

Metal colorization using picosecond laser pulses

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I dedicate this thesis to my wonderful wife and the love of my life, Alena, et à ma famille, surtout à vous papa et maman, pour tout votre soutien durant toutes ces années.

Statement of Originality

I certify that all the content of this thesis is my own. I stand by all the contents and its originality. Work and findings by other groups and colleagues are properly cited with respect to ethical standards.

Abstract

In the last few decades, the nanoscale fabrication of metallic structures has demonstrated promising applications in security (*e.g.* cryptography), photochemistry (*e.g.* plasmon-assisted photo-chemistry), decoration (*e.g.* colouring), biocompatibility of implants and more. To fabricate such subwavelength nanostructures, we typically resort to the use of several nanolithography techniques that are lengthy and incompatible with large-scale production on complex substrates. For this purpose, we invented an innovative technique for the fast fabrication of nanostructures via the use of a picosecond laser. We used this technique to produce colourful coins for the Royal Canadian Mint which were presented at the World Money Fair in Germany in 2015 as a world first. To ensure the long-term survival of these plasmonic colours, a new dual-layer passivation technique was conceived based on an atomic deposition process, to meet the commercialisation requirements of our industrial partner. A new burst colouring technology was also invented that allows for the creation of more visually appealing colours. These laser burst colours were also shown to have a high sensing potential and an overall better visual response to the application of the passivation layer.

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Publications

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- Jaspreet Walia, Jean-Michel Guay, Oleksiy Krupin, Fabio Variola, Pierre Berini and Arnaud Weck, “*Visible light driven plasmonic photochemistry on nano-textured silver*”, Physical Chemistry Chemical Physics, **20**, 238-246 (2018)
- Jean-Michel Guay, Graham Killaire, Peter G. Gordon, Sean T. Barry, Pierre Berini, and Arnaud Weck, “*Passivation of Plasmonic Colors on Bulk Silver by Atomic Layer Deposition of Aluminum Oxide*”, Langmuir, **34**, 17, 4998-5010 (2018)
- Jean-Michel Guay, Antonino Calà Lesina, Joshua Baxter, Graham Killaire, Lora Ramunno, Pierre Berini, and Arnaud Weck, “*Topography tuning for plasmonic colour enhancement via picosecond laser bursts*”, Advanced Optical Materials, 1800189 (2018)
- Jean-Michel Guay, Jaspreet Walia, Guillaume Côté, Daniel Poitras, Fabio Variola, Pierre Berini, Arnaud Weck, “*Effect of laser repetition rate on colour rendition, nanoparticle morphology and surface chemistry on silver*”, Optical Materials Express, 9(2) 456-468 (2019) (**invited** contribution)
- Jean-Michel Guay, Antonino Calà Lesina, Graham Killaire, Peter G. Gordon, Choloong Hahn, Sean T. Barry, Lora Ramunno, Pierre Berini, Arnaud Weck, “*Laser-written colours on silver: optical effect of alumina coating*”, Nanophotonics (2019)

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- Guay, J.-M., Calà Lesina, A., Côté, G., Charron, M., Ramunno, L., Berini, P., Weck, A., “*Picosecond Laser Angle Dependent/Independent Coloring of Metals: Road to Large Scale Application*”, Photonics North, Quebec City, Canada (2016)
- Guay, J.-M., Calà Lesina, A., Côté, G., Charron, M., Ramunno, L., Berini, P., Weck, A., “*Plasmonic Coloring of Silver using Picosecond Laser Pulses*”, CLEO: Topical Review on Laser in Materials Processing II, San Jose, USA (2016)
- Guay, J.-M., Côté, G., Charron, M., Ginn, M.L., Baxter, J., Weck, A., “*Tailoring Colors of Silver Surface via Nanoparticle Formation upon Picosecond Pulses*”, Photonics North, Ottawa, Canada (2015)

Book Chapter

- A. Calà Lesina, J.-M. Guay, A. Weck, P. Berini, L. Ramunno, “*Modeling of Coloured Metal Surfaces by Plasmonics Nanoparticles*”, Book: Quantum Nano-Photonics (2018)

Patents

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- 1st prize - University of Ottawa 3-minute thesis competition, "*Painting Metals Without Paint*", Ottawa, Canada (2018) (**Oral presentation**)
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- 1st prize - 8th Engineering and Computer Science Graduate Poster Competition, "*Coloring of metals using ultrafast lasers*", Ottawa, Canada (2015) (**Poster presentation**)

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Introduction

1.1 Thesis Scope and Outline

In a recent editorial article published in Nature Photonics, the editor and lead researchers in academia discussed the crashing hype and wave of the plasmonic field.[33] In its infancy, this field promised much and still continues to offer more avenues of research. To date, only a handful of companies have commercialized plasmonic based devices. Limited fabrication times and work area have presented difficulties that have severely hindered the commercialization of plasmonic based products. For this reason, the hype of the plasmonic field has remained largely isolated to the academic field and the lab setting. The work in this thesis aimed to break this stagnated trend; to produce and commercialize plasmonic goods with a production time that is compatible with industry. In partnership with the Royal Canadian Mint, this thesis brings insight into the journey that lead to the commercialization of the first set of plasmonic collectible coins to be released on the near future and the application of a patent. Additionally, while keeping focus on the main goal of producing plasmonic coins, other findings lead us to research the same surfaces for various other commercial applications and for other purely academic interests. The scope of thesis comprises multiple important points:

- *Developing a process that allows for the fast production of plasmonic surfaces.* The most common fabrication method for plasmonic surfaces is currently lithography. Lithographic techniques are usually slow, limited to small areas, costly and must be done in a clean room environment. Such processes are incompatible with industry production times. Recently, two other research groups were able to produce some plasmonic colours on the surface of metals using lasers.[20, 21] In both cases the colour palettes were very limited and in one case the speeds were very low. This thesis presents a method of scaling up the plasmonic colouring of metals using picosecond lasers, which is compatible with industry whose production rate consists of producing thousands of items a day. The colours are demonstrated to be linked to a total accumulated fluence value which allows for the fast production of plasmonic devices. The colouring technique was applied to a 5 kg silver coin with a topography of 1.5 cm.
- *Surface protection of plasmonic products from the environment.* Scaling up production of plasmonic devices is only one of many challenges towards achieving commercialization. For certain metals, exposure to the environment will have the effect of changing the chemical composition of the nanofeatures. Additionally, the low temperature melting points of the nanofeatures[34, 35, 36] and oil from hands will also have detrimental effect on the well-functioning of the plasmonic surface. For this reason, this thesis presents a new coating technique using atomic layer deposition that passed rigorous testing at the Royal Canadian Mint, preserving the integrity of the colours. This technique has a multi-layer approach, where the first layer serves to trap the heat sensitive nanoparticles for the subsequent higher temperature (and denser) alumina layer.
- *Colour optimization for better visual quality.* The colouring of metals by lithographic technique displays a wide colour palette with high Chroma values (i.e. saturation). Laser-induced plasmonic surfaces did not have the same range and quality of colours. This thesis presents a novel technique using laser bursts to increase the quality of the surface colours rivaling the colours produced by lithographic techniques with a fraction of the time. These colours are now being applied to the production of plasmonic coins at the Royal Canadian Mint.
- *High applicability of the colour surfaces.* The surface created using the technique in this thesis has proven to be widely applicable to other fields such as: pho-

tochemistry, sensing, bio-sensing, wetting, lab-on-a chip and much more. These applications will be the topic of upcoming publications that are in the works, but will not be part of this thesis.

- *Effect of laser parameters on colour rendition, nanoparticle morphology and surface chemistry.* The realization of direct-laser writing of colours on metal surfaces have been to date achieved by the random trial of various laser parameters. This thesis presents, experimentally, the impact of the various laser parameters on colour rendition. In particular, the effect of laser repetition rate which is shown to affect surface chemistry. The possible creation of core/shell structures over large surface areas could have wide application in catalytic applications.

This thesis consists of a collection of scientific publications, each one presented as a separate chapter. The entirety of this thesis is structured as follows: Chapter 2 is the Literature Review, consisting of previous work on the colouring of metals using various techniques. Chapter 3 is the experimental section which describes in more detail the methods and scientific equipment used in the studies. Chapter 4 discusses the two laser colouring techniques employed for the surface colouring of metals (nonburst and burst) and, the link between Hue and total accumulated fluence value. While the colouring method is applied to a 5 kg silver coin, the same colouring method is shown to colour copper, aluminum and gold. A finite-difference time-domain (FDTD) model is used to explain the nature of the plasmonic colours using the statistics of the coloured regions. Chapter 5 discusses a new passivation method for the protection of silver colours. A multi-layer ALD approach is reported for the deposition of alumina to trap the heat sensitive silver nanoparticles. The method consists of, first, depositing a low-density alumina film at low-temperature to trap the nanoparticle and provide heat stability for the second, subsequent deposition of a denser alumina film at a more elevated temperature. The surfaces underwent testing using the established practices at the Royal Canadian Mint (RCM), showing the successful passivation of the surfaces. The technique is demonstrated on a coloured 5 kg silver coin. The use of short laser burst for the creation of various surface structures is presented in Chapter 6. The colours produced using this technique are shown to increase colour saturation by up to 100%. The laser-induced periodic surface structures (LIPSS) produced on the surface of silver are attributed to the increase in electron-phonon coupling which depends on the energy distribution within the burst pulses. FDTD simulations of the surfaces show the LIPSS structures to be responsible for the increase colour saturations due to the field enhancement at the surface.

Chapter 7 assesses the potential application of the coloured surfaces as radiometric and colourimetric sensors. The article also attempts to shed light on the interesting observation of the burst surfaces to recover colour with increasing thickness of alumina. This recovery is observed only for the burst coloured surfaces. Chapter 8 demonstrates the effect of laser repetition rate on the colours, chemistry and morphology within the machined regions. While silver oxides and silver carbonates are found within the coloured regions, the colours are observed to be dependent on the nanoparticles present and re-deposited on the surface. Finally, Chapter 9 presents the conclusion of the thesis and suggestions for future work. The co-authored publications can be found in Appendix A. Chapter 1 presents and explains the fundamentals of localized surface plasmon resonance (LSPR) and laser-induced periodic surface structures (LIPSS). These two distinct physical phenomena can render colours to metal surfaces. The theoretical work contained within this Chapter was largely based on well-known sources.[37, 38, 39, 40, 41]

Early in life, every scientist learns that metals can carry current because of the weakly bound electrons. As we progress in our scientific careers and continuously learn, we discover that metals are in fact natural plasmas much like Earth’s ionosphere.[42] The story behind this thesis starts from this simple concept.

1.2 Classical electrodynamic interaction with matter

The interaction and propagation of electric and magnetic fields in vacuum is well described by Maxwell’s equations. However, the interaction and propagation in matter cannot be as adequately described due the changes induced in the propagating medium by the field themselves, requiring an extended classical electrodynamic interpretation. For example, classical electrodynamics fails to consider d-band transitions[38] in silver and frequency dependent permittivity[42, 43] if the surfaces were to be exposed to white light. Material response to EM fields and dependence on frequency, for example, requires the understanding and knowledge of solid state physics in order to adequately modify the classical electrodynamic interaction with matter.[39, 42]

1.2.1 Maxwell's equation

The classical electrodynamic interpretation of EM field interaction with matter and the formation of local fields can be described by the following Maxwell's equations[37]:

$$\vec{\nabla} \cdot \vec{D} = \rho_{ext} \quad (1)$$

$$\vec{\nabla} \cdot \vec{B} = 0 \quad (2)$$

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (3)$$

$$\vec{\nabla} \times \vec{H} = \vec{J}_{ext} + \frac{\partial \vec{D}}{\partial t} \quad (4)$$

where $\vec{B}$ is the magnetic flux density, $\vec{E}$ is the electric field, $\vec{D}$ is the dielectric displacement, $\vec{H}$ is the magnetic field, ρ_{ext} is the external charge density and $\vec{J}_{ext}$ is the external current density.

While these relations are convenient and sufficiently explain the propagation of EM fields in free space, for interactions with matter it is often useful to separate the applied external fields and the material response to the applied fields. For this purpose, polarization ($\vec{P}$) and magnetization ($\vec{M}$) are introduced.

Thus, to describe the interaction of EM fields with matter we introduce the following relations[37]:

$$\vec{D} = \underbrace{\epsilon_o \vec{E}}_{\text{External field}} + \underbrace{\vec{P}}_{\text{Local material response}} \quad (5)$$

and

$$\vec{H} = \underbrace{\frac{\vec{B}}{\mu_o}}_{\text{External field}} - \underbrace{\vec{M}}_{\text{Local material response}} \quad (6)$$

For propagation in free space (i.e. $\vec{P} = 0$ and $\vec{M} = 0$) we return to the well known relation of $\vec{D} = \epsilon_o \vec{E}$ and $\vec{B} = \mu_o \vec{H}$, where ϵ_o and μ_o are the permittivity and permeability of free space, respectively.

For this thesis, we will ignore the effect of local magnetization since the materials considered are nonmagnetic. Thus, while the $\vec{P}$ is introduced to describe the interaction of matter with an applied field, the quantification of the material response to an applied external field must be done via measurable quantities. These relations are known as the

constitutive relations defined as[39]:

$$\vec{J} = \sigma \vec{E} \quad (7)$$

$$\vec{P} = \epsilon_o \chi \vec{E} \quad (8)$$

where $\vec{J}$ is the current density, χ is the material susceptibility and σ is the material conductivity. Replaced in equation 5, we obtained the important relation $\vec{D} = \epsilon_o \epsilon \vec{E}$, where $\epsilon = (1 + \chi)$. Together $\vec{J}$ and $\vec{P}$ can describe the material response in the presence of an applied external electric field. However, under its current form it would seem that ρ and ϵ are constant values. Experimentally, it was observed that when metals are exposed to optical radiation they exhibit responses that are highly dependent on frequency[44, 42] of the incoming light and on spatial non-localities requiring the relations to add a dependence on $\vec{K}$ and ω .

$$\vec{D}(\vec{K}, \omega) = \epsilon_o \epsilon(\vec{K}, \omega) \vec{E}(\vec{K}, \omega) \quad (9)$$

$$\vec{J}(\vec{K}, \omega) = \sigma(\vec{K}, \omega) \vec{E}(\vec{K}, \omega) \quad (10)$$

Where $\vec{K}$ is the wave vector and ω is the angular frequency. The principal metal considered in this thesis, silver, has a lattice arrangement that is face-centered cubic with a lattice constant of $a = .409$ nm. Therefore, for wavelength greater than a single unit cell (i.e. $\lambda \gg a$) or mean free electron path the relation can be simplify by replacing $\vec{K} = \vec{0}$ obtaining relations describing the material response that only depends on the frequency. Where $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ and $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ are the complex permittivity and conductivity functions of the material exposed to an EM field. It is important to point out that the imaginary term of the permittivity, ϵ_2 , describes losses in the material (*i.e.* absorption) which consequently contributes to the real part of the conductivity, σ_1 . The two complex functions can be distinguished as the response of the bound charges (χ) and free charges (σ) when exposed to electromagnetic fields.

1.3 Solid state physics and determination of the optical constants of metals

As stated in the previous section, the response of matter to EM fields are not constant values. This is especially true for metals when exposed to optical radiation where important interband transitions occur. This section will show the mathematical work and physical concepts behind the parameters used to describe the response of matter when exposed to EM fields starting from the basic Drude model.[45, 46]

1.3.1 Drude-Sommerfeld model

The Drude model was developed to describe the losses and the optical response of the bulk to different frequencies. The original model by Paul Drude was based on independent and free electrons oscillating around an ionic core.[45, 46] However, the model was over simplified and failed to consider the important interband transitions in noble metals. Arnold Sommerfeld later modified the theory by adding a damping term, γ , to the harmonic oscillator whose value depends on τ^{-1} with τ being the electron relaxation time (about 40 fs for Ag).[47, 48, 49, 50] This damping term assumes the electron to be moving freely in-between collisions. Assuming that the bulk is exposed to a time dependent varying field, $\vec{E}(t) = \vec{E}_o e^{-i\omega t}$, we obtain the following equation for a damped harmonic oscillator:

$$m_{eff} \frac{d^2 \vec{x}(t)}{dt^2} + m_{eff} \gamma \frac{d\vec{x}(t)}{dt} = -e \vec{E}(t) \quad (11)$$

The solution to the harmonic oscillator, considering the Fourier domain relation that $\partial/\partial t \rightarrow -i\omega$, is:

$$\vec{x}(t) = \frac{e}{m_{eff}\omega^2 + im_{eff}\omega\gamma} \vec{E}(t) \quad (12)$$

Where m_{eff} is the electron effective mass and e is the electron charge. The electrons in a metal can be seen as free electrons (i.e. electron gas) or very weakly bonded. The electron gas, when exposed to optical radiation, will be pulled away from the ionic core which will want to bring it back, causing an oscillatory behavior. This restoring force and the oscillation motion driven by the optical field will cause a resonance. The collective displacement of the electrons away from the ionic core induces a polarization that is:

$$\vec{P} = -n_e e \underbrace{\frac{e}{m_{eff}\omega^2 + im_{eff}\omega\gamma}}_{x(t)} \vec{E}(t) \quad (13)$$

Where n_e is the free electron density. By introducing equation 13 into equation 5 and simplifying we obtain the following relation for the frequency dependent permittivity, $\epsilon(\omega)$:

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (14)$$

where

$$\omega_p = \sqrt{\frac{n_e e^2}{\epsilon_o m_{eff}}} \quad (15)$$

is the bulk plasma frequency. A plasma is defined has a mixture of positive and negative charges, for which either the negative or positive charges, of equal concentration, are free

Table 1:

	Ag
n_e/m^{-3}	$5.76 \cdot 10^{28}$
m_{eff}/m_e	0.96

to propagate and are unbound. In the case of metals, the free propagating charges are the electrons and the ion cores are bound and of equal concentration for a net charge of zero. The bulk plasma frequency of each metal is governed by the free electron density and the electron effective mass specific to each metal. The longitudinal motion of the bulk plasma is called a plasmon.

For incoming optical radiation on the surface of a metal, if the optical frequency is higher than that of the bulk plasma; the electron gas is unable to respond, and the light is transmitted. For lower optical frequencies, the light is reflected by the bulk plasma.[39, 43] This distinctive optical behaviour can be observed in the reflectance spectra of different metals. It is also important to note that semi-conductor and dielectrics can have metallic behaviour if the free electron density is increased, such behaviour is observed when semi-conductors[51, 52, 53] and dielectrics[54] are exposed to high intensity fields. In the limit where $\omega \gg \omega_p$, the free electron model gives the prediction that $\epsilon(\omega) \rightarrow 1$, see equation 14. However, for metals this is somewhat untrue. For noble metals such as Ag, Cu and Au, in the limit where $\omega > \omega_p$, important polarization effects are caused by the d-band[38] (close to the Fermi surface) and the positive ion cores causing a highly polarized local environment, thus, requiring a correction to equation 14.[43]

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (16)$$

where ϵ_∞ encompasses the effects of the polarized contribution of the d-band. In most material, other than mostly noble metals, the assumption that $\epsilon_\infty \approx 1$ is usually correct.

In its current form the model still does not accurately describe the response of the metals when exposed to optical radiation. Equation 16, only considers intraband transitions giving the bulk plasma frequency of silver to be roughly 9.4 eV compared to the measured experimental value of 3.2 eV.[40] This discrepancy is attributed to the neglect of the standard Drude model to consider interband transitions. These transitions from the d-band to the s-shell are significant for metals such as silver, copper and gold. To

consider these transitions, an extra term is added to the damped harmonic oscillator (equation 11) describing the oscillatory motion of the d-band to the s-shell.

$$m_{eff} \frac{d^2 \vec{x}(t)}{dt^2} + \underbrace{m_{eff} \gamma \frac{d\vec{x}(t)}{dt}}_{\text{damping term}} + \underbrace{m_{eff} \omega_o^2 \vec{x}(t)}_{\text{d-band to s-shell transitions}} = -e \vec{E}(t) \quad (17)$$

where ω_o is the resonant frequency describing the interband transition from the d-band to the s-shell. Solving equation 17 and repeating the same steps described earlier in this section, we obtain the following frequency dependent relation for the permittivity.

$$\epsilon(\omega) = \underbrace{\epsilon_\infty}_{\text{residual polarization from ionic core}} - \underbrace{\frac{\omega_p^2}{\omega^2 + i\gamma\omega}}_{\text{intraband contribution}} + \underbrace{\sum_{j=1}^l \frac{A_j \omega_p^2}{(\omega^2 + i\omega\gamma - \omega_{oj}^2)}}_{\text{interband contribution}} \quad (18)$$

where A_j is a weighting factor. The last term of equation 18 (i.e. interband contribution) is referred to as the Lorentz oscillator.[55, 56] To have an accurate response of the material to EM fields it is often enough to add 2 term (j=1,2) contribution from the Lorentz oscillator.

1.3.2 Wave propagation

The electromagnetic wave equation is a solution to the Maxwell's equation and is useful in describing the propagation of an electromagnetic wave through matter or empty space. The wave equation is also a powerful tool that can be used to obtain the dispersion relations of the system that are very important in understanding the field of plasmonics. Starting from the relation[37]:

$$\vec{\nabla} \times \vec{\nabla} \times \vec{E} = -\mu_o \frac{\partial}{\partial t} (\vec{\nabla} \times \vec{B}) \quad (19)$$

For simplicity, we assume no external charge and propagation in free space. We obtain using equation 3 and 4 with some simple derivations the following relation:

$$\nabla^2 \vec{E} = \mu_o \epsilon_o \frac{\partial^2 \vec{E}}{\partial t^2} \quad (20)$$

which is widely known as the wave equation. We also assume that the electromagnetic wave is a propagating time-dependent plane wave, i.e. $\vec{E}(\vec{r}, t) = \vec{E}_o e^{i(\vec{k}\vec{r} - \omega t)}$, where $\vec{k}$ is the wave vector. Substituting the electric field into equation 20 and simplifying, we obtain the important relation:

$$\omega = ck \quad (21)$$

which is the dispersion relation of light traveling in free space, also known as the light line.

The wave equation can then also be generalized for electromagnetic waves propagating inside matter

$$\nabla^2 \vec{E} = \mu_o \epsilon_o \epsilon(\omega) \frac{\partial^2 \vec{E}}{\partial t^2} \quad (22)$$

giving the dispersion relation

$$\omega = \frac{ck}{\sqrt{\epsilon(\omega)}} = \frac{ck}{n} \quad (23)$$

where n is the refractive index of the propagating medium. This ends the section with the wave equation which is an important introductory concept for the next section on surface plasmon polaritons.

1.4 Surface Plasmon Polaritons

Surface plasmon polariton (SPP) waves are evanescent waves confined in the perpendicular direction of a metal-dielectric interface.[39, 42, 3] More precisely, SPP are propagating and dispersive electromagnetic waves at a conductor-insulator interface coupled to the electron plasma of the conductor. In the previous section, we described the propagation of an electromagnetic wave through matter as:

$$\nabla^2 \vec{E} = \mu_o \epsilon_o \epsilon(\omega) \frac{\partial^2 \vec{E}}{\partial t^2} \quad (24)$$

where we assumed a time-dependent harmonic field to give

$$\nabla^2 \vec{E} + k_o \epsilon(\omega) \vec{E} = 0 \quad (25)$$

Now, while the SPP is confined to the transverse direction (z-direction) the evanescent wave may still propagate in either the x- or y-direction. For demonstration purposes, let's assume the wave to be propagating in the x-direction. The wave propagating at the interface can be represented by

$$\vec{E}(x, y, z) = \vec{E}(z) e^{i\beta x} = \vec{E}_o e^{i(kz - \omega t)} e^{i\beta x} \quad (26)$$

where β is the propagation constant of the wave at the metal-dielectric interface. By substituting relation 26 into equation 25, we obtain:

$$\frac{\partial^2 \vec{E}(z)}{\partial z^2} + (k_o^2 \epsilon(\omega) - \beta^2) \vec{E} = 0 \quad (27)$$

However, since the wave is propagating at the interface of 2 mediums, a solution or dispersion relation for medium 1 and medium 2 can be obtained by substituting k for k_1 or k_2 in relation 26 giving 2 independent relation

(medium 1)

$$k_1^2 = \beta^2 - k_o^2 \epsilon_1(\omega) \quad (28)$$

and

(medium 2)

$$k_2^2 = \beta^2 - k_o^2 \epsilon_2(\omega) \quad (29)$$

which are the dispersion relations for a wave propagating in medium 1 and medium 2. In its current form the relations are decoupled given no insight on the conditions required to sustain an evanescent or SPP wave at the interface of medium 1 and medium 2. To find solutions and conditions that would sustain an evanescent wave at the interface we must revert back to Maxwell's equations using the electric field in eq. 26 ($\partial/\partial t = -i\omega$) where the wave is propagating in the x-direction ($\partial/\partial x = i\beta$ and $\partial/\partial y = 0$) and confined in the z direction. Replacing relation 26 into equation 3 and 4, we obtain:

$$\vec{\nabla} \times \vec{E} = \left(\frac{\partial E_z}{\partial y} - \frac{\partial E_y}{\partial z}\right)\hat{x} - \left(\frac{\partial E_z}{\partial x} - \frac{\partial E_x}{\partial z}\right)\hat{y} + \left(\frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y}\right)\hat{z} = i\omega\mu_o(H_x\hat{x} + H_y\hat{y} + H_z\hat{z}) \quad (30)$$

and

$$\vec{\nabla} \times \vec{H} = \left(\frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z}\right)\hat{x} - \left(\frac{\partial H_z}{\partial x} - \frac{\partial H_x}{\partial z}\right)\hat{y} + \left(\frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y}\right)\hat{z} = i\omega\epsilon_o\epsilon(\omega)(E_x\hat{x} + E_y\hat{y} + E_z\hat{z}) \quad (31)$$

From eq. 30 and 31, a set of 6 relations are obtained which can be separated into 2 sets of coupled solutions for the different polarization of the propagating wave. In equations 28 and 29, we found the dispersion relations for the waves traveling in both medium 1 and medium 2, however, it is not clear if a solution exists in which the interface may support the evanescent waves and for this the relations of equations 30 and 31 must be resolved. To resolve these relations, we separate the appropriate terms to solve the wave equation for both transverse electric (TE) and transverse magnetic (TM) modes.[39] For the TE (or s) polarization solution to the wave equation at the interface, we isolate the H_x , H_z and E_y and solved them independently of the other terms. For TM (or p) polarization solution to the wave equation at the interface, we isolate and solve for the inter-dependent

terms E_x , E_y and H_y . Solving for each of the terms in 30 and 31 enforcing continuity at the metal-dielectric interface using the appropriate boundary conditions; conditions on both k_1 and k_2 are obtained for the SPP waves to exist for TE and TM polarization.[39]

For a TE polarization solution to the wave equation, the following condition on k_1 and k_2 must be satisfied:

$$A_1(k_1 + k_2) = 0 \quad (32)$$

where A_1 is the amplitude of the field inside the conductor. However, the confinement of the wave at the interface requires that $Re(k_1)$ and $Re(k_2)$ be greater than 0, and gives that A_1 must be 0, instating that A_2 must also be zero in the insulator medium. The significance of this result is quite important; no TE modes solution for the wave equation for a confined surface wave exists. This will be the subject of an important discussion later in this section.

For a TM polarization solution to the wave equation, the following condition on k_1 and k_2 must be satisfied:

$$\frac{k_2}{k_1} = -\frac{\epsilon_2}{\epsilon_1} \quad (33)$$

where $A_1 = A_2$ due to the boundary conditions and continuity at the interface. Once again, due to the confinement of the wave at the interface, conditions on $Re(k_1)$ and $Re(k_2)$ requires that they be greater than 0. Hence, this means that of one the permittivity $Re(\epsilon_1(\omega))$ or $Re(\epsilon_2(\omega))$ must be positive while the other needs to be negative. This important result states that an SPP wave can only exist at the interface of 2 materials if their permittivity is of opposite signs (one positive and one negative). By substituting 33 into the dispersion relations of 28 and 29 and isolating for β , we obtain the important dispersion relation for an SPP wave which is given by:

$$\beta = k_o \sqrt{\frac{\epsilon_2 \epsilon_1}{\epsilon_2 + \epsilon_1}} \quad (34)$$

It is important to point out that the SPP waves can only exist for TM polarization modes. A concept that is important in order to understand the orientation of the grating vector of the laser-induced periodic surface structures (LIPSS) on the surface of the metals after laser exposure, which will be discussed later in this thesis.

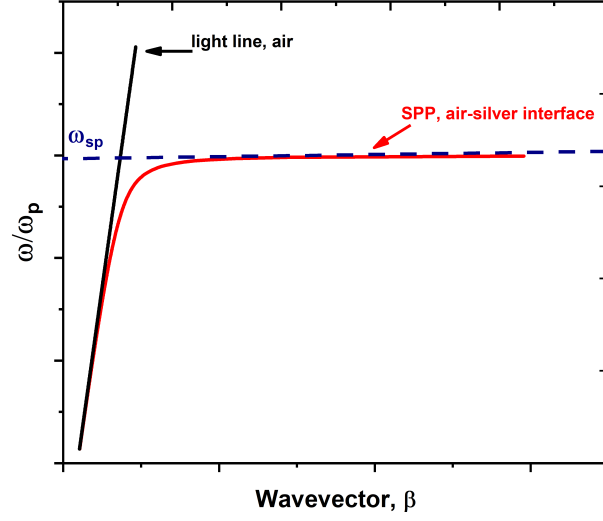


Figure 1: Graphical representation of the light line and dispersion curve of an SPP at an air-silver interface. ω_{sp} is the surface plasmon frequency at the asymptote of the SPP dispersion curve. The permittivity values of silver with respect to frequency were taken from Johnson and Christy.[1]

In figure 1, we plot the light line for a wave propagating in air and SPP wave propagation at a silver-air interface. The frequency is normalized by dividing by the bulk plasma frequency ω_p . The values for calculating ω_p were taken from [40] and tabulated in table 1.

For small wavevectors (mid-infrared or lower), the SPP propagation constant β is close to but on the right of the light line. As β increases, the separation between the light line and the SPP dispersion curve increases, straining the condition required for phase-matching and proper coupling. In the large wavevector limit, we observed β to reach an asymptote becoming constant over all wavevectors resulting in a 0 group velocity, $\frac{\partial \omega}{\partial k} \rightarrow 0$. As the group velocity reaches zero, a localized electrostatic condition is set on the surface where no evanescent wave can propagate.[38, 39] The frequency at which this happens is called the surface plasmon, ω_{sp} , which will be the topic of the next section of this thesis. The surface plasmon frequency where the group velocity goes to 0 is given by the following relation:

$$\omega_{sp} = \frac{\omega_p}{\sqrt{1 + \epsilon_2}} \quad (35)$$

where ϵ_2 is the permittivity of the dielectric media. It should be noted that equation 35 is

a rough estimation since damping is ignored ($\gamma \approx 0$). For a more accurate determination of the surface plasmon frequency, the complete relation of the permittivity (equation 18) would have to be used.

1.4.1 Surface Plasmon Polariton excitation at a planar interface

In the previous section, we saw that SPP waves could be excited by light if the SPP dispersion curve and the light line intersect to have phase-matching. In air, phase-matching at the metal-air interface is less strained for low wavevectors, see Figure 1, corresponding to mid-infrared light. Furthermore, noble metals have low melting temperatures scaling down with size which makes the integrity of the metallic nanostructures questionable at such wavelengths.[34, 36] Hence, the intrinsic properties of metals require the use of larger wavevectors for the excitation of SPP waves. Under these conditions the confined wave are evanescent since the SPP dispersion lies to the right of the light line where $\beta > k$. [39] Therefore, in practice, SPP cannot be directly excited by light beams as more momentum is needed to properly couple light with the SPP. Even angling the impinging light at the metal surface does not provide the necessary photon momentum, $k_x = k \sin \theta$, for proper phase-matching/coupling with the SPP wave. Therefore, additional momentum to the photon is required to provide the necessary phase-matching to couple and excite SPP at the metal-dielectric interface. Next, we present 2 methods to achieve the efficient coupling and excitation of SPPs.

Prism Coupling

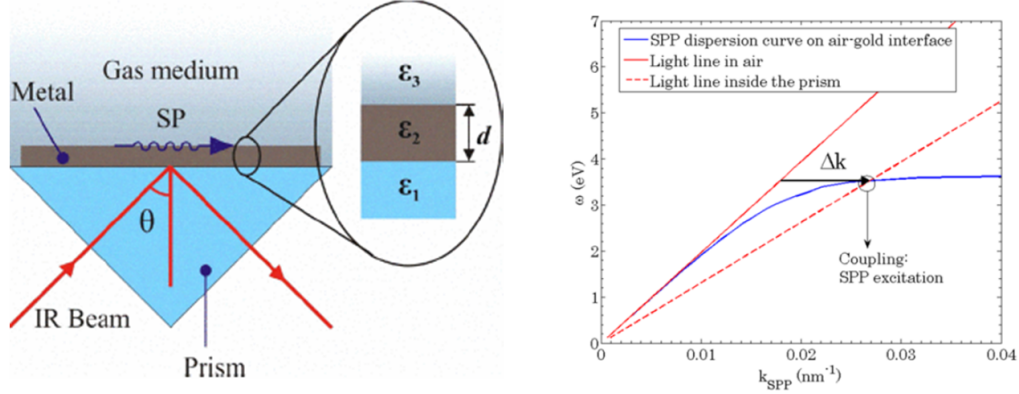


Figure 2: (left) Schematic representation of SPP waves excited via a prism using the Kretschmann configuration. A thin metal film is placed at the surface of the prism, in contact with another dielectric medium. The dielectric medium on the other side of the metal surface does not necessarily have to be a gas. Image reprinted from [2] with permission from © 2009 IEEE. (b) Graphical representation of the dispersions curves of SPP waves at an air-gold interface and the light lines for light traveling outside (*i.e.* air) and inside the prism. The prism is shown to impart extra momentum, Δk , to the photons allowing for the proper excitation of SPP waves. Image taken from [3] in agreement with the creative common license.

Figure 2 (left) shows the arrangement used for the excitation of an SPP wave at a metal-air interface via the use of a prism. The setup consists of a thin metal film deposited on the surface of a prism where one face is exposed to air. The light enters the prism and impinges onto the metal film at a certain angle θ . The prism imparts a momentum of k_x to the photon.

$$k_x = k\sqrt{\epsilon}\sin\theta \quad (36)$$

where ϵ is the permittivity of the prism. From figure 2 (right) we can see that the light line inside the prism is tilted with a lesser slope with a good part of the SPP dispersion curve laying to the left of the light line. The sustained excitation of SPP wave occurs at the intersection of the light line of the prism and the metal-air SPP dispersion curve where phase-matching is achieved (*i.e.* $\beta = k$). It should be pointed out that since the

added photon momentum originates from the prism and the excitation of the SPP is at the metal-air interface that the metal film needs to be thin.

grating and roughness coupling

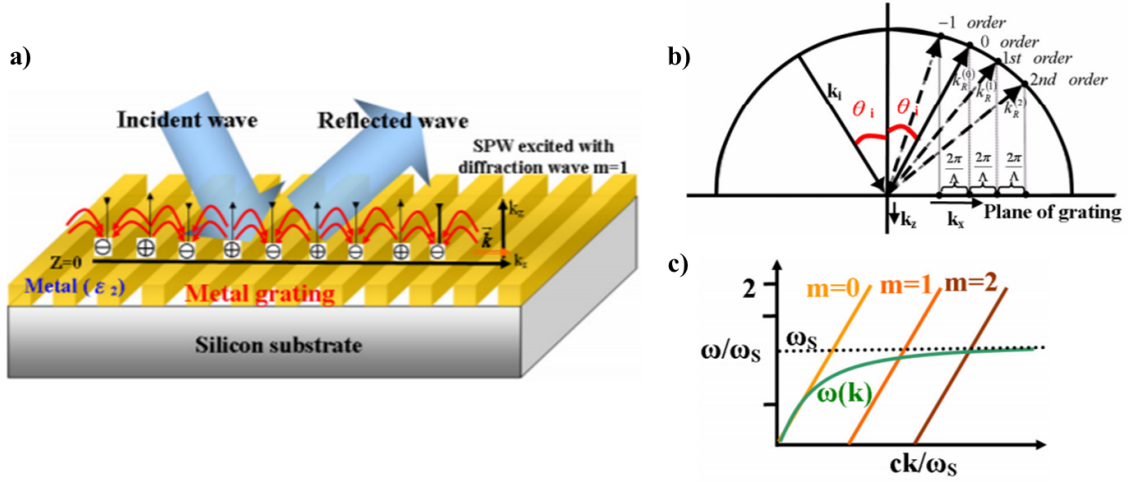


Figure 3: (a) Schematic of grating assisted excitation of SPP wave at a metal-dielectric interface. The added momentum imparted to the incident photons depends on the (b) incident angle (θ_i), grating vector (Λ) and the order of diffraction. (c) Graphical representation of the dispersion curves showing the line light and that of the diffracted light. The added momentum to the photon is $\Delta k = m2\pi/\Lambda$ where m is the order of diffraction. Images were taken and modified from [4] with permission from © 2007 IEEE.

This next method of SPP excitation is extremely important for understanding the concept of LIPSS formation. The photon momentum can be increased by a network of periodic grooves (or grating) on the metal surface, see Figure 3 (a). [4, 57, 39] From the grating, the photon acquires added momentum of $\Delta k = mg$ where $g = 2\pi/\Lambda$ is the reciprocal grating vector, and Λ is the grating period and m is an integer representing the order of diffraction, see Figure 3 (b). Figure 3 (c) shows the effect of the grating on the light line essentially translating it by Δk . The intersection between the translated light line (due to the grating) and the SPP dispersion curve corresponds to the sustained excitation of the SPP wave at $\beta = k \sin \theta \pm mg$. It should be noted, however, that the grooves should not be too deep since more complex physics may be introduced which lies outside the scope of this thesis. [39] The grooves should be kept shallow (< 100 nm). [3]

The excitation of SPP waves at the metal grating air interface can be directly measured by capturing reflectance and observing dips in the spectrum.[58, 3]

The presence of a grating on the surface and the shift of the light line by an integer number of the grating period is an important concept in the understanding of the LIPSS structure that are much smaller than the wavelength of light[20, 59, 60] that we observed with ultrafast laser with pulse durations below the thermal expansion time.[61]

Alternatively, SPPs can also be excited on metal surfaces with random roughness adding photon momentum of Δk_x provided via the scattering of light.[18] The excitation of SPP waves occurs for the phase-matching of $\beta = k \sin \theta \pm \Delta k_x$. The extra momentum imparted to the photon by the roughness is, however, lower than the periodic grating (i.e. $\Delta k_{x,roughness} < \Delta k_{x,grating}$).[39] Omitting the large ohmic losses of metals, surface roughness could provide enough momentum to excite SPP at low wavevectors, see Figure 1. Nonetheless, with this concept the complete picture of LIPSS formation is obtained: (1) LIPSS are formed by the presence of an initial surface roughness, (2) LIPSS smaller than the wavelength are achieved by the presence of grating formed on the metal for subsequent laser pulses and (3) the grating vector is perpendicular to the polarization of light (i.e. TM).[39, 24] The interference between of the incoming light with scattered surface electromagnetic waves (SEW)[62] presented by Sipe[63] was in fact nothing else than the interference of incoming light with SPP waves at the interface.

1.4.2 Laser-Induced Periodic Surface Structures

Classical Model

The creation of laser-induced periodic surface structures (LIPSS) has been widely studied in the last decade. The well accepted classical model for their formation was explained by Sipe et al.[63] as an interference phenomena between a scattered surface electromagnetic wave (SEW)[62] and incoming laser light. In the classical model, the periodicity of LIPSS is given by:

$$\Lambda = \frac{\lambda}{n \pm \sin(\theta)} \quad (37)$$

where n is the refractive index of the surrounding dielectric medium, θ is the angle of incidence of the incoming laser light, λ is the wavelength of light and $\pm$ is the propagation direction. In air ($n = 1$) and under normal incidence ($\theta = 90$) the grating period is $\Lambda = \lambda$. It should be noted that Sipe et al.[63] stated that for the LIPSS to form that it was necessary to have an initial roughness in order to have the SEW waves[62] (see

SPP section). In the absence of roughness LIPSS cannot form through the described interference phenomena. Therefore, LIPSS formation occurs through a surface feedback mechanism. In this mechanism, the first laser pulses on the surface create the initial roughness and the required surface for the formation of LIPSS.

This model was widely accepted as it described well the LIPSS formation mechanism until the introduction of ultrafast lasers. It was discovered that femtosecond laser irradiation of metal surfaces, at normal incidence and in air, produced LIPSS with grating periods below the wavelength of light. These LIPSS were named femtosecond laser-induced periodic surface structures (FLIPSS) or low spatial frequency laser-induced periodic surface structures (LSFL).[\[26, 64, 59, 20, 60, 27, 65\]](#) Such grating periodicity could not be explained by the classical model formulated by Sipe et al.[\[63\]](#) since the SEW wave in their model did not take the characteristic properties of the SPP.

Modified Model

To explain the creation of the sub-wavelength grating (i.e. LSFL) an alternate model was proposed based on the classical model. This model explains the creation of the grating on the surface of materials as an interference phenomenon between the electron oscillating plasma (or SPP) and the incoming laser light, see Figure 4. For metals, valence electrons are loosely bound and can be regarded as an electron gas. When exposed to electromagnetic radiation this electron gas can oscillate through the ionic lattice. Simply, SPP waves are also SEW, hence, the classical model while still valid required slight modifications. The modified model was proposed by Huang et al.[\[24\]](#)

From the assumption that the interference phenomena occurred between the SPP waves and incoming laser light, the modified model was changed to the following relation:

$$\Lambda = \frac{\lambda}{\frac{\lambda}{\lambda_s} \pm \sin \theta} \quad (38)$$

where λ_s is the plasmon wavelength, from equation 34, given by:

$$\lambda_s = \lambda \left(\frac{\epsilon_1 + \epsilon_2}{\epsilon_1 \epsilon_2} \right)^{\frac{1}{2}} \quad (39)$$

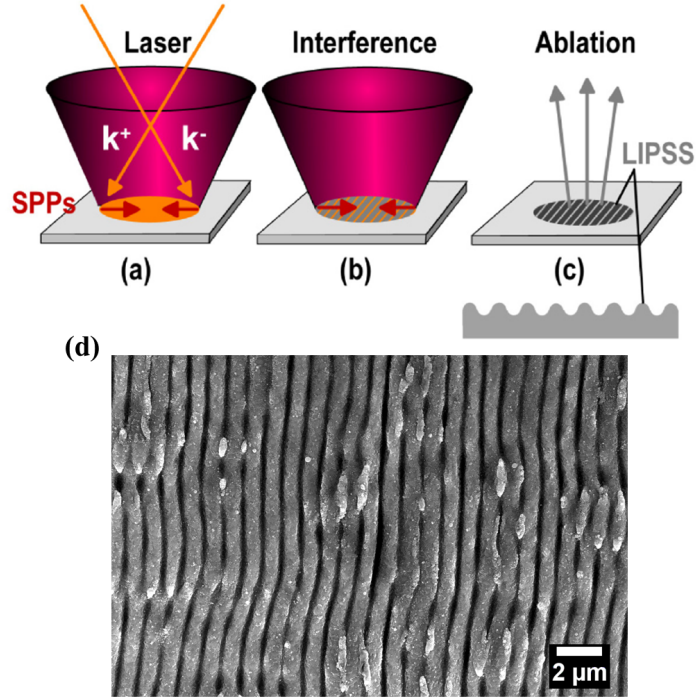


Figure 4: Schematic representation of the model for the formation of LIPSS. (a) The scattering of the incoming laser light, on the roughen surface, couples light into counter-propagating SPP waves. (b) The interference of the two counter-propagating wave results in a spatially modulated energy deposition pattern resulting in a (c) spatially modulated ablation and the formation of LIPSS. Reprinted/Adapted with permission from ref. [5], Optical Materials Express. (d) SEM image of LIPSS created on the surface of copper.

Under normal irradiation and for machining in air (*i.e.* $\epsilon_2 \approx 1$), the grating periodicity is equal to the plasmon wavelength, $\Lambda = \lambda_s$, which is lower than the wavelength of light. This claim is supported experimentally for the machining of ultrafast lasers on semi-conductors[51, 52, 53], metals and dielectrics.[54] The modified model using SPP interference also serves to explain the change in the periodicity of the gratings across the laser modified areas. In an area of overlapping laser shots, it is observed that the periodicity of the LIPSS grating is smaller at the periphery than at the center of the laser modified area.[24] This observation can be explained by the definition of the SPP wavelength. When exposed to intense fields, material permittivity will be modified, see equation 18. The change in the material permittivity, for intense field, originates from

the bulk plasma frequency which depends on the free electron density.

$$\omega_p = \left(\frac{e^2 n_e}{m_{eff} \epsilon_o} \right)^{\frac{1}{2}} \quad (40)$$

where e is the electron charge, n_e is the free electron density, m_{eff} is the electron effective mass and ϵ_o is the permittivity of free space.

Thus, the SPP wavelength and the periodicity of the grating would vary depending on the free electron density. As experimentally observed, materials machined with a Gaussian beam, the center of the irradiated area would have a grating periodicity on the order of the SPP wavelength due to the high n_e . As per the edges of the irradiated region, where the beam intensity is at the lowest, the SPP wavelength would decrease with n_e following the intensity of the Gaussian beam. As a result, the grating periodicity would decrease moving from the center of the irradiated region going outwards.[24] It is important to note that, the modified model serves to explain the creation of LIPSS not only on metals but also on semi-conductors[51, 52, 53] and dielectrics[54]. Semi-conductors and dielectrics exposed to intense fields will exhibit metallic behaviour, thus, explaining the SPP-light interference and the formation of LIPSS when exposed to light. Furthermore, the SPP-light interference model also explains the orientation of the ripple structures. From the classical model, it was normally accepted that the grating orientation was perpendicular to the polarization of the incoming light. For the modified model, the orientation of the gratings can be explained and determined by the traverse magnetic (TM) characteristic of the SPP (see SPP section).

The model of Huang et al.[24] also explains the creation of LIPSS (LSFL) that are much smaller than the wavelength of light with the use of ultrafast laser. In the previous section of SPP waves, we saw that gratings could be used to impart additional momentum to photons to efficiently couple them with SPP waves at larger wavevectors. For pulses under the thermal expansion time[61], the LIPSS remain intact from shot-to-shot since the structures are not destroyed by the successive melting and re-formation of LIPSS. Thus, for pulse duration under the thermal expansion time[61], a grating is maintained to impart this added momentum. With each laser shot the grating is slightly modified in depth and pitch, changing the condition for SPP coupling. As a result, the LIPSS periodicity is continually evolving with each laser shot creating LIPSS structures that are much smaller than the wavelength of light. However, as described by Huang et al.[24], a wave eventually crashes. Hence, there are still limitations on the period

of LIPSS that cannot be continuously diminished from shot-to-shot. Additionally, due to field-enhancement in the crevices of LIPSS, the depth of the ripples become deeper with each successive laser shot causing the grating coupling to become more strained. This field-enhancement could also be used for the dipole enhancement of nanoparticles in proximity of the groove which was the topic of the burst work presented in this thesis.[31]

It is important to point out that LIPSS that are much smaller than the wavelength of light are usually not found on surfaces exposed with laser pulses that are longer than the thermal expansion time of the material.[61] For that reason, the gratings are erased (by melting) from shot-to-shot resulting in no additional momentum to the light photons. This can also occur in materials with low electron-phonon coupling since the hot electrons do not transfer their energy locally to the lattice. As a result, the definition of the LIPSS is not very good from shot-to-shot.[66] The metals used in this thesis were plagued with the property of low electron-phonon coupling coefficients which we successfully increased using laser bursts.[67, 68] It should be noted, however, that the use of burst may have the opposite effect of decreasing the electron-phonon coupling in certain metals.[69, 70]

1.5 Nanoparticles and Localized Surface Plasmon Resonance

Compared to SPPs discussed in the previous section, localized surface plasmon (LSP) are non-propagating at the material surface, hence, the reason they are termed localized. Instead, when exposed to EM fields the electrons at the surface of nanostructures are coupled to the EM field producing non-propagating excitations.[39, 43] The electron cloud is pulled away from the curved surfaced and the ionic core inducing a restoring force causing the electron cloud to oscillate in the presence of the EM field. Additionally, since there is no need for momentum matching, unlike SPP, LSP resonances (LSPR) of the nanostructures can be excited via direct light exposure.

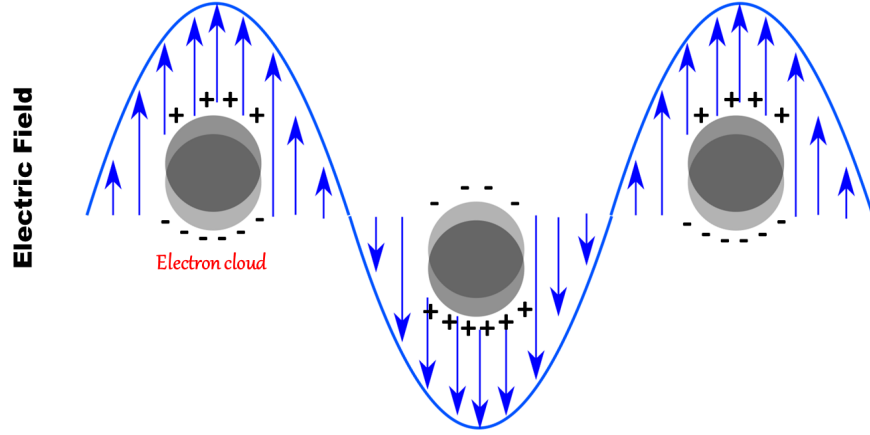


Figure 5: Schematic of the surface plasmon resonance of a spherical nanoparticle showing the displacement of the electron cloud with respect to the ionic core when exposed to an electric field. A restoring force is imparted bringing the electron cloud back, creating a resonant condition.

1.5.1 Quasi-electrostatic approximation

To describe the response of the nanofeatures when exposed to EM field, a quasi-electrostatic approach is often used. This approach, however, is only applicable in the limit where the features or nanoparticles are much smaller than the wavelength of light ($d \ll \lambda$).^[37] If this condition is satisfied, we may use the Laplacian of the electrical potential, Φ , to determine the fields outside and inside a spherical nanoparticle using the following relation^[39, 56]:

$$\nabla^2 \Phi = 0 \quad (41)$$

where

$$\vec{E} = -\nabla \Phi \quad (42)$$

The solution of the electrical potential at the surface of the nanoparticles is formulated in spherical coordinates using the Legendre polynomials by^[39]:

$$\Phi(r, \theta) = \sum_{l=0}^{\infty} [A_{lr}^l + B_{lr}^{-(l+1)}] P_l(\cos \theta) \quad (43)$$

The above relation is the solution for spherical nanoparticles, hence, due to symmetry there is no dependence on the azimuthal angle, ϕ .

Additionally due to the requirement of continuity at the interface, solutions must satisfy

the following boundary conditions:

$$\frac{-1}{a} \frac{\partial \Phi_{in}}{\partial \theta} \Big|_{r=a} = \frac{-1}{a} \frac{\partial \Phi_{out}}{\partial \theta} \Big|_{r=a} \quad (44)$$

and

$$-\epsilon_o \epsilon \frac{\partial \Phi_{in}}{\partial \theta} \Big|_{r=a} = -\epsilon_o \epsilon_m \frac{\partial \Phi_{out}}{\partial \theta} \Big|_{r=a} \quad (45)$$

where a (i.e. $d/2$) is the radius of the spherical nanoparticles. From the relation of the electrical potential and the boundary conditions, we obtain the relations for the electrical potential inside and outside the spherical nanoparticle.

$$(inside) \Phi_{in} = \frac{-3\epsilon_m}{\epsilon + \epsilon_m} E_{or} \cos \theta \quad (46)$$

and

$$(outside) \Phi_{out} = -E_{or} \cos \theta + \frac{\vec{p} \cdot \vec{r}}{4\pi\epsilon_o\epsilon_m r^3} \quad (47)$$

where

$$\vec{p} = 4\pi\epsilon_o\epsilon_m a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon} \vec{E}_o \quad (48)$$

In the quasi-electrostatic approach, the displacement of the electron cloud from the curved surface of the nanoparticle can be represented as a point like dipole. Additionally, from equation 26, we find an important relation that is fundamental in plasmonics: polarizability. The polarizability, α , defined as:

$$\alpha = 4\pi a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \quad (49)$$

The ratio of $(\epsilon - \epsilon_m)/(\epsilon + 2\epsilon_m)$ is called the Clausius-Mossotti relation[71, 38] differentiating the polarizability of the material compared to its local environment. From this point forth, it would be important to distinguish both the polarizability (α) and the susceptibility (χ) of the exposed material. χ describes the induced polarization of the material in the presence of a local EM field. Alternatively, α describes the induced polarization to the external field caused by the nanostructure.

From equation 27, a nanoparticle is said to be at resonance when the denominator $\epsilon + 2\epsilon_m = 0$ or $\epsilon = -2\epsilon_m$ requiring the real part of the permittivity of the metal to be negative. Metals with this property for the real permittivity are referred to as plasmonic metals. On a side note, non-plasmonic metals (e.g. tungsten) have been shown to produce LIPSS when exposed to intense fields raising the possibility that non-plasmonic metals may become plasmonic if exposed to a sufficiently high EM field.[72] The resonant enhancement

at $\text{Re}[\epsilon(\omega)] = -2\epsilon_m$ is called the dipole surface plasmon. However, from equation 27, it would incorrect to assume that a particle may be infinitely polarized under the condition $\epsilon = -2\epsilon_m$ due to the imaginary part of $\epsilon(\omega) \neq 0$. In fact, the imaginary part of the metal's permittivity as the effect of damping the resonance and to broaden it. Furthermore, one can easily see that the polarizability of the nanoparticle is extremely sensitive to any change in the refractive index of the surrounding medium (*i.e.* ϵ_m). As a rule of thumb, increasing the refractive index of the local medium has the effect of red-shifting the plasmon resonance.

Replacing the value of $\epsilon(\omega) = -2\epsilon_m$ in equation 16, assuming no ionic background (*i.e.* $\epsilon_\infty = 1$) with no damping ($\gamma = 0$) and surrounded by air ($\epsilon_m \approx 1$), we obtain the natural plasmon resonance predicted by the free electron model of $\omega_o = \omega_p/\sqrt{3}$.

The electric fields inside and outside the nanoparticles can be determined using equation 20 which gives:

$$(inside)\vec{E}_{in} = \frac{3\epsilon_m}{\epsilon + 2\epsilon_m}\vec{E}_o \quad (50)$$

$$(outside)\vec{E}_{out} = \vec{E}_o + \frac{3\vec{n}(\vec{n} \cdot \vec{p}) - \vec{p}}{4\pi\epsilon_o\epsilon_m r^3} \quad (51)$$

where $\vec{n}$ is an arbitrary point around the surface of the nanoparticle. From the electric field relation of inside and outside the nanoparticle, it is clear that the electric field is enhanced by the resonance. The field enhancement outside the particle falling by a factor of r^{-3} away from the nanoparticle surface. In the presence of harmonic external applied field, $\vec{E}(r, t) = \vec{E}_o e^{-i\omega t}$, an oscillating dipole is induced on the nanostructure creating a time-dependent oscillating dipole, $\vec{p}(t) = \epsilon_o\epsilon_m\alpha\vec{E}_o e^{-i\omega t}$. In the quasi-electrostatic case, spatial retardation effects are neglected removing the spatial dependence of $\vec{p}$. The oscillating motion of the electron cloud around the nanoparticle will generate EM radiation. The radiation of the dipole can result in the scattering of the plane wave by the sphere, which can be represented as radiation from a point dipole.

From the EM fields formed by the oscillating dipole, a set of coefficients can be obtained to describe the absorption (C_{abs}) and scattering (C_{sca}) by the nanoparticles.[41, 39, 73]

$$C_{sca} = \frac{k^4}{6\pi}|\alpha|^2 = \frac{8\pi}{3}k^4 a^6 \left| \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right|^2 \quad (52)$$

and

$$C_{abs} = k\text{Im}[\alpha] = 4\pi k a^3 \text{Im}\left[\frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m}\right] \quad (53)$$

where $k = 2\pi/\lambda$ is the wavevector. From relation 30 and 31, we can observe that the contribution of scattering and absorption are proportional to the size of the nanoparticle by a factor of a^6 and a^3 , respectively. Hence, for increasing nanoparticle size the scattering term dominates over absorption. The loss exacerbated by the nanoparticle is often written as the extinction coefficient which is the sum of both the scattering and the absorption term.

$$C_{ext} = C_{abs} + C_{sca} = \frac{12\pi\omega}{c}\epsilon^{3/2}a^3 \frac{Im[\epsilon(\omega)]}{(Re[\epsilon(\omega)] + 2\epsilon_m)^2 + (Im[\epsilon(\omega)])^2} \quad (54)$$

1.5.2 Mie Theory

In the previous section, the quasi-electrostatic approach was used to determine the extinction coefficient. This approach, however, is valid only in the limit where the wavelength is much greater than the dimension of the nanoparticle (i.e. $d \ll \lambda$). For larger nanoparticles, typically larger than 100 nm, the quasi-electrostatic approach is no longer valid and Mie theory[74] of an EM wave scattering of the surface of a sphere needs to be used to determine the scattering and extinction coefficient of the particle. Mie derived an analytical electro-dynamical solution for uncharged particles in an homogeneous environment.[74, 39]

$$Q_{sca}^{(n)} = \frac{2}{(kr)^2}(2n+1)(|a_n|^2 + |b_n|^2) \quad (55)$$

$$Q_{ext}^{(n)} = \frac{2}{(kr)^2}(2n+1)Re(a_n + b_n) \quad (56)$$

where a_n and b_n are the Mie coefficients given by[74, 75, 76]:

$$a_n = \frac{m\psi_n(mx)\psi'_n(x) - \psi_n(x)\psi'_n(mx)}{m\psi_n(mx)\xi'_n(x) - \xi_n(x)\psi'_n(mx)} \quad (57)$$

$$b_n = \frac{\psi_n(mx)\psi'_n(x) - m\psi_n(x)\psi'_n(mx)}{\psi_n(mx)\xi'_n(x) - m\xi_n(x)\psi'_n(mx)} \quad (58)$$

where $x = kr$ and $m = \sqrt{\epsilon_r} = n_{particle}/n_{medium}$. ϵ_r is the relative permittivity, $n_{particle}$ and n_{medium} are the refractive index of the particle and the surrounding medium, respectively. The terms ψ_n and ξ_n are the Riccati-Bessel functions.

The treatment of a spherical particle suggests spherical symmetry and the use of a multipole extension of the fields, referred to as the letter n in the Mie relations. In the

quasi-static limit discussed in the previous section, the nanoparticles were treated as point dipoles corresponding to an $n = 1$ (i.e. dipole) in the Mie relations.[76] These are referred to as Rayleigh-type plasmon resonances.

The size of 100 nm earlier was largely based on the use of noble metallic nanoparticles whose resonance falls within the visible spectrum and is widely used within that spectrum for various applications. However, the validity of the quasi-electrostatic approach is relative to the incoming wavelength (λ) impeding onto a nanoparticle of a certain dimension (d).[76] For example, IR light on a 200 nm particle may still use the quasi-electrostatic approach.

Additionally, for the sake of completeness, quantum effects may become important if the nanoparticle size or if the gap between two nanoparticles is smaller than 2 nm. Quantum effects arise in metallic nanoparticles when the size of the particles are small enough that the continuous density of states is broken up into discrete energy levels.[56] For this thesis, such effects are neglected but may become important to explain the colours on gold obtained using the laser texturing process.

1.5.3 Gans Theory

For the case of more complex structures, other than a sphere, Gans theory is used to describe the scattering and extinction of EM waves incident on the nanoparticle.[77] Gans theory[77] is an extension of the Mie theory[74] for particles other than that of a sphere. The polarizability of the nanoparticle of different shape is generalized by the following relation[78, 43, 76, 79, 80]:

$$\alpha_k(\omega) = \frac{4\pi}{3}abc \frac{\epsilon_m - \epsilon_d}{\epsilon_d + (\epsilon_m + \epsilon_d)L_k} \quad (59)$$

where the factor L_k is the depolarization (or geometrical factor) for each of the axis and abc are the different lengths defining the complex structure. For a sphere, see equation 57, we would have the condition where $a = b = c$ ($L_a = L_b = L_c = 1/3$). Under these conditions we retrieve equation 47. For ellipsoids, we would have $a \neq b \neq c$ where such a particle would have 3 distinct SP modes corresponding to the 3 polarizabilities along the main three axes. For spheroids ($a = b \neq c$), there would be two distinct SP modes corresponding to the 2 polarizabilities along the 2 main axes.[43, 79] The excitation of the SP modes of each of the different shapes will depend on the incident polarization and the direction of the main axes with respect to polarization. In the case where the

main axis of an ellipsoid is oriented parallel to the incident polarization, only a single SP mode would be excited out of the possible three. For a perfect sphere, the SP resonance is independent of the incident polarization.

1.5.4 Core/Shell

So far, we have seen the polarizability of a metal sphere and of other complex shapes that were surrounded by a single homogeneous medium. In this section, we introduce the polarizability of core/shell nanoparticle (i.e. dielectric core and metallic shell or vice-versa). For simplicity we will present only the case of a sphere, but the same principle can be extended to other shapes. The concept of the core/shell nanoparticle is important in the context of this thesis and for future work since experimental evidence would suggest that the nanoparticle redeposited on the surface may have a core/shell structural composition (e.g. $\text{Ag}_2\text{O}/\text{Ag}$).[\[81, 82\]](#) The use of core/shell has recently seen great interest in the plasmonic community due to the wider tunability of the plasmon resonance in such a structural arrangement.[\[83, 84, 78, 85, 79, 83\]](#)

The polarizability of a core/shell sphere is given by[\[85\]](#):

$$\alpha = 4\pi r_s^3 \left(\frac{(\epsilon_s - \epsilon_m)(\epsilon_c + 2\epsilon_s) + (r_c/r_s)^3(\epsilon_c - \epsilon_s)(\epsilon_m + 2\epsilon_s)}{(\epsilon_s + 2\epsilon_m)(\epsilon_c + 2\epsilon_m) + (r_c/r_s)^3(2\epsilon_s - 2\epsilon_m)(\epsilon_c - \epsilon_s)} \right) \quad (60)$$

where r_s and r_c are, respectively, the radius of the shell (i.e. outer radius) and the core (i.e. inner radius), ϵ_c is the permittivity of the core, ϵ_s is the permittivity of the shell and ϵ_m is the permittivity of the surrounding medium outside the nanoparticle.

The extinction coefficient of the core/shell nanoparticle is given by[\[85\]](#):

$$Q_{ext} = \frac{8\pi^2 r_s^3}{\lambda \sqrt{\epsilon_m}} \text{Im} \left[\epsilon_m \left(\frac{(\epsilon_s - \epsilon_m)(\epsilon_c + 2\epsilon_s) + (r_c/r_s)^3(\epsilon_c - \epsilon_s)(\epsilon_m + 2\epsilon_s)}{(\epsilon_s + 2\epsilon_m)(\epsilon_c + 2\epsilon_m) + (r_c/r_s)^3(2\epsilon_s - 2\epsilon_m)(\epsilon_c - \epsilon_s)} \right) \right] \quad (61)$$

From relation 38 and 39 the core/shell structure has more tuning knobs, so to speak, to control plasmonic resonances. For the core/shell spherical nanoparticle, two resonances are obtained for $\epsilon_s = -2\epsilon_m$ and $\epsilon_c = -2\epsilon_m$. In the case where $\epsilon_c = \epsilon_s$ equation 54 is retrieved, the dependence of the permittivity on ω is assumed in the equations.

1.5.5 Size dependent plasmon resonance

So far in this section we have seen only the polarizability, the scattering and absorption coefficients to be dependent on the size of the nanoparticles. However, the position of

the plasmon resonance (for a given frequency) would currently be fixed since $\epsilon(\omega)$ in equation 18 is independent of size for the resonant condition where $Re[\epsilon(\omega)] = -2\epsilon_m$. Experimentally, the position of the plasmon resonance is clearly observed to be dependent on the size of the nanoparticles. Hence, the Drude model requires modifications to consider the effect of size on the plasmon resonance and to make $\epsilon(\omega)$ dependent on r (the radius of the nanoparticle).[\[50, 43\]](#) The size dependence is added to the Drude model by introducing two size dependent terms to the damping.

$$\gamma' = \underbrace{\gamma}_{\text{free electron scattering}} + \underbrace{A \frac{v_F}{l_{eff}}}_{\text{surface scattering}} + \underbrace{2B\hbar \frac{4}{3}\pi r^3}_{\text{radiative}} \quad (62)$$

where A and B are phenomenological factors unique to the composition of the nanoparticle, v_F is the Fermi velocity and l_{eff} is the reduced effective mean free path. For a sphere, the classical model gives $l_{eff} = r$. The two terms added to the damping are the contribution of the surface scattering and radiative effects.[\[56\]](#) The effect of surface scattering leads to additional collisions of the conduction electrons which become more important with decreasing particle size. The loss of coherence by scattering is contained within A . The value of A is found to depend strongly on surface chemistry. The radiative contribution to damping is due the acceleration and the deceleration of the electrons in the presence of the time-dependent EM field.[\[79\]](#) This acceleration of the electron, from classical electrodynamics, will have the effect of emitting radiation in all directions. The emission of radiation will induce a deceleration force on the oscillating dipole. The fitting factor B is obtained from direct experimental measurement. Considering these size dependent terms, the Drude model is now written as:

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i(\gamma + A \frac{v_F}{r} + B\hbar \frac{8}{3}\pi r^3)\omega} + \sum_{j=1}^l \frac{A_j \omega_p^2}{(\omega^2 + i\omega(\gamma + A \frac{v_F}{r} + B\hbar \frac{8}{3}\pi r^3) - \omega_{oj}^2)} \quad (63)$$

1.5.6 Near-field interaction of closely spaced nanoparticles

Thus far we have considered the instance of a lone single nanoparticle. Here we explore the effect of nanoparticles in close proximity. We saw that when a metal nanoparticle is exposed to optical radiation and is at resonance, a strong electric field is generated in close proximity to the nanoparticle surface. This field outside the nanoparticle is given

by:

$$\vec{E}_{out}(t) = \underbrace{\vec{E}(t)}_{\text{applied external field}} + \underbrace{\frac{3\vec{n}(\vec{n} \cdot \vec{p}(t)) - \vec{p}(t)}{4\pi\epsilon_o\epsilon_m r^3}}_{\text{field enhancement from oscillating dipole}} \quad (64)$$

This equation is the same as equation 51 but with a time dependence to represent the time-dependent harmonic electric field. The enhancement of the field by the oscillating dipole will be felt by nanoparticles in close proximity. The field enhancement drops by a factor of r^{-3} away from the oscillating nanoparticle. For a nanoparticle in close proximity to the resonant particle, the local field, E_{loc} , perceived by the nanoparticle will be:

$$E_{loc}(t) = E(t)(1 + E_{nf}(t)) \approx E(t)(1 + \alpha\beta) \quad (65)$$

where α is the polarizability, β is the interaction constant and E_{nf} is the near-field contribution from all nanoparticles in proximity. The interaction constant β is a complex parameter that considers the influence of all the nanoparticles in close proximity. Higher order interaction constants can be added to the relation in order to consider the effects of particles at different distances. However, their effects to the local field are less important than the closer nanoparticles.

Until now we have treated the nanoparticles as point-like oscillating dipoles which is still valid. However, for particles in close contact it may be useful to add higher order multipole for a more accurate description of the interaction given the actual finite-size of the nanoparticles.[43]

$$E_{nf}(t) = \underbrace{\frac{2\alpha}{4\pi\epsilon_o r^3} E(t)}_{\text{dipole}} + \underbrace{\frac{3\sigma \frac{dE}{dt}}{4\pi\epsilon_o r^4}}_{\text{quadrupole}} + \underbrace{\frac{4\gamma \frac{d^2 E}{dt^2}}{4\pi\epsilon_o r^5}}_{\text{oct upole}} \dots \quad (66)$$

where σ and γ are the higher order polarizability tensor of the nanoparticle. From equation 64, we can see that the contribution of the higher poles to the enhancement field felt by the surrounding particles becomes more important with decreasing inter-particle separation. For large inter-particle separation, the higher order can be dropped returning to the treatment of the nanoparticle as point-like oscillating dipoles. In general, the plasmon resonance is red-shifted when surrounded by other nanoparticles.[86] However, for only two nanoparticles in close proximity, the plasmon resonance can either red-shift or blue shift depending on the polarization of the incoming light with respect to the gap separating the two particles.[43, 87] This is due to the increase or decrease of the restoring force acting on the oscillating electrons by the charge distribution of the neighbouring nanoparticle.[88, 89] In the work presented in this thesis, based on the

statistical analysis of the surfaces, this principle is crucial for understanding the origin of the different colours since the size of the nanoparticles are fixed and only the inter-particle distance changes. The use of higher order poles is also required in symmetry breaking conditions where a nanoparticle is held above a substrate.[90, 91, 92] In such a scenario, an image dipole of the nanoparticle is created in the substrate. This image dipole excites the quadrupole mode of the nanoparticle which is then imparted onto the image on the substrate. This quadrupole then excites octupole modes and so on. Alternatively, when the nanoparticle is brought into contact or “embedded” into the substrate, the substrate acts as a depolarization field reducing the oscillatory motion of the electron cloud.[93, 94, 50]

Literature Review

For the past several decades, the production of colours by plasmonic means for the intent of mass production has been a hot topic, with much potential in a growing field of applications. In this Chapter, a Literature Review covering some select relevant works will be presented.

2.1 Plasmonic coloured surfaces

2.1.1 Fabrication of plasmonic coloured surfaces without direct laser writing

This section covers the fabrication of coloured surfaces by means other than direct laser machining. Currently and for the last decade, the most common methods of fabrication of coloured and metamaterial surfaces have been by electron beam lithography (EBL)[95], ion beam lithography (IBL)[6, 8, 96] or milling[9] and hot embossing or nanoimprint lithography (NIL).[6, 9] While the control of the structures and the shape of the nanofeatures is unrivalled by these fabrication techniques, the vast introduction of plasmonic devices into the consumer market has been inordinately slow due to the incompatibility of these techniques for mass production or the fabrication of large surface areas.[33]

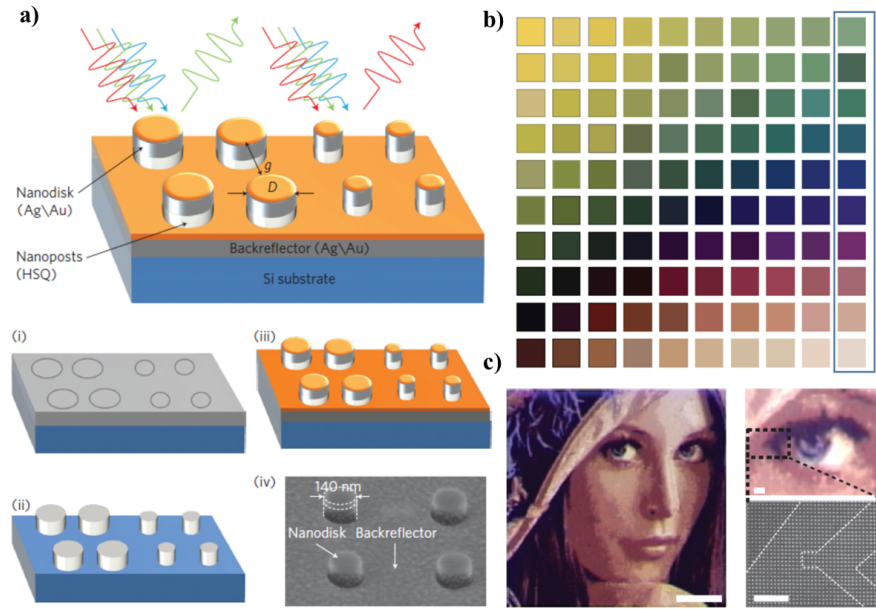


Figure 6: (a) Schematic representation of the surfaces composed of electron-beam fabricated HSQ nanopillars covered with an evaporated Ag/Au layer. (b) Colour was obtained for a fixed thickness of Ag/Au, the different colours were obtained by increasing the diameter of the nanopillar (bottom-to-top) and by increasing the periodicity of the nanopillars (left-to-right). (c) Image of Lena coloured applying the colouring technique with a resolution as high as $\sim 100\,000$ DPI. Reprinted (adapted) with permission from Nature Ref.[6] © 2012.

Kumar et al.[6] fabricated a coloured surface with a resolution of $\sim 100\,000$ dots per square inch using plasmonic nanostructures. The structures responsible for the plasmonic colours consisted of nano-pillars fabricated on-top of a silicon wafer. A thin 95 nm film of hydrogen silsesquioxane (HSQ) was spin-coated on the surface of the silicon wafer and patterned by EBL. The nano-pillars and the silicon wafer were subsequently covered by a 1 nm Chromium, 15 nm silver and 5 nm gold capping layer using an electron beam evaporator, see Figure 6. The plasmonic metal layers (Ag and Au) on the flat silicon wafer were referred by the authors as a “holey” backreflector onto which the nano-pillars sit. By modifying the gap between the pillars and the diameter of the nano-pillars, the authors obtained a wide colour palette. To prove their plasmonic colouring method, the authors fabricated pixels of 250 nm by 250 nm in dimension which is at the diffraction limit of optical systems using white light. The image fabricated measured only a few

microns. However, the authors claimed the process to be scalable by the means of nano-imprint lithography.

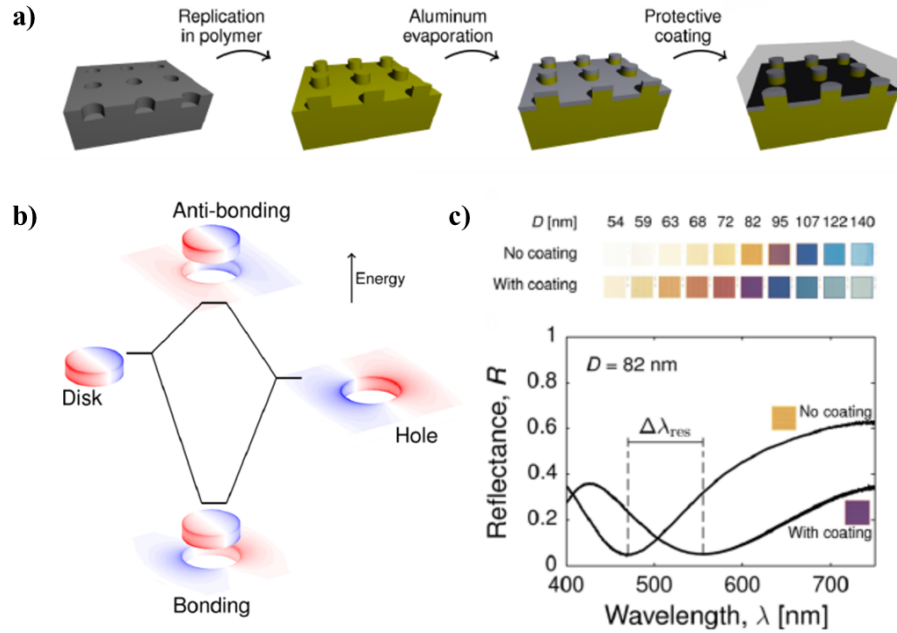


Figure 7: (a) Schematic representation of the fabricated surfaces composed on PMMA nanopillar capped with an aluminum disk and an aluminum film covering the surrounding areas. (b) Representation of the “bonding” and “anti-bonding” resonances caused by the hybridization of the hole and disk plasmonic resonances. The bonding resonance was observed to be responsible for the creation of colours and was found to be stronger with decreasing nanopillar height. (c) Colours and selected reflectance for colours with and without a coating of PMMA. The colours were obtained by changing the diameter of the aluminum disk and nanopillar. A red-shift in the reflectance spectra is observed after the application of the PMMA coating. Reprinted (adapted) with permission from Ref.[7]. © 2014 American Chemical Society.

In a subsequent study, Clausen et al.[7] fabricated similar surfaces but with a layer of aluminum instead of silver or gold. The authors claim that aluminum properties are advantageous over silver and gold for the following reasons: first, the interband transition of aluminum compared to gold finds itself to be outside of the visible spectrum and second, compared to silver, SPPs supported on aluminum have their frequency in the visible spectrum closer to the light line allowing for less angle-dependence on the resulting plasmonic colours. For this reason, the authors chose to deposit aluminum on the surface of

PMMA. The masters were fabricated by electron beam lithography and the dry etching of silicon using a single spot writing technique with speeds of up to $1 \text{ cm}^2/\text{hour}$. The masters were then used to do hot embossing and to transfer the features onto PMMA. The PMMA surfaces were then coated with an aluminum film using an electron beam evaporator. The different colours were obtained by changing the periodicity, diameter and height of the nano-pillars, see Figure 7. Like Kumar et al.[6], the authors refer the film on low areas of the substrate as the “holey” film. The authors explain the colours as a combination of dipolar resonances originating from both the hole and disk. With decreasing nano-pillar height, the authors claim that two new modes are created due to hybridization: a “bonding” and “anti-bonding” mode. The “bonding” mode resonating at a lower frequency and the “anti-bonding” mode resonating at a higher frequency. The authors claim the “bonding” resonant mode to be key for the creation of tunable colours. Reflectance spectra showed no “bonding” resonant modes for nano-pillar height over 70 nm. The strength of the bonding was found to be stronger for lower height nano-pillars. However, due to the issue of short circuiting the disk (top of the nanopillar) and the holey film, a limitation on the height of the nano-pillars is discussed. In the intent of demonstrating the industrial viability of the technology, the authors, deposited a protective coating layer on the surface of their nanostructure red-shifting their plasmonic resonances.

Roberts et al.[8] obtained plasmonic colours based on metal-insulator-metal (MIM) interfaces capable of supporting gap-surface plasmons. The surfaces were fabricated by the electron beam evaporation of a 100 nm thick film of gold on a silicon substrate followed by a sputtering of a SiO_2 film, see Figure 8. For the creation of the gold disk, a 30 nm film of gold was deposited by thermal evaporation and the lift-off done by immersing the fabricated surfaces in acetone. For the experiments, the authors chose to have a fixed periodicity of 340 nm between gold disks. The gap-plasmon resonance and colours were tuned by changing the diameter of the gold disk. The authors also briefly showed that the gap-plasmon resonance to be tuned by changing the thickness of the insulator layer of the MIM. A full colour palette was obtainable by the presence of two dips in the reflectance spectrum. The first dip was due to the Fabry-Perot resonance in the MIM gap which is dependent on the size of the gold disk, and the second dip was due to the resonance attributed to the interband transition of gold. For chemical and mechanical protection, a 100 nm layer of PMMA was spin-coated onto the MIM surface resulting

in a reduction in the red (R) contribution of the colours. The author claims the surface was originally designed to have no coating and that better colour could be obtained by designing MIM structures especially designed to compensate for the PMMA layer.

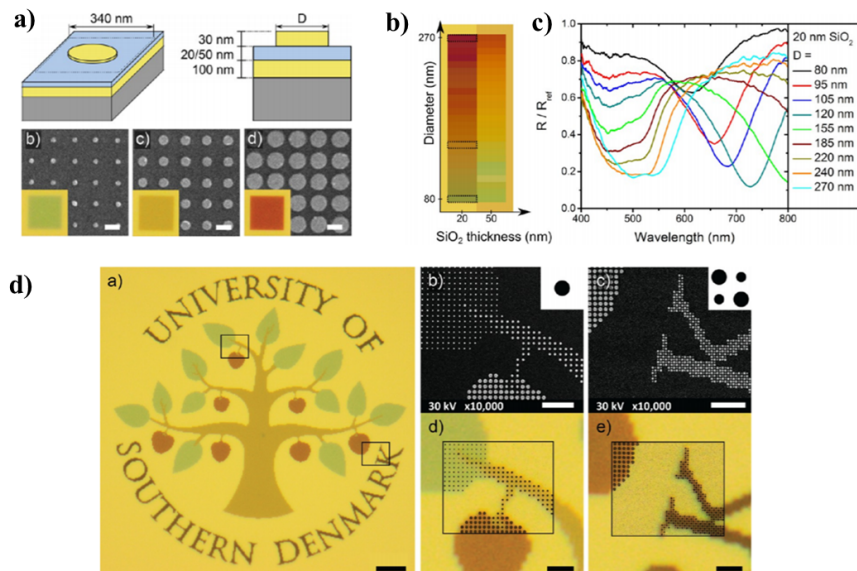


Figure 8: (a) Schematic representation of the fabricated surfaces consisting of gold nanodisks on a thin film of SiO₂ deposited on a thin film of gold. The gold nanodisks were fabricated by EBL. The authors kept the periodicity of the nanodisks constant at 340 nm throughout the experiments. (b) Graphical representation of the colours obtained by changing the size of the gold nanodisks and the thickness of the SiO₂ layer in the MIM. (c) Reflectance spectra of varying sizes of the gold nanodisks for a fixed SiO₂ thickness of 20 nm. (d) Image of the University of Southern Denmark logo fabricated by the authors using their colouring technique. Reprinted (adapted) with permission from Ref.[8]. © 2014 American Chemical Society.

In a similar study, Cheng et al.[9] produced plasmonic colours by fabricating MIM surfaces using holes instead of disks, see Figure 9. The metal-insulator-metal interface consisted of a 30 nm aluminum layer, a 45 nm alumina layer and a 100 nm of aluminum layer all deposited by sputtering onto a silicon wafer. The hole arrays were machined into the 30 nm aluminum layer using a focused ion beam (FIB). By varying the periodicity of the holes and their size, the authors obtained a palette of 70 distinct colours. The origin of the colours by the MIM is explained by the authors has a highly confined propagating SPs excited by the periodic hole arrays.

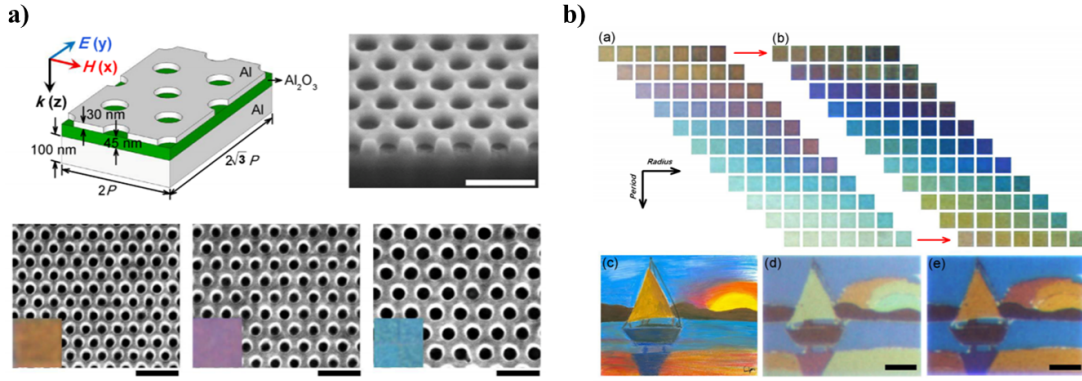


Figure 9: (a) Schematic of the fabricated MIM surfaces by Ref.[9] consisting of a 45 nm thick alumina film sandwiched in-between 2 aluminum films. The top 35 nm aluminum film was machined by FIB to create the so called “holey” film. The colours obtained by the MIM were observed to be dependent on the periodicity and the size of the holes. (b) Demonstrates the colour palettes obtained by varying the periodicity and the size of the holes (top-left) before and (top-right) after the deposition of a passivation layer of PMMA. The authors applied their colour palettes to an image of a sail boat on the waters at dusk. The authors demonstrate the effect of the PMMA layer with a side-by-side comparison of the fabricated image before and after the application of the passivation layer. Reprinted (adapted) with permission from Ref.[9]. © 2015 Optical Society of America.

The dielectric spacer acting as a bridge to couple SPs on two separate metal-insulator interfaces resulting in an optical magnetic resonance. The hole arrays are fabricated in a triangular arrangement to separate the first two SP resonances in the gap. To protect the MIM surface, a layer of 100 nm of PMMA is deposited onto the MIM metal interface. The plasmon resonances were observed to red-shift with the introduction of the PMMA layer. In addition, surprisingly, the colour saturation is observed to be significantly improved with the introduction of the PMMA layer. The authors explained this phenomenon by the higher degree of symmetry at the hole interface (PMMA-alumina, air-alumina) creating a stronger coupling which in consequence causes a stronger magnetic dipole enhancing absorption. This increase in absorption is paired by a broadening of the spectrum due to a slightly weaker confined electric field. Murthy et al.[97] demonstrated the transfer

of such features in a rolling process they claim meets industry requirements.

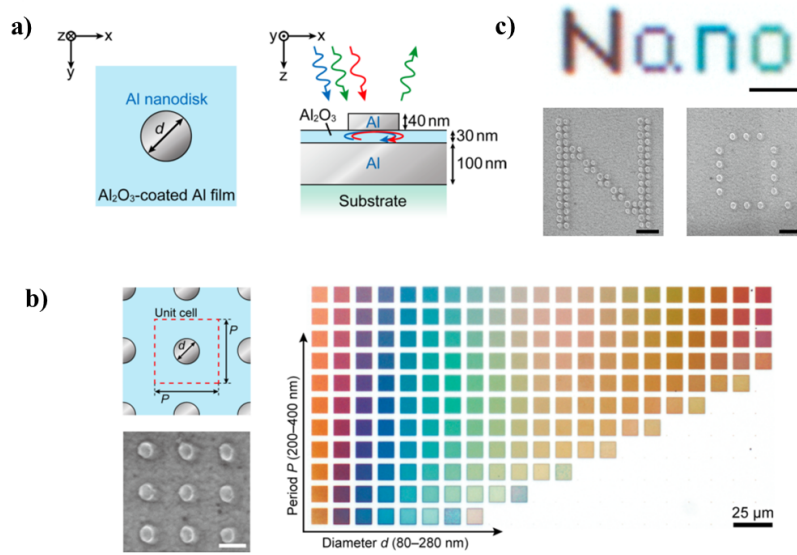


Figure 10: (a) Schematic of the MIM surfaces fabricated by Ref.[10] consisting of a layer of 30 nm of alumina sandwiched between a 40 nm top and 100 nm bottom layer of aluminum. The top layer of aluminum is machined by EBL to create an array of aluminum nanodisks. (b) Colour palettes obtained by varying the period and diameter of the aluminum nanodisks. (c) The authors used their fabrication technique and surfaces to spell the word “Nano” in colour. Reprinted (adapted) with permission from Ref.[10]. © 2016 American Chemical Society.

Miyata et al.[10] proposed and demonstrated the colouring of surfaces via single nano-antenna pixels using MIM interfaces. The metal-insulator-metal interface was fabricated by depositing a 40 nm thick layer of aluminum onto a 30 nm film of alumina deposited onto a 100 nm film of aluminum, see Figure 10. The use of the MIM concepts confines strong standing-wave resonances into the MIM insulator gap. The strong light absorption of the two distinct frequencies in the nanogap of the single nano-antenna pixel is shown to allow for the creation of saturated and distinct colours. The resonances condition and the different colours are obtained by changing the size of the single nano-antennas. Due to the strong confinement of gap-plasmon, very weak coupling is observed between close proximity nano-antennas. Hence, to increase the absorption and saturation of the colour, more single nano-antennas are placed in the nanostructure coloured area with an

optimized periodicity of 300 nm. With a square arrangement of 3 different size of nano-antennas, the authors created dark pixels with a reflectance of $\sim 30\%$ with no distinctive features. To protect the surfaces, a film of PMMA was deposited on the MIM resulting in a distinctive red-shift of the colours. The authors claim that the shift could be compensated prior to the deposition of PMMA in order to obtain the desired colour outcome.

Lu et al.[11] produced plasmonic colours in transmission by the fabrication of inverse nano-pillars in a 200 nm thick PMMA film placed onto a quartz substrate. The holes were fabricated using EBL and a 60 nm metal film was subsequently deposited creating a flat metallic top surface and a bottom metallic disk, see Figure 11. The authors studied the creation of transmitted plasmonic colours using 3 different metal films: Au, Ag and Al. The colours produced using Au was deemed of lesser quality due to the interband transitions of gold at 525 nm. While both Ag and Al produced large colour palettes, the authors claimed Ag to be better at creating plasmonic colours in transmission. The different colours were obtained by varying the periodicity and the diameter of the holes. During fabrication, the authors observed severe colour degradation in the transmitted colours for hole-depth lower than 100 nm which they attributed to plasmon hybridization originating from the interference of the plasmon resonance coming from the top and bottom metallic surface. This hybridization (or interference) is explained to create a “bonding” resonance associated to an out-of-phase charge oscillation and an “anti-bonding” resonance associated to in-phase charge oscillation from the separated metallic layers. FDTD simulations were made to demonstrate this phenomenon. A systematic study on different hole-depth revealed that hole deeper than the longest visible wavelength lacked near-field interactions causing the transmittance spectrum features to split. Hence, to achieve colour stability a depth of 200 nm to 350 nm was good enough to limit hybridization and maximize near-field interactions. To study the evolution of the colours using Ag which creates a natural oxide layer of 1 to 2 nm, the authors conducted FDTD simulations to observe the change of colour over time. To demonstrate industrial viability of the technology, the authors produced a mole and transferred the coloured features via NIL with the highest resolution of 127 000 dpi.

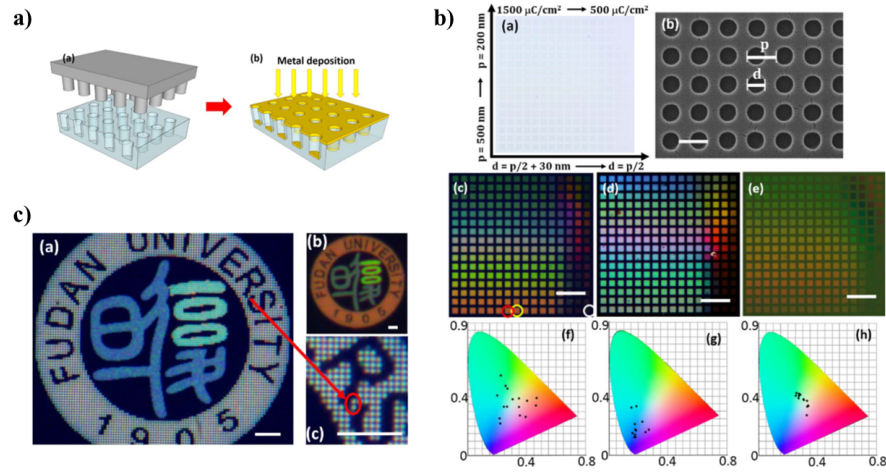


Figure 11: (a) Schematic representation of the fabricated surfaces by Ref.[11]. The “holey” film is created via a hot embossing process followed by the deposition of the metallic film. (b) Compares colour palettes obtained using the 3 different metallic films: (c,f) Ag, (d,g) Al and (e,h) Au. The different colours were obtained by changing the periodicity and size of the holes. (c) The authors using NIL fabricated a colourful logo of the Fudan University with a resolution of 127 000 dpi. Reprinted (adapted) with permission from Ref.[11]. © 2016 Optical Society of America.

Yu et al.[12] demonstrated plasmonic colour tuning by controlling the contact angle of silver nanocaps via a dewetting process, see Figure 12. Films of silver were deposited on the surface of SiO_2 using a magnetron sputtering technique. The nanogaps were produced by the heating of the samples at certain temperatures and durations. During heating, the film would break down and with a high surface energy merge into silver islands creating nanocaps. The size and density of the nanocaps (or nanoparticles) is found, by the authors, to be controllable by varying the silver film thickness. For thicker films, it is observed that larger nanocaps are created at a much lower surface density. Additionally, the reflectance is red-shifted with increasing thickness and colours are also observed to be much lighter. Hence, the authors choose thicknesses between 3 to 10 nm in order to optimize colour rendition. Due to the nature of the assembly (*i.e.* silver on glass), the authors observed a strong degree on dichroism like the famous Lycurgus cup.[98, 99] The authors were able to obtain a full colour palette by tuning the contact angle of the silver nanocap with the SiO_2 substrate for a fixed diameter of 10 nm. The study also extended to other diameters of varying contact angles. The control of the contact

angle and the nanocap size during the dewetting process was accomplished by varying the temperature and duration of heat exposure. Simulations of the geometry based on SEM analysis, for $D = 10$ nm at different contact angles, showed very good agreement with experimental reflectance and transmittance. The surface was also protected by the sputtering deposition of a 150 nm layer of PMMA.

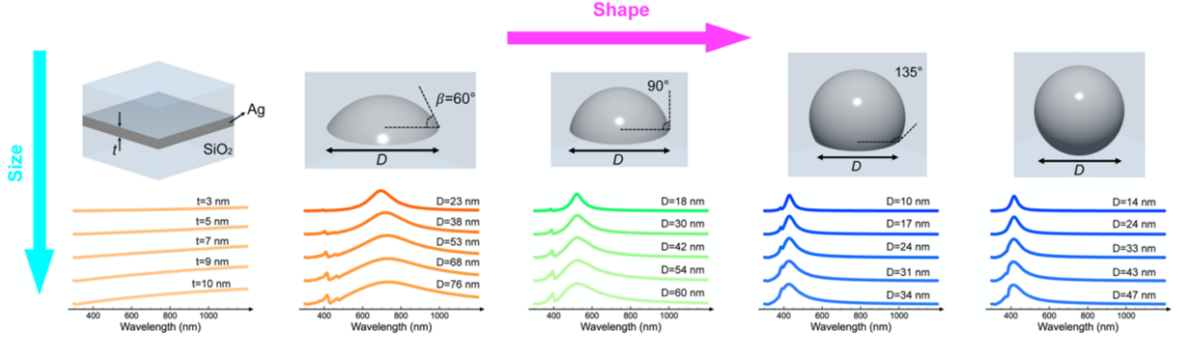


Figure 12: The far-left panel demonstrates the surfaces prior to subjecting the silver film to elevated temperatures. After exposure to elevated temperature, the silver film is observed to dewet, resulting in the formation of NPs. The contact angle is controlled by the temperature and duration of exposure. The size of the NPs is controlled by the thickness of the silver film. The colour obtained with this technique is shown to be highly dependent on the contact angle and not so much on the size of the particles. Reflectance spectra for a fixed contact angle and varying NP sizes are presented. Reprinted (adapted) with permission from Ref.[12]. © 2016 American Chemical Society.

The dewetting approach for tuning plasmonic resonances has had growing interest in the field. Zhu et al.[13] used lasers to dewet their aluminum disks and control the contact angle between the disk and the surface of nanopillars (discussed earlier in this section, see Ref.[12]). The dewetting of the aluminum capping disk and the contact angle is controlled by the energy of a ns laser pulse, see Figure 13. A wide range of colours was obtained for a fixed nanopillar size, height and periodicity. Han et al.[100] dewetted nanoparticles directly from a gold film deposited onto a SiO_2 substrate using a dual-wavelength interference approach. The different colours were obtained by controlling the nanoparticle size and contact angle via different laser energy pulses. Wang et al.[101] cleverly created nanovoids by focusing the laser into the SiO_2 substrate instead of the gold film lifting the gold film by the nanopotrusion of the SiO_2 . The nanofeatures orig-

inate from the nanovoids created from the confined plasma located close to the surface instead of the dewetting approach. The different colours were obtained by controlling the height of the nanofeatures via the laser pulse energy and the pressure of the confined plasma slightly below the surface.

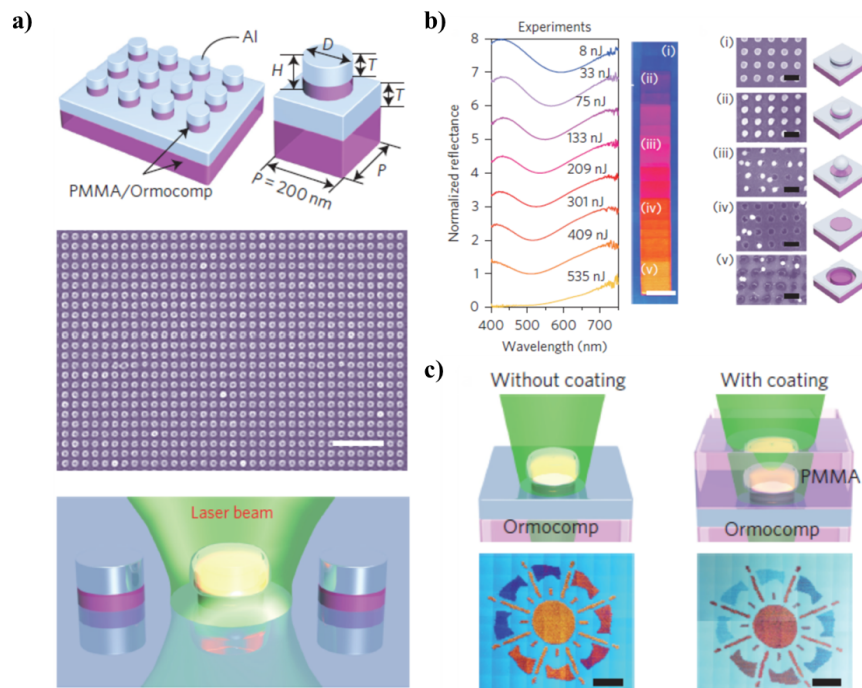


Figure 13: (a) Schematic representation of the fabricated surfaces composed on PMMA nanopillars capped with an aluminum disk and an aluminum film covering the lower surrounding areas. The capped aluminum disks are modified through a dewetting process by exposing the disks to a nanosecond laser source. (b) Reflectance spectra for different laser pulse energy exposure of the nano-aluminum disks. The morphological transformation of the disks by dewetting are represented in the right panel. (c) Colour design with and without the protection layer of PMMA. The colours are observed to lose vibrancy and shift with the PMMA coating. Reprinted (adapted) with permission from Nature Ref.[13] © 2015

Olson et al.[14] fabricated vivid colours for potential applications in televisions using plasmonic nanorods, see Figure 14. The surfaces were fabricated via the deposition of 30 nm of aluminum using an electron beam evaporator onto an EBL patterned PMMA

substrate. The authors chose aluminum due to low cost and their ability to create vivid colours. The downside of using aluminum was the red region, which is spectrally broad due to the interband transitions of aluminum beyond 600 nm. The authors proposed the use of nanorod arrays to exploit the far-field diffractive coupling to narrow the spectral response in the red region and produce more vivid colours. The far-field diffractive coupling can be tuned by the disposition (y-direction) of the aluminum array of nanorods while the plasmonic resonance is controlled by the aspect ratio of the nanorods.

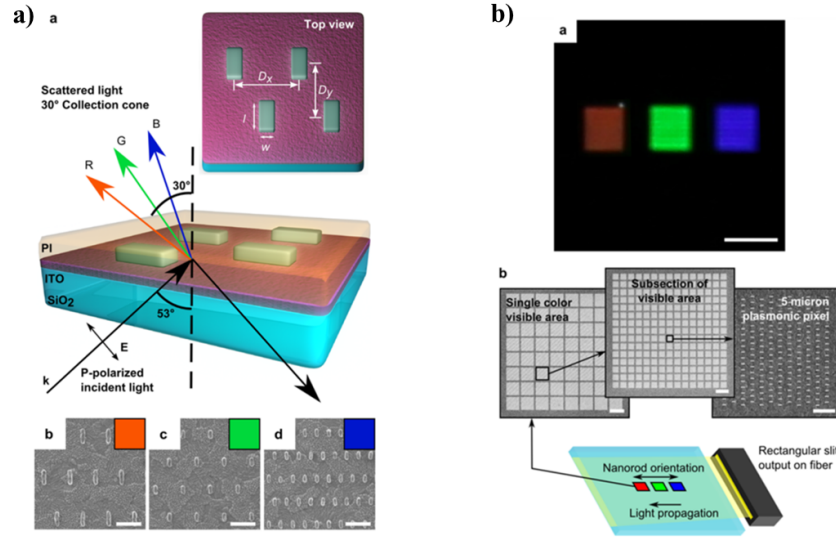


Figure 14: (a) Schematic representation of the surfaces fabricated by Ref.[14]. The surface consists of aluminum rods fabricated by EBL. The different colours were obtained by offsetting the nanorods in both the x and y direction to tune the Fano resonance and the diffractive coupling. (b) RGB pixels were fabricated by the authors to provide proof of concept to the introduction of the technology into LCD displays. Reprinted (adapted) with permission from Ref.[14]. © 2016 American Chemical Society.

To narrow the spectral response in the blue region, the authors shifted the nanorods (x-direction) introducing an extra tuning element to the surface: Fano resonances. The disposition in both lateral directions combined with the aspect ratio allowed the authors to create an impressive range of colours. Due to better performance of gold in the red regions, the authors discussed combining 2 arrays of aluminum and 1 array of gold to create an RGB pixel. Due to the polarization sensitivity of the nanorods, the surfaces were deemed ideal for their introduction into an LCD. The colours were observed to

disappear with the application of a voltage in the LCD. The colours were, however, angle-dependent. The authors claim that a diffuser could be used to render the colours angle-independent.

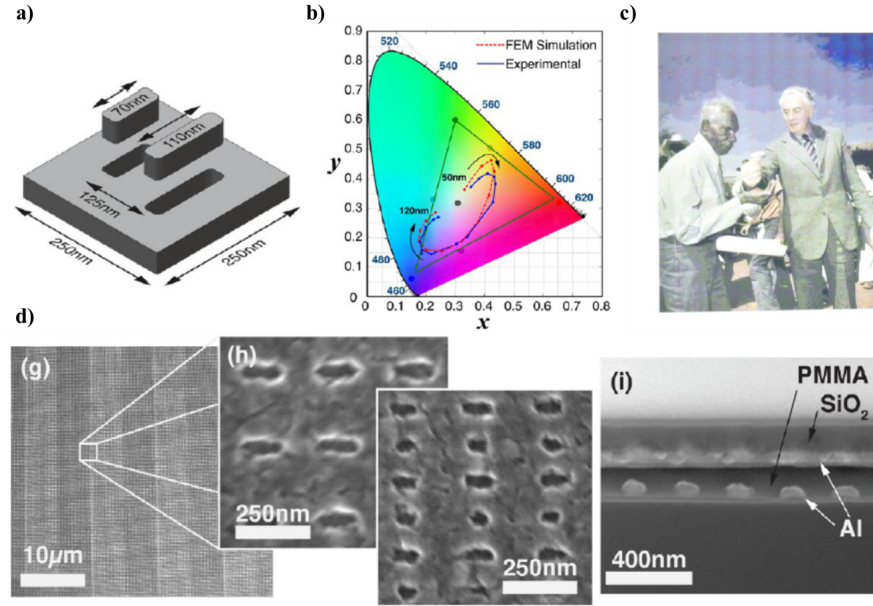


Figure 15: (a) Schematic representation of the fabricated MIM surface. The aluminum nanorods are held above the metallic aluminum film using a PMMA layer. (b) CIE xy diagram of the colours obtained by changing the dimensions of the nanorods. Very few green colours are obtained with this technique. (c) Image fabrication obtained by the disposition of proper nanorod configurations to create the desired pixel colours. (d) SEM close-up of (c) showing the different arrangements of the surface to create the desired colours. Reprinted (adapted) with permission from Ref.[15]. © 2016 American Chemical Society.

The use of nanorods for colouring was also demonstrated in the work of James et al.[15] where the authors used aluminum nanorods and placed them above the metallic surface in a technique they call floating dipoles. The aluminum rods are held above a metallic surface by 30 nm. The bottom metallic surface is patterned with hole features that are of the same dimension as the nanorods located above them. The different colours were obtained by changing the dimension of the nanorods, see Figure 15. Like Olson et al.[14], the plasmonic response and colours were sensitive to incident light polarization. Black like colours were obtained by placing 2 floating nanorods of different

dimensions in proximity of each other. The surfaces were fabricated by EBL on PMMA and the aluminum was deposited by evaporation before being capped by a layer of SiO_2 . Alternatively, Li et al.[102] demonstrated polarization sensitive colours by fabricating cross-shaped apertures in an aluminum film. The colours observed with the different polarization was tuned by changing the lengths of the cross arms. The authors also showed that a combination of different apertures could be used to tune colours in the far-field.

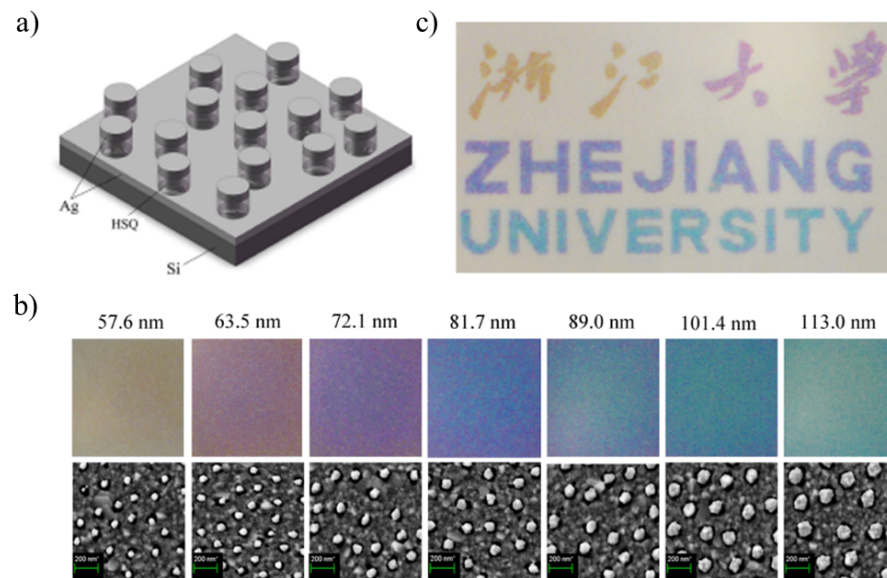


Figure 16: (a) Schematic of the surfaces fabricated by Ref.[16]. Silver is deposited on pillars of hydrogen silsesquioxane creating a silver nanodisks hovering above a holey film. The nanofeatures were randomly placed on the surface giving an angle-independence to the produced colours. (b) Colour palette produced by changing the diameter of the nanodisks randomly dispersed on the surface. (c) Randomly dispersed nanodisks of various sizes were used to spell out “Zhejiang University” in colour. Reprinted (adapted) with permission from Ref.[16]. © 2017 Institute of Physics.

Wu et al.[16] demonstrated the creation of angle-independent colours by the fabrication of randomly placed nanopillars. The surface and nanofeatures were fabricated by the machining of hydrogen silsesquioxane (40 nm in height) using EBL and by the deposition of a 20 nm Ag film by electron-beam evaporation. The end result of this fabrication, like other groups in this section, consists of metallic disks hovering above a “holey” metallic film, see Figure 16. The authors discuss that reflection colour filters often exhibit angle

sensitivity due to the momentum-matching of SPPs caused by the underlying periodic structures. The authors proposed that the creation of randomly placed nanopillars would hinder long range SPPs and favour uncoupled localized SPPs (LSPPs) necessary to render the colour angle-independent. A systematic simulation study of varying disk diameters and inter-disk distances showed that strong short range SPP (SRSPs) dominated over LSPPs at inter-spacing of 40 nm. For inter-disk spacing over 80 nm only LSPPs were observed. From the simulations, the authors, chose to maintain an inter-disk spacing of 80 nm between the randomly place nanopillars to maximize the nanopillar density within the fabricated areas. A full colour palette was obtained by changing the size of the capping silver disks. The author confirmed the angle-independence of their surface by recording their colours at various angle from 0 to 70 degrees.

Duan et al.[17] demonstrated the fabrication of dynamic colour display based on the use of magnesium nanoparticles. The surface arrangement responsible for the colours consists of square magnesium nanoparticles placed in between a capping layer of Ti/Pd and an adhesion layer of Ti. The nanofeatures were placed on a 100 nm film of SiO₂ supported by a Si substrate, see Figure 17. The different colours were obtained by changing the size of the squared Mg nanoparticles and the inter-distance between each of the Mg nanoparticles. The authors show the colours were erased by exposing the nanostructures surface to hydrogen gas. The rate of colour change was observed to be dependent on the size of the Mg nanoparticles. The authors explained this phenomenon by the intrinsic property of Mg which undergoes a metal-to-dielectric transition when exposed to hydrogen forming MgH₂. The capping layer of Ti/Pd was cleverly introduced in the design due to the catalytic properties of Pd. Pd dissociates the hydrogen molecules into hydrogen atoms which are then allowed to diffuse through the Ti adhesion layer forming MgH₂. Subsequently, when the surface is exposed to oxygen, the colours are observed to return via a dehydrogenation process. This was explained by the exposure of MgH₂ to O₂ which will form Mg and H₂O resulting in the recovery of the original structures. However, it was observed that the colours did not fully recover after dehydrogenation. The authors claim that the dimensions of the Mg nanoparticle may have slightly changed during the hydrogenation and dehydrogenation process.

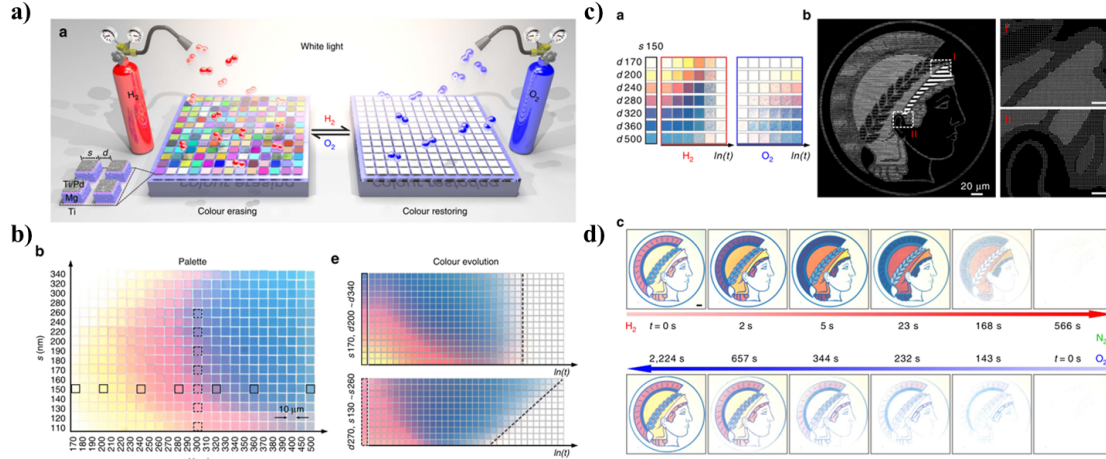


Figure 17: (a) Cartoon representation of exposing the fabricated Mg NPs to gases of H₂ and O₂. (b) The colour palette is obtained by varying the size, s , and the inter-particle distance, d , of the Mg NPs. (c-d) Demonstrates the evolution of the colours with exposure to H₂ gaz. Various colour designs were used to demonstrate the fading and recovery of the colours; one of the designs was the Max Plank crest. The authors demonstrate the evolution of crest over time when exposed to the H₂ gas. Reprinted (adapted) with permission from Nature Ref.[17] © 2017

Xue et al.[18] demonstrated the colouring of surfaces using a method they named “confugate two-phase modulation” (CTPM). This method consists of placing a dielectric film on a metallic substrate to maximize peak-valley ratio in the reflection spectra and to place a thin metallic layer on the dielectric to act as a broadband plasmonic absorber, to narrow the peaks of the reflection spectra. The surfaces were fabricated by the electrochemical growth of a film of anodize alumina oxide (AAO) followed sputtering of a thin film of silver, see Figure 18. The authors explain that the thickness of each layer be such that constructive interference should occur at both the reflection interfaces of the dielectric and destructive interference occurs at the metallic interference for the same wavelength. This thickness of the silver film should, however, not be thick enough to significantly change the phase of the light. The authors demonstrated this interference colouring scheme and showed that large light absorption could be achieved and could be tuned to the desired part of the spectrum. However, for flat metallic films only a sharp narrow absorption peak could be obtained. To narrow the reflection peaks, the authors

replaced the flat film and introduced a rough film composed of various shapes and sizes of nanoparticles causing a broadening in absorption. The colours could be tuned by changing the thickness of the AAO film. Furthermore, the authors also demonstrate that the colour could be tuned by changing the refractive index of the AAO film. The change in the refractive index was obtained by producing pores and changing the volume fraction of pores by immersing the AAO film in acid for different periods of time. Additionally, filling the pores with different liquids was also observed to change the perceived colours.

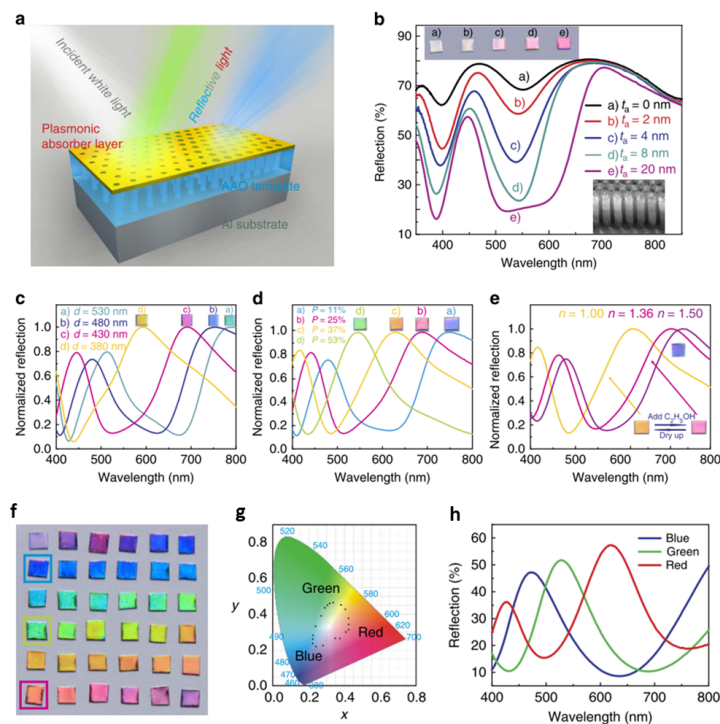


Figure 18: (a) Schematic representation of the MIM fabricated by Ref.[18] consisting of an aluminum substrate with a deposited AAO film covered by a “holey” silver film. The authors demonstrate that the colours can be tuned by varying the thickness of the (b) Ag film, (c) the thickness of the AAO film, (d) the porosity of the AAO film and (e) by changing the refractive index. (f) The authors demonstrated the colour palette obtained with increased etching time of the AAO film. (g) CIE xy diagram of the colours obtained by the authors and (h) reflectance spectra of the RGB colours. Reprinted (adapted) with permission from Nature Ref.[18] © 2016

Li et al.[103] produced colours by the direct machining of an aluminum surface. The aluminum film was deposited by electron beam evaporation onto a substrate of SiO_2 .

The trapezoid shaped aluminum nanostructures were then fabricated by focused ion beam milling. The authors demonstrated the creation of colour palettes by changing the height, size and periodicity of the aluminum trapezoid like structures. However, due to the periodicity of the nanostructured surface, the colours were observed to be highly angle-dependent. Simulations of the structures revealed a strong magnetic dipole resonance concentrated in the trench located in between adjacent nanostructures. Similarly, a strong electric dipole resonance was observed at the top of the aluminum trapezoid. In a follow-up study, Wang et al.[104] used tapered v-grooves in between the aluminum trapezoid nanostructures. They showed that the plasmonic resonance shifted linearly with the groove depth. The authors additionally showed that the use of two groove depths, orthogonal to each other, around the aluminum trapezoids generated polarization dependent colours. The authors claim that such effects could be used in security marking applications.

Yun et al.[19] demonstrated the ingenious colouring of surface by the fabrication of a small nanoaperture within metal cavities. The surfaces were fabricated by the electron beam evaporation of a silver film and by the machining of cavities by focused ion beam milling. The authors fabricated the metal cavities to generate within it standing waves by the excitation of SPP waves. Within the cavity, small apertures were placed strategically in order for it to fall at a node or anti-node to select certain wavelength of the standing wave. For a standing wave where the nanoaperture coincided with a anti-node, the light was re-emitted on the other side of the nanoaperture. This technique allowed the extraction of light from the cavity and to selectively choose a specific wavelength and amplitude. Additionally, such cavities were polarization sensitive which the authors claim would have applications in colour display. The concept was tested on a multiplexed cavity aperture. An asterisk like feature composed of 3 distinct arms of different lengths with a common nanoaperture was fabricated. The 3 length of the arms were designed to support green, red and blue colours with a common anti-node at the center nanoaperture. From these structures, the authors showed the selective colours (RGB) could be transmitted by controlling the incident light polarization.

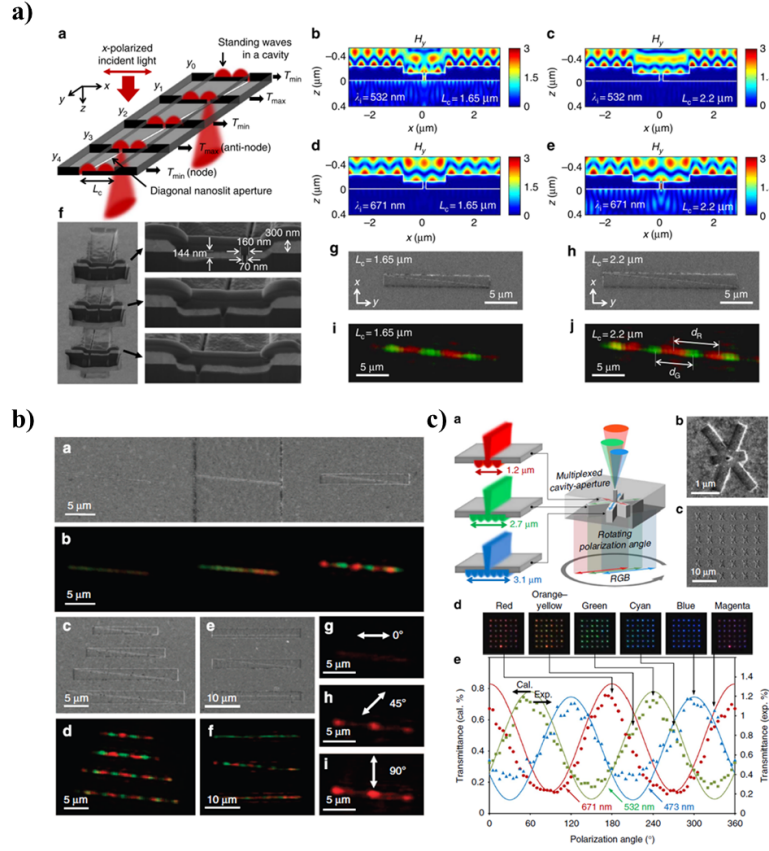


Figure 19: (a) Schematic representation of the surfaces fabricated by Ref.[19]. The surfaces consist of a cavity trench with an aperture located in the approximate center. With white light exposure, a standing wave is created in the cavity. For wavelengths with anti-nodes coinciding with the aperture, the light is re-emitted on the other side of the aperture. (b) The location of the aperture is moved within the cavity in order to selectively choose the wavelength emitted through the aperture or by controlling the length of the cavity. Furthermore, given the condition for supporting a standing wave inside the cavity, the transmission of light was highly polarization dependent. (c) The authors demonstrate that overlapping cavities can be designed to have a common anti-node for multiple wavelengths permitting the creation of a single RGB pixel. Reprinted (adapted) with permission from Nature Ref.[19] © 2015

2.1.2 Fabrication of coloured surfaces by direct laser writing

In the previous section, the nanostructures were generally prepared using lengthy procedures which are mostly incompatible with industry and present a significant challenge to scale-up. The colouring of metals using continuous wave (CW) and pulsed lasers with pulse duration longer than a few hundredths of picoseconds have shown to produce colour on the surface of metals through the formation of thick oxides. However, it wasn't until recently with the commercialization of ultrafast lasers, with pulses shorter than a few tenths of picoseconds, that the colourization of metals by plasmonic means has been achieved. The literature review on the direct laser writing of fixed angle-independent colours on the surface of metals rendered by plasmonic means is virtually non-existent. Additionally, the role of oxides on the ablation products (i.e. NPs) and the observed colours is still an open question.

Vorobyev et al.[20] were able to produce gold and grey aluminum[105], blue titanium[20] and the now famous “black” metal, see Figure 20. The famously “black” metal was produced on the surface of platinum, gold, aluminum and titanium.[20, 106] In their publications, the authors never clearly mention the different parameters used in order to obtain the different colours and black surfaces. They state that the parameters were carefully chosen without giving any detail on the parameters used. Nonetheless, the authors claimed the colours to be plasmonic in nature. The origin of the colours was attributed to the deposition of nanoparticles on top of the femtosecond-LIPSS (FLIPSS). The authors would later refer to them as NC-LIPSS or nanostructure covered LIPSS. In a subsequent study,[107] from the same group, showed that the femtosecond ablation of aluminum in air, produced oxidized material. Surface comparison of the machined aluminum in both air and argon showed the presence of nanoparticles next to the ablated lines. The authors explained the interaction between the ejected material and the ambient gas as nanochemical effects where the most chemically active products were from the ejection are the ions and atoms due to their increasing area-to-volume ratio. In this study they showed that a fraction of the incident laser energy was observed to transit into chemical energy. At lower fluence this amount was said to be very low, however, it is observed to increase linearly with laser fluence. For a laser fluence of 12.12 J/cm^2 , the authors claim that 13% of the incident energy takes the chemical energy path and that 50 % of the released ablated aluminum is oxidized. The authors claimed that oxidation played no role in the direct colouring of metal's surface with femtosecond lasers.

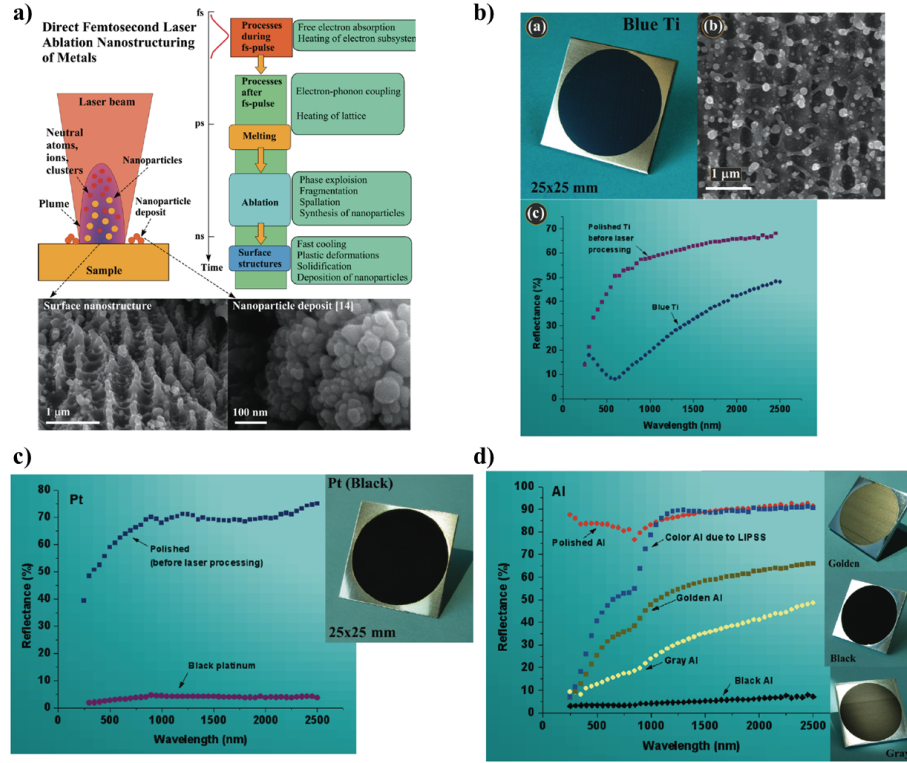


Figure 20: (a) Model proposed by the authors on the process of ablation, creation and re-deposition of NPs on the material's surface. (b) Blue titanium, (c) black platinum, (d) gray, golden and black aluminum and their appropriate reflectance obtained by the authors by exposing the material surfaces to different laser parameters. The colours are said to be plasmonic in origin and from the re-deposition of NPs on the modified region after ablation. Reprinted (adapted) with permission from Ref.[20]. © 2013 John Wiley and Sons.

The creation of fixed colours rendered by plasmonic effect was believed for many years to be unique to femtosecond lasers. In 2013, Fan et al.[108, 109, 21] showed the colouring of copper using a picosecond laser producing 10 ps pulses. While they add only a limited colour palette, the number of colours obtained on copper already surpassed the few colours obtained by Guo et al.[20]. The colours were obtained by raster scanning the copper surface with speeds up to 5000 mm/s. The different colours were obtained by changing the line spacing, the energy and machining speed. The authors attributed the colours to the nanoparticles redeposited on the surface of copper following laser ablation, see Figure 21. A statistical analysis of the different coloured surfaces was provided and showed the particles to increase in size and proximity with decreasing machining speed.

The surfaces were machined in air using a laser repetition rate of 2 MHz which was claimed to cause no heat effect.[61]

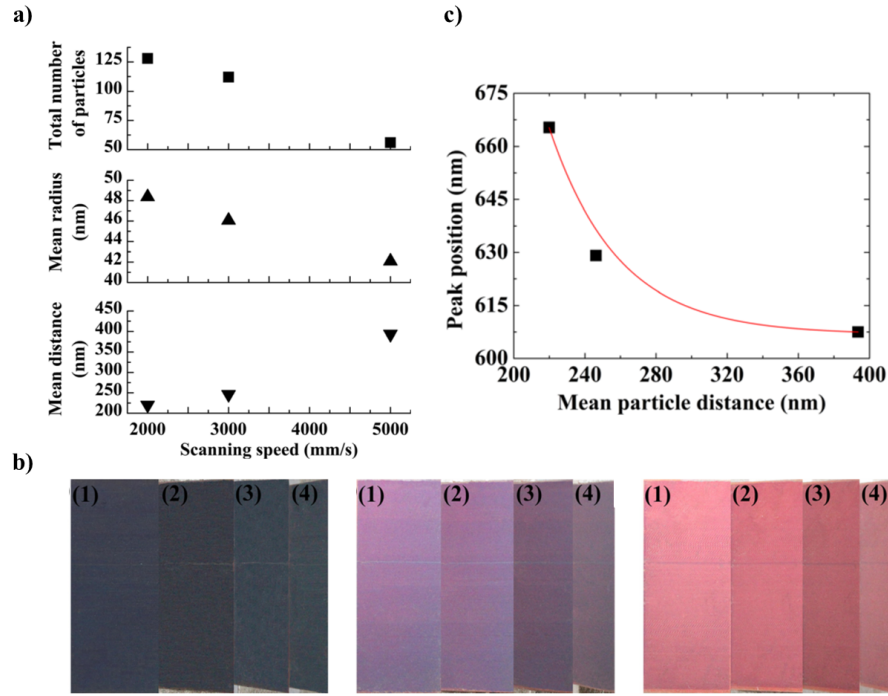


Figure 21: (a) NP statistics presented by the authors of the coloured regions obtained on copper. (b) Blue, purple and pink angle-independent colours obtained on the surface of copper. The different colours were obtained by changing the machining speed of the raster mirrors for fixed line spacing. (c) Graph of surface plasmon resonance versus inter-particle distance presented by the authors and obtained from the reflectance spectra of the colours and the statistics of the surfaces. Reprinted (adapted) with permission from Ref.[21]. © 2014 American Institute of Physics.

The direct colouring of metals by the previous groups mentioned in this section are said to come from plasmonic effects, however, the production of full colour palettes by controlling oxide thickness using lasers has long been demonstrated. Antonczak et al.[110] and Gorny et al.[111] both showed the formation of full colour palettes on the surface of stainless steel via the use of 100 ns laser pulses. The authors explain the different colours by the different thickness of the induced oxides. They establish a set of parameters to generate a wide range of colours and demonstrated the colouring technique to create different logos. In a similar study, Laakso et al.[112] demonstrated the colouring of stainless steel using a MOPA laser using a pulse duration of 200 ns up to 1 μ s. The

oxide thickness produced, for the colours, was measured to be 310 nm to 340 nm thick. In both cases the colours were observed to be angle dependent due to the nature of oxide films.

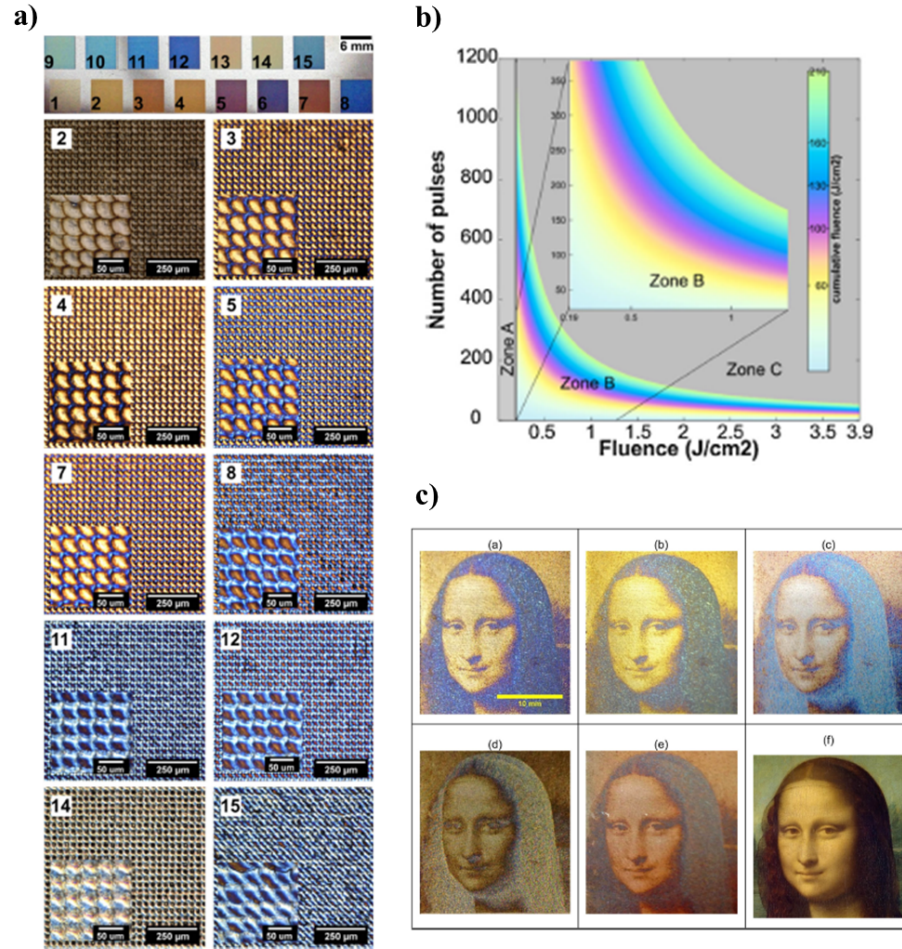


Figure 22: (a) Colours obtained by Jwad et al.[22] using their so called single spot colorization technique. The colours were obtained by changing the cumulative fluence via the pulse energy, fluence and the repetition rate of the laser. (b) Graphical representation of the number of pulses versus fluence to create the different colours. The graphs are a representation of the colours obtained with total accumulated fluence. (c) Mona Lisa fabricated by the authors using their single spot colouring technique. The colours are angle-dependent as can be observed from the different viewing angle of the Mona Lisa. Reprinted (adapted) from Ref.[22], © 2016, with permission from Elsevier.

Jwad et al.[22] demonstrated the colouring of titanium using a 1064 nm laser producing pulses duration between 15 to 200 ns, see Figure 22. The colouring of titanium was

widely studied by other groups prior to this publication[113, 114]. The authors presented the colouring of titanium via a process they call single spot colourization. Each colour produced by this method is said to be dependent on a cumulative fluence similar to that of Guay et al.[115]. In order to produce the colours, the authors kept the laser fluence below ablation threshold, otherwise no colours were produced. To control the value of the cumulative fluence Jwad et al. changed pulse energy, fluence and the laser repetition rate of the laser from 1 MHz to 500 kHz. The colours produced by this method were angle-dependent. The authors claimed that this method to be transferable to other metals such as: niobium, steel, tantalum and chrome.

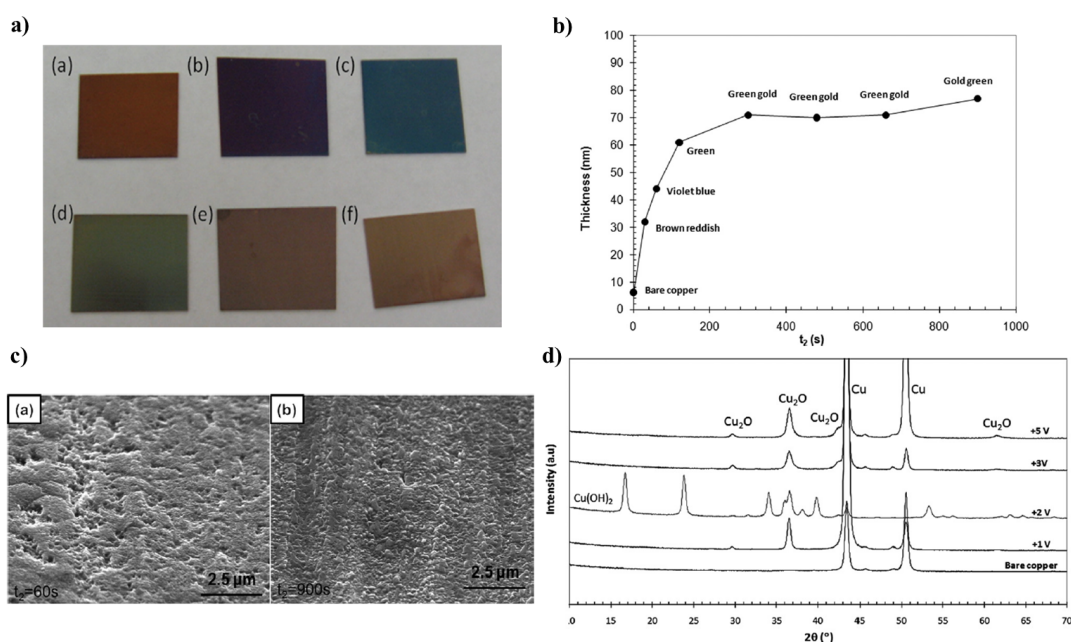


Figure 23: (a) Colours obtained by Fredj et al.[23] by controlling the thickness of the copper oxide via an electrochemical process. (b) Graphical representation of the oxide thickness as a function of immersion time after the removal of the potential bias. The colours for the different oxide thicknesses are identified. (c) SEM images of a blue (left) and green (right) colour copper surface. (d) XRD of the copper film for different potential bias showing the presence of copper oxides. Reprinted (adapted) from Ref.[23], © 2011, with permission from the ElectroChemical Society.

The following research article demonstrates the colouring of copper without the use of a laser. The article is placed in this section to prove a later point. Fredj et al.[23]

demonstrates the colouring of copper by the electrochemical growth of a copper oxide film. This was achieved by placing a piece of copper inside a hot concentrated solution of sodium hydroxide and by applying a potential bias to the copper, see Figure 23. With the applied potential and immersed in solution, a copper oxide film is formed, stripped away and dissolved in the solution. After the potential is dropped to zero, the oxide film is grown back into the surface of the immersed copper. The time the copper is left after the removal of the potential bias dictates the thickness of the oxide film. With this method the authors produced a wide palette of colours on copper. The surfaces were carefully examined using XRD, XPS and FESEM.

The point to be made with the previous paper is very simple: both chemistry and plasmonics have the ability to produce colour and both mechanisms are important to understand. The field of colouring metals via ultrafast lasers is still in its infancy but it requires a rigorous approach to properly understand the true mechanism behind the origin of the colours especially when machined in air. Both Vorobyev et al.[20] and Jwad et al. [22] produced colours on titanium and both Fan et al.[21] and Fredj et al.[23] produced colours on copper. It may be that both are right to claim the origin of the colours to be chemical and plasmonic. However, both Vorobyev et al.[20] and Fan et al.[21] claimed the surfaces to be plasmonic without providing chemical information of the surface or try to model their surface via FDTD to support their claims. The work presented in this thesis aims at providing a better understanding of the role played by both morphology and chemistry on colour formation.

2.2 Laser-Induced Periodic Surface Structures and their applications

The work contained in this thesis clearly sheds light on the use of lasers to produce fixed angle-independent colours on the surface of metals. However, the idea of using burst came to me during my initial work of painstakingly trying to produce quality LIPSS on the surface of silver at the beginning of my PhD. This story started with the directive of the RCM to generate diffractive gratings directly on the surface of silver, a metal plagued with a low electron-phonon coupling coefficient. In the quest to generate quality LIPSS I attempted to use the burst technology which we found enabled the creation of a wider colour palette with more intense colours.

2.2.1 LIPSS formation

The fundamental framework for the creation of LIPSS on the surface of materials was first proposed by Sipe et al.[63] They formulated the theory to explain the periodic structures observed on the surface of aluminum, germanium, silicon and brass. To create the structures, the authors irradiated the surface of the materials using a 20 ns, $\lambda = 1.06 \mu\text{m}$ laser source. The theory explained the formation of the LIPSS as an interference effect between the surface scattered waves and the incoming laser light. Their model is still used to explain the periodicity of the LIPSS structures.

Once ultrafast lasers that were capable of producing pulses shorter than the thermal expansion time[61] of metals were introduced to the scientific community, it was not long after that such lasers were used to study light-matter interaction on various materials. Vorobyev and co-workers[20] pioneered the work of studying light-matter interaction of femtosecond pulses with metal surfaces. In 2005, they first irradiated the surface of metals using a Ti:sapphire. They showed that the metals, when irradiated with femtosecond pulses, produced well defined LIPSS structures that were shorter or significantly shorter than the wavelength of light. The experimental study had been done in air with a normal incident laser beam. The findings were incompatible with the widely accepted model of Sipe et al.[63] The authors named the ripple structures as femtosecond laser-induced periodic surface structures (FLIPSS).[20] The authors claimed that such ripples could only be created using femtosecond lasers. In parallel, the authors showed that metals could be coloured by the FLIPSS by the diffraction of light from the periodic structures. The same authors pioneered the field and continued to study the effect of the exposure of various metals to femtosecond pulses and under various incident angles.[116, 117] Their comparison of the FLIPSS created on silver, gold and copper showed that the electron-phonon coupling properties played a crucial role on the definition of the ripple structures.[66, 118]

Less than a decade after the discovery of the FLIPSS structures, Huang et al.[24] provided an alternative interpretation and modification to the classical Sipe model.[63] The authors theorized that the surface plasmon polaritons were at the origin of the interference phenomena. It was theoretically demonstrated that the interference between surface plasmons and the incoming light would produce grating periodicities smaller than the wavelength of light. The model introduced by the authors, added to the classical model since SPP are by definition also SEW.[62] From the new interpretation of the interference

phenomena the authors explained the origin of the changing periodicity of the LIPSS. The authors claimed the period of the gratings to be directly linked to the free electron density, n_e . The higher the free the electron density the larger would be the LIPSS periodicity, see Figure 24. The grating periodicity changed depending on the intensity of the inbound laser beam. Later in this paper, the authors would describe the concept of SP-grating assisted coupling were the light and the SP wave are coupled more efficiently by the LIPSS as they remain and are not destroyed after each subsequent laser shot.

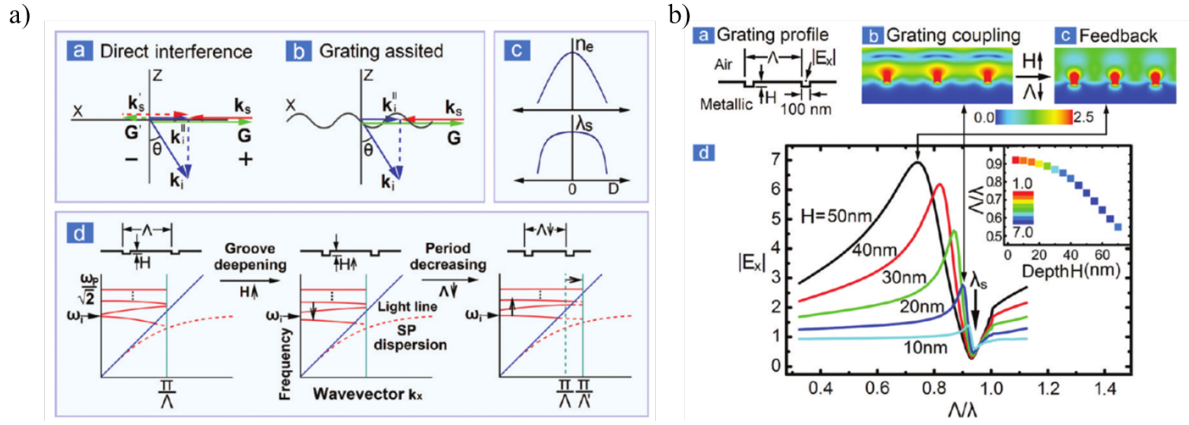


Figure 24: (a) Schematic demonstrating the origin of the LIPSS and the feedback of the surface by grating-assisted coupling to create LIPSS with periods that are smaller than the wavelength of light. The original LIPSS periodicity is said to be dependent on the free electron density causing the periodicity to change from the center of the modified region to the edge when the surface is irradiated with a Gaussian beam. (b) The presence of LIPSS for the feedback mechanism of grating-assisted coupling is explained to depend on the depth of the crevices due to field-enhancement. For deeper crevices, larger field-enhancements are observed leading to smaller LIPSS periodicity. Reprinted (adapted) with permission from Ref.[24]. © 2009 American Chemical Society.

2.2.2 LIPSS applications

The use of LIPSS for the purpose of decoration, anti-counterfeiting, sensing, and much more has been and continues to be widely studied[119, 120, 121, 54]. The field is currently saturated and therefore only a small fraction of the work is presented in this section.

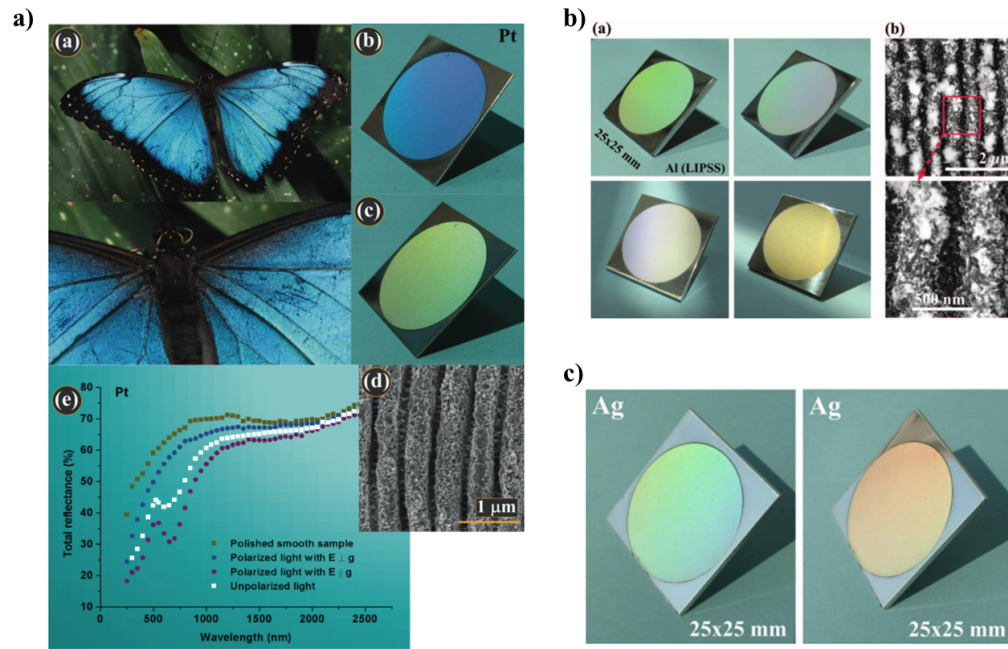


Figure 25: (a) Photograph, SEM images, and reflectance spectra of LIPSS structures and angle-dependent colours obtained by Vorobyev et al.[20] on platinum. (b) LIPSS and the diffractive angle-dependent colours obtained on the surface aluminum. (c) Photograph of angle-dependent colours obtained on the surface of silver. Reprinted (adapted) with permission from Ref.[20]. © 2013 John Wiley and Sons. Reprinted (adapted) from Ref.[25], with the permission of AIP publishing. Reprinted (adapted) from Ref.[26], with the permission of AIP publishing.

Vorobyev et al.[20] discovered the fixed colouring of metals while working on the creation of laser-induced periodic surface structures (LIPSS), see Figure 25.[20, 25, 26] While the creation of LIPSS was known from the work on Sipe et al.[63] many decades before, Vorobyev et al.[20, 25, 26] shown that the periodicity of the gratings could be smaller than the wavelength when exposing metal's surfaces to ultrafast laser irradiation. They used a Ti:sapphire laser with a central wavelength of $\lambda = 800$ nm producing pulse duration of 65 fs with a repetition rate of 1 kHz. The authors would later refer to them as femtosecond LIPSS (FLIPSS). The authors also demonstrated the creation of angle-dependent colours on the surface of silver, copper, aluminum and titanium due to the FLIPSS. The FLIPSS acting as a diffraction grating causing the viewer to see iridescence. The work by Vorobyev et al.[20, 25, 26] was the trigger that started the research into the application of LIPSS for security, anti-counterfeiting and much more.

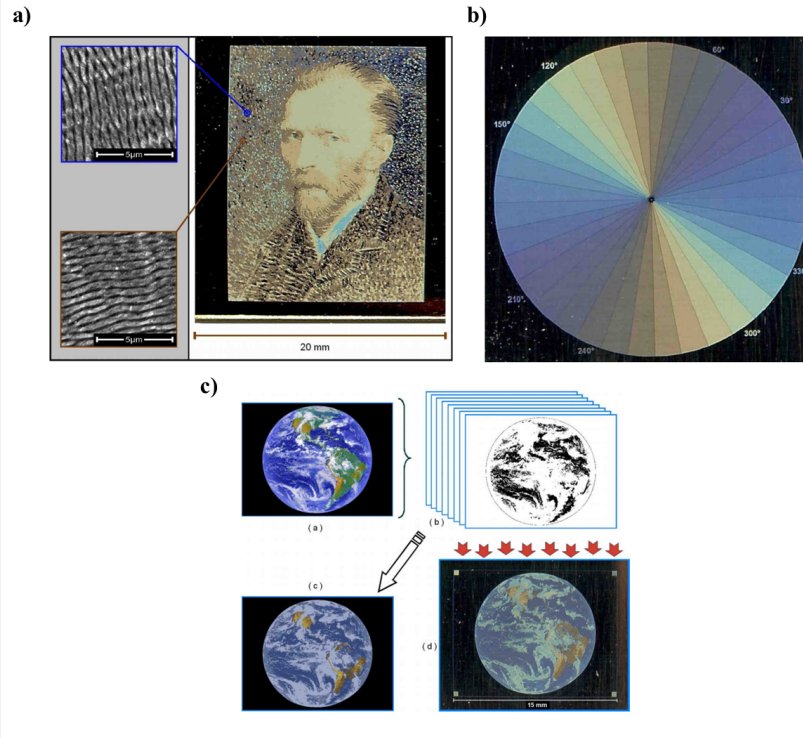


Figure 26: (a) Portrait created using LIPSS by Dusser et al.[27] viewed at a fixed viewing angle. The different colours were obtained by changing the orientation of the LIPSS purposely designed to give the desired colour at a specific viewing angle. (b) Circle composed of LIPSS created on the surface of 316L stainless steel written at different angles using a polarizer. The Circle was then placed on a typical white light scanner to determine the diffractive colours for a specific illumination and viewing angle. (c) The authors made a colourful reproduction of Earth by dividing the different colour into separated slices to facilitate the machining of the surface with the desired colours for a fixed viewing angle. Reprinted (adapted) with permission from Ref.[27]. © 2010 Optical Society of America.

In 2009, Dusser et al.[27] used a Ti:sapphire laser, $\lambda = 800$ nm producing pulse of 150 fs in duration at a repetition rate of 5 kHz, to colour the surface of 316L stainless steel. The colours were produced by FLIPSS and therefore were angle dependent. The authors showed that by controlling the polarization and as a result the orientation of the gratings, they were able to reconstruct famous paintings, see Figure 26. Dusser et al.[27] studied perceived colours for a fixed viewing angle and built a colour palette to generate the paintings. The colour palette was found by placing a stainless steel puck composed of various LIPSS orientation on the surface of a typical scanner.

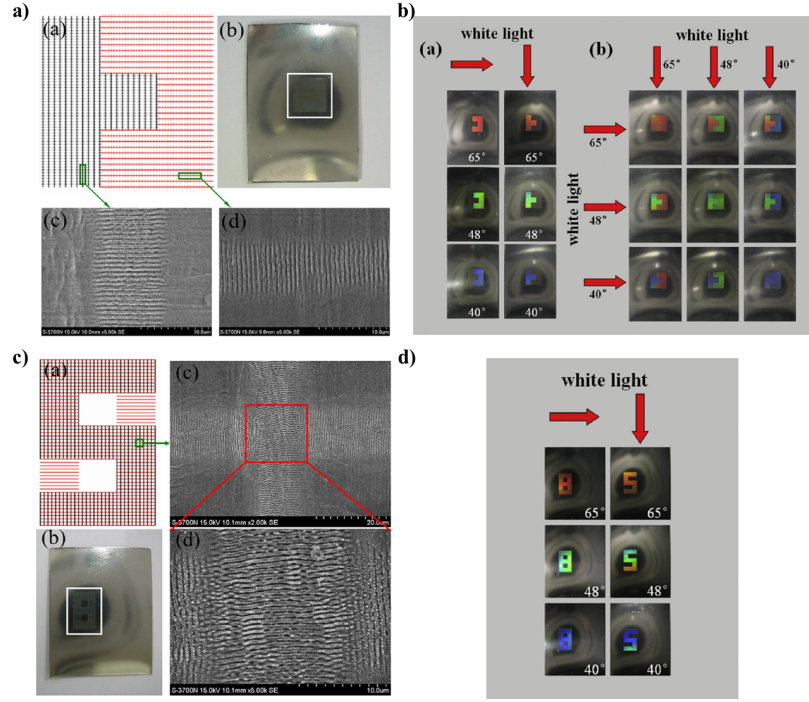


Figure 27: (a) Schematic representation, photograph and SEM images of the machined surface. Two features are machined at 90 degrees, such that when illuminated, some features are (b) turned on and off. However, for illumination other than 0 and 90 degrees with respect to the diffraction grating, both features are observed. (c) Schematic representation, photograph, and SEM images of a machined surface with region of overlap where LIPSS of orthogonal grating vectors are machined. This region of overlap allows for the creation of features that can change with different angle of illumination. For example, (d) the number “8” becoming a “5” when changing the angle of illumination. Reprinted (adapted) from Ref.[28], © 2012, with permission from Elsevier.

The overlapping of LIPSS structures for selective appearances for potential security applications on metals was first introduced by Yao et al. in 2012.[28] The authors showed that LIPSS of different grating orientation could be overlapped to create features that would change with viewing angle, see Figure 27. It was showed that an “8” could become a “5” simply by changing the angle illumination of the light. Their work on overlapping features and selective appearance would pioneer the use of LIPSS to generate motion on the surface of metals. The features were fabricated on the surface of 301L stainless steel using a Ti:sapphire laser producing a pulse duration of 90 fs at a repetition rate of 1 kHz.

Ionin et al.[51] demonstrated the formation of the femtosecond angle-dependent colouring

of Ti, Cu, Al and the semiconductor Si via the formation of LIPSS. The authors used a Ti:sapphire laser with a central wavelength of 744 nm producing laser pulses of 100 fs at a laser repetition rate of 10 Hz. Their study on the formation of LIPSS showed that the use of high fluences broke the definition of the LIPSS structures and that pulses slightly above threshold produced better LIPSS definition. The authors showed the evolution of the LIPSS which originate from the initial formation of a surface roughness evolving to form periodic surfaces, after a couple of laser shots. The authors observed the early LIPSS structures to form non-harmonic reliefs. These non-harmonic reliefs were said to come from the universal near-threshold nanostructuring phenomenon. The diffractive colours were said to be optimal for laser fluence slightly above threshold and that higher fluence led to a gradual and significant darkening of the angle-dependent colours.

Methods

This Chapter provides detail on the research equipment and the numerical simulations used during the research studies. More precisely, this chapter defines the machining apparatus and characterization equipment used for the creation of the plasmonic colours and their surface statistics. In addition, it provides specification on the methods and equipment used for the passivation of the coloured surfaces.

The beginning of the partnership between the University of Ottawa and the Royal Canadian Mint (RCM) initially started from the purchase of a picosecond laser system by the RCM whom envisioned leading the minting industry in the age of laser technology. However, lacking laser knowledge, the RCM reached out to Dr. Weck to start a collaboration. In the early months of the partnership much time was spent to evaluate and characterize the laser system, and to modify it for better performance. Soon after the initial assessment of the laser, several interesting applications were identified that could serve both academia and create profits for the RCM. The fixed colouring of metals was only one of these applications.

3.1 Laser system

The laser source used in this research project was a Master Oscillator Power Amplifier (MOPA) (Duetto, Time Bandwidth[®] Products) lasing using a Nd:YVO₄ gain medium. The MOPA was seeded by a Nd:YVO₄ oscillator functioning at a repetition rate of 8.2 GHz and mode-locked using semiconductor saturable absorber mirror (SESAM) technology. The laser is capable of producing a maximum energy per pulse of 0.5 mJ with a pulse duration of 10 ps at the fundamental wavelength of 1064 nm. The laser was fitted with an autoNLO box (Time Bandwidth[®] Products) with the appropriate internal optical elements to produce a frequency doubled (532 nm) and frequency tripled (355 nm) beam. However, while each wavelength was observed to obtain distinctive results that could be of further interest in the future, the research presented in this thesis concentrates only on the 1064 nm source. The laser repetition rate was tunable from 50 kHz to 8.2 MHz. For frequencies under 50 kHz, a pulse picker option could be used to block N shots out of M laser pulses. For example, a pulse picker of 2 at a repetition of 50 kHz would block half of the shots producing a laser repetition rate (as seen by the sample surface) of 25 kHz. In such a case, the pulse energy at 50 kHz and 25 kHz are equal due the same time passed in the gain medium and the laser cavity. Throughout this work, the majority of the experiments were conducted in between the laser repetition rate of 1 and 400 kHz.

3.1.1 Burst and FlexburstTM

The laser used during the experiments had the added feature and capability of producing laser bursts. The time separation between each of the pulses contained within the burst train is governed by the laser oscillator (8.2 GHz) for an intra-burst time separation of $t_{ib} = 12.8$ ns, see Figure 28. For the burst train, a selection of 1 to 8 bursts could be chosen to compose the burst train. A burst of 1 would be what laser physicists would normally know as a typical functioning pulsed laser producing a single laser shot at the set laser repetition rate. In our publications, a burst of 1 is referred to as nonburst. The idea of burst technology was patented to Peter Hermann from the University of Toronto. His group demonstrated the laser machining of glass without cracking using burst technology.[122] Following this discovery, burst was integrated into certain laser systems. The advantage of a burst laser was notable in areas of machining where it was shown to significantly increase the ablation yield of materials by increasing the electron-phonon coupling.[67, 123, 124, 125] Kerse et al.[126] also showed the use of burst in

medical application describing it as making “cold” ablation.

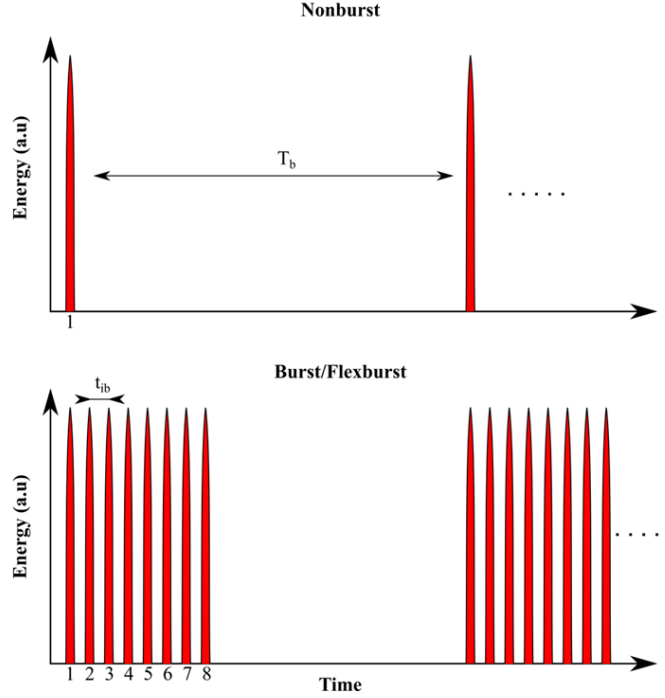


Figure 28: Schematic representation of the (top) nonburst and (bottom) burst pulse. The pulse-to-pulse time separation between the nonburst laser pulses is defined by $T_b = 1/f$ where f is the laser repetition rate of the laser in normal operation. In burst mode, 2 to 8 pulses can be selected. The time separation between each pulse within the burst is governed by the oscillator (8.2 GHz) and in this case $t_{ib} = 12.8$ ns.

The burst train exits the laser at the repetition rate of the laser, $f = 1/T_b$. The laser repetition rate was kept between 1 to 400 kHz. The creation of the burst pulse is shown in Figure 29. A series of 1 to 8 seed pulses (i.e. burst number) is sent from the oscillator into the amplifier. Each seed pulse enters the cavity and is amplified traveling back and forth inside the gain medium. However, due to the depletion of the gain medium (i.e. population inversion) the first seed pulse is more amplified than the second seed pulse, and the second seed pulse is more amplified than the third seed pulse, and so on. As a result, the burst energy distribution for each pulse within the burst train appears to form a trace of laser pulses of exponentially decreasing energy, see Figure 29.

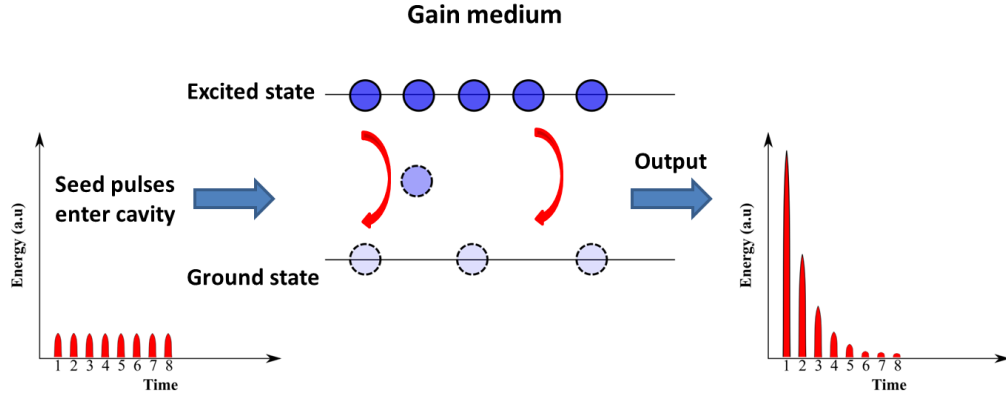


Figure 29: Schematic representation of the creation of the burst pulse. 1 to 8 seed pulses from the oscillator with a time separation of 12.8 ns is sent into the cavity and gain medium of the amplifier. The gain medium is depleted by the back and forth travels of the burst pulses within the cavity. Each pulse within the burst is amplified less than the pulse before it, due to the depletion of the gain medium by the previous pulses resulting in a burst pulse trace composed of laser pulses of decreasing energy.

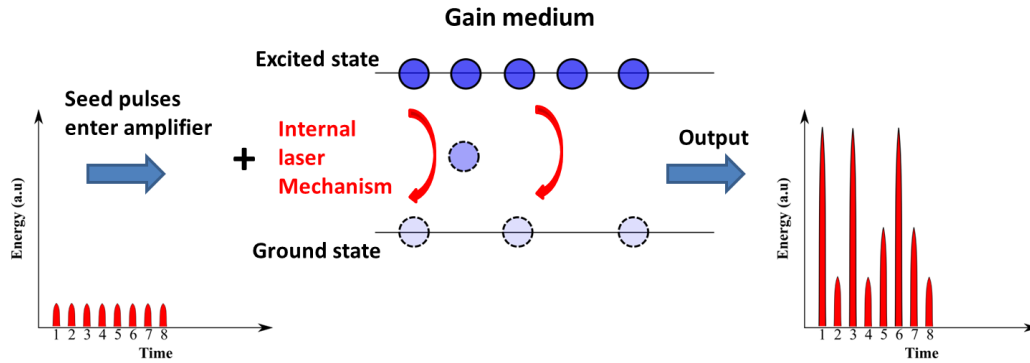


Figure 30: Schematic representation of the creation of a Flexburst. 1 to 8 seed pulses from the oscillator with a time separation of 12.8 ns is sent into the cavity and gain medium of the amplifier. An internal laser mechanism allows for the selected amplification of the different pulses within the burst train creating Flexburst traces of different energy distributions. The energy distribution of each pulse within the laser burst is selectively entered by the user on the laser controller.

Conversely FlexburstTM, compared to regular burst, allows for the control of the energy distribution within each of the laser pulses composing the burst, see Figure 30. The

exact mechanism and optics inside the laser that allows for such control on the energy distribution within the laser burst is only known to the manufacturer.

The control on the energy distribution of each pulse within the burst is done by manually entering a value from 0 to 255 in 1 to 8 bins depending on the desired number of pulses wanted within the burst train, see Figure 31. These values were entered directly into the laser controller. The energy allocated to each pulse ranged from 255 (maximum energy) to 0 for a zero-energy pulse. Zero-energy pulses were used to conduct temporal studies and its effect on colour formation.

Flexburst pattern entry

	Pulse 1	Pulse 2	Pulse 3	Pulse 4	Pulse 5	Pulse 6	Pulse 7	Pulse 8
0 to 255	100	38	100	38	100	38	100	38

Figure 31: Schematic of the Flexburst pattern as entered in the laser controller. Each pulse is given a value of 0 to 255 where 0 gives a zero-pulse energy and 255 gives the maximum energy to the specific pulse within the burst pulse. The energy can be distributed to a maximum of 8 pulses within the burst. The pattern entered (red text), for example, would produce a burst of periodically modulated high to low pulses or “zigzag” pattern, see Figure 32.

It was observed, however, that for frequencies under 200 kHz FlexburstTM did not function as intended by the manufacturer. The use of an oscilloscope (tds3033b, Tektronix) and a fast photodiode (DET10A2, Thorlabs) revealed traces that were much different than what was supposed to be a zigzag pattern composed of pulses of the same energy (i.e. same 0 to 255 numbers) for a laser repetition rate of 50 kHz, see Figure 32. For frequencies over 200 kHz, all traces appeared as expected from the values entered. I suspect the depletion of the gain medium by the burst pulses traveling back and forth in the cavity for longer time periods (i.e. lower repetition rates). To address this problem the values within each of the bins were adjusted in the laser controller in such a way to form the wanted trace on the oscilloscope. The total energy of the burst always remains constant.

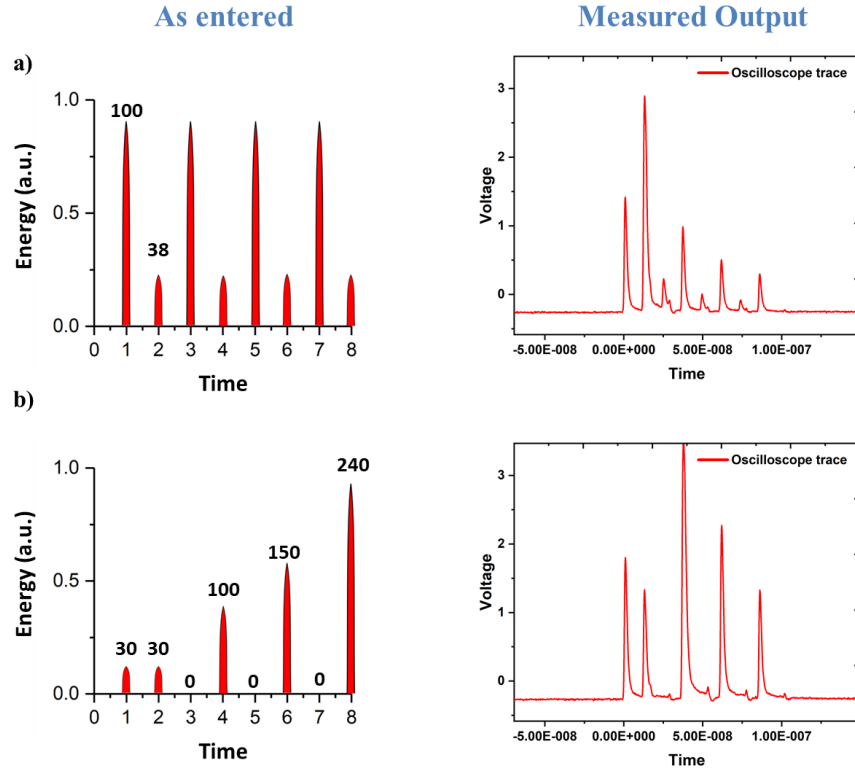


Figure 32: Representation of the flexburst burst patterns (left) as entered into the laser controller and the (right) actual measured output obtained using a fast photodiode and oscilloscope. The entered energy distributions were to be for a (a) zigzag pattern and (b) our current best energy distribution to achieve highest Chroma colours. Located above each pulse is the 0 to 255 values entered in the laser controller in order to control the energy distribution within each pulse composing the laser burst.

3.2 Experimental setup

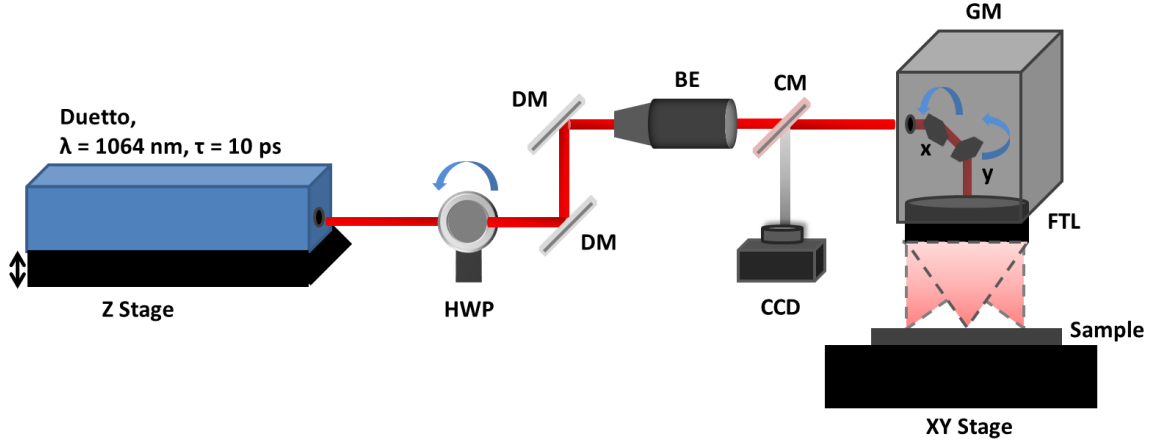


Figure 33: Schematic diagram of the experimental and machining setup. The Duetto laser and optical assembly are placed on an aluminum slab that can be moved up and down using an AC servo motor to give the laser and machining system a z-axis. The output of the laser first enters a half-wave plate (HWP) for beam polarization control and directed by dielectric mirror (DM) into a beam expander (BE). The half-wave plate (HWP) was mounted on a mechanical rotary stage controlled by Thorlabs APT software via an external servo motor controller (KDC101, Thorlabs). The beam is then expanded from 1.2 mm to 12 mm and sent into the back of the galvanometric xy mirror assembly (GM). The xy mirrors raster scans the back entrance of the F-Theta-Ronar lens (FTL) which is then focused into the sample surface. For real time view and monitoring, the back reflected light was collected by a cold mirror (CM) and sent into a CCD camera.

Figure 33 is a schematic representation of the mechanical and optical components comprising the apparatus used in these studies. The laser system and optical setup were originally purchased from FOBATM. The laser itself was purchased by the company and placed within a proprietary enclosure with all the components, software and hardware integrated, to simultaneously control all devices. While the system was purchased with all optical components installed, certain modifications to the laser path were done to improve the performance of the laser and to add other capabilities. For example, a half-wave plate (WPH10M-1064, Thorlabs) was mounted into a motorized rotating stage (PRM1Z8, Thorlabs) and placed in the beam path in order to give control on beam po-

larization important for LIPSS formation and thus the dependence of the fixed colours with respect to the direction of the polarization in regards to the machining direction.

The laser 1064 nm output beam of 1.2 mm in diameter exits the laser passing through the half-wave plate and is directed using dielectric mirrors (BB1-E03, Thorlabs) into a beam expander (LINOS G038662000, QIOptiq). The beam is expanded from 1.2 mm to 12 mm (10X), transmits through a cold mirror (M254C45, Thorlabs), and enters the back of the galvanometric assembly (TurboScan 10, Raylase). The light is focused on the samples using an F-Theta-Ronar lens (4401-261-000-21 for 163 mm lens and 4401-288-000-20 for the 254 mm lens, QIOptiq). The galvanometric mirrors raster scans the materials with speeds ranging from 2 to 3000 mm/s. The line-to-line resolution of the raster scan was roughly $0.5\ \mu\text{m}$. The surfaces were raster scanned in a top-to-bottom unidirectional fashion to eliminate any cumulative heating effects that could have occurred by the bi-directional scanning of the metal's surface, see Figure 34. The surface and machining of the surface were displayed in real time using a CCD camera (Lt365R, Lumenera) collecting the back-reflected light via the cold mirror (M254C45, Thorlabs). Debris ejected far above the surface during the writing of the surfaces were removed by a suction hose (TKFVA103, FuchsUmwelttechnik) placed far enough away as too not affect the outcome of the colours.

The samples were placed on an XY stage. The majority of the work was carried out on silver and gold with purities of 99.99 and 99.999%, respectively. Experiments on other metals such as: copper, aluminum alloys, copper-nickel alloys, titanium and tantalum were also carried out. The surface quality of the samples was observed to not play a role on colour outcome.^[115] That being said, the experiments were carried out on a fairly smooth flat struck silver surface off the production line at the RCM. The diameters of the samples were 38 mm diameter for Ag and 16 mm in diameter for Au. The thickness of the samples was of 3 mm.

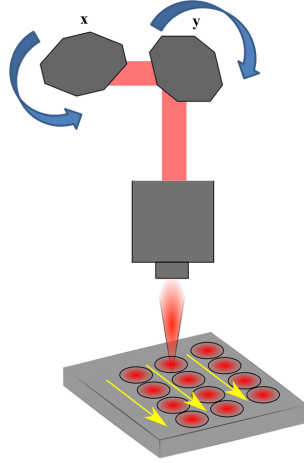


Figure 34: Schematic representation demonstrating the machining of the metal surfaces using a top-to-bottom raster scanning pattern. The unidirectional machining of the surface was implemented to eliminate the possible heat accumulation effect caused by the bidirectional machining of the surface. The galvanometric mirrors could raster scan surfaces with speeds ranging from 2 to 3000 mm/s.

3.2.1 XYZ Stages

The laser and optics are mounted on a large aluminum z-stage with a resolution specification at $1\text{ }\mu\text{m}$ with a maximum travel distance of 350 mm. The XY stage (HF-MP23, Mitsubishi AC servo motor) had a resolution of $1\text{ }\mu\text{m}$ in both the x and y direction. All stage axes were controlled via FOBATM EMC software or manually using a rotary controller.

3.2.2 Touch probe and surfaces

The surface of the samples was found using a touch probe (Best-Nr 80360, Universal 3D-Taster), see Figure 35. The touch probe was calibrated to be at the focus of the F-theta lens used. The touch probe was attached to the z-stage and lowered until the two needles on the touch probe aligned to 0, see Figure 35. The calibration of the touch probe to the focus was periodically verified to ensure reproducibility.

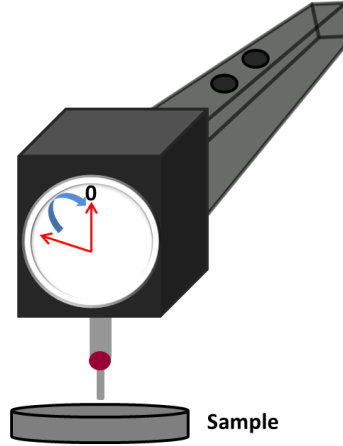


Figure 35: Representation of the touch probe used to locate the surface of the machined samples. The touch probe was calibrated to be at the focus of the F-Theta lenses. To find the surface of the samples the touch probe is lowered using the z-stage until the 2 red needles both point to 0.

3.3 Energy deposition and focus properties

The calibration of the laser system was done by measuring the average laser power at the exit of the objective. The power meter (3A-P-Quad, Ophir) was placed in an out-of-focus region of the lens to prevent any damage to the sensor. The power was displayed on a hand-held digital device (Vega, Ophir) or using the Starlab (Ophir) software. The average laser power, P_{ave} measured by the power meter is given by the following relation:

$$P_{ave} = Ef \quad (67)$$

where E is the laser pulse energy and f is the repetition rate of the laser.

The pulse energy is then defined as

$$E = \frac{P_{ave}}{f} \quad (68)$$

Due the capability of changing the repetition rate of the laser from 50 kHz to 8.2 MHz, the laser pulse energy varied strongly with the amount of time each pulse spent in the cavity. The laser pulse energy increases with lower laser repetition rates. The main body of the work presented in this thesis was for energies at the laser repetition rates of 50 kHz to 400 kHz producing a maximum pulse energy of 114 and 16 μ J, respectively.

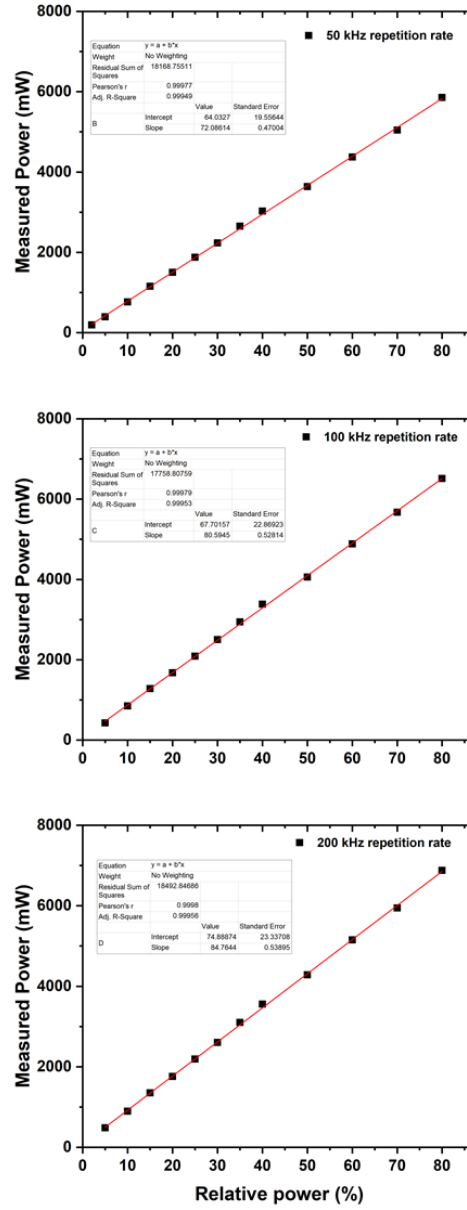


Figure 36: Calibration graphs of the power measured by the power meter with respect to the different relative power entered in the user interface for the laser repetition rates of (left) 50, (middle) 100 and (right) 200 kHz. Multiple points were taken to extrapolate a linear relation of power vs laser relative power. The R^2 value of the graphs is nearly 1.

The laser fluence delivered to the surface of the metals is defined by

$$\phi = \frac{2E}{\pi\omega_o^2} \quad (69)$$

where ω_o is half of the laser spot size (i.e. beam radius) as focused by the lens.

For ablation on any types of material, it is necessary that the laser fluence, ϕ , exceeds a certain fluence threshold, ϕ_{th} , in order to have ejection. If the laser fluence were to be under this threshold, material may still be modified, *e.g.* melting, but will not meet the necessary critical temperature, T_c , for material ejection.[124, 125] The threshold fluence for material ejection is unique to the material and the number of shots delivered to the region. For the latter, melting and the introduction of a roughness on the surface of the metal will increase the surface area perceived by the following laser shots, thus, augmenting the energy deposited locally effectively lowering the threshold fluence required to ablate.

The modified regions caused by single shot ablation, assuming a Gaussian beam profile, is related to the laser fluence delivered to the surface and the threshold fluence required for ablation by the following relation[127]:

$$D^2 = 2\sigma_o^2 \ln\left(\frac{\phi}{\phi_{th}}\right) \quad (70)$$

where D^2 is the square diameter of the modified region and $\sigma_o = 2\omega_o$ is the laser spot size.

Furthermore, since both ϕ and ϕ_{th} assume the same spot size, the relation can be simplified as follows:

$$D^2 = 2\sigma_o^2 \ln\left(\frac{E}{E_{th}}\right) \quad (71)$$

where E_{th} is the minimum laser energy required to initiate the removal of material from the material's surface.

Hence from this relation, the true spot size can be estimated from the graph of D^2 versus $\ln(E/E_{th})$. The slope of such a graph (i.e. $2\sigma_o^2$) can be used to find an approximate $1/e^2$ value for a Gaussian beam.

To find the ablation threshold value, a series of spaced out lines was made on the surface of silver with decreasing pulse energy. The relative power was decreased in steps of 5% between each line. To ensure the single shots were delivered locally to the surface, the galvanometric mirrors deflected the beam onto the material's surface with speeds much faster than the repetition rate of the laser. The threshold value was initially approximated by looking at the surface of silver under a microscope. The single shot energy

threshold for silver was observed to be $40 \mu J$. Images of the modified regions and a more accurate threshold value was obtained by SEM, see Figure 37. The dimensions of all the modified regions were obtained from the SEM pictures using ImageJ.[29]

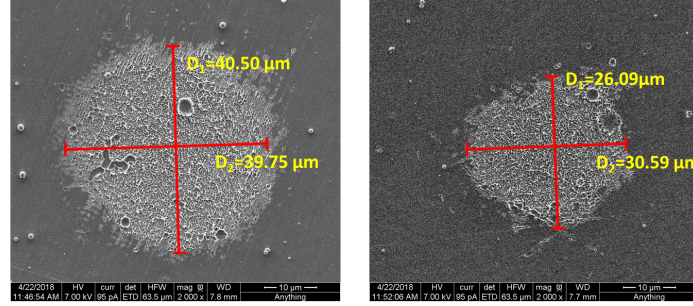


Figure 37: Measurements of the modified regions. The values of the modified regions were done using ImageJ[29] with the appropriate calibrations using the SEM scale bars. The value of D^2 obtained by multiplying the lateral dimensions of the modified regions (i.e. $D_1 * D_2$).

The values of D^2 as a function of $\ln(E/E_{th})$ were then plotted for each lens, see Figure 38.

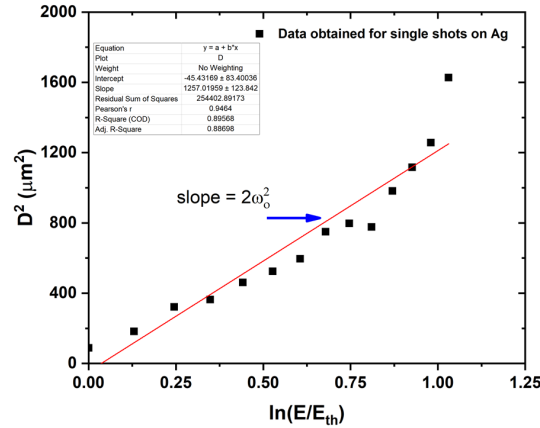


Figure 38: Graph of the modified regions, D^2 , versus $\ln(E/E_{th})$ for the 254 mm lens. The slope of the linear fit is defined as $2\sigma_o^2$. From the linear extrapolation of the multiple measured diameters, the spot size of the 254 mm lens is measured to be $25 \mu m$.

From these graphs and by extrapolation, spot sizes of 14 and $25 \mu m$ were found for

both the 163 and 254 mm lens, respectively. The measured spot sizes were in agreement with the specs of the lenses. These spot sizes were periodically verified throughout the research project. Deviation from a linear slop is believed to originate from the surface quality of the sample and its flatness across the surface.

In the recently published article of Guay et al.[115], a relation between total accumulated fluence and Hue was established. The total accumulated fluence relation was given by

$$\Phi = \frac{a^2 E f}{v L_s} \quad (72)$$

where v is the scanning speed of the galvanometric mirrors, L_s is the line spacing between lasered lines and a is a correction factor. This correction factor was quantified using the D^2 versus $\ln(E/E_{th})$. The origin of a comes from changes in the size of the modified region with increasing pulse energy. Hence, when the pulse energy is much higher than threshold, the surface is modified over larger spatial dimensions. Therefore, the increase in the modified region augments the overlap between successive laser shots and successive lines. The value of a is extracted from the ratio of the actual measured modified region, D^2 , to that of the measured spot size.

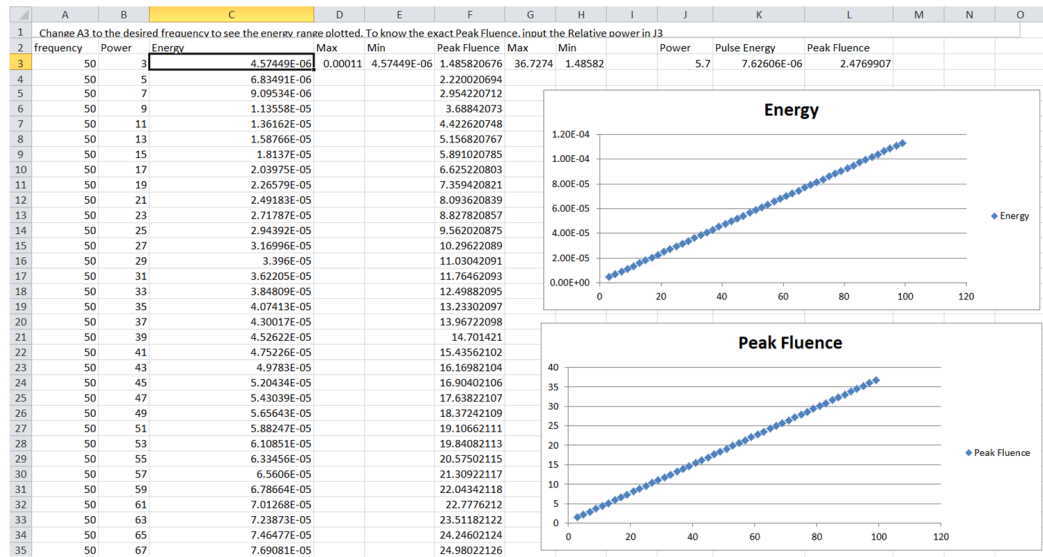


Figure 39: Excel code written to give the laser fluence depending on relative power used and the laser repetition rate. The user could change between the different calibrations for each laser frequency by entering the laser frequency sought in cell A3.

From the spot size measurement and power calibration, an excel code was written to give the fluence for any relative power entered in the user interface of the laser, see

Figure 39. The calibration was periodically verified for fluctuations or changes in laser output.

For the frequency study, the effect of bulk residual heat on the colour outcome was done by selecting a fixed laser repetition rate and by introducing different integer numbers in the pulse picker. For example, a repetition rate of 200 kHz was obtained by applying a laser repetition of 400 kHz with a pulse picker of 2. The importance of this method, instead of simply going to 200 kHz without the use of the pulse picker, is that the pulse energy of both the 200 and 400 kHz are the same, therefore isolating the temporal effects. This was confirmed by the 50% drop in average power for each dividing pulse factor of 2. From equation 70, the total accumulated fluence delivered to the surface can, therefore, be maintained by adjusting the machining speed to compensate for the new frequency knowing that the pulse energy remains unchanged.

$$\Phi = \frac{aE f'}{v' L_s} \quad (73)$$

where $f' = f/N$ is the frequency of the pulse picker, $v' = v/N$ is the new machining speed and N is the divider or pulse picker number. Replacing the values in equation 71 we obtain the same relation as in equation 70.

3.4 Material ejection and metal colouring

This section of this Chapter aims to provide a detailed explanation on the ejection process of nanoparticles, the important and influential parameters for the colouring of metal surfaces and the process of controlling the re-deposition of nanoparticles on the metal surface.

To eject nanoparticles from a metal surface through the process of ablation, we must first expose the metal surface to a focused and highly intense laser beam. The laser energy impinging on the metal's surface is predominantly absorbed by the electrons becoming hot electrons (or energetic electrons) in the process. The electrons dominantly absorb the laser energy due to their higher thermal capacity than that of the lattice. The lattice only serves as a heatsink for the hot electrons who seek to cool down by transferring their energy via phonon collisions.[\[128\]](#)

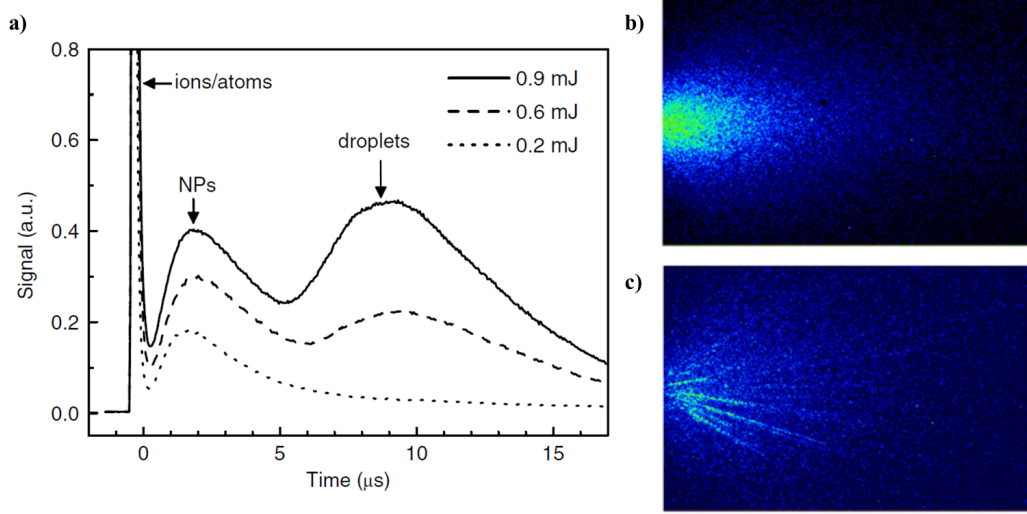


Figure 40: (a) Graphical representation of the signals obtained Perriere et al.[30] using a fast thermal camera and looking at the ejection of material due to laser ablation. They observed 3 phases of material ejection at different time: (1) ions by Coulomb explosion ($\sim ns$), (2) nanoparticles and (3) droplet due to phase explosion. Notice the reduction in the number of droplets observed we decreasing laser pulse energy. (b) and (c) are frames of the fast-thermal camera showing the ejection of material from the surface using a (b) large and (c) small spot size. The larger spot size is observed to eject material preferentially in the forward direction while the smaller spot size ejects material over a larger angle. Reprinted (adapted) from Ref.[30], © 2007, with permission from the Institute of Physics.

The efficiency to which the hot electrons transfer their energy to the lattice is a characteristic of the material and is defined by the electron-phonon coupling.[67] Thus, for material with a high characteristic electron-phonon coupling (*e.g.* Nickel and Copper), the hot electrons can efficiently transfer their energy within the top layer of the material. In that case, the hot electrons and lattice rapidly reaches thermal equilibrium resulting in the energy being deposited within a smaller volume close to the surface.[67] Alternatively, for materials with low electron-phonon coupling, the thermal energy is transferred to the deeper part of the lattice below the surface due to the longer time between collisions (or longer mean free path) resulting in the deposition of energy over a larger volume.[67] Furthermore, as the pulse creates the hot electrons; the atoms are stripped bare of their electrons resulting in a net positive charge. The large number of positive ions in close

proximity, within the interaction region, leads to a large repulsive force causing the ions to be expelled from the surface, a process known as Coulomb explosion.[129, 30] This process occurs relatively quickly during the interaction of the laser pulse with the surface ($\sim$ a few ns), see Figure 40.[30, 130]

Following Coulomb explosion, the hot electrons will cool down by transferring their energy to the material lattice via the process of collisions increasing the temperature of the lattice. As the lattice reaches 0.9 times the critical temperature (T_c), phase explosion occurs resulting in the ejection of material from the interaction volume.[124, 129, 130] The ejection of material also occurs when the shock-wave generated is strong enough to lift the molten material off the surface. The shock-wave is induced in the material by the expanding plasma and its reflection at the solid-liquid boundary within the interaction region.[30] During this process, the material ejected is in the form of nanoparticles. This process occurs on the μs time scale, see Figure 40.[30, 130] It is important to note that the size of the particles ejected from the surface is dependent on thermal conductivity and pressure of the ambient gas.[131, 132, 30] The colouring of silver in an argon environment produced significantly different structures to those produced in air, see Figure 41.

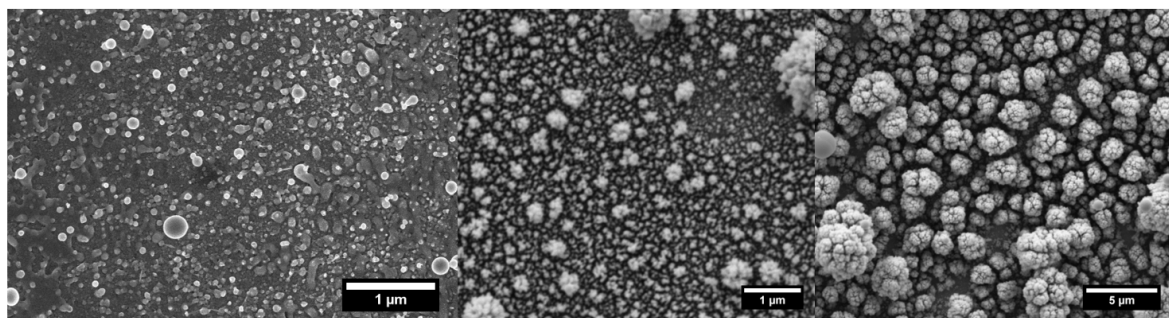


Figure 41: SEM images of nanoparticles re-deposited on the silver surface following laser ablation. Ablation was done in a (left) air and (middle, right) argon environment. The SEM in (left) and (right) was taken for the nanoparticles re-deposited close to the ablated line and (middle) for nanoparticles ejected further away. The nanoparticle can be observed to be very morphologically different depending on the ambient gas during the ablation of material.

In our research we observed that each Hue value was attributed to a unique total

accumulated fluence value which also controlled the particle distribution re-deposited on the surface.[115, 133] At first the link between Hue value and total accumulated fluence may be difficult to accept without truly understanding the simplicity and elegance of the colouring process. Firstly, the energy of the laser pulse controls the expansion of the plasma, and in consequence the shock-wave velocity and pressure responsible for the ejection of the nanoparticles.[130] Thus, the larger the incident pulse energy E , see equation 73, sent to the surface; the further the nanoparticles are ejected. Hence, for a fixed E the area of ejection can be assumed to be constant, therefore, speed (v) and line spacing (L_s) then controls the number of nanoparticles accumulated on the surface from shot-to-shot and line-to-line, respectively. Similarly, if E is increased the area of nanoparticle re-deposition is larger requiring a proportional increase in v and L_s to deposit the same amount of nanoparticle density onto the surface. It is also important to note that the increase in E also increases the laser interaction volume within the material resulting in the ejection of a larger number of nanoparticles. To compensate for this increase in the number of nanoparticles ejected, v and L_s must be appropriately changed to deposit the proper nanoparticle density corresponding to the desire colour.[133] The larger interaction region using a higher laser pulse is captured in the term a of equation 73. In summary, the total accumulated fluence formula is a tool to quantify this process of ejection and accumulation on the material surface. It links the colours to the nanoparticle density on the surface which can be controlled by the total accumulated fluence formula.[115] The bimodal nanoparticle statistics of similar Hue values were found to be identical when using different laser parameters.[115, 133] With this understanding of the ejection and how to control the re-deposited density of the particles on the surface, we have successfully applied this technique to fully colour other plasmonic metals such as: copper, gold, nickel, niobium, aluminum, tantalum and titanium.[115] The only important parameter that requires modification for the different metal is the laser pulse energy that is required to eject nanoparticles from the surface which is unique to every metal. The nanoparticle density on the surface can then be controlled via the appropriate laser marking parameters (*i.e.* v and L_s). It should also be noted that the increase in E not only results in a higher number of nanoparticles being ejected from the surface via laser ablation but also results in a larger melting layer during the interaction causing the ejection of a smaller number of larger nanoparticles.[30, 130, 129] The amount of larger nanoparticles is strongly dependent on the incident laser energy E . [30, 130, 129] This ejection of larger nanoparticles still

only adds a few nanoparticles to the tail of the bimodal distribution of nanoparticles found on the coloured surfaces (see Chapter 4). The origin of the bimodal nanoparticle distribution is believed to originate from the 2-stage ejection of material from the surface. The small nanoparticles are believed to originate from the condensation of the plasma (*i.e.* from the Coulomb explosion) like in pulse-laser-deposition (PLD).[129] The medium nanoparticles from the phase explosion. Both re-deposited and fused to the surface due to the process of ablation occurring in air or a gas environment during this thesis. The presence of larger nanoparticle, with higher E , causes the colours to appear lighter.[115] For example, a navy blue colour created using a lower E will appear sky blue using a larger E for the same total accumulated fluence. The augmentation in Lightness is attributed to the increase scattering of nanoparticle with larger size.[39]

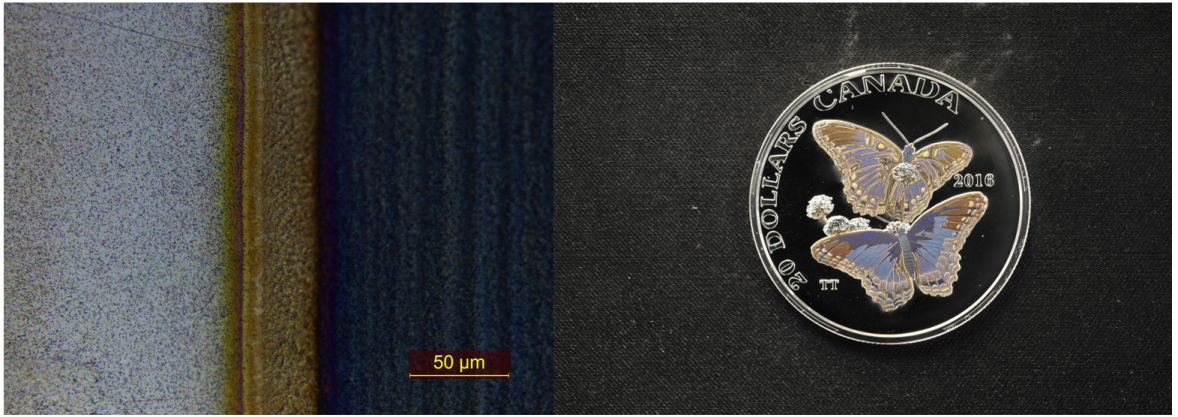


Figure 42: (a) Microscope image of a coloured square showing the last line of the raster pattern. Due to the absence of accumulation of nanoparticle and melting of the nanoparticles previously deposited, the last line of the raster scan always appears yellow. (b) Butterfly design from the RCM coloured using the laser colouring method. Yellow demarcation lines can be seen between features of different colours due the absence accumulation of nanoparticles in the last line of the raster scan. This can be remedied by modifying the underlying topography to control the total accumulated fluence delivered locally effectively controlling the colours within have to colour different areas separately.

The accumulation process of nanoparticle from shot-to-shot and line-to-line can also be seen visually under the microscope and in the absence of the last line of a raster scanning pattern, see Figure 42. The ejection is symmetric around the point of ejection resulting in equal ejection on the right and left of the ejection site. However, during the

raster scanning of the surface, the nanoparticles ejected to the right or left of the line will be exposed to the laser by the subsequent marking line of the pattern. Observations shows that the nanoparticles subjected to the laser, after re-deposition, are melted and altered during this process causing the last line of the raster pattern to be absent of colours. Therefore, the accumulation of nanoparticles on the surface occurs behind the front of the marking laser and in the direction opposite to the raster pattern. The colours could also be erased by subsequently passing the laser on top of the coloured surfaces. It should also be noted that the absorption of laser energy by the surface is strongly dependent on the roughness of the surface. Therefore, for overlapping section of the surface from shot-to-shot or line-to-line accumulation is not always the same. For example, the surface will absorb less of the first laser pulse but will suffer structural modification that will make the surface absorb more laser energy when exposed to the following laser shots. The same occurs for areas where nanoparticles have been deposited and are exposed to the laser beam. The presence of the nanoparticles not increases the surface roughness (*i.e.* area) but also enhances local fields when exposed to optical radiation which can cause local heating and the sintering of the nanoparticles. The sintering of the nanoparticles and their agglomeration due to local heating is believed to be responsible for the brown/yellow colour observed in the last line of the raster scan pattern.[134]

The total accumulated fluence formula, however, has also certain limitation. First, it does and does not consider the spot size of the focusing lens. It does consider the focusing lens by adding the correction factor a in equation 73 to consider the overlapping between laser shots and laser lines. But also, it fails to consider the important role of the spot size on nanoparticle ejection. From the formula, one could assume that changing the lens and spot size would have no effect on the colouring results if the laser parameters were modified to deliver the same total accumulated fluence to the surface. However, this would be an incorrect and naive assumption. In fact, the laser plume expansion angle is dependent on the spot size.[129, 30] For increasing spot size, the expansion angle is reduced, and the ejection of material is dominantly forward directed.[129, 30] For a smaller spot size, the angle of ejection is larger and less forward directed. Furthermore, the smaller spot sizes will favorably eject droplets (*i.e.* larger particles) while the larger spot size favorably ejects nanoparticles.[129, 30] This would have a significant impact on the resulting nanoparticle array on the material's surface and perceived colour. In this study, the 2 lenses used had very large spot sizes which made this effect negligible. This

is supported by a reduction of almost half in the marking time by doubling the spot size.

The total accumulated fluence formula also another significant flaw: it has no temporal dependence. In Chapter 6 and Chapter 8, we see that different burst arrangements with the same total laser energy resulted in significantly different outcome, and that different laser repetition rates delivering the same total energy to the surface resulted in different nanostructured surfaces and surface chemistry.[133, 135] This suggests a strong temporal dependence. The chemistry can be explained by the ejection of positively charged particles (stripped of electrons) and the ionization of air leading to the creation of exotic chemical species.[135] The time spacing between the pulse within the burst (12.8 ns) and from pulse-to-pulse dictated by the laser repetition rate ($\sim \mu s$) significantly complicates the ejection dynamics.[30, 130] First, the burst time separation is on same time scale as the ejection of ions from the surface during Coulomb explosion.[30, 130] This would have the subsequent pulses of the burst interacting with the initial plume. Second, the laser repetition rate used in this study was of the same time scale as the ejection of nanoparticles from the surface following phase explosion.[30, 130] This would have each subsequent pulse interacting with the cloud of nanoparticle ejected from the surface. Hartmann et al.[136] observed with a thermal camera that the interaction of subsequent pulses with the nanoparticle cloud increased its volume resulting in the re-deposition of nanoparticles over a larger area. Thus, the interaction of the laser pulses with the plume and ejected nanoparticle can be very complex. This was initially remedied by keeping the keeping the laser repetition rate fixed.[115] In the laser repetition rate study this effect could, however, not be neglected and remains an important factor.[135] Additionally, following the re-deposition of nanoparticles on the surface, it is known that heat can accumulate in the bulk with increasing laser repetition rate. This effect was observed in the laser repetition rate study by the smoothing of the nanoparticle covered surfaces and the suppression of chemical species within the exposed regions.[135]

The use of the burst colouring technique method also had multiple advantages. For one, it increased the electron-phonon coupling of silver and gold permitting the creation of LIPSS structures that would normally not properly be formed.[66] As discussed earlier, this occurs due to the heating of the lattice and a reduction in the mean free path of the electrons bringing the interaction volume closer to the surface.[67, 124] This as the effect of concentrating the absorbed energy to a smaller volume closer to the surface. Secondly,

the increase in the electron-phonon coupling is also very important in the ejection of nanoparticles and their re-deposition on the material's surface. This is because material is ejected from the surface only when $0.9\epsilon_c$ is reached.[124, 129, 130] For materials plagued with a low electron-phonon coupling (*e.g.* gold), the ejection volume is very small since most of the energy is delivered to the deeper layers melting and heating the material.[67] Only a small volume will actually reach the required $0.9T_c$ necessary for ejection. We believe that gold could only be coloured using burst for this reason. The use of burst increased the electron-phonon coupling of gold concentrating the deposited energy closer to the surface increasing the ejected volume.

3.5 Atomic layer deposition of alumina

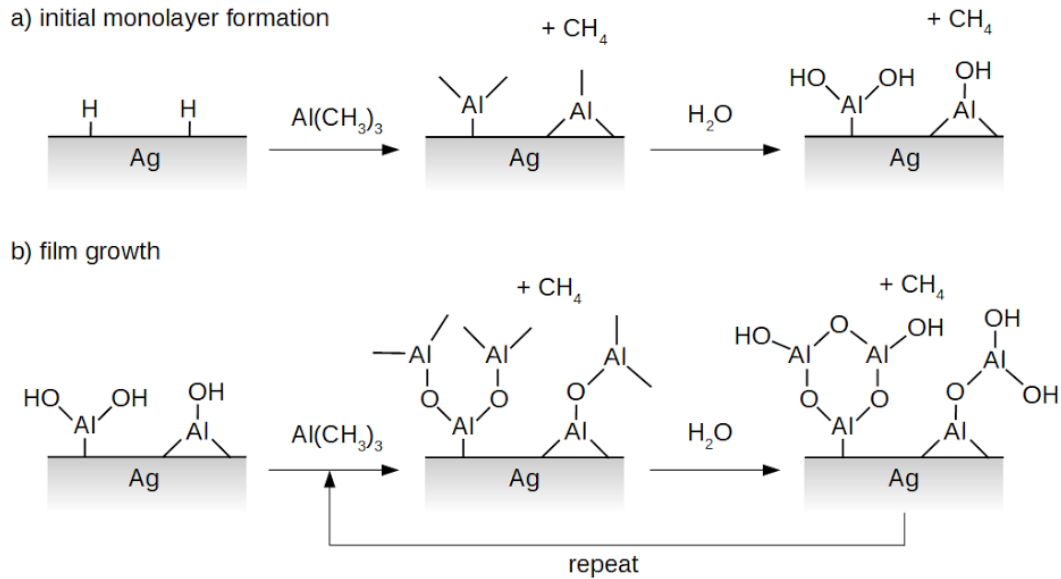


Figure 43: Schematic of the atomic layer deposition of alumina on the surface of silver. The alumina film is grown in a cyclic fashion by the periodic introduction of TMA and water into the deposition chamber. Reprinted (adapted) with permission from Ref.[31].
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The passivation of the coloured surfaces was done using atomic layer deposition (ALD). ALD was selected due to its ability to deposit films at low temperature and achieve conformal coating on complex surfaces.[137] The films deposited were that of aluminum oxide (*i.e.* alumina). Two passivation methods were used to protect the integrity of the coloured surfaces, the single and dual layer approach. In the single layer approach, a film

of alumina was deposited (PicoSun R150) at a temperature of 60°C. The alumina film was grown by cyclically exposing the coloured surfaces to 1 second pulses of trimethylaluminum (TMA) and water, see Figure 43. The purge time for TMA and water were that of 1 and 90 seconds, respectively. In the dual-layer approach, a second denser alumina layer was deposited at a temperature of 100°C. The water purge time was reduced to 10 seconds in order to reduce thermal effects on the nanostructure.[31] For silver (and other materials), the injection of water vapor into the chamber hydroxylates the silver surface initiating the formation of the alumina layer, see Figure 43.

3.6 Measurements and surface analysis

3.6.1 Colourimetric and radiometric data

Colourimetric

A method was required to quantify the colours, the change in colours with the application of a coating, and to improve the colours with new sets of laser parameters.

All colours can be described in terms of 3 values. This is what is referred to the tristimulus.[138] An example of the tristimulus is the human eye. The cones of the human eyes capture the 3 values of red, green and blue to construct what we perceive as colours. The advantage of the tristimulus or colourimetric information over radiometric information is that the tristimulus can be represented in 3-dimensional space, in addition to being more representative of the human eye. This 3-dimensional space is what we refer to as the colour space. In this work, the colours produced via direct laser writing were quantified using the LCH colour space, see Figure 44. Where L is colour Lightness ranging from 0 to 100, C is colour Chroma (i.e. saturation ranging from 0 to 100 and H is Hue (colour value associated with a 360° scale). The LCH colour space was chosen due to its simplicity in describing colours. However, like changing from Cartesian to a cylindrical coordinate system, the colour spaces can be transformed from one colour space to another by applying the proper relations or transformation matrices. Such transformations were required to make xyl CIE diagrams from the LCH values. These transformations were done in matlab.

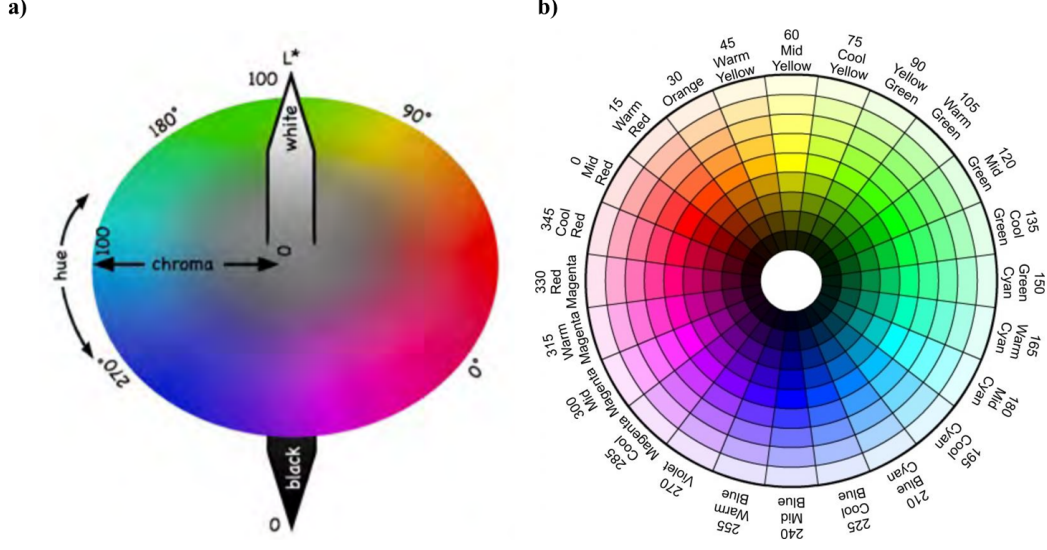


Figure 44: (a) Representation of the LCH colour space. The Chroma ranges from 0 to 100 (gray to saturated) and the Lightness from 0 to 100 (black to white). The Hue is colour on a 360° scale. Image was taken from Ref.[32]. (b) Demonstrates the separation of the Hue regions over the rotation of 360°.

To test the sensitivity of the surfaces and to determine the effect of the coatings on colours, the change in colour before and after coating deposition (or for various other tests) was quantified using the following relation:

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2} \quad (74)$$

where a and b are defined as

$$a = C \cos\left(\frac{2\pi H}{360}\right) \quad (75)$$

and

$$b = C \sin\left(\frac{2\pi H}{360}\right) \quad (76)$$

In equation 72, the subscripts 1 and 2 are used to identify the colours before and after a test or the deposition of a coating, respectively. A value of $\Delta E \sim 1$ is the minimum value for the human eye to perceive any colour change.[138] For industrial application a maximum of $\Delta E \sim 6$ or 7 is often accepted. [138]

Radiometric

In this work, the radiometric measurements of the surfaces were taken from 2 distinct sets of instruments. One is a high-end commercially available spectrophotometer while

the second was home-built using a spectrometer.

High quality reflectance measurements of the colours were carried out using a high-end spectrophotometer (CARY 7000 UV-Vis-NIR, Agilent technologies) equipped with an integrating sphere using a 1 nm step size. The reflectance data and measurements were corrected against reference samples of silicon and bare silver. The reflectance data was transformed into LCH values using a matlab code weighting each wavelength to the sensitivity of the human eye (*i.e.* cone and rod light receptors) in the photopic regime.[139]

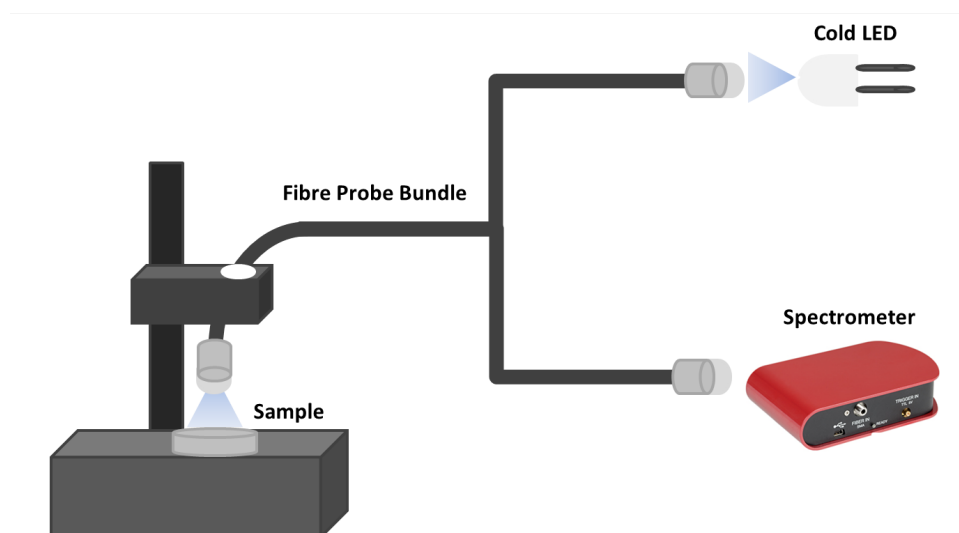


Figure 45: Schematic representation of the house-built spectrometer design to obtain reflectance spectra of the coloured metal surfaces. The design consists of a spectrometer, a cold LED source and a fibre optic reflection bundle.

Reflectance measurements were also conducted using an in-house built spectrometer, see Figure 45, composed of a spectrometer (CCS200, Thorlabs) with a resolution of 2 nm over the range of 200-1000 nm. The illumination light source was a cold LED (MCWHF2, Thorlabs). The light was sent and collected via a fibre optic reflection probe bundle (RP28, Thorlabs). The reflectance measurements were corrected against the illumination of the bare silver.

3.6.2 SEM and statistical analysis

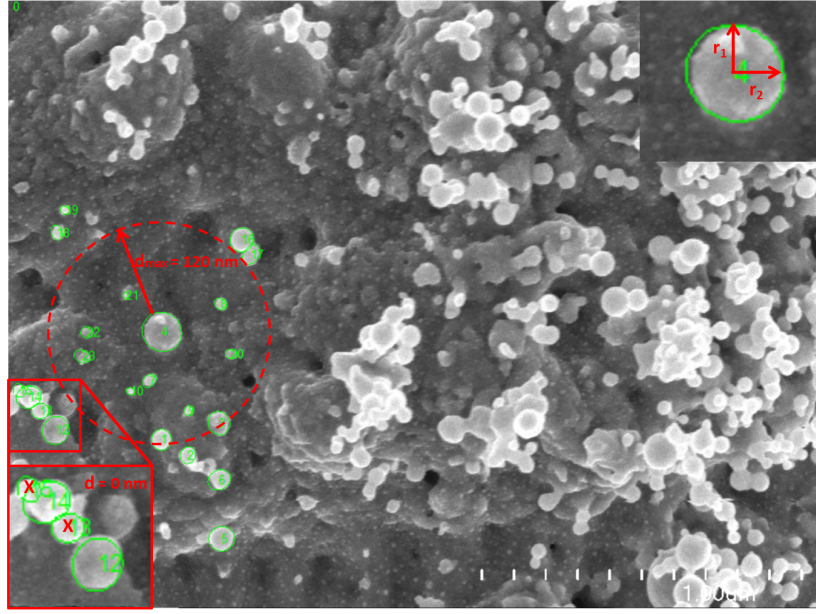


Figure 46: Demonstrates the functioning of the matlab code used to count and gather information about the NP such as: position and size. For a complete statistical analysis of the surface, all the NP in the SEM images would be surrounded by an ellipse. The statistics of the medium and small NPs were done at 2 different magnifications; here only the medium particles were accessed due to the low-magnification SEM image of the coloured surface. For each NP the matlab code would record the major (r_2) and minor (r_1) diameter of the ellipse (see inset in top-right corner). The mean radius values of each NP were then calculated using eq. 75. The mean inter-particle distance was determined using a matlab code by considering the position of the particles in close proximity, minus the size of each of the particle (i.e. only the gap). Only particles within a 0.05 to 120 nm distance were considered since touching particles were deemed to be a single particle (see inset in lower-left corner) and therefore ignored. The maximum radius (d_{max}) of 120 nm around each of the NP was determined from FDTD simulation where it was shown that NPs did not interact for inter-particle distances higher than this value.

The images of the irradiated surfaces were taken using various SEM throughout the project (GeminiSEM 500, Zeiss - JSM-7500F FESEM, JEOL - Quanta 450, FEI). However, problems with contrast in the SEM images due to the rough nature of the coloured surfaces made it impossible for software such as ImageJ to properly discern the bound-

aries of each of the NPs. To address this problem, a matlab program was written to manually place ellipses around each of the NPs in the SEM images. The dimension of the ellipse and the position of each NP were saved into a .mat file, see Figure 46. The mean radius of the NP was obtained from the drawn ellipsoid using the following relation:

$$r_{mean} = \frac{\sqrt{\frac{r_1^2 + r_2^2}{2}}}{p} \quad (77)$$

where r_1 and r_2 are the minor and major axis of each of the ellipse recorded in the .mat file and p is the calibration factor with units of nm/pixel obtained from the scale bar of the SEM images using ImageJ.

The values for the NP radii's were then plotted in histograms or used in graphs of mean particle size. For inter-particle spacing data, a matlab code was written to take the position of each of the NP (i.e. ellipse) saved in the .mat file and to consider only NP within 0.05 to 120 nm in proximity. The minimum value of 0.05 nm was justified to ignore particles that are touching, making them a single NP. The maximum distance of 120 nm was deduced from the FDTD simulations which showed that NP no longer interacted over such inter-particle distances. This approximation was necessary, given the chaotic nature of the surfaces and the large distribution of inter-particle distances for each NP.

3.6.3 Environmental testing

The longevity and stability of the colours over time was tested by exposing the samples to harsh environmental conditions. These tests were conducted to mimic the exposure of the colours over a time period of many years in normal environmental room conditions. In addition, the tests were used to evaluate the performance of the passivation films placed on the colours. Prior to the marking of the colours, the surfaces were thoroughly washed using a multi-step process: (step 1) isopropanol wash, (step 2) acetone wash, (step 3) cleaned by deionized water, (step 4) isopropanol wash and (step 5) nitrogen dried. The samples to be passivated were placed in plastic capsules with high purity nitrogen and placed in plastic bags filled with nitrogen. The samples were then transported to the group of Dr. Sean Barry at Carleton University where an alumina film was deposited via atomic layer deposition (ALD). The careful washing of the surfaces were observed to be important for the proper adhesion of the alumina films to the surface of the silver samples.

The environmental tests conducted on the coloured samples were the standard used by the RCM. To test the tarnishing resistance of the passivation layer and the colour evolution of unpassivated samples, the samples were placed in a sulphur rich environment for a period of 20 hours. The sulphur rich environment was created in a dessicator (NalgeneTM, ThermoFisher) with a mixture of 6 mL of H₂S saturated water (742546, Aldrich) and 394 mL of deionized water. The mixture was poured at the bottom of the desiccator and the samples placed on the holder elevated above the mixture. The dome was sealed for the period of the test. For each test, multiple passivated and control samples were placed on the holder to ensure reproducibility and to evaluate the failure rate for the eventual release of a coin product.

To test the effect of humidity on the colours and the protection of the passivation layer, the coins were exposed for a period of 72 hours to a relative humidity of 85% and a temperature of 38 °C. The environmental conditions were precisely controlled using an accelerated aging temperature humidity weather test chamber (TH-100, LIB). Similarly, to the tarnish test, multiple control samples and passivated samples were placed in the chamber to evaluate reproducibility and failure rates. Failures in the tarnish and humidity tests determined visually, complete or partial discoloration of the surface was deemed a failure.

To study the effect of heat on the colours, heating tests were carried out in two separate ovens working in parallel (Sentry Xpress 4.0, Orton; and Gravity Convection General Incubator, VWR Symphony). The samples were exposed to temperatures of 40 to 100 °C for a time period of up to 2000 hours. The temperature inside the ovens was monitored using a thermocouple (type K thermocouple, Thermometrics) attached to an infrared thermometer (ST-8835, Reed). Like the previous tests, multiple control and passivated samples were placed inside the ovens for each test to ensure reproducibility and to obtain a failure rate.

3.6.4 Surface compositional analysis

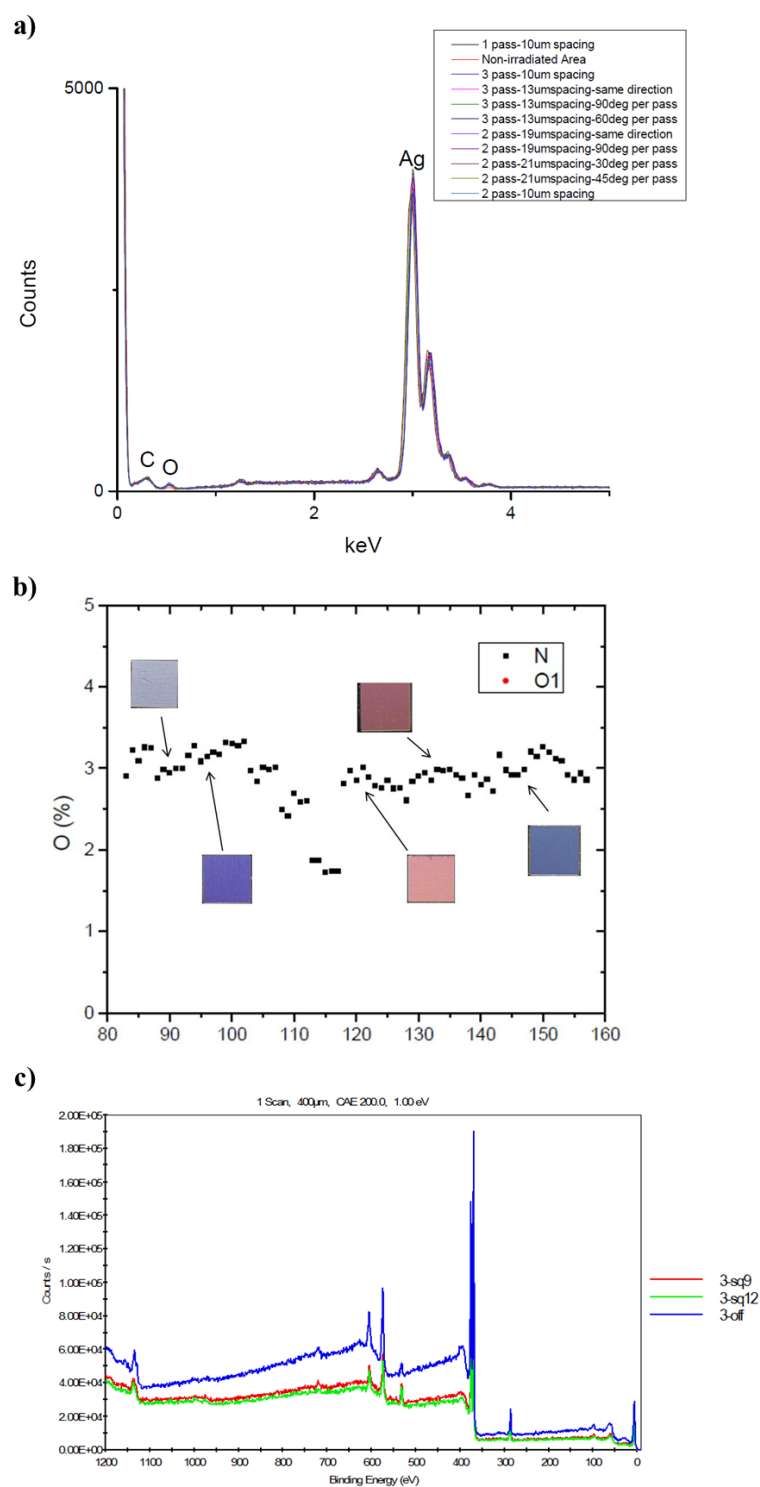


Figure 47: The compositional analysis of non-irradiated surfaces and coloured surfaces were done using (a) energy-dispersive X-ray spectroscopy (EDS), (b) wave-dispersive X-ray spectroscopy (WDS) and X-ray photoelectron spectroscopy (XPS).

The compositional analysis of the irradiated and coloured surfaces was done by (XPS) X-ray photoelectron spectroscopy (K-ALPHA, Thermofisher Scientific), (WDS) Wave-dispersive X-ray spectroscopy (8230 Superprobe, JEOL) and (EDS) Energy-dispersive X-ray spectroscopy (X-MaxN 80, Oxford), see Figure 47.

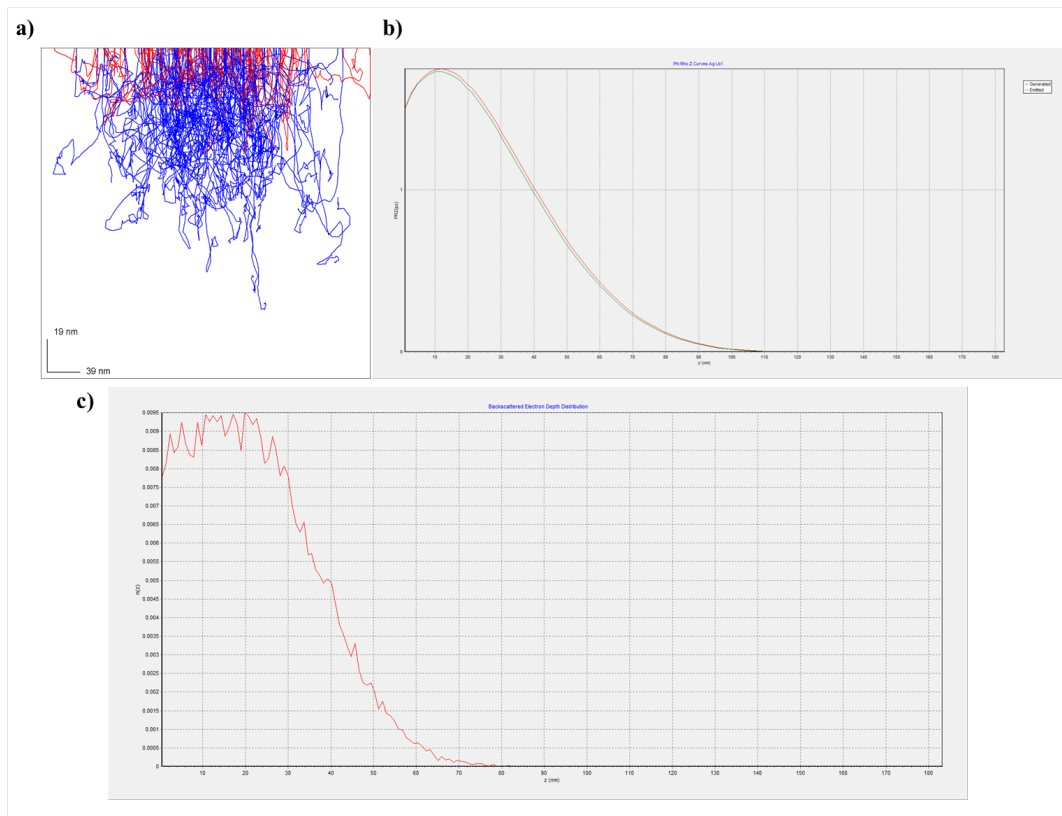


Figure 48: (a) Results of a Monte-Carlo simulations using the Casino software. The simulation is for a 6 keV electron beam striking a surface, generating backscattered electrons and X-ray emissions. The simulations allow for the determination of the (b) probing depth using the same probing conditions and (c) the backscattered electron distribution. Additionally, the depth at which the X-rays may escape and counts from inside the material were calculated.

To determine the probing depth and film thickness of species such as silver oxide (Ag_2O), for example, Monte-Carlo simulations on the software Casino were by entering the characteristic parameters used during the EDS scan (i.e. take-off angle, beam voltage, etc...). The oxygen counts from the EDS measurements were compared to the oxygen counts from the Monte-Carlo simulations assuming a silver oxide film in the interaction region, see Figure 48. From these comparisons, an estimated thickness of the film could

be obtained.

3.6.5 Surface chemical analysis

The chemical analysis of the irradiated and coloured surfaces was performed by grazing angle (Nexus 870, Thermo Nicolet) Fourier-transform IR (FTIR) spectrometer with the incident light illuminating the surface of the sample at 80° . The back of the sample or a similar non-irradiated sample was used for background correction. The signal was integrated 256 times to reduce noise and augment the definition of the peaks. The samples were carefully oriented to avoid diffraction effects, as a result of the LIPSS, throughout the analysis of the surfaces.

Laser-induced plasmonic colours on metals

4.1 Summary

This chapter demonstrates the angle independent colouring of silver using two distinct laser colouring methods: nonburst and burst. The burst method is showed to generate significantly more saturated colours than the nonburst method. A link between total accumulated fluence and Hue is established making this process viable for industrial applications. The colouring process is applied to various coin designs with and without topography. A 5 kg coin with a topography of ~ 1.5 cm is also coloured. Finite-difference time-domain simulations using the statistical data from the SEM images are explored. The simulations support and explain the plasmonic nature of the colours and their delicate sensitivity. A good agreement between theoretical and experimental results is established. The supplementary information discusses burst, the colouring of copper, aluminum and gold, and provides the statistical data used in the simulation.

4.2 Contributions

The results provided in this section were published in the open access journal Nature Communications. The quality of the publication is the result of collaborations with the groups of Profs. Ramunno, and Berini. In this publication, I invented (see patent) and discovered the process used for the colouring of metals (see appendix for patent application). Under the direction of Dr. Arnaud Weck, I supervised the research team at the Royal Canadian Mint and taught COOP students Guillaume Côté and Martin Charron how to colour the surface of silver using the nonburst and burst colouring techniques. Guillaume and I established the relation between total accumulated fluence and Hue. Guillaume, Martin and I gathered the experimental data and the statistical analysis of the coloured silver surfaces. I discovered and established the complex laser parameters for the colouring of gold, copper and aluminum presented in the supplementary materials. Dr. Lora Ramunno and Dr. Pierre Berini co-directed the study, contributing with their extensive knowledge of plasmons, and supervising the simulations. Dr. Antonino Calà Lesina established the theoretical framework and conducted the FDTD simulations based on the statistical data of the silver coloured surfaces. Dr. Calà Lesina and I discussed and analyzed the results and correlation between the experimental and simulation results. Dr. Daniel Poitras and I conducted the spectrophotometer measurements of the surfaces. Dr. Berini, Dr. Ramunno and Dr. Calà Lesina formulated the theoretical conclusion of the simulations. All the the authors discussed both the experimental and theoretical results. Dr. Berini, Dr. Weck, Dr. Ramunno, Dr. Calà Lesina and I co-wrote the paper. The figures were made by Guillaume, Dr. Calà Lesina and myself.

4.3 Article

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ARTICLE

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OPEN

Laser-induced plasmonic colours on metals

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Plasmonic resonances in metallic nanoparticles have been used since antiquity to colour glasses. The use of metal nanostructures for surface colourization has attracted considerable interest following recent developments in plasmonics. However, current top-down colourization methods are not ideally suited to large-scale industrial applications. Here we use a bottom-up approach where picosecond laser pulses can produce a full palette of non-iridescent colours on silver, gold, copper and aluminium. We demonstrate the process on silver coins weighing up to 5 kg and bearing large topographic variations (~ 1.5 cm). We find that colours are related to a single parameter, the total accumulated fluence, making the process suitable for high-throughput industrial applications. Statistical image analyses of laser-irradiated surfaces reveal various nanoparticle size distributions. Large-scale finite-difference time-domain computations based on these nanoparticle distributions reproduce trends seen in reflectance measurements, and demonstrate the key role of plasmonic resonances in colour formation.

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Metal nanoparticles (NPs) are used in a multitude of applications, but perhaps the oldest is as a colourizing agent when dispersed in a host dielectric, as in the (dichroic) Lycurgus cup^{1,2}. Exposed to optical radiation, metal NPs exhibit scattering properties due to excited plasmons that depend on their shape, size, composition and the host medium^{3–6}. Producing colours by exploiting plasmonic effects on metal nanostructures⁷ is of interest because the colours can last a long time (for example, the Lycurgus cup), can be rendered down to the diffraction limit⁸ and can be used in any metal colouring or marking application where inks, paints or pigments should be avoided for environmental, health cost or other reasons.

Fabrication techniques to render plasmonic colours include laser interference lithography⁹, electron beam lithography^{8,10,11}, ion beam lithography or milling¹² and hot embossing or nanoimprint lithography^{9,12}. Kumar *et al.*⁸ fabricated coloured images via electron beam lithography having a resolution as high as $\approx 100,000$ dots per inch. However, the production of large coloured surfaces with such techniques is challenging, time consuming and the methods may be incompatible with the

demands of low-cost mass manufacturing. Furthermore, such processes generally require flat surfaces, and with the exception of periodic structures below the diffraction limit of visible light^{13,14}, the colours produced are often angle dependent (iridescent).

Femtosecond (fs) lasers have been used for metal colourization because of their ablation characteristics, for example, the tendency to preferentially release NPs, compared with the large clusters and chunks produced by nanosecond pulses^{15–17}. Vorobyev and Guo¹⁸ showed that exposing metals to fs pulses could produce highly absorptive surfaces (the so-called ‘black metals’) and surfaces producing a specific colour. However, the colour palette that can be produced by such lasers appears to be limited and angle dependent due to the underlying regular structure¹⁹, and the low pulse energy of fs lasers makes the colouring process time consuming.

Picosecond (ps) lasers have lower costs and higher pulse energies, and offer much faster processing times. Fan *et al.*^{20,21} used single laser pulses to demonstrate colours on copper, where each colour was associated with a single set of laser parameters. Plasmonic effects were mentioned as a mechanism underlying



Figure 1 | Laser colouring of large areas having significant topographic variations. (a) Photograph of a coloured silver coin featuring a representation of an eagle. (b,d) Photographs of silver coins bearing a frosted butterfly (b) before and (d) after laser colouring. The topography on these coins has an overall height of ~ 2 mm. The distinctive white areas on the butterfly are due to the frosted (that is, melted) finish; (c) optical microscope image of the frosted regions, having topographic variations of up to 2 mm in height and a roughness of ~ 1 to $2 \mu\text{m}$. (e) Photograph of a laser-coloured 5 kg silver coin of diameter 21 cm and thickness 2.5 cm (the butterfly coin of (d) is also shown for comparison). (f) Close-up of (e) showing crevices ~ 5 mm deep of black-and-white-coloured eyes. (g) Alternate colouring of another 5 kg coin over topographic relief ~ 1 cm in height. (h) Close-up of (g) near the nose and brow, the highest points on the coin. (i) Angle-independent colours produced on the surface of a gold coin.

colour production, arising from NPs of medium size. Work by a different group showed that oxide production on copper could also generate colours²².

Thermal effects for ps pulses are likely to play a role in the creation of colours, unlike for fs laser pulses that have durations that are shorter than the thermal expansion time²³. The use of closely time-spaced laser pulses (bursts) then presents an interesting method of manipulating the laser–metal interaction. The use of laser bursts on tissue surfaces was recently shown to rapidly ablate the hot interaction region with little heat damage in a process called ‘cold ablation’²⁴. The use of burst for machining metals is of interest due to its increasing ablation yield and faster cutting times²⁵. The advantage of burst compared with the nonburst (single pulse) regime is linked to the increase in electron–phonon coupling²⁶.

Here, we report a widely applicable high-throughput and deterministic process for producing a comprehensive angle-independent (that is, non-iridescent) colour palette composed of many colours via ps laser nonburst and burst colouring methods. This is achieved on unpolished metal surfaces, including silver, gold, copper and aluminium, and surfaces with frosting and centimetre-scale topographic features. We demonstrate the process by colouring silver coins produced at the Royal Canadian Mint, including large 5 kg coins. Scanning electron microscopy (SEM) images of laser-irradiated surfaces reveal the formation of random NPs having size and separation distributions that are statistically controllable through the laser parameters. In addition, we show significant increase in colour quality using the burst colouring method over the nonburst. Colour saturation (Chroma), increased by up to $\sim 70\%$ in some cases, and colour lightness is observed to extend in range by almost 60%. Our experiments on nonburst demonstrate that a large set of laser parameter combinations can produce a given Hue, as long as the total accumulated fluence remains the same, making the process scalable and time efficient. To understand the colour formation, we used large-scale computational electrodynamics to simulate the scattering from periodic distributions of different sized NPs, with geometrical parameters based on statistical analyses of several SEM images of irradiated surfaces. Simulations show that plasmonic resonances in arrangements of NPs play the main role in the colour formation process. We were able to reproduce trends in experimental reflectance spectra for a range of statistical parameters, thus explaining the origin of different colours.

Results

Applications. Figure 1a shows the application of our colouring process to the selective colouring of a silver coin featuring a representation of an eagle. Figure 1b,d shows images before and after colouring a silver coin displaying a butterfly having topography variations of up to 2 mm in height. The colours were selected before laser colouring using a master curve of hue versus total accumulated fluence (see discussion below) for available colour palettes. The colouring process can be applied to surfaces of varying quality, allowing, for example, the uniform colouring of rough frosted surfaces (that is, melted, Fig. 1c) or of large surfaces having significant topographic variations. For example, Fig. 1e–h shows the laser colouring of 5 kg silver coins displaying a representation of a bear, using different colour designs. These 5 kg coins are 21 cm in diameter and 2.5 cm thick, and they have topographic features as high as 1 cm above the flat regions of the surface (nose of the bear), crevices as deep as 5 mm below the flat regions of the surface (topmost eyes), and thus of overall topographic variations of ~ 1.5 cm.

Precise colouring of features on coins was done using vision alignment software with pattern recognition. The vectors were

obtained from an artist at the Royal Canadian Mint. The process is capable of making angle-independent colours on elevated and complex surfaces that are difficult or impossible to colour via traditional paint-based or bottom-up manufacturing processes. Moreover, colour gradients can easily be produced by focusing the laser beam slightly above the surface, outside the confocal volume, making the colouring process sensitive to topography (for example, see Fig. 1g,h). The number of colours in a colour gradient is governed by the distance between the surface and the laser focus. At small distances (while still out of the confocal region) the colour gradient has a smooth transition in colours over a large area—see stripes next to the ears of the bear in Fig. 1e,f. Flat and topographical surfaces situated within the confocal volume are, however, coloured uniformly. In the case of extreme topography, the laser energy can be increased or the focus altered to uniformly colour topographic features.

Colour palettes were also produced on gold samples, as shown in Fig. 1i, and on copper and aluminium surfaces, as shown in Supplementary Fig. 2. The creation of purple, blue and green angle-independent gold and copper is interesting, especially given the onset of vertical electronic transitions in these metals within the visible range (that is, an absorption edge), and will be the subject of further investigation.

Unprotected colours were observed to be unstable over a short timeframe. Passivation coatings formed via atomic layer deposition or evaporation on coloured silver surfaces protected the colours during aggressive humidity and tarnish tests carried out at the Royal Canadian Mint. The colours were, however, slightly red-shifted due to the passivation layer, an effect that is consistent with the shifting of plasmonic resonances on the surface. These shifts can be pre-compensated by altering the appropriate laser parameters during the initial writing.

Colours and burst versus nonburst. The exposure of pure silver to different laser parameters is observed to produce vivid angle-independent colours, as shown in Fig. 2. Figure 2a–c shows colour palettes obtained using our technique, specifically, with nonburst (Fig. 2a) and burst irradiation (Fig. 2b,c). Supplementary Figure 1 shows a schematic illustrating these irradiation schemes. Comprehensive colour palettes were produced through a variation of different machining techniques such as: (1) changing the line spacing, L_s , between each successive line (Fig. 2a); (2) changing the laser marking speed, v , while maintaining a fixed line spacing (Fig. 2b); (3) varying the light polarization with respect to the machining direction; and (4) passing multiple times on the same area, changing the angle between the machining direction and the light polarization, or changing the laser parameters, between each pass (for example, cross-hatching) (Fig. 2c). The same processes were used to produce colour palettes on gold, copper and aluminium.

These colours are highly reproducible and found to depend on the size and density of ablated metal NPs covering the surface (discussed further below). During laser ablation by raster scanning the sample surface, the number of metal NPs redeposited and accumulating from one line to the next is dictated by the inter-line spacing L_s (or marking speed v); that is, the spacing between two consecutive laser lines. The change in particle density with increasing distance from the laser ablated line can be seen in Supplementary Fig. 3 (see Supplementary Note 1).

Figure 2a shows the colours produced with nonburst irradiation of silver by raster scanning the surface, where the different colours are produced by simply increasing L_s . Increasing L_s from 1 or 2 μm in increments of 0.5 μm up to 13.5 μm , at a laser marking speed of $v = 100 \text{ mm s}^{-1}$ results in a production rate of $\eta = 0.1$ to $1.6 \text{ mm}^2 \text{ s}^{-1}$, where the production rate is defined as $\eta = L_s v$. Augmenting the laser marking speed in increments of

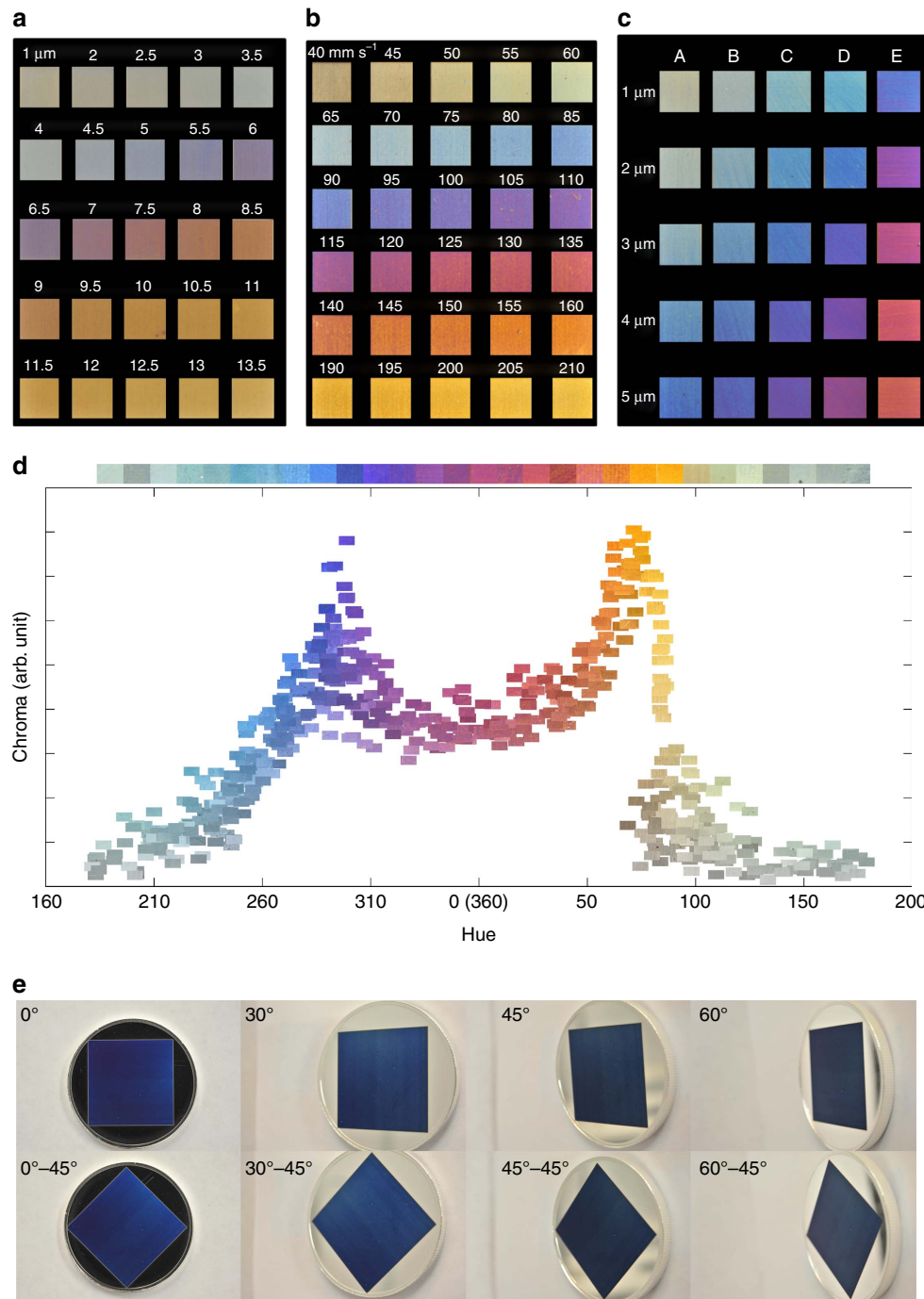


Figure 2 | Colour palettes on Ag. Coloured squares 25 mm^2 in area produced using (a) nonburst and (b,c) burst irradiation. (a) The different colours were obtained by changing the line spacing, L_s , in steps of $0.5 \mu\text{m}$ (as marked above each panel) for a laser fluence of $\phi = 1.29 \text{ J cm}^{-2}$ and a marking speed of $v = 100 \text{ mm s}^{-1}$. (b) Colour palette obtained using bursts containing 5 laser pulses by varying the machining speed in increments of 5 mm s^{-1} starting at 40 mm s^{-1} (as marked above each panel) with a fixed line spacing of $L_s = 7 \mu\text{m}$ and a laser fluence of $\phi = 5.6 \text{ J cm}^{-2}$. (c) Colour palette obtained by maintaining the line spacing fixed (row-wise, as marked) and varying the machining angle between each successive pass (that is, the angle between the light polarization and machining direction), where column A = 2 pass at 270° , column B = 1 pass at $270^\circ + 1$ pass at 234° , column C = 1 pass at $270^\circ + 1$ pass at 191° , column D = 1 pass at $270^\circ + 1$ pass at 162° and column E = 1 pass at $270^\circ + 1$ pass at 126° . The burst parameters in c were identical to the parameters used in b and the marking speed was $v = 150 \text{ mm s}^{-1}$. (d) Graph of Chroma versus Hue, using as markers photographs of the colours obtained by applying the different machining processes of (a–c) and using the same burst parameters and fluence as in b,c. The horizontal colour bar was constructed from a collection of photographs of the 30 highest Chroma colours in d, covering the entire Hue range (0 to 360°). (e) Photographs of a blue-coloured coin taken at four tilt angles (0° , 30° , 45° and 60°) for two coin orientations.

5 mm s^{-1} from 40 to 160 mm s^{-1} , and from 190 to 210 mm s^{-1} , with $L_s = 7 \mu\text{m}$ results in production rates of $\eta = 0.3$ to $1.5 \text{ mm}^2 \text{ s}^{-1}$ for the colours shown in Fig. 2b. The colours shown in Fig. 2c, obtained by the cross-hatching method,

maintained the line spacing fixed (as marked for each row) while varying the machining angle between each successive pass, at a laser marking speed of $v = 150 \text{ mm s}^{-1}$ for a production rate of $\eta = 0.38 \text{ mm}^2 \text{ s}^{-1}$ to $0.69 \text{ mm}^2 \text{ s}^{-1}$. The energy distribution of

each pulse within the bursts and the laser fluence were the same for both Fig. 2b,c). The energy distribution was chosen based on the quality of the colours produced. The colour palettes in Fig. 2a,c can be extended by reducing the line spacing (marking speed in Fig. 2b, or angle in Fig. 2c) between each successive line that also increases the total accumulated fluence.

Figure 2d plots Chroma versus Hue obtained from a collection of colour palettes. The colours were created using the various colouring process described above using a single fluence for the same burst energy distribution as in Fig. 2b,c). A complete Hue palette is produced, covering the entire spectral and nonspectral regions (for example, magenta). The colour bar above Fig. 2d was constructed by selecting a subset of 30 colours having the highest Chroma. Green and cyan colours have the lowest Chroma. High-quality white and black were also achieved using the appropriate laser parameters, as can be observed on the eyes in Fig. 1f.

The burst colours (Fig. 2b,c) are of higher quality, showing greater saturation than the nonburst colours (Fig. 2a). Figure 3a,b plots Chroma and Lightness versus Hue, respectively, for a large collection of colours produced using burst and nonburst irradiation using multiple laser parameters (beyond those used to produce Fig. 2d). A significant increase in Chroma values is achieved over the entire Hue range using burst irradiation compared with nonburst; for example, the Chroma of Hue values near 285 is increased by $\sim 70\%$ (Fig. 3a). Similarly, the range of Lightness values is also increased, for example, by $\sim 60\%$ for Hue values near 100 (Fig. 3b). Fig. 3c shows a CIE xy chromaticity diagram of the colours plotted in Fig. 3a,b) produced using burst and nonburst irradiation. The range of colours achievable is significantly larger using burst irradiation, and the range is expected to increase further as more work using this approach is pursued. The enhancement of colours using burst was also observed in the creation of colour palettes on gold, copper and aluminium.

Our chromaticity diagram on silver (Fig. 3c) is comparable to the chromaticity diagram obtained by bottom-up lithographic techniques using aluminium^{27–29} with the exception of the green colours. The creation of extended colour palettes on aluminium was achieved by tuning the interspacing of fabricated bimodal nanostructures¹¹—interestingly, we find that laser-induced bimodal distributions of NPs are essential to the creation of a broad colour palette, as discussed in the forthcoming sections. An advantage of bottom-up techniques to render plasmonic colours is their ability to achieve high resolution by defining nanoscale features^{8,10}. Our top-down technique holds advantages in process simplicity (single-step direct laser write), and in that no cleanroom infrastructure, moulds, stamping die or chemical processing are required. The existence of a master curve allows colouring processes that tradeoff laser fluence against writing speed. Our technique is capable of colouring large areas bearing high topographic relief (Fig. 1) that may be challenging to work with using bottom-up techniques or paint application methods (for example, ink-jet spray over large areas when encountering sharp relief).

Nonburst colouring of silver and total accumulated fluence.

We focus now on the nonburst colouring process applied to silver to build an understanding of the nanostructures induced on irradiated surfaces and of their ability to render colour. For this purpose, colours were produced using nonburst irradiation at a fixed repetition rate of 50 kHz, keeping the light polarization parallel to the laser machining direction. Colour palettes were produced following the approach of Fig. 2a where L_s was changed in fixed intervals. During production of the colour palettes, it was

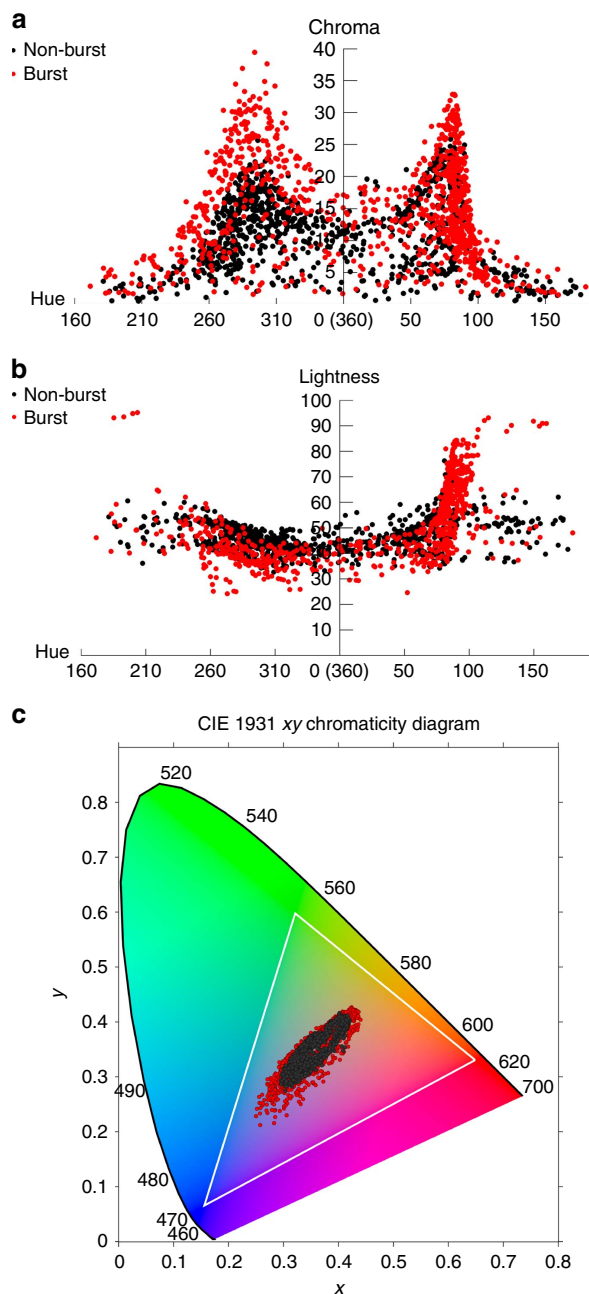


Figure 3 | Nonburst versus burst colours. Graphs comparing (a) Chroma and (b) Lightness values versus Hue for nonburst and burst produced colours. The burst colouring method is observed to significantly increase the Chroma of each Hue value by up to $\sim 70\%$ compared with the nonburst colouring method. (c) CIE xy Chromaticity diagram comparing the burst (red dots) and nonburst (black dots) colours. The white triangle shows the gamut of the sRGB colour space, representing colours achievable by common computer monitors.

noticed that similar Hue values were often obtained using different laser parameters. Each Hue value was subsequently found to be linked to a unique total accumulated fluence value, as plotted in Fig. 4a.

The total accumulated fluence Φ is defined as:

$$\Phi = \varphi N_{\text{eff}} = \frac{a^2 E f}{v L_s} \quad (1)$$

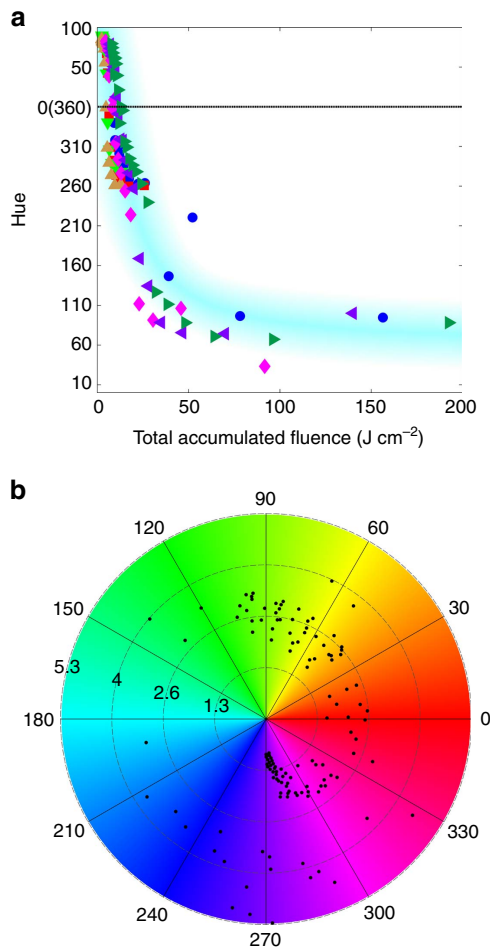


Figure 4 | Hue versus total accumulated fluence. (a) Hue versus total accumulated fluence for (blue circle) $\varphi = 1.12 \text{ J cm}^{-2}$ at $v = 11 \text{ mm s}^{-1}$, (red star) $\varphi = 1.67 \text{ J cm}^{-2}$ at $v = 50 \text{ mm s}^{-1}$, (green downward pointing triangle) $\varphi = 2.59 \text{ J cm}^{-2}$ at $v = 100 \text{ mm s}^{-1}$, (brown left pointing triangle) $\varphi = 6.26 \text{ J cm}^{-2}$ at $v = 250 \text{ mm s}^{-1}$, (pink asterisk) $\varphi = 13.23 \text{ J cm}^{-2}$ at $v = 500 \text{ mm s}^{-1}$, (purple left pointing triangle) $\varphi = 20.58 \text{ J cm}^{-2}$ at $v = 750 \text{ mm s}^{-1}$ and (green right pointing triangle) $\varphi = 29.75 \text{ J cm}^{-2}$ at $v = 1,000 \text{ mm s}^{-1}$. The Hue value completes a full 360° rotation. (b) Polar plot representation of (a) with Hue plotted azimuthally and the logarithm of the total accumulated fluence plotted radially. A full rotation in Hue is observed with increasing total accumulated fluence.

where the laser fluence φ is given by:

$$\varphi = \frac{2E}{\pi\omega_0^2} \quad (2)$$

and the effective number of laser shots N_{eff} is

$$N_{\text{eff}} = \sqrt{\frac{\pi a\omega_0 f}{2v}} \sqrt{\frac{\pi a\omega_0}{2L_s}}. \quad (3)$$

where E is the laser pulse energy, ω_0 the beam waist radius, f the laser repetition rate and a a correction factor due to the modification of a larger area when using a higher pulse energy. This correction factor was obtained from semi-logarithmic plots used to determine the laser spot size, following the procedure detailed in ref. 30. The intraline component of N_{eff} encompasses the shot overlap within a local region, where f/v is the distance travelled between successive laser pulses in a single laser line. The interline component, in comparison, considers the geometrical overlap, $a\omega_0/L_s$, between successive laser lines. At large spacings,

that is, for a lower total accumulated fluence and as $a\omega_0/L_s \rightarrow 1$, the colours converge to yellow due to the absence of overlap between consecutive laser lines. Further evidence of this accumulation process can be observed from the absence of colours, other than yellow, in the last line of each of the coloured squares (not shown). The last line does not undergo the process of particle accumulation as there are no subsequent laser lines.

We find that a very large number of laser parameter combinations can be used to obtain a given Hue, as long as the total accumulated fluence remains the same, under the condition that the repetition rate remains fixed—this is highlighted by the light blue trend band (master curve) on Fig. 4a. Figure 4b shows a polar plot of Fig. 4a with Hue plotted azimuthally and the logarithm of the total accumulated fluence plotted radially; a full 360° rotation in Hue is observed.

The master curve is useful, for example, to tradeoff writing time versus laser write parameters; that is, from equation (1), v , L_s and E can be changed independently to obtain a specific total accumulated fluence and the master curve used to relate the fluence to the Hue. The largest production rates attained in producing a comprehensive colour palette from the master curve were in the range from $\eta = 3 \text{ mm}^2 \text{ s}^{-1}$ to $36 \text{ mm}^2 \text{ s}^{-1}$, achieved by setting $v = 3,000 \text{ mm s}^{-1}$ (the highest speed of our galvo-metric mirrors). The master curve can also assist with the aesthetic control of a single colour, as the Lightness increases with laser fluence, φ , for a constant Hue; for example, various ‘types’ of blue (navy blue, sky blue) can be realized in this manner. Chroma, however, was observed to remain unaffected for each Hue when using different laser fluences, φ . The rotation and overlapping of the data points on Fig. 4b show explicitly that the xy values of CIE XYZ colour space (Fig. 3c) can be recovered for a fixed laser fluence, φ , by simply adjusting the marking speed or line spacing.

Deviations from the master curve in Fig. 4a are attributed to the increasingly chaotic nature of the surface with increasing total accumulated fluence. Also, while we are able to render reds reproducibly, there is less variety in the reds than for other colours due to the high slope in the red region on the master curve (Hue values from 345 to 15 —modulo 360°). In fact, the rate of change of Hue per μm (or mm s^{-1}), in the red region, is twice as high as the rate of change in all other Hue regions, explaining the absence of red colours in Fig. 2a.

Changing the repetition rate, f , along with v , L_s and E to obtain a desired total accumulated fluence resulted in colours other than what was expected based on the master curve of Fig. 4a. To study the effect of the laser repetition rate on the colours, f was changed proportionally with speed, v , to maintain a fixed total accumulated fluence, while E and L_s were kept constant. The colour palette obtained was similar to that shown in Fig. 2a but with fewer colours. Increasing f and keeping it fixed while changing v , L_s and E would only create reduced colour palettes. The baseline in Fig. 4a increased with increasing repetition rate gradually cutting off the lower colours (that is, blues, purples and reds). No colours other than yellow were observed at repetition rates above 400 kHz , suggesting a local thermal accumulation effect.

Surface analysis. Extensive SEM analyses of regions exhibiting different colours on silver reveal 3 distinct classes of particles differentiated by size: large ($R \geq 75 \text{ nm}$), medium ($10.7 \leq R < 75 \text{ nm}$) and small ($R < 10.7 \text{ nm}$), where R is the radius of a particle. These particle classes were obtained from statistical analyses of SEM images, producing histograms with well-defined ranges of particle sizes (see Supplementary Figs 4 and 5).

Figure 5a–c shows three coloured surfaces with corresponding low- and high-magnification SEM images. The particle density is

found to change significantly with line spacing, as shown in Fig. 5. In Fig. 5d–i, the small and medium particles are seen to form random networks with the medium-sized particles sparsely covering the surface and the small ones more densely distributed across the irradiated region (see Supplementary Note 2). The formation of NPs is believed to come from the combination of thermal effects^{31–34} and the redeposition of particles following laser ablation^{17,15}. Upon close examination of the SEM images, it appears that the small particles are in reality approximately hemispherical, an observation supported by a cross-section of a coloured silver sample obtained through focused ion beam milling and imaging. Thus, they can be modelled as spheres partially embedded into the silver surface.

SEM analyses of coloured regions reveal that the number density of the small particles, produced using different laser parameters, follows its own distinctive trend with total accumulated fluence (see Supplementary Fig. 4a), similar to that of Fig. 4a, whereas the number density of the medium particles does not (see Supplementary Fig. 4b). This observation suggests that the small particles play a role in the colours perceived. The mean radius of small and medium particles was found to remain approximately constant as a function of line spacing (Supplementary Fig. 4c,d, determined from the analysis of three SEM images per line spacing). However, the mean interparticle distance (wall-to-wall) changes with line spacing (Supplementary Fig. 5e,f), that is, it decreases for small particles and increases for medium particles, suggesting that the colours are affected by near-field interactions between nanoparticles in close proximity^{6,35–37}, particularly the associated surface plasmon resonance⁶.

Wavelength-dispersive spectroscopy analysis of the different colours in Figs 2a and 4a showed no difference in the amount of oxidation measuring $2.8 \pm 0.4\%$ oxygen content for all Hue values tested. Monte Carlo simulations (WinXray) of silver oxide layers, under the same wavelength-dispersive spectroscopy operating conditions, gave an equivalent oxide thickness of ~ 2 nm. The same conclusion was gathered from the invariability of the oxygen content in separate energy-dispersive spectroscopy and X-ray photoelectron spectroscopy measurements of the different coloured surfaces. The X-ray photoelectron spectroscopy analyses of the coloured surfaces also showed no sulfur content.

FDTD simulations. Our finite-difference time-domain (FDTD) simulations show that colour formation can be viewed as spectrally selective absorption processes involving plasmonic resonances. White light incident on a nanostructured surface is not fully reflected, as it would be for a smooth silver surface. Rather, narrow-band spectral components (colours) are subtracted due to plasmonic resonances on the surface, and absorption processes in the medium, as also reported in another study³⁸. What survives these absorptive processes is reflected (there is no transmittance).

In Fig. 5j we show a high-magnification SEM image for the case of $\varphi = 1.67 \text{ J cm}^{-2}$ at $\nu = 50 \text{ mm s}^{-1}$ with $L_s = 8 \mu\text{m}$, from which we observe the presence of NPs having a random distribution. The analysis of SEM images produced statistics of the NP distributions, that is, number of particles per unit area, particle dimensions and interparticle distances, from which the average radii and average interparticle distances were obtained. Three sets of NPs were identified based on their dimensions, that is, small, medium and large NPs. The large particles are neglected in our analysis due to their low number on the surface, as suggested by the bimodal distribution for small and medium NPs in the histograms (Supplementary Fig. 5a–c). We carried out simulations considering only small and medium Ag NPs uniformly distributed on a perfectly flat Ag substrate following the statistics retrieved from the SEM images. The average radii of small and medium NPs used in simulations are denoted R_s and R_m , and the

average interparticle distances (centre-to-centre) are denoted D_s and D_m , respectively.

Images such as Fig. 5j inspired us to construct a model of surfaces where NPs were periodically arranged in a hexagonal configuration that produces a hexamer unit cell. The hexamer has D_{6h} symmetry, and based on group theory, exhibits polarization independence (isotropy), as verified by simulations³⁹. We chose D_m as an integer multiple of D_s to allow the application of periodic boundary conditions to the unit cell defined by the medium NPs. The periodicity of the unit cell ($\sim D_m$) is small enough to preclude coupling by diffraction into propagating surface plasmon waves on the Ag surface. Perfect periodicity of the NPs gives isotropy with respect to the incident polarization, narrowband resonances and ultimately colour selectivity. This can be considered a good qualitative approximation to actual surfaces.

By changing the surface density and/or the radius of small and/or medium NPs, several types of arrangements can be formed. An arrangement is homogeneous when it is formed by an aggregate of small NPs only or medium NPs only, and heterogeneous when it is formed by an aggregate of medium and small NPs. A heterogeneous arrangement, for example, is formed by a central medium NP with nearby small NPs arranged in a ring. Furthermore, by modifying the level of embedding of the NPs into the substrate, the geometry changes because the NPs are gradually transformed from spheres to hemispheres. Plasmonic arrangements embedded in a homogeneous medium or on a dielectric have been extensively studied (dimer, trimer, quadrumer, tetramer, hexamer, heptamer)^{39–41}, but not on a metal substrate and not arranged and embedded as inspired by SEM images of laser-processed metal surfaces. We have observed different types of resonant modes in our simulation of arrangements; we will refer to them as collective resonances.

In Fig. 6a,b we demonstrate the interplay between medium and small NPs on colour formation, and the effect of embedding the small NPs on the collective resonance, respectively, by showing simulation results for the statistical average parameters associated with the line spacing $L_s = 5 \mu\text{m}$, marked at $\nu = 50 \text{ mm s}^{-1}$ with a laser fluence $\varphi = 1.67 \text{ J cm}^{-2}$: $R_s = 4 \text{ nm}$, $R_m = 34.3 \text{ nm}$, $D_s = 13.5 \text{ nm}$ and $D_m = 108 \text{ nm}$.

In Fig. 6a we show the computed reflectance spectrum considering small NPs only, medium NPs only and the combination of both NP sizes; the small and medium NPs are embedded by half their radius. We observe the resonance of the medium-sized NPs at $\lambda = 390 \text{ nm}$ (black curve), shifted slightly from the prediction of Mie theory for the same sphere in air, due to the presence of the substrate. The interaction between small and medium NPs drastically alters the computed reflection spectrum, as noted by the appearance of a deep dip at $\lambda = 650 \text{ nm}$ in Fig. 6a (red curve) that is due to a new collective resonance. In Fig. 6b we show how the reflectance response evolves as the small NPs are embedded in steps of 0.5 nm . A very high sensitivity of collective resonances on embedding is observed as the large shift in the associated dip. By embedding the small NPs, the size of the nanogaps between the central medium NP and the surrounding small NPs increases. This changes dramatically the geometry of the arrangement and, consequently, their resonances. A blue shift in the collective resonance is observed with increasing embedding (a blue shift due to cluster expansion was reported in previous work³⁹). In the laser-generated surfaces, we would expect the location and embedding of the small NPs to vary across the surface, and thus the overall effect of the sharp absorption dip to be averaged out; we take this into account below. In Fig. 6b we also note other smaller features in the reflectance curves. These are due to resonances arising from homogeneous arrangements of small NPs only.

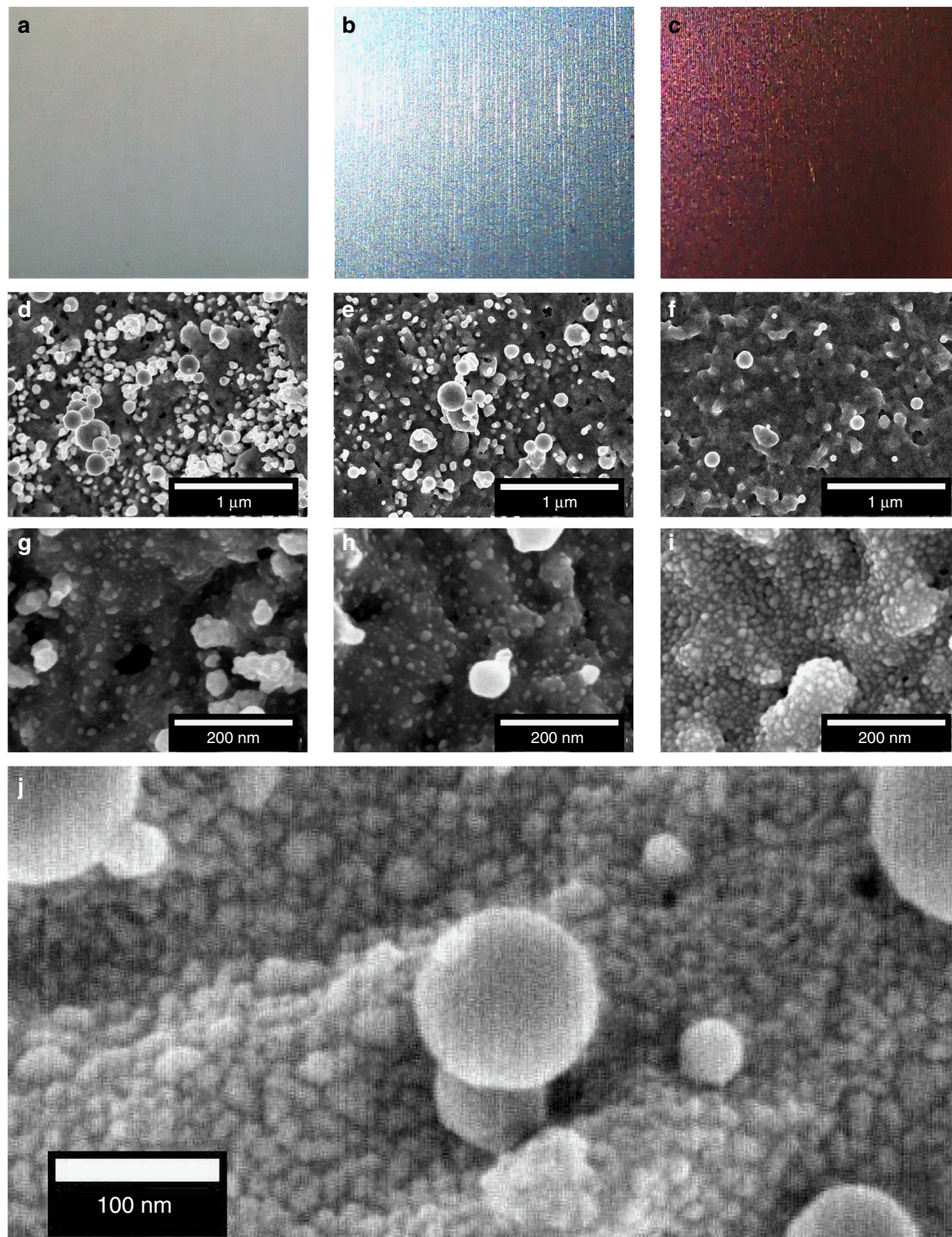


Figure 5 | Nanoparticle networks on coloured silver surfaces. (a–c) Low-magnification optical microscope images of coloured surfaces; (d–f) low-magnification and (g–i) high-magnification SEM images of corresponding surfaces. Surfaces processed using $\varphi = 1.12 \text{ J cm}^{-2}$ at $v = 11 \text{ mm s}^{-1}$. (a,d,g) $L_s = 5 \mu\text{m}$ (Hue = 216.5, Cyan); (b,e,h) $L_s = 10 \mu\text{m}$ (Hue = 269.3, Blue); and (c,f,i) $L_s = 30 \mu\text{m}$ (Hue = 17.2, Red). The number of medium NPs is observed to decrease with increasing L_s (d,e,f, scale bar, 1 μm), and the number of small NPs to increase with L_s (g,h,i, scale bar, 200 nm). (j) High-magnification SEM image for $\varphi = 1.67 \text{ J cm}^{-2}$ at $v = 50 \text{ mm s}^{-1}$ with $L_s = 8 \mu\text{m}$.

In Fig. 7a–d we show the electric field distribution at the free-space optical wavelengths of $\lambda = 390 \text{ nm}$ (Fig. 7a,c) and $\lambda = 650 \text{ nm}$ (Fig. 7b,d), where we observe absorption dips in Fig. 6a. We show xz planes cut 2 nm above the silver surface for medium NPs only (Fig. 7a,b), and for medium and small NPs (Fig. 7c,d). In Fig. 7a we show the response of the surface to illumination with $\lambda = 390 \text{ nm}$, the resonance of the medium-sized NPs only.

Figure 7b shows that medium NPs only do not produce any absorption when illuminated with $\lambda = 650 \text{ nm}$, and where the reflectance in Fig. 6a is shown to be very high. In Fig. 7c we observe that the near-field intensity of the medium NPs at $\lambda = 390 \text{ nm}$ is reduced by the presence of the small NPs that act as plasmonic waveguides⁴², coupling the medium-size NPs. When small and medium NPs are illuminated at $\lambda = 650 \text{ nm}$ (Fig. 7d), a

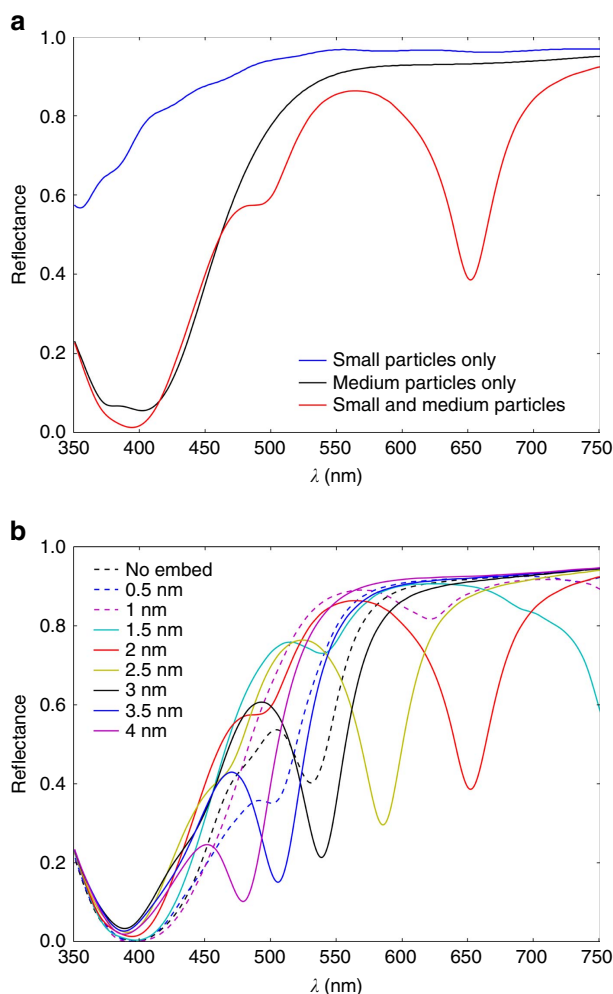


Figure 6 | Computed reflectance responses. (a) Computed reflectance spectra considering only small NPs embedded by $R_s/2$; only medium NPs embedded by $R_m/2$; and medium and small NPs embedded by $R_m/2$ and $R_s/2$, respectively. (b) Reflectance spectra computed by varying the embedding of the small NPs in steps of 0.5 nm (the medium NPs are embedded by $R_m/2$).

collective resonance is excited, producing field enhancement in the nanogaps, and ultimately the smaller absorption dip observed in Fig. 6a. The interaction of a z -polarized and y -propagating plane wave pulse with the nanoparticles on the surface (medium and small NPs are embedded into the surface by $R_m/2$ and $R_s/2$, respectively) is shown in Supplementary Movies 1 and 2, for an xz plane 2 nm above the silver substrate, and a yz plane through the middle of the medium particles, respectively. In Fig. 7e we show a snapshot extracted from Supplementary Movie 2; the plane wave excitation pulse has just hit the nanostructures, inducing localized surface plasmons in all NPs that are clearly visible.

In Fig. 8a we show measured reflectance spectra of 6 coloured squares produced with line spacings of 4, 5, 6, 8, 10 and 14 μm . These reflectance spectra show a transition from blue to yellow with increasing line spacing. The same transition has already been shown in Fig. 4a as a function of the total accumulated fluence. Magenta and yellow are the colours that can be produced with the highest Chroma (note the bimodal distribution of Fig. 3a).

In Fig. 8b we reproduce the qualitative features of Fig. 8a by modelling the response of two-particle periodic surfaces according to the statistical trends observed from the corresponding SEM

images. Exact quantitative comparisons are not possible, as the experiments are on rough surfaces (for example, burnished then laser-coloured surfaces), whereas we consider a flat surface with NPs in our simulations. This also explains why the overall reflectance levels in the experiments are lower. To account for the statistical nature of embedding, we repeated the simulations for small NP embedding values ranging between 0.5 and 3.5 nm in 0.5 nm increments; the medium NPs were all embedded by 30% of their radius. We averaged over the resulting reflectance spectra to produce each curve in Fig. 8b. Averaging over nm scale embedding washes out the effect of the collective medium/small NP resonances, resulting in a broadened response, consistent with what was observed in random clusters⁴³. The Hues in Fig. 8b of 276, 328, 14, 55, 65, 81 and 87 were obtained for $D_m = 81, 86, 90, 96, 100, 113$ and 139 nm, and D_m/D_s ratios of 5, 5, 6, 7, 8, 10 and 13, respectively, with $R_m = 36$ nm and $R_s = 4$ nm. As in the experimental reflection spectra, a transition from blue to yellow occurs with increasing D_m and decreasing D_s , supported by the statistical analysis of the coloured surfaces (see Supplementary Fig. 4).

Simulations show that blue originates when medium NPs are very close to each other (edge-to-edge distance ~ 10 nm), and yellow originates when medium NPs are farther apart ($D_m > \sim 110$ nm). This dependence on interparticle distance is in agreement with experimental trends. However, we use somewhat smaller values of D_m compared with those reported in Supplementary Fig. 4. Since the statistical SEM analysis averages D_m over a large surface, the interparticle distances information for very close medium NPs (which are visible, for example, in Fig. 5) is lost. This suggests that arrangements of very closely spaced medium NPs play the main role in the blue/violet colour formation, acting as colour hot spots on the surface. The colours in between blue and yellow are created with small changes in D_m , and thus harder to obtain experimentally with a random distribution of nanoparticles. Thus, we would expect that it would be more difficult to get a red with high Chroma, and this is precisely what is noted in experiments (Figs 2d and 3a).

In conclusion, we described a broadly applicable and deterministic process for the non-iridescent colouring of metal surfaces and demonstrated the process by colouring silver coins produced at the Royal Canadian Mint, as well as gold, copper and aluminium surfaces. In the case of nonburst irradiation, each individual colour can be linked to a total accumulated fluence that can then be exploited to decrease the colouring time of large metal surfaces or to fine-tune the colour perceived for a specific Hue. The colours originate from random distributions of small and medium nanoparticles embedded into the surface, induced and controlled by laser exposure. The randomness of the nanoparticle networks is modelled effectively by assuming a periodic structure defined by statistical averages of nanoparticle size and separation. We have demonstrated that plasmonic effects arising in nanoparticle arrangements explain the palette of experimental colours. The medium nanoparticles in particular play a fundamental role in the colour formation, as their interparticle distance modifies plasmonic resonance conditions and then the perceived colour. Irradiation using short time-spaced laser bursts was shown to increase significantly the Chroma for all Hue values, in some cases by up to $\sim 70\%$. Furthermore, burst irradiation allowed for the creation of colour palettes on surfaces of gold, copper and aluminium. This laser colouring process was demonstrated on several silver coins, including a large 5 kg coin bearing significant topographic features (~ 1.5 cm). The proposed method opens the door to large-scale industrial applications of laser colouring for anti-counterfeiting, biosensing, biocompatibility and the decoration of consumer products such as jewels, art, architectural elements and fashion items.

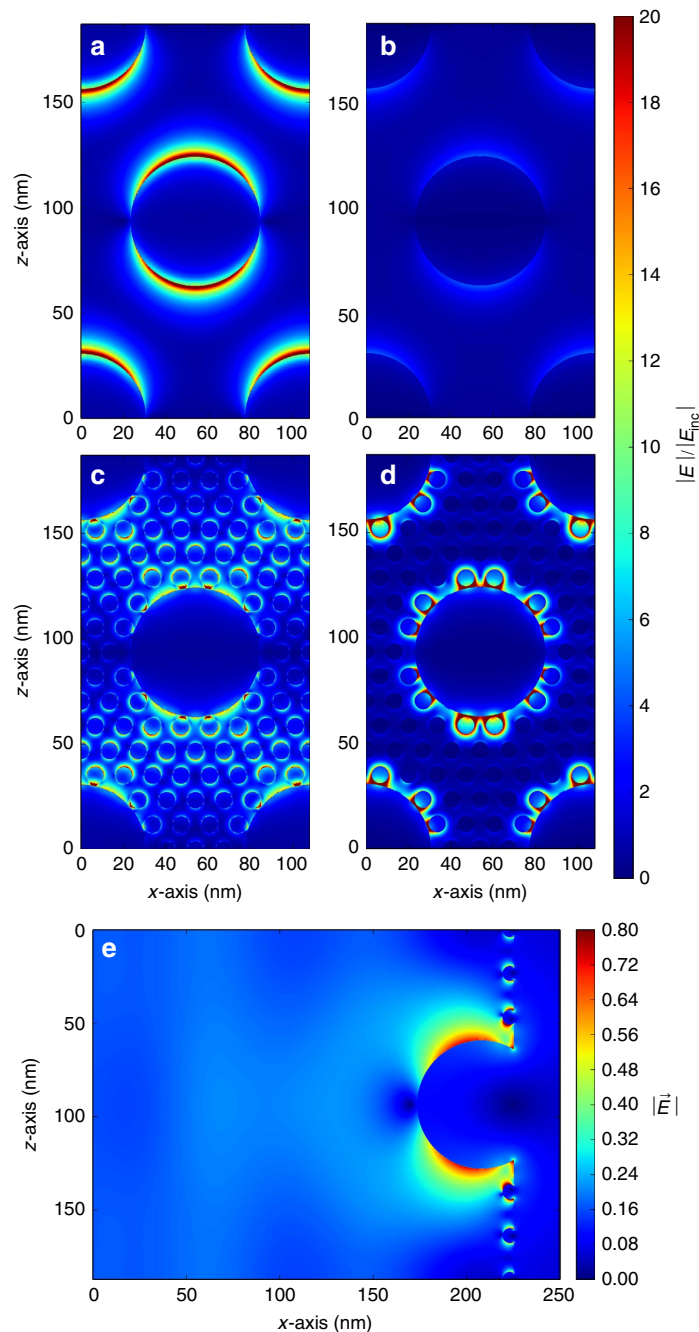


Figure 7 | Computed near-field distributions for arrays of nanoparticles. FDTD simulations showing the electric field distribution for only medium NPs at (a) $\lambda = 390$ nm and (b) $\lambda = 650$ nm, and for medium and small NPs at (c) $\lambda = 390$ nm and (d) $\lambda = 650$ nm. (e) Snapshot from the time-domain simulation for medium and small NPs. All NPs are embedded into the surface by half of their radius.

Methods

Laser specifications. In our experiments, we used 1,064 nm light from a 15 W Duetto (Nd:YVO₄, Time-Bandwidth Product) mode-locked MOPA laser, operating at a fixed burst repetition rate of $f_b = 1/T_b = 50$ kHz (T_b is the burst period) of 10 ps pulses. The time separation between each pulse within a burst is $t_{ib} = 12.8$ ns (see also Supplementary Fig. 1). A selection of 1 to 8 pulses within each burst is available. The setting of 1 pulse per burst corresponds to the normal mode of operation of the laser and will be defined as nonburst (that is, a burst of 1 pulse). The energy distribution of each pulse within a burst was controlled using the software provided by the manufacturer (FlexBurst). A spot size of 14 μm for the 163 mm lens (28 μm for the 254 mm lens) was obtained from semilogarithmic plots of the square diameter of the modified region, measured with SEM, as a function of energy, following the procedure described in ref. 30.

Laser colouring process. The light was focused on the metal surface using an F-theta lens ($f = 163$ and 254 mm, Rodenstock). The pulse energy for the results

presented ranged between 3.4 and 91.4 μJ . The laser was fully electronically integrated and enclosed by a third party for industrial applications (GPC-PSL, FOBA). For accurate focusing, the surface of a sample was located using a touch probe system. The silver and gold samples were of 99.99% and 99.999% purity, respectively, and not polished before machining to meet requirements of reproducibility in industrial applications. The aluminium samples were from the 7000 alloy series. For machining, a sample was placed on a 3-axis translation stage with a resolution of 1 μm in both the lateral and axial directions. Samples were raster scanned using galvanometric XY mirrors (TurboScan 10, Raylase) displacing the beam in a top to bottom fashion with a mechanical shutter blocking the beam between successive lines. The laser power was computer controlled via a laser interface and calibrated using a power meter (3A-P-QUAD, OPHIR).

Surface imaging and statistics. High-resolution SEM (JSM-7500F FESEM, JEOL) images were obtained using secondary electron imaging mode. For analysis of the SEM images, a Matlab program was written to locate the position of each

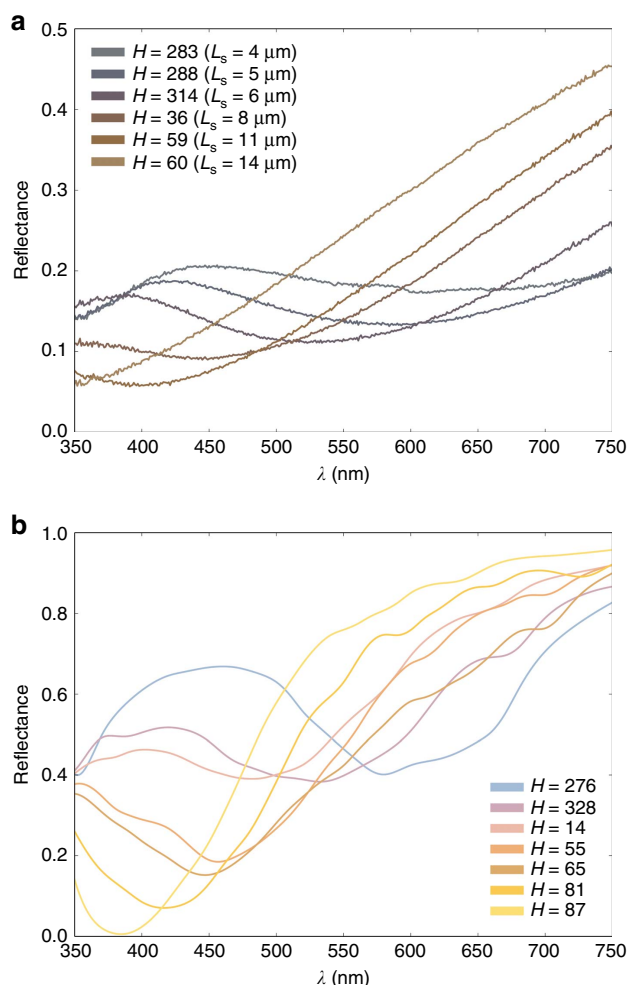


Figure 8 | Experimental and theoretical reflectance spectra.

(a) Measured reflectance spectra of colours produced with the line spacings of 4 (Hue = 283), 5 (Hue = 288), 6 (Hue = 314), 8 (Hue = 36), 10 (Hue = 59) and 14 μm (Hue = 60). (b) Computed reflectance spectra, each curve averaged over a few values of small NP embedding for increasing D_m (Hue). The colour scheme of the curves follows the measured/calculated Hues.

particle and record its diameter and the average wall-to-wall inter-distance spacing to its nearest neighbours.

Photometric characterization. Colours were quantified using a Chroma meter (CR-241, Konica Minolta) in the CIELCH colour space, 2 observer and illuminant C (North sky daylight); where L is colour Lightness, C is Chroma (colour saturation) and H is Hue (colour value associated with a 360° polar scale).

Radiometric characterization. The reflectance measurements were performed using a CARY 7000 UV-Vis-NIR spectrophotometer (Agilent Technologies) equipped with an integrating sphere detector (Labsphere) for collecting simultaneously the specular and diffuse reflectance signals from the samples. An aperture was used in front of the samples to ensure that only the treated surface area was probed with the incident light beam. The reflectance data were calculated taking into account this aperture, and corrected against reference samples of silicon and silver.

Numerical simulations. Three-dimensional FDTD simulations^{44,45} were performed to determine the origin of the colour rendering process. We used in-house 3D-FDTD parallel code^{46,47} on an IBM BlueGene/Q supercomputer (64k cores) part of the Southern Ontario Smart Computing Innovation Platform (SOSICIP). In the model, metal NPs were arranged in the xz plane, as inspired by SEM images of irradiated surfaces and the corresponding statistics of the metal NP distributions, and the system was excited by a z -polarized plane wave. A broadband electromagnetic pulse propagating along the y -direction from air and impinging on the nanostructured surface was used. The analysis was performed over the

wavelength range 350–750 nm in a single run of the code using in-line discrete Fourier transform. Space-steps in the range of 0.125–0.5 nm were used for the simulations. The dispersion of silver was introduced by the Drude + 2CP model⁴⁸. This model was implemented in FDTD by the auxiliary differential equation technique⁴⁹. The simulation domain in the direction of propagation of the plane wave was truncated by convolutional perfectly matched layer absorbing boundary conditions⁵⁰. The simulations required up to 16k cores. The theoretical reflectance spectrum was calculated by integration of the Poynting vector in the backward far-field region. The theoretical reflectance spectra were reconstructed as colours using in-house Matlab code, weighting each frequency composing the spectra to the spectral sensitivity of the human eye.

Data availability. The data that support the findings presented in this paper are available. Restrictions apply to data availability due to the commercial nature of the technology and are not publicly available. Data are however available from the authors on reasonable request and with permission from the Royal Canadian Mint.

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Author contributions

J.-M.G. conceived the laser colouring process. J.-M.G. and G.C. developed the laser colouring technology. A.W. proposed and directed the project, and supervised the experiments. L.R. proposed the computational study. L.R. and P.B. co-directed the study and supervised the simulations. J.-M.G., G.C. and M.C. carried out the statistical analysis of the surfaces. G.C. wrote the Matlab codes. D.P. obtained reflectance measurements on coloured surfaces. A.C.L. set up the FDTD code, conducted the simulations and generated the movies. A.C.L. and J.-M.G. analysed the results. A.C.L., L.R. and P.B. formulated the theoretical conclusions. J.-M.G., A.C.L., L.R., P.B. and A.W. co-wrote the paper and J.-M.G., A.C.L. and G.C. prepared the figures. All authors discussed the experimental and theoretical results.

Additional information

Supplementary Information accompanies this paper at <http://www.nature.com/naturecommunications>

Competing interests: The authors declare no competing financial interests.

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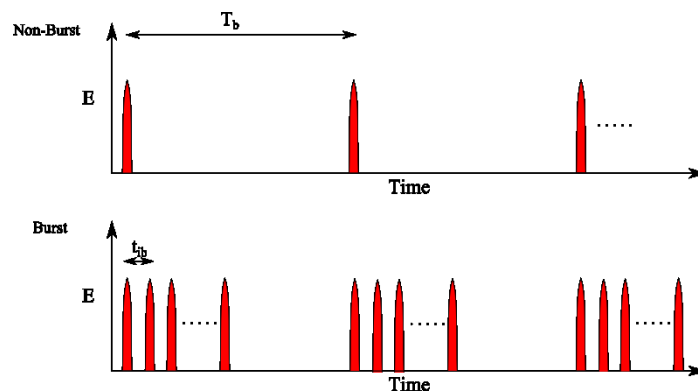
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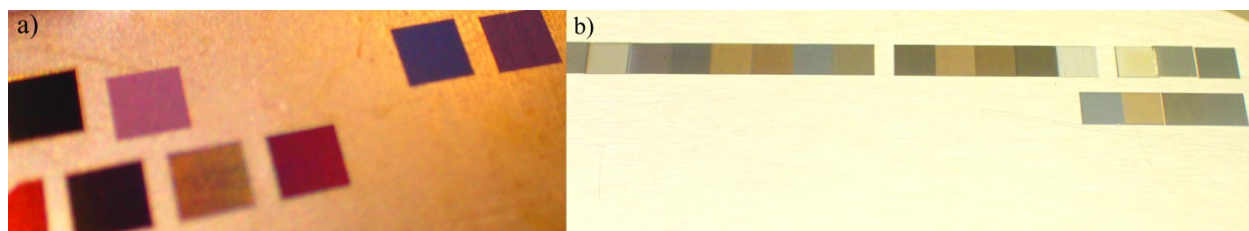


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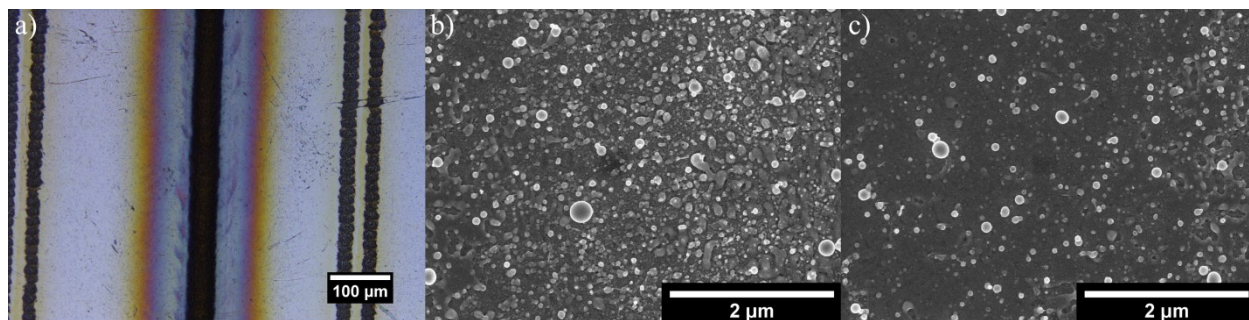
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Supplementary Figure 1 | Schematic representation comparing the non-burst and burst operation of the machining laser. The repetition rate of the laser in normal operation (*i.e.*, non-burst) is defined by $f = 1/T_b$ where T_b is the burst period. In these experiments, f was fixed at 50 kHz. In burst mode a choice of 2 to 8 pulses could be chosen with a fixed time separation of $t_{ib} = 12.8$ ns. The energy of each pulse within the burst could be controlled via FlexBurstTM.



Supplementary Figure 2 | Photographs of colours obtained on (a) copper and (b) aluminum using the burst colouring method. The different colours were obtained by varying the spacing between successive laser lines.

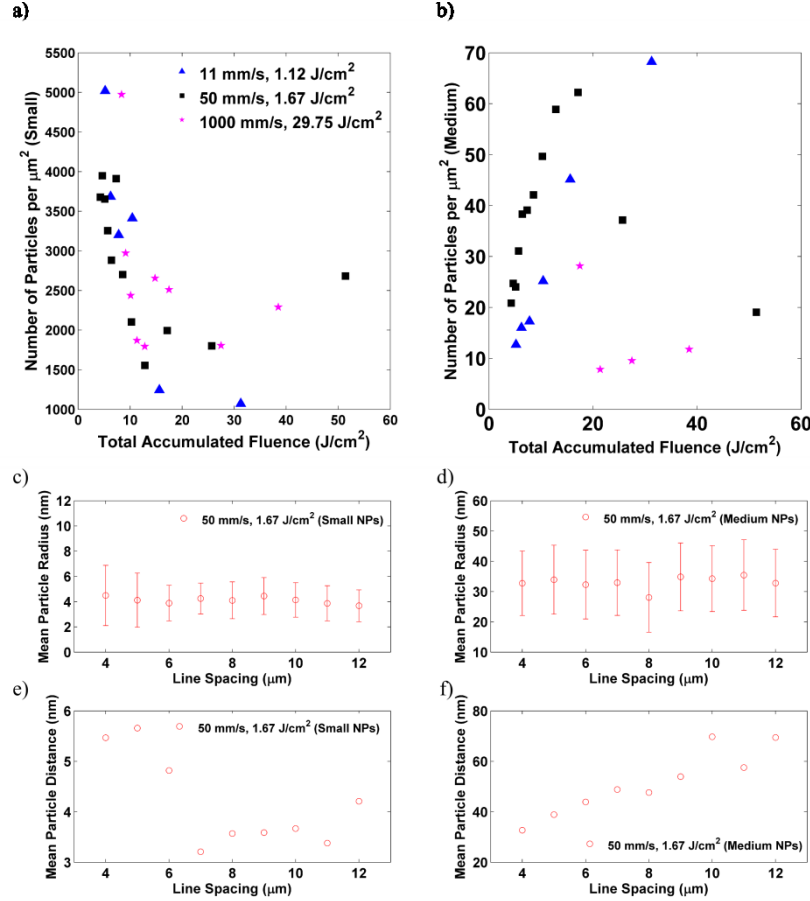


Supplementary Figure 3 | (a) Photograph of a laser ablated line on silver taken under 50x magnification. (b) SEM image of the nanoparticles deposited close to the ablated line shown in (a). (c) SEM image of the nanoparticles deposited further away from the ablated line shown in (a).

Supplementary Note 1 | Particle density distribution

The particle density resulting from the laser ablation of a single line was observed to differ along the direction normal to the line, Supplementary Figure 3 (b,c). The different particle densities can be inferred by the color gradient next to the ablated line, Supplementary Figure 3 (a). From this information the proper spacing between subsequent lines can be determined in order to tune to the desired colour. In the case of Supplementary Figure 3 (a), a

very slow speed was used in order to compensate for the lack of subsequent lines which as a result produced a groove.

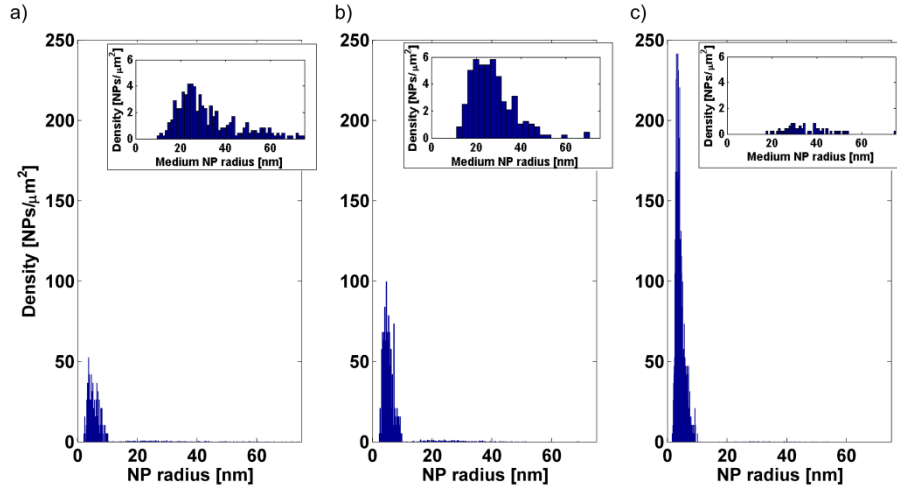


Supplementary Figure 4 | Number of particles per μm^2 versus total accumulated fluence for (a) small nanoparticles and (b) medium nanoparticles for a fluence $\phi = 1.12 \text{ J/cm}^2$ at laser marking speed $v = 11 \text{ mm/s}$; $\phi = 1.67 \text{ J/cm}^2$ at $v = 50 \text{ mm/s}$; and $\phi = 29.75 \text{ J/cm}^2$ at $v = 1000 \text{ mm/s}$. Mean particle radius versus line spacing for (c) small NPs and (d) medium-large NPs for $\phi = 1.67 \text{ J/cm}^2$ at $v = 50 \text{ mm/s}$. Mean inter-particle distance (wall-to-wall) versus line spacing for (e) small NPs and (f) medium-large NPs for $\phi = 1.67 \text{ J/cm}^2$ at $v = 50 \text{ mm/s}$. The errors bars are standard deviation obtained from the statistical analysis of 3 SEM images within different areas of the same coloured squares.

Supplementary Note 2 | Particle Statistics

Surface analysis of coloured regions reveal that the number density of small particles, produced using different laser parameters, follows its own trend, Supplementary Figure 4 (a), similar to that of Fig. 4 (a), whereas the number density of the medium particles does not, Supplementary Figure 4 (b). This observation suggests that the small particles play a major role in the colours perceived. The mean radius of small and medium nanoparticles was found to remain approximately constant as a function of line spacing, as observed in Supplementary Figure 4 (c,d) (determined from the analysis of 3 SEM images per line spacing, *i.e.*, per colour). However, the mean inter-particle

(wall-to-wall) distance changes with line spacing, so the colours are believed to be caused by near-field interactions between nanoparticles in close proximity^{1,2,3,4}, particularly the associated surface plasmon resonance frequency⁴.



Supplementary Figure 5 | Histogram of the number of particles on the substrate relative to their radius over a surface area of $1 \mu\text{m}^2$ for a fluence $\phi = 1.12 \text{ J/cm}^2$ and line spacing (a) $L_s = 5 \mu\text{m}$, (b) $L_s = 10 \mu\text{m}$, and (c) $L_s = 30 \mu\text{m}$, at a marking speed $v = 11 \text{ mm/s}$. Two discernible bumps (bimodal distribution) are noted in the histograms, corresponding to the small and medium particles. The inserts are magnifications of the medium particle distributions.

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Passivation of Plasmonic Colours on Bulk Silver by Atomic Layer Deposition of Aluminum Oxide

5.1 Summary

This chapter demonstrates the protection of plasmonic coloured surfaces using a novel two-step deposition process of alumina by atomic layer deposition for the intent of mass production. Coloured silver surfaces are demonstrated to be sensitive to heat and vulnerable to chemical attacks if left unprotected. The deposition of a conventional single layer of alumina is demonstrated to conserve colours, protect against heat but is shown to be inefficient at protecting the nanostructured silver against chemical attacks. A novel two-step process was conceived which consists of (1) the deposition of a low-density film of alumina (*i.e.* low temperature deposition) to act as a heat barrier for (2) the deposition of a denser film of alumina (*i.e.* higher temperature). This two-step approach is shown to provide protection against both heat and environmental chemical attacks while preserving the colours. The technique is applied to a 5 kg laser coloured coin with a

topography of ~ 1.5 cm. The supplementary information document gives an in-depth description of the burst train and provides additional information on the chemical composition of the coloured surfaces, the adhesion of the alumina coating to the coloured surfaces and SEM images of the surface morphology before and after heating.

5.2 Contributions

The results provided in this section were published in the journal *Langmuir*. In this publication, I coordinated the efforts between the Royal Canadian Mint, Carleton University and the University of Ottawa. Under the direction of Dr. Weck and Dr. Berini, I supervised the research team at the Royal Canadian Mint and taught COOP student Graham Killaire how to colour metals and the functioning of the laser system. Graham Killaire and I provided the Carleton group with samples to be coated. I analyzed the data contained in this manuscript and, from the data, I conceived the two-step process described in this paper. Dr. Gordon applied the alumina coatings to the coloured surfaces under the supervision of Dr. Barry. The tarnish tests were conducted under the supervision of Raine Kampmann at the Royal Canadian Mint. In this manuscript, I made all the figures at the exception of the CIE diagrams with a coloured background and the ALD attachment schematic. The coloured background CIE diagrams were made by Graham Killaire. All authors discussed the results. Dr. Gordon and Dr. Barry provided the chemical explanation for the attachment of alumina onto the silver surface and the visual schematic. Dr. Weck, Dr. Berini and I co-wrote the publication.

5.3 Article

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Passivation of Plasmonic Colors on Bulk Silver by Atomic Layer Deposition of Aluminum Oxide

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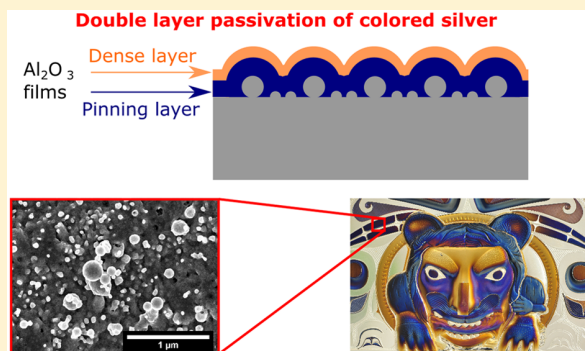
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Supporting Information

ABSTRACT: We report the passivation of angle-independent plasmonic colors on bulk silver by atomic layer deposition (ALD) of thin films of aluminum oxide. The colors are rendered by silver nanoparticles produced by laser ablation and redeposition on silver. We then apply a two-step approach to aluminum oxide conformal film formation via ALD. In the first step, a low-density film is deposited at low temperature to preserve and pin the silver nanoparticles. In the second step, a second denser film is deposited at a higher temperature to provide tarnish protection. This approach successfully protects the silver and plasmonic colors against tarnishing, humidity, and temperature, as demonstrated by aggressive exposure trials. The processing time associated with deposition of the conformal passivation layers meets industry requirements, and the approach is compatible with mass manufacturing.



INTRODUCTION

The use of nanofeatures to control plasmonic resonances has been an important research topic for the past decade, targeting various applications in, e.g., medicine^{1,2} and energy conversion.^{3–6} Of recent interest is the use of plasmonic nanostructures to render color.^{7–15} Plasmonic colors have yet to be applied in an industrial context, but the effort and time required for creating metal nanostructures has been significantly reduced by the use of lasers^{9,11} or nanoimprinting technology.^{12–14} Both methods have sufficiently cut production times to satisfy manufacturing requirements; however, passivation is necessary to protect the surfaces. In recent work on colored surfaces fabricated using bottom-up techniques, the surfaces produced were passivated using polymers deposited by evaporation¹² or spin coating;^{16–19} however, no tribological or chemical testing was conducted to test their passivation efficacy, which is a major consideration for industrial applications. Contrary to bottom-up coloring techniques, direct laser coloring produces very chaotic surfaces due to the complex nanostructures and 3D topography formed.^{9,11,7} It is therefore expected that evaporated or spin-coated polymers^{12,16–19} would not be very effective to passivate such surfaces because these coatings are not conformal.

Furthermore, laser colored surfaces can exhibit a wide range of wetting properties, which can make film deposition challenging.^{7,20}

Atomic layer deposition (ALD) is a gas-phase stepwise thin film deposition method that yields highly conformal coverage of complex surfaces.²¹ ALD is an effective method for creating nanoscale coatings on a wide variety of substrates.^{22–31} Compared to, e.g., chemical vapor deposition (CVD), which is a continuous deposition process, ALD distinguishes itself by the self-limiting nature of the molecular monolayer formed at each step. Another aspect to take into account is the film deposition temperature. The stability of the colored surfaces can in some cases be poor and prone to morphology change with temperature,³² especially in the case of high purity metals such as silver³³ and gold,³⁴ making them vulnerable to high temperature processes. The ALD of thin films has also been useful for protective and cosmetic purposes.^{35,36} Conformal and complete coatings using a minimal thickness of material have generated recent interest in ALD coatings as barriers to

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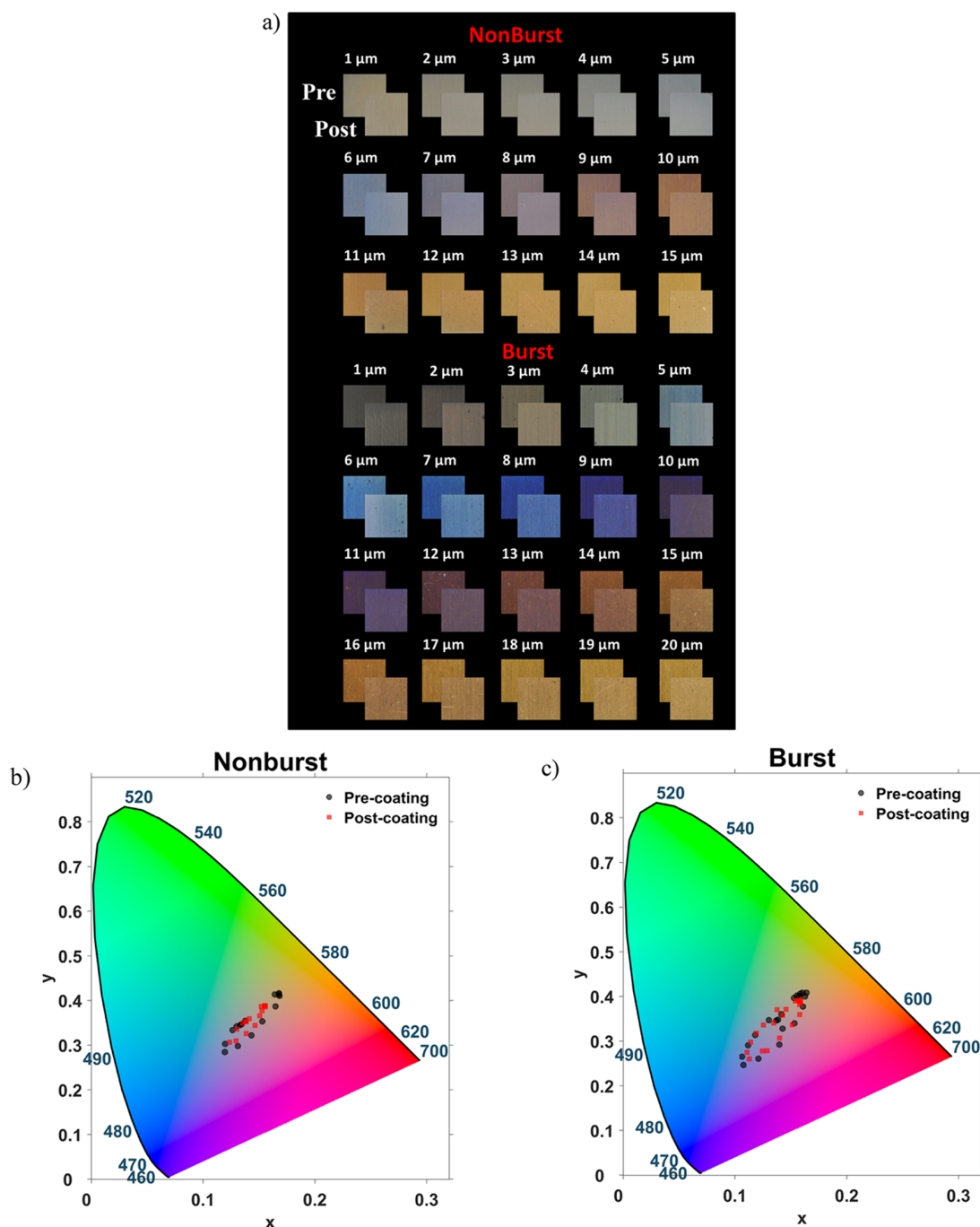


Figure 1. Color palettes before and after ALD of a single film of alumina. (a) Color palettes obtained using the nonburst (top) and burst (bottom) laser coloring methods. The different colors were obtained by changing the line spacing of the raster scan by intervals of 1 μm . The nonburst palette was obtained using a marking speed of 100 mm/s and a laser fluence of 5.73 J/cm². The burst palette was obtained with a marking speed of 150 mm/s and a laser fluence of 12.12 J/cm². The ~ 10 nm thick alumina layer was deposited at a temperature of 60 $^{\circ}\text{C}$ over a period of 10 h and a purge time of 90 s. CIE diagrams of (b) nonburst and (c) burst colors, before and after ALD of the alumina layer.

corrosion and mechanical wear. The literature provides numerous examples of efforts to protect a wide variety of materials including plastics for use in space,³⁶ wood,³⁷ ball bearings,³⁸ and brain implants.³⁹ More importantly, ALD allows for the deposition of some thin films at room temperature,⁴⁰ making it ideal for the passivation of heat sensitive surfaces. The passivation and application of some kind of protective coating is crucial if plasmonic colors are to be used in mainstream applications. However, a protective coating (e.g., a

dielectric) is expected to have a significant effect on plasmonic resonances,¹⁶ and therefore on the rendered colors, so its incorporation should be understood in terms of its optical effects.

Here, we report the passivation of laser-induced plasmonic colors on the surface of bulk silver via the ALD of thin conformal coatings of aluminum oxide (alumina) at low temperatures. These coatings have been demonstrated on collectible silver samples (substrate) as large as ~ 21 cm in

diameter and weighing 5 kg. Typical ALD processes were observed to either significantly degrade the plasmonic colors through thermal damage or fail to meet reasonable processing times as required for mass production. Therefore, a new two-step approach was conceived in order to protect nanotextured silver surfaces against chemical attack while conserving their quality and meeting the time scale requirements for mass production. Conventional coating deposition methods, such as the spraying of PMMA or the evaporation of SiO₂, failed to protect the surfaces against chemical attack and severely degraded the colors upon application. The passivation of plasmonic colors on bulk silver is an important step toward practical application and industrial adoption of this coloring process for decorative, anticounterfeiting, or sensing applications, for example.

RESULTS AND DISCUSSION

ALD of a Single Al₂O₃ Film. Figure 1a shows two color palettes obtained on the surface of bulk silver, comparing the colors pre and post ALD of an alumina layer. The colors were produced using a nonburst (top) and burst (bottom) laser coloring method.^{9,10} The colors were obtained using a laser marking speed of 100 mm/s with a laser fluence of 5.7 J/cm² and a marking speed of 150 mm/s with a laser fluence of 12.1 J/cm², respectively. The burst sequence was composed of a five-burst pulse train of increasing energy with the first two laser pulses at the same energy. At the exception of the first pulses, the pulses within a burst were separated by 25.6 ns (i.e., separated by pulses of zero energy; see Supporting Information Figure 1). The different colors composing the palette were obtained by changing the raster scan line spacing by intervals of 1 μm, as described previously.⁹

The layer of alumina was deposited at a temperature of 60 °C, requiring a total deposition time of 10 h. Pulse times for trimethyl aluminum (TMA) and water were 1 s. The purge times for TMA and water were 1 and 90 s, respectively. The thickness of the alumina film was found to be 10 nm, as measured at multiple locations by GMRFilm software using *k*-ratios from electron-dispersive X-ray spectroscopy (EDS).⁴¹ The film thicknesses were subsequently verified by ellipsometry measurements. The process of ALD was chosen for passivation due to the need for a conformal protective layer on the complex three-dimensional nanostructures formed on the surface, which are responsible for the colors (see Methods). Conventional coating processes (e.g., spray, sputtering, evaporation, spin-coating) may not seal the surface because these processes are not conformal and the 3D topography of the surface creates shadows, thus potentially leaving regions of the surface at the mercy of chemical attacks.

Commission International de l'Éclairage (CIE) diagrams of the colors obtained by both lasing methods are shown in Figure 1b (nonburst) and c (burst), comparing the color palettes before and after ALD of the 10 nm layer of alumina. On the CIE diagram, the burst color palette is observed to cover a larger area than the nonburst colors due to their higher chroma values.^{9,10} In both cases, the color palettes are relatively unchanged following the ALD of the alumina film—only the yellow colors are slightly more affected. The change in colors is linked to the combined effects of the change in the local permittivity on the nanostructures and heating of the temperature-sensitive nanostructures during ALD of the alumina layer. The higher chroma of the burst colors can be

perceived in the vivacity of the color palette compared to the nonburst case (cf. Figure 1a).

X-ray photoelectron spectroscopy (XPS) measurements (Supporting Information Figure 2) revealed the presence of carbon and oxygen on colored and uncolored silver surfaces, prior to ALD of alumina. Fourier-transform infrared (FTIR) spectroscopy further revealed that colored silver surfaces have silver oxides (Ag₂O and AgO)⁴² and silver carbonate (Ag₂CO₃),⁴³ as well as hydroxyl defects (e.g., AgOHAg₂CO₃),⁴³ as observed in Figure 2. The presence of

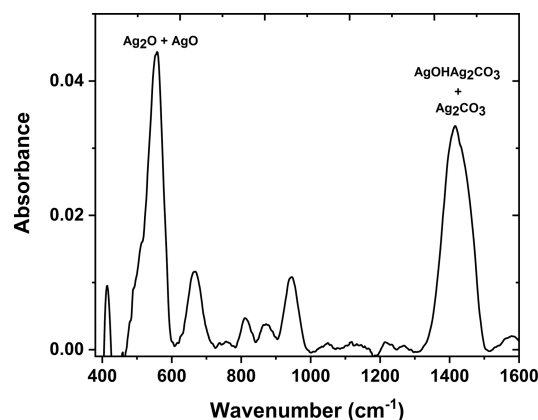
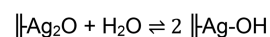
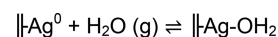


Figure 2. Surface composition. Grazing-angle IR absorbance spectrum of a colored silver surface prior to ALD of alumina. The spectrum shows the presence of Ag₂O, AgO, AgOHAg₂CO₃, and Ag₂CO₃.

AgOHAg₂CO₃ is identified from the peak at 820 cm⁻¹.⁴³ The measurements were obtained on a blue-colored square, such as shown in Figure 1a. FTIR measurements of different colors within a palette revealed that the ratios between oxides, carbonates, and hydroxyl defects differ for each color (not shown). The variation of hydroxyl defects from color to color is believed to originate from the total energy deposited locally in order to generate the desired color. In previous work, we showed that each color was linked to a total accumulated fluence value.⁹ For example, for blue, more laser energy is delivered to the surface to create the required nanostructuring than for yellow, increasing the amount of chemical defects present for the former. Thus, with decreasing total accumulated fluence (i.e., less exposure), the amount of chemical defects was observed to decrease.

Our nominal (initial) ALD process uses a cyclical injection of trimethyl aluminum (TMA, C₆H₁₈Al₃) followed by a purge of water.⁴⁰ Ideally, the presence of oxygen or hydroxyls on the metal surface assists in favorably initiating the formation of the alumina layer, but a hydrogen-terminated surface also serves this purpose. Under a pulse of water vapor at process temperatures (and even room temperature), the conversion of both Ag⁰ and Ag₂O to hydroxylated and water-covered species is favorable:⁴⁴



The hydroxylated surface is the archetype surface reaction group, and while all surface reactivity can be very complex, the presence of easily generated surface hydroxyls suggests that the initial surface interaction likely occurs at this moiety.

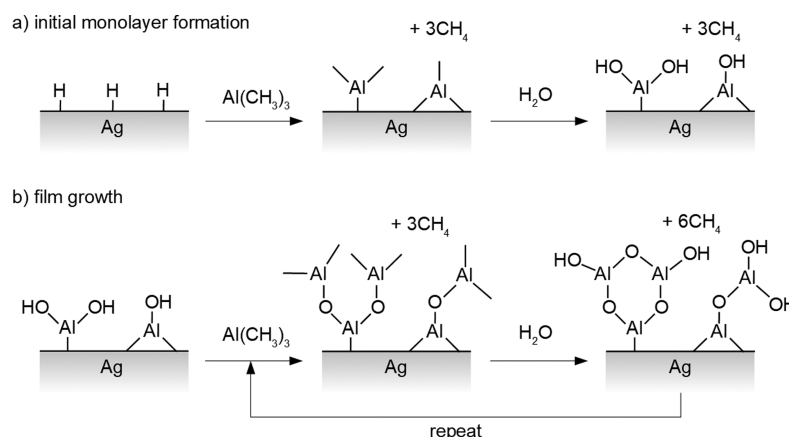


Figure 3. ALD of alumina on silver. A schematic depicting the growth of the alumina film on the surface of silver, using a TMA and water ALD process. The alumina film is grown in a cyclic fashion. Gas-phase byproducts consisting primarily of methane and excess precursor are removed by purge/evacuation steps.

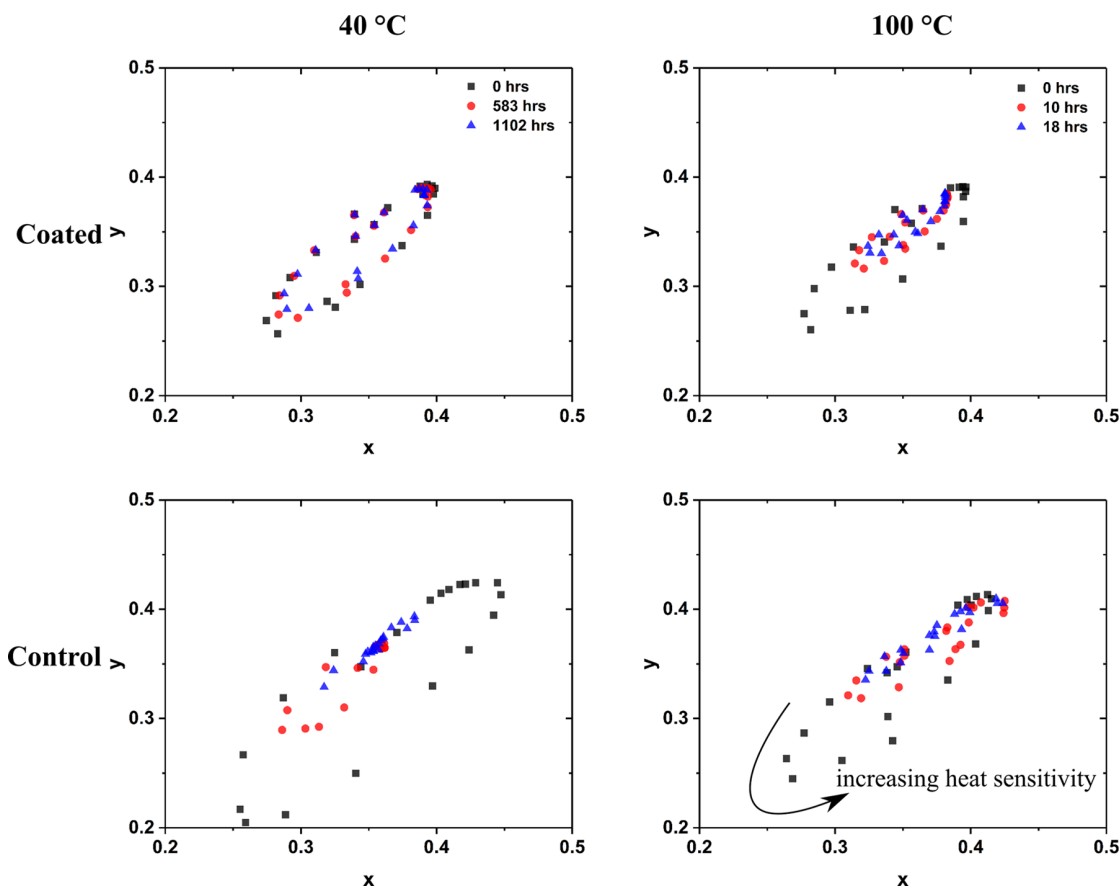
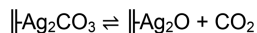


Figure 4. CIE diagrams of coated and uncoated (control) samples exposed to different temperatures. CIE diagrams of coated (top) and uncoated (bottom) colored silver samples exposed to 40 and 100 °C for prolonged periods of time. For 40 °C, after 1095 h, the colors on the uncoated control are observed to fully collapse. The sensitivity of the colors to heat is observed to increase from yellow to blue.

Ag_2CO_3 shows significant decomposition to Ag_2O and CO_2 at around 175 °C, but the onset of this reaction could occur at much lower temperatures.⁴⁵



Given that there is evidence of both Ag_2O and Ag_2CO_3 at the surface, it is not unreasonable to expect the surface oxide to be

present in a high enough abundance to initiate formation of the alumina layer.

In Figure 3, the initial atomic layer is shown forming on a hydrogen-terminated surface.^{46,47} The adhesion of the coating to the surface was tested using a simple tape test followed by an EDS map of the surface. The EDS map showed no difference in the aluminum content between the taped and nontaped regions (Supporting Information Figure 3), indicating strong adhesion.

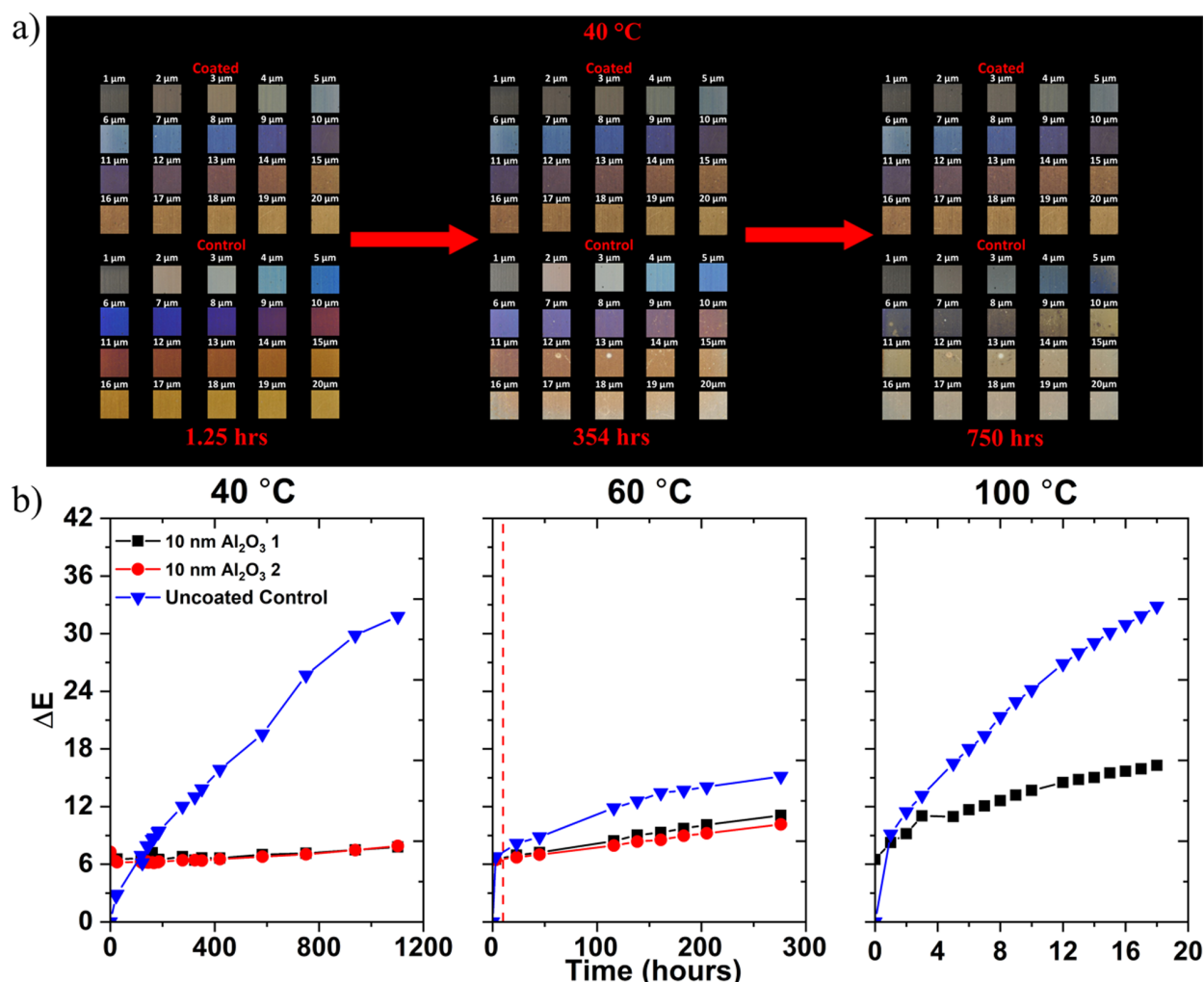


Figure 5. Color evolution for three temperatures of coated and control (uncoated) samples. (a) Color palette evolution at 40 °C comparing coated (top) and uncoated (bottom) samples for time intervals of 1.25, 354, and 750 h. (b) Graphs of the average change in color (ΔE) vs time for coated and uncoated samples exposed to 40, 60, and 100 °C. The ALD process produced a 10 nm thick alumina film.

Henceforth, only burst color data will be shown, since nonburst and burst exhibited the same behavior in all tests. To test the effectiveness of the alumina coatings to protect against high temperatures, colored silver samples were exposed for prolonged periods to temperatures of 40, 60, and 100 °C. The goal of these experiments was to determine if the layer could protect against temperature-induced morphological changes.

Figure 4 shows CIE diagrams comparing protected silver samples coated with 10 nm of alumina (top) with uncoated samples (bottom) for different exposure times to 40 and 100 °C. The area spanned by the color palettes in the CIE diagram is smaller for the coated samples due to their initial exposure to 60 °C for ~10 h in the chamber during ALD of the alumina film. We observe relatively little change in the colors of the protected samples after 1095 h at 40 °C, whereas a complete collapse of the colors is observed for the unprotected samples at this temperature, demonstrating the effectiveness of the coatings against prolonged heat exposure. The results observed for the trials at 60 °C (not shown) are similar. The trials carried out at 100 °C resulted in significantly reduced coverage of the CIE diagram in both cases, revealing the passivation limit of the alumina film. The color changes observed in this case are believed to be morphological and chemical in origin. Conventional

coating techniques, such as spraying a layer of PMMA or evaporating SiO_2 , were observed to destroy the colors (i.e., produced a large ΔE).

A visual evolution of the colors for prolonged exposures to 40 °C is shown in Figure 5a. A clear degradation over time of the uncoated control sample is observed. The same was observed for samples exposed to 60 and 100 °C (not shown). The time required for complete destruction of the colors decreases with increasing temperature.

Figure 5b plots the average color change (ΔE) of the full color palette over time, caused by heating the samples to 40, 60, and 100 °C. The change in color (ΔE) is defined as⁴⁸

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2} \quad (1)$$

where a and b are

$$a = C \times \cos\left(\frac{2\pi H}{360}\right) \quad (2)$$

and

$$b = C \times \sin\left(\frac{2\pi H}{360}\right) \quad (3)$$

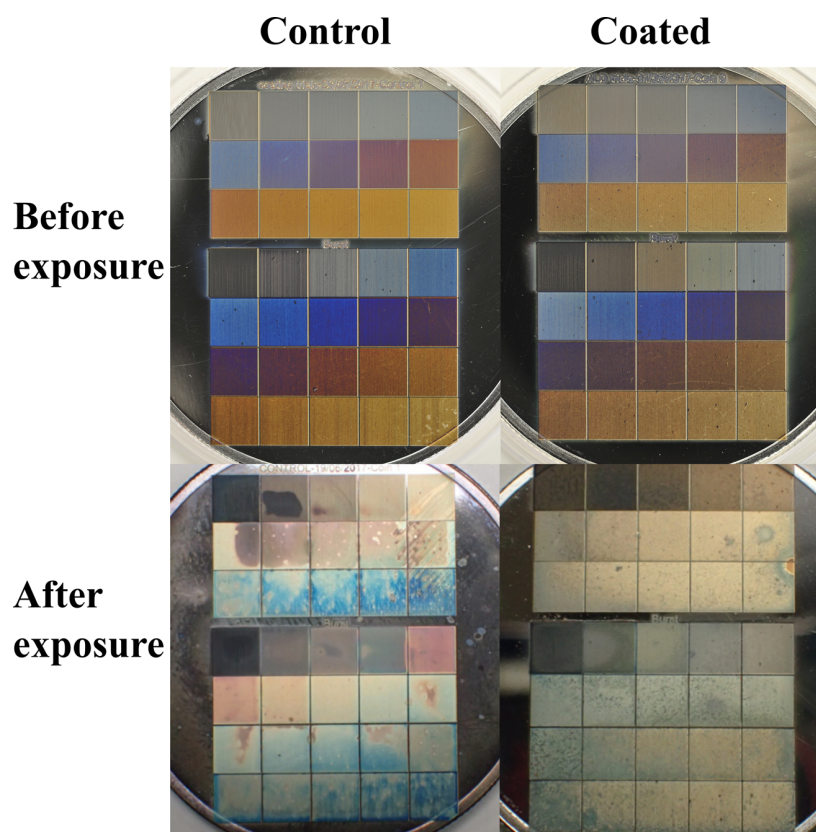


Figure 6. Tarnishing of uncoated and coated silver samples. Side-by-side comparison of an uncoated control sample (left) and a coated sample (right) bearing 10 nm of alumina before (top) and after (bottom) tarnishing. The samples were exposed to a sulfur rich gas for a period of 20 h. The plasmonic colors on the surface of the uncoated and coated samples were not conserved.

In the above, L is lightness, C is chroma, and H is hue—the three components of the LCH color space. In eq 1, subscripts 1 and 2 are used to identify the before and after values, respectively. From color theory, a ΔE of ~ 1 is the minimum change needed for the eye to discern a variance in color.⁴⁸ For ΔE values higher than 2, a change in color can be perceived without meticulous inspection of the surface. Statistically, it was demonstrated that a ΔE of 6 or 7 was acceptable for some industrial applications.⁴⁸

From Figure 5b, we observe that the average change in color for the control (uncoated) samples is significant for all temperatures. In the case of the coated silver samples, the average change in color at time zero is the change due to the deposited alumina film. Postdeposition, we observe that ΔE changes very little ($\Delta E < 1.3$) over 1095 h for the 40 °C tests. For coloring applications, minimal color changes due to deposition of the passivation layer and to environmental influences are highly desirable. Therefore, a delicate balance between minimal color change upon deposition and maximum surface protection is sought.

Furthermore, the results of the heat test suggest that the alumina begins to provide protection during the 10 h ALD process. Indeed, a direct comparison with the uncoated control exposed for the same amount of time at 60 °C shows a higher ΔE (Figure 5b, 60 °C panel, vertical dashed line). Each atomic layer deposited on the surface builds upon the protection provided by previously deposited layers, which helps to conserve the integrity of the colors throughout the deposition process.

As noted above in relation to Figure 4 and as observable from Figure 5b, the passivation limit of the ALD alumina coating seems to occur at an environmental temperature of about 100 °C, which suggests the onset of morphological changes to the surface. Previous work identified the colors as plasmonic in nature based on simulations assuming a statistical distribution of redeposited silver nanoparticles on the silver substrate.⁹ Plasmonic resonances were found to be highly sensitive to the contact angle between the silver nanoparticles and the substrate, resulting in significant resonance shifts for a small variation in angle (i.e., embedding). This would suggest that any changes in morphology would greatly affect the colors perceived in the far field.

The heat sensitivity of the colors increases from yellow to blue (blue colors are more sensitive to heat than any other color). This can be explained by the unique surface required for each color and their specific nanoparticle statistics.⁹ For blue, the interparticle distance is much smaller than that for other colors, e.g., yellow. Due to this characteristic, small morphological changes caused by heating will cause a greater change in the plasmonic resonance, making blue more sensitive to elevated temperatures and yellow less sensitive, as observed experimentally.

To further investigate the heat sensitivity of the colors, scanning electron microscope (SEM) images of uncoated colored samples were placed on a heating stage inside the SEM under a vacuum and held at 200 °C for about 1 h. The images observed in real time showed the embedding or sintering of nanoparticles and the islandization of topographical features,

ultimately leading to loss of color (see [Supporting Information Figure 4](#)). The rate of change of the surface was observed to depend on the stage temperature, where increasing temperature resulted in faster morphological changes on the surface.

Passivation film deposition at elevated temperatures or the use of hot liquids could be, in principal, enough to sinter and embed the nanoparticles, causing a significant shift in colors. For ALD, the deposition can be done at room temperature, reducing the possibility of severe morphological changes to the nanostructure. Furthermore, compared to other coating techniques, the conformal coating of the nanostructures via ALD should provide more stability against the sintering (or embedding) of the nanoparticles.

To test the tarnishing resistance of the alumina passivation layer, the silver samples were placed in a sulfur rich environment for a period of 20 h (following a standardized aggressive tarnish test proprietary to the Royal Canadian Mint). [Figure 6](#) shows a side-by-side comparison of an uncoated control (left) and a coated silver sample (right) before (top) and after (bottom) going through the tarnish test. The uncoated controls and the coated samples failed the test. The colors of the alumina coated sample are observed to turn brown. It should be noted, however, that the uncolored (untextured) regions of the coated sample remained intact and untarnished compared to the control sample. Thus, while the flat silver regions were protected, the same could not be said about the nanostructured color-producing regions. The nanostructures have a highly variable surface free energy, so deposition on nanostructure could vary from deposition on Si witness samples used to monitor film growth during deposition.

The success of the ALD alumina coating in the temperature tests but its failure in the tarnish test is attributed to the low density of the alumina film.⁴⁰ The ALD of alumina at 60 °C may form a low-density porous film that adequately pins the nanotextured surface yet allows sulfur gas to permeate and directly attack the silver. Thicker layers (57 nm or more) were deposited at 60 °C and shown to protect the surface; however, such thick coatings took 48 h to deposit. Furthermore, complex reflection and interference effects were observed to play a detrimental role on the colors. Therefore, a thin but denser film is desirable to protect against chemical attacks, which requires the use of higher deposition temperatures. Trials to deposit directly at higher temperatures a denser layer on colored silver surfaces rapidly destroyed the colors, so a two-step ALD process was developed, as described in the next section.

ALD of Two Al_2O_3 Films. From [Figure 5b](#), it was observed that a thin low-density porous film deposited at 60 °C effectively traps or delays changes in colors on samples exposed to high temperatures. From this, we speculated that a second denser film could be deposited at a higher temperature on top of the first to improve protection against chemical attacks. The second film depositions were carried out at a temperature of 100 °C. The purge time between cycles was modified to minimize thermal effects on the colors and reduce process time. Tests revealed that shorter purge times resulted in better color palettes, as shown in [Figure 7c](#). In [Figure 7c](#), the effect causing the colors to change is purely thermal, since the overall thickness of the alumina remains roughly the same. For shorter purge times, the deposition of the second film occurs much more rapidly and therefore limits the exposure of the porous film to the process temperature of 100 °C. The best result was achieved for a purge time of 10 s between cycles, resulting in a

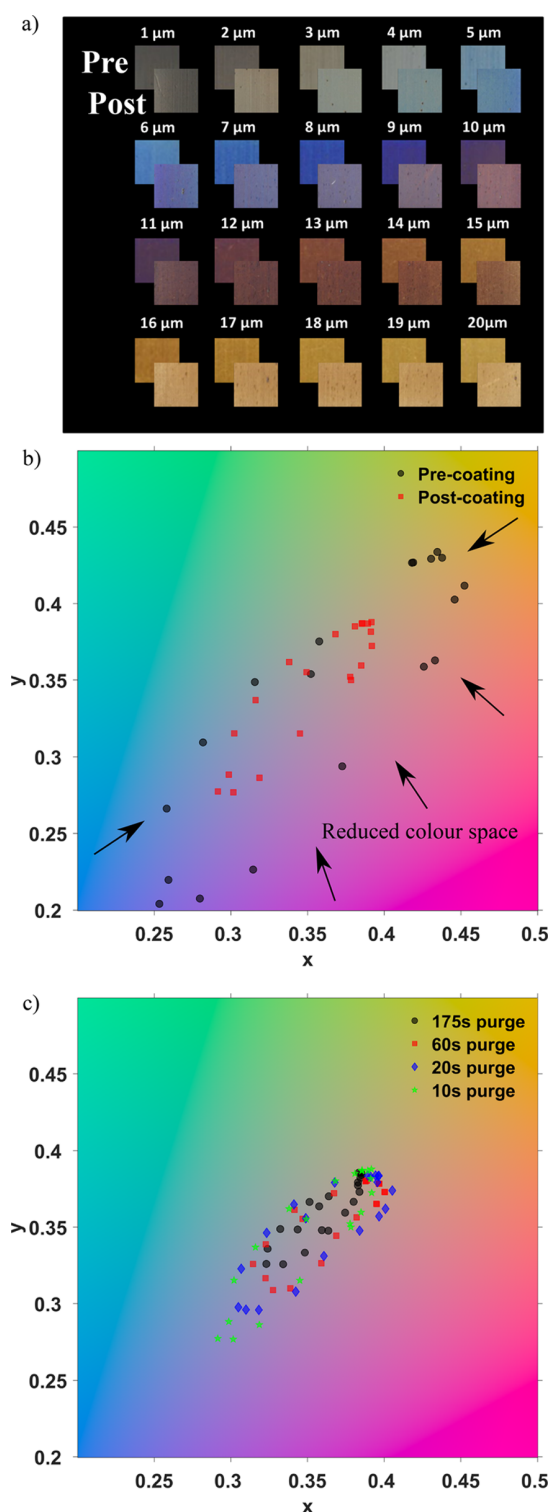


Figure 7. Color palettes before and after two-step ALD of alumina. (a) Color palette before (top) and after (bottom) the deposition of a second denser film. The second film was deposited at 100 °C with a purge time of 10 s. (b) Zoom-in of the CIE diagram representing the color palette before and after ALD of the second film of alumina. (c) CIE diagram comparing the color palettes obtained for purge times of 175, 60, 20, and 10 s at a temperature of 100 °C.

total deposition time of ~ 2 h for a final film thickness of 15–17 nm.

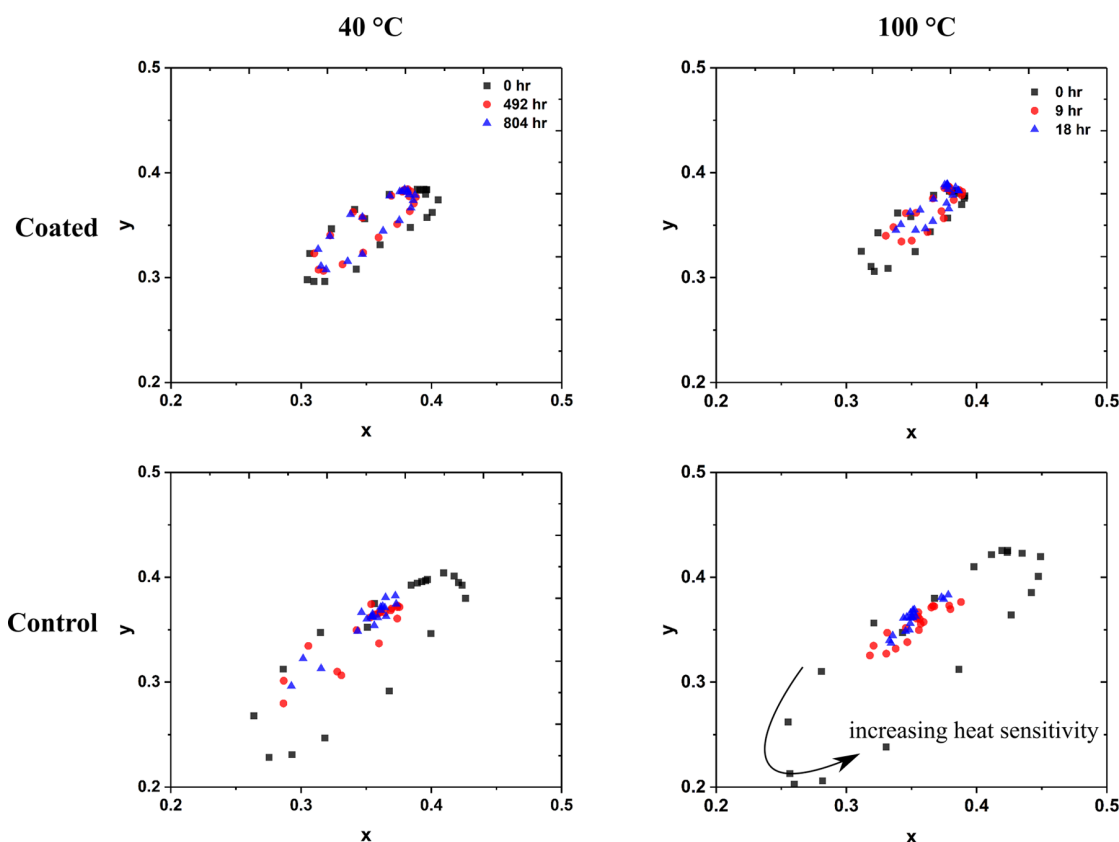


Figure 8. CIE diagrams of coated (two-step ALD of alumina) and control (uncoated) samples exposed to different temperatures. Coated (top, purge time of 20 s) and uncoated (bottom) colored silver samples exposed to 40 and 100 °C for prolonged periods of time. Again, the sensitivity of the colors to heat is observed to increase from yellow to blue. The two-step ALD process produced a composite alumina film (porous and dense) 13 nm thick.

Figure 7a shows the color palettes on silver before (top) and after (bottom) two-step ALD of the denser alumina. Clearly, the effect of heat exposure can be observed; however, compared to a single deposition of alumina at 100 °C (not shown), the color palette remains essentially intact. Once again, the blue colors were the most sensitive to heat. The extent of the color palette is nonetheless reduced, as observed from Figure 7b. The reduction in the area spanned by the colors was directly influenced by the purge time and the overall exposure of the sample to 100 °C, as seen in Figure 7c. The effect of reducing the purge time significantly increased the quality of the colors and the outcome. Interestingly, the area spanned by the burst colors post passivation is similar to that spanned by the nonburst process pre passivation.⁹

The two-step alumina film samples were subjected to the same heat tests as described in the previous section. Figure 8 shows CIE diagrams comparing coated samples (top) and uncoated controls (bottom) exposed for prolonged periods of time to temperatures of 40 and 100 °C. For 40 °C, no changes to the coated samples are observed, unlike the control samples for which significant changes are observed. In the case of 100 °C, the area spanned is observed to reduce over time for the coated samples but to fully collapse for the control samples.

Degradation of the uncoated (or control) samples is visually apparent in Figure 9a at 40 and 100 °C. Conversely, little to no visual change is observed for the coated samples over the same time period. An aspect that is not captured on the CIE diagrams of Figure 8 is the “whitening” (increased lightness) of

the colors with time observed in Figure 9a. For the protected colors, the changes occur primarily in the chroma or hue and less in the lightness. This can be observed for the case of exposure to 100 °C where the colors on the coated samples are relatively unchanged but those of the controls change to white and some are completely destroyed.

The effectiveness of the coating is captured in the graphs of Figure 9b which plot ΔE vs time for exposure to 40, 60, and 100 °C. The color changes caused by the two-step deposition of the alumina films are plotted at time zero. The uncoated controls exhibit the same behavior with time (as in Figure 5), but the coated samples show little to no change over these long exposures. SEM images comparing an uncoated and coated surface after 1444 h exposed at 40 °C (see Supporting Information Figure 5) show the destruction of the underlying topography and the islandization of the surface in the case of the control silver sample. For the ALD coated colored silver surface, the surface is kept intact and no sign of islandization is observed, providing protection against elevated temperature and long exposures.

Humidity experiments conducted in a chamber with 85% relative humidity at 38 °C for a period of 72 h showed that the alumina protected the surface of silver and the colors. The color changes on the controls were much less severe than the effect of temperature and tarnishing. Only white spots were observed to randomly form on the surface of the unprotected silver (not shown). Results on the protected silver were independent of the single- or two-step deposition process of the alumina film.

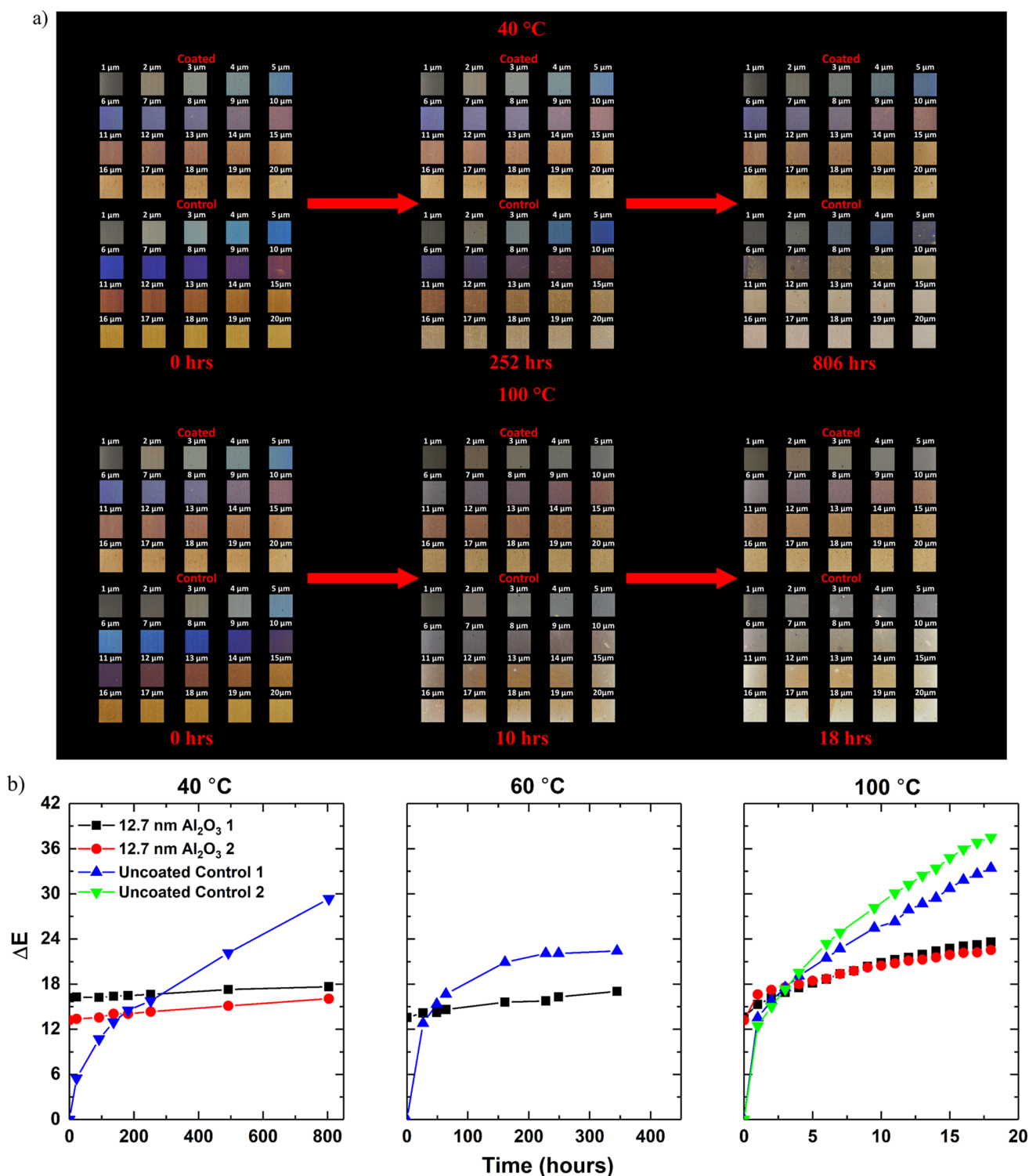


Figure 9. Color evolution for three temperatures of two-step coated and control (uncoated) samples. (a) Color palette evolution over time at 40 and 100 °C comparing coated (top) and uncoated (bottom) samples for time periods of 0, 252, and 806 h and 0, 10, and 18 h, respectively. (b) Graphs of the average change in color (ΔE) vs time for coated and uncoated samples exposed at 40, 60, and 100 °C. The two-step ALD process produced a composite alumina film (porous and dense) 13 nm thick.

The assumption of a better chemical protection by a denser conformal alumina film was verified using the same sulfur test described in the previous section. The color properties (LCH values) were measured at various times during the experiment, as described in the schematic shown in Figure 10a. Figure 10b

shows the results of the tarnish test, comparing uncoated (left) and coated (right) samples, before (top) and after (bottom) tarnishing. The coated samples were observed to survive the tarnishing test, while the uncoated controls failed.

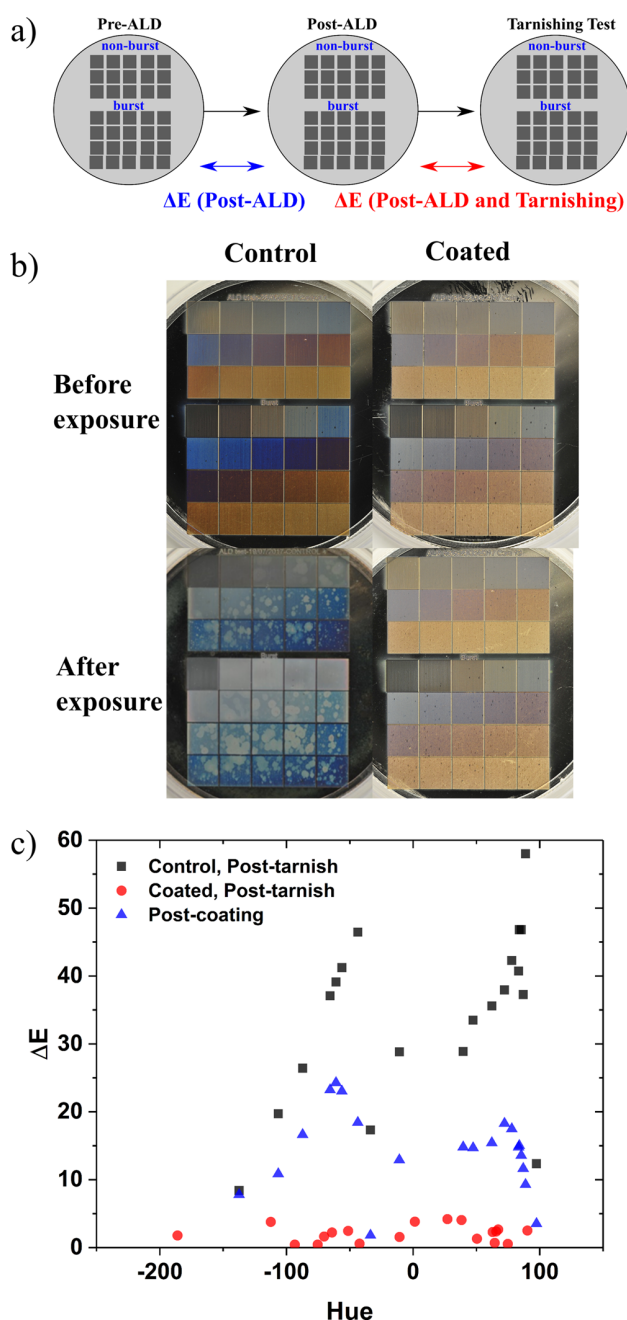


Figure 10. Tarnishing of two-step coated and control (uncoated) samples. (a) Schematic of the experiment and LCH measurement. (b) Side-by-side comparison of an uncoated control (left) and two-step coated (right) samples before (top) and after (bottom) tarnishing. The two-step ALD process produced a final alumina film 15 nm thick. The samples were exposed to a sulfur rich gas for a period of 20 h. (c) ΔE versus hue for the steps schematically presented in part a.

The measured effects on the colors of samples coated with the two-step passivation process and subsequent exposure to the tarnishing agent are summarized in Figure 10c, and compared to the color changes incurred by the uncoated control due to tarnishing. Post-tarnishing data demonstrates that the coated samples were minimally affected by the sulfur gas, proving the effectiveness of the process. The deposition of a conformal layer on the heat sensitive structures is key to the protection of the complex three-dimensional nanostructures

formed on the surface from chemical attack. The change in color of the uncoated sample is significant, and all of the colors are shifted toward blue. By comparison, the change in colors caused by the two-step ALD of the alumina films is much lower and a full color palette is conserved.

The two-step ALD process, which consists of first depositing a porous alumina film at low temperature to stabilize and pin the nanotextured surface, followed by the deposition of a second denser alumina film at higher temperature produces an effective passivation coating. The process can be further optimized for protection and color conservation by, e.g., incrementally increasing the temperature during the ALD cycle.

Figure 11 demonstrates application of the two-step ALD passivation process to a laser-colored 5 kg collectible silver



Figure 11. Pre (left) and post (right) ALD of alumina on a sample (two-step ALD process). Photograph of a laser colored 5 kg collectible silver sample before (left) and after (right) the two-step ALD of a composite alumina passivation film (porous and dense) 15 nm thick.

sample (21 cm diameter, 1.5 cm topography). Before and after photographs reveal that the alumina film shifts the colors slightly; however, they remain vibrant and appealing.

In conclusion, we have demonstrated a new two-step ALD process for passivating the surface of laser-induced silver nanostructures that render plasmonic colors on bulk silver, without destroying the color palette. A first porous film of alumina is deposited by ALD at low temperature and serves to pin (trap) the nanostructures on the surface to delay color degradation upon heating, while a second denser film of alumina deposited at a higher temperature completes passivation. This two-step approach allows for the deposition of conformal thin films that passivate the surface against humidity, temperature, and chemical attack, as demonstrated via a series of experiments including aggressive tarnish tests. This process not only protects colors but also allows for the deposition to be done in a time frame that is compatible with industrial manufacturing constraints. Application of the process was demonstrated on a large-area high-topography silver surface addressing the collectibles market.

METHODS

Laser Specifications. The coloring of the silver surfaces was carried out in a raster-scanning pattern using a wavelength of 1064 nm from a Duetto mode-locked laser (Nd:YVO₄, Time-Bandwidth Products) producing 10 ps pulses. The laser repetition rate of the

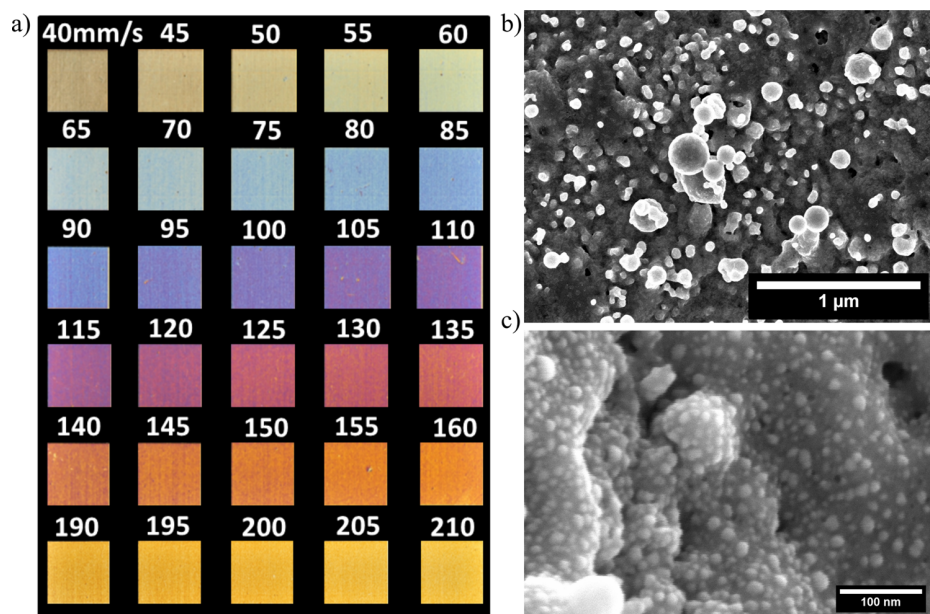


Figure 12. Color palette and plasmonic surface. (a) A full color palette obtained using the burst method with a laser fluence of 5.6 J/cm^2 and a laser line spacing of $7 \text{ } \mu\text{m}$. The different colors were obtained by changing the total accumulated fluence (via machining speed) delivered to the silver surface.⁷ (b) Low- and (c) high-magnification SEM of the plasmonic surfaces responsible for the angle-independent colors.

laser was kept at 25 kHz throughout the experiments. The time separation between each pulse within the burst is fixed at 12.8 ns, and one to eight pulses within each burst can be selected. The setting of 1 pulse per burst is equivalent to the normal functioning of the laser and is defined as nonburst. For burst mode (a burst containing more than one pulse), the energy distribution of each laser pulse within the burst was controlled by the software provided by the manufacturer (FlexBurst, Time-Bandwidth Product). A Gaussian beam radius of $\sim 22 \text{ } \mu\text{m}$ was measured using the semilogarithmic plot of the modified region, following ref 49.

Sample Preparation. The silver samples were of 99.99% purity. Prior to the laser machining of the silver samples, the surfaces were thoroughly cleaned using a multistep cleaning approach: (step 1) isopropanol wash, (step 2) acetone wash, (step 3) cleaning by deionized water, (step 4) second isopropanol wash, and (step 5) nitrogen-drying. For transport and to prevent surface contamination, the samples were placed in nitrogen filled bags and plastic capsules.

Laser Coloring Process. The colors on silver were produced using nonburst and burst methods described in previous publications.^{7,10} Figure 12a demonstrates the creation of a full color palette on silver obtained by simply changing the total accumulated fluence delivered to the surface.⁷ The colors are rendered by the complex plasmonic nanostructured surfaces formed by the machining process; see Figure 12b and c. The light was focused on the silver surface using an F-theta lens ($f = 254 \text{ mm}$, Rodenstock). The laser was fully electronically integrated and enclosed by a third party for industrial applications (GPC-PSL, FOBA). For accurate focusing, the surface of a sample was located using a touch probe arrangement. For coloring, the samples were placed on a three-axis stage with a resolution of $1 \text{ } \mu\text{m}$ in both the lateral and axial directions. The samples were raster scanned using galvanometric XY mirrors (Turboscan 10, Raylase) displacing the beam in a top to bottom fashion. The laser power was computer-controlled via a laser interface and calibrated using a power meter (3A-P-QUAD, Ophir).

Colorimetric Data. LCH (L = lightness, C = chroma, H = hue) values were measured using a Konica Minolta CR-241 chroma meter in the CIELCH color space, 2 observer and illuminant C (North sky daylight).

Heating Apparatus. The heating tests were conducted in two separated ovens working in parallel (Sentry Xpress 4.0, Orton; and Gravity Convection General Incubator, VWR Symphony). The

temperature inside the ovens was monitored using a thermocouple (type K thermocouple, Thermometrics) attached to an infrared thermometer (ST-8835, Reed).

Atomic Layer Deposition Specifications. ALD depositions were performed using a Picosun R150 thermal deposition tool with a capacity of coating 2400 samples (38 mm in diameter) without placement optimization. Trimethylaluminum (TMA, >98%) was purchased from Strem and used as received. The TMA and distilled water were held at $18 \text{ } ^\circ\text{C}$ in stainless steel bubblers for all depositions. Purge and line flows used 99.998% N_2 (150 sccm for TMA, 200 sccm for water). Si(100) “witness” wafers were used to confirm the expected growth rate. A stainless steel mesh was used to support the samples and ensure complete coverage. The reflectance spectra of the different alumina thicknesses were simulated using the open source software TFCompanion (Semiconsoft Inc.).

Layer Thickness Measurements. The alumina layers were probed by electron dispersive X-ray spectroscopy (EDX). The alumina layer thicknesses were estimated by entering the values of SEM probe voltage, takeoff angle, element, element k -ratio, and estimated density in the software GMFilm. The EDS alumina thickness measurements were confirmed by ellipsometry (FUV-NIR, Horiba Uvisel).

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b00210.

Figures showing a schematic representation of the nonburst and burst pulse arrangements used to the color the silver surfaces in this study, XPS measurements, EDS map of the tape test interface on a colored silver surface, and SEM images (PDF)

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Notes

The authors declare no competing financial interest.

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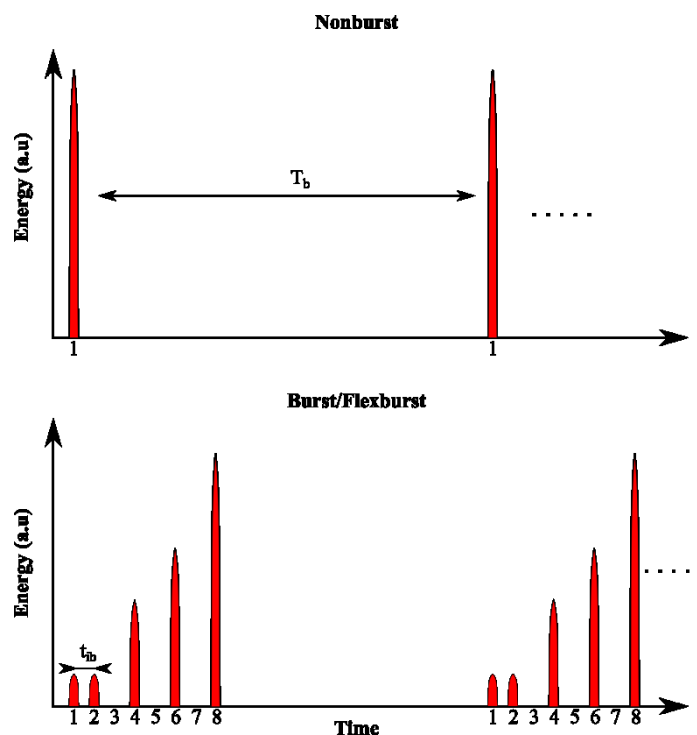
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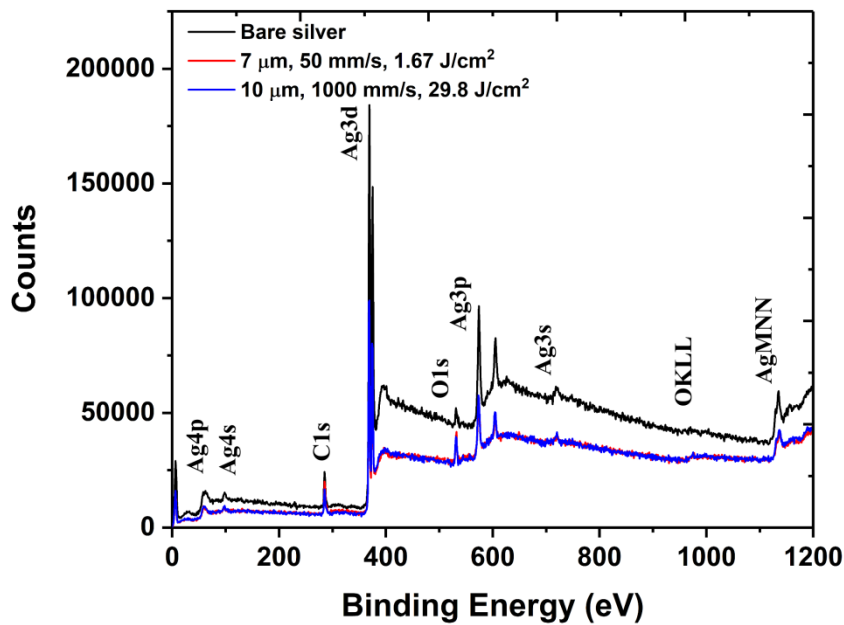
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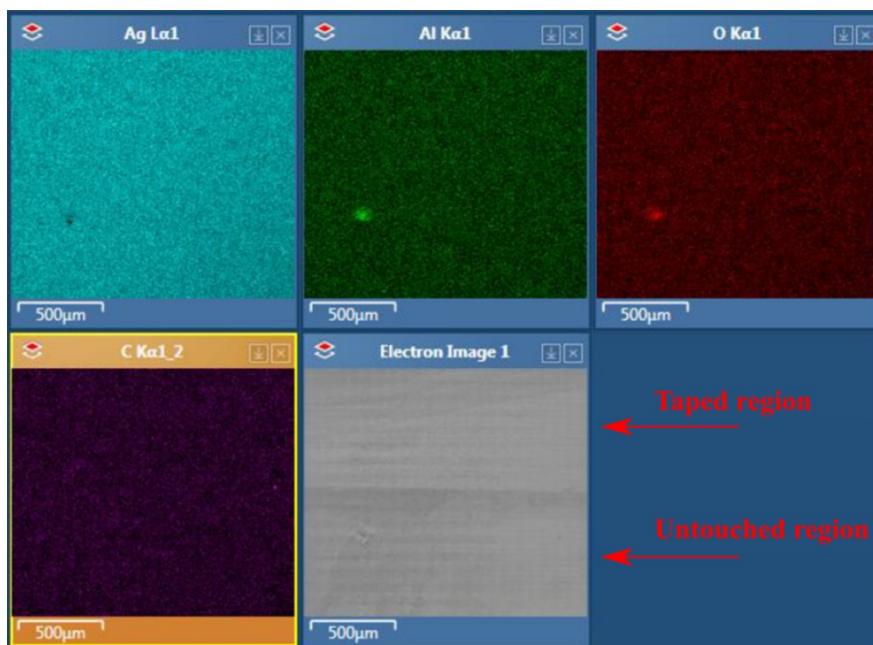
Supplementary material



Supplementary Figure 1 | Schematic representation of the (top) nonburst and (bottom) burst pulse arrangement used to color the silver surfaces in this study. The pulse-to-pulse time separation of the nonburst is defined by $T_b = 1/f$ where f is the repetition rate of the laser in normal operation. In the burst mode 2 to 8 pulses could be selected where the energy of each pulse within the burst could be controlled via FlexBurstTM. The time separation between each pulse within a burst is governed by the repetition rate of the oscillator and in this case is $t_{ib} = 12.8$ ns. The burst colors were produced using the burst arrangement sketched above where the 3rd, 5th and 7th pulses were set to zero energy and the energy of the remaining pulses was distributed following the schematic representation.

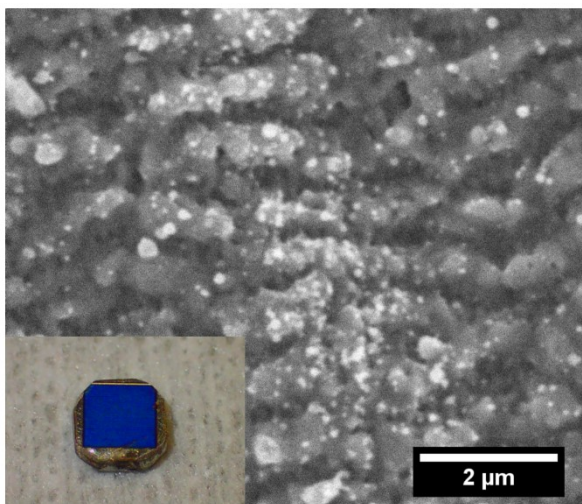


Supplementary Figure 2 | XPS measurements of a bare silver surface and of 2 blue colored areas produced with 2 sets of laser parameters but delivering the same total accumulated fluence. The blue colors were produced using a line spacing of 7 μm, a marking speed of 50 mm/s and a laser fluence of 1.67 J/cm²; and a line spacing of 10 μm, a marking speed of 1000 mm/s and a laser fluence of 29.8 J/cm². Oxygen and carbon peaks are observed on the bare silver surface and on the colored areas. The amount of oxygen is higher on the colored areas compared to bare silver.

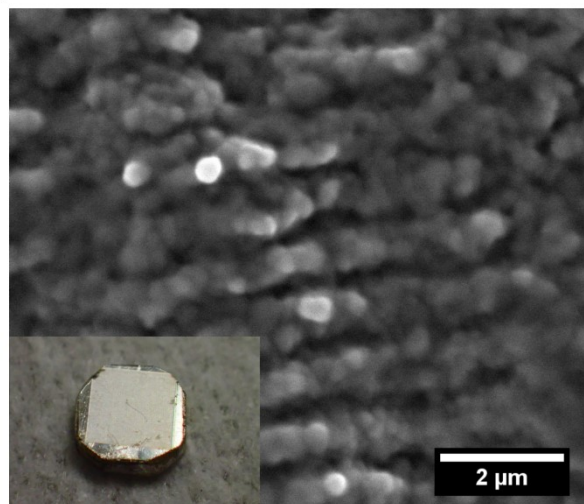


Supplementary Figure 3 | EDS map of the tape test interface (see arrows) on a colored silver surface. The boundary between the untouched and taped regions can be observed on the SEM image (bottom middle), where the slight contrast originates from the removal of dust on the surface by the tape. No differences in elemental composition are observed between the taped and untouched regions, demonstrating strong adhesion of the alumina film to the colored surface. The elemental composition in % weight was: 84.2% Ag (top left), 12.4% O (top right), 2.1% Al (top middle) and 1.2% C (bottom left).

a)

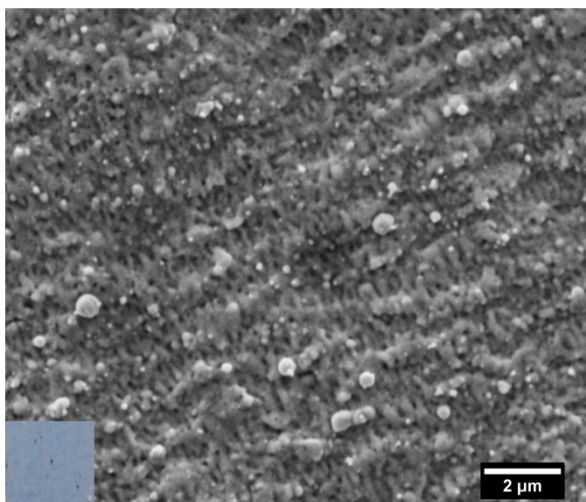


b)

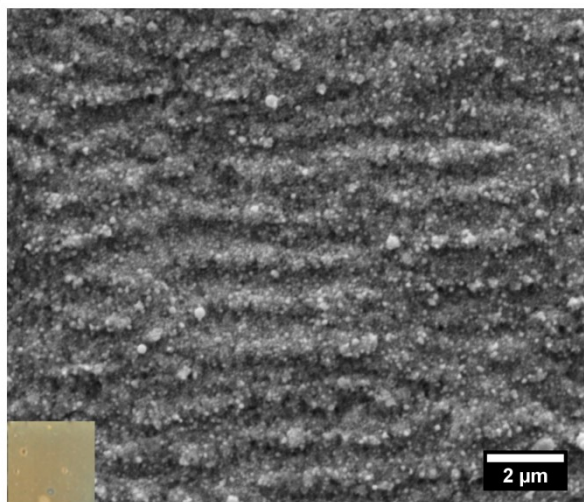


Supplementary Figure 4| SEM images of a blue colored surface (a) before and (b) after heating the sample on a heating stage inside the SEM at 200 °C for about 1 hour. After 1 hour of heating, the blue color (bottom left inset) turned white (bottom right inset). The images reveal increased islandization of the surface and the disappearance of nanoparticles thought to be responsible for the colors. The colored surface was uncoated.

a)



b)



Supplementary Figure 5 | SEM images of an originally blue-colored square after exposure to 40 °C for 1444 hours (a) with and (b) without a protective alumina coating. The colors after this long exposure are shown as insets in the respective bottom-left corners of the SEM images. The ALD protected surface maintained its original nanostructuring and color, whereas the uncoated sample was degraded by increased islandization and the disappearance of nanoparticles thought to be responsible for the blue color.

Topography tuning for plasmonic colour enhancement via picosecond laser bursts

6.1 Summary

This chapter demonstrates the tuning of the underlying topography, onto which the nanoparticles redeposit, by controlling the energy distribution within a laser burst of up to 8 pulses each separated by 12.8 ns. We show that distinct colour palettes can be obtained by changing the energy distribution of each shot within the burst while keeping the same total energy delivered on the sample. While only a fraction of pulse energy distributions has thus far been investigated, an increase in colour saturation of up to $\sim 100\%$ across the full Hue range has been obtained when compared to the traditional non-burst colouring method (burst of 1). Two temperature model (TTM) simulations of the burst pulse interaction with the silver surface reveals the increase in the electron-phonon coupling of silver. Distinctive topographical features unique to the burst surfaces are observed for different burst arrangements. Finite-difference time-domain (FDTD) sim-

ulation of the burst surfaces show that grating coupling, field enhancement and the increased area caused by the topography is responsible for the enhanced light absorption explaining theoretically the reason behind the increased colour saturation observed in the far-field. The supplementary information document provides the statistical and comparison data of the nonburst and burst coloured surfaces. It also provides SEM images of the surface exposed to different burst arrangements, in addition to an FDTD image showing the excitation of SPP waves on the topographical features that are unique to the burst surfaces.

6.2 Contributions

The results presented in this section were published in the journal *Advanced Optical Material*. In this publication, I initially discovered experimentally the colour enhancement produced on the surface of metals via the use of small time-spaced laser bursts. Under the direction of Dr. Arnaud Weck and Dr. Pierre Berini, I supervised a team of COOP student (Joshua Baxter and Graham Killaire) at the RCM. To explain the formation of LIPSS via the use of burst, I proposed the theory of enhanced electron-phonon coupling and, supervised and directed the writing of a two-temperature model code by Joshua Baxter. Graham Killaire and I gathered the flexburst and burst data for the manuscript. Graham Killaire found the best burst arrangement for optimal colour rendition to date. The LCH data and pictures were taken by me and Graham. The SEM images of the burst surfaces were taken by me at the RCM. From experimental observation of the burst surface, I proposed to Dr. Antonino Cala Lesina the simulation of the LIPSS structures covered by NPs. Dr. Antonino Cala Lesina conducted an in-depth study of the role of the LIPSS on the colours. The simulation study was directed by Dr. Lora Ramunno and Dr. Pierre Berini. The simulation and experimental results were discussed by all the authors. The theoretical conclusions were drawn by Dr. Pierre Berini, Dr. Lora Ramunno, Dr. Antonino Cala Lesina and myself. I wrote the experimental section of the paper and prepared the figures. Dr. Antonino Cala Lesina wrote the theoretical section of the manuscript.

6.3 Article

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Topography Tuning for Plasmonic Color Enhancement via Picosecond Laser Bursts

Jean-Michel Guay,* Antonino Calà Lesina,* Joshua Baxter, Graham Killaire, Lora Ramunno, Pierre Berini, and Arnaud Weck

The tuning of 3D topographical features on silver for the production of plasmonic colors is reported. The topography is produced by applying closely time-spaced laser bursts. Using laser bursts increases the Chroma of the colors produced by up to 100% compared to the nonburst coloring method. By adjusting the energy distribution of the laser pulses in a burst, while maintaining the total burst energy constant, significantly different color palettes and topographical structures are produced. Scanning electron microscope analysis of the surfaces produced reveals the creation of three distinct sets of laser-induced periodic-like surface structures (LIPSS): low spatial frequency LIPSS (LSFL), high spatial frequency LIPSS (HSFL), and large LIPSS that have a period about 7× that of the laser wavelength. Two-temperature model simulations of silver irradiated by a laser burst show a significant increase in the electron–phonon coupling which is mainly responsible for the creation of LIPSS. Finite-difference time-domain simulations of a model of the surface, consisting of nanoparticles arranged on a sinusoidal-modulated surface of varying amplitude (0 to 150 nm) and period (200 and 1000 nm), elucidate the importance of the HSFL and LSFL structures for color formation, including the increase in Chroma (saturation) observed experimentally.

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1. Introduction

Metallic nanoparticles (NPs) exhibit unique plasmonic responses when exposed to optical radiation, leading to promising applications in many fields, such as material processing,^[1–3] solar cells,^[4,5] medicine,^[6,7] and plasmon-assisted photochemistry.^[8] It was shown that the surface plasmon (SP) resonance of nanoparticles is influenced by factors such as particle size, shape, and permittivity.^[9–13] Coloring metal surfaces by exploiting surface plasmon resonances is an emerging topic and multiple fabrication techniques exist to tune the plasmonic response.^[14–18] However, bottom-up processes can be tedious and time consuming. The use of lasers for coloring metals via direct irradiation is still a relatively new concept that has been described by a three-step process: 1) laser-induced melting, 2) spallation, and 3) redeposition and fusion of NPs onto the substrate.^[1] The exposure of metals to laser light can also produce

laser-induced periodic surface structures (LIPSS).^[1,19] Their formation is understood as resulting from the interference between the laser light and a surface scattered wave.^[20–23] Recently, it has been suggested that surface plasmon polaritons (SPPs) excited during laser irradiation could play a crucial role in the formation of LIPSS and that grating-assisted coupling would be responsible for the creation of LIPSS with periods smaller than the wavelength of light (i.e., low spatial frequency LIPSS [LSFL]).^[20] Such structures are typically oriented perpendicular to the light polarization and governed by the transverse magnetic characteristics of excited SPPs.^[20] Periodic-like structures with a periodicity of $\lambda/10$, called high spatial frequency LIPSS (HSFL) were also observed; however, their origin is still debated.^[24,25]

Laser bursts, where each burst is comprised of closely time-spaced laser pulses, have found many applications in the machining of glasses and metals.^[26,27] The use of laser bursts in the machining of metals was shown to increase the ablation rate due to interactions of subsequent pulses within a burst with the heated surface.^[28,29] The diffusion of energy between the electronic and lattice systems and the pulse-to-pulse interaction on a surface can be modeled by a two-temperature

model. Typical two-temperature models are known to neglect the temperature dependence of many parameters,^[28] a valid assumption when modeling light-matter interactions with a long pulse-to-pulse separation. However, in burst mode, a modified two-temperature model is needed in order to handle the temperature dependence of the interaction. Hu et al.^[29] showed that the use of bursts, where the interpulse separation is of the order of picoseconds, significantly decreased the electron relaxation time, and increased the electron–phonon coupling in copper by a factor of 11, due to the higher electron temperature perceived by the next pulse within a burst. Electron–phonon coupling plays a crucial role in the creation of LIPSS and an increase in this coupling could play an important role in metals such as silver and gold, where LIPSS formation upon laser irradiation is known to be difficult.^[30] In addition, pulses in a burst were shown to interact with the ablation plume causing the plume to augment significantly in volume,^[26] redepositing nanoparticles onto a larger area.

In this paper, we report the coloring of silver using picosecond laser burst. The use of burst on silver is shown to increase the Chroma values by $\approx 100\%$ compared to the nonburst (NB) coloring method. Comparisons between colored surfaces produced by burst and nonburst reveal similar statistical distributions of nanoparticles, but vastly different underlying topographies involving LIPSS. These topographies include i) LSFL, ii) HSFL, and iii) large LIPSS (LLIPSS). By adjusting the energy distribution of laser pulses within a burst, we produce significantly different LIPSS and color palettes. Two-temperature simulations of the burst irradiation process are observed to increase the electron–phonon coupling, which in turn is believed to be responsible for the increase in the definition of the LIPSS. Finite-difference time-domain (FDTD) simulations of the surfaces identify the LSFL and HSFL, unique to burst, as playing an important role in the increased Chroma observed experimentally.

2. Results and Discussion

2.1. Nonburst, Burst, and Flexburst

In previous work, we showed that each Hue value was bound to a total accumulated fluence curve and that by simply tuning the energy density delivered to the surface one could generate full color palettes.^[3] The total accumulated fluence delivered to the metal surface via raster scanning (see Figure 1a), can be tuned by varying the laser fluence, marking speed and line spacing. Color longevity and stability are normally limited to a couple of weeks if not passivated.^[31] In this paper we address the aspect of increasing the vivacity and the range of colors produced on silver using burst trains composed of closely time-spaced laser pulses, see Figure 1b (see the Experimental Section).

Figure 2a shows a graph of Chroma versus Hue values for colors produced on silver using the nonburst, burst, and flexburst (FB) coloring methods. Compared to nonburst, the burst and flexburst coloring methods are observed to enhance the Chroma across the full Hue range by up to $\approx 70\%$ and $\approx 100\%$, respectively. Figure 2b shows a Commission Internationale de l'Eclairage (CIE) xy chromaticity diagram composed of all the colors found in Figure 2a. The range of colors produced by the flexburst coloring method is observed to be larger than those produced by the two other coloring methods. However, the increase in area covered on the CIE diagram is much less important between burst and flexburst. On a CIE diagram, the color saturation (i.e., Chroma) increases from the center going outwards. The highest increase in Chroma values is observed to be within the blue and magenta regions. Burst and flexburst are both readily observed to form significantly more vivid colors. However, the advantage of flexburst over burst arises from the control over the energy distribution within the burst pulse, which can be tuned for optimal color production. To identify the origin of the increased Chroma, three blue

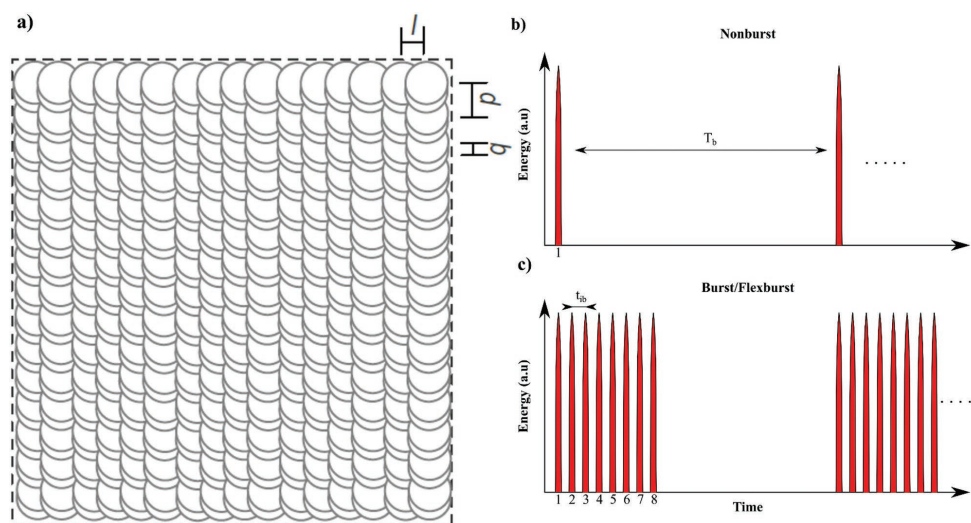


Figure 1. Coloring process and methods. a) Schematic of the coloring process for coloring metals. Raster scanning of the surface is done in a top to bottom fashion where l is the spacing between each successive laser line, d is the distance between successive laser bursts and b is the distance between the pulses within the bursts (d and b are set by the beam translation speed, and the burst and pulse periods, respectively). Schematic of a b) nonburst and c) burst pulse train produced by the laser at a given repetition rate of f_b , where $f_b = 1/T_b$ with T_b the burst period. The separation between the pulses within the burst is $t_{ib} = 12.8$ ns.

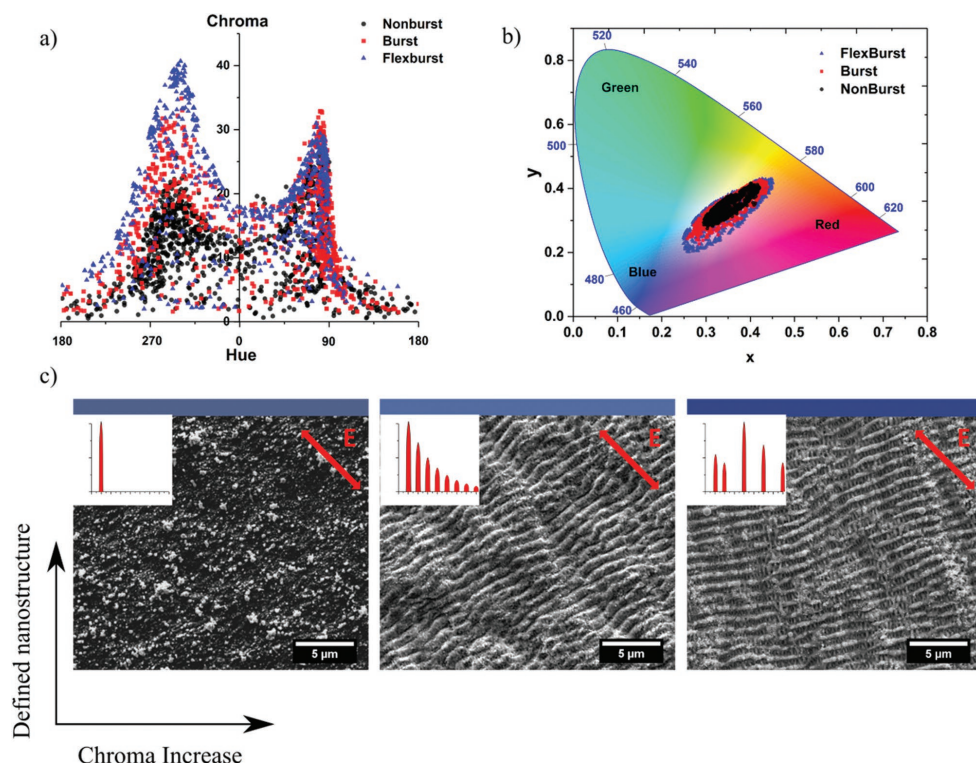


Figure 2. Colors and topography. a) Graph of Chroma versus Hue comparing colors obtained using the nonburst (●), burst (■), and flexburst (▲) coloring methods. b) CIE xy Chromaticity diagram comparing the nonburst (●), burst (■), and flexburst (▲) coloring methods of (a). c) SEM images of blue surfaces produced using the nonburst (left), burst (middle), and flexburst (right) coloring methods. The Hue is roughly the same for all squares ($H \approx 295^\circ$) whereas the Chroma values are 22.3, 31.2, and 39.44. Significant nanostructures are observed on the surfaces for the cases of burst and flexburst. The relative energy distribution of the burst pulses is shown as insets along with the orientation of the electric field (E) applied during writing.

colors were produced on the same silver sample using the nonburst, burst and flexburst coloring methods, as shown on the overbars on Figure 2c. The three colors have roughly the same Hue value ($H \approx 295^\circ$) but their Chroma increases from 22.3, 31.2 to 39.44 for the nonburst, burst, and flexburst colors, respectively. In this Hue range, a Chroma of 23 is generally the maximum value achievable by the nonburst coloring method, see Figure 2a.

The surface of the nonburst blue (Figure 2c, left) is observed to be almost devoid of any distinctive underlying topography and is relatively flat. This property was observed consistently on the nonburst colored surfaces. In the case of burst and flexburst, the surfaces are observed to have significant topography. For burst, the topography on the colored region is dominated by the combination of well-defined LSFL and HSFL structures (Figure 2c, center). For flexburst, the surface topography is dominated by well-defined HSFL structures with periods of ≈ 200 and ≈ 1000 nm, respectively (Figure 2c, right). The relative pulse energy distribution within the burst trains are shown as insets in Figure 2c.

In previous work, scanning electron microscope (SEM) analyses of similar colors produced by the nonburst coloring method revealed similar nanoparticle statistics for the a similar total accumulated fluence.^[3] Here, the nanoparticle statistics of a color palette produced by a single set of burst parameters was compared to the nanoparticle statistics of the nonburst colored surfaces, see Figure S1 in the Supporting Information.

The burst statistics of the medium and small nanoparticles were taken from high and low-magnification SEM images of the colored surfaces, see Figure S2 in the Supporting Information. The trends and number of nanoparticles per unit area, for small and medium nanoparticles, are observed to agree for the same Hue values (Figure S1, Supporting Information). The distribution of nanoparticle radii clearly demonstrates the consistency of the nanoparticle network for each color; see Figure S3 in the Supporting Information. Deviations between the burst and nonburst nanoparticle densities on the surface can be explained by the increase (or decrease) in surface area due to the underlying structure of burst/flexburst surfaces. To limit this effect, a burst arrangement that produced lower quality structures, but higher Chroma, was used in the comparison. For higher Chroma values, the number of particles in the 2D projection SEM images is expected to increase due to the larger underlying structures and surface area.

The Hue is produced by the nanoparticle networks formed on the surface,^[3] but the increase in Chroma is believed to originate from the topographical features unique to burst/flexburst. Moreover, the Chroma increases with the increasing definition of the LIPSS (i.e., HSFL and LSFL). Huang et al.^[20] showed that crevasses create stronger electric fields than nontopographical surfaces when exposed to optical radiation. Therefore, nanoparticles on and between the LIPSS would be exposed to enhanced fields, consequently enhancing the resonances and the absorption and resulting in more vivid colors in the far-field. In certain instances

where the LIPSS were strongly defined, an overlap of a fixed background color and of diffracted colors could be observed.

The effect and importance of burst irradiation on the creation of vivid colors are captured in Figure 3. Color palettes

were obtained on the silver surface using NB and FB. To study the effect of the partial-pulse (PP) train on the color rendition, the highest energy pulse (i.e., middle pulse) of the flexburst was removed. Also, the energy of the nonburst pulse and the

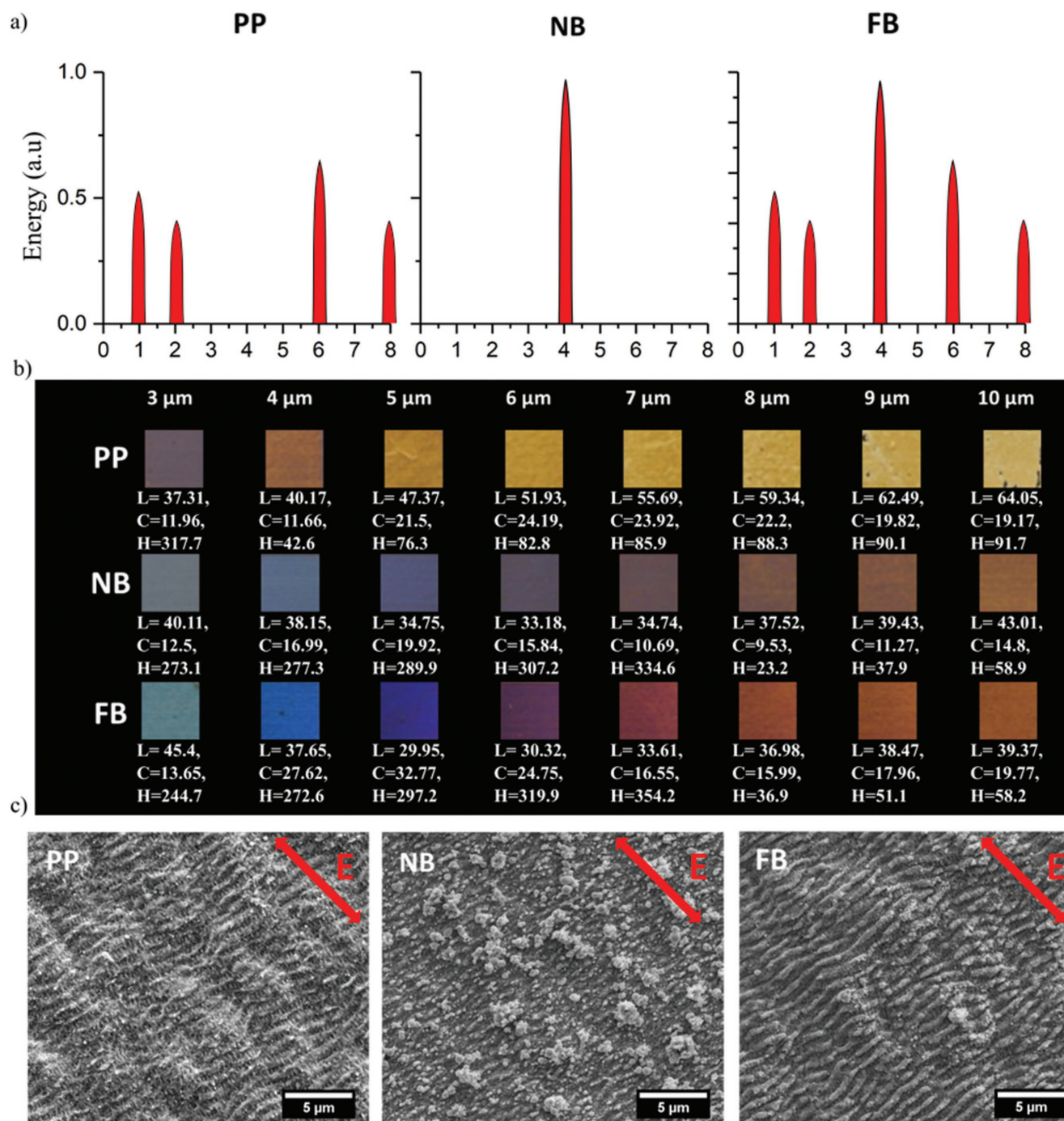


Figure 3. Effect of burst on color and topography. a) Schematic of the relative pulse energy distributions used to produce different color palettes. b) Different colored squares, $3 \times 3 \text{ mm}^2$, are obtained by changing the line spacing in steps of $1 \mu\text{m}$ with a marking speed of 150 mm s^{-1} . The partial-pulse (PP) train was isolated from the flexburst train (FB) to study the effect of the partial-pulse train on the color outcome. The pulse energy of the nonburst (NB) was the same as the last pulse of the flexburst pulse train (FB). The LCH values of each color are given below each square. c) SEM images of the surfaces produced by the partial-pulse (left), nonburst (middle) and flexburst (right). Significant topography is observed to be formed by the partial-pulse train evolving to form distinctive LIPSS with the full flexburst train (FB). No defined topography is observed on the surface of silver using nonburst (NB). The orientation of the electric field (E) applied during writing is sketched.

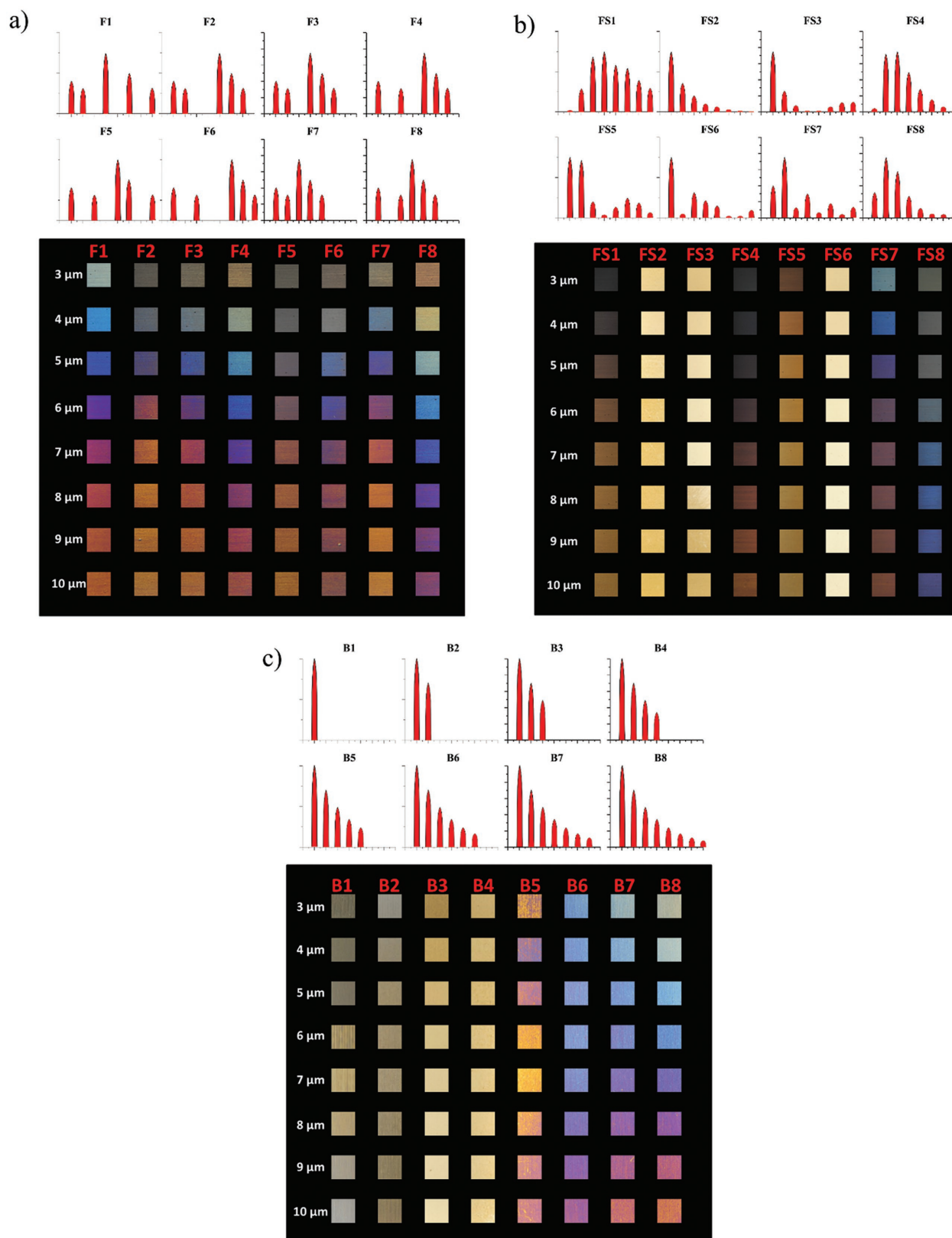


Figure 4. Palettes created via different burst configurations. a–c) Color palettes composed of $3 \times 3 \text{ mm}^2$ squares obtained by varying the pulse relative energy distribution in the burst following the sketches above each color panel. The total energy of the burst remains the same in all cases. a) The effect of time delays on the color is studied by placing zero energy pulses in the burst. b) Color palettes produced using different profiles for the pulse energy distribution. c) Color palettes created by changing the number of pulses in the pulse train.

middle pulse of flexburst were set to be the same, see Figure 3a. The palette created using only the PP train is limited to very few colors. The different colors were obtained by changing the line spacing between each of the squares in intervals of $1\text{ }\mu\text{m}$ with a marking speed of 150 mm s^{-1} . Interestingly, the machining of the surface using flexburst and nonburst created color palettes of similar Hue but different Chroma. In all instances the Chroma is higher for the flexburst colors, consistent with Figure 2, thus indicating that the partial-pulse train contributes to the Chroma increase. SEM images of the surfaces, shown in Figure 3c, reveal a distinctive trend. Surfaces exposed to the partial-pulse train bear distinctive LSFL and HSFL that are absent on the nonburst colored surface. In the case of flexburst, the surface contains even better defined LSFL and HSFL. From these observations, it would appear that the partial-pulse train assists in the creation of the underlying topography while the highest energy pulse (i.e., middle pulse) generates the final color and improves the definition of the structures formed by the partial-pulse train. In addition, we observed that the underlying topography can be tuned depending on the energy distribution within the burst. In other words, the vivacity of the colors can be adjusted by varying the underlying topography.

Figure 4a–c shows different burst configurations that were applied and the resulting color palettes. In all cases, the total energy of a burst configuration remained constant. The pulse relative energy distributions adopted are sketched above each color panel. The color produced is observed to depend on the pulse energy distribution within the burst. In Figure 4a, the burst configuration remains the same, but time delays are introduced by inserting zero energy pulses. The colors are observed to shift depending on the time delay, revealing a temporal dependence on the production of color. The most intense colors were obtained for the F1, F4, and F8 burst configurations. Figure 4b shows another set of burst configurations and the colors produced, which are also observed to vary significantly. For example, a double Gaussian (FS5) produces dark colors while a zigzag distribution (FS7) produces a broader palette. Figure 4c shows the colors achieved by changing the number of pulses per burst while maintaining the same total energy per burst. For burst (B), the highest Chroma values were generally obtained with the highest number of pulses per burst (e.g., B6–B8). In the case of flexburst (F and FS), higher Chroma values could be obtained with a fewer number of pulses per burst. The Flexburst allows better control over the energy distribution in the pulse chain compared to the regular burst, thus decreasing the number of pulses needed to generate high color saturation. For burst and flexburst, the relation between color and total accumulated fluence is no longer applicable, as the relation does not take into account temporal effects originating from the various pulse energy configurations within bursts.^[3] Each burst configuration produced different underlying topography.

SEM images of the surfaces produced by the burst configurations of Figure 4c reveal surprising structures that are not present on the nonburst colored surfaces (Figure S4, Supporting Information). In addition to LIPSS, large periodic-like structures (i.e., LLIPSS) are observed that are roughly $7\times$ larger than the wavelength of the incoming laser light and that are ori-

ented along the direction of the laser polarization (red arrow). At normal laser incidence, their creation cannot be explained by light-scattering interference or light-plasmon interference theories.^[20–23] The structures appear only when using burst (or certain flexburst patterns). The LIPSS structures are more defined with a decreasing number of pulses within the regular burst (to a minimum of 2 pulses) due in part to the higher energy per pulse within the burst. The evolution of the structures with decreasing number of pulses per burst (i.e., higher energy per pulse) gives insight into the creation of these LLIPSS structures. For an 8 pulse burst (Figure S4a, Supporting Information), random hole-like structures are observed on the surface. With a decreasing number of pulses per burst (Figure S4b,c, Supporting Information), the number of random hole-like structures increases and they eventually coalesce (Figure S4d, Supporting Information) to form structures that are roughly $7\times$ the wavelength of light. This indicates not only a feedback mechanism in the process but possibly dynamic interaction with the molten surface.

Figure 5 shows SEM images of the surfaces created by the different burst arrangements presented in Figure 4b. The surface features are observed to be significantly different for each burst configuration. In one case, micro-‘spike’ features can be observed (FS3) while in other instances features that are roughly $7\times$ the wavelength of light (FS2, FS6, and FS7) or well-defined LSFL and HSFL (FS1, FS2, FS5, and FS8) can be observed. The microfeatures (i.e., LLIPSS) are generally observed for burst arrangements starting with high energy laser pulses. While FS1, FS2, FS5, and FS8 had similar underlying features as in Figure 2c, the lack of vivid colors could be explained by the particle distribution redeposited on the burst features. The SEM images were taken for a line spacing of $3\text{ }\mu\text{m}$. In general, the distinct features of the burst/flexburst surfaces are observed to be more pronounced for smaller line spacing due to the higher degree of overlap between each successive machined line. With increasing line spacing, the distinctive features of each burst arrangement gradually disappear, in part, explaining why the increase in Chroma is more pronounced for colors produced at smaller line spacings (i.e., blue and purple), see Figure 2.

Less discernable differences could be observed on the surfaces produced by the burst arrangements of Figure 4a, see Figure S5 in the Supporting Information. This is not surprising because changes to the temporal distribution of the burst pulses only created slight variations in the color palettes. Only small differences in the shape and definition of the LIPSS are observed. For example, F1 appears to have thinner LSFL while F5 has more fragmented LSFL.

2.2. Two-Temperature Model

In previous work, we explained the origin of nonburst produced colors as a plasmonic effect coming from the coupling of small and medium nanoparticles formed on the Ag surface.^[3] SEM image analysis and FDTD simulations of colored surfaces suggested that the different colors originated from different particle arrangements on the surface and were due to collective plasmonic resonances. In contrast to burst, the surfaces of the nonburst colored regions of silver were relatively flat with

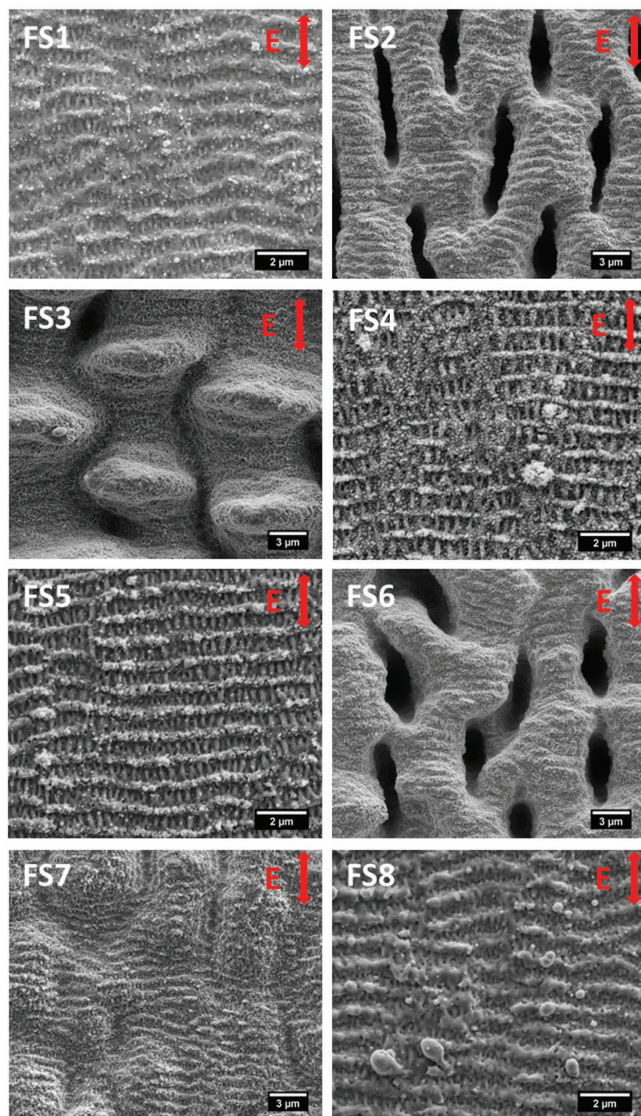


Figure 5. SEM images of surfaces machined by different burst arrangements. SEM images of the surfaces produced using the burst arrangements of Figure 4b for the line spacing of 3 μm and the same total laser energy. Each surface was machined using a laser fluence of 12.12 J cm^{-2} with a marking speed of 150 mm s^{-1} . The surface features are observed to be strikingly different for each burst arrangement. Note the different scale bars to properly capture the distinctive features of each surface and their respective laser burst arrangements. The light polarization during machining is indicated by red arrows.

no distinctive or significant topography. It is believed that the emergence of topography under burst irradiation is linked to the increase of electron–phonon coupling in the metal which is known to play a vital role in the quality of ripple structures.^[1,30]

The two-temperature model (TTM) is a 1-D heat diffusion model that can be applied to represent the diffusion of the laser energy in the electron and lattice subsystems.^[32] The dynamics of diffusion are governed by coupled differential equations where the laser energy is diffused mainly through the electron system. The electron energy is then transferred to the lattice via collisions (electron–phonon coupling). The coupled differential equations^[29] are

$$C_e \frac{\partial T_e}{\partial t} = \frac{\partial}{\partial z} \left(k_e \frac{\partial T_e}{\partial z} \right) - g(T_e - T_l) + S(z, t) \quad (1)$$

$$C_l \frac{\partial T_l}{\partial t} = \frac{\partial}{\partial z} \left(k_l \frac{\partial T_l}{\partial z} \right) + g(T_e - T_l) \quad (2)$$

where C_e and C_l are the electronic and lattice thermal heat capacities respectively, k_e is the electronic thermal conductivity, k_l is the lattice thermal conductivity, g is the electron–phonon coupling, S is the energy deposited on the surface by the laser, and T_e and T_l are the electronic and lattice temperatures, respectively. The lattice thermal conductivity is assumed to be negligible in comparison to the electron thermal conductivity and is usually neglected in TTM simulations.^[33] The electronic thermal heat capacity versus temperature was taken from ref. [34]. The electronic thermal conductivity and electron–phonon coupling were calculated using the relations found in ref. [33]. The lattice thermal heat capacity was calculated in the high temperature limit by applying the Debye model.^[35] The laser absorption by the material was calculated using the following relations^[29,36]

$$S(z, t) = (1 - R) \alpha I(t) e^{-\alpha z} \quad (3)$$

and

$$I(t) = 0.94 \frac{J_0}{\tau} e^{-2.77 \left(\frac{t}{\tau} \right)^2} \quad (4)$$

where R is the surface reflectivity, α is the absorption coefficient, I is the laser intensity, τ is the pulse length, and J_0 is the laser fluence. The material reflectivity and absorption were continuously calculated using the temperature dependence of the electron relaxation time in the Drude + 2 Critical Point model.^[37]

As the lattice temperature approaches 0.9 times the critical temperature (T_c), critical point phase separation (phase explosion) occurs and material is ejected from the surface.^[28,29] In our simulations, when the material reaches $0.9 T_c$ (in the lattice), the regions with this temperature are ignored for the remainder of the simulation and the layer below is assumed to be the new surface for the next laser pulse. The different colors created using a different number of pulses per burst for a fixed total energy is believed to result from the interaction between the already hot surface and the subsequent laser pulses within a burst. **Figure 6a** shows a 1D TTM simulation of the temperature field with respect to time for a burst of 8 pulses, each pulse separated by 12.8 ns. For simplicity, each pulse within the burst was taken to be of equal amplitude. It is readily observed that the lattice temperature increases significantly as more pulses irradiate the surface. In **Figure 6b**, we see during the laser irradiation that the electron temperature is significantly higher than that of the lattice. This is due to the assumption that the electrons absorb the laser energy before transferring it to the lattice. The excited electrons transfer their energy to the lattice by collisions until the lattice accumulates more energy than the electron system near the surface. With time the system

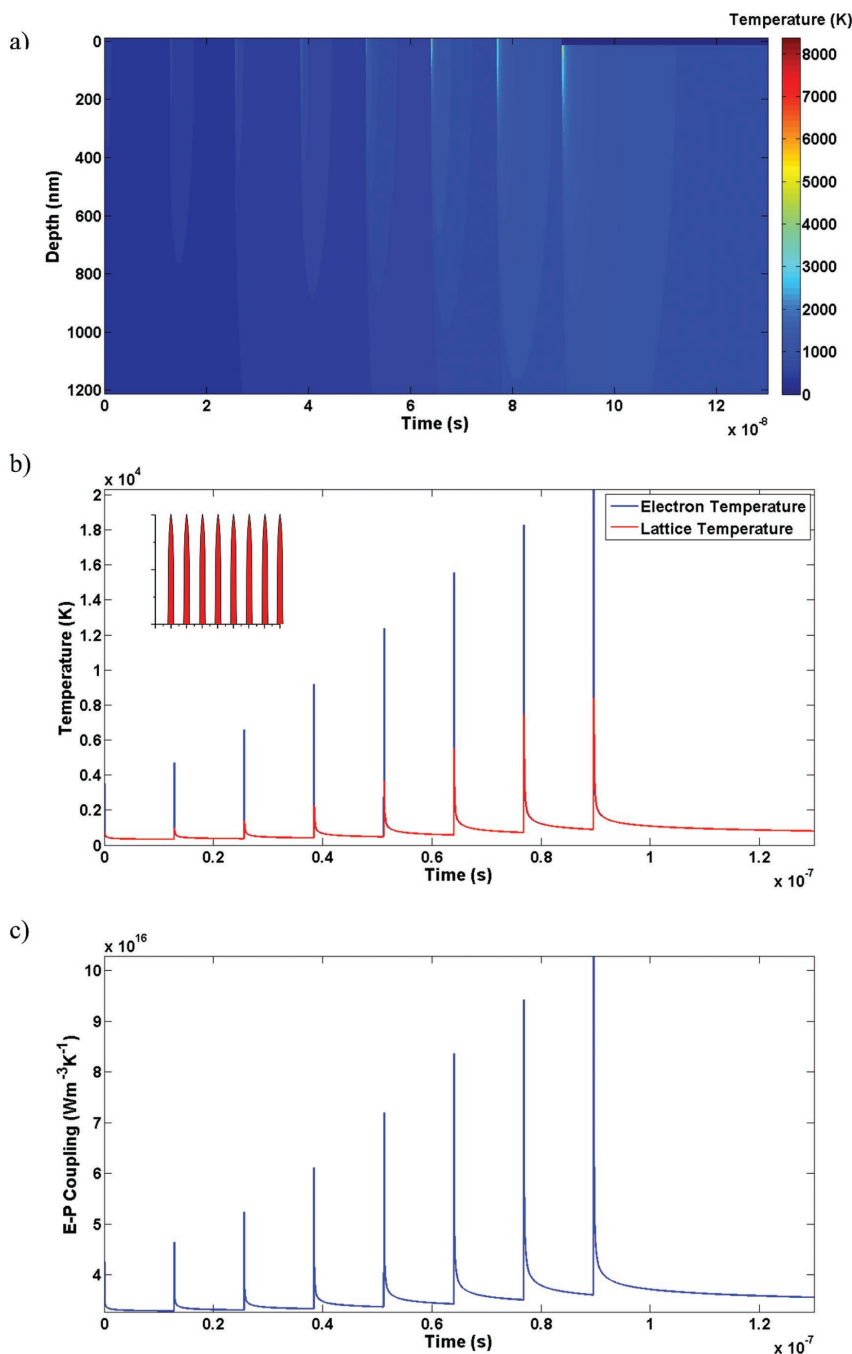


Figure 6. Electron–phonon coupling increase due to burst exposure. a) 1D temperature field with respect to time simulated using the TTM, for an 8 pulse burst where each pulse within the burst is separated by 12.8 ns and has a total energy of 244 μJ (or a fluence of 1 J cm^{-2} per pulse). b) Graph showing electron and lattice temperatures, and c) electron–phonon coupling (g) with respect to time.

tends to equilibrium. In the case of burst, another pulse hits the surface before equilibrium is reached. The electron–phonon coupling values for burst in Figure 6c show an increase of up to $\approx 150\%$, contributing to higher and better defined LIPSS observed in burst. The pulse separation being much shorter than the time for silver to return at room temperature, heat accumulation is seen to occur in the metal causing the electron–phonon coupling to increase. The

increase in the electron–phonon coupling would make silver comparable to copper ($g_{\text{Cu}} = 10 \times 10^{16} \text{ W m}^{-3} \text{ K}^{-1}$),^[30] a metal known for forming well-defined LIPSS. Moreover, control of the pulse energy distribution within the burst allows to control the enhancement of the electron–phonon coupling and by association the definition of the LIPSS. The tuning of the LIPSS with different burst configurations was observed experimentally. The link between LLIPSS and higher electron–phonon coupling is however not clear. Other groups have observed similar structures from the accumulation of laser shots on a surface,^[38] however, our experiments showed no such structures in the nonburst case even for the same amount of shots delivered locally, indicating that the structures may arise from interaction with the already melted surface. Previous coloring of silver surfaces in the nonburst case failed in all instances to produce such structures.^[3] This suggests that the use of burst could be highly effective in creating well defined LIPSS on metals that normally do not respond well to LIPSS formation.

2.3. FDTD Simulations

As in our previous work,^[3] we utilized SEM statistical analyses of the nanoparticles distributed on the silver surface to create a model suitable for FDTD simulations. The SEM statistical analyses of the colored regions reveal similar nanoparticle densities for the same Hue values, following burst and nonburst laser processing (Figures S1 and S3 in the Supporting Information). The main differences originate from the underlying modulated silver surface and the resulting larger surface area. In our experiments, a laser wavelength of 1064 nm was used, which produces surface ripples with a periodicity of $\approx 1000 \text{ nm}$ (LSFL), as informed by SEM images and atomic force microscope (AFM) scans. The other periodic structures, perpendicular to the LSFL, observed on the surface have a periodicity of $\approx 200 \text{ nm}$ (HSFL). In ref. [3], we considered both small

and medium NPs showing how their interplay can create dips in the reflectance due to cluster resonances. These dips were not observed in experiments due to the random nature of the distributions. A model with only medium NPs is used here, which can still explain the color transition from blue to yellow reported in ref. [3].

To mimic a typical surface (see Figure 2c, center), we simulate medium NPs arranged on an xz surface

modulated by a sinusoidal function in the x -direction, i.e., $f(x,z) = A \cdot \sin(2\pi x/L_p)$, where L_p is the spatial period of the sinusoid and A its amplitude. The medium NPs are embedded by 30% of their radius, which we take as $R_m = 35$ nm, with the embedding direction normal to the surface.^[3] The center-to-center distance between NPs is D_m . Based on the fact that NPs arranged in square and hexagonal lattices on a flat surface produce the same color transition from blue to yellow for increasing D_m , in this paper, the medium NPs are arranged following a square lattice. This is more convenient for the application of periodic boundary conditions in x and z due to the sine-modulated surface. The dispersion of silver is taken into account by using a Drude+2CP model as in ref. [44], the simulation domain was discretized with a space step of 0.5 nm, and the system was excited by a y -propagating plane wave pulse to calculate the reflectance in the optical range 350–750 nm. The presence of the surface modulation makes the system polarization-dependent, so we considered two linear polarizations of the incident light, i.e., x - and z -polarization.

The geometric parameters of relevance, i.e., D_m , A , and L_p , are highlighted in **Figure 7a,b** for different cases (the field distributions are discussed in detail further below). We considered HSFL and LSFL, i.e., $L_p = 200$ nm and $L_p = 1000$ nm, and conducted a parametric study to understand the effect of ripples on color formation for different interparticle spacing (D_m) and ripple amplitude (A).

Simulations of a sine-modulated surface only (no NPs) produced the same reflectance as a flat surface for z -polarization, but constructive interference spots were noted at different locations close to the surface for different wavelengths (not shown). No field enhancement on the surface was observed for z -polarization. Conversely, for x -polarization, features are observed in the reflectance depending on L_p and A due in part to the excitation of SPPs, and some field enhancement is justifiably always present. For example, for $L_p = 200$ nm, we observe an increasing absorbance at shorter wavelengths as a function of A , due to the increased metal surface exposed to the incident radiation. This means higher field enhancement in the crevices over a broader spectrum with increasing A (see field distribution at 450 nm for $A = 40$ nm in Figure S6a in the Supporting Information).

A full parametric study was also performed for a rectangular ridge (nonsinusoidal) grating with characteristic dimensions between 10 and 200 nm to understand the effect of HSFL without nanoparticles, and the only color observed was a light yellow Hue, which is due to increased absorbance in the blue region (≈ 400 nm), and is angle-independent due to the sub-wavelength size of the grating as previously reported.^[18,39]

Simulations for $L_p = 200$ nm in presence of NPs were also conducted by considering five HSFL periods (see Figure 7a). For z -polarization, the absorbance slowly increases at all wavelengths due to a slight increase in the NP areal density as a function of A (for the same D_m), which also implies darker colors. By increasing A , the ripples modify the resonance of the NPs, which corresponds to a color shift. For higher A , simulations show out-of-plane plasmonic resonances, i.e., involving nanoparticles which are arranged on the surface with a component along the direction of propagation y . These out-of-plane

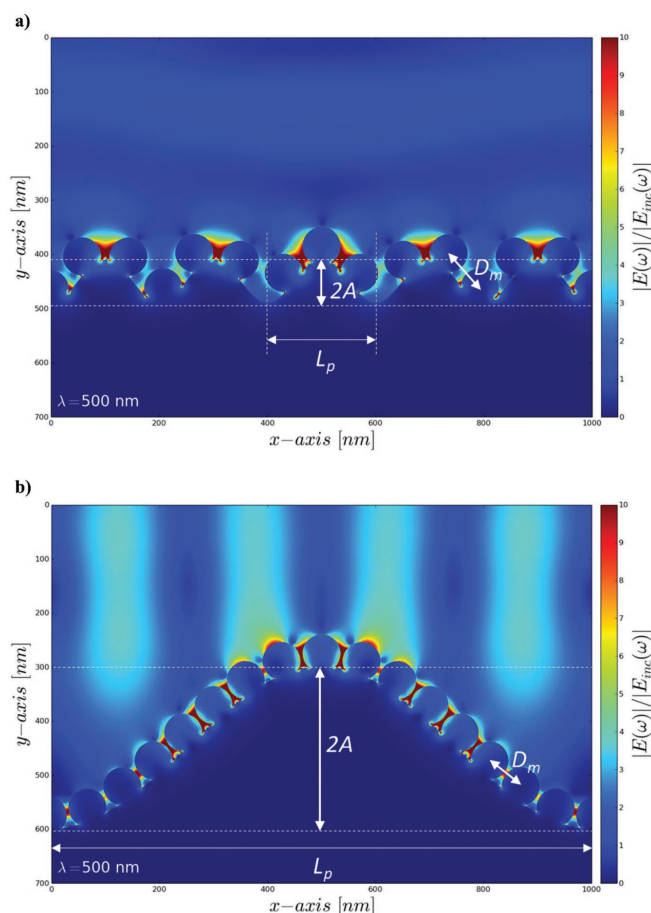


Figure 7. Simulation setup and computed near-field for NPs on a sine-modulated surface. Electric field distribution (magnitude) at $\lambda_0 = 500$ nm under x -polarization for a) $L_p = 200$ nm, $D_m = 85$ nm, $A = 40$ nm, and b) $L_p = 1000$ nm, $D_m = 75$ nm, $A = 150$ nm.

resonances are not observed in experiments due to the random nature of the surface.

For x -polarization, we observe higher absorbance at shorter wavelengths for increasing A , which is due to the field enhancement in the crevices and produces a reduction of the reflectance in the blue region of the spectrum. We also observe cluster resonances at longer wavelengths responsible for new dips in the reflectance (not observed in experiments because of the random nature of the surface).

In Figure 7a we show the field distribution for x -polarization excitation at $\lambda_0 = 500$ nm in an xy plane cut through the center of the spheres for $L_p = 200$ nm, $D_m = 85$ nm, and $A = 40$ nm (Media 1 shows the field distribution from $\lambda_0 = 350$ to 750 nm in steps of 10 nm). In general, HSFL having dimensions comparable to the NPs (e.g., Figure 2c, right) can modify the resonance conditions producing a shift in the absorbance dip, creating new plasmonic resonances and modifying the color, while field enhancement effects on top of the ridges (the enhancement increases for sharper geometries) or in gaps between NPs, in troughs between grating ridges, and for NPs in a trough, are responsible for increased absorption.

The dimensions of LSFL are of the order of the laser wavelength and thus can act as a grating coupler for

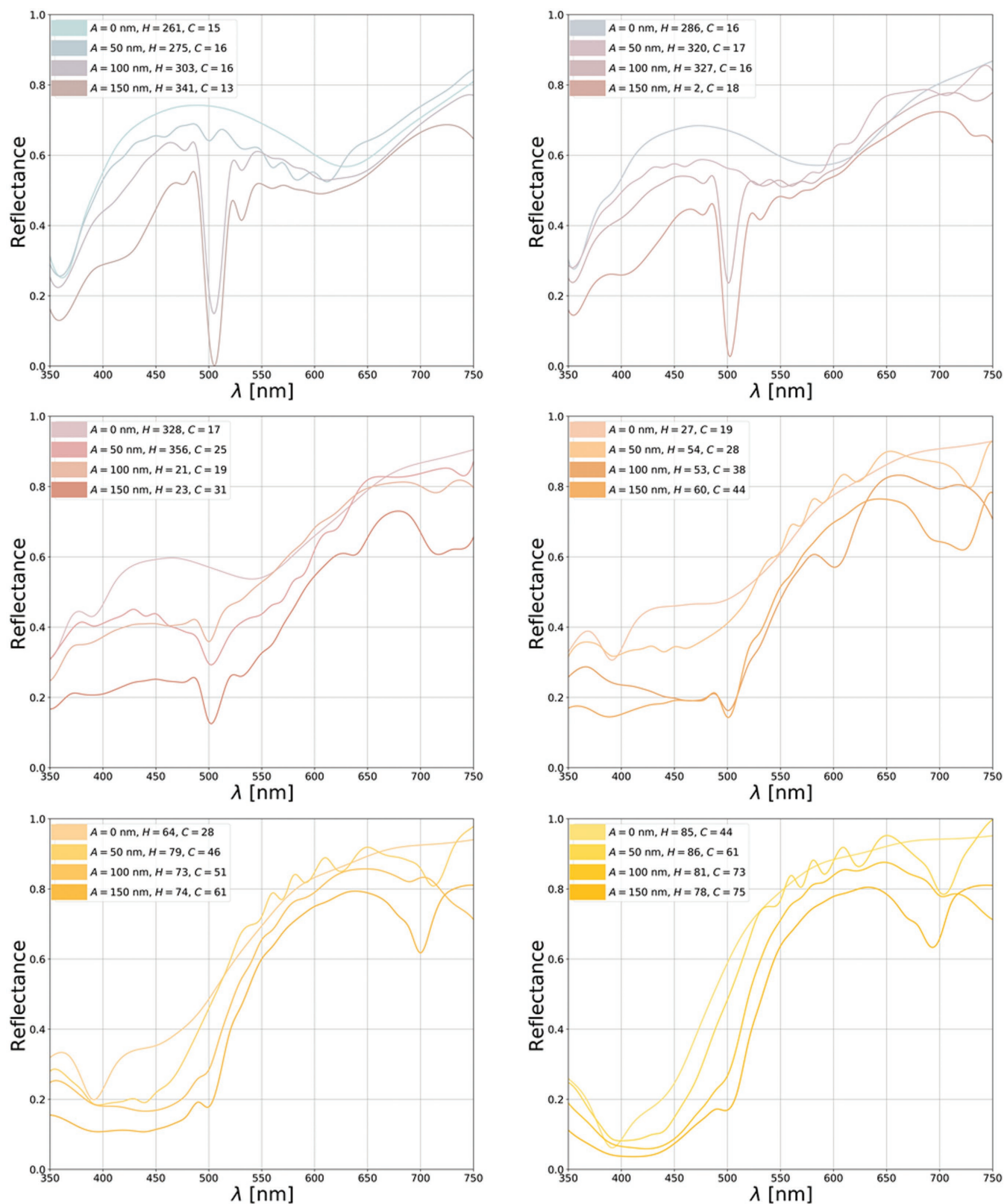


Figure 8. Theoretical reflectance spectra for x-polarized excitation. a) Blue ($D_m = 75$ nm), b) violet ($D_m = 77$ nm), c) magenta ($D_m = 80$ nm), d) red ($D_m = 85$ nm), e) orange ($D_m = 90$ nm), and f) yellow ($D_m = 100$ nm) color evolution (Hue and Chroma) as a function of A for x-polarized excitation. The linestyle colors were rendered by converting the reflectance spectra to a color and using the associated RGB values.

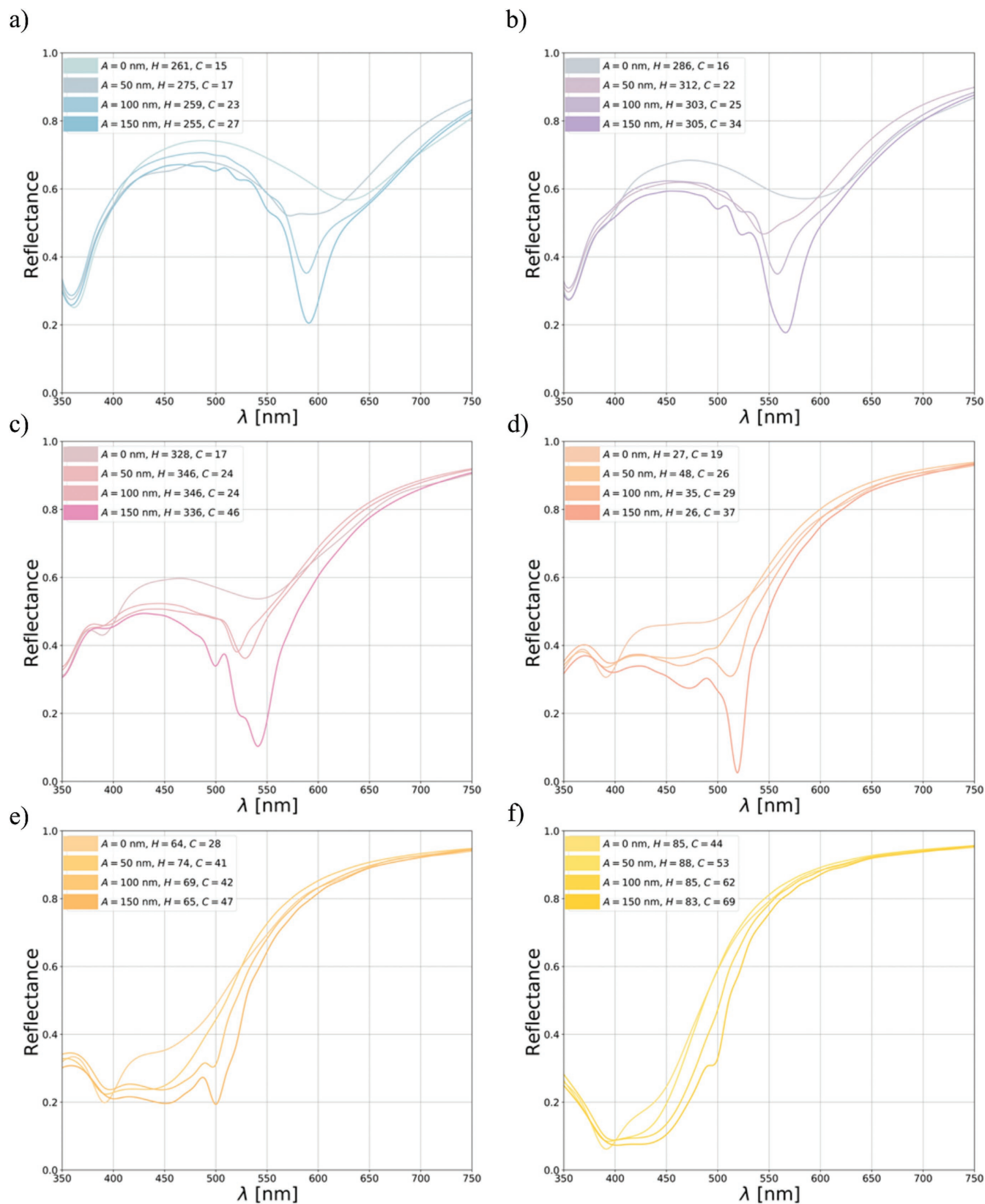


Figure 9. Theoretical reflectance spectra for z-polarized excitation. a) Blue ($D_m = 75$ nm), b) violet ($D_m = 77$ nm), c) magenta ($D_m = 80$ nm), d) red ($D_m = 85$ nm), e) orange ($D_m = 90$ nm), and f) yellow ($D_m = 100$ nm) color evolution (Hue and Chroma) as a function of A for z-polarized excitation. The linestyle colors were rendered by converting the reflectance spectra to a color and using the associated RGB values.

surface plasmons. The coupled wavelength can fall in the visible range producing a dip in the reflectance spectrum. The absorptance dip due to grating coupling can affect the colors dramatically and can be exploited to tune the color even further.

The simulation of a sine-modulated surface with $L_p = 1000$ nm without NPs under x -polarization reveals increasing absorptance at shorter wavelengths as a function of A , and a coupling to propagating SPPs which become increasingly perturbed as A increases (grating coupling to SPPs on a flat surface is observed for small A). These perturbed propagating SPPs produce field enhancement on the surface which can be responsible for higher absorption in the NPS. For example, for $A = 100$ nm, we observe a dip at $\lambda_0 = 540$ nm with 72% reflectance (see field distribution in Figure S6b, Supporting Information). The presence of NPs can bring this reflectance to 15% and almost 0 as observed in Figure 8a at $\lambda_0 = 505$ nm for $A = 100$ and 150 nm, respectively.

Thus grating coupling can be seen as a strategy to enhance absorptance and Chroma. In Figure 7b we show the field distribution at $\lambda_0 = 500$ nm for x -polarized excitation for $L_p = 1000$ nm, $D_m = 75$ nm, and $A = 150$ nm, which reveals a grating-coupled SPP propagating along the surface (Media 2 shows the field distribution from $\lambda_0 = 350$ to 750 nm in steps of 10 nm).

In Figure 8a,f we show the evolution of the reflectance responses and the corresponding color rendered as the linestyle color for each response for the cases $D_m = 75, 77, 80, 85, 90, 100$ nm and $A = 0, 50, 100, 150$ nm. Grating coupling produces a dip in the reflectance spectra, for instance at $\lambda_0 = 500$ nm for the period selected ($L_p = 1000$ nm) as shown in Figure 8a, with the consequence that colors are modified (Figure 7b plots the field distribution at the location of the dip in Figure 8a for $\lambda_0 = 500$ nm, $D_m = 75$ nm and $A = 150$ nm). In general, the dip at $\lambda_0 \approx 500$ nm affects the blue and red colors (Figure 8–c) more than orange-yellow (Figure 8d–f) for which only an increase in Chroma is observed.

In Figure 9 we show the evolution of the colors as a function of A for different D_m values ($D_m = 75, 77, 80, 85, 90, 100$ nm) which produce a transition from blue to yellow in the flat case ($A = 0$) for z -polarized excitation. We note that for this polarization there is no grating coupling and all colors show an increase in Chroma as a function of A , which is due to the higher density of NPs due to the increased surface available.

The interaction between the incident x - and z -polarized plane wave pulse and the silver surface with NPs ($D_m = 75$ nm, $A = 100$ nm, $L_p = 1000$ nm) is shown in movies Media 3 and Media 4, respectively.

In general, the increase in Chroma with A is due to increased absorption from the nanoparticles caused by the field enhancement generated by the underlying topography under x -polarization for both L_p values investigated. However, given the orthogonal nature of the ripple orientation for the 2 sets of ripple structures, the effect of field enhancement caused by the structures are always present. Increased absorptance due to a larger surface area with increasing A , which can contain a larger number of NPs, is present for any incident polarization.

3. Conclusion

Colors covering the full spectrum were obtained using closely time-spaced laser pulses (burst mode). The use of burst mode to color silver is observed to increase Chroma values by $\approx 100\%$ over most of the color spectrum. These increases are accompanied by the creation of 3 kinds of LIPSS on the surface of silver, i.e., LSFL, HSFL and LLIPSS. Different pulse energy distributions within the laser burst, while maintaining the total energy constant, is observed to create significantly different nanostructures. The NP statistics of the burst and nonburst colors are observed to be similar pointing to the underlying structure as responsible for the increase in Chroma observed. TTM simulations of the burst interaction support that electron–phonon coupling enhancement is responsible for the formation of well-defined LIPSS structures on the surface of colored silver. FDTD modeling of representative surfaces corroborate the involvement of surface plasmons in color rendering and show the importance of the crevices (i.e., LSFL of $L_p = 1000$ nm and HSFL of $L_p = 200$ nm) to enhance absorptance and enrich plasmon resonances for the creation of new colors. The Chroma value of the colors is generally observed to increase with increasing LSFL and HSFL amplitude. The presence of the LSFL on the surface and the absence of angle-dependent colors suggest that selective absorption dominates over diffraction.

4. Experimental Section

Laser Specifications: The irradiation of silver surfaces was carried out in a raster-scanning fashion, as sketched in Figure 1a, with 1064 nm light from a Duetto mode-locked laser (Nd:YVO₄, Time-Bandwidth Product) producing 10 ps laser pulses. The burst repetition rate $f_b = 1/T_b$ (T_b is the burst period) was tunable from 50 to 8200 kHz but was kept at 25 kHz (50 kHz with a pulse picker of 2) throughout the experiments. The time separation between each pulse within a burst is $t_{ib} = 12.8$ ns, which is fixed, Figure 1b. A selection of 1 to 8 pulses within each burst is available. A burst of 1 is defined as “nonburst” irradiation, whereas 2 or more pulses within a burst constitute “burst” or “flexburst” irradiation. In burst, the energy distribution is uncontrolled but governed by the normal laser amplification process resulting in the first pulse being amplified more than the subsequent ones. For flexburst, the energy distribution of the pulses within the burst is controlled using software provided by the manufacturer (FlexBurst, Time-Bandwidth Product).

Laser Coloring Process: Colors were produced on silver using a method described in a previous publication,^[3] where different colors were obtained by controlling (statistically) interparticle distances. The laser light was focused on the silver surface using an F-theta lens (254 or 163 mm, Rodenstock). The laser was fully electronically integrated and enclosed by a third party for industrial applications (GPC-PSL, FOBA). For accurate focusing, the surface of the samples was located using a touch probe system. The silver samples used in this study were of 99.99% purity measuring 38 mm in diameter with a thickness of 3 mm. For machining, the samples were placed on a 3-axis stage with a resolution of 1 μ m in both the lateral and axial directions. The samples were raster scanned using galvanometric XY mirrors (TurboScan 10, Raylase) displacing the beam in a top to bottom fashion, Figure 1a. The laser polarization was kept parallel to the laser machining direction. The laser power was computer-controlled via a laser interface and calibrated using a power meter (3A-P-QUAD, OPHIR). A Gaussian beam radius of ≈ 28 μ m (≈ 14 for the 163 mm lens) was obtained from a semi-logarithmic plot of the square diameter of the modified region, measured with an SEM, as a function of laser pulse energy following the method described in ref. [40].

Surface Imaging and Statistics: High-resolution SEM (JSM-7500F FESEM, JEOL) images were obtained using secondary electron imaging (SEI) mode. SEM low- and high-magnification images were used to obtain NP statistics on several colored surfaces using a Matlab program that was written to identify the location and dimensions of the NPs on the surface.

Photometric Characterization: Colors were quantified using a Konica Minolta CR-241 Chroma Meter in the CIELCH color space, 2 observer and illuminant C (North sky daylight), where *L* is color Lightness, *C* is Chroma (i.e., color saturation) and *H* is Hue (color value associated with a 360° polar scale).

Two-Temperature Model Simulations: TTM simulations were done using an in-house code parallelized using compute unified device architecture (CUDA) to be run on a graphic processing unit (GPU) cluster (SciNet's Gravity cluster). The TTM model equations were solved using the finite-difference method using a space discretization step size of 2.5 nm.^[41] The time step was chosen to be on the order of attoseconds for numerical stability.

Finite-Difference Time-Domain Numerical Simulations: 3D finite-difference time-domain simulations^[42,43] were performed to determine the origin of the Chroma increase. An in-house 3D-FDTD parallel code,^[44,45] running on an IBM BlueGene/Q supercomputer (64k cores) part of the Southern Ontario Smart Computing Innovation Platform (SOSCIIP), was used.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

plasmonic colors, surface colorization, ultrafast laser machining

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ADVANCED OPTICAL MATERIALS

Supporting Information

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Topography Tuning for Plasmonic Color Enhancement via
Picosecond Laser Bursts

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Graham Killaire, Lora Ramunno, Pierre Berini, and Arnaud
Weck*

Supporting Information

Topography tuning for plasmonic colour enhancement via picosecond laser bursts

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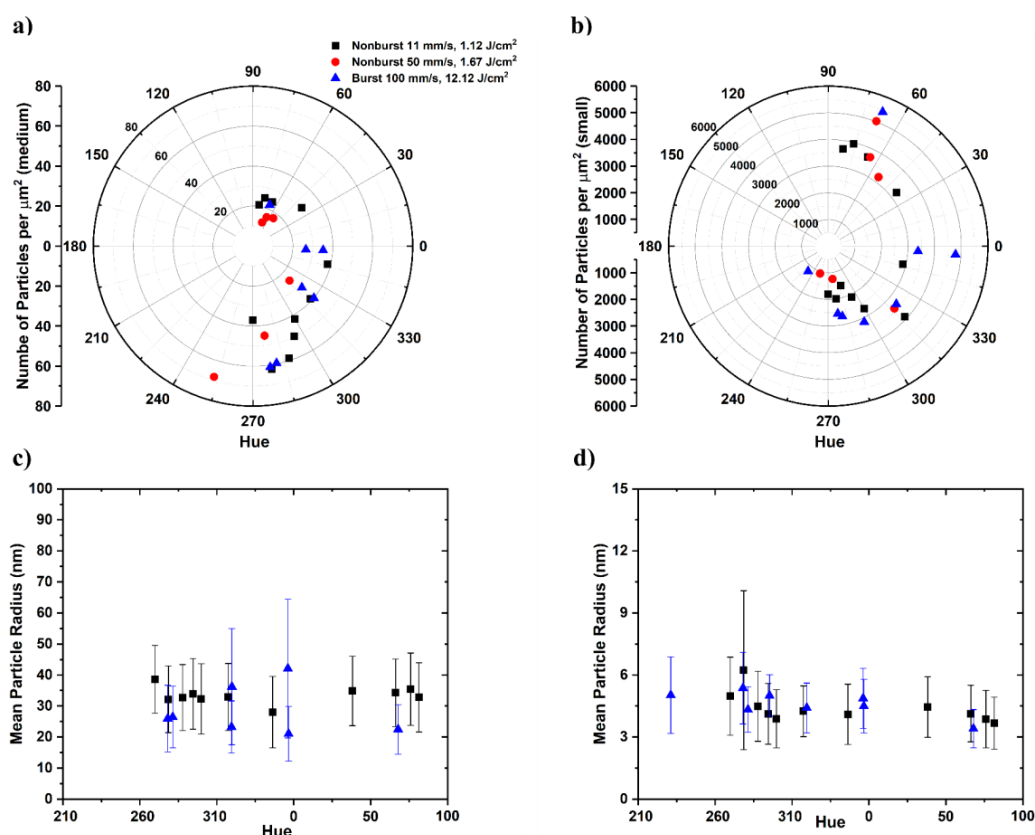


Figure S1| Polar plot of number of particles per μm^2 versus Hue for (a) medium and (b) small nanoparticles for 2 sets of nonburst laser parameters and 1 set of burst laser parameters. The nonburst colours were obtained using a laser fluence of (●) 1.12 J/cm² with a marking speed of 11 mm/s, and a laser fluence of (■) 1.67 J/cm² with a marking speed of 50 mm/s. The burst colours (▲) were obtained with a burst of 5 laser pulses with a laser fluence of 12.12 J/cm² and a marking speed of 100 mm/s. Mean particle radius versus Hue for the (c) medium NPs and (d) small NPs for the nonburst and burst colours. The error bars are the standard deviations obtained from the statistical analyses of the SEM images.

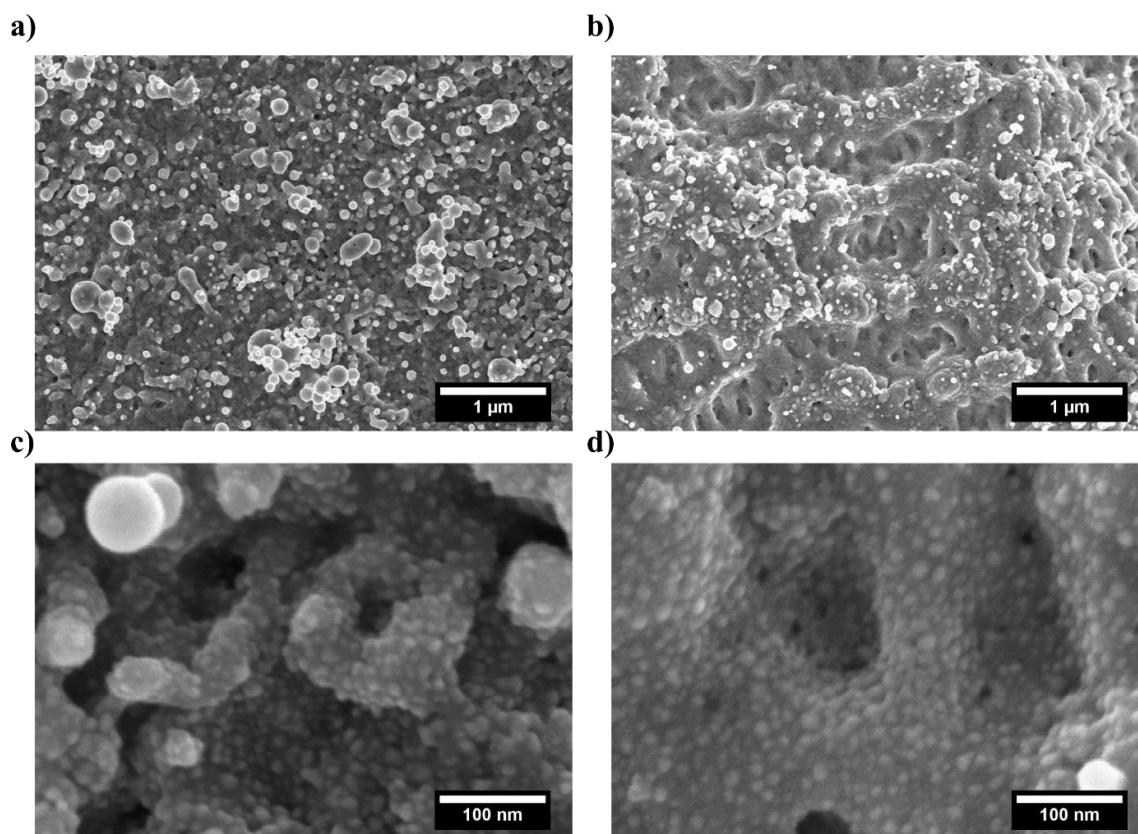


Figure S2 | (a,b) Low-magnification and (c,d) high-magnification SEM images of a (a,c) nonburst ($H = 317.9$) and (b,d) burst ($H = 319.6$) coloured surfaces. The surfaces were processed using a laser fluence of 1.67 J/cm^2 with a marking speed of 50 mm/s for the nonburst colour and a laser fluence of 12.12 J/cm^2 with a marking speed of 100 mm/s for the burst colour using a standard burst of 5 pulses. The medium particle statistics are counted from the low-magnification SEM images (a,b, scale bar $1 \mu\text{m}$) and the small nanoparticle statistics from the high-magnification SEM images (c,d, scale bar 100 nm).

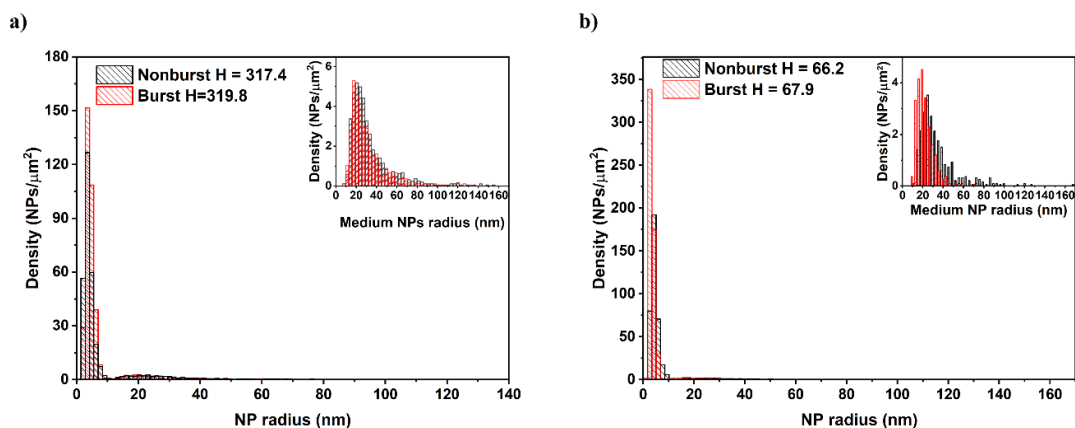


Figure S3 | Histograms of the number of nanoparticles on the substrate relative to their radius obtained from the low- and high-magnification SEM images of the coloured surfaces. The nonburst colours were obtained

with a laser fluence of 1.67 J/cm^2 and a marking speed of 50 mm/s . The burst colours were obtained with a regular burst of 5 pulses, a laser fluence of 12.12 J/cm^2 and a marking speed of 100 mm/s . The statistics compared in the histograms are for nonburst and burst colours of roughly the same Hue. Two discernable bumps (bimodal distribution) are observed, corresponding to the small and medium nanoparticles. The insets are magnifications of the medium particle distributions.

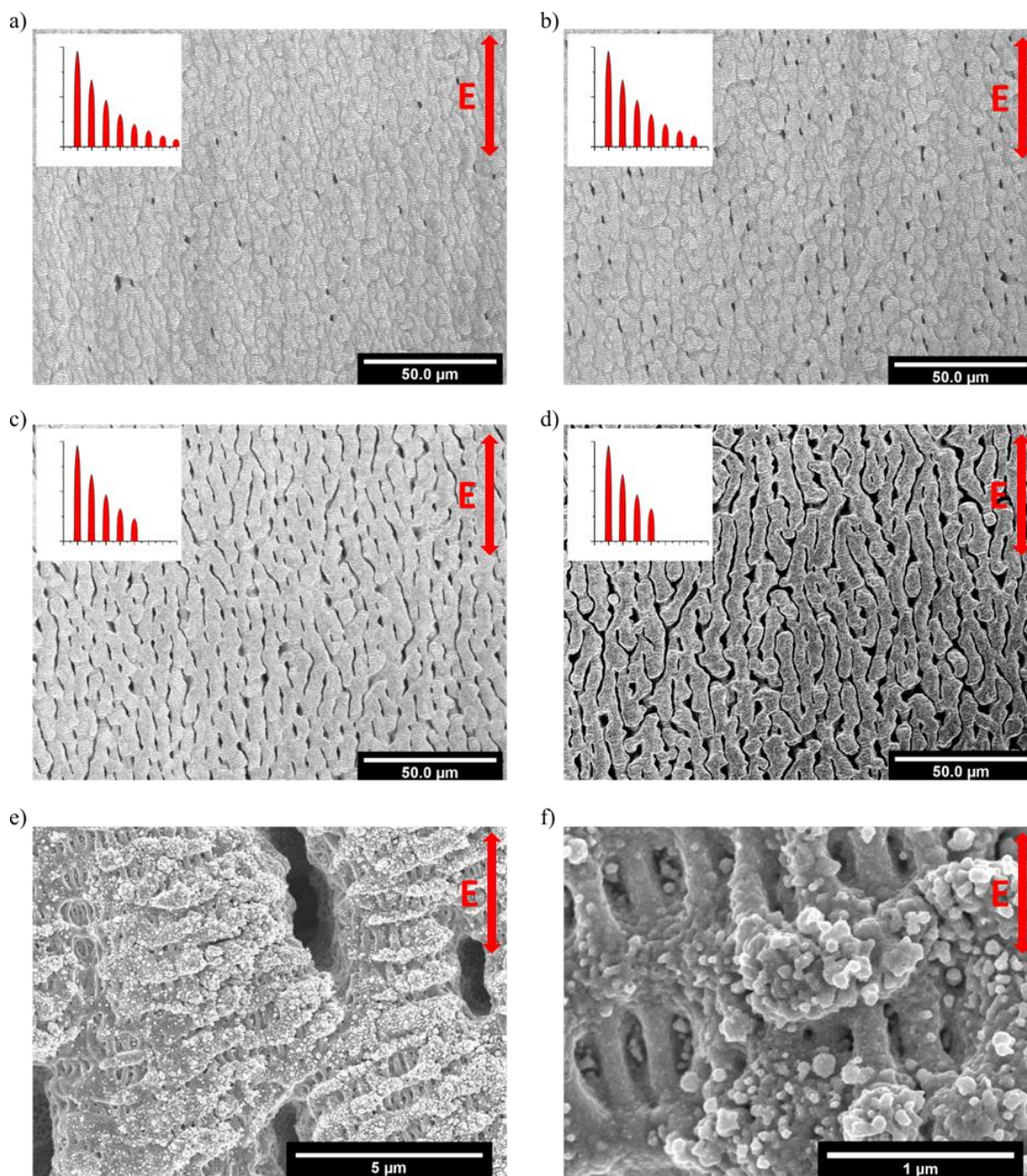


Figure S4 | SEM images of coloured surfaces produced following (a) 8, (b) 7, (c) 5 and (d) 4 pulse burst exposures with a writing speed of 100 mm/s , a laser fluence of 12.12 J/cm^2 and a line spacing of 5 μm . Random melted structures are observed to form on the surface and coalesce into large LIPSS with a periodicity roughly

7× the wavelength and oriented parallel to the laser polarization (represented by the red arrow). (e,f) High-magnification SEM images of surfaces coloured using 5 pulse bursts at a writing speed of 100 mm/s, a laser fluence of 12.12 J/cm² and a line spacing of 5 µm.

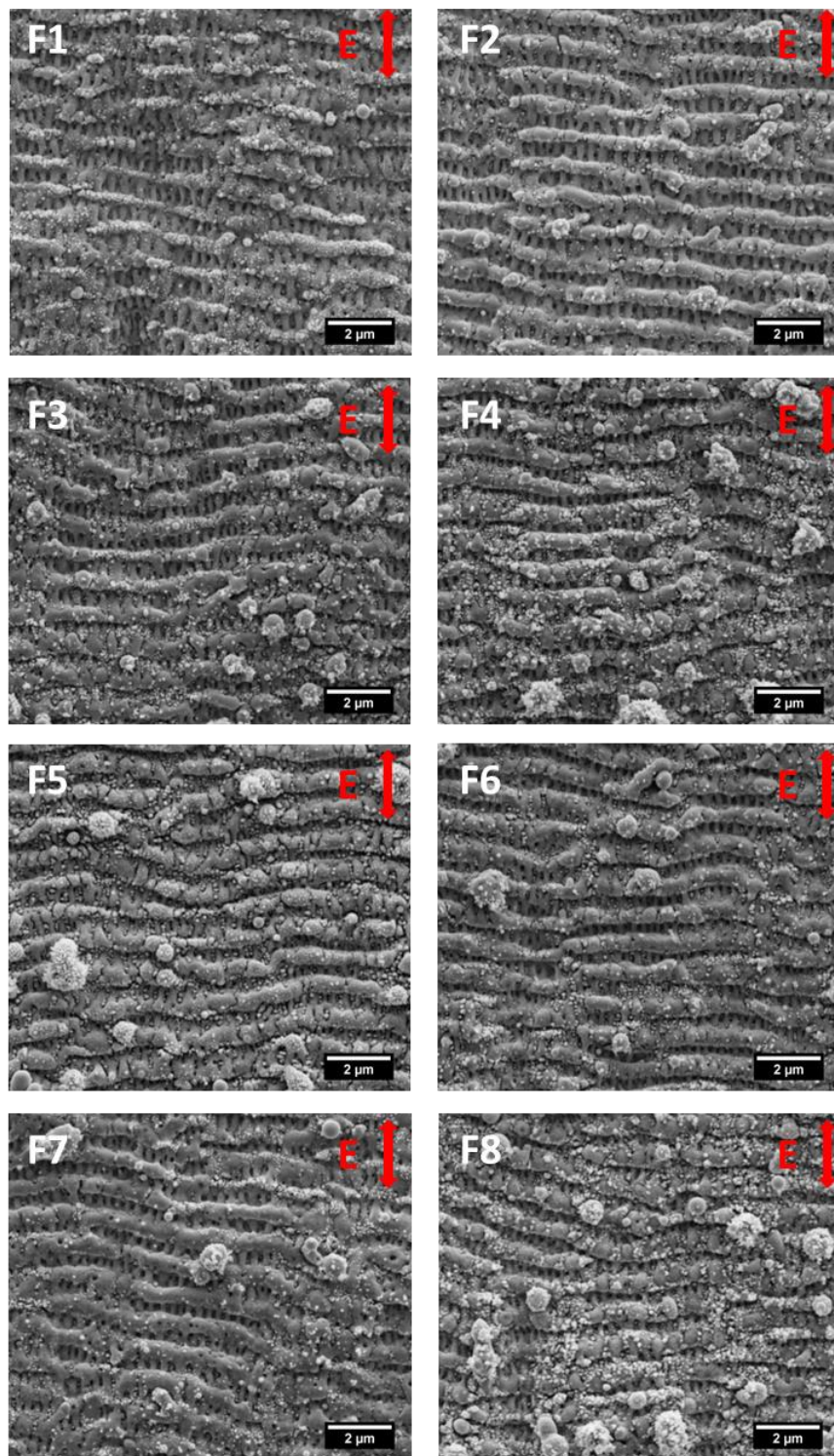


Figure S5| SEM images of coloured surfaces produced using the burst arrangements of Fig. 4(a) for the line spacing of 3 μm and the same total laser energy. Each surface was machined using a laser fluence of 12.12 J/cm² with a marking speed of 150 mm/s. Slight differences in the LIPSS structures can be observed between the different burst temporal arrangements. The light polarization during the machining of the surfaces is indicated by the red arrows.

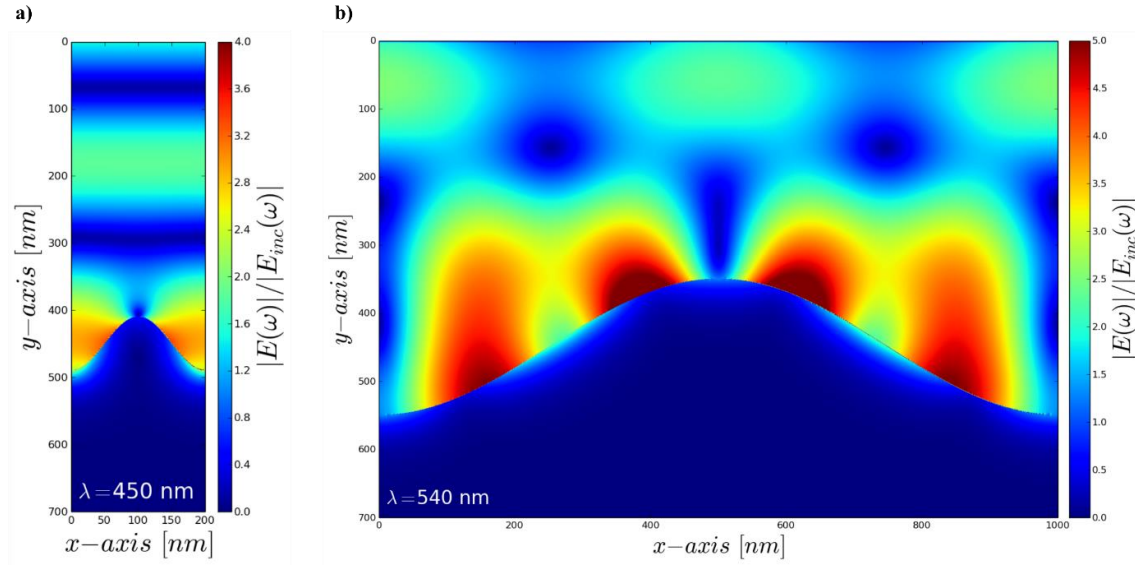


Figure S6| Field distribution for two ripple periods: (a) $L_p = 200$ nm and $A = 40$ nm at $\lambda_0 = 450$ nm, (b) $L_p = 1000$ nm and $A = 100$ nm at $\lambda_0 = 540$ nm, showing field enhancement on the surface. Periodic boundary conditions are applied along x .

Laser-written colours on silver: optical effect of alumina coating

7.1 Summary

This chapter evaluates the potential application of the coloured surfaces for radiometric and colourimetric sensing applications. Different thicknesses of alumina films were deposited on identical coloured silver samples to monitor colour evolution. The evolution of the colours was monitored both radiometrically using a spectrometer and colourimetrically using a Chroma meter. For a small alumina thickness, the colours of the burst surfaces are slightly faded. With increasing alumina thickness, the Hue of the burst coloured surfaces is observed to make a full rotation, with a return to the original colour saturation values (*i.e.* Chroma). This demonstrates that a film could be used as a fine-tuning knob to control the final colours while providing the necessary protection for real world applications. For nonburst coloured surfaces, the colours are observed to fade and are never recovered. Finite-difference time-domain simulation of the burst surfaces shows that the grating coupling, field-enhancement and the excitation of SPP waves are responsible for the recovery of the colours unique to the burst surfaces. The colourimetric

response of the coloured surfaces is observed to be colour dependent with a maximum sensitivity of 3/nm requiring less than 1 nm of material for the human eye to perceive a colour shift. The radiometric sensitivity of the colours was also observed to be colour dependent with a maximum sensitivity of 3.16 nm/nm.

7.2 Contributions

The manuscript has been accepted in the journal Nanophotonics. The successful completion of this manuscript was due to the combined effort of all of the people involved. In this publication, I initially proposed the experiment to the Carleton team to evaluate the evolution of the colours with increasing alumina thickness. I coordinated the efforts between the University of Ottawa, Carleton University and the Royal Canadian Mint. Under the direction of Dr. Arnaud Weck and Dr. Pierre Berini, I supervised the COOP student Graham Killaire at the RCM. Dr. Antonino Cala Lesina conducted the FDTD simulations under the supervision of Dr. Lora Ramunno and Dr. Pierre Berini. The theoretical conclusions were drawn by Dr. Pierre Berini, Dr. Lora Ramunno, Dr. Cala Lesina and myself. Dr. Peter Gordon applied the alumina coating to the coloured silver samples under the supervision of Dr. Sean Barry. The experimental data was collected by Graham Killaire and me. Dr. Choloong Hahn conducted the ellipsometer measurements of the alumina films. I wrote the experimental section of the manuscript and Dr. Antonino Cala Lesina wrote the theoretical section. In this manuscript, I made all the figures at the exception of the FDTD simulation figure. All authors discussed the results.

7.3 Article

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Research article

Jean-Michel Guay*, Antonino Calà Lesina*, Graham Killaire, Peter G. Gordon, Choloong Hahn, Sean T. Barry, Lora Ramunno, Pierre Berini and Arnaud Weck

Laser-written colours on silver: optical effect of alumina coating

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Abstract: In this paper we discuss the optical response of laser-written plasmonic colours on silver coated via the atomic layer deposition of alumina. These colours are due to nanoparticles distributed on a flat surface and on a surface with periodic topographical features (i.e. ripples). The colours are observed to shift with increasing alumina film thickness. The colours produced by surfaces with

ripples recover their original vibrancy and hue after the deposition of film of thickness ~60 nm, while colours arising from flat surfaces gradually fade and never recover. Analysis of the surfaces identifies periodic topographical features to be responsible for this behaviour. Finite-difference time-domain simulations unravel the role played by the alumina thickness in colour formation and confirm the rotations and recovery of colours for increasing alumina thickness. The coloured surfaces were evaluated for applications in colourimetric and radiometric sensing showing large sensitivities of up to 3.06/nm and 3.19 nm/nm, respectively. The colourimetric and radiometric sensitivities are observed to be colour dependent.

Keywords: Plasmonic colouring; Nanostructures; Thin Films; Colour sensors; Computational Nanophotonics.

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1 Introduction

Plasmonic devices based on the unique optical properties of metallic nanoparticles (NPs) have been a topic of interest in the last decade, casting a wide net of promising applications in fields such as chemical and biomedical sensing [1–5], photochemistry [6–8], colouring [9–17] and surface-enhanced spectroscopy [18, 19]. Localised surface plasmon resonances (LSPRs) are due to collective oscillations of free electrons when metal nanoparticles are exposed to optical radiation. They are sensitive to the shape and size of the nanoparticles, the proximity of any surrounding nanoparticles and the refractive index of the local surrounding medium [20–22]. The use of plasmonic nanoparticles in sensing applications exploits the latter for the detection of target analyte. Research on optimising the sensitivity of plasmonic nanoparticles by seeking the largest possible LSPR shift has been an important driver in the development of plasmonics. Researchers have explored the fabrication of nanowires [23], nanoshells [24, 25], nanodisks [26] and other distinctive shapes and arrangements [27] to achieve the best LSPR sensor. Typical fabrication methods of such structures include lithography [14, 28–31] and the

growth of nanoparticles via chemical means [32]. While nanoimprint lithography [14, 31] has promising scale-up potential, the initial step of mould fabrication is lengthy and often limited to small surface areas.

Recent advances in ultrafast laser technology and the creation of single-step plasmonic surfaces via the fast direct laser writing [9–11] of large areas [12, 17] show great promise in increasing production and cutting down of the fabrication time and cost of plasmonic devices. In addition, compared to ordered surfaces commonly fabricated using lithographic methods, surfaces coloured by ultrafast lasers are random. For colouring applications, this implies that under certain conditions such surfaces do not exhibit angle-dependent colours typical of ordered surfaces [12]. However, using different laser parameters, the exposure of metals to laser light can also result in angle-dependent colours via the creation of laser-induced periodic surface structures (LIPSS) [9] that originate from the interference of the incoming light with a scattered surface wave [33, 34]. Recently, Guay et al. [35] demonstrated that these LIPSS, combined with nanoparticles, enhance plasmon resonances, and that they could be tuned via

different laser burst arrangements. Colour arising from light interacting with LSPRs on noble metals is sensitive to the local environment, so colour changes can be monitored in colourimetric sensor applications [32].

Plasmonic colours created via laser pulses on Ag require a coating layer to passivate the surface [17]. Here, we investigate the optical response of plasmonic colours coated by alumina layers of different thicknesses formed via atomic layer deposition (ALD) on laser-coloured silver surfaces. The colour palettes investigated were created via the burst and nonburst colouring methods [12, 35]. We observed, with increasing alumina thickness, a broadening of the spectrum of burst colours and witnessed an initial fading of the colours followed by the recovery of the original chroma in the case of the burst colours. Finite-difference time-domain (FDTD) simulations were conducted to understand the role of an alumina layer in colour recovery, and to identify that the difference in behaviour between burst and nonburst coloured surfaces originates from the LIPSS that are formed using burst. We also consider our laser-coloured Ag surfaces as colourimetric and radiometric sensors, based on their responses to different alumina thicknesses.

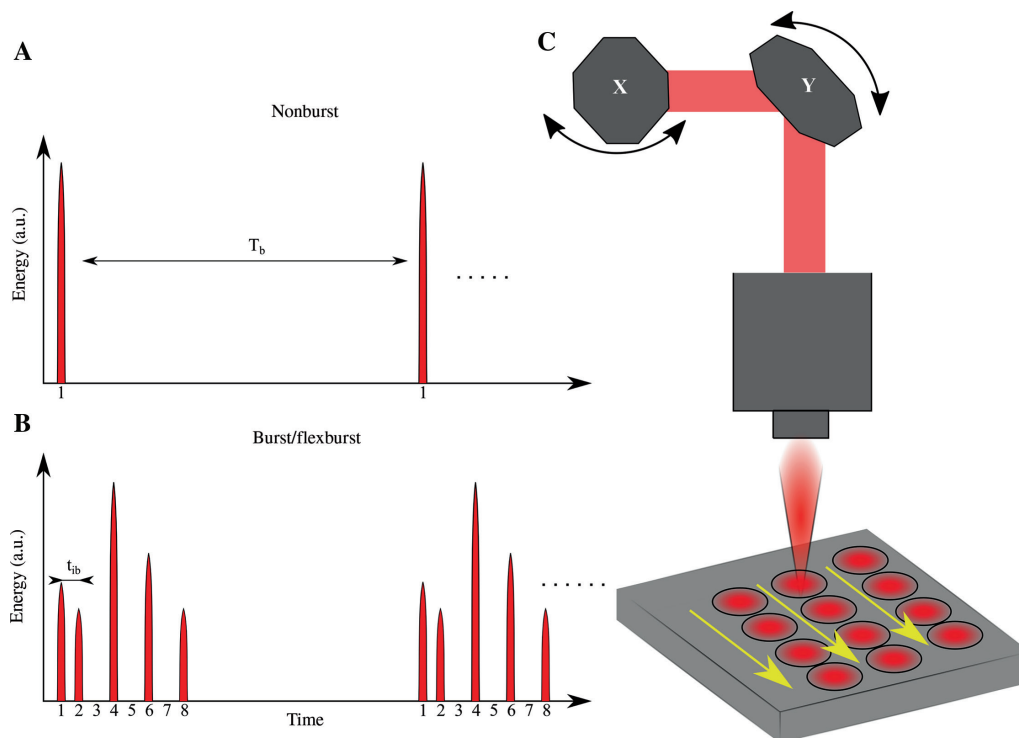


Figure 1: Experimental setup.

Schematic representation of the pulse energy distribution used for the (A) nonburst and (B) burst colours. The nonburst colours were written using a burst of 1 pulse (i.e. nonburst) with a laser repetition rate, $f=1/T_b$, of 50 kHz, while the burst colours were written using a burst pulse energy distribution shown in (B) with each pulse separated by 12.8 ns. The number of pulses within each burst can be set from 1 to 8. To increase the time separation between shots within the burst, the energy of pulses within the burst can be set to zero. (C) Schematic demonstrating the machining of samples using a top to bottom, unidirectional, raster scanning pattern.

2 Experimental methods

Silver surfaces were coloured by exposing large areas of the samples to laser irradiation by raster scanning the surfaces in a unidirectional top to bottom fashion (Figure 1). The machining of the surfaces was carried out using a wavelength of 1064 nm emitted by a Duetto mode-locked laser (Nd:YVO₄, Time Bandwidth® Products, Zurich, Switzerland) outputting 10 ps pulses. Two laser colour marking schemes are investigated: the ‘burst mode’ composed of a train of closely time-spaced pulses and the standard ‘nonburst mode’. The colouring of silver using these two marking techniques is described in previous work [12, 17]. The time separation between each of the pulses within the burst train is governed by the oscillator and is set to $t_{ib} = 12.8$ ns. One to eight pulses within a laser burst can be selected and the energy distribution among the pulses can be adjusted using Flexburst™. The burst pattern (i.e. energy distribution) used to create the colours is shown in Figure 1B. The repetition rate, $f = 1/T_p$, of the laser was set to 25 kHz using a pulse picker of 2 kHz for the burst colours and 50 kHz for the non-burst colours. After going through the XY galvanometric mirrors (TurboScan 10, Raylase, Webling, Germany), the light was focused onto the silver surface using an F-theta lens ($f = 254$ mm, Qioptic, Goettigen, Germany). For accurate focusing, the surface of a sample was located using a touch probe arrangement. The silver samples were of 99.99% purity with a diameter of 38 mm and a thickness of 3 mm. For machining, the silver samples were placed on a three-axis stage (HF-MP23, Mitsubishi Electric, Tokyo, Japan) with a translation resolution of 1 μ m in the lateral and axial directions. The laser power was controlled by a user interface and monitored using a power meter (3A-P-QUAD, Ophir, Jerusalem, Israel). The spot size was measured to be ~ 28 μ m following the semi-logarithmic plot approach of the modified region following previous work [36].

The colours were quantified using a Konica Minolta CR-241 Chroma meter (Tokyo, Japan) in the CIELCH colour space, 2-observer and illuminant C (North Sky Daylight). The instrument outputs LCH values of the measured colours, where L is lightness, C is chroma (i.e. colour saturation) and H is hue (colour value associated with a 360° polar scale). The LCH values were converted to the XYZ tristimulus colour space using Matlab (Natick, MA, USA) for the plotting of the Commission de l'éclairage (CIE) diagrams. The reflectance measurements were taken via an in-house setup comprising a spectrometer (CCS200, Thorlabs, Newton, NJ, USA) and a cold LED source (MCWHF2, Thorlabs, Newton, NJ, USA). The light was sent and collected

via a fibre-optic reflection probe bundle (RP28, Thorlabs, Newton, NJ, USA).

The ALD of alumina was performed using a Picosun R150 (Picosun Oy, Espoo, Finland) thermal deposition tool. Trimethylaluminium (TMA, >98%) and distilled water were held at 18°C in stainless steel bubblers for all of the depositions on the silver surfaces. Purges and line flows used 99.998% N₂ (150 sccm for TMA, 200 sccm for water). For all the depositions, there were six initial 1 s pulses of TMA followed by a 30 s purge. After the initial cycle, pulses and purge times for TMA and water were 1 s and 90 s, respectively. The depositions were performed with the temperature of the chamber set to 60°C. In addition, Si (100) “witness” wafers were placed in the chamber to confirm the expected growth rate of the alumina films. The silver samples were placed on a stainless-steel mesh during deposition in order to support the samples and ensure complete coverage.

The alumina films were probed by electron X-ray dispersive microscopy (EDX) (Oxford Instruments, Abingdon, UK). The alumina layer thicknesses were estimated by entering the values of the EDX probe, voltage, takeoff angle, element, element k-ratio, and estimated density in the software GMSI (Cambridge University, Cambridge, UK) [37]. The EDX alumina thickness measurements were confirmed by ellipsometry (FUV-NIR, Horiba Uvisel, Kyoto, Japan), which was also used to measure the refractive index of the alumina films at an incident angle of 70° over the spectral range of 235–2000 nm in steps of 5 nm. Grazing angle measurements were performed with an FTIR spectrometer (Nexus 870, Thermo Nicolet, Waltham, MA, USA) with the incident light hitting the surface of the sample at an angle of 80°.

3 Results and discussion

3.1 Colourimetric response to the atomic layer deposition of alumina

In a previous study, a multi-layer coating method was developed to minimise morphological and colourimetric changes on the sample surface while protecting the surface against chemical attacks in order to target a specific industrial application [17]. The mechanism of island formation and film growth on the silver surface during ALD was discussed [17]. Here, a layer of alumina is deposited over pre-existing silver colours to investigate its effect on colour changes in order to compensate or predict the final image canvas. Figure 2 is a side-by-side comparison of

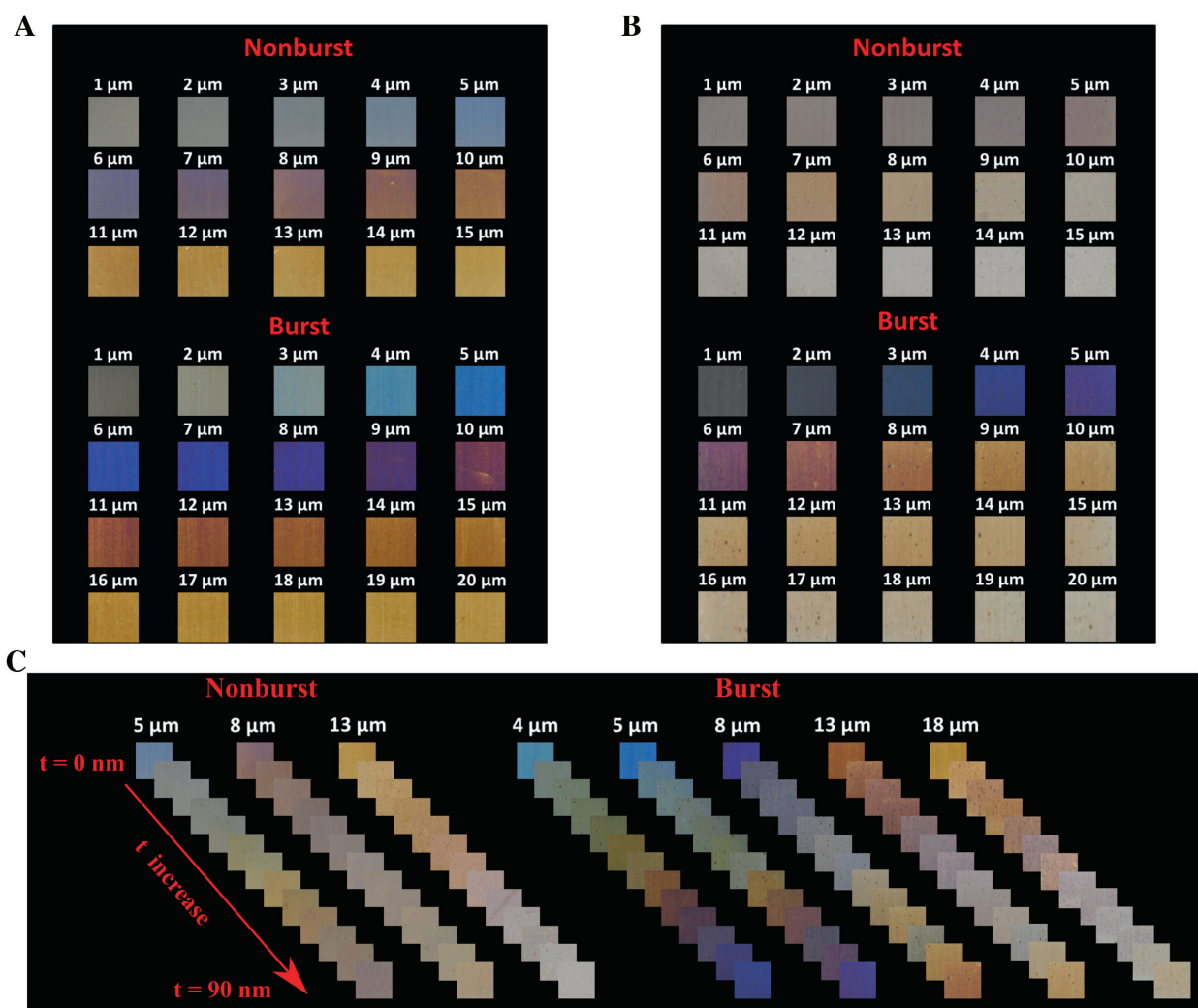


Figure 2: Colour evolution with alumina thickness.

(A, B) Colour palettes obtained using the (top) nonburst and (bottom) burst laser colouring methods (A) before and (B) after the deposition of 90 nm of alumina. The different colours were obtained by changing the line spacing, L_s , in steps of 1 μm , creating squares 4×4 mm² in area. The colours were written using a laser fluence of 5.73 J/cm² with a marking speed of 100 mm/s and a laser fluence of 12.12 J/cm² with a marking speed of 150 mm/s for the nonburst and burst colours, respectively. (C) Colour evolution with increasing alumina thickness from 0 to 90 nm in steps of ~ 7 nm.

a full colour palette (a) without and (b) with a 90-nm-thick film of alumina deposited via ALD. The colours on the surface of the silver samples were obtained using the nonburst (top in Figure 2A and B) and burst (bottom in Figure 2A and B) laser colouring methods, discussed in a previous publication [12, 35]. The nonburst and burst laser parameters used were a marking speed of 100 mm/s with a laser fluence of 5.73 J/cm² and a marking speed of 150 mm/s with a fluence of 12.12 J/cm², respectively. The different colours were obtained by changing the line spacing, L_s , between successive lines, controlling the density of nanoparticles re-deposited onto the metal's surface [12].

As shown in Figure 2A and B, the colours are observed to change significantly for both nonburst and burst colours

following the application of the 90 nm layer of alumina. For the burst case, intense colours are still observed after deposition of the 90 nm alumina film. Conversely, for nonburst, the colours are observed to be greyish and lighter. In industrial applications where visual colours are required, a smaller change in colour (i.e. ΔE) is preferred [38], thereby conserving the vivid colour palette. Figure 2B suggests that burst coloured surfaces are the preferred choice in applications where protective coatings or tagging agents are to be placed on the coloured surface. Conversely, in colourimetric sensing applications, large changes in colour are desired. Figure 2C shows the evolution of colour with increasing alumina thickness in steps of ~ 7 nm for a few selected line spacings. Twelve identical

colour palettes on 12 silver samples were placed in the ALD chamber and one sample was removed after each deposition of ~ 7 nm. The nonburst colours are observed to gradually lose their chroma with increasing alumina thickness. This decrease in the visual quality of the colours is largely consistent with groups who created colours by lithographic fabrication techniques and covered their surfaces with a passivation layer [13, 29]. Alternatively, for the burst case, the chroma of the colours is mostly recovered at larger film thicknesses. Indeed, the burst colours are observed to rotate in hue by almost 360° going from blue ($H=249.2$) to purple ($H=291.4$) with increasing alumina thickness (as discussed further below). Green colours can be distinctively observed during the colour transition with increasing ALD thickness, e.g. burst colours in Figure 2C for the case $L_s=4\ \mu\text{m}$. For nonburst, only blue is observed to rotate in colour; however, the chroma of the colours is significantly reduced and does not recover with increasing alumina thickness. Green colours with

this direct laser colouring method have, in the past, been difficult to obtain [12]. Thus, the alumina layer can serve as a tuning element to obtain colours over a wider range of hue values. Furthermore, techniques for controlling the thickness of ALD in selective areas were previously demonstrated via the use of self-assembled monolayer (SAM) films. The selective deposition of the ALD layer was controlled by etching the SAM layers at the metal surface [39, 40]. In a previous publication, we demonstrated that our surfaces could be used to cleave SAM molecules by a plasmon-assisted mechanism, making the deposition of selective thicknesses of alumina a real possibility [6].

Figure 3 shows CIE xy chromaticity diagrams for nonburst and burst colours as the alumina film thickness increases. The data points in the CIE diagram were obtained from the LCH measurement of each colour using the unpolarised light of the chromameter. Initially, the area covered by the colours on the CIE diagrams for each of the colouring methods is observed to decrease

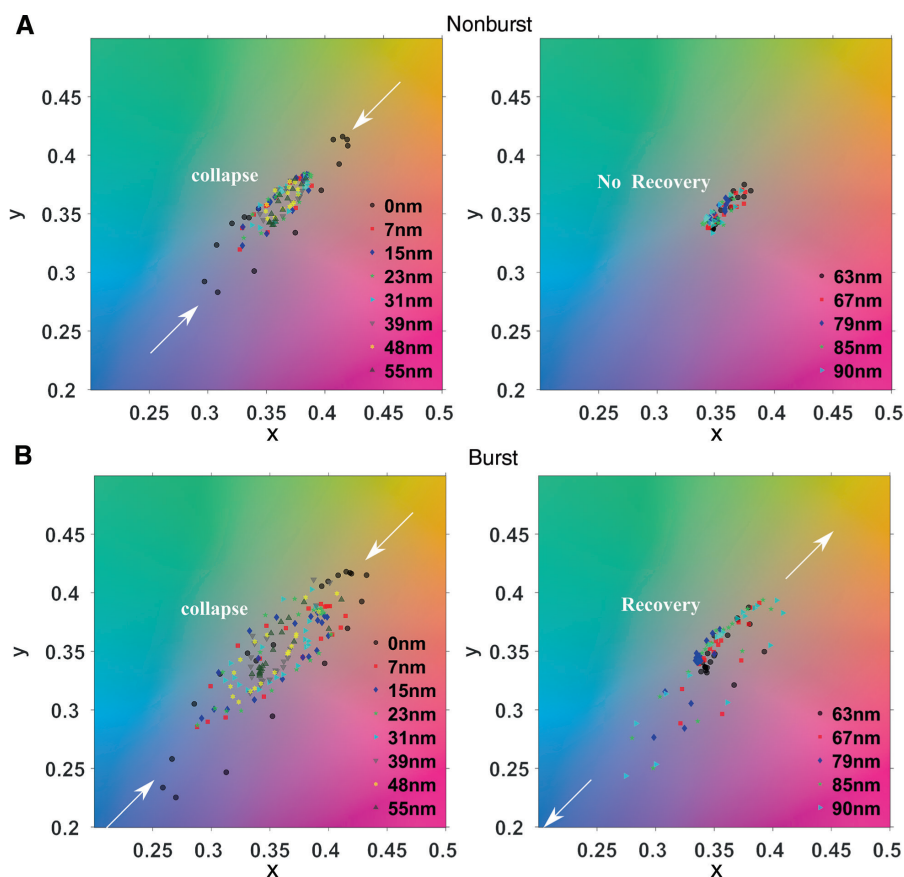


Figure 3: CIE of colours with increasing ALD thickness.

CIE xy chromaticity diagrams showing the evolution of the (A) nonburst and (B) burst colours with increasing ALD thickness. The area on the CIE diagram spanned by the nonburst colours is observed to collapse with increasing alumina thickness. For the burst colours, the area spanned is observed to recover after 55 nm of alumina. The LCH values used in the CIE diagram were obtained by the unpolarised light source of the chromameter.

with increasing alumina thickness. This observation is consistent with other studies where a passivation layer was deposited on nanostructures responsible for colours [13]. In a CIE xy chromaticity diagram, the chroma (i.e. saturation) increases from the centre outwards. For burst, the area covered by the colours extends over more of the green region after the initial deposition of alumina. In addition, the decrease in covered area was observed up to a thickness of 55 nm before gradually recovering up to the maximum applied thickness of 90 nm. The reduction in the area is caused by a reduction in the chroma. The point of recovery for the burst colours appears to occur around ~55 nm of alumina. At 90 nm, the chroma is largely

recovered. In the nonburst case, the chroma decreased and never recovered, yielding colours that are mostly grey. In addition, the area spanned by the colours continuously decreased with increasing thickness, collapsing into a small region of the CIE diagram.

Figure 4 shows polar plots of hue (θ) versus total accumulated fluence (r) for the nonburst and burst colours with increasing alumina thickness. For the nonburst colours, the evolution of the hue values is observed to follow a brushing/sweeping motion (red arrow) with increasing alumina thickness. The brushing/sweeping motion initially moves to the right, until the thickness of 55 nm, before reversing direction to sweep left. At the thickness

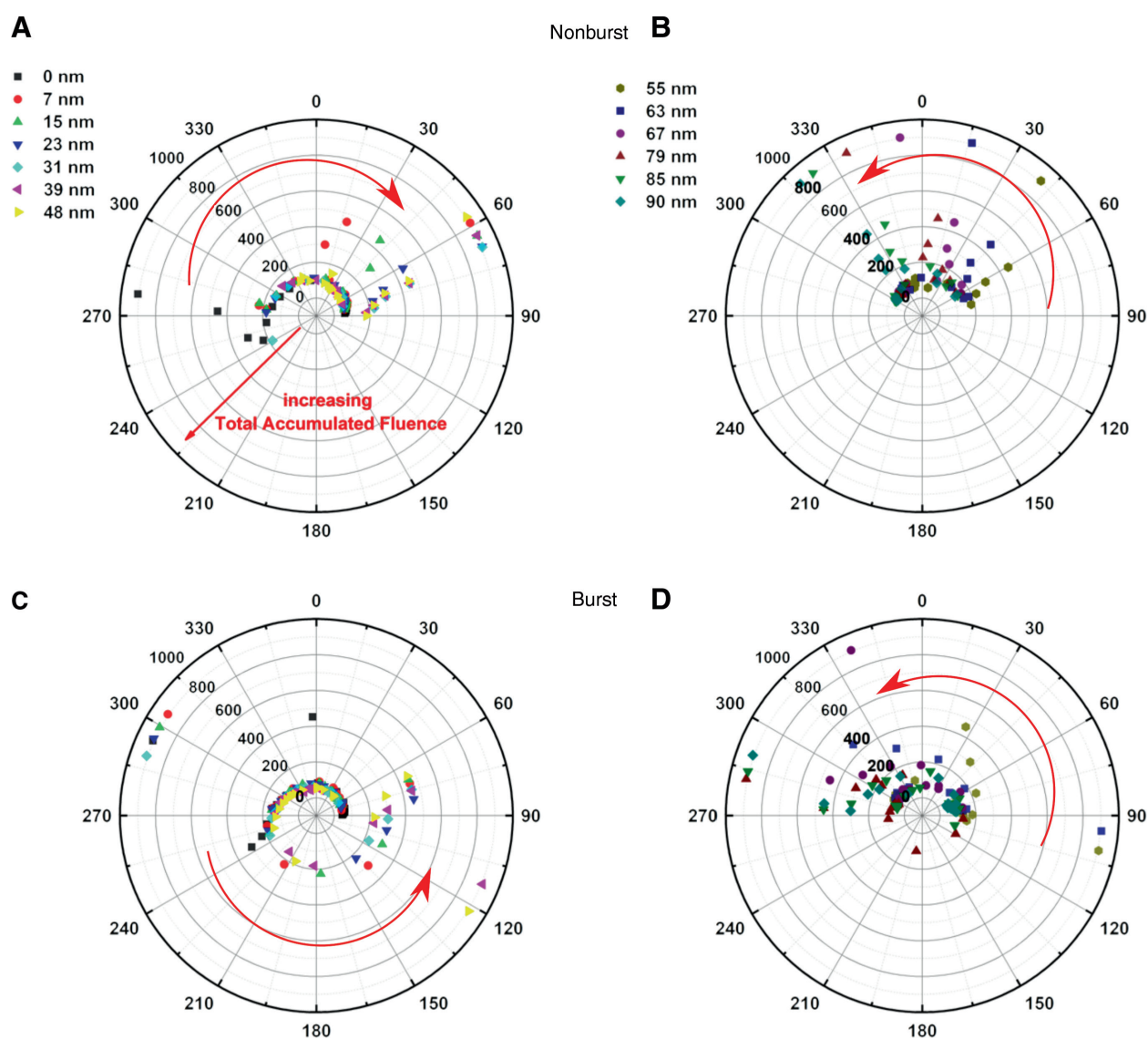


Figure 4: Hue values of colours with increasing ALD thickness.

Polar plots of hue (θ) versus total accumulated fluence (r) for the (A, B) nonburst and (C, D) burst colours with increasing alumina thickness. The different points in the plots represent the hue range of the colour palette for a certain alumina thickness. The evolution and displacement of the hue values with increasing alumina thickness is displayed by the red arrow.

of 90 nm, the hue values have almost recovered their original values. It should be pointed out that throughout the motion in the nonburst case, new hue values are never added. For burst colours, however, the evolution of the hue values is different, exhibiting a counter-clockwise rotation with increasing alumina thickness. This counter-clockwise motion allows access to the green hue range ($90\text{--}150^\circ$) that is usually very difficult to achieve with direct laser machining alone. A chroma gain of up to 61% can be observed in the green colour region ($H=90$ to 150) compared to the best green colours obtained to date [12]. Hence, the burst colours are tunable to cover hue values outside the normal range depending on the thickness of the alumina layer. Similarly, to the nonburst colours, the original hue range is mostly recovered after deposition of 90 nm of alumina, with a distinctive crossing point at 55 nm.

It is widely known that changes in the local permittivity can be used to tune the plasmonic response of nano-textured surfaces [22]. While both colouring methods recovered their original hue values (Figure 4), recovery of the chroma values was observed solely in the burst case (Figure 3). The results were observed to be reproducible in multiple trials demonstrating the deterministic process of the colour recovery of the burst surfaces. However, since the burst and the nonburst surfaces have similar nanoparticle statistics [17] and alumina film thicknesses, it would be expected that both should present a similar behaviour. The only difference between the two lies with the underlying topography of the burst surfaces [17]. The LSFL and HSFL structures found on the burst coloured surface is the key to understanding the different behaviours with increasing alumina thickness. The structures would serve to increase the area covered by the nanoparticles and cause field enhancement in the crevices, both increasing absorption [17]. The colours produced by the burst method are largely angle independent; however, if the colours are observed under intense white light, it is possible to see faint diffraction. The suppression of diffraction by the underlying periodic structure was previously explained as selective absorption dominating over diffraction [35]. We observed experimentally, for burst arrangements that produced the best-defined LSFL and HSFL structures, a dichroism in the perceived colours (e.g. blue-purple; purple-red; red-yellow) by simply rotating the coloured samples by 90° . The effect of diffraction is ruled out due to the absence of the majority of the colour spectrum while rotating the sample. The dichroism of the surface could originate from selective absorption by the defined LSFL and HSFL periodic structures. It is important to note that the burst colours used in this paper did not exhibit any dichroism.

In a colouring application, the passivation of the nonburst coloured surfaces would necessitate the deposition of a thickness lower than 7 nm in order to minimise the change in the colours and retain the original visual appeal of the colours (see Figure 3). For burst, the alumina layer could either be below 7 nm or around 90 nm (see Figure 3B), the latter providing better passivation. Furthermore, while the coloured surfaces have been previously shown to be sensitive to heat and to irreversibly degrade with prolonged exposure [17], the recovery of the colours with increasing film thickness rules out heat as being responsible for the colour change. In a previous publication, it was demonstrated that alumina films deposited at 60°C required a minimum layer thickness of ~ 60 nm in order to protect coloured surfaces against chemical attack [17]. In an application, it is important that the protective layer has a minimal effect on the colours. For example, a colour design featuring a blue sky should still be blue following the deposition of the protective layer. The introduction of a protective layer usually shifts and shrinks the colour gamut rendering some colours inaccessible [13]. This has been a significant problem for plasmonics in decorative applications. A strategy to counter these issues has been to pre-compensate for the protective layer by modifying the nanostructure responsible for the colours [29]. This approach is certainly good in practice; however, coating techniques often demonstrate certain variability between runs which can counteract and negate the effect of the pre-compensated nanostructure. For instance, in our trials, we observed a significant change in colour for just a few nm of alumina. Alternatively, metal-insulator-metal (MIM) structures supporting gap plasmons and used to render colour are largely insensitive to changes in the local permittivity above the metal layer [41]. However, like most approaches based on nanolithography, the fabrication of MIM structures can be lengthy, complex and is limited to small planar areas. Therefore, recovery of the original colours of the burst surfaces reduces the difficulty of conserving the original colour design and provides an elegant solution to the problem. It does not require any pre-compensation of the nanostructure for the application of the protective layer while providing the necessary protection against the environment, but tight tolerances are required in the formation of the layer.

Figure 5 shows reflectance measurements of selected coloured squares with different alumina thicknesses. The reflectance measurements using unpolarised light in Figure 5 are for blue ($L_s = 5\text{ }\mu\text{m}$) and purple ($L_s = 8\text{ }\mu\text{m}$) colours prior to the deposition of the alumina film, produced using the nonburst and burst colouring methods [12]. The features in the reflectance curves appear to

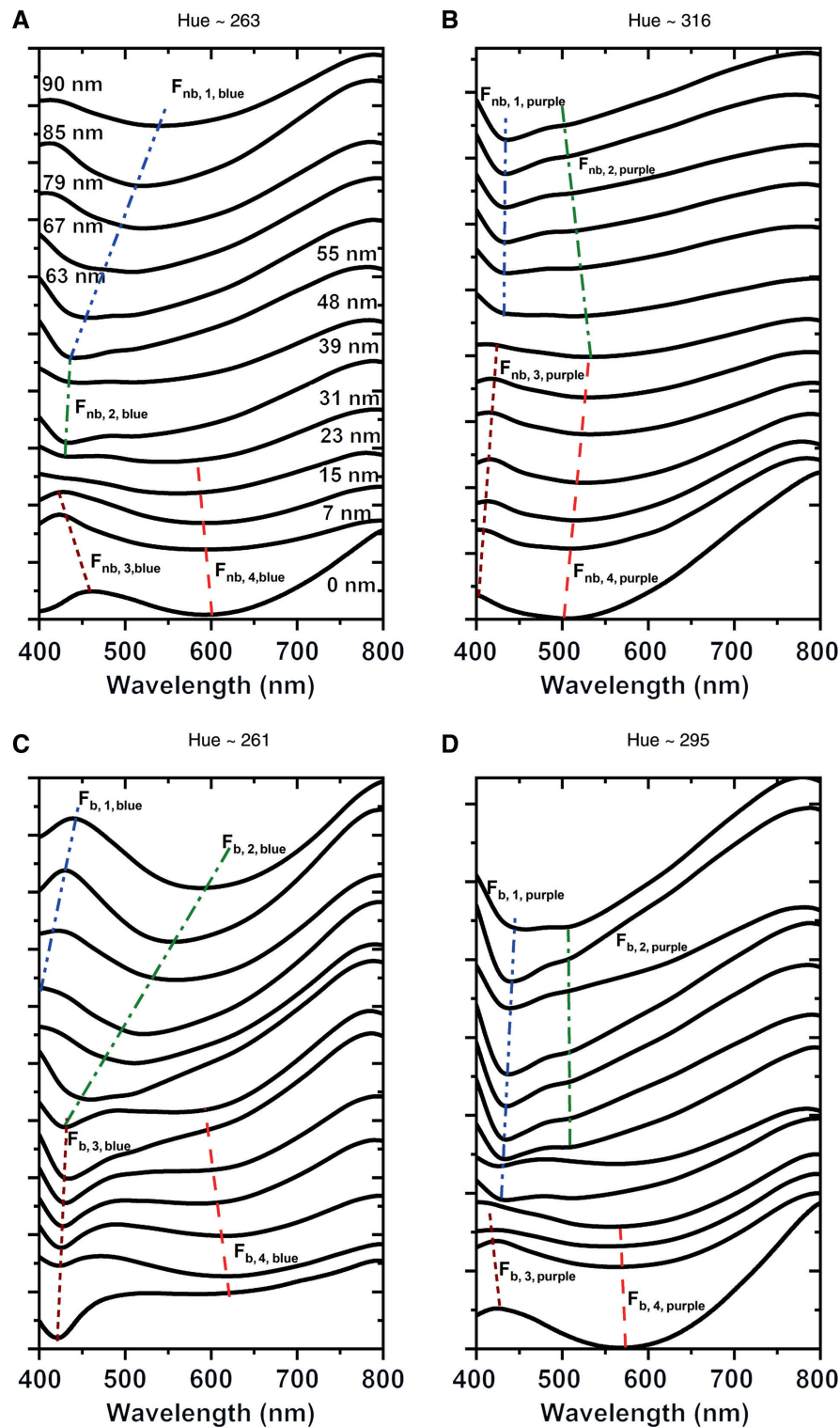


Figure 5: Experimental reflectance spectra.

Measured reflectance spectra using unpolarised light with increasing alumina thickness for blue (left) and purple (right) colours written using (A, B) the nonburst method (laser fluence of 5.73 J/cm², marking speed of 100 mm/s), and (C, D) the burst method (laser fluence of 12.12 J/cm², marking speed of 150 mm/s). The blue colours were written using a line spacing of 5 μ m and the purple colours were written using a line spacing of 8 μ m. The shifting of spectral features with increasing alumina thickness is tracked with straight lines of different line styles (as a guide to the eye). The original hue values are identified at the top of each panel.

follow similar trends for the different colours. The burst colours showed more defined features and larger variations between the peaks and valleys, explaining the higher chroma. With increasing film thickness, various features in the reflectance spectra emerge or shift (dotted lines); some of these features are more active than others. The shifts in the peaks/troughs are observed to be colour dependent with the blue colours being the most active.

3.2 Surface chemical analysis

FTIR measurements of coated surfaces, plotted in Figure 6A, clearly show the presence of Al_2O_3 on the surface of coloured silver. A peak at 952 cm^{-1} representative of Al–O vibration can be distinguished [42, 43]. The alumina film was deposited at the low temperature of 60°C in order to limit any colour change caused by thermal damage to the nanostructure during deposition (the melting temperature of small silver nanoparticles is lower than the bulk [44, 45]). Silicon witness wafers were placed in the deposition chamber and one was removed systematically at the same time as a silver sample. The thickness of each film was measured using a multi-point measurement approach and determined using GMRFilm software using K-ratios from electron dispersive X-ray spectroscopy [37]. The thickness of each film was also determined by ellipsometry measurements, along with their refractive index dispersion. Figure 6B compares the refractive index of thin films of Al_2O_3 deposited via pulsed laser deposition [46], to the refractive index of our Al_2O_3 layers deposited

by ALD on our witness wafers. The thicknesses obtained by ellipsometry on the silicon witnesses are in agreement with the EDX measurements obtained on the silver samples. In every case, the measured refractive index of the deposited films is lower than the films measured by Boidin et al. [46]. The low refractive index of our alumina is explained by the low deposition temperature used [47]. The refractive index of the deposited alumina layer can be modified by changing the deposition temperature; e.g. see the case for 250 cycles deposited at 100°C in Figure 6B.

3.3 Numerical simulations

Numerical simulations using the FDTD method were conducted to give insight into the experimental observations. We use a 3D model with a silver surface in the xz plane, which can be a flat surface or a surface with a ripple structure, representing nonburst and burst morphologies, respectively. In Figure 7, we show the setup for a burst simulation and highlight the geometric parameters. We model burst by a sine-modulated surface $f(x, z) = A \cdot \sin(2\pi x/L_p)$, where L_p is the spatial period of the sinusoid and A its amplitude. The nonburst simulation is obtained for $A = 0$. Silver nanoparticles of radius R are distributed on the burst silver surfaces following a square lattice with centre-to-centre distance D_m and an embedding length into the surface R_{emb} expressed as a fraction of the nanoparticle radius. We consider a y -propagating plane wave excitation (normal incidence) and periodic boundary conditions are applied in the x - and z -direction. We excite the system with

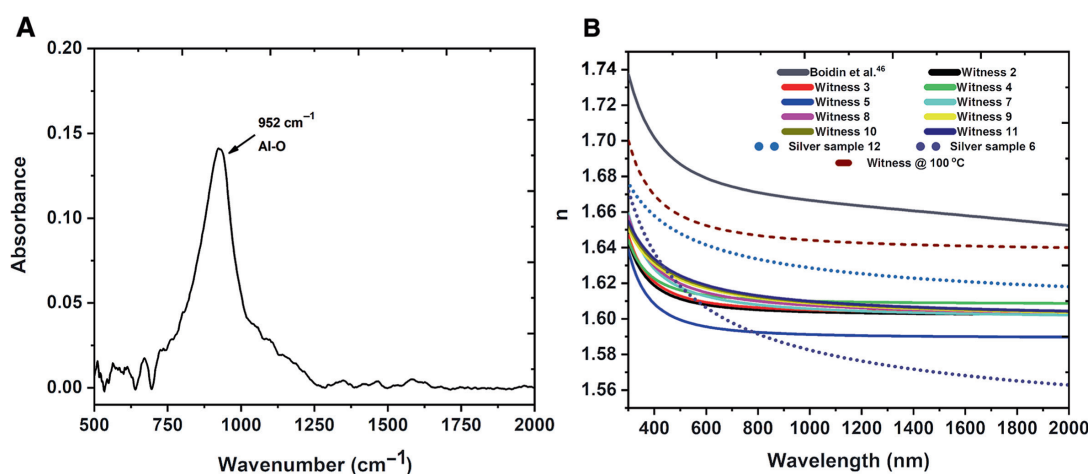


Figure 6: Alumina film measurements.

(A) FTIR measurement of a coloured silver sample covered with an alumina film deposited by ALD. The peak at 952 cm^{-1} can be attributed to Al–O vibrations. (B) Plot comparing the refractive index of amorphous Al_2O_3 as measured by Boidin et al. [46] and the refractive index of the deposited films measured by ellipsometry on the witness silicon wafers and the two silver samples. The difference in the refractive index is attributed to the low-temperature deposition of the alumina film producing lower density and porous films.

a broadband pulse to get results in the optical spectrum in a single run of the code. For the simulations, we used in-house parallel FDTD software [48]. An alumina layer of thickness t_{ALD} is applied conformally to cover the surface of the silver samples [49]. The optical parameters of alumina are modelled in FDTD by fitting the data in Figure 6B (case of 250 cycles at 100°C) to a Lorentz model with relative permittivity $\epsilon_r(\omega) = \epsilon_\infty + (\epsilon_s - \epsilon_\infty) \frac{\omega_0^2}{\omega_0^2 - 2i\delta_0\omega - \omega^2}$, where $\epsilon_s = 2.6872$, $\epsilon_\infty = 1$, $\omega_0 = 1.9833 \times 10^{16}$ rad/s, and $\delta_0 = 1.325 \times 10^6$ rad/s. The Ag is modelled using the Drude model with two critical points (Drude+2CP) [48]. A space step of 0.5 nm was used to discretise the simulation domain.

In particular, Figure 7 shows the electric field magnitude for the x -polarised excitation at $\lambda_0 = 500$ nm for $L_p = 1000$ nm, $R = 35$ nm, $R_{\text{emb}} = 0.3R$, $D_m = 100$ nm, $A = 100$ nm and $t_{\text{ALD}} = 50$ nm. In the figure we see a surface wave propagating in the x -direction directly above the alumina layer due to grating coupling. This figure is also extracted from Media 1, which shows the field distribution as a function of λ_0 for x -polarization, while Media 2 shows the field distribution as a function of λ_0 for z -polarization. In Media 1 and Media 2 we observe that for shorter wavelengths the field is more diffused in the alumina layer, while for longer wavelengths the field is confined in the vicinity of the nanoparticles. In Media 1 we also see the complexity of the resonant modes for nanoparticles arranged on a sinusoidal surface. In Media 3 we show the time domain evolution of the electric field in the case

of an x -polarised plane wave pulse interacting with the surface for $L_p = 1000$ nm, $D_m = 100$ nm, $A = 100$ nm and $t_{\text{ALD}} = 100$ nm. This movie helps in understanding the simulation setup and the physics involved. We consider here only LSFL ($L_p = 1000$ nm), but simulations for HSFL ($L_p = 200$ nm) were also conducted and they show similar trends (see Figure S3 and Media S1).

As shown in Figure 2, the colours obtained with the burst technique are more saturated than the colours obtained with nonburst [35], and this is valid also when an alumina layer is applied. In Figure 8A and B, we show the simulation results for nonburst and burst ($L_p = 1000$ nm, $A = 150$ nm), respectively. The simulations were performed for $R = 35$ nm, $R_{\text{emb}} = 0.3R$ and $D_m = 75$ nm for increasing t_{ALD} . In our simulations, we find that the colours in the burst case (when the burst surface is excited through a plane wave linearly polarised in the z -direction) are more saturated than in the nonburst case for most alumina thicknesses. This is due to the underlying ripples which produce field enhancement in the crevices [35] and to the alumina layer which further confines the field close to the nanoparticles.

The local minima in the reflectance curves are due to the fact that the random surface is approximated by a perfectly ordered array of nanoparticles. The reflectance becomes smoother by averaging the curves associated with the variation of a geometric parameter, e.g. L_p , but the overall trend of the reflectance is not altered. Thus, the result of a single simulation (without performing averages) is enough to describe the behaviour of the surface.

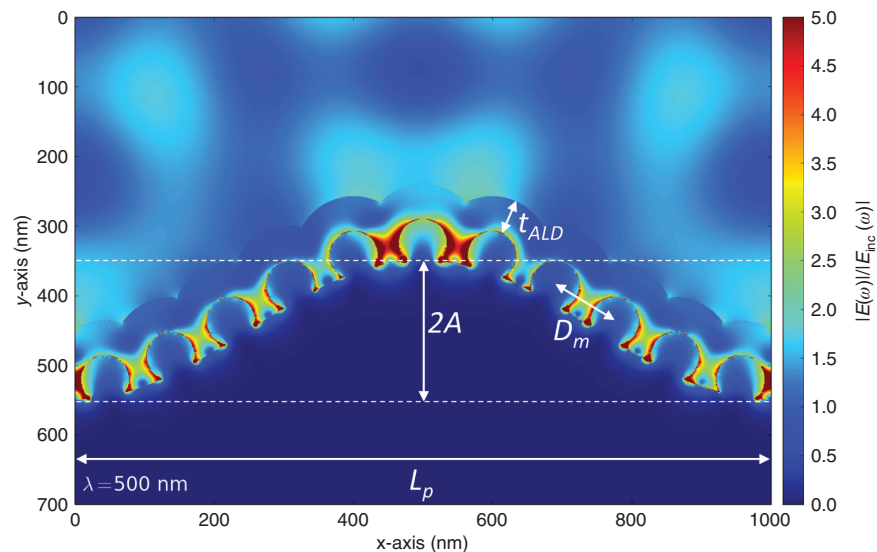


Figure 7: Simulation setup and computed near-field for NPs on a sine-modulated surface covered with a film of alumina. Electric field (magnitude) distribution at $\lambda_0 = 500$ nm under x -polarised excitation for $L_p = 1000$ nm, $R = 35$ nm, $R_{\text{emb}} = 0.3R$, $D_m = 100$ nm, $A = 100$ nm, $t_{\text{ALD}} = 50$ nm. The xy plots are taken through the centre of the spheres. This figure is extracted from Media 1, which shows the field distribution as a function of the wavelength.

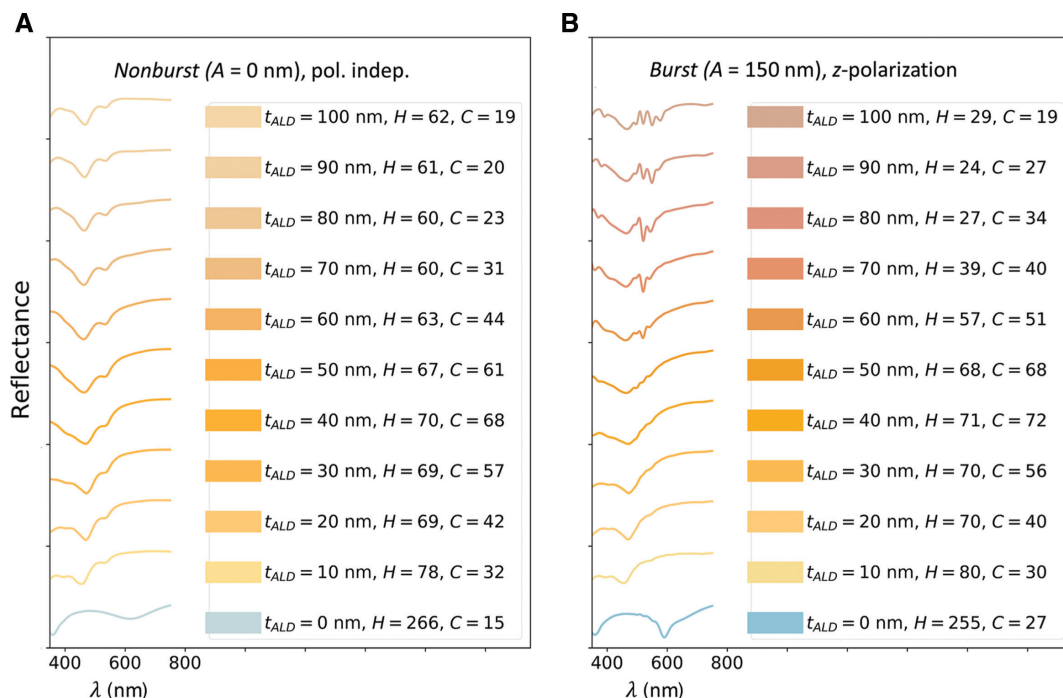


Figure 8: Reflectance spectra and colour evolution for increasing t_{ALD} (nonburst vs. burst). The simulation setup is $R = 35$ nm, $R_{\text{emb}} = 0.3R$ and $D_m = 75$ nm for (A) nonburst (flat surface) and (B) burst ($L_p = 1000$ nm, $A = 150$ nm, and z-polarization).

In simulations, the colour is strongly dominated by shifts in plasmonic resonances up to a certain alumina thickness $t_{\text{ALD}} \sim 0.5D_{ee}$ (D_{ee} is the edge-to-edge distance, defined as $D_m - 2R$). In fact, a small increment of t_{ALD} between 0 and $\sim 0.5D_{ee}$ produces a quick filling of the gaps in between the nanoparticles and a rapid change in colour. For example, in the case of silver nanoparticles in Figure 8 ($R = 35$ nm, $R_{\text{emb}} = 0.3R$ and $D_{ee} = 5$ nm), the conformal growth of the alumina layer increases the optical thickness between nanoparticles and a transition from blue to yellow is observed (see Figure 8), which mimics the trend previously reported [12], where we found that increasing interparticle distance of surfaces without alumina changes the colour from blue to yellow. For $D_m = 90$ nm ($D_{ee} = 20$ nm, see Figure 9), we see a transition from yellow to blue due to an increase of the effective nanoparticle size. In simulations, when we increase the alumina layer thickness from $t_{\text{ALD}} = 0$ nm to $t_{\text{ALD}} \sim 0.5D_{ee}$, we do not consider any modification of the geometry and distribution of the nanoparticles and we observe a sharp colour transition. In experiments, the surface could be modified when the alumina deposition process starts due to a temperature increase [17]. This may modify the geometry and distribution of nanoparticles, for example, the nanoparticles could embed further into the surface, which may cause a drastic colour change. Recently, it was observed that the

nanoparticles may consist of a core/shell ($\text{Ag}/\text{Ag}_2\text{O}$ or $\text{Ag}/\text{AgOHAg}_2\text{CO}_3$) structure which could significantly alter its dielectric environment [50]. The presence of the oxide and hydroxyls would help the initial growth of the alumina but at the same time chemical changes may be incurred at the surface [17]. On the basis of these considerations, we will not try to compare our simulations to the experimental results for an alumina thickness less than $\sim 0.5D_{ee}$, and we will rather focus on the colour evolution for $t_{\text{ALD}} \geq 0.5D_{ee}$ (~ 10 nm). Under this condition the colour evolution as a function of t_{ALD} becomes more gradual.

In the case of x-polarised excitation of a burst surface, the grating-coupling (see Figure 7) may produce narrow-band dips in the reflectance spectrum at $\lambda_0 \sim 0.5L_p$ that modifies the colour with respect to z-polarised excitation [35]. Figure 9A and B show this effect in burst simulations as a function of t_{ALD} for x-polarization and z-polarization, respectively, for $L_p = 1000$ nm, $A = 150$ nm, $R = 35$ nm, $R_{\text{emb}} = 0.3R$ and $D_m = 90$ nm. The polarization dependence arising in burst simulations is observed also in experiments, though not as strongly, and only for burst arrangements with very defined and continuous ripple structures. In Figure 2C, despite the low saturation of the nonburst colours (the colours seem to bleach), we still notice similar colour trends for nonburst and burst for increasing t_{ALD} ; this was also observed in our simulations over a wide

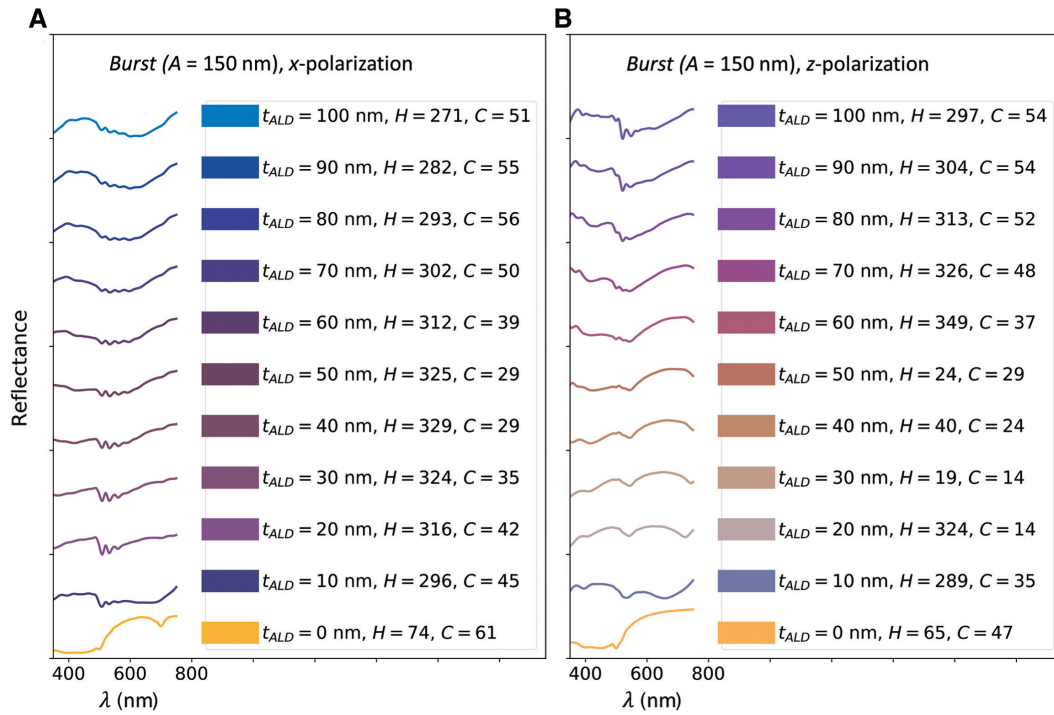


Figure 9: Reflectance spectra and colour evolution for increasing t_{ALD} (burst for two incident linear polarizations).

The simulation setup is $R = 35$ nm, $R_{emb} = 0.3R$ and $D_m = 90$ nm for (A) x-polarization and (B) z-polarization on a burst surface ($L_p = 1000$ nm, $A = 150$ nm).

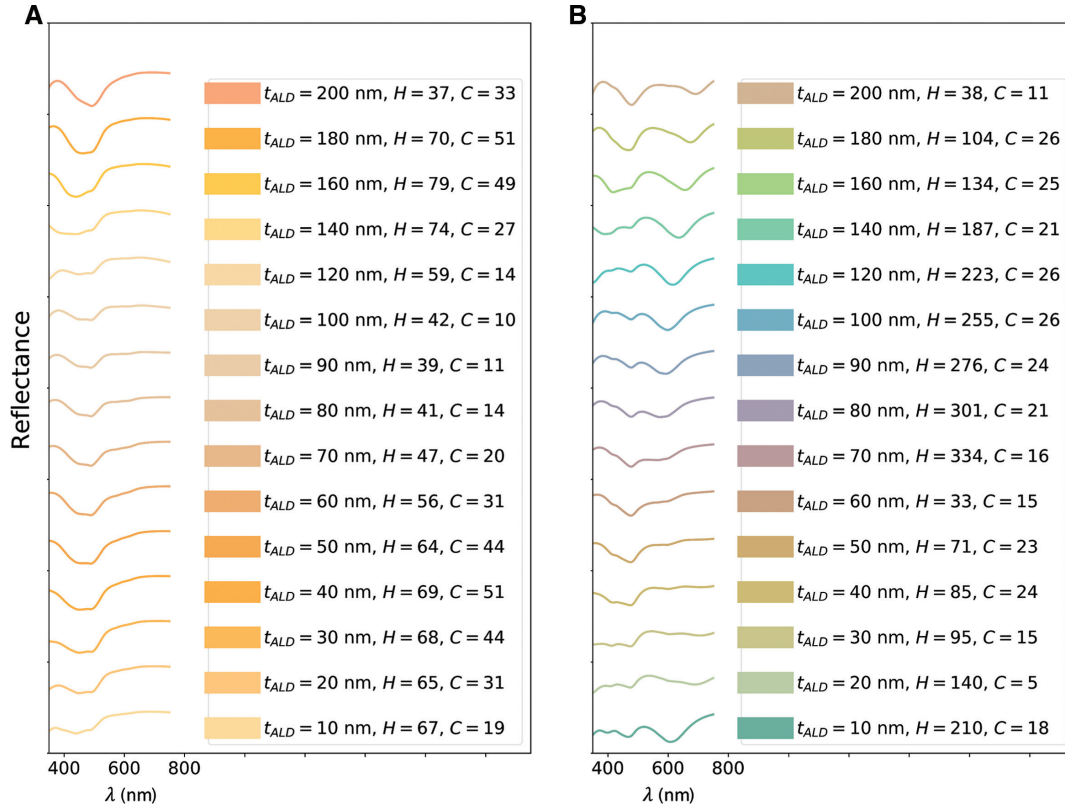


Figure 10: Reflectance spectra and colour evolution for increasing alumina thickness (two experimental trends).

The simulation setup is $R = 35$ nm, $A = 0$ nm (flat surface), (A) $D_m = 75$ nm ($R_{emb} = 0.5R$), (B) $D_m = 90$ nm ($R_{emb} = 0.6R$).

range of parameters (see Figure 8 for example). Since the contribution of the ripples to the hue is somewhat marginal as they primarily contribute to the colour saturation, nonburst simulations would be sufficient to study the mechanism of the colour evolution with increasing t_{ALD} . For all these reasons, we consider nonburst surfaces in the following discussion.

In Figure 10A and B, we show the colour evolution as a function of t_{ALD} for $D_m = 75$ nm ($R_{\text{emb}} = 0.5R$) and $D_m = 90$ nm ($R_{\text{emb}} = 0.6R$), respectively; the nanoparticles are arranged in a hexagonal lattice, and we consider $R = 35$ nm and $A = 0$ nm (i.e. a flat surface) in both cases. The trend in Figure 10A is observed in Figure 2C for nonburst 18 μm and burst 13 μm . The trend in Figure 10B is observed in Figure 2C for nonburst 5 μm and burst 4 μm . While the experimental palettes are shown up to $t_{\text{ALD}} = 90$ nm, we have performed our simulations up to $t_{\text{ALD}} = 200$ nm to confirm the colour recovery and rotation. In fact, in Figure 10A, we see that the orange for $t_{\text{ALD}} = 40$ nm ($H = 68$, $C = 51$) recovers at $t_{\text{ALD}} = 180$ nm ($H = 70$, $C = 51$) with a rotation over an alumina thickness of 140 nm. In Figure 10B, we see that the green for $t_{\text{ALD}} = 20$ nm ($H = 140$, $C = 5$) recovers at $t_{\text{ALD}} = 160$ nm ($H = 134$, $C = 25$) with higher saturation and with a rotation over an alumina thickness of 140 nm. The rotation of the colour palette over $t_{\text{ALD}} \sim 140$ nm (which is $\sim 0.5 \lambda/n$, where $n \sim 1.65$ is the refractive index of alumina measured in Figure 6B) suggests that it may be due to the interference between the reflected wave at the air/alumina interface and the reflected wave at the alumina/silver interface. While the colour is strongly influenced by the plasmonic dip above $t_{\text{ALD}} = 10$ nm, which does not seem to change, it is also affected by the condition of maximum constructive interference, which depends on the alumina thickness as well as the phase of the plasmonic reflection coefficient that is highly dependent on frequency. This maximum constructive interference condition will then move to different colours as the thickness increases, eventually returning to the original colour when the thickness has increased by $\sim 0.5 \lambda/n$. To summarise, for a small t_{ALD} the colour is primarily dominated by changes in plasmonic resonances, and starting from a certain t_{ALD} threshold the plasmonic resonance is less perturbed by adding more alumina. Thus, the evolution of the colour is dominated primarily by interference between the wave reflected at the air/alumina interface and the wave reflected at the alumina/plasmonic interface, where we can imagine the plasmonic layer as a composite layer made by metal and alumina with all the gaps filled by alumina.

The evolution of the colours as a function of t_{ALD} can also be used as a fingerprint to retrieve the nanoparticle

distribution, since the sequence of colours is intimately connected to the surface characteristics. Another interesting aspect about the use of a coating layer is the fact that the rotation of the colour can be exploited for tunability and creation of colours which are difficult to create on the bare surface, for example green. Tunability means that starting from a colour (hue), there is an alumina thickness which is able to create any other colour. This is not true for all the initial colours, as we can see in Figure 10. For example, we find that it is true for the case in Figure 10B, where we see that the palette covers the full hue spectrum, and it is not true for the case in Figure 10A, where the range of hues is limited.

3.4 Surface sensitivity

The visual differences in the colours and the changes observed in the reflectance spectra with increasing alumina thickness (Figures 2C and 5) suggest that the surfaces could be used in colourimetric sensing applications (e.g. colour change biosensors). To examine the potential for this application, we plot in Figure 11 the change in colour, ΔE , versus hue with increasing film thickness for nonburst and burst colours. The change in colour is defined by the following relation [38]:

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2}, \quad (1)$$

where a and b are given as

$$a = C \times \cos\left(\frac{2\pi H}{360}\right) \quad (2)$$

and

$$b = C \times \sin\left(\frac{2\pi H}{360}\right). \quad (3)$$

L is lightness, C is chroma and H is hue – the three components of the LCH colour space. In Eq. (1), subscripts 1 and 2 are used to identify the colours before (1) and after (2) ALD coating. $\Delta E \sim 1$ is the minimum colour change that the human eye can discern [38]. A significant change in colour can be observed for both the nonburst and burst colours with increasing alumina thickness. ΔE is observed to depend on the starting colour before deposition of the alumina film. In both cases, the most sensitive hue region is in the purple colour range ($H = 270$ – 330). The sensitivity of the burst colours is observed to be higher in the blue ($H = 210$ – 270) and purple region ($H = 270$ – 330), by 96%

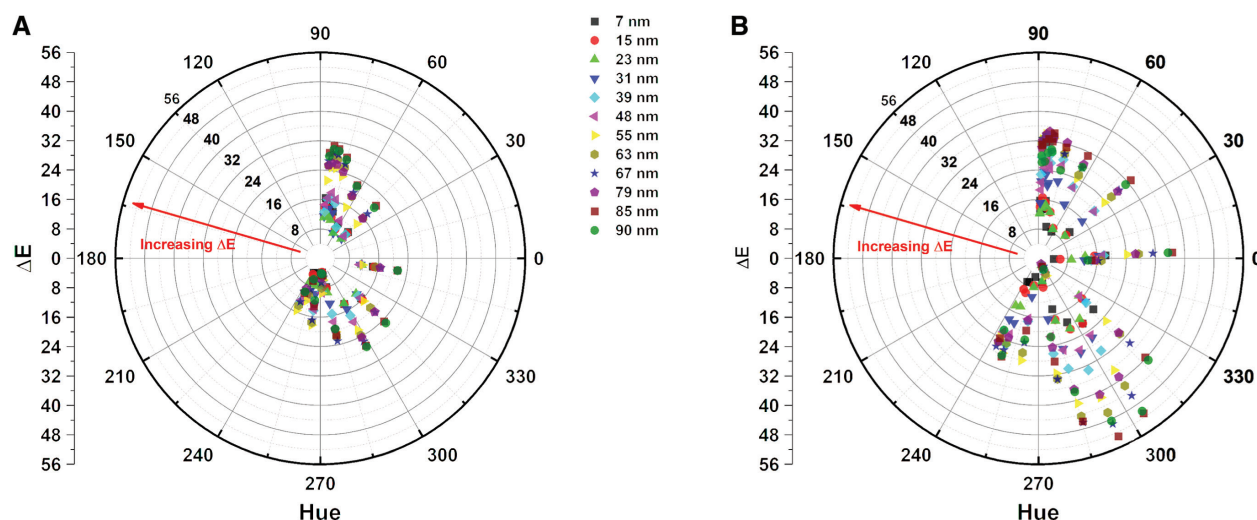


Figure 11: Colourimetric sensing response of the coloured surfaces.

Polar plot of the change in colour (i.e. ΔE) versus hue for the (A) nonburst and (B) burst colours with increasing alumina thickness. The change in colour, ΔE , increases radially outward as represented by the red arrow. The change in colour with alumina thickness is observed to be dependent on the initial hue value.

and 75%, respectively, compared to the nonburst colours of the same hue regions. The increase in ΔE for the burst colours is believed to come from the periodic structures in the burst coloured surfaces. The ability to tune these structures with different burst arrangements [35] could potentially serve to increase their sensitivity for better performance in colourimetric sensing applications. Yellow ($H=30-90$) and red ($H=330-30$) colours do not produce a significant enhancement in ΔE for burst, yielding 13% and 64% increases, respectively. The similar sensitivities of the nonburst and burst surfaces in the yellow and red hue regions is attributed to the disappearance of the periodic features present in burst with increasing line spacing [35]. Interestingly, the improvement in sensitivity of the burst colours follows the improvement in chroma compared to the nonburst colours. These results suggest that burst purple (Figure 11B) is the ideal choice for colourimetric sensing applications with a sensitivity of 3.06/nm (2.02/nm for nonburst – ΔE is dimensionless), implying that less than 1 nm of material on the surface is required for the change in colour to be perceived by the human eye. The sensitivity of the coloured surfaces is, however, not linear with increasing alumina thickness. For a film thickness of 90 nm, the sensitivity of the purple colours drops to 0.56/nm and 0.30/nm for burst and nonburst, respectively, requiring about 2 nm of material to produce a perceivable change in colour. Blue colours are observed to change the least with increasing film thickness.

Interestingly, while blue surfaces do not perform well as a colourimetric sensor, the surface is best as a

radiometric sensor (see Figure 5). For the blue surfaces, the highest sensitivities observed are for the resonant features identified as $F_{nb,1,blue}$ and $F_{b,2,blue}$, yielding 2.58 and 3.19 nm/nm for the nonburst and burst cases, respectively. These sensitivities rival sensors fabricated via nanolithography techniques. For the purple cases, the features producing the highest sensitivities are $F_{nb,4,purple}$ and $F_{b,4,purple}$, yielding 0.63 nm/nm and 1.02 nm/nm, respectively. The sensitivity of the different features identified in the reflectance spectra varies significantly with thickness. For example, $F_{nb,2,blue}$ and $F_{b,3,blue}$ produce sensitivities of 0.31 nm/nm and 0.35 nm/nm, respectively. The plasmon shift, with increasing alumina thickness, is observed to decrease for colours produced with larger line spacings (i.e. lower nanoparticle densities – blue to yellow) making the blue colours better for radiometric sensing. In addition, while the current colours were chosen because they were aesthetically pleasing, colours can be produced with marking speeds as fast as 3000 mm/s making this process viable for industrial applications and the marking of large surface areas. Furthermore, while silver cannot be used directly in bio-sensing applications due to its reactivity, a thin passivation layer could be formed by ALD on the surface.

4 Conclusion

Colour palettes produced on the surface of silver using nonburst and burst colouring methods were modified by alumina films produced via ALD. The colour

and reflectance changes were characterised as a function of alumina film thickness. For burst, the colours first degrade with increasing film thickness but recover at larger thicknesses and the colour range is expanded, whereas for nonburst the colours keep degrading. Underlying periodic structures specific to burst are responsible for this behaviour. FDTD modelling of representative surfaces, including a conformal alumina layer, helps explain the colour rotation and recovery observed in experiments with increasing alumina thickness. For alumina thicknesses smaller than the nanoparticle gaps, the changes in the perceived colours are due to the perturbation of plasmonic resonances. For alumina thicknesses larger than the nanoparticle gap, the change in colours originates from the complex reflectance response of the alumina-coated structures due to plasmonic resonances and interference effects in the multi-layer system.

In addition, the surfaces are thought to be good candidates for colourimetric sensing. The sensitivity of the surfaces depends on the initial colour prior to deposition. The colourimetric response of the burst surfaces is increased by up to 96% relative to the nonburst surfaces. The purple colours are the most sensitive, yielding a sensitivity of 3/nm, which implies that less than 1 nm of alumina is needed to produce a colour shift perceivable by the human eye. The coloured surfaces could also perform well as radiometric sensors, yielding sensitivities as high as 3.19 nm/nm for the blue colours. The ability to tune the structures for grating-assisted coupling and improve colours using burst makes laser-written surfaces very versatile for specific sensing application.

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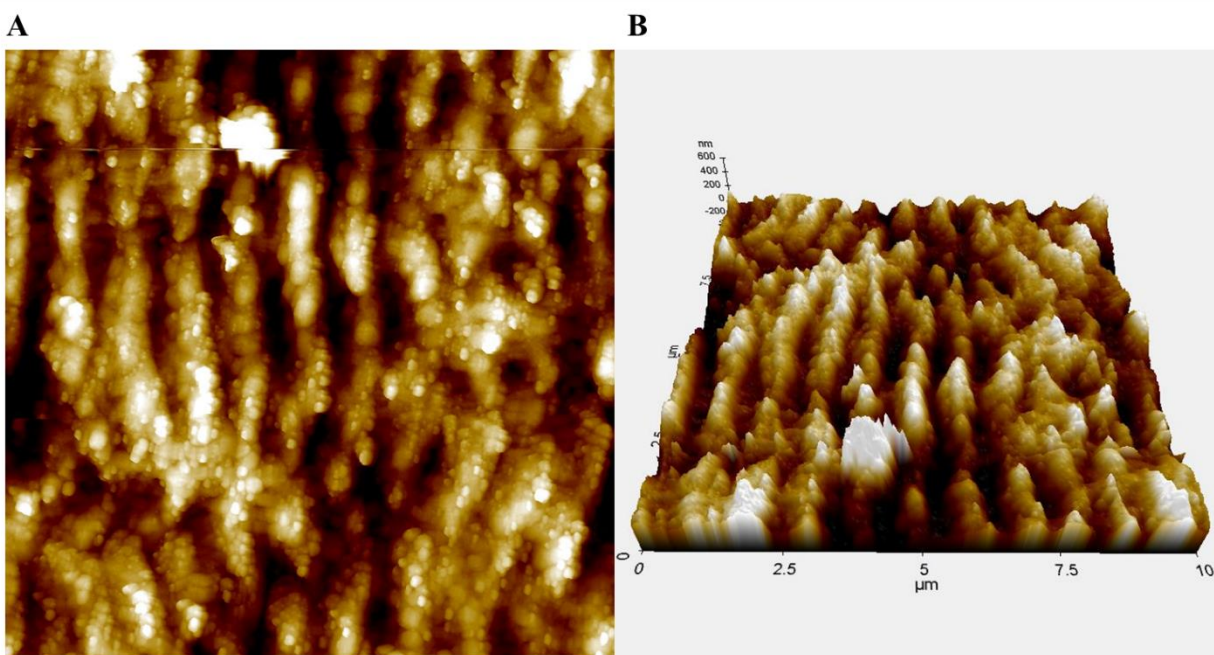
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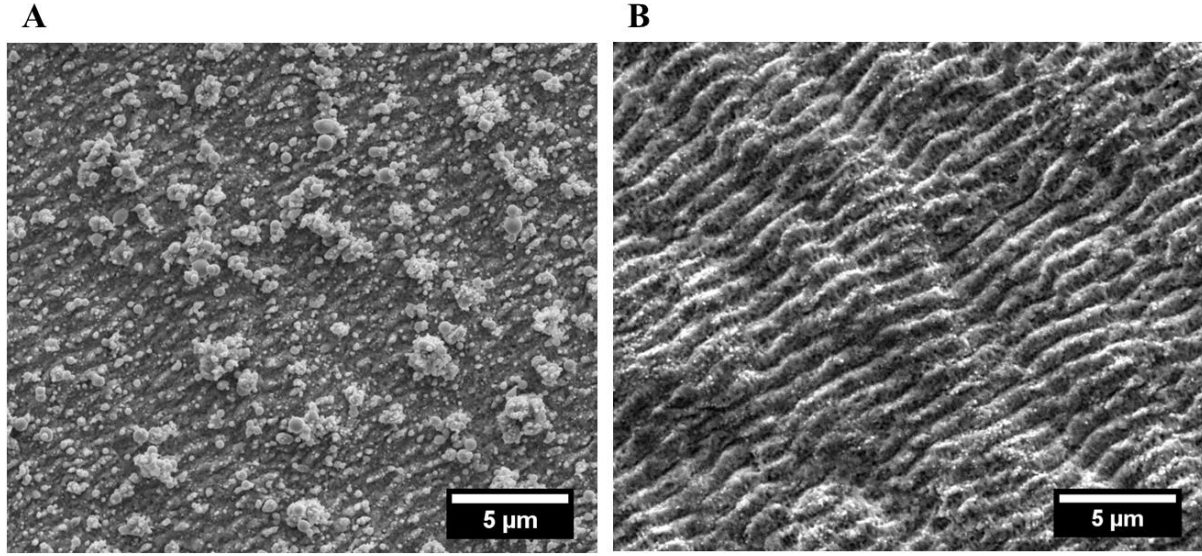
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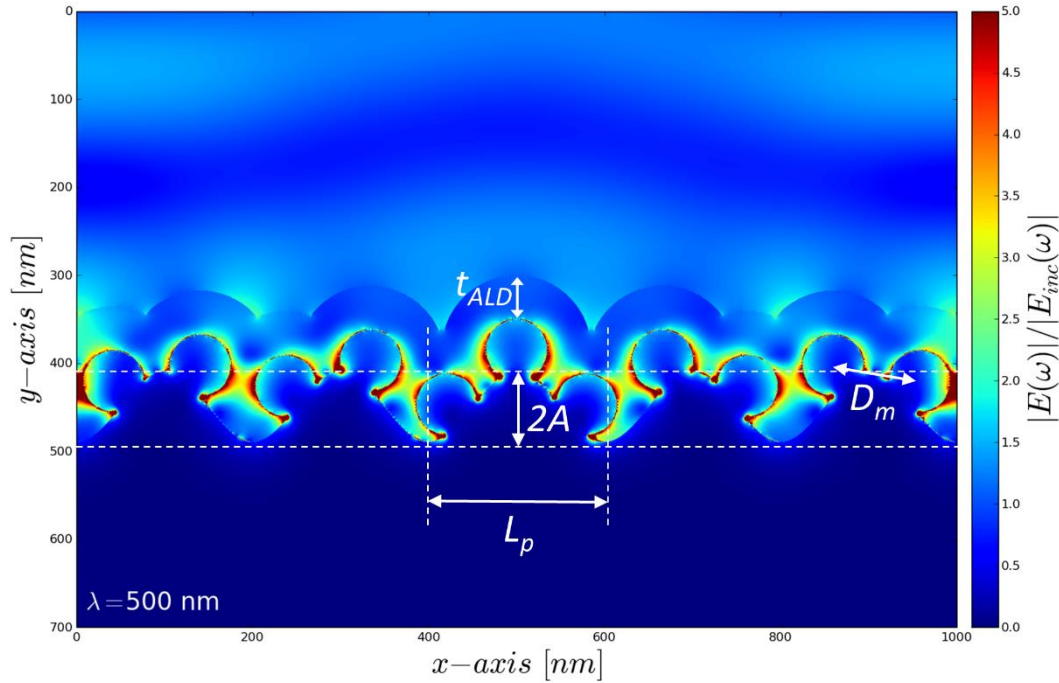
Supplementary material



Supplementary Figure 1|(A) Atomic force microscope (AFM) measurement of a burst blue colored square. (B) The data of the AFM scan of the surface was imported into the Gwyddion software to extrapolate a height profile of the LIPSS structures. A height of 150 nm was found for this particular burst pulse arrangement.



Supplementary Figure 2| SEM images of blue surfaces created using the (A) nonburst and (B) burst colouring method. The Hue value was roughly the same, $H \sim 295^\circ$, whereas the Chroma values of each blue was measured to be 22.3 and 31.2 for the nonburst and burst surface, respectively. Significant differences in the underlying topographical features can be observed between the nonburst and burst surfaces.



Supplementary Figure 3| Simulation setup and computed near-field for NPs on a sine-modulated surface covered with a film of alumina. Electric field (magnitude) distribution at $\lambda_0 = 500$ nm under x-polarized excitation for $L_p = 200$ nm, $R = 35$ nm, $R_{emb} = 0.3R$, $D_m = 100$ nm, $A = 40$ nm, $t_{ALD} = 50$ nm. The xy plots are taken through the center of the spheres. This figure is extracted from Media S1, which shows the field distribution as a function of the wavelength.

Effect of laser repetition rate on colour rendition, nanoparticle morphology and surface chemistry on silver

8.1 Summary

This chapter demonstrates the effect of the laser repetition rate on the colours, chemistry and morphology of the irradiated silver surfaces. The lower laser repetition rate is observed to incrementally add to the colour gamut enabling the production of the elusive cyan and green colours. Chemical analysis of the coloured surfaces showed the laser repetition rate dependent formation of silver oxides and silver carbonates. Identical colours with distinctive chemical compositional surfaces suggest that the surface chemistry is not responsible for the colours. Scanning electron microscope images of the surfaces machined using the same total accumulated fluence, but different laser repetition rates, is observed to have significantly different topography. The surfaces of the coloured areas were observed to become smoother with increasing laser repetition rate. The combination of the smoothing of the surfaces with the disappearance of the chemical

species at higher laser repetition rates suggest the sintering of the nanoparticles due to the accumulative heating of the bulk.

8.2 Contributions

The results provided in this section were published in the journal Optical Materials Express as a invited contribution. The successful completion of this manuscript was due to the combine effort of the people involved. In this publication, I and Guillaume Côté made the initial visual observation of the laser repetition rate effect on the colours. For this publication and the proposed explanation, I prepared the samples, made the experiments and gathered the LCH and RAIRS measurements. I made and took photographs of the coloured surfaces produced using different laser repetition rates. Dr. Berini's lab technician, Anthony Olivieri, and I took the SEM images of the surfaces. Dr. Daniel Poitras and I conducted the spectrophotometer measurements of the surfaces. Dr. Jaspreet Walia and myself discussed and analyzed the chemical section of the paper. From the data, I established the theoretical conclusion explaining the observations. All the the authors discussed the experimental results. Dr. Berini, Dr. Ramunno, Dr. Weck, Dr. Variola, Dr. Walia and I co-wrote the manuscript. The figures were made by me.

8.3 Article

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Effect of ps-laser repetition rate on colour rendition, nanoparticle morphology and surface chemistry on silver [Invited]

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Abstract: We investigate the effects of the laser repetition rate on the creation of angle-independent colours on bulk silver samples, and characterize the coloured surfaces in terms of the associated morphology and oxidation products produced. The laser used produces pulses 10 ps in duration at $\lambda = 1064$ nm, and the repetition rate was varied over the range from 5 to 400 kHz. Decreasing the laser repetition rate creates a colour palette on silver with a significantly wider gamut, including green and cyan colours, which were previously difficult to obtain. Scanning electron microscope analyses of these surfaces show an increase in topographical features (roughening) with decreasing laser repetition rate. Chemical analyses of the coloured areas show that the amounts of oxide and carbonate species formed depend on the laser repetition rate.

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1. Introduction

The collective oscillation of the electron cloud around a metal ionic core, also known as a surface plasmon, allows for the manipulation of light at the sub-wavelength scale [1]. Plasmon resonances are sensitive and can be tuned by varying characteristics such as particle size, shape and permittivity [1–3]. In the past decade, the nanostructuring of metallic surfaces or the use of sub-wavelength metallic structures have seen growing applications, such as in photo-chemistry [4–6], colouring [7–12], medicine [13,14], sensing [15,16] and anti-counterfeiting [17,18].

The fabrication of nanostructured plasmonic surfaces is usually achieved by lithographic techniques [10,11]. Recently, ultrafast lasers demonstrated the ability of producing nanostructures by direct-laser writing of metal surfaces to create colours [19–23]. These colours are believed to be plasmonic in origin due to the random re-deposition and fusion of metallic nanoparticles onto the metal substrate following surface laser irradiation and ablation [19]. The colours rendered depend strongly on the type of laser used to produce them, and on the laser parameters which are typically determined through trial and error [19–23]. Moreover, compared to colours generally produced by periodic nanostructured surfaces, such as laser-induced periodic surface structures (LIPSS) [19,24], the randomness of the re-deposited metal nanoparticles makes the rendered colours insensitive to viewing angle.

To date, a comprehensive understanding of the effects of laser parameters on the direct-laser colouring of metals is still lacking. In particular, the effects of the laser repetition rate are ill-understood; yet this parameter is of high importance as it controls throughput, yield, energy delivery and the timing of the delivery. It is expected that the colours produced on the

surface of metals exhibit a temporal dependence on the deposition of laser energy thereon. The machining of materials using high laser repetition rates is known to increase the bulk and surface temperatures due to heat accumulation [25–27]. The increase in temperature and the response (deformation) of the bulk are determined in part by the laser repetition rate.

Guay *et al.* [22] showed through computer simulations that the plasmonic resonances and colours originating from arrays of re-deposited nanoparticles are highly sensitive to embedding depths as small as 0.5 nm. Specifically, the plasmon resonance is sensitive to the angle formed between the surface-bound nanoparticles and the substrate. Thus the presence of metallic nanoparticles of lower melting temperature than that of the bulk [28,29], combined with the sensitivity of the colours to slight sintering variations or changes in the nanoparticle contact angle, indicate that all laser parameters in the laser-colouring process are impactful, including the laser repetition rate. Furthermore, laser colouring of metals is commonly achieved in ambient air. The ionization of material and air during the irradiation/ablation process suggests the creation of exotic chemical species [30]. To date, little chemical analyses have been done on laser-coloured, or more generally, laser-nanostructured surfaces [31,32]. In previous work, colours produced on metals by ultrafast lasers were thought to be solely rendered plasmonically, although similar colour palettes could be produced by controlling the thickness of metal-oxide layers [33–35]. Thus, the presence of chemical species on laser-machined surfaces and their effect on colour or on the behavior of nanostructured surfaces are of strong interest. Moreover, the amount of chemical species formed during the ablation process could produce purely plasmonic [22], core/shell [36–38] or semiconductor [39–41] (*i.e.* quantum dot) nanostructures. Each of these different compositions can exhibit a different and unique behavior, but all of them are in principle capable of producing structural colours.

In this paper, we investigate the effects of laser repetition rate on the production of colours on silver (Ag). In parallel, we also study the effect of the laser repetition rate on the morphology and surface chemistry of the coloured silver surfaces. For the same total accumulated fluence [22] delivered to the surface, the colours, morphology and surface chemistry are observed to change depending on the time between subsequent laser shots. With decreasing laser repetition rate, we observe a widening of the colour gamut to include obtain green and cyan colours (previously difficult to obtain). Scanning electron microscope (SEM) images of the colours produced using the same total accumulated fluence but with different laser repetition rates reveal the creation of significantly different nanostructures. Spectroscopic analyses of the coloured surfaces reveal that an increasing amount of silver oxide and silver carbonate species are formed by increasing the time between laser shots (*i.e.* lower laser repetition rates). The morphological and chemical analyses of the surface suggests that the origin of the colours to be morphological in nature.

2. Experimental sections

2.1 Laser specifications and fabrication

The machining of the silver samples was carried out by irradiating the surface with 1064 nm light from a Duetto mode-locked laser (Nd:YVO₄, Time-Bandwidth Product) and a pulse duration of 10 ps. The repetition rate of the laser is tunable from 50 to 8200 kHz. For the lower repetition rates, a pulse picker option was used to reduce the laser repetition rate by an integer factor *N*. In our experiments, the repetition rate of the laser was fixed to 400 kHz and the pulse picker was used to control the laser repetition rate at the output. This approach ensured that the laser pulse energy remained the same throughout the experiments. This was verified by reading a factor of 2 drop in the average power (3A-P-QUAD, Ophir) for every factor of 2*N* of the pulse picker. The operation of the pulse picker was also verified and monitored using an oscilloscope (tds3033b, Tektronix). The silver samples were 38 mm in diameter, 3 mm thick and of 99.99% purity. The flat silver surfaces were produced via a high-tonnage press with a resulting silver surface roughness of 20-100 nm (average). Prior to machining the silver surfaces, the surfaces were cleaned using a multistep cleaning approach:

(step 1) isopropanol wash, (step 2) acetone wash, (step 3) de-ionized water rinse, (step 4) second isopropanol wash and (step 5) dried using nitrogen. For transport, the silver samples were placed in nitrogen filled plastic capsules and placed in nitrogen filled bags. Colours machined by the raster-scanning of the silver surfaces were achieved following the same method previously described in ref [22], where the different line spacing is observed to produce distinct nanostructures that are unique to each colour [22,23]. The laser was fully electronically integrated and physically enclosed by a third party for industrial applications (GPC-PSL, FOBA). To machine the silver surface, the laser light at the output was expanded from a 3 to 12 mm diameter spot using a fixed beam expander (LINOS G038662000, QIOptiq) and directed into the back of the XY galvanometric mirrors (TurboScan 10, Raylase). The light was then focused onto the silver surface using an F-theta lens ($f = 254$ mm, Rodenstock). The light was displaced over the surface in a top-to-bottom raster-scan pattern at a maximum speed of 3000 mm/s. For accurate determination of the silver surface, the surface of the silver was located using a touch probe system. Throughout the experiments, the polarization of the laser light was kept parallel to the machining direction. For machining, the samples were placed on a 3-axis stage of resolution of 1 μm in the lateral and axial directions. The laser power was computer-controlled via a user interface and calibrated using a power meter. A Gaussian beam radius of $\sim 28 \mu\text{m}$ was obtained using a semi-logarithmic plot of the square diameter of the modified region, measured using a SEM, as a function of laser pulse energy [42].

2.2 Characterization

The Lightness (L), Chroma (C) and Hue (H) values of each coloured square were measured using a Konica Monilta CR-241 chroma meter in the CIELCH colour space, 2 observer and illuminant C (North sky daylight). The Hue is representative of colour associated with a 360° polar scale [43]. The LCH values were converted to the XYZ tristimulus colour space using Matlab for the plotting of the Commission Internationale de l'Éclairage (CIE) diagrams. The reflectance measurements of the coloured silver surfaces were carried out using a CARY 7000 UV-Vis-NIR spectrometer (Agilent Technologies) equipped with an integrating sphere detector (Labsphere) to collect both the specular and diffuse reflectance signals from the samples. The reflectance data was corrected against reference samples of silicon and silver. Grazing angle measurements of the coloured surfaces were performed using an FT-IR spectrometer (Nexus 870, Thermo Nicolet) with the incident light source hitting the surface of the sample at an angle of 80°. In this approach (RAIRS - Reflection Absorption Infrared Spectroscopy), the sharp angle is utilized to predominantly generate an electric field that is oriented perpendicular to the probed surface, such that vibrational modes of the chemical species on the surface that have transition dipole moments parallel to the electric field are excited, and featured in the IR spectra [44]. Each spectrum is the average of 256 accumulations recorded with a spectral resolution of 2 cm^{-1} , taken from a coloured square of surface area of 0.5 cm^2 . A smooth and polished silver sample was used for background correction. High-resolution SEM (Gemini SEM 500 FESEM, Zeiss) images of the coloured surfaces were obtained by using secondary electron imaging mode. To obtain additional information on the nanoparticles deposited within the machined surface, SEM images of the surfaces were taken with a stage tilt of 70°.

3. Results and discussion

3.1 Laser repetition rate dependent colours

Significant progress has been made towards the understanding of the colourimetric response of laser coloured silver and copper surfaces. However, studies focusing on the colouring of such surfaces by ultrafast lasers have overlooked the effects of the laser repetition rate [21] as the pulse-to-pulse separation time was longer than the thermal expansion time of the metal

[45]. Yet, the heating of a material with increasing laser repetition rate is well known [25–27]. In addition, due to the low melting point of nanoparticles with respect to the bulk [46,28,29], the effect of cumulative heating on the metallic nanostructures responsible for the colours should not be neglected. Moreover, the interaction of the laser pulse with the ablation plume and the ejected debris occurring within the same time scale should also be considered [47]. In our previous work [22], we presented the colouring of silver using a fixed repetition rate in order to leave out any temporal effect on the energy deposition. With this approach, each colour could be linked to a unique total accumulated fluence (TAF) value [22]. The TAF was observed to control the nanoparticle density re-deposited on the surface and from this observation a model based on nanoparticle sizes and distributions was proposed suggesting that the perceived colours are plasmonic in origin [22]. Even though the model simplified the disordered topography of the machined surfaces and neglected the presence of oxides and carbonates, it nonetheless successfully reproduced the salient features observed in measured reflectance spectra [22]. The TAF relation is given by:

$$\phi = \frac{a^2 E f}{v L_s} \quad (1)$$

where a is a dimensionless correction factor accounting for the dependence of the modified region area on the laser pulse energy E (J), f (Hz) is the laser repetition rate, v (mm/s) is the laser marking speed along the surface and L_s (μm) is the line spacing between successive lines in the raster scan. In these experiments E was fixed and, therefore, a was also constant due to its dependence on the laser pulse energy.

The surfaces shown in Fig. 1(a) were irradiated with a laser TAF of 5.16 J/cm^2 and a laser pulse energy of $E = 15 \text{ }\mu\text{J}$. The laser pulse energy and TAF were kept constant throughout the experiments using the laser pulse picker to control the repetition rate at the output of the laser. A decrease of half in the average power for each integer of 2 on the pulse picker was confirmed using a power meter, ensuring constant pulse energy at the laser output. To deliver the same TAF to the surface, the laser repetition rate was changed by $f' = f/N$ and the marking speed was modified proportionally as $v' = v/N$, where N is the pulse picker number. Replacing the modified repetition rate and marking speed into Eq. (1), we obtain the following relation:

$$\frac{a^2 E f'}{v' L_s} = \frac{a^2 E f}{v L_s} \quad (2)$$

The number of overlapping shots within a single line was 5 for each of the different combinations of f and v . In Fig. 1(a), significant changes in colour can be seen for the same TAF deposited on the surface, but using different laser repetition rates. This suggests a strong temporal dependence on colour formation most likely from cumulative heating of the surface, which could in turn affect the contact angle of the nanoparticles sitting on the substrate.

The colours are observed to evolve in a counter-clockwise manner on a colour Hue polar plot representation (*i.e.* yellow $\rightarrow$ purple $\rightarrow$ blue) with decreasing laser repetition rate, see Fig. 2(a). The rate of change in Hue with decreasing laser repetition rate is observed to increase as the line spacing decreases. In addition, a full Hue rotation can be observed for the line spacing $L_s = 5 \text{ }\mu\text{m}$. Figures 1(b)-1(d) show reflectance spectra from surfaces with the line spacings of Fig. 1(b) $L_s = 5 \text{ }\mu\text{m}$, Fig. 1(c) $L_s = 8 \text{ }\mu\text{m}$ and Fig. 1(d) $L_s = 13 \text{ }\mu\text{m}$, using different laser repetition rates. Features in the reflectance spectra can be followed as the repetition rate changes, and thus as the time between laser pulses delivered to the surface changes. The features are observed to red-shift with decreasing laser repetition rate. The red-shift in the features are smallest at the highest repetition rates (400 to 200 kHz), but are significantly larger for laser repetition rates lower than 50 kHz.

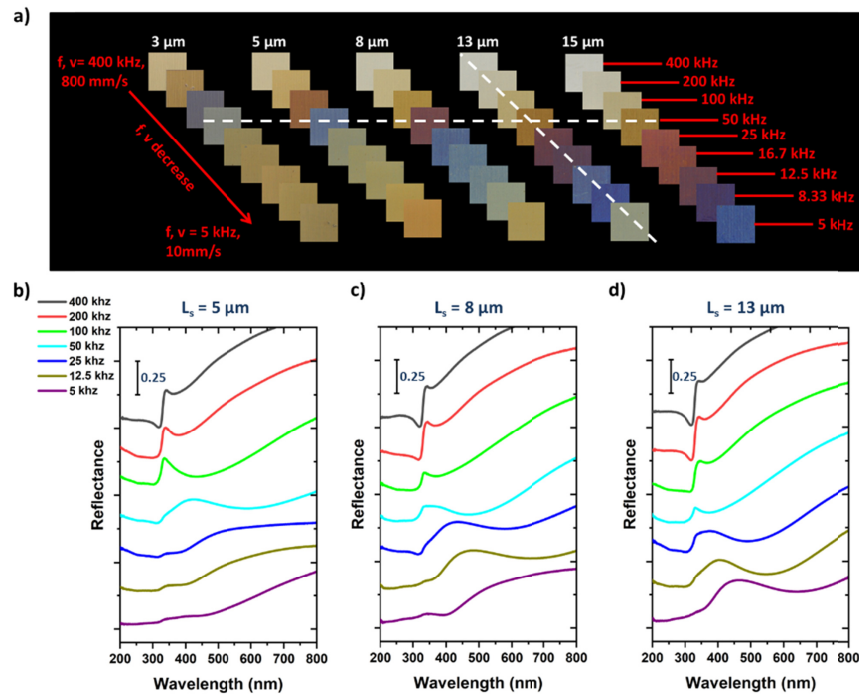


Fig. 1. (a) Colour evolution for different laser repetition rates, f (red text), for selected raster line spacing (white text). To deliver the same total accumulated fluence to the surface, the laser marking speed was adjusted proportionally to the laser repetition rate. The colours were created with a fixed fluence of 5.16 J/cm^2 and a laser pulse energy of 15 μJ . The coloured surfaces created were $3 \times 3 \text{ mm}^2$. Similar colour palettes were obtained by changing the line spacing, and fixing the laser repetition rate, or by fixing the line spacing and changing the laser repetition rate (horizontal and vertical white dashed line, respectively). Reflectance spectra are shown for selected line spacing values of (b) $L_s = 5 \text{ μm}$, (c) $L_s = 8 \text{ μm}$ and (d) $L_s = 13 \text{ μm}$, written using different laser repetition rates but with the same total accumulated fluence. The main features in the reflectance spectra can be followed distinctively and are observed to red-shift with decreasing frequency with more sensitivity to laser repetition rates of 50 kHz and lower. The scale bar of (b), (c) and (d) is located in the upper-left corner of each panel.

Radial plots of Hue (θ) as a function of the logarithm of the TAF (r) using different laser repetition rates are shown in Fig. 2(a). The TAF deposited on the surface increases radially outward. The range of colours covered by the highest repetition rate of 400 kHz is observed to be significantly limited and reduced to the yellow Hue region. Alternatively, with decreasing rate much wider colour palettes are obtained. We previously reported the colouring of silver using a fixed repetition rate of 50 kHz, where only a small number of green and cyan colours could be obtained (when the process was modified by changing the angle of polarization with respect to the machining direction or by performing multiple overlapping passes) [22]. In Fig. 2(a), the colour palette (Hue) is extended simply by decreasing the repetition rate of the laser. Furthermore, the Chroma values of the cyan and green colours obtained using lower repetition rates are higher than those obtained with previously reported non-burst colouring techniques [22]. Additionally, the TAF used to produce the full range of colours is significantly reduced. For example, at $L_s = 15 \text{ μm}$ and $f = 50 \text{ kHz}$, a yellow colour is obtained. By decreasing the laser repetition rate and marking speed accordingly (keeping the same TAF), a blue colour is obtained instead, which would have normally required a higher TAF (*i.e.* smaller line spacing). This feature can be observed by the tightening of the spiral in the radial plots at lower laser repetition rates, see Fig. 2(a).

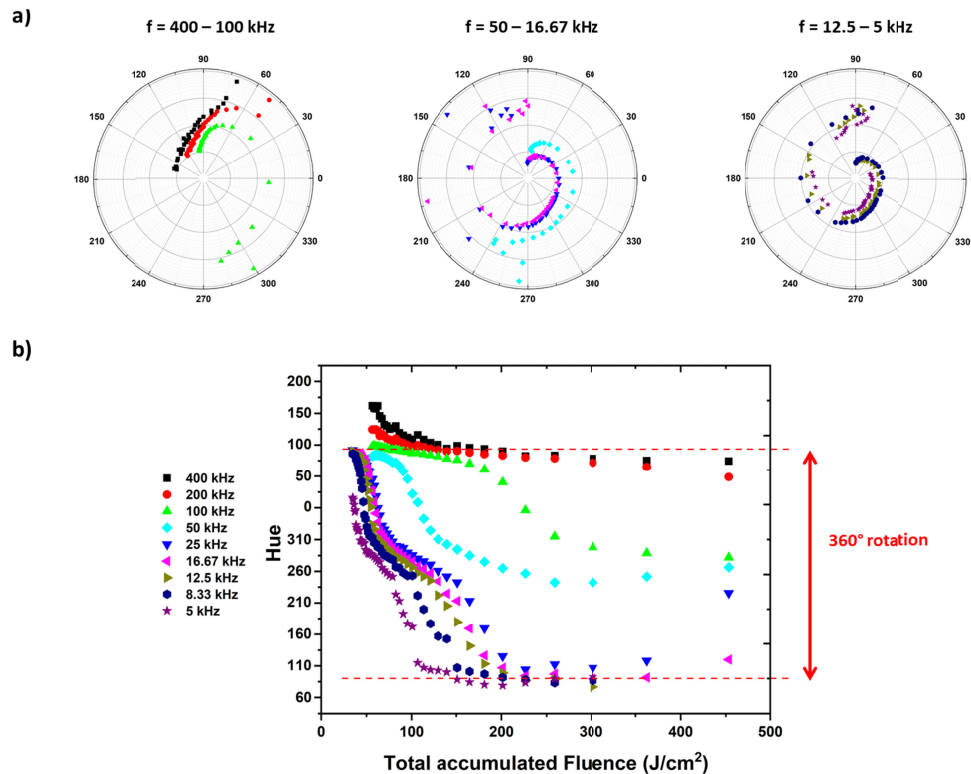


Fig. 2. (a) Polar plot of Hue (θ) versus the logarithm of total accumulated fluence (r) using different laser repetition rates as indicated above the plots [and the legend in part (b)]. The different points in the plots represent the colours in each respective colour palette obtained using different frequencies. The different colours were obtained by changing the raster line spacing of each coloured square by $0.5 \mu\text{m}$. The colour gamut is observed to widen with decreasing laser repetition rate. (b) Plot of Hue versus total accumulated fluence using different laser repetition rates. At lower frequencies, a full rotation in Hue can be observed (red arrow). The cutoff in the colours obtained is determined by the laser repetition rate. At higher frequencies, the colour palette is effectively reduced to the yellow Hue region.

In addition, with decreasing rate a full 360° rotation in Hue is achieved, see Fig. 2(b). At much lower rates, the gain in the colour range is not as significant, however, control of the slope in the Hue region of 235° to 110° (cyan and green) could be useful since they are the most difficult colours to obtain [22]. By controlling the slope, the sensitivity of the colours to slight variations in the TAF could be decreased in favour of reproducibility while extending the colour range obtainable, see Fig. 2(b). As a result, in an industrial environment where the ambient conditions and vibration may not be well controlled, variations in laser output and its effect on the colour (*i.e.* ΔE) could be minimised.

Of note is the reduction of the palette with increasing repetition rate. The colour palette is observed to collapse and to produce only yellow colours for rates higher than about 200 kHz, as seen on Fig. 3(b). Figure 3(a) is a CIE xy chromaticity diagram of the colours obtained using different repetition rates. The points are representative of the colours shown in the previous figures. The area covered by the colours produced with the laser repetition rate of 400 and 200 kHz is seen to collapse into a small region of the CIE diagram in the yellow section. An increase in the area covered by the colours is observed by decreasing the laser repetition rate from 200 to 50 kHz. No significant gain in area is observed after decreasing the repetition rate below 50 kHz. Although, lowering the repetition rate below 50 kHz does not expand the covered area, more colours (*i.e.* markers) are added (Fig. 2), resulting in a complete rotation (ring) in the CIE diagram. However, the increase in the green and cyan

regions is not as well captured in the CIE diagram. This is due to the low Chroma values of the green and cyan colours since Chroma values in the CIE diagram always increases outward.

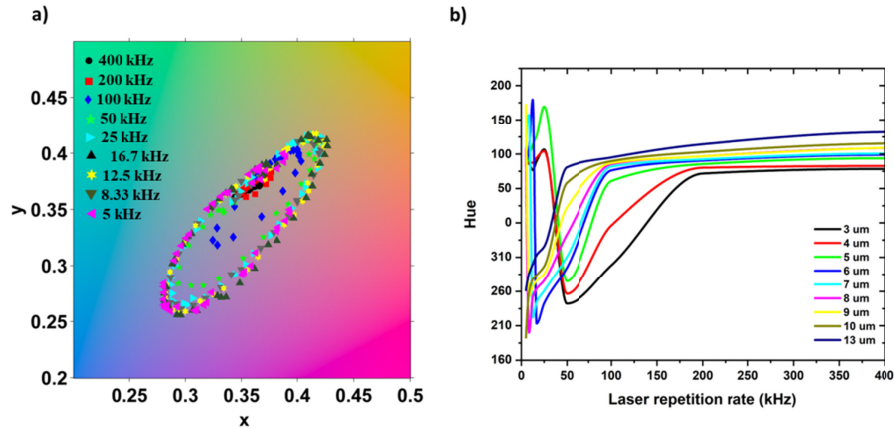


Fig. 3. (a) CIE xy Chromaticity diagram showing the area covered by the colours produced using the different laser repetition rates. The area covered increases with decreasing repetition rate starting from a small area in the yellow region. For lower frequencies, the area is increased to cover more of the green region. (b) Graph of Hue versus laser repetition rate for different raster line spacing. The colour palette is observed to reduce to the yellow Hue region for laser repetition rates over ~200 kHz.

3.2 Surface characterization

High magnification images of the surfaces, as given in Fig. 4, show that the nanostructures produced by the lower laser repetition rates are more disorganized. While round particles are distinctively present for all laser repetition rates, the underlying roughness is significantly different. With increasing laser repetition rate, the roughness is observed to smooth out. In a previous publication, this roughness was modeled as nanoparticles with a statistical distribution of embedding ratios [22]. The effect of embedding was demonstrated in computer simulations to play an important role in determining which colours might be observed. In fact, changes in embedding as small as 0.5 nm were enough to significantly shift the plasmon resonance and consequently the far-field colours. The embedding could suggest that a high enough temperature was produced on the surface having the effect of sintering the nanoparticles whose melting temperature is lower due to their size [28,29].

The direct laser machining to produce coloured surfaces is conducted in ambient air. The ionization of silver atoms and the ejection of charged silver nanoparticles during ablation [48] favours the creation of Ag-based chemical species [30]. The species can form a broad range of nanoparticles, including purely metallic [22], core/shell [36–38], semiconductor [39–41] or more chemically-complex structures [49]. Combinations of different types of nanoparticles can also produce colour [50]. Additionally, metals processed using direct-laser machining or electro-deposition also produce colours but via oxide formation [33,34,51].

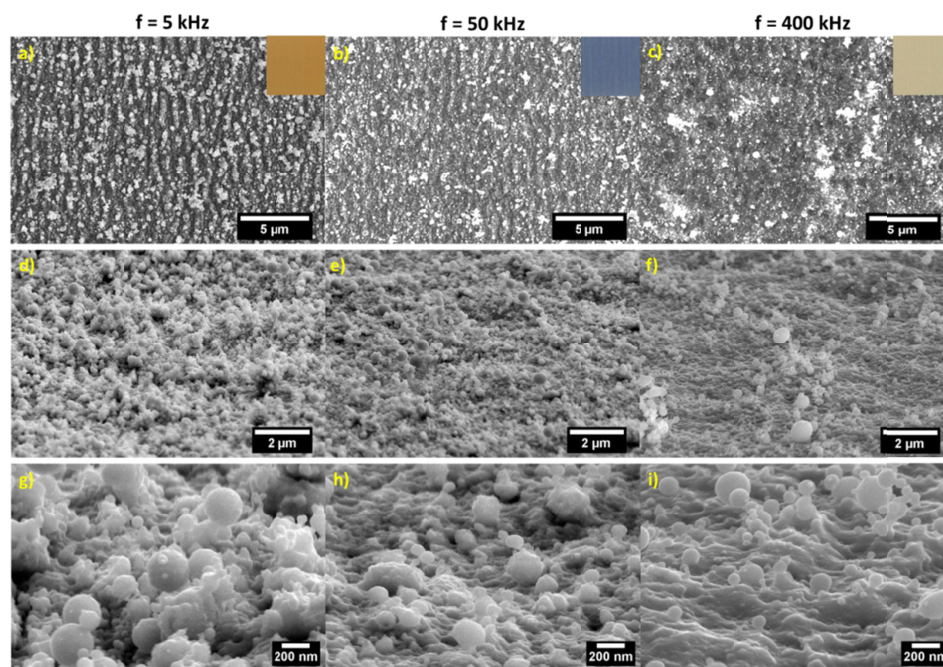


Fig. 4. (a-c) Top-down SEM images of the coloured surfaces produced using laser repetition rates of (left-column) 5 kHz, (middle-column) 50 kHz and (right-column) 400 kHz, respectively. The surfaces were machined using a raster line spacing of $L_s = 5 \mu\text{m}$ and a laser fluence of 5.16 J/cm^2 . (d-f) Low-magnification and (g-i) high-magnification SEM of the same surfaces with a tilt angle of 70° . The roughness of the surfaces is observed to decrease with increasing laser repetition rate. The colour of each surface can be seen in the insets.

We performed chemical analyses of our coloured surfaces using grazing angle reflection absorption infra-red spectroscopy (RAIRS). Colours produced using two distinct sets of laser parameters were characterized to determine their surface chemistry. Figure 5(a) is a plot of the RAIRS measurements from samples fabricated with a line spacing $L_s = 5 \mu\text{m}$ and different laser repetition rates. Figure 5(b) is a plot of the RAIRS measurements from a full colour palette obtained on the surface of silver by varying the line spacing, L_s , from 2 to $11 \mu\text{m}$, and using a fixed laser repetition rate of 50 kHz. The absorbance results shown in Fig. 5 are plotted over the 500 to 2000 cm^{-1} spectral range. In both cases, two main absorbance bands centered at 560 cm^{-1} and 1450 cm^{-1} appear [52]. The peak at 565 cm^{-1} corresponds to the longitudinal optical vibration of the Ag-O bond in silver oxide, Ag_2O [52]. The broad feature centered at 1450 cm^{-1} is the result of two distinctive spectral contributions at 1400 cm^{-1} and 1465 cm^{-1} . The origin of these bands were formally assigned to the splitting of asymmetric stretching of the carbonate ion, CO_3^{2-} , which would otherwise be centered at 1410 cm^{-1} [53]. Alternatively, in another study it was shown that the splitting can result from the formation of basic silver carbonate, $\text{AgOHAg}_2\text{CO}_3$, which can readily evolve when silver carbonate, Ag_2CO_3 , is exposed to water vapor [53]. As the ejection of the nanoparticle is conducted in an ambient environment the formation of such chemical species is expected. In the past, the exposure of the coloured silver surface to humid conditions consistently showed a significant increase in carbonate signals that are consistent with the doublet observed in the literature [55]. Therefore, we assign the two spectral contributions at 1400 cm^{-1} and 1465 cm^{-1} to basic silver carbonate. The creation of these chemical species during machining is currently the subject of a separate study. No chlorine or sulfur compounds were detected on the silver

surfaces prior or following the laser machining using X-ray photoelectron (XPS), IR and Raman spectroscopic techniques.

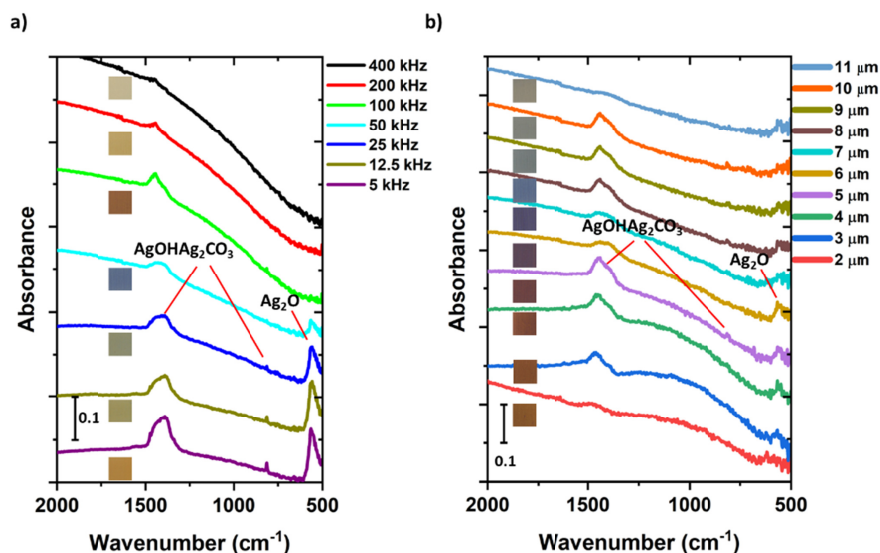


Fig. 5. (a) RAIRS measurements of the coloured surfaces produced using different laser repetition rate for the same line spacing of 5 μm and the same total accumulated fluence. With decreasing laser repetition rate, two distinctive chemical species can be observed: Ag_2O and $\text{AgOHAg}_2\text{CO}_3$. (b) RAIRS measurements of coloured surfaces obtained by changing line spacing by intervals of 1 μm and machined with a fixed laser repetition rate of 50 kHz. The coloured square corresponding to each spectrum is placed as an inset below their respective trace. The scale bar of is located in the bottom-left corner of each panel.

The RAIRS measurements in Fig. 5 show a significant variation in the presence of chemical species with changing laser repetition rate, but that the same chemical species are relatively insensitive to changes in line spacing. In Fig. 5(a), a concomitant decrease in peaks assigned to silver oxide and basic silver carbonate is observed as the laser repetition rate is increased from 5 to 400 kHz. Surfaces machined at 400 kHz showed only very weak signals from carbonates and the total disappearance of oxides. The results clearly show that longer times between pulses can result in significant increases in the amounts of detected oxides and carbonates. For Ag_2O to dissociate into pure Ag a temperature of $\sim 400^\circ\text{C}$ [54] is required on the surface. Figure 5(a) suggests that the dissociation temperature is reached when the time between laser pulses is reduced to 10 μs (*i.e.* 100 kHz), where silver oxide and basic silver carbonate begin to be suppressed. This chemical information and trend would support the heating of the bulk and the smoothing or sintering of the roughness in Fig. 4. The dissociation of the chemical species could be understood by the systematic erasing of the chemicals by the following laser pulses and subsequent laser lines due the heating of the bulk in close proximity of the previously formed chemical compounds.

Referring back to Fig. 1, the different colours generated by the machined surface of silver are produced using a fixed laser repetition rate and by changing only the line spacing. Similarly, the same color palette is created when the line spacing is fixed to $L_s = 13 \mu\text{m}$ and the laser repetition rate is changed (horizontal and vertical white dashed lines, respectively). In contrast, the oxide and carbonate content of the colours obtained by changing the line spacing was not found to vary appreciably compared to those obtained by changing the laser repetition rate. The strong colour response to variations in line spacing, combined with a relatively consistent surface chemistry, suggests that the observed colours are not the result of thin-film interference effects or varying amounts of silver oxide or carbonate. Furthermore,

the colours produced using a repetition rate of 5 kHz and 400 kHz are both yellow in Hue, yet they have very different surface chemical composition, which suggests the colours to be morphological in nature. Additionally, SEM images of the coloured surfaces (see Fig. 4 and previous work [22,23]) consistently show the formation of nanoparticles on a roughened surface. The spectroscopic results, however, show that silver oxide and basic silver carbonate are present on these surfaces. The creation of these chemical species likely results from the ionization and ejection of charged particles through ambient air during laser ablation [50]. It is unlikely that all of the silver material ejected from the surface would be oxidized. Instead, a surface composed of regions of silver, as well as silver oxides and silver carbonates are to be expected. We cannot discount the possibility that the ejected material takes the form of core/shell nanoparticles, which is not uncommon to form during laser ablation [54,55]. For silver in particular, even more chemically-complex nanoparticles could be formed [49]. The nanoparticle model developed based on statistical measurements of the coloured surfaces [22,23] should include this new chemical information - a mixture of silver, silver oxide and silver carbonate nanoparticles should be considered. Additionally, the formation of chemical species on the nanostructured surface warrants further research within the context of plasmon-assisted photochemistry.

4. Conclusion

The colour response, morphology and chemistry of laser-machined bulk silver surfaces were observed to be dependent on the repetition rate of the marking laser. Incremental reduction in the repetition rate was observed to broaden the colour palette on silver covering the evasive and difficult-to-obtain green and cyan colours before completing a full 360° rotation on the colour wheel. For the same total accumulated fluence, analysis of the surface reveals significant differences in the nanostructures produced within the irradiated areas. The nanostructured surfaces are observed to become smoother with increasing laser repetition rate. The reduction of chemical species combined with smoothing of the surface suggests local temperatures in excess of 400 °C, which is enough to sinter the heat sensitive nanoparticles. Additionally, due to the full 360° rotation in colour, the presence of 2 distinct chemical signatures for the same colour supports the morphological nature of the colours.

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Disclosures

The authors declare no conflicts of interest.

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Conclusions

The use of ultrafast lasers for the plasmonic colouring of metal surfaces shows great promise for the fast machining and commercialization of plasmonic devices. The work in this thesis pioneered the understanding and the use of lasers for the creation of plasmonic coloured surfaces on metals. The objective of this thesis was to use our understanding of the plasmonic colours for the possible commercialization of a set of new collectible coins at the Royal Canadian Mint. The technology was presented at the World Money Fair in Germany. The technology and the application were developed internally by this group. The work in this thesis led to 17 prizes, 1 patent and many articles that have been published, or are still in the process of being written.

9.1 Summary and contributions

Recently an editorial article published in Nature Photonics[33], discussed the crashing hype of the plasmonic wave due to fabrication times that are currently incompatible with industry despite its great promise. The article discussed that only a few companies were spin-offs of plasmonic technology and that few others were selling plasmonic devices. The problem comes from the low production rate of making plasmonic surfaces, typically done

by lithographic methods. Chapter 4 presented *an alternate fast marking method for the plasmonic colouring of metal's surfaces using a picosecond laser*. The colouring method of raster scanning the surface of metals achieved production rates of up to $36 \text{ mm}^2\text{s}^{-1}$ which is more than compatible with industry requirements. Each Hue values were observed to be linked to a total accumulated fluence value. This process was observed to be universal for all plasmonic metals investigated to date. For each metal, a full colour palette was created. The analysis of the coloured surfaces showed the presence of a bi-modal distribution of nanoparticles unique to each colour. The FDTD simulation of the surfaces, using the statistical data, explained the role of each nanoparticle distribution and the plasmonic nature of the colours. The medium nanoparticles were found to be dominantly responsible for the colours while the small nanoparticles were found to create new resonances by acting as plasmonic waveguides. In the past, groups that have produced colours by fabricating nanostructures using lithography, have more than often used spraying methods to passivate their surfaces. For laser machining, however, surfaces have more than often been observed to be hydrophobic following laser exposure making these surfaces incompatible with spraying methods for the passivation of the surface. Furthermore, groups that have claimed passivation of their plasmonic surfaces never actually tested their passivation layers against aggressive environmental conditions. Chapter 5 presented *a novel multi-layer approach deposited by atomic layer deposition that is compatible with laser machined surfaces*. A new method of passivation based on atomic layer deposition was conceived. Due to the low temperature stability and melting point of nanoparticles, a low-density alumina layer was deposited by ALD at low temperatures. Aggressive environmental testing against the single low-density layer failed to conserve the integrity of the colours. A layer of 57 nm was observed to be necessary to appropriately protect the surfaces against environmental attacks requiring long deposition times that were incompatible with industry. Heat testing of the single layer, however, showed that the layer provided stability against long heat exposure. Thus, it was conceived that the low-density alumina layer could provide stability while another higher density alumina layer could be deposited at higher temperatures. This proved to be successful. The two-layer deposition approach was tested against the same aggressive environmental tests and passed with great success. Only 13 nm was required, at a fraction of the time, to protect the integrity of the colours. The two-layer approach was tried on a 5 kg coin showing the before and after colours. A reduction in colour quality was also visually observed. The plasmonic colours obtained by laser exposures

have thus far produced colour palettes with very low Chroma (i.e. saturation) compared to lithographic techniques. Chapter 6 presents *significant colour enhancement rivaling lithographic techniques using picosecond laser bursts*. The laser burst pulses are separated by 12.8 ns governed by the repetition rate of the oscillator. The energy distribution of each pulse within the laser burst could be controlled using FlexburstTM. The use of burst to create colours gave an increase of up to $\sim 100\%$ over the full colour palette compared to the nonburst colours. Analysis of the surfaces that for a given Hue the same nanoparticle statistics is obtained. The only difference between the burst and nonburst colours is the LIPSS structures formed, which are unique to the burst surfaces. TTM simulations of the burst interaction with the silver surfaces showed a significant increase in electron-phonon coupling, a metal property that is crucially important in the well formation of LIPSS structures. Different burst energy configurations were tried, with the same total energy, resulting in different underlying structures. The different structures were explained to come from the different pulse-to-pulse interaction with the surface leading to a different electron-phonon coupling coefficient. FDTD simulation of the HSFL and LSFL structures showed field enhancement caused by the crevices, explaining the observed enhancement in Chroma due to higher absorption. The surfaces have so far been used for visual decorative purposes. However, the potential commercialization power behind this rapid technique shouldn't be limited to decorative purposes. Chapter 7 presents *the potential use of the surfaces for possible sensing application*. A low-density film of varying thicknesses is placed on the surface of the colours. The layer of ALD film is observed to shift the colours and shows it has the potential to be used a colour tuning element. Interestingly, burst colours are observed to be recovered with increasing thickness of alumina while the nonburst colours did not. This observation, confirmed by FDTD simulations, is explained by the SPP supported by the LIPSS structures. The radiometric and colourimetric response of the coloured surfaces with increasing alumina thickness shows a colourimetric sensitivity of up to 3/nm and a radiometric sensitivity of up to 3.6 nm/nm making these surfaces potentially great sensors. Chapter 8 presents *the colour, chemistry and morphological dependence of the surface to the laser repetition rate*. The colour gamut is widened with decreasing laser repetition rate to encompass the elusive cyan and green colours. The chemical analysis of the coloured regions revealed the presence of silver oxides and silver carbonate within the coloured regions. The observation of identical colours with vastly different chemical composition suggests the nature of the colours to not be from the chemistry but from the morphology. Appendix A (article 1)

presents the *plasmon assisted photochemistry potential of the coloured surfaces*. A self-assembled monolayer of thiol was placed on the coloured surfaces. The exposure of the surfaces to visible light was observed to initiate chemical reactions and produce Ag₂S. A reaction that without the coloured surfaces would necessitate the use of UV light.

9.2 Suggestions and Future work

In Chapter 4, the colour palette produced on the surface of silver was observed to be limited in both the green and red regions due to their low Chroma values. A wider palette of green colours was observed using different polarization angles with respect to the machining direction. The effect of the angle should be further studied as a potential solution for the absence of vibrant green colours. For red, more vibrant colours were produced by the successive cross-hatching of the surface at various angles. Thus, the effect of polarization-machining angle and the number of passes should be further studied to understand their effect and to widen the colour palettes. In Chapter 6, SPP excitation by the presence of periodic topography (~ 1064 nm) was shown to occur in the green region (~ 532 nm). Tuning the underneath periodicity of the LIPSS by using different laser wavelengths could change the excitation wavelength of the SPP, resulting in more vivid colour in the green and red regions. This in fact, could explain the quasi-absence of vivid green colours on the surface of silver. Furthermore, colours produced using UV wavelength displayed colours that are unique to the laser wavelength. It would warrant further study at different laser wavelengths. In Chapter 4-8, the nanoparticles were assumed to be pure metals. The latest experimental results suggest that the nanoparticles could be core/shell nanoparticles where the shell structure is a thin oxide. This would make sense as the ablation of the surface is made in air. Hence, the theoretical modeling would need to be modified to consider this new reality. Additionally, since the core/shell structure would explain the visible assisted photochemistry observed on the coloured surface. It would be a good idea to try to control the thickness of the oxide shell by conducting ablation in controlled environment with specific gas mixtures. In Chapter 6, burst parameters are shown to produce enhanced colours due the simultaneous creation of LIPSS structures. The LIPSS and other structures were found to be dependent on the different burst energy distribution arrangements resulting in different electron-phonon coupling enhancement of the metal. These results were supported by TTM simulations of the metal-laser burst interaction. While the different types of surface structures could be used in different applications, TTM simulations should be done to find the optimal

electron-phonon coupling to create the best LIPSS and colours. Furthermore, colours on aluminum and gold were only observed to be possible with the use of burst. Hence, a systematic study on the use of burst and the creation of different structures should also be conducted on different metals. The creation of micro-spikes on different metals could be useful for making anti-bacterial surfaces. The creation of LIPSS on metals with low electron-phonon coupling could significantly increase their bio-compatibility. In Chapter 5, the multi-layer deposition process achieved the desired result of protecting the surfaces. However, the resulting colours, compared to the original, are not as aesthetically pleasing. The process consisted of depositing a first layer of alumina at 40°C followed by a deposition at 100°C . Experimental results showed that exposing the surfaces to 100°C for a certain period of time had detrimental effect on the colours. Therefore, a second layer at 80°C could be attempted instead. Moreover, a gradual increase in temperature could be tested to better conserve the colours. For example, increasing the temperature from 40°C to 100°C at a rate of $1^{\circ}\text{C}/\text{min}$. The slow increase in the density layer-by-layer could potentially result in better heat stability of the surface and protection of the colours against harsh environmental conditions. It would also be highly recommended that trials be done with lower refractive index material to diminish the effect of colour change by reducing the plasmon shift. Furthermore, the layering of different material could also be tried following the deposition of a pinning layer adding extra protection to the colours. In Chapter 7, silver was assessed as a potential sensor which can have different real-world applications. However, silver is not medically friendly but could be made so using an appropriate spacer between the surface and the biological specimen being sensed. Alternatively, our coloured gold surfaces could be good candidate for bio-sensing and should be investigated in future trials. On the same topic, the creation of blue and green should not exist given the d-transition of gold, therefore, a theoretical study based on the surface structures should be envisioned to explain their existence. In Chapter 8, the presence of silver oxides and silver carbonates within the coloured regions necessitates the revision of our model to incorporate these chemical species within the simulation. In Appendix A, plasmonic assisted photochemical reactions occurred on our coloured surfaces producing Ag_2S . While this is an interesting observation and is very promising, the surfaces should be used to produce targeted and more industrially interesting chemical reactions. Due to the universal nature of the colour process to other metals, plasmonic assisted reaction should also be tested using different coloured metal surfaces.

A

Co-authored publications



Visible light driven plasmonic photochemistry on nano-textured silver

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Plasmon assisted generation of silver sulfate from dodecanethiol is demonstrated on a nano-textured silver substrate with a strong surface plasmon resonance in the visible range. The observed photo-physical processes are attributed to hot charge carriers that are generated from the excitation of surface plasmon resonances using 532 nm laser light. Excited charge carriers are responsible for cleaving the alkane chain, and for generating reactive oxygen species which rapidly photooxidize the exposed sulfur atoms. The ability to drive photochemical reactions with photon energies in the visible range rather than in the UV, on nano-textured silver surfaces, will enable researchers to study photochemical transformations for a wide variety of applications. The strong optical absorbance across the visible range, combined with the fact that the substrates can be fabricated over large areas, naturally makes them candidates for solar driven photochemical applications, and for large scale plasmonic reactors.

Introduction

Our current understanding of surface plasmon resonances (SPR) on gold (Au) and silver (Ag), combined with the recent surge in realizing various noble metal nanostructures has generated interest in both academia and industry that is focussed on real-world applications. The type of metal, geometry, and surrounding environment all influence the wavelength which generates maximum excitation of SPR. The classic examples of size dependant plasmon resonances are nanoparticles in solution. The shift in resonance resulting from a change in refractive index at the surface has found considerable success when used for molecular detection on nano-textured metals.^{1–5}

More recently, plasmon assisted photochemistry on nano-textured metal surfaces has received considerable attention.^{6–12} On resonance, very strong electric fields are generated near nano-textured features, and even stronger fields have been reported in gaps between nanostructures.^{13–16} The metal regions where significant electric field enhancement occurs also contain an elevated density of excited charge carriers, which in turn can be used to drive photo-physical processes in adsorbed molecules. Charge transfer can occur *via* tunneling processes, where charge carriers are transferred to/from frontier orbitals

in the adsorbate. When considering charge transfer dynamics between metallic surfaces and molecules (*e.g.*, a metal–organic interface), self-assembled monolayers (SAM) of alkanethiols on highly conductive substrates represents a good model system. Scanning tunneling microscopy,^{17–19} and conducting probe force microscopy²⁰ experiments are usually performed to determine the position of the Fermi level in a metal relative to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).²¹ Although these measurements provide a consistent value for the HOMO–LUMO gap in alkanethiols, the position of the Fermi level remains under debate, and therefore it is unknown if tunneling processes are dominated by holes or electrons.

In this study, the formation of silver sulfate (Ag₂SO₄) *via* CW visible laser irradiation of a dodecanethiol (HS[CH₂]₁₀CH₃) layer on nano-textured Ag in air is reported. The surfaces are nano-textured using picosecond laser pulses, which generate spherical nanoparticles of varying sizes and SPR throughout the visible range. Previously, it was shown that by varying the fabrication parameters, many different colours could be produced on silver surfaces.²² In the past, photooxidation of dodecanethiol was observed in samples irradiated by UV photon energies,^{23–28} and significant progress has been made in connection with UV photo-patterning of alkanethiol monolayers for various biological and chemical applications.^{29–32} Here, we demonstrate that a 532 nm (2.33 eV) source producing an output power of 0.5 mW can drive the formation of sulfate species from an alkanethiol monolayer formed onto a nano-textured Ag surface that generates strong SPR in the visible. During laser irradiation, acquired Raman spectra clearly reveal the formation of R-SO₄^{2–} units,

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purported to be Ag_2SO_4 , consistent with other views.^{23,33,34} We conclude that hot carriers, efficiently generated within silver nanostructures near the surface due to strong coupling of the incident light to SPR modes thereon, are responsible for the observed photochemical transformations.

The demonstration that chemical reactions on large-area nano-textured silver surfaces can be driven by 0.5 mW of visible laser radiation represents a significant step towards realizing new photochemical reactors for potential industrial use. In this connection, catalytic oxidation reactions are of interest. Namely the partial oxidation of ethylene to form ethylene oxide. Furthermore, UV radiation can be hazardous to work with, and requires special optics and materials to perform experiments, driving up costs. The ability to photooxidize alkanethiols using visible light rather than UV light will now enable researchers to examine photooxidation and photo-patterning of thiols for a wide variety of biochemical applications.

Sample fabrication

High purity (99.99%) silver samples approximately 4 mm thick and 38 mm in diameter were obtained from the Royal Canadian Mint (Ottawa, Canada). Nanotexturing of the silver surfaces was recently reported, and a detailed account of the process is available in the literature.^{22,35} Briefly, we used a 15 W Duetto (Nd:YVO₄, Time-Bandwidth Product) mode-locked MOPA pulse-burst laser at the fundamental wavelength of 1064 nm, operating at a fixed frequency of 25 kHz. The time separation between each of the pulses contained within a burst is fixed at 12.8 ns. The energy distribution of each pulse contained within a burst was controlled using FlexBurst™. An F-theta lens ($f = 254$ mm, Rodenstock) was used to focus the light to a measured spot size of 28 μm . The spot size was determined from semilogarithmic plots of the modified regions as described in the literature.^{22,36} The samples were placed on a 3-axis translation stage with a resolution of 1 μm on each of the individual axis. Each sample was raster scanned in a top to bottom pattern using galvanometric mirrors (TurboScan, Raylaser) at a speed of 150 mm s^{-1} .

To modify the surfaces of the nano-textured silver, samples were immersed in a 2 mM solution of 1-dodecanethiol, $\text{HS}[\text{CH}_2]_{11}\text{CH}_3$, dissolved in IPA for 3 hours. To avoid the formation of multilayer alkanethiols at the surface, the sample was thoroughly washed by placing it in three separate IPA baths for 20 minutes each. After each immersion, the sample was agitated for approximately 2 minutes to allow un-reacted alkanethiol molecules to diffuse out into the IPA solution. All the experiments were carried out in glass (Pyrex) Petri dishes.

RAIRS and Raman measurement

Grazing angle IR measurements were performed on a Thermo Nicolet Nexus 870 FT-IR spectrometer with the incident light beam hitting the surface of the sample at 86° . Raman spectroscopic data was recorded using a WiTec Alpha a300 system in the backscattering configuration, at an incident wavelength of 532 nm, focused through a 20×0.4 N.A. objective. Photooxidation was initiated using an irradiance of 15 kW cm^{-2} in ambient conditions. During photooxidation, spectra were acquired using an integration time of 2 s, and 3 accumulations were averaged. Spectra were taken at 1 minute intervals for 60 minutes.

Results

The plasmonic nature of the substrate is readily seen in the images of Fig. 1. The topography and the structural colour generated by the surface are clearly observed in the bright-field microscope image of Fig. 1(a). The surface consists of nano-particle clusters scattered over underlying laser-induced periodic surface structures (LIPSS), as observed in the SEM image of Fig. 1(b), resulting in the generation of the blue/gold hues observed in Fig. 1(a) and its inset which shows a photograph of the surface as perceived by the naked eye. The measured reflectance spectrum covering the 300 to 800 nm range is plotted in Fig. 1(c), and shows that there is a significant increase in the amount of light absorbed in this range relative to bulk silver

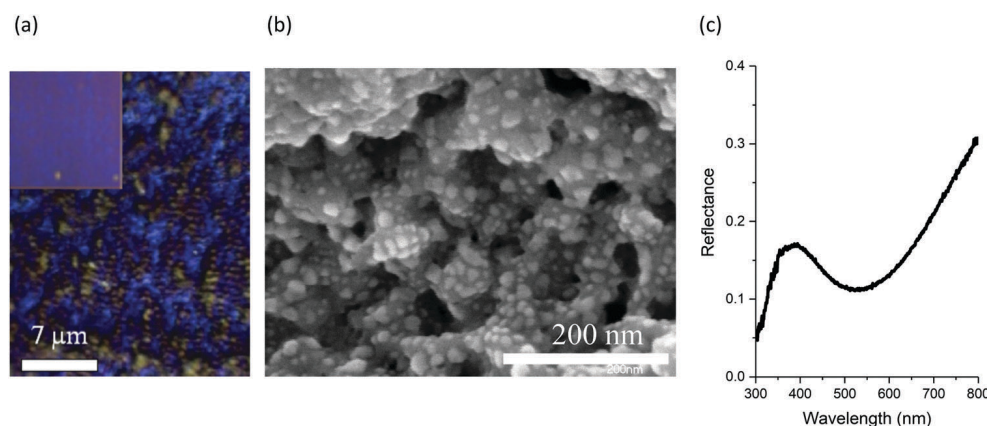


Fig. 1 (a) Nano-textured silver producing a blue hue due to plasmonic resonances that are excited in ambient light; image taken with a bright field microscope at $100\times$ magnification. The inset is a photograph of the surface as seen by the naked eye. (b) SEM image showing the highly topographical nature of the surface after the laser machining process. (c) Corresponding measured reflectance spectrum displaying a strong plasmonic resonance centred at ~ 530 nm. The peak in reflectance centred at ~ 400 nm is responsible for producing the blue hue perceived in (a).

which has near unity reflectance over the visible range. More importantly, the spectrum displays a maximum absorbance at ~ 530 nm, a peak in reflectance at ~ 400 nm, and a gradually increasing reflectance throughout the yellow and red regions of the visible spectrum. These features are consistent with the colours observed in Fig. 1(a). Moreover, the spectral line shape observed in Fig. 1(c) is indicative of a plasmonic resonance. The mechanisms responsible for rendering colours on similar surfaces has been discussed in detail previously.^{22,36} The most salient feature is the highly absorptive nature of this silver surface, where less than 25% reflectance is seen over the 400–800 nm range, with values decreasing to as low as 10% on resonance. Another interesting feature of these surfaces is the colour perceived by the naked eye does not depend on viewing angle.

To confirm the presence of dodecanethiol on the surface, a grazing angle IR absorbance spectrum was recorded and is shown in Fig. 2. A background spectrum was recorded from a coloured silver surface that was maintained under the same conditions. Emphasis was given to the 3050–2750 cm^{-1} spectral region, where the strongest IR absorbance bands in dodecanethiol occur and are associated with C–H stretching vibrations. The assignment of specific vibrational modes of various alkanethiols in this spectral region has been reported previously.^{37–40} There are nine vibrational modes that can potentially be observed, all corresponding to CH vibrations in the methylene chain and methyl headgroup. Spectral deconvolution of the data was performed to accurately determine the center frequency positions of the various peaks, and is also shown in Fig. 2. Center frequencies for the symmetric and asymmetric CH stretching vibrations in the methylene groups were assigned values of $\nu_s(\text{CH}_2) = 2848 \text{ cm}^{-1}$ and $\nu_a(\text{CH}_2) = 2917 \text{ cm}^{-1}$. Frequencies related to asymmetric CH vibrations of the methyl terminal headgroup were assigned values of $\nu_a(\text{CH}_3, \text{ip}) = 2963 \text{ cm}^{-1}$ and $\nu_a(\text{CH}_3, \text{op}) = 2955 \text{ cm}^{-1}$, where ip and op denote in-plane and

out-of-plane stretching vibrations.³⁸ The band related the symmetric CH stretching mode in the methyl group is actually split into two modes resulting from Fermi resonance interactions, commonly denoted as $\nu_s(\text{CH}_3, \text{FR})$, and have previously are observed at 2938 cm^{-1} and 2879 cm^{-1} in alkanethiol monolayers.^{37,38}

It is generally accepted that a well-defined SAM of *n*-alkanethiol chains on a flat surface will form a closely packed structure in the all-*trans* conformation with all of their alkyl chains forming a well-defined tilt angle, α , away from the surface normal as shown in inset of Fig. 2. The molecule can also be twisted along its molecular axis r' defined by the angle β . Previous works have shown that RAIRS can be used to estimate α on flat surfaces.⁴⁰ In RAIRS, a grazing angle of incidence is used, so the generated electric field is mostly perpendicular to the surface, and vibrational modes that have transition dipole moments parallel to the electric field are observed in IR spectra.⁴⁰ This forms a set of selection rules for molecules which have a preferential orientation. For the case of the *n*-alkyl thiols in the all-*trans* conformation, the transition dipole moment of the $\nu_s(\text{CH}_2)$ mode lies in the molecular plane, and is orthogonal to the molecular plane for an asymmetric stretch. The transition dipole moment for symmetric stretch in the methyl group, $\nu_s(\text{CH}_3)$, also lies in the molecular plane, oriented along the long axis of the molecule. Correspondingly, for $\alpha, \beta = 0^\circ$, only the symmetric CH vibrations in the methyl group would be seen, whereas for $\alpha = 90^\circ$ and $\beta = 0^\circ$, only the symmetric CH vibrations in the methylene groups would be observed. In general, the chain tilt and twist angles are determined by fitting experimental results to a model capable of simulating experimental spectra for various values of α and β . However, on nano-textured metal surfaces that enable resonant coupling into plasmonic modes, the electric field may be oriented along several directions depending on the local nanostructure. The high topography of the surface will also influence the local orientation of the molecule. In this connection, there is a breakdown of the selection rules described above and the spectrum plotted in Fig. 2 can be deconvolved into all possible observable modes. The excellent agreement between the measured IR absorbance frequencies and the frequencies reported in the literature for closely packed *n*-alkyl thiols not only confirms that dodecanethiol is present on the Ag surfaces, but also suggests that the alkyl chains favour a *trans* conformation.³⁷

Photooxidation of the dodecanethiol layer was initiated using an irradiance of 15 kW cm^{-2} (0.5 mW power) in a beam focussed through a 20 $\times$, 0.4 N.A. objective at a wavelength of 532 nm. The products of the reaction were monitored using Raman spectroscopy using the same laser. In contrast to previous works,^{23,41,42} Raman scattering signals from C–C stretching modes in the thiol layer were not resolvable. A coloured silver sample that did not undergo the thiolation procedure, was also measured for comparison. Unlike the coloured silver surfaces, smooth bulk silver does not support surface plasmonic resonances, and therefore surface enhanced Raman scattering (SERS) effects cannot be observed, making it very difficult to obtain a measurable signal from any type of species which may be on

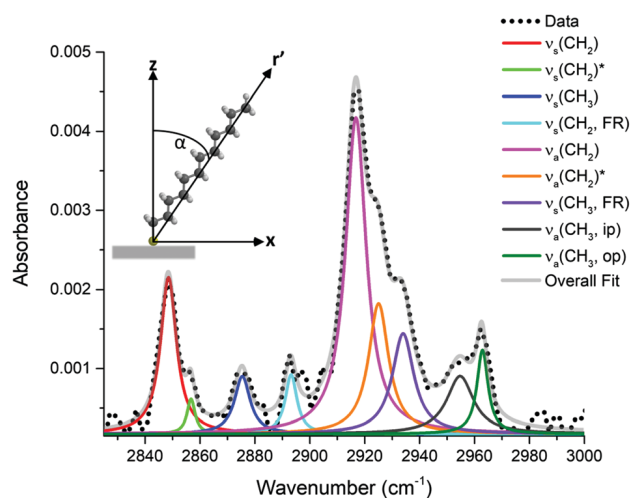


Fig. 2 Grazing angle IR absorbance spectrum of dodecanethiol, $\text{CH}_2(\text{CH})_{11}\text{S}/\text{Ag}$ (black dots), and a corresponding spectral deconvolution into various vibrational modes as shown in the legend and discussed in the text.

such a surface. In contrast, the plasmonic nature of the silver surface used in this study generates enhanced local electric fields^{22,36} which amplify Raman scattering intensities. In keeping with this, previous studies in which Raman spectroscopy was used to study UV induced photooxidation of alkanethiol monolayers required the use of roughened silver substrates.²³ It is also instructive to note that quantitative analysis of any products or reactants can be very difficult to achieve due to highly localized and variable field intensities, commonly referred to as hotspots throughout the literature. From a qualitative perspective, Raman scattering signals provide strong evidence for the presence for molecular species of interest.

Raman spectra from the two samples (with and without the thiol layer), after 3 s and 1 h of exposure to the 532 nm laser are plotted in Fig. 3(a) and (b), respectively. During the first acquisition, neither sample generated any detectable Raman

scattering signal. However, after 1 hour, clear spectral differences are seen between the samples. On surfaces where no dodecanethiol was present, a Raman spectrum that is relatively featureless is observed, whereas the irradiation of dodecanethiol on the coloured silver surface generates a spectrum containing high intensity narrowband lineshapes, and confirms that spectral differences result from the presence of the alkanethiol layer. Specifically, five new peaks centred at 470, 635, 711, 973, and 1190 cm^{-1} appear and are easily resolved in the spectrum, and represent the products of alkanethiol photooxidation that has taken place on the surface.^{23–28} Time evolution Raman spectra over the course of one hour were recorded every minute and are plotted in Fig. 3(c). For the purpose of clarity, twelve spectra are plotted over five-minute intervals. One can see that the photooxidation process begins within the first five minutes of exposure. The most intense feature appearing in the 975 cm^{-1} region is assigned to the symmetric stretch of a sulfate (SO_4^{2-}) ion.^{23,42} The peaks at 470, 635 and 1190 cm^{-1} are also assigned to Raman scattering from SO_4^{2-} , and follow the previous assignments in the literature.²³

Locally normalized Raman intensities as a function of time for the five peaks associated with scattering from sulphate species is shown in Fig. 4(a) for an incident power of 0.5 mW. All of the peaks essentially grow at the same rate, consistent with the assignment that they are all from the same surface species. The data were then fit to a single exponential, from which the rate was determined for each of the five peaks. The rates were then averaged to calculate a rate for a given incident power. This calculation was repeated for incident laser powers of 0.75, 1, 1.5, 2 and 2.5 mW and is plotted on a logarithmic scale in Fig. 4(b). The slope of this plots is ~ 1.5 and suggests a strong non-linear dependence on light intensity. Generally, for a chemical reaction whose rate depends on temperature, a strong non-linear dependence of this type is expected.⁴³ Both thermal and hot carrier induced processes can generate various power laws.

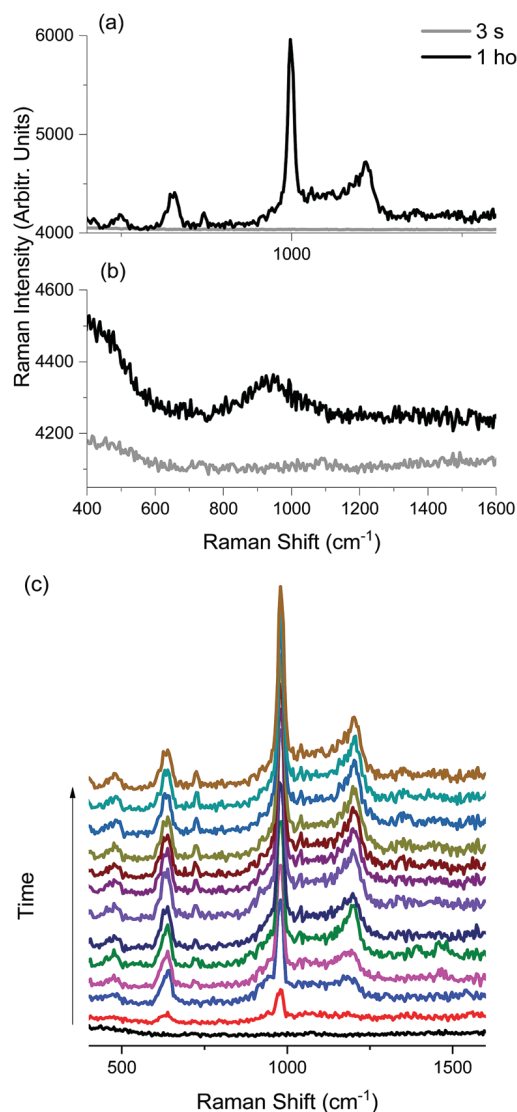


Fig. 3 Raman spectra after three seconds (grey traces) and 1 hour (black traces) of laser exposure from a silver surface with dodecanethiol (a) and without (b). Time evolution of the photooxidation process over the course of an hour (c).

Discussion

The observation of Raman scattering from sulfate species provides clear evidence that a chemical reaction takes place in areas which experienced laser irradiation, and suggests that the sulfur atom from the dodecanethiol layer remains bonded to the silver surface during the chemical transformation. This idea is supported by the fact that no evidence of any silver sulfate (Ag_2SO_4), silver sulfite (Ag_2SO_3) or silver sulfide (Ag_2S) was observed from surfaces which were not treated with dodecanethiol, and therefore the origin of sulfur was not from the surrounding environment. The lack of any signal from hydrocarbon units forming the tail end of the dodecanethiol molecule suggests that the molecule has been cleaved at the S–C bond. Cleaving of this bond has been previously reported in the literature^{23,41} for SAMs of alkanethiols illuminated using UV light (photon energies > 4.7 eV). It was proposed that photooxidation of alkanethiol species on silver under UV irradiation occurs *via* a two-step process.²³ First, C–S bond scission occurs

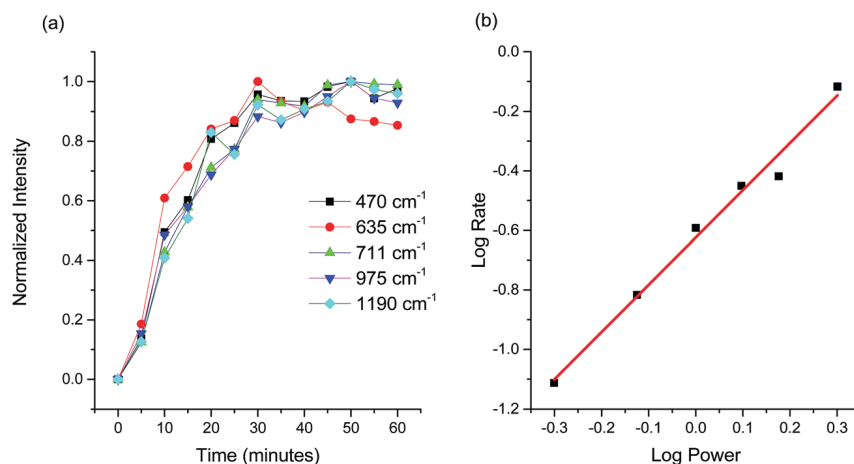


Fig. 4 (a) Locally normalized Raman scattering intensity as a function of time for each of the five peaks associated with Raman scattering from SO_4^{2-} units. (b) Average rate of reaction versus laser power on a logarithmic scale.

resulting in removal of the alkyl chain, after which oxidation of the exposed sulfur atoms proceeds. Expanding on this, another study has suggested that in addition to bond cleaving, a significant amount of alkylsulfonates were formed under UV excitation.²⁴ We did observe a contribution at 711 cm^{-1} from sulfite species, however since no scattering from units formatting the hydrocarbon were observed, this peak is tentatively assigned to Ag_2SO_3 . Correspondingly, we assign the rest of the spectrum to Raman scattering from Ag_2SO_4 .

Previous studies have attributed photooxidation of the S–C bond in alkanethiols on Ag to hot electron excitation.²³ In our study, the same chemical transformation is observed, but using a photon energy of only 2.33 eV. However, in contrast to previous literature on the subject, our surfaces consist of nano-textured silver supporting strongly localized plasmons in the visible, so care must be taken to understand their role in a photochemical reaction. Plasmonic excitations can decay non-radiatively by giving up their energy to carriers in the metal. These carriers can then be emitted into an adsorbate, thereby inducing a chemical reaction, or they can thermalize (heating of the lattice) with the resulting heat inducing a chemical reaction.

The silver surface used in this work exhibits a very strong optical absorbance in the visible which may lead to significant local heating of the sample surface. If indeed the observed chemical changes are driven by thermal effects, then identical chemical transformations should be observed when thermal energy only is supplied to the sample *via* resistive heating.⁶ The results of such an experiment indicate that this is not the case. A sample was placed on a heating stage and raised to various temperatures ranging from 40 to 160 °C in 30 °C increments. Raman spectra were acquired at each temperature after 40 minutes of heating. Up to temperatures of 130 °C, all recorded Raman spectra were featureless, showing no evidence of sulfur compounds. Subjecting the sample to elevated temperatures did however significantly alter its colour. No colour changes were observed when samples were irradiated with the laser. It is instructive to note however, that the onset of thermal damage

was found to occur when the irradiance was increased to $45\text{--}60\text{ kW cm}^{-2}$. Based on these observations, the energy supplied for the observed S–C bond cleavage and subsequent photooxidation of the exposed sulfur atom is not thermal. This is somewhat expected since the nano-textured Ag surface is effectively in direct contact with a relatively large high purity (99.99%) Ag substrate which has a very high thermal conductivity of $429\text{ W m}^{-1}\text{ K}^{-1}$.⁴⁴

Ruling out thermally-driven reactions, we now consider photochemistry involving charge carriers, specifically, what their role might be in cleaving the S–C bond in adsorbed dodecanethiol molecules. In understanding photochemistry on metal surfaces, the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the adsorbate molecule relative to the Fermi level of metallic surface is of central importance. In addition, if the metallic surface is nano-textured or consists of nanoparticles, then knowledge of LSPR frequencies and the corresponding enhancements in local electric field intensities are also required. Generally, when molecules adsorb onto metal surfaces, transition energies between the HOMO and LUMO level in the adsorbed molecule can be either blue- or red-shifted from their gas phase energies by as much as 1 eV. Lastly, these orbitals experience broadening when the metal–adsorbate complex forms and no longer consist of discrete energies. The HOMO–LUMO gap for adsorbed molecules on metal surfaces can be determined using scanning tunnelling microscopy (STM). In particular, the HOMO–LUMO gap for dodecanethiol has been reported to lie between ~ 7 to 8 eV.²¹ The Fermi level of Ag is 4.3 eV and lies between the HOMO and LUMO levels of the adsorbed molecule.

Although the experimentally-measured HOMO–LUMO gap energies appearing in the literature for alkanethiol monolayers on gold and silver are consistent, the position of the Fermi energy with respect to these orbitals remains an open question. For example, conducting-probe atomic force microscopy (CP-AFM) measurements have shown that higher work function metals, such as Pt, decrease the contact resistance, and therefore barrier heights to tunnelling, compared to Au and Ag. It was

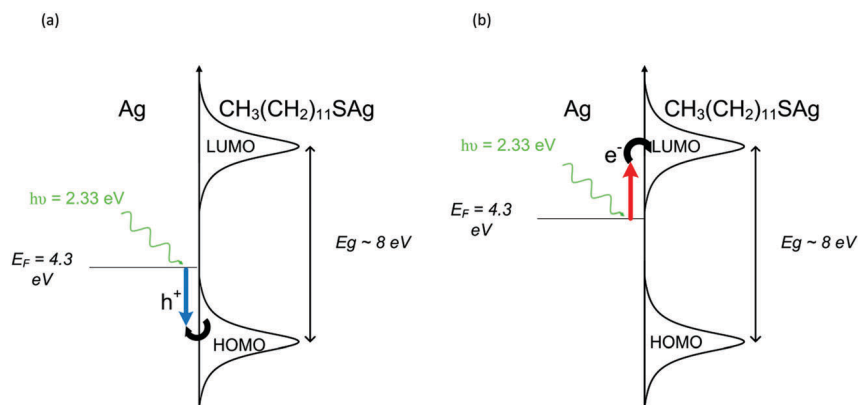


Fig. 5 Schematic of plasmon mediated charge transfer. Plasmons and photons with an energy of 2.33 eV generate hot holes (a) and hot electrons (b) over a range of energies. (a) Hot holes can capture electrons from occupied states (HOMO) in the molecule. (b) Excited electrons can tunnel into unoccupied electronic states in the molecule (LUMO). The direction of charge transfer in adsorbed dodecanethiol is unknown.

suggested that such trends are indicative that the Fermi level lies closer to the HOMO, and that charge transport is dominated by hole tunnelling.⁴⁵ On the other hand, the results of ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) experiments suggest that the main mechanism is electron tunneling and therefore the Fermi level is positioned closer to the LUMO.

When plasmons are excited on the surface of a metal, hot electrons and hot holes are created and become available to drive chemical reactions within the adsorbate. As shown in Fig. 5, excited carriers will be excited to a maximum energy of $h\nu$ above the Fermi level. Three mechanisms that lead to chemical transformations in adsorbed molecules are then possible: (i) a hot electron (Fig. 5a) can be excited from the Fermi level to the LUMO of the molecule. (ii) A hot hole (Fig. 5b) enables electron transfer to the metal from the HOMO of the adsorbate. These two scenarios are referred to as indirect adsorbate excitation, and generally require the corresponding frontier orbitals to lie near the Fermi level.⁶ (iii) The coupling of surface plasmon energy into electronic states in the molecule enabling direct transitions is also possible.^{7,8,43} In addition to this, an increasing number of reports are appearing in the literature discussing the effect of high intensity electric fields and increased charge-carrier yields.¹² Spaces between plasmonic nanostructures can generate higher intensity fields than on isolated nanoparticles and are thought to be areas of increased photochemical activity.

In our study, there are two reactions of interest. First, the cleaving of the S–C bond leading to the formation of silver sulfide, Ag_2S , followed by an oxidation reaction producing Ag_2SO_4 . Quantum chemical calculations using time domain density functional theory (TDDFT) provide values for allowed UV/Vis transitions of molecules adsorbed on Ag clusters,⁴⁶ allowing to determine if charge transfer is from the metal to the molecule or *vice versa* for a given reaction. For example, theoretical calculations have shown that visible light driven reactions involving ArNO_2 on Ag clusters are due to electron transfer from silver to the LUMO of ArNO_2 . On the other hand, it was also shown that electrons are transferred from the

HOMO levels in adsorbed ArNH_2 molecules to unoccupied levels in silver.⁴⁷ Unfortunately, a detailed TDDFT calculation to confirm the direction of charge transfer for each reaction step is beyond the scope of this work. The experimental results demonstrate that the entire reaction can be driven with photon energies of 2.33 eV, and therefore the energy separation between the Fermi energy and either the HOMO or LUMO must lie within this energy range for bond cleaving to proceed, as sketched in Fig. 5. It is unlikely that the HOMO–LUMO energy gap for dodecanethiol would be reduced by $\sim 5 \text{ eV}$ after adsorption, therefore direct excitation is ruled out. To our knowledge, this is the first demonstration of S–C bond scission in thiol molecules by visible light (532 nm radiation). The key to this reaction is a nano-textured Ag surface capable of strong absorption through SPR at visible wavelengths.

In addition to hot carriers, the reaction involving the oxidation of Ag_2S to Ag_2SO_4 requires the presence of oxygen species. From Fig. 4a, the Raman scattering intensity from sulfate species reaches a maximum after 20 minutes. Since an increase in reaction rate is observed as irradiance is increased, the limiting factor must be the concentration of hot carriers to drive the reaction forward and not molecular species in the surrounding environment. In previous works, alkanethiol oxidation on gold and silver surfaces in air, under UV excitation, required the presence of ozone (O_3).^{48,49} It has been suggested that UV excitation leads to decomposition of O_3 into O_2 molecules in the singlet state. Oxygen molecules in the singlet state are known to be highly reactive. Plasmonic decomposition of O_3 has not been reported previously, and to assign the observed plasmonic photooxidation to ozone decomposition is premature; carefully designed experiments where the environment is controlled are required. Furthermore, metal sulfide oxidation will readily proceed in aqueous conditions, and therefore water molecules in the surrounding environment, or hydrogen bonded to the surface may play a role.

From a fabrication standpoint, laser machining represents a high throughput process capable of patterning large areas and requires minimal fabrication steps. When considering industrial scale operations, these attributes are essential if

the technology is eventually going to scale-up. On the other hand, nanofabrication tools like electron beam lithography and focused ion beam milling can produce extremely well-defined structures at the nanoscale to support strong optical resonances in the visible range. This in turn would lower the power input requirement to initiate photooxidation. Self-assembled plasmonic silver structures with tunable resonances have also been realized,⁵⁰ and can be fabricated over large areas as well. Along these lines, the best fabrication tool for photochemical applications involving silver remains an open question and requires further investigation.

Conclusions

We demonstrated that plasmonic resonances in the visible can be used to drive photochemical reactions on nano-textured silver. Specifically, it was found that hot carriers in silver, of maximum excess energy of 2.33 eV (corresponding to irradiation with 532 nm light), are responsible for cleaving the S–C bond, and the subsequent desorption of alkyl chains, in adsorbed dodecanethiol. It is also proposed that hot carriers are responsible for the rapid oxidation of the exposed sulfur atom, however it is unclear if ozone decomposition plays a role. Photochemical transformations on plasmonic metal surfaces is a relatively new field. The large-area, easy to fabricate, nano-textured silver substrates capable of photochemical activity will enable researchers in many different fields to examine plasmon-assisted chemical processes in greater detail. In general, the ability to drive reactions with visible light instead of UV light (as used in past work, e.g., on dodecanethiol) is significant, as visible light is safer due to the lower photon energy involved, and inexpensively generated, detected and managed.

Conflicts of interest

There are no conflicts to declare.

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Glossary of Terms

AAO Anodize Alumina Oxide	LSPR Localized Surface Plasmon Resonance
ALD Atomic layer deposition	NIL Nano-Imprint Lithography
EBL Electron Beam Lithography	NP Nanoparticle
EDS Energy-dispersive X-ray spectroscopy	MIM Metal-Insulator-Metal
FDTD Finite-Difference Time-Domain	PMMA Poly(methyl methacrylate)
FESEM Field-Emission Scanning Electron Microscope	RCM Royal Canadian Mint
FIB Focused Ion Beam	RGB Red, Green, Blue
FLIPSS Femtosecond LIPSS	SEW Surface Electromagnetic Wave
IBL Ion Beam Lithography	SP Surface Plasmon
LCH Lightness, Chroma, Hue	SPP Surface Plasmon Polariton
LFSL Low Frequency Structure LIPSS	SPR Surface Plasmon Resonance
LIPSS Laser-induced periodic surface structures	TTM Two-temperature model
LSP Localized Surface Plasmon	WDS Wavelength-dispersive X-ray spectroscopy
LSPP Localized Surface Plasmon Polariton	XPS X-ray photoelectron spectroscopy

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