

Plasmonic Nano-Resonators and Fano Resonances for Sensing Applications

by

Akram Hajebifard

Thesis submitted to the University of Ottawa
in partial Fulfillment of the requirements for the
Doctor of Philosophy

Department of Physics
Faculty of Science
University of Ottawa

Abstract

Different types of plasmonic nanostructures are proposed and examined experimentally and theoretically, with a view towards sensing applications. First, a self-assembly approach was developed to create arrays of well-ordered glass-supported gold nanoparticles (AuNPs) with controllable particle size and inter-particle spacing. Then, a periodic array of gold nano-disks (AuNDs) supported by a Bragg reflector was proposed and examined in a search for Fano resonances in its optical response. Arrays of heptamer-arranged nanoholes (HNNH) in a thin gold film were also proposed and explored theoretically and experimentally, revealing a very rich spectrum of resonances, several exhibiting a Fano lineshape.

A commercial implementation of the vectorial finite element method (FEM) was used to model our plasmonic structures. Taking advantage of the periodic nature of the structures, a unit cell containing a single element was modelled. The transmittance, reflectance or absorbance spectra were computed, and the associated electromagnetic fields were obtained by solving the vector wave equations for the electromagnetic field vectors throughout the structures, subject to the applicable boundary conditions, and the applied source fields. The sensing performance of the structures, based on the bulk sensitivity, surface sensitivity and figure of merit (FOM) was calculated.

First, a novel bottom-up fabrication approach was applied (by our collaborators) to form a periodic array of AuNPs with controllable size over large areas on SiO₂ substrates. In this method, self-assembly of block copolymer micelles loaded with metal precursors was combined with a seeding growth route to create ordered AuNPs of desired size. It was shown that this new fabrication method offers a new approach to tune the AuNP size and edge-to-edge inter-particle spacing while preserving the AuNP ordering. The optical characteristics of the AuNP arrays, such as their size, interparticle spacing, localized surface plasmon resonance (LSPR) wavelength, and bulk sensitivity, were examined, numerically and experimentally. This proposed novel fabrication method is applicable for low-cost mass-production of large-area arrays of high-quality AuNPs on a substrate for sensing applications.

Then, we proposed and examined the formation of Fano resonances in a plasmonic-dielectric system consisting of uncoupled gold nano-disk (AuND) arrays on a quarter-wave dielectric stack. The mechanism behind the creation of Fano resonances was explained based on the coherent interference between the reflection of the Bragg stack and the LSPPs of the AuNDs. Fano parameters were obtained by fitting the computational data to the Fano formula. The bulk sensitivities and figure of merit of the Fano resonances were calculated. This plasmonic structure supports Fano resonances with a linewidth around 9 nm which is much narrower than the individual AuND LSPP bandwidth (~ 80 nm) and the Bragg stack bandwidth (~ 100 nm). Supporting Fano resonances with such a narrow linewidth, the structure has a great potential to be used for sensing applications. Also, this metallic-dielectric nanostructure requires no near-field coupling between AuNDs to generate the Fano resonances. So, the AuNDs can be located far enough from each other to simplify the potential fabrication process.

The optical properties of HNH arrays on an SiO_2 substrate were investigated, numerically and experimentally. Helium focused ion beam (HeFIB) milling was applied (by Dr. Choloong Hahn) to fabricate well-ordered and well-defined arrays of HNHs. Transmittance spectra of the structures were obtained as the optical response, which exhibits several Fano resonances. Then, the mechanism behind the formation of the Fano resonances was explained, and the sensing performance of the structure was inspected by measuring the bulk sensitivities. This array of nanohole cluster is exciting because it supports propagating SPPs and LSPPs, and also Wood's anomaly waves, which makes the optical response very rich in excitations and spectral features. Also, as a periodic array of sub-wavelength metallic nanoholes, the system produces extraordinary optical transmission - highly enhanced transmission through (otherwise) opaque metallic films at specific wavelengths, facilitating measurement acquisition in transmission.

Acknowledgements

First and foremost, I would like to thank my dear supervisors, Prof. Pierre Berini, for all his patient guidance, support and encouragement. He is likely the most positive person I will ever meet. He has always been understanding and supportive during the entire time working with him. I am incredibly grateful for all that I have learned so much from him during my PhD study.

I would also like to appreciate Dr. Choloong Hahn, the post-doctoral fellow in Berini's group at the University of Ottawa, who fabricated my samples and assisted me in experimental measurements. I have always appreciated his patience, willingness and help.

I am also grateful to my dear colleagues in Berini's group, specifically to Saba Siadat, who is one of my best friends and colleagues. She is kind of person you can always rely on, whenever you need help.

I would like to express my gratitude to my Dad and especially to my Mom, who I lost during my PhD, for their emotional support and continues encouragement. I also thank for heart-warming kindness from my sisters and brothers.

I owe thanks to a special person, my beloved husband, Yasser, for all his support and care. I thank him for being in my life and for making my life full of joy. I thank my dear daughter, Sama, for all her warm hugs and kisses, for all beauty she has brought to my life, and for being such a good girl always cheering me up. I consider myself the luckiest in the world to have such a lovely and caring family, standing beside me with their love and unconditional support.

Table of Contents

Abstract.....	ii
Acknowledgements	iv
List of Figures.....	vii
1. Introduction.....	1
2. Literature review	8
Surface plasmon	8
A. Propagating surface plasmon	9
B. Localized surface plasmon	11
Principle of Plasmonic Sensors	14
Plasmonic Nanostructures	17
A. Single Nanoparticles/Nanoholes	19
B. Nanoparticle/ Nanoholes Aggregates	22
C. Arrays of Nanoparticles/Nanoholes	24
Nanofabrication methods.....	25
A. Top-down nanofabrication techniques	25
a. Patterning techniques in resist.....	25
b. Resist-free patterning techniques	33
B. Bottom-up nanofabrication	35
a. Atomic layer deposition	35
b. Self-assembly	37
c. Sol–gel nanofabrication.....	38
Fano resonance.....	39
A. History of Fano resonance.....	40
B. Origin of Fano resonance	41
a. Single oscillator.....	41
b. Two coupled oscillators	43
C. Plasmonic Fano resonance	46
a. Symmetry-broken geometries	47
b. Periodic array of nanostructures.....	49

c. NP near a metallic surface.....	50
d. Nanostructure clusters	52
e. Nanoparticles on reflecting dielectric	59
2. Ordered gold nanoparticle arrays on glass and their characterization.....	60
A. Summary	60
B. Contribution	60
C. Article.....	60
3. Plasmonic Fano interference produced by gold nano-disks on a dielectric Bragg stack.....	71
A. Summary	71
B. Contribution	71
C. Article.....	71
D. Correction.....	Error! Bookmark not defined.
4. Fano resonances in gold heptamer nano-hole arrays	80
A. Summary	80
B. Contribution	80
C. Article.....	80
5. Helium focused ion beam direct milling of plasmonic heptamer-arranged nanohole (HNH) arrays.....	96
A. Summary	96
B. Contribution	96
C. Article.....	96
6. Optical response and Fano resonances in arrays of plasmonic heptamer-arranged nanoholes	104
A. Summary	104
B. Contribution	104
C. Article.....	104
7. Conclusions and future work.....	121
A. Concluding remarks	121
B. Future work	124
References.....	126

List of Figures

FIGURE 1 (A) SURFACE PLASMON POLARITONS PROPAGATION AT THE METAL-DIELECTRIC INTERFACE [2] (B) DISPERSION CURVE OF PROPAGATING SP AND INCIDENT LIGHT [4] NATIONAL TSING HUA UNIVERSITY - MANLAB COPYRIGHT @ 2006 MANLAB RIGHT RESERVED.....	2
FIGURE 2 THE LSPR WAVELENGTH VS REFRACTIVE INDEX OF THE SURROUNDING MEDIUM OF THE GOLD NPS, BASED ON THE DRUDE MODEL.....	3
FIGURE 3 (A) SCHEMATIC REPRESENTATION OF AN ELECTRON DENSITY WAVE PROPAGATING ALONG A METAL-DIELECTRIC INTERFACE, AND (B) DISPERSION CURVE OF SURFACE PLASMON POLARITONS AND INCIDENT LIGHT. (NATIONAL TSING HUA UNIVERSITY - MANLAB COPYRIGHT @ 2006 MANLAB RIGHT RESERVED).....	10
FIGURE 4(A) SPP EXCITATION BY GRATING COUPLER AND (B) THE EXTRA WAVE MOMENTUM IS PROVIDED BY THE GRATING. (NATIONAL TSING HUA UNIVERSITY - MANLAB COPYRIGHT @ 2006 MANLAB RIGHT RESERVED).....	10
FIGURE 5 (A) OTTO CONFIGURATION, (B) KRETSCHMANN CONFIGURATION OF AN ATTENUATED TOTAL REFLECTION SETUP FOR COUPLING SURFACE PLASMONS. (C) THE EXTRA WAVE MOMENTUM IS PROVIDED BY THE PRISM TO COMPENSATE MOMENTUM MISMATCH BETWEEN SPP AND INCIDENT PHOTONS.. (NATIONAL TSING HUA UNIVERSITY - MANLAB COPYRIGHT @ 2006 MANLAB RIGHT RESERVED).....	11
FIGURE 6 CALCULATED EXTINCTION (BLACK), ABSORPTION (RED), AND SCATTERING (BLUE) SPECTRA OF SILVER NANOPARTICLES WITH DIFFERENT SHAPES. (A) AN ISOTROPIC SPHERE HAS A SINGLE RESONANCE PEAK. (B) ANISOTROPIC CUBES, (C) TETRAHEDRA, AND (D) OCTAHEDRA HAVE MULTIPLE, RED-SHIFTED RESONANCE PEAKS. (E) THE RESONANCE WAVELENGTH OF A HOLLOW SPHERE RED-SHIFTS RESPECT TO A SOLID SPHERE, (F) AND IT EVEN MORE RED-SHIFT FOR THINNER SHELL WALLS [51].....	20
FIGURE 7 EXTINCTION (BLACK), ABSORPTION (RED), AND SCATTERING (BLUE) SPECTRA OF SILVER (A) TRIANGULAR PLATE AND (B) CIRCULAR DISC AND (C, D) NANORINGS OF TWO DIFFERENT THICKNESSES [51].....	21
FIGURE 8 EXTINCTION SPECTRA OF GOLD NAN SPHERES OF INCREASING RADIUS R IN WATER, COMPUTED WITH THE MIE THEORY [6].....	22
FIGURE 9 (A) E-FIELD ENHANCEMENT OF SILVER NANOPARTICLE MONOMERS WITH A TRIANGULAR PRISM AND A RECTANGULAR ROD SHAPE. THE ARROWS SHOW THE MAXIMUM OF THE E-FIELD [55]. E-FIELD ENHANCEMENT OF A (B) DIMER OF AG NANOPARTICLES SEPARATED BY 2 NM, AT ITS RESONANCE WAVELENGTHS (430NM AND 520NM), (C) A “TIP-TO-TIP” PRISM DIMER AT ITS RESONANCE WAVELENGTHS (550NM AND 932NM), (D) “TIP-TO-SIDE” PRISM DIMER AT ITS RESONANCE WAVELENGTHS (653NM AND 852NM) .IN THE 3D PLOTS, THE AXIS PERPENDICULAR TO THE SELECTED PLANE REPRESENTS THE AMOUNT OF E-FIELD ENHANCEMENT AROUND THE DIMER.	23
FIGURE 10 (A) SEM IMAGES OF SELF-ASSEMBLED GOLD NANOPARTICLE CHAINS CONSISTING OF 1 TO 6 PARTICLES. MEAN DIAMETER OF GOLD PARTICLES IS 64 NM, AND THE INTER-PARTICLE GAP IS ~ 1 NM. SCALE BAR IS 250 NM. (B) NORMALIZED SCATTERING INTENSITY OF THE NANOPARTICLE CHAINS CONSISTING OF 1 TO 6 PARTICLES. SPECTRA ARE NUMERICALLY LABELED ACCORDING TO THE CHAIN LENGTH.....	24

FIGURE 11 SCHEMATICS OF THREE MAIN METHODS USED FOR NANOFABRICATION (A) A METAL LAYER IS DEPOSITED BEFORE THE NANOPATTERNING STEP, WHICH IS FOLLOWED BY EITHER A WET OR DRY ETCHING. (B) NANOPATTERNING STEP IS FOLLOWED BY METAL DEPOSITION, WHICH IS FOLLOWED BY THE FORMATION OF METALLIC NANOFEATURES THROUGH LIFT-OFF PROCESS. (C) FABRICATION OF NHs ARRAY IN A SUSPENDED MEMBRANE, MOSTLY IN Si_3N_4 , IS DONE THROUGH A COMBINATION OF PHOTOLITHOGRAPHY AND WET CHEMICAL ETCHING OF Si , FOLLOWED BY NANOPATTERNING AND METAL DEPOSITION STEPS [64].	26
FIGURE 12 EXAMPLE OF (A) ISOTROPIC AND (B) IDEAL ANISOTROPIC ETCHING: ILLUSTRATING THE EVOLUTION OF SIDEWALL. HTTPS://LINK.SPRINGER.COM/CONTENT/PDF/10.1007%2F978-0-387-48998-8_751.PDF	27
FIGURE 13 SCHEMATICS OF LIFT-OFF PROCESS STEPS: (A) SUBSTRATE PREPARATION (B) DEPOSITION OF THE RESIST LAYER (C) PATTERNING THE RESIST TO CREATE (D) AN INVERSE PATTERN (E) METAL DEPOSITION (F) WASHING OUT THE UNWANTED AREA FROM THE SUBSTRATE.	28
FIGURE 14 SCHEMATIC ILLUSTRATION OF RESIST/METAL BILAYER LIFT-OFF PROCESS. HERE, AL HAS BEEN USED AS THE METAL IN THE RESIST/METAL BILAYER (A) ELECTRON BEAM RESIST OR PHOTORESIST, AND THE AL LAYER IS PREPARED ON A SUBSTRATE. (B) RESIST IS PATTERNED BY ELECTRON BEAM OR PHOTOLITHOGRAPHY, THEN DEVELOPED. (C) FORMATION OF UNDER-CUT IN THE WET ETCHING OF THE AL LAYER (D) METAL DEPOSITION (E) RESIST LIFT-OFF. (F) REMOVAL OF RESIDUAL AL.	28
FIGURE 15 SUSPENDED PLASMONIC NANO HOLE ARRAYS ARE FABRICATED USING A LITHOGRAPHY PROCESS CONSISTING OF: (A) PATTERNING OF THE FREESTANDING Si_3N_4 MEMBRANE FOLLOWED BY RIE ETCHING, (B) OXYGEN PLASMA CLEANING OF THE SURFACE FOLLOWED BY METAL DEPOSITION. (C_D) SEM IMAGES OF THE FABRICATED NANOHOLES ARRAY (IN DIFFERENT ANGLES). HOLES DIAMETER AND PERIODICITY IS 200 NM AND 600 NM, RESPECTIVELY [71]	29
FIGURE 16 SCHEMATIC OF PHOTOLITHOGRAPHY STEPS, IN GENERAL,	30
FIGURE 17 (A) THE GENERAL SCHEME OF THE TWO-BEAM AND FOUR-BEAM TRANSMISSION-DIFFRACTION IL METHOD TO PRODUCE LINE AND HOLE/DOT PATTERNS, RESPECTIVELY [76]. (B) (TOP PANEL) SCHEMATIC OF DIFFERENT CONFIGURATIONS FOR MULTIPLE-BEAM INTERFERENCE LITHOGRAPHY AND SEM IMAGES EXHIBIT THE CORRESPONDING EXPOSURES IN PHOTORESIST [77].	31
FIGURE 18 SCHEMATIC OF E-BEAM LITHOGRAPHY PROCESS. (SEM IMAGE ON THE BOTTOM LEFT IS THE ARRAY OF GOLD NANORODS DEPOSITED ON A GLASS SUBSTRATE) [79].	32
FIGURE 19 SCHEMATIC OF NANOIMPRINT LITHOGRAPHY PROCESS OF (A) THERMAL NIL, (B) UV-CURABLE NIL [86]	33
FIGURE 20 COMPARISON BETWEEN (A) CONVENTIONAL FIB MILLING TECHNIQUE AND (B) “SKETCH AND PEEL”-BASED FIB MILLING PROCESS, TO FABRICATE A PLASMONIC NANOPARTICLE. (A) IN THE CONVENTIONAL METHOD, A LARGE AREA OF THE METAL FILM SHOULD BE MILLED TO OBTAIN AN ISOLATED PARTICLE. (B) IN “SKETCH AND PEEL” APPROACH, ONLY A NARROW AREA NEEDS TO BE MILLED FOLLOWED BY SELECTIVELY PEELING OFF THE MAJORITY OF THE METAL FILM TO CREATE AN ISOLATED PARTICLE.	34
FIGURE 21 (TOP PANEL) SCHEMATIC FOR THE FABRICATION OF AG NANOWELL ARRAYS WITH A GEOMETRIC GRADIENT, USING THE COLLOIDAL LITHOGRAPHY COMBINED WITH AN INCLINED RIE PROCESS. (BOTTOM PANEL)	

THE SEM IMAGES OF THE PS MICROSPHERE MASKS ON DIFFERENT POSITIONS ALONG THE SUBSTRATE. (THE SCALE BARS FOR SEM IMAGES ARE 1MM) [91].	35
FIGURE 22 SCHEMATIC ILLUSTRATION OF ONE ALD CYCLE OF THE TMA/H ₂ O PROCESS. STEP 1: THE FIRST REACTANT A (TMA) REACTS IN A SELF-TERMINATING WAY WITH THE AVAILABLE FUNCTIONAL GROUPS ON THE OH-TERMINATED SURFACE. STEP 2: THE EXCESS OF REACTANT A (TMA) AND THE GASEOUS BY-PRODUCTS (CH ₄) ARE PURGED OR PUMPED AWAY. 3. STEP 3: THE SECOND REACTANT B (H ₂ O) REACTS IN A SELF-TERMINATING WAY WITH THE ADSORBED SPECIES (A) ON THE SURFACE. 4. STEP 4: THE EXCESS OF REACTANT B (H ₂ O) AND THE GASEOUS BY-PRODUCTS (CH ₄) ARE PURGED OR PUMPED AWAY	36
FIGURE 23 SCHEMATIC OF THE FABRICATION PROCESS OF Au NPs/NANOGAP/Au NPs STRUCTURE WHICH CONSIST OF ALD TECHNIQUE (I) GOLD FILM IS DEPOSITED ON THE SUBSTRATE, USING SPUTTERING (II) Au NPs ARE FABRICATED USING RTA PROCESS; (III) VERY THIN Al ₂ O ₃ LAYER IS FORMED ON Au NPs VIA ALD PROCESS; (IV, V) SECOND THIN Au FILM IS DEPOSITED ON THE Al ₂ O ₃ COATED Au NPs, THEN RTA PROCESS IS USED TO FORM A STRUCTURE OF AuNPs/Al ₂ O ₃ /AuNPs; (VI) Al ₂ O ₃ IS PARTIALLY ETCHED TO CREATE THE FINAL AuNPs/NANOGAP/AuNPs STRUCTURE [92].	37
FIGURE 24 TO ASSEMBLE THE CLUSTERS, NANOSHELLS IN AQUEOUS SOLUTION IS PLACED ON A HYDROPHOBIC SUBSTRATE AND EVAPORATED [98].	38
FIGURE 25 A SCHEMATIC ILLUSTRATION OF THE LINE SHAPE OF A FANO RESONANCE FOR VARIOUS Q-PARAMETER [107].	40
FIGURE 26 (A) THE RESONANT LINE SHAPE OF THE AMPLITUDE FOR THE SINGLE OSCILLATOR. THE DRIVEN FREQUENCY IS IN UNITS OF THE NATURAL FREQUENCY OF THE OSCILLATOR, ω/ω_0 . (B) THE PHASE JUMPS BY π WHEN THE FREQUENCY PASSES THROUGH THE RESONANCE.	42
FIGURE 27 (A) SCHEMATIC VIEW OF TWO COUPLED OSCILLATORS WITH A DRIVING FORCE APPLIED TO THE FIRST ONE. THE RESONANT BEHAVIOUR OF THE AMPLITUDE OF THE (B) FIRST OSCILLATOR AND (D) SECOND OSCILLATOR IN TWO COUPLED OSCILLATOR SYSTEM; WHERE THE FREQUENCY IS IN UNITS OF THE NATURAL FREQUENCY, ω/ω_0 . THERE IS A ZERO- AMPLITUDE AT $\omega_{ZERO}=\omega_2 = 1.2$ FOR THE FIRST OSCILLATOR, WHICH CAUSES THAT THIS OSCILLATOR EXPERIENCES AN ASYMMETRIC LINESHAPE NEAR $\omega=1.21$. THE PHASE BEHAVIOUR OF THE (C) FIRST OSCILLATOR AND (E) SECOND OSCILLATOR AMPLITUDE HAVE BEEN PROVIDED, AS WELL [10].	46
FIGURE 28 EXTINCTION SPECTRA FOR AG CENTRIC RING/DISK CAVITY (DASHED LINES) AND AG NONCONCENTRIC RING/DISK CAVITY (SOLID LINES) [129].	48
FIGURE 29 (A) SKETCH OF AN ALIGNED AND A TILTED NANOANTENNA DIMER. (B) EXPERIMENTAL EXTINCTION SPECTRA OF THE DIMERS FOR DIFFERENT TILTING ANGLE, Δ . (C) SEM IMAGES OF DIMERS FOR VARIOUS TILTING ANGLES 0° (i), 70° (ii), 80° (iii), AND 90° (iv) (SINGLE ANTENNA SIZES: LENGTH $L = 160$ NM, WIDTH $w = 80$ NM, HEIGHT $H = 60$ NM, AND INTERPARTICLE GAP IS 5 NM) [130].	48
FIGURE 30 (A) EXTINCTION SPECTRA OF A SINGLE ISOLATED NP (GREEN LINE) AND A PARTICLE IN A 480 NM SQUARE LATTICE (BLUE LINE). THE NPs ARE SILVER DISKS WITH A DIAMETER OF 120 NM AND A HEIGHT OF 30 NM	

EMBEDDED IN A HOMOGENEOUS MEDIUM ($n = 1.515$). (B) EXTINCTION SPECTRA OF 50 NM SILVER NPs ARRAY OF 400 PARTICLES WITH INTERPARTICLE SPACING (PERIODICITY) RANGING FROM 200 TO 700NM. THE ISOLATED PARTICLE SPECTRUM IS INCLUDED FOR REFERENCE; IT IS EVIDENT THAT SLR IS PROFOUND FOR SPECIFIC PERIODICITY, WHICH IS AT $P=500\text{nm}$, IN THIS CASE [131].	49
FIGURE 31 (A) SCHEMATIC OF AN ARRAY OF NANOHOLE ON SiO_2 SUBSTRATE (B) SEM IMAGE OF THE ARRAY (C) FDTD AND EXPERIMENTAL TRANSMISSION SPECTRA FOR $n_{\text{III}} = 1.29$ (n_{III} IS THE REFRACTIVE INDEX OF THE SUPERSTRATE). THIS STRUCTURE SUPPORTS SEVERAL FANO-SHAPE RESONANCES ORIGINATING DUE TO THE COUPLING OF SPR OR LSPR AND THE LIGHT DIRECTLY TRANSMITTED THROUGH THE HOLES [137].	50
FIGURE 32 (A) SCHEMATIC OF THE COUPLED SYSTEM OF AUNPs ON A 50-NM-THICK AU FILM WITH A 6-NM-THICK SiO_2 SPACER. (B) SEM IMAGES OF AN ARRAY OF AUNPs WITH A PERIODICITY OF 300 NM AND DIAMETERS OF 110 NM (C) EVOLUTION OF EXTINCTION SPECTRA FOR A VARIOUS INCIDENT ANGLE OF ILLUMINATION FOR TE ILLUMINATION [140].	51
FIGURE 33 (A) SCHEMATIC OF THE NANO SHELL-METALLIC FILM INTERACTION WITH A DIFFERENT ASPECT RATIO (A/B). THE BLACK CURVES SHOW THE ABSORPTION SPECTRUM RESULTING FROM THE PLASMONIC INTERACTION BETWEEN THE NANOSHELL AND THE FILM.	52
FIGURE 34 FANO RESONANCES IN PLASMONIC NANOPARTICLE CLUSTERS. (A) CALCULATED DIPOLE AMPLITUDES OF THE BONDING AND ANTIBONDING PLASMON MODES IN A GOLD NANOSHELL HEPTAMER[98]. (B) MEASURED AND (C) CALCULATED SCATTERING SPECTRA OF A GOLD NANOSHELL HEPTAMER [98]. (D) SEM IMAGES OF THE FABRICATED GOLD NANODISK HEPTAMER. (TOP) VIEW OF THE SAMPLE, (BOTTOM) ENLARGED VIEWS OF THE SAMPLE AT A TILTING ANGLE OF 70° . (E) AND (F) TRANSMISSION SPECTRA ARE SHOWING THAT THE HEPTAMER SUPPORTS A PROFOUND FANO RESONANCE FOR SMALL INTERPARTICLE DISTANCES [98].	54
FIGURE 35 CALCULATED EXTINCTION SPECTRA FOR DIFFERENT OLIGOMERS OF SILVER NANOSPHERES (A) SHOWING THE FORMATION OF FANO FEATURE WHEN THE OLIGOMER IS A HEPTAMER (B) ILLUSTRATING THAT BY CHANGING THE SIZE OF THE CENTRAL HOLE, THE OLIGOMER CAN SUPPORT A FANO RESONANCE. ALL PERIPHERAL PARTICLES HAVE $R = 50\text{ nm}$, AND THEIR INTERPARTICLE GAPS ARE 5 NM. THE RADIUS OF THE CENTRAL PARTICLE IS VARYING IN THE RIGHT PANEL TO LET THE CLUSTER HAVE A ZERO NET DIPOLE MOMENT FOR ANTIBONDING MODE, AND THEN SUPPORT A FANO RESONANCE.	55
FIGURE 36 EXTINCTION SPECTRA OF THE AG HEPTAMER OLIGOMER FOR SURROUNDING MEDIA WITH DIFFERENT DIELECTRIC PERMITTIVITY. THE HEPTAMER IS COMPOSED OF AG SPHERE WITH RADIUS = 50 NM AND AN INTERPARTICLE GAP OF 5 NM. THE GLASS SUBSTRATE HAS A PERMITTIVITY OF 2.09.	56
FIGURE 37 (A) SCHEMATIC OF THE OLIGOMER STRUCTURE CONSISTING OF A DIPOLE ANTENNA (YELLOW) AND TWO NANORODS (BLUE). THE ANTENNA HAS AN ARM LENGTH OF 70 NM AND A GAP $D=25\text{nm}$, AND THE OTHER HAS AN ARM WITH A LENGTH OF $L = 120\text{ nm}$. THE WHOLE SYSTEM IS MADE OUT OF GOLD. (B) SIE SIMULATION (SOLID RED LINE) AND ECO MODEL FIT (BLACK DASHED LINE) OF THE SCATTERING SPECTRUM FOR A STRUCTURE. (C-G) THE REAL PART OF THE NORMAL COMPONENT OF THE ELECTRIC FIELD AT SOME WAVELENGTHS ILLUSTRATED IN PANEL B [143].	57

FIGURE 38 SCATTERING SPECTRUM OF THE SYSTEM (SHOWN IN FIGURE 37 (A)) (A) DARK-FIELD EXPERIMENTAL MEASUREMENTS, (B) SIE SIMULATIONS, (C) ECO MODEL SIMULATION, AND (D) SEM IMAGES OF GEOMETRIES WITH NANORODS LENGTH $L = 120\text{nm}$ AND VARYING ANTENNA GAP SIZE FROM 5 TO 50 NM (SCALE BAR IS 100 NM).	57
FIGURE 39 (A) SCHEMATIC OF A QUADRUMER NANO HOLE CLUSTER IN A GOLD FILM. (B) SCATTERING SPECTRA OF THE CLUSTER AS A FUNCTION OF (B) HOLE DIAMETER D (FOR $S = 6\text{ nm}$ AND $H = 30\text{ nm}$), (C) GOLD FILM THICKNESS H (FOR $D = 100\text{ nm}$ AND $S = 30\text{ nm}$), AND (C) INTER HOLE DISTANCE S (FOR $D = 100\text{ nm}$ AND $H = 6\text{ nm}$). A Y-POLARIZED NORMAL INCIDENCE FIELD ILLUMINATES THE WHOLE SYSTEM. DASHED LINES INDICATE THE POSITIONS OF THE DARK MODES (BLACK) AND BRIGHT MODES (BRICK RED).	58
FIGURE 40 (A) SCHEMATIC OF GOLD NANODISKS ON GLASS SHOWING FANO INTERFERENCE DUE TO THE INTERACTION BETWEEN LOCALIZED PLASMONS AND AN INTERFACE REFLECTION. (B) SEM IMAGE OF GOLD NANODISKS ON GLASS (C) SCHEMATIC OF THE EXPERIMENTAL MEASUREMENT CONFIGURATION. (D-G) REFLECTANCE SPECTRA FOR VARIOUS INCIDENT ANGLES. THE ASYMMETRIC LINE-SHAPES IS SEEN FOR ANGLES CLOSE TO THE CRITICAL ANGLE OF THE GLASS_AIR INTERFACE, $\theta_c = 41.1^\circ$. DOTTED LINES CORRESPOND TO EXPERIMENTAL DATA, AND SOLID LINES ARE THE FANO FORMULA FITS [151].	59

AcronymsCases

ALD : Atomic layer deposition.....	46
AuND : Gold nano-disk	2
AuNP : Gold nanoparticle.....	2
CCO : Conventional coupled oscillator	66
CL : Colloidal lithography	45
CRDC : Concentric ring/disk cavity	57
EBL : Electron beam lithography	38
ECO : Extended coupled oscillator.....	66
EOT : Extraordinary optical transmission	19
FDTD : Finite-difference time-domain.....	60
FEM : Finite element method	2
FIB : Focused ion beam	15
FOM : Figure of merit.....	2
fwhm : full width at half-maximum.....	23
HeFIB : Helium focused ion beam	3
HNH : Heptamer-arranged nanohole	2
HSQ : Hydrogen silsesquioxane	42
LSPR : Localized surface plasmon resonance	2
NCRDC : Nonconcentric ring/disk cavity	57
NIL : Nanoimprint lithography	43
NIR : Near-infrared.....	20
NP : Nanoparticle.....	14
PMMA : Polymethyl methacrylate	42
PR : Photo-resist	40
RI : Refractive index	17
RIE : Reactive-ion etching.....	38
RIU : Refractive index unit.....	64
RTA : Rapid thermal annealing	46
SERS : Surface-enhanced Raman scattering	24
SIE : Surface integral equation	66

SLR : Surface lattice resonance	35
SP : Surface plasmon	20
SPP : Surface plasmon polariton.....	13
SPR : Surface plasmon resonance.....	20
TM : Transverse magnetic	13
TMA : Trimethylaluminium	46
WA : Wood's anomaly	17

1. Introduction

Plasma oscillations of conduction electron gas on the surface of a metallic structure can couple to incident light and form coupled excitations called surface plasmon polaritons (SPPs). SPPs are usually categorized into two main groups, propagating surface plasmon polaritons and localized surface plasmon polariton (LSPP). Propagating SPPs are (transverse magnetic) TM-polarized waves propagating along a metal-dielectric interface [1]. As illustrated in Figure 1(a), the SPP fields peak at the metal-dielectric interface and decays exponentially away. The properties of propagating SPPs can be derived using Maxwell's equations, which eventually results in obtaining the wave number, k , of the propagating SPP as follows [2]:

$$k = \frac{\omega}{c_0} \left(\frac{\epsilon_r \epsilon_d}{\epsilon_r + \epsilon_d} \right)^{\frac{1}{2}} \quad (1)$$

where ϵ_d is the relative permittivity of the dielectric, ω is the optical frequency, c_0 is the speed of light in free space, and ϵ_r is the real part of the relative permittivity of the metal. Based on the Drude model [3], ϵ_r can be expressed as:

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

where ω_p is the plasma frequency, and γ is the damping parameter of the bulk metal. For visible and near-infrared light, $\gamma \ll \omega_p$, so the above is often simplified to:

$$\epsilon_r = 1 - \frac{\omega_p^2}{\omega^2} \quad (3)$$

Inserting equation (3) in equation (1), the dispersion curve of the propagating SPP can be plotted, as shown in Figure 1 (b). At low frequencies, the SPP behaves like a free space photon, but as frequency increases, the dispersion curve moves increasingly to the right of the light line, and k reaches an asymptotic limit at the "surface plasma frequency", $\omega_{sp} = \frac{\omega_p}{\sqrt{2}}$ [4]

.Since the dispersion curve bends to the right of the light line, the SPP has a larger momentum than the incident light, which means it cannot be excited by directly incident light. Usually, a prism or a grating coupler is used to add extra k (momentum) to the incident light. Using

these mechanisms, the momentum mismatch is compensated, and light can couple into the propagating SPPs, which travel along the dielectric-metal interface [1].

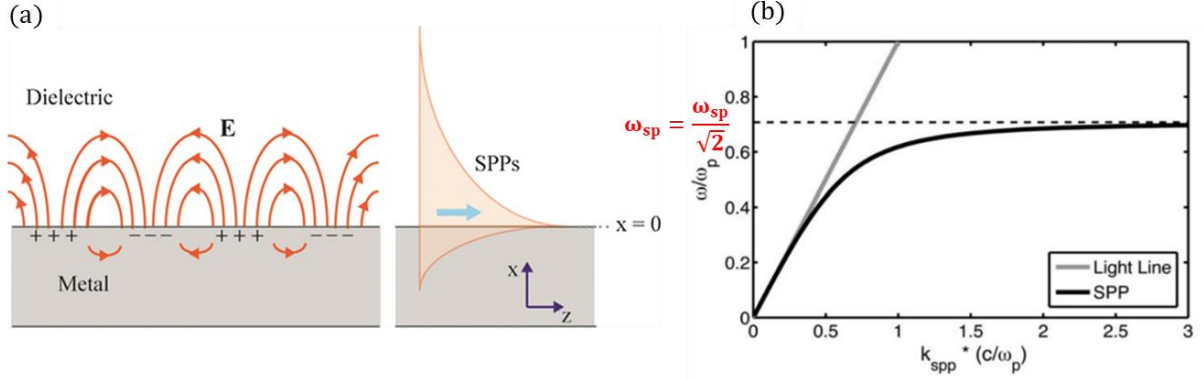


Figure 1 (a) Surface plasmon polaritons propagation at the metal-dielectric interface [2] (b) Dispersion curve of propagating SP and incident light [5]

Unlike propagating SPP, LSPPs are resonant modes localized to the vicinity of metal nanoparticles (NPs) of dimensions much smaller than the excitation wavelength [6]. LSPPs have two key characteristics: First, they generally have strong field enhancement near the particle surface, being greatest at the surface, and rapidly decaying away. Secondly, the optical response of a noble metal NP exhibits a resonance within the visible spectral range. The resonant characteristics of LSPPs depend on the refractive index of the surrounding dielectric medium, which is the basis for sensing applications. This dependency can be determined using Mie theory [7], which expresses the dipole polarizability, α , of a spherical metallic NP as:

$$\alpha = 3\epsilon_0 V \frac{(\epsilon_r - \epsilon_d)}{(\epsilon_r + 2\epsilon_d)} \quad (4)$$

where V is the NP volume, ϵ_0 is the permittivity of free space, ϵ_d is the relative permittivity of the surrounding dielectric, and ϵ_r is the real part of the relative permittivity of the metal. The resonant wavelength of the LSPP is determined occur when the denominator of equation (4) is zero, that is, when:

$$\epsilon_r = -2\epsilon_d \quad (5)$$

This is the condition for which the dipole polarizability of the NP and its optical response (scattering) will be maximized. For instance, for gold NPs in water, the LSPP resonance occurs

at ~ 520 nm [8]. To find the LSPR wavelength as a function of the dielectric constant of the surrounding medium, one can combine equation (5) with equation (3) resulting in:

$$\omega_{\max} = \frac{\omega_p}{\sqrt{2\varepsilon_d + 1}} \quad (6)$$

which can be rewritten as:

$$\lambda_{\max} = \lambda_p \sqrt{2n_d^2 + 1} \quad (7)$$

where $\lambda_{\max}$ is the LSPR wavelength, and λ_p is the wavelength corresponding to the bulk plasma frequency. Based on equation (7), the LSPR wavelength is linearly related to the refractive index of the surrounding medium, as illustrated in Figure 2 for gold NPs. This is the basis for sensing applications using plasmonic NPs. The resonant wavelength and the linewidth of LSPR can be tuned by changing geometrical parameters of the NPs such as the size and shape. The recent improvement in the imaging and fabrication of nano-sized structures led to fabricating and engineering plasmonic nanostructures, which support LSPs with strong field enhancement, sharp resonances and high sensitivity to the surrounding environment, suitable for sensing applications.

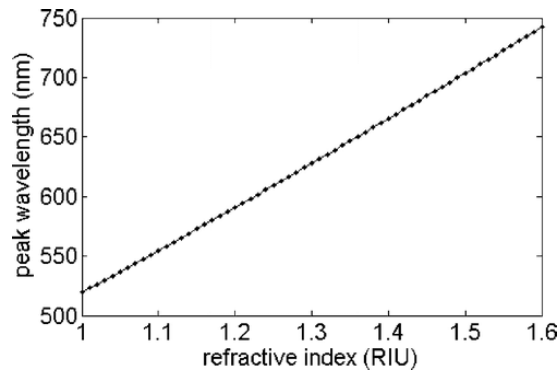


Figure 2 The LSPR wavelength vs refractive index of the surrounding medium of the gold NPs, based on the Drude model.

Nanofabrication methods can be categorized into two main approaches: Top-down and Bottom-up. In the former, a piece of the base material is gradually selectively eroded and miniaturized to the nanoscale until the desired structure is produced. Focused ion beam (FIB) milling is a conventional method used in this category. FIB milling is a resist-free, maskless nanofabrication technique which uses high energy focused ion beams to directly mill nanoscale

patterns on the desired substrate [9]. This technique is widely used for milling well-defined nanoholes in metallic films, with high resolution. He^+ ion beams have recently been used to create holes with diameter as small as 5 nm in a 100 nm thick gold film [10].

In the bottom-up approaches, atoms or molecules are self-assembled to form the desired nanostructure. Unlike top-down approaches, which typically require expensive tools and are time-consuming, bottom-up methods are more suitable for low-cost mass-manufacturing. They can be used for fabricating large-area arrays of well-ordered and high-quality nanoparticles on a substrate. The fabrication approach is selected based on the materials involved in the structure, fabrication costs, and target applications. For instance, for bio-sensing applications, it is critical to engineer structures which support excitations with high field enhancement ("hot spots") to increase the interaction of electromagnetic fields with the sensing material. Some plasmonic nanostructures, which support Fano resonances in their response can provide high field enhancement in the structure, suitable for sensing applications.

Fano resonances in plasmonic systems have an asymmetric line shape with unique characteristics such as a narrow linewidth, nanometer-scale field confinement, high field enhancement, and also high sensitivity to changes in the local dielectric medium. The physical origin of Fano resonances can be understood using a simple system of coupled damped oscillators in which one oscillator is driven by an external force [11]. In this classical model, the coupling between oscillators results in the formation of an asymmetric Fano-shape resonance in the motion of one oscillator. This simple model of coupled oscillators could be extended to any system exhibiting a Fano feature. For instance, the origin of the Fano feature in some nanoplasmonic structures is explained based on the coupling and interaction of subradiant and superradiant modes of the structure. Superradiant modes, which are spectrally broad, can directly and easily couple to incident light. They are broadband because of radiative damping [12]. Conversely, subradiant modes, which are spectrally narrower [12, 13], cannot be directly excited by incident light. However, they are excited via the coupling interaction with superradiant modes. This interaction leads to far-field interference between scattering by the modes, which results in a Fano feature due to constructive and destructive interference. This phenomenon, which is manifested by a maximum adjacent to a minimum in an optical spectral

response, is the key factor in the formation of the asymmetric line shape of a Fano resonance. Due to the typically narrow line shape and high field enhancement of Fano resonances, a new family of plasmonic structures has been designed [14, 15].

One of these families consists of a cluster of nanostructures. When NPs are close-packed in a cluster, their plasmons can couple through near-field interaction, forming a new set of hybridized LSPPs. Heptamer arrangements of nanoholes (HNH) in a metal film, organized in a periodic array are a very promising structure in this regard. Such an array of nanohole clusters produces a complex spectral response due to supporting various excitations, including LSPPs in the vicinity of holes, propagating SPPs along the metal surfaces, and Wood's anomaly (WA) waves. The Fano features in this structure arise due to the interference between light directly transmitted through the holes, and light indirectly scattered through the various plasmon excitations. HNH arrays can be considered for use as a biosensor allowing for a high degree of multiplexing, parallel optical detection, and the ability to integrate microfluidics [31–34].

NPs on a reflecting dielectric is another promising geometry supporting Fano resonances. In this kind of system, the Fano resonance arises due to interaction between the dipolar LSPPs of the NPs and the "white" continuum caused by the dielectric reflection. The main advantage of this structure is that no near-field coupling between NPs is required for the generation of Fano resonances. Then, the NPs can be placed far enough from each other to facilitate and simplify fabrication. The array of nanodisks (NDs) on a Bragg reflector is interesting in this regard because the linewidth and the Fano resonance wavelength can be tuned by altering the thickness and refractive index (RI) of the alternating layers in the Bragg stack, in addition to other tuning parameters such as the thickness and diameter of the NDs.

Thesis scope and outline

This thesis aims to provide a deeper understanding of plasmonic nanostructures supporting SPPs and LSPPs, and their coupling to form Fano resonances. Theoretical and experimental studies are conducted to design, optically characterize and evaluate several proposed metallic nano-arrays with a view toward sensing applications. The finite element method (FEM) is widely used throughout this thesis for the design and simulation work. The thesis consists of a collection of scientific articles; each presented as a chapter. The remainder of this document is organized as follows:

In chapter 3, a novel approach has been developed in which we create ordered gold nanoparticle (NP) arrays of controllable size over large areas on solid SiO₂ substrates. In this method, self-assembly of block copolymer micelles loaded with metal precursors is combined with a growth technique to create ordered gold nanoparticles of suitable size. A journal article co-authored with Jie Yuan on the fabrication of gold nanoparticles using this self-assembly approach was published. We show that this fabrication method offers a new approach to tune the AuNP size and edge-to-edge inter-particle spacing while preserving AuNP ordering. The properties of AuNP arrays on glass, including their size, interparticle spacing, LSPP wavelength, and bulk sensitivity, were fully characterized. Theoretical study and numerical simulations were carried out to determine the size and pattern of NP arrays and predict the LSPR peak. E-beam lithography or focused ion beam milling is commonly used to fabricate metallic nanostructures, but these are costly and time-consuming nanofabrication methods. The proposed fabrication technique is suitable for low-cost mass-manufacturing of large-area arrays of well-ordered and high-quality AuNPs on a substrate for biosensor or other applications.

In chapter 4, we examine the generation of Fano interferences in a system consisting of a periodic array of uncoupled gold nano-disks (AuNDs) supported by a Bragg stack. It is shown that the Fano resonance could arise due to coherent interference between the reflection spectrum of the Bragg stack and the scattering from LSPPs on the AuNDs. The Fano parameters of the resonance were deduced by fitting the computational data to the Fano formula. The sensitivity of the structure was investigated by calculating bulk sensitivities and the figure of merit of Fano resonances. A critical advantage of the proposed architecture is that

the linewidth of its Fano resonances is ~ 9 nm which is much narrower than the individual nano-disk LSPR bandwidth ~ 80 nm and the Bragg stack bandwidth ~ 100 nm. This makes the structure potentially attractive for sensing applications. In most plasmonic structures, the Fano resonance is due to strong near-field coupling between elements of the structure when the interparticle gap is minimal, which poses fabrication and application challenges. However, in this proposed structure no near-field coupling between particles is needed to generate the Fano resonances. So, the AuNDs can be spread far enough from each other to facilitate fabrication.

In Chapters 5, 6, and 7, we investigate the optical response of periodic arrays of heptamer-arranged nanoholes (HNH) in a Au film on a SiO_2 substrate. We explain in detail how Helium (He) focused ion beam (HeFIB) milling is used to fabricate these plasmonic HNH arrays. The optical and plasmonic responses of this structure are investigated numerically and experimentally. We describe the mechanism behind the formation of Fano resonances in such structures, and we examine its application to biosensors. A journal article co-authored with Choloong Hahn on the fabrication of plasmonic HNH arrays using a HeFIB direct milling process is presented in chapter 5, explaining in detail how HeFIB direct milling has been applied to create well-ordered and well-defined arrays of nanoholes in a heptamer arrangement. This complementary plasmonic structure - nanohole clusters - is attractive due to its potential to support both propagating SPPs and LSPPs, and also Wood's anomaly waves, which makes its optical response very rich in resonances. Also, the array of sub-wavelength metallic nanoholes can support extraordinary optical transmission (EOT), which provides enhanced transmission through (normally) opaque metallic films. It makes it convenient to observe transmittance spectra for data acquisition.

A Conclusion and future work are provided finally in Chapter 6.

2. Literature review

Surface plasmon

Valence electrons in metal solids form a high-density electron gas which moves freely (with scattering) about the positively charged ionic lattice [16]. This free electron gas can oscillate collectively, resulting in plasma oscillations or plasmons [17]. Surface plasmons (SPs) are plasma oscillations at the interface between a metal and dielectric.

Surface plasmon resonance (SPR) is the resonant oscillation of free electrons at the metal-dielectric interface stimulated by incident light. The surface plasmon polariton (SPP) is a non-radiative transverse-magnetic (TM) electromagnetic surface wave that propagates parallel to the metal-dielectric interface. Unlike the radiative mode, k_{spp} for the non-radiative SPP mode is higher than the momentum of the incident light, so it cannot decay into photons in general [18].

For SPPs to exist, the metal should have a negative real part of the permittivity, and its magnitude must be greater than the permittivity of the dielectric. This condition is met in the infrared-visible wavelength region for some metals such as Au, Ag, Cu, and Al [19]. Gold is one of the most popular plasmonic metals due to its superior chemical stability under ambient conditions, and an abundant amount of free electrons, and then supporting SPPs in near-infrared (NIR) spectral range [20].

The volume plasmon frequency ω_p is given by:

$$\omega_p = \left(\frac{4\pi N e^2}{\epsilon_{\infty} m^*} \right)^{1/2} \quad (8)$$

where e and m^* are the charge and the effective mass of carriers, respectively, N is the density of carriers (electrons or holes), and ϵ_{∞} is the permittivity of the metal at high frequency ($\omega \gg$

ω_p). For noble metals such as gold or silver, the carriers are electrons and N ranges from 10^{22} to 10^{23} cm^{-3} which results in supporting plasmon resonance wavelength in the NIR and visible spectral regions. For doped semiconductors, the typical value of N is 10^{16} – 10^{21} cm^{-3} which locates the plasmon wavelength in the THz and NIR region. The plasmon wavelength of

semiconductors can be tuned over a wide range by changing the doping density (density of impurities introduced into an intrinsic semiconductor for the purpose of modifying its electrical, optical or structural properties).

SPPs hold promise in many new technology areas such as nanophotonics, biosensing, and integrated optical circuits. Also, SPPs offer useful and interesting characteristics, such as subwavelength confinement, field enhancement, high surface and bulk sensitivities, and field localizations [21]. SPPs are often categorized into two main groups: propagating or delocalized surface plasmon polaritons (propagating SPPs), and localized surface plasmon polaritons (LSPPs) [22]. When excited by light, the induced surface plasmons can propagate along the surface of the bulk metal-dielectric interface as propagating SPPs. The oscillating charges can also be confined and enhanced on the surface of a nanoparticle, in which case it is termed LSPPs.

A. Propagating surface plasmon

Propagating SPPs are waves along a metal-dielectric interface. This surface wave is a transverse magnetic (TM)-polarized wave considered as a coupled excitation of a charge density wave in the metal and electromagnetic fields that peak at metal-dielectric interfaces and decay exponentially away, as illustrated in Figure 3(a). This wave propagates along the interface until its energy is lost, either absorbed in the materials or scattered away.

SPPs have larger momenta than the incident light. Thus, the light cone of incident light can't intersect with the dispersion curve of SPP (*i.e.*, the two don't possess the same k_x component for the same frequency), as illustrated in Figure 3(b). This momentum mismatch results in forbidden excitation of SPPs by free incident waves. Also, for the same reason, a propagating SPP along a smooth metal-dielectric interface cannot emit energy as a free-space photon into a uniform dielectric.

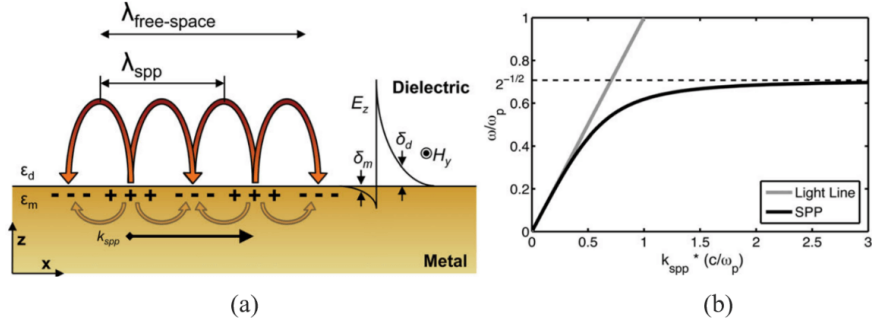


Figure 3 (a) Schematic representation of an electron density wave propagating along a metal-dielectric interface, and (b) Dispersion curve of Surface plasmon polaritons and incident light [4].

To overcome this problem, the mismatch in momentum should be compensated through a mechanism which can add an extra k_x component to the incident light. This process can be done using a coupling medium such as a prism or a grating. A grating coupler can provide an extra parallel momentum ($G = 2n\pi/p$) related to its grating period, as shown in Figure 4(a), where n is an integer and p is the periodicity. This extra momentum is added to the light cone to shift and intersect with the dispersion curve of the SPP, as illustrated in Figure 4(b). So, simply creating some defects such as a groove, a slit or a corrugation on the planar surface can play the role of a grating coupler by which free-space photons and SPPs can couple and exchange energy.

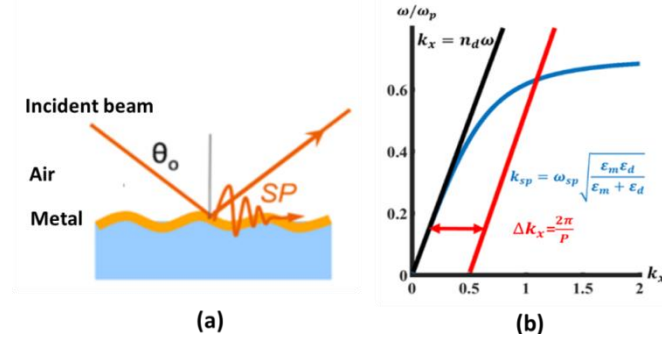


Figure 4(a) SPP Excitation by Grating Coupler and (b) The extra wave momentum is provided by the grating [4].

Another way of matching the momentum of the incoming beam to that of the plasmon is prism coupling, which is commonly used in two well-known configurations, Kretschmann or Otto configuration, schematically shown in Figure 5. In both configurations, a thin metallic film is illuminated in total internal reflection through a prism. So, the parallel component of the

incident light momentum, shown as k_x in Figure 5(b), is increased and then compensates the free-space/SPPs momentum mismatch. So, the propagating SPs are excited on the metal-air interface through the evanescent-wave coupling. In the **Otto configuration**, the metal film and the prism surface are positioned close enough to each other so that the evanescent wave can reach and interact with the surface and hence excite the SPPs [23]. In the **Kretschmann configuration**, the metal film is deposited onto the prism base. So, the evanescent wave directly tunnels through the metal film to interact with the opposite surface and excite SPPs at the metal/air interface [24]. This configuration is used in most practical applications [23].

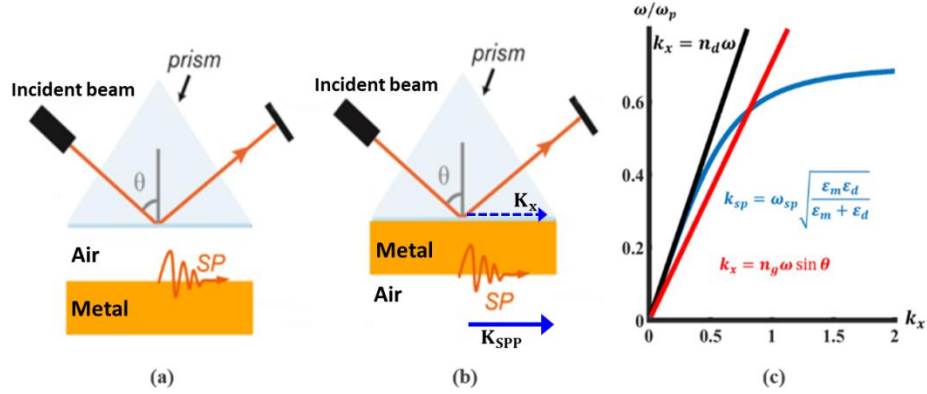


Figure 5 (a) Otto configuration, (b) Kretschmann configuration of an Attenuated Total Reflection setup for coupling surface plasmons. (c) The extra wave momentum is provided by the prism to compensate momentum mismatch between SPP and incident photons [4].

In both configurations, the excitation of propagating SPPs is revealed as the appearance of a dip in the reflectance spectrum, for a fixed angle of incidence. The spectral width of this dip is typically ~ 50 nm full width at half-maximum (FWHM) for Au films [25], and it is accompanied by an apparent phase change near the minimum of the resonance for the reflected light. Due to the high sensitivity of SPR to change in the refractive index (RI) of the bounding dielectric medium, SPR has a critical role in the development of biosensing methods [26].

B. Localized surface plasmon

Localized surface plasmon polaritons (LSPPs) are collective free electron charge oscillations in metallic nanoparticles, which are excited by the incident light. For a small metallic nanosphere surrounded by air, the incident electromagnetic field induces a dipole moment p , whose magnitude is proportional to the amplitude of the applied electric field ($|E_0|$). So the

polarizability of the particle, α , defined as $p = \alpha E_0$ can be derived in the quasistatic approach, in which the size of the particles is less than the wavelength of the incident light [27]:

$$\alpha = 4\pi\epsilon_0 a^3 \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} \quad (9)$$

Here a is the radius of the sphere and $\epsilon(\omega)$ is the dielectric constant of the particle, which is frequency-dependent. When the denominator of equation (9) approaches zero, a dramatic increase in the polarizability, α , occurs, which is the condition for the excitation of an LSPP.

Hence, the spectral position of the LSPP can be anticipated from the condition $\text{Re}[\epsilon(\omega)] = -2$. This condition is met in the infrared-visible wavelength region for some metals such as Au, Ag, Cu, and Al [19].

There is a remarkable near-field enhancement at the LSPP wavelength, which is highly localized at the nanoparticle surface and decays rapidly away from the nanoparticle/dielectric interface into the dielectric medium. Far-field scattering by the particle is also enhanced at the resonant wavelength. One of the advantages of LSPPs with respect to propagating SPPs is that the momentum matching condition does not apply. Also, strong enhancement of LSPP, in a subwavelength localized region, has made it suitable for various applications, such as refractive index (RI) measurement [28], fluorescence enhancement [29, 30], surface-enhanced Raman scattering (SERS) [31, 32], biomolecular interaction detection [33], and so on. The LSPP wavelength is controlled by the free electron density (N), and by the nanostructure shape, dimensions, and bounding medium. Nanostructures implemented in the plasmonic metals gold, silver and copper have corresponding LSPPs in the visible and near-infrared regions [34]. LSPRs excitation is not fundamentally limited to metals, as it can occur in semiconductors or conductive metal oxides [35] with appropriate free carrier densities. Free carrier concentrations of semiconductors for nanoplasmonics can be tuned by doping, temperature, and/or phase transitions, which allow LSPP tailoring [36]. However, the LSPP response of a metal nanostructure can only be engineered by the choice of nanostructure and its parameters, such as shape, size, dimensions or metal type. Promising structures [37] include the ring, disk and hole, in which the resonance can be tuned into the near-infrared spectral region by altering the width of the disk or ring, for instance.

Plasmonic nanostructures could be engineered to support new kind of resonance, called Fano resonances, for instance by symmetry breaking. Fano resonances usually have asymmetric line shapes with a narrow linewidth, and exhibit intense field enhancement and subwavelength localized fields. So, types of nanostructures which support Fano resonances are very promising to be used as plasmonic sensors.

Principle of Plasmonic Sensors

Nano-plasmonic based structures are considered promising for the development of biological and chemical sensors for label-free detection, multi-analyte sensing and point-of-care applications [38-40]. These kinds of biosensors work based on the sensitivity of SPPs or LSPPs to near-surface refractive index (RI) changes [39, 41, 42]. Due to the subwavelength field confinement and intense field enhancement associated with these excitations at the metal/dielectric interface, plasmonic resonances depend strongly on the environment of the system.

Plasmonic sensors work based on two primary configurations: the Kretschmann (prism-coupling) configuration or the grating coupling configuration [43-45]. In general, the grating coupling configuration may be more suitable than the Kretschmann one, because the latter requires bulky instrumentation, which prevents developing miniaturized sensor devices for lab-on-a-chip and point-of-care applications [39]. Recently, advanced nanofabrication techniques have made it possible to fabricate plasmonic nanostructures containing subwavelength gratings, which is suitable for plasmonic sensor applications [46-48]. The main advantage of grating-based nano-plasmonic sensors is miniaturization, enabling lab-on-a-chip commercial applications such as biosensing, hazard and chemical detection.

For both configurations, four primary optical interrogation methods can be used: (1) **Spectral interrogation**, in which a polychromatic light source is used for plasmon excitation and the shift in the resonant wavelength of the reflectance/transmittance spectrum indicates the change in refractive index near the metal/dielectric interface. (2) **Angular interrogation**, in which a single wavelength (monochromatic) laser source is used and the angular shift of the reflected/transmitted signal is measured as the indication of refractive index change. (3) **Intensity interrogation**, where the change in the transmitted/reflected light intensity is measured, while both the wavelength and the angle at which the signal is collected are maintained constant. (4) **Phase interrogation**, where a phase shift in the collected light is considered as the indication of refractive index change, and the wavelength and the angle in which the signal is collected are constant [45].

To characterize the performance of a structure for sensing applications, parameters such as the **bulk sensitivity**, **surface sensitivity** and **figure of merit** (FOM) could be used. The bulk sensitivity is defined as a resonant wavelength (λ_{res}) shift vs. the refractive index change ($d\lambda_{\text{res}}/dn_c$) of the bounding medium. To find the bulk sensitivity, the refractive index of the bounding medium is changed from a nominal value to other values, step by step. Then the shift of the resonance wavelength vs. this change is calculated. The surface sensitivity determines how the resonances shift with the change in the thickness of an adlayer which grows at the interface between the metal and the bounding medium. In biosensing experiments, the metal surface is in contact with a sensing solution (bounding medium) and is functionalized chemically to react with a target analyte selectively. As analyte attach, an adlayer of refractive index higher than that of the sensing solution forms, which causes a shift in the resonance wavelengths. The surface sensitivity is defined as the shift in λ_{res} relative to the change in the adlayer thickness growing at the metallic/solution interface.

However, the overall sensing performance of a system depends on the spectral width of the resonance as well. A narrower resonance allows for more accurate measurement of small shifts in the resonance wavelength caused by refractive index changes in the bounding medium. The FOM is defined as the ratio of the resonance wavelength shift per unit refractive index change (bulk sensitivity), divided by the spectral width of the resonance, and is used as an overall measure of quality of a sensor.

In this thesis, we focus on studying periodic arrays of nanoparticles and nanoholes. The periodicity in an array inherently creates “grating coupling”. Spectral interrogation is generally employed by calculating and/or measuring the transmitted/reflected spectrum of an array. In chapter 3, nanoparticle (NP) arrays are fabricated by self-assembly to form periodic arrangements. The sensing performance of this structure is reported as the LSPP shift with respect to the change in the refractive index of the medium that covers the nanoparticles. Chapter 4 focuses on studying periodic arrays of uncoupled nano disks on a Bragg stack supporting Fano resonances. The performance of the structure as a plasmonic sensor is represented by its bulk sensitivity and figure of merit (FOM). In chapters 5 and 6, heptamer nanohole arrays also operate as a grating coupler to excite a variety of plasmonic excitations in

the system. The Fano resonances supported by this structure have been studied and their optical properties and sensing performances have been examined.

A large number of theoretical and experimental studies have been reported as researchers proposed, engineered and tested plasmonic nanostructures supporting SPPs, LSPs and Fano resonances for various applications, especially sensing. The following section reviews some of these studies

Plasmonic Nanostructures

The term nano has etymological origins in Greek and means dwarf. The physical dimension of a billionth of a meter (10^{-9} m or nanometer) is colloquially called the nanometric scale or simply the nanoscale. Figure 6 compares the size of objects and natural organisms at different scales.

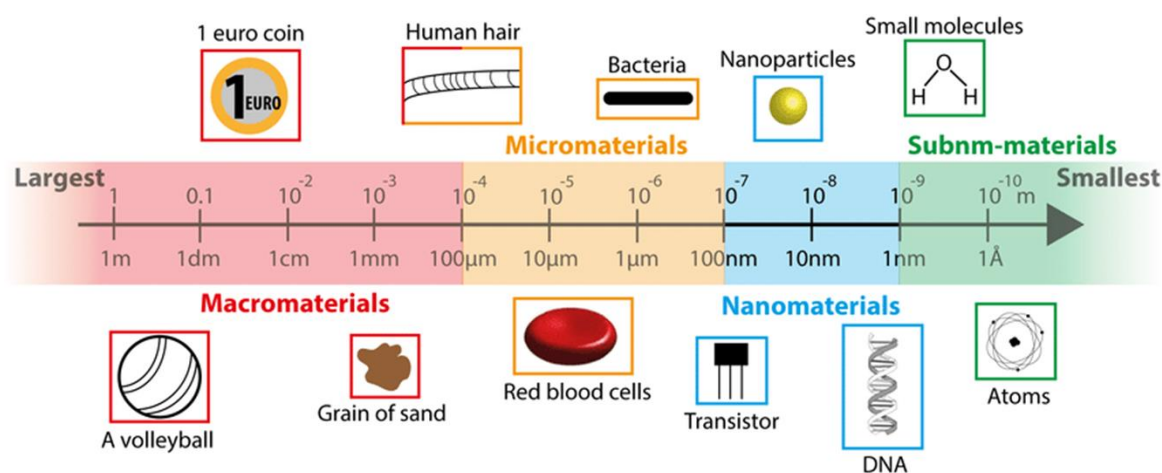


Figure 6 Nanomaterials with dimension in the range from 1 to 100 nm [49]

The properties of a material on the nanometer scale differ from those at the macroscopic scale. There are several reasons for this difference. For instance, the nanomaterials have a relatively larger surface area when they are compared to the same mass of material produced in a larger form. Reducing dimensions often makes a material more chemically (bio) reactive and affects its electrical, optical, magnetic, thermal, structural, and mechanical properties.

The Lycurgus cup is one of the most significant examples of using plasmonic nanoparticles in the ancient world. When lit from the outside, the cup appears greenish (Figure 7(a)), but when lit from the inside, the cup appears reddish and purple (Figure 7(b)). This dichroic effect is achieved by the presence of nanoparticles, silver 66.2%, 31.2% gold, and 2.6% copper, up to 100 nm in size, dispersed in colloidal form throughout the glass material [50]. The red color observed is due to the absorption of light (at $\lambda = 520$ nm) by the gold particles, and the purple color is due to absorption by the larger particles. In contrast, the green color is associated with the light scattering by colloidal dispersions of silver particles of size > 40 nm. Figure 7(c) and

7(d) show an example of using gold and silver nanoparticles of different sizes by medieval artisans to produce different colors in stained glass windows [50].

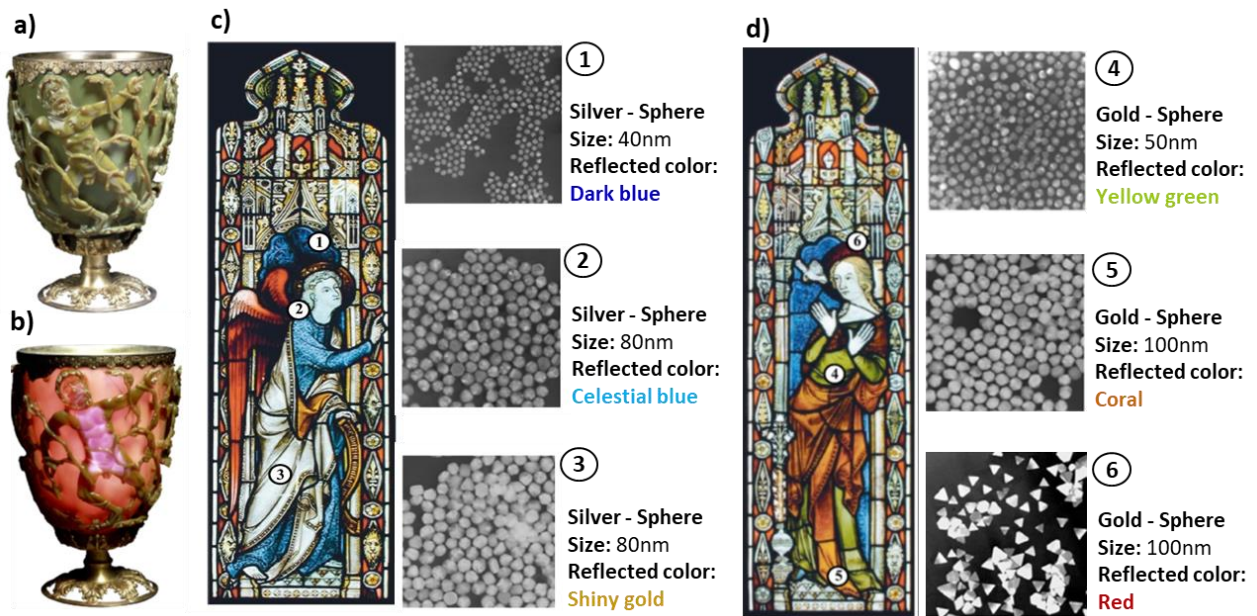


Figure 7 The Lycurgus cup looks (a) green when illuminated from the outside and (b) purple-red when illuminated from the inside. (c) Silver nanoparticles of different sizes have been used to produce different colors in stained widows. (d) The color obtained in stained windows varies Gold nanoparticles with nanoparticle size and shape (sphere, prism) [50].

The recent improvement in the imaging and fabrication of nano-sized structures led to the novel and fast-emerging field of nanoplasmonics. Their optical properties are explained based on coherent oscillations of conductive electrons, known as plasmons [51]. Nanostructured materials have unique characteristics different from the constitutive material. They show many unique properties in their morphological, electrical, thermal, electromagnetic, and optical properties. For instance, as the size of metal structures reaches the nanoscale, not only can they support SPPs at different wavelengths, but also their resonant wavelengths depend strongly on the size and shape of the structure. The properties of SPPs and LSPs on nanoscale structures depend strongly on the morphology of the structure. So, sub-wavelength metal structures have attracted significant research interest due to their fascinating optical properties originating due to the excitation of SPPs and LSPs [52].

In the case of the noble metals, especially gold and silver, the plasmon modes occur in the visible to the infrared wavelength range, making them suitable for applications, such as biosensing, near-field microscopy [53], and surface-enhanced Raman scattering [54]. The plasmonic properties of structures such as nanoparticles depend strongly on the objects' geometrical parameters, such as its size and shape. These dependencies have been studied in numerous experiments on plasmonic structures such as nanoparticles, disks, shells, rods, rings, other shapes [55-57], and even the complementary structures, which consist of nanoholes milled into a planar metal film [58, 59]. Plasmonic nanostructures behave differently when they are positioned in different arrangements. When they are alone or randomly located with respect to each other, their plasmonic properties, such as their plasmonic modes, are different than when they are sitting in a periodic array or form clusters. Here we categorized nanoplasmonic structures into three main categories, *single nanostructures*, *nanostructure aggregates*, and *arrays of nanostructures*, where the nanostructures could be nanoparticles or nanoholes.

Numerous theoretical and experimental works have been reported on these categories of plasmonic nanostructures which support SPPs, LSPs and Fano resonances. Here, we review some of them as investigated by different research groups. We also review nanofabrication techniques common to their fabrication.

A. Single Nanoparticles/Nanoholes

LSPs on metallic nanoparticles and nanostructures can be tuned by their geometric parameters, which has been extensively explored to shape and manipulate plasmonic properties. Figure 8 and Figure 9 give the calculation of extinction, absorption, and scattering spectra of Ag nanoparticles with various geometric shapes such as cube, tetrahedron, octahedron and diversified topologies such as solid, hollow, and core-shell [60]. These results show the strong relationship between plasmonic properties and the structural parameters of a metallic nanoparticle.

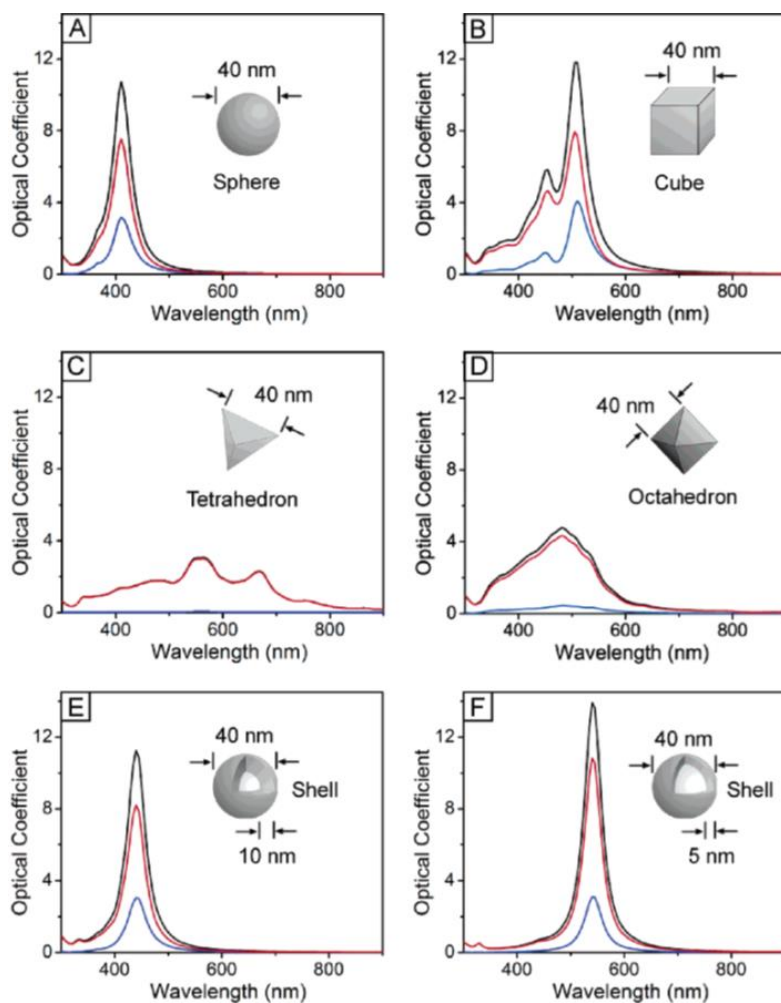


Figure 8 Calculated extinction (black), absorption (red), and scattering (blue) spectra of silver nanoparticles with different shapes. (A) An isotropic sphere has a single resonance peak. (B) Anisotropic cubes, (C) tetrahedra, and (D) octahedra have multiple, red-shifted resonance peaks. (E) The resonance wavelength of a hollow sphere red-shifts respect to a solid sphere, (F) and it even more red-shift for thinner shell walls [60].

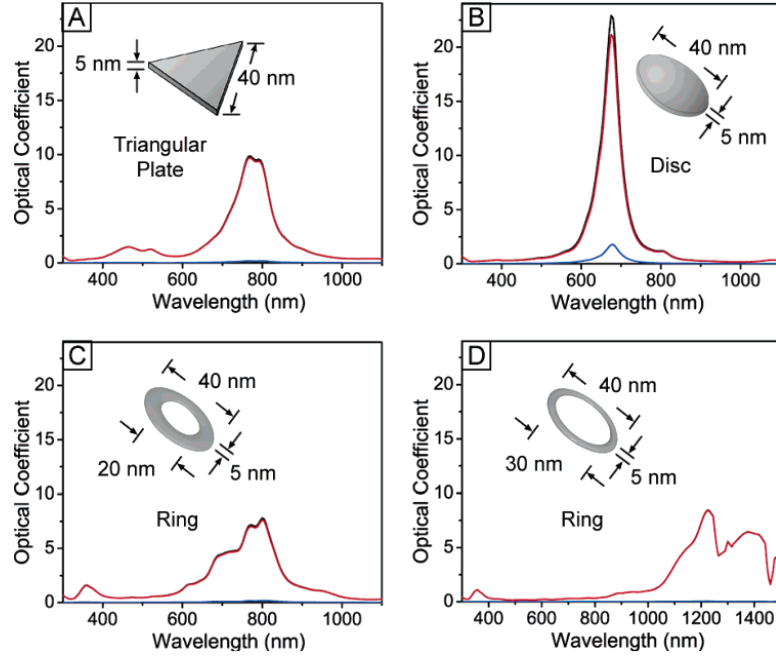


Figure 9 extinction (black), absorption (red), and scattering (blue) spectra of silver (A) triangular plate and (B) circular disc and (C, D) nanorings of two different thicknesses [60].

For nanoparticles with a size much smaller than the excitation wavelength, retardation effects are negligible, so the particle just shows a dipolar resonance. But, as the size of the particle increases, retardation effects should be considered, resulting in higher-order modes such as the quadrupole mode, hexapolar mode, and so on. Figure 10 shows the extinction spectra computed using Mie theory [7] for a spherical gold nanoparticle in water, with an increasing radius up to $R = 100$ nm. The particle with small R , only supports a dipolar mode, seen as a resonance around $\lambda = 520$ nm, which redshifts with increasing radius. However, for $R > 50$ nm, the quadrupole mode at shorter wavelengths show up as a shoulder on the main dipolar resonance.

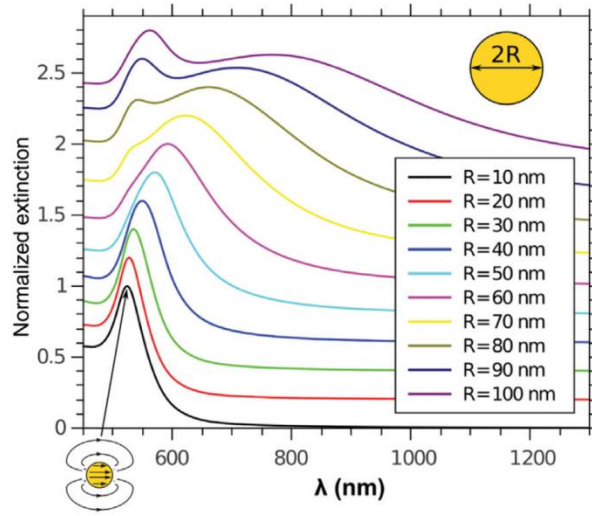


Figure 10 Extinction spectra of gold nanospheres of increasing radius R in water, computed with the Mie theory [7].

B. Nanoparticle/ Nanoholes Aggregates

A key feature of LSPs is their ability to squeeze or “focus” electromagnetic energy into a nanometer-scale volume. This locally enhanced energy leads to the formations of "hot spots", usually generated at sharp tips of metal particles [8] or inside the gaps between NHs or NPs [9] or between a metal NP and a metal film. Significant enhancement of local field intensity is found around the sharp corners, edges, and conical tips of metallic nanoparticles, which is desired for applications in fluorescence and Raman scattering. Even more significant field enhancements can be achieved inside gaps between nanoparticles [61] or between a metal nanoparticle and a thin metal film [62]. So, various arrangements of metallic nanoparticles, such as dimers and aggregates, have been designed and fabricated to promote plasmonic enhancements to a very high level [63]. For instance, Hao *et al.* [64] investigated the electromagnetic fields induced by the excitation of LSPs in silver nanostructures, including monomers and dimers composed of triangular prisms or rectangular rods. They tried to figure out what size, shape, and arrangement of particles result in the most extensive local electric field enhancement. Most of their calculations were on triangular prisms, which exhibit distinct dipole and quadrupole resonances. The electric field enhancement of a silver triangular prism and a rectangular rod shape is given in Figure 11(a). For individual particles they determined that the field enhancement values for triangular prisms, oblate spheroids, or cylindrical rods,

was always being less than 10^4 . However, arranging particles in a dimer yields field enhancements of up to 10^5 for structures where the particles are separated by 2 nm. It was shown that the enhancement is a strong function of separation distance.

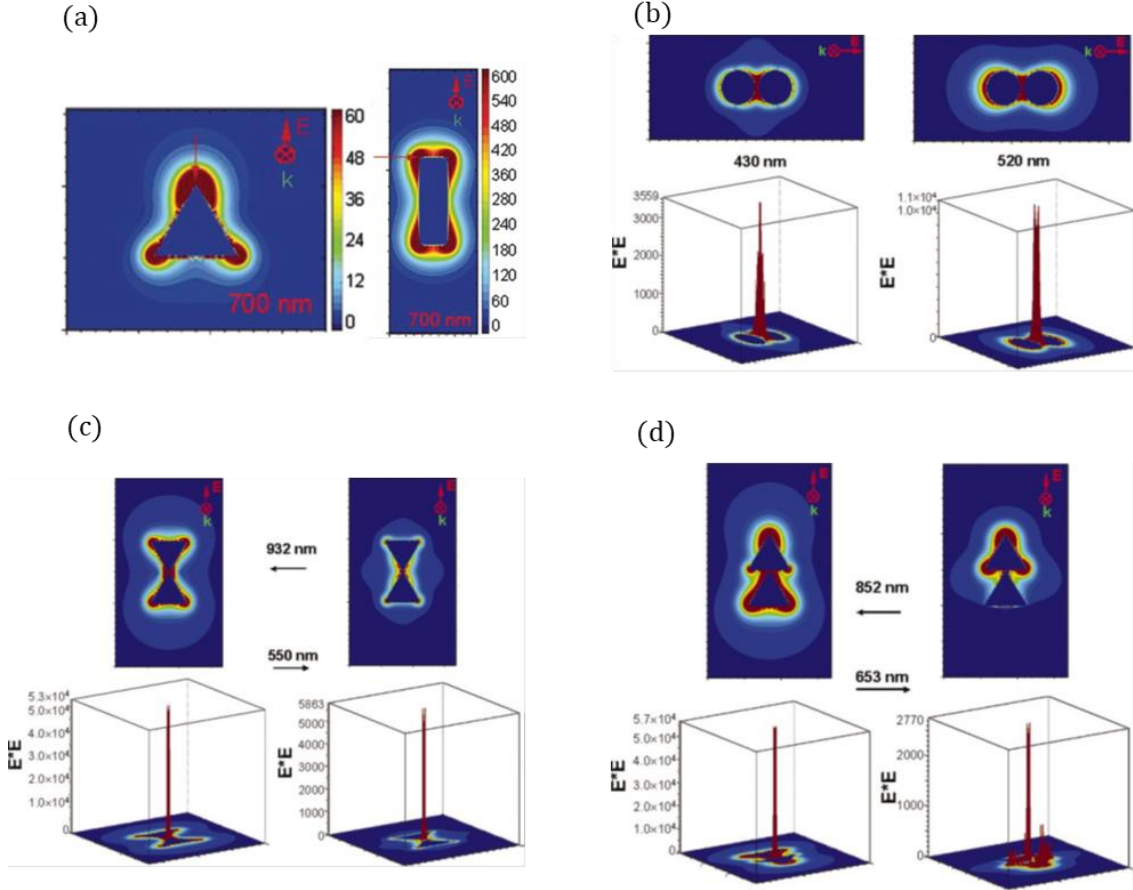


Figure 11 (a) E-field enhancement of silver nanoparticle monomers with a triangular prism and a rectangular rod shape. The arrows show the maximum of the E-field [64]. E-field enhancement of a (b) dimer of Ag nanoparticles separated by 2 nm, at its resonance wavelengths (430nm and 520nm), (c) a “tip-to-tip” prism dimer at its resonance wavelengths (550nm and 932nm), (d) “tip-to-side” prism dimer at its resonance wavelengths (653nm and 852nm) .In the 3D plots, the axis perpendicular to the selected plane represents the amount of E-field enhancement around the dimer.

In another study, Barrow *et al.* [65] have measured the light scattering properties of gold nanoparticles self-assembled into chains of differing length from monomer to hexamer, in which the inter-particle gaps were 1 nm, as shown in Figure 12(a). When the chains were illuminated by light with a polarization parallel to the chain axis, a redshift of the surface plasmon resonance was observed for increasing chain length, as shown in Figure 12(b). They

showed that higher-order modes and retardation effects need to be considered in order to find a good agreement between experimental and theoretical results. This study indicates that the LSPs of the structure are very sensitive to the number of particles in the chain, and very large shifts are observed by adding one particle to the chain.

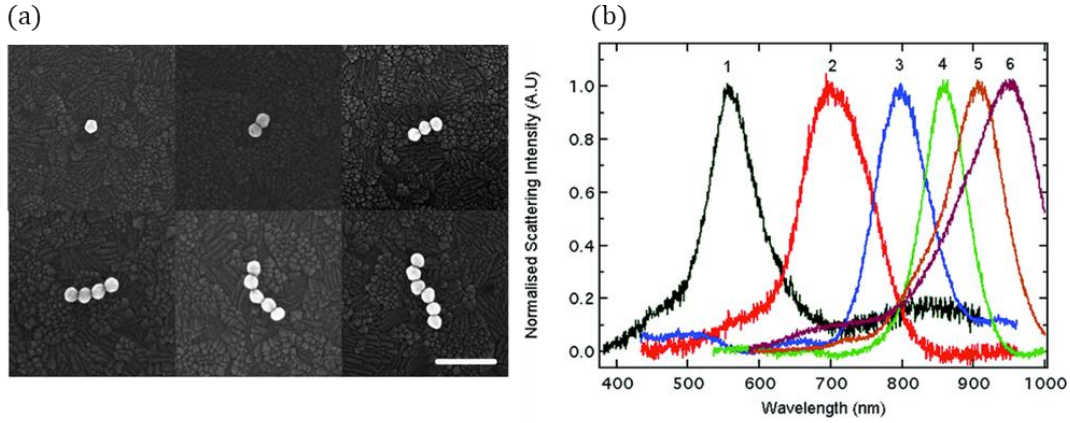


Figure 12 (a) SEM images of self-assembled gold nanoparticle chains consisting of 1 to 6 particles. Mean diameter of gold particles is 64 nm, and the inter-particle gap is ~ 1 nm. Scale bar is 250 nm. (b) Normalized scattering intensity of the nanoparticle chains consisting of 1 to 6 particles. Spectra are numerically labeled according to the chain length.

C. Arrays of Nanoparticles/Nanoholes

The plasmonic properties of nanostructures can be tailored by creating aggregates. By changing their dielectric environment, dimensions, and morphology, the local EM field enhancement could be increased to $10^4 - 10^6$ for metal nanospheres [66]. Another common method to tailor the plasmonic characteristics of nanostructures is putting them in a periodic array to form a nano-array pattern. In addition to SPPs, LSPs and Fano resonances which can be supported by individual nanostructures or nanoparticle clusters, array architectures can be tailored to produce surface lattice resonances (SLRs). The optical response of an array depends not only on size and shape but also on the periodicity, resulting in additional flexibility and tunability of plasmonic and optical properties [67].

Nanofabrication methods

Nanofabrication methods can be categorized into two main groups: Top-down and Bottom-up. Top-down nanofabrication is most common, where the base material is gradually eroded and miniaturized to the nanoscale until the desired structure is achieved. One of the most used top-down fabrication techniques is lithography, in which a mask usually protects the material, and the undesired material is etched away. In bottom-up fabrication techniques, nano-metric structures such as atoms or molecules are placed one at a time through a process of self-assembly or assembly to build the desired nanostructure higher than the initial ones. The physical and chemical forces at the nanoscale are driving mechanisms for this atomic/molecular arrangement. Some of the fabrication methods in this category include sol-gel, atomic layer deposition, and self-assembly techniques.

The fabrication of plasmonic nanostructures usually requires several steps, such as deposition/coating, etching, micromachining, and nanofabrication steps. The method to fabricate a specific nanostructure is selected based on the materials involved in the structure, fabrication costs, and its target application. Also, the selection of the fabrication techniques depends on other parameters, such as the process steps of etching and deposition.

A. Top-down nanofabrication techniques

Following the goal of this thesis, we focus on fabrication techniques of periodic nanostructure arrays, which can be classified into two main groups, *patterning techniques in resist* and *resist-free patterning techniques* [68]. While the former uses a resist which, *e.g.*, is patterned before depositing the metal film (lift-off), the latter consists of directly patterning a metal film, *e.g.*, by milling.

a. Patterning techniques in resist

In this category, three primary methods are usually used to fabricate an array of nanostructures, which are illustrated in Figure 13. In the first method, shown in Figure 13(a), the resist which is deposited on top of a metal layer is patterned, and then this nano-patterned resist is used as a mask to etch the metal layer and achieve desired nano features [69-71]. In a second method,

illustrated in Figure 13(b), a nano-patterned resist is followed by metal deposition, and the nano features are achieved through a lift-off process [72]. The third method is a combination of two previous methods. One example is fabricating NHs in a freestanding membrane performed by Kumar et al. [73]. This suspended membrane can be used as an optofluidic substrate, which lets the fluidic access from both sides of the membrane. Using the third method, a suspended plasmonic membrane, on silicon nitride is fabricated in two steps. The first step includes wet chemical etching of Si and photolithography, and the second step is nano-patterning, followed by metal deposition, as illustrated in Figure 13(c).

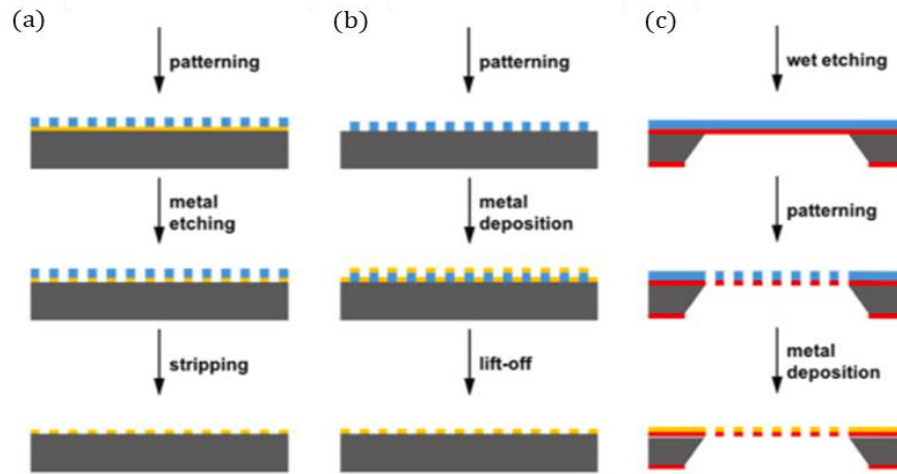


Figure 13 Schematics of three main methods used for nanofabrication (a) A metal layer is deposited before the nanopatterning step, which is followed by either a wet or dry etching. (b) Nanopatterning step is followed by metal deposition, which is followed by the formation of metallic nanofeatures through lift-off process. (c) Fabrication of NHs array in a suspended membrane, mostly in Si_3N_4 , is done through a combination of photolithography and wet chemical etching of Si, followed by nanopatterning and metal deposition steps [73].

Metal etching process is categorized into two types, wet and dry etching. In the wet etching process, a wet chemical etchant dissolves a metal film through the patterned resist in a highly selective manner. Specific etchants can be used for each metal. Wet etching is commonly used in microfabrication process. Still, it is limited in nanofabrication due to isotropic nature of this etching method which etches a large undercut the resist layer and form cavities with sloping sidewalls in the metal film, as shown in Figure 14 (a). It can also define grains and create roughness. Another problem is that control of etch time is not easy to achieve.

1. Alternatively, dry etching is an anisotropic process with high selectivity that leaves the underlying material untouched. Dry etching or Reactive-ion etching (RIE) requires a plasma-assisted system, which exposes the material to a bombardment of ions to etch the desired layer. RIE processes are mostly used for nanofabrication in semiconducting materials. However, there is no well-defined RIE process for plasmonic metals, such as Au and Ag, due to the large amount of redeposition during etching [74].

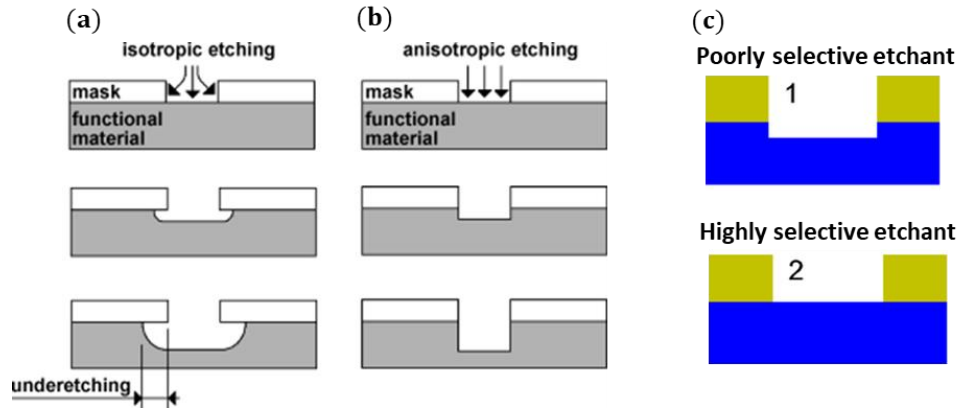


Figure 14 Example of (a) isotropic and (b) ideal anisotropic etching: illustrating the evolution of sidewall [75].

Lift-off processes use a solvent to remove the resist layer after metal deposition, as illustrated in Figure 15(F). During this process, lifted-off metals can be redeposited on the sample surfaces in the bath, which can contaminate the remaining materials on the substrate [76]. Another problem is that the resist often partially remains undissolved. Also, during metal deposition, the sidewalls of the resist can be covered by metal, which can prevent the resist from being lifted off appropriately [77, 78]. Also, metal deposition on the sidewalls could fall on the surface, forming unwanted features.

Recently Hahn et al. [79] developed a resist-on-metal bilayer lift-off technique, illustrated in Figure 16, facilitating the fabrication of nano plasmonic structures on insulating substrates. Electron beam lithography (EBL) is a well-know and standard method to write directly on a resist. However, using EBL on transparent or insulating substrates (e.g. glass or polymer) is difficult, due to charging caused by the accumulation of static electric charge on the substrate surface during exposure. The main advantage of metal/resist bilayer is that EBL is enabled on insulating substrates by eliminating charging during electron beam exposure. Also, it provides

an under-cut for clean lift-off. They selected Al as the metal in the metal/resist bilayer, because it (i) minimally reactive with the substrate, (ii) can be wet-etched to form the under-cut (iii) is etched with high selectively with respect to other materials used in the structure.

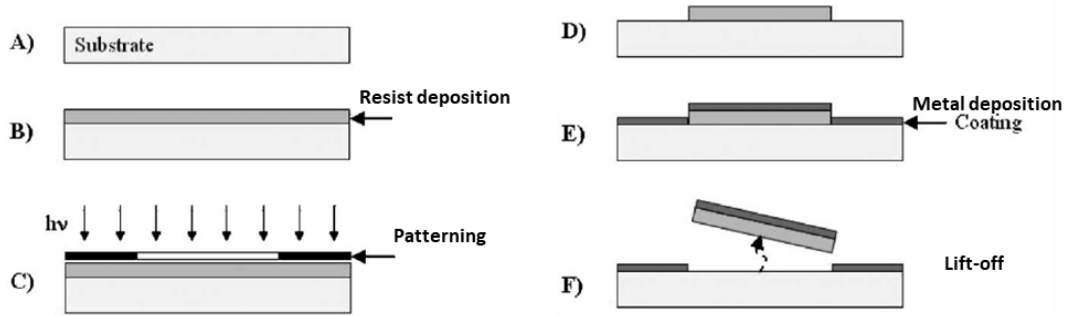


Figure 15 Schematics of Lift-off process steps: (A) Substrate preparation (B) Deposition of the resist layer (C) Patterning the resist to create (D) an inverse pattern (E) Metal deposition (F) Washing out the unwanted area from the substrate.

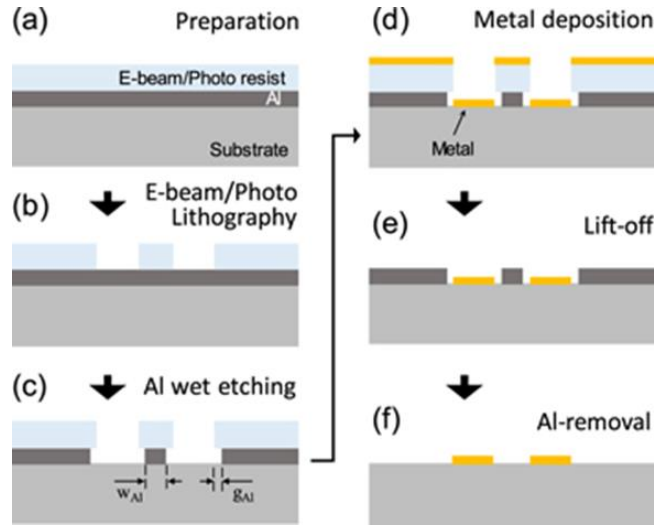


Figure 16 Schematic illustration of resist/metal bilayer lift-off process. Here, Al has been used as the metal in the resist/metal bilayer (a) Electron beam resist or photoresist, and the Al layer is prepared on a substrate. (b) Resist is patterned by electron beam or photolithography, then developed. (c) Formation of under-cut in the wet etching of the Al layer (d) Metal deposition (e) Resist lift-off. (f) Removal of residual Al.

Because of some issues mentioned before, and also because the lift-off process is a tedious process for plasmonic nanofabrication, Yanik et al. [80, 81] have developed a fabrication

technique which eliminates the need for a lift-off process after metal deposition. They used a freestanding Si₃N₄ membrane patterned with NH array structures as a stencil mask for metal deposition. So, during metal deposition, the metal flows out through the NH array in the stencil mask and only remains on the surface. One issue related to this technique is the re-usability of stencil masks for multiple metal depositions, which prevents this technique to be used widely for nan-patterning.

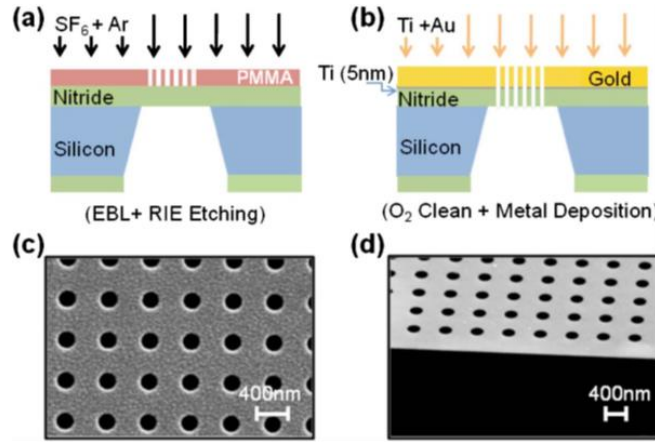


Figure 17 Suspended plasmonic nanohole arrays are fabricated using a lithography process consisting of: (a) patterning of the freestanding Si₃N₄ membrane followed by RIE etching, (b) oxygen plasma cleaning of the surface followed by metal deposition. (c_d) SEM images of the fabricated nanoholes array (in different angles). Holes diameter and periodicity is 200 nm and 600 nm, respectively [81]

i. UV lithography

UV lithography makes use of a photoresist (PR) layer that is spin-coated on a substrate and then is exposed to UV light using a photomask which is patterned with a metal such as chromium (Cr), as shown in Figure 18. PR can be a positive or negative tone. For the positive tone, the area exposed to UV light through the photomask will be dissolved during developing, while for the negative tone, PR will remain during developing. Usually, the smallest feature that can be patterned is limited by the wavelength of the UV light source. The smallest feature size is roughly equal to the square root of the illumination wavelength [82]. To overcome this limitation, short UV wavelengths such as deep UV light produced by an excimer laser (*e.g.* KrF, ArF, and F₂) can be used [82]. Using deep UV light, an array of nano features with 200 nm diameter and 600 nm period on Si₃N₄/Si [83] and glass substrates [70] have been reported.

However, this kind of lithography requires nanoscale precision alignment systems as well as an expensive photomask.

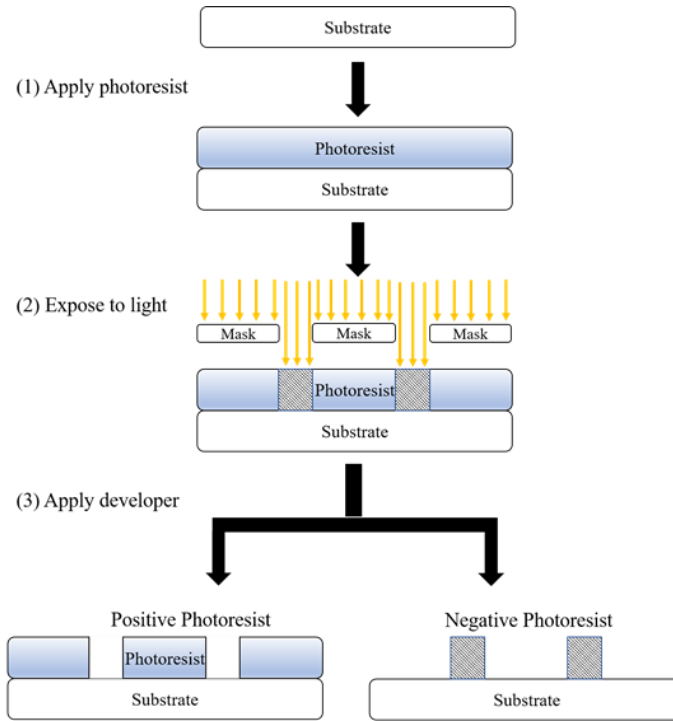


Figure 18 Schematic of photolithography steps, in general,

ii. Interference lithography (IL)

This technique can be used for the fabrication of nano-arrays in a large area without using any photomasks [84]. As shown in Figure 19, in this method, two or more coherent incident beams interfere to create an interference pattern in the photoresist layer. The period of the interference pattern can be controlled by the wavelength, the angles of incidence, or a combination of both [84]. UV lasers with different wavelengths (Ar laser at 244 nm and Nd:YAG laser at 213 nm) have been reported for creating interference patterns. The smallest feature size fabricated with those wavelengths are 122 and 96 nm, respectively [85]. One of the main advantages of interference lithography is that it allows the fabrication of large-area arrays without requiring any photomasks [70]. A limitation is that only features that can be defined by interference patterns can be realised.

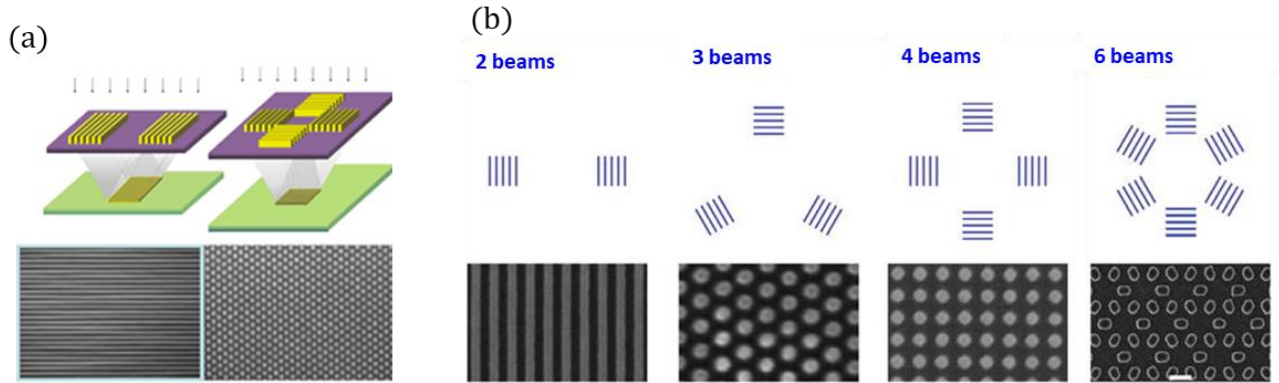


Figure 19 (a) The general scheme of the two-beam and four-beam transmission-diffraction IL method to produce line and hole/dot patterns, respectively [86]. (b) (top panel) Schematic of different configurations for multiple-beam interference lithography and SEM images exhibit the corresponding exposures in photoresist [87].

iii. Electron beam lithography (EBL)

EBL is a direct writing method which does not require any photomask and uses an electron beam to write nanoscale patterns on an e-beam sensitive resist deposited on a substrate, as illustrated in Figure 20. In this technique, polymethyl methacrylate (PMMA) and hydrogen silsesquioxane (HSQ) are widely used as a positive and negative resists, respectively. Due to the small wavelength of the electron beam, EBL can be used to pattern tiny (nanoscale) features [72], which cannot be created using optical lithography and IL. To achieve small dimensions (sub-10 nm features), the thickness of the resist should be minimal to minimize the electron scattering effects in the resist [72, 88]. However, achieving high-resolution features and well-defined nanoarrays requires an appropriate selection of resist/developer and a careful post-exposure process.

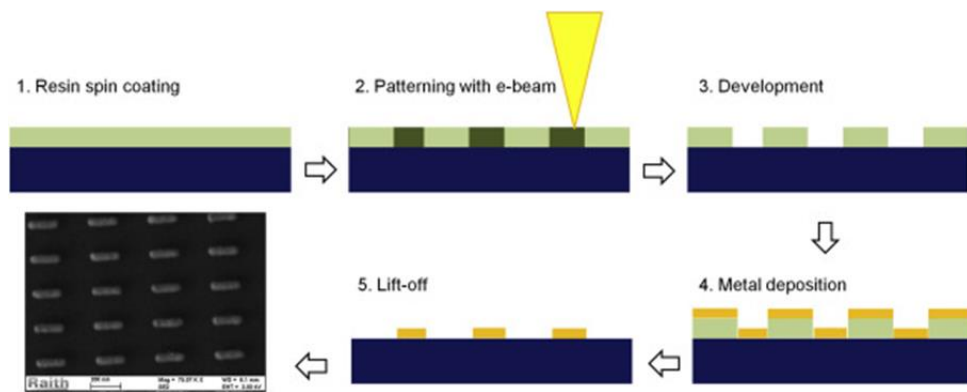


Figure 20 Schematic of E-beam lithography process. (SEM image on the bottom left is the array of gold nanorods deposited on a glass substrate) [89].

iv. Nanoimprint lithography (NIL)

Nanoimprint lithography (NIL) is a high-resolution patterning method providing an effective and low-cost technique for replicating features less than 10 nm over large areas with long-range order. This method is considered promising as a solution to the practical limits of photolithography and e-beam lithography. Since this lithography method does not require any light or high energy particle beams, the feature resolution is not limited or controlled by factors such as diffraction, interference, or scattering [90, 91]. There are two common types of NIL, thermal and UV, and both usually involve two steps: molding and demolding. In thermal NIL, the imprint resist, which is a thermoplastic polymer, is coated onto the substrate, followed by an imprint or molding step. Then the resist is masked and heated above the glass transition temperature (T_g) to form a viscous, flowable liquid. For the demolding step, the resist is cooled down, and the mask is pulled off, to separate the mold from the molded resist, to be reused for the next molding cycle. PMMA is a common thermoplastic resist material, for thermal NIL, due to its low cost and availability in a wide range of molecular weights, which can produce 10 nm resolution patterning [92]. In contrast to thermal NIL, in UV-NIL, the resist hardens by cooling and UV-curing. Both thermal and UV-NIL have been used by various research groups to produce large-area metallic structures [73, 93, 94]. The nanofabrication of metallic structures using NIL suffers from issues such as the presence of a residual layer after imprinting which needs a subsequent RIE process to remove [95]. Schematic illustrations of both thermal and UV nanoimprint lithography processes are given in Figure 21.

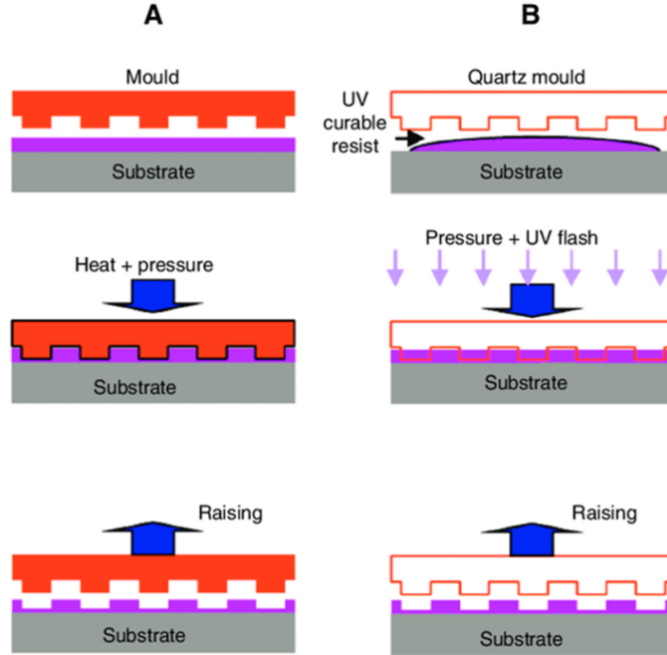


Figure 21 Schematic of Nanoimprint lithography process of (A) thermal NIL, (B) UV-curable NIL [96]

b. Resist-free patterning techniques

i. Focused ion beam (FIB) lithography

FIB lithography is a resist-free, maskless nanofabrication technique which uses high energy focused ion beams to directly mill nanoscale patterns on a desired substrate [9], as illustrated schematically in Figure 22(a). Ga and He ions are commonly used in this technique. Because ions are more massive than electrons, FIB milling is less affected by scattering. FIB milling using gallium (Ga) ions is a common approach to nanofabrication [97, 98]. The typical nanohole size obtained using Ga^+ ions is limited to ~ 50 nm. Ga FIB milling suffers from limited resolution, material redistribution and unwanted implantation of Ga ions into the substrate [99]. He^+ ion beams have been used by Ananth *et al.* [10] for creating 5 nm holes in a 100 nm thick gold film. Also, Hahn *et al.* [9] used He FIB milling to fabricate arrays of plasmonic heptamer-arranged nanoholes with 15 nm inter-hole spacings in a 55 nm thick gold film. While FIB milling is widely utilized to make isolated metallic nanoholes, it cannot be used to create isolated metallic nanoparticles and assemblies. To solve this problem, Chen *et al.* [100] proposed and developed an approach to defining plasmonic nanoparticles and also

nanoparticle assemblies using FIB milling via a "sketch and peel" strategy, as shown in Figure 22(b).

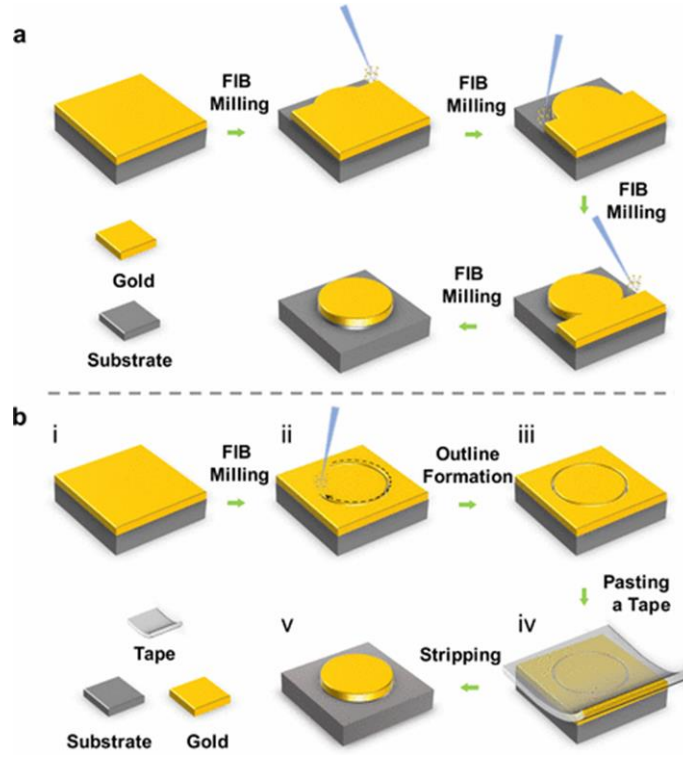


Figure 22 Comparison between (a) conventional FIB milling technique and (b) “sketch and peel”-based FIB milling process, to fabricate a plasmonic nanoparticle. (a) In the conventional method, a large area of the metal film should be milled to obtain an isolated particle. (b) In “Sketch and peel” approach, only a narrow area needs to be milled followed by selectively peeling off the majority of the metal film to create an isolated particle.

ii. Colloidal lithography (CL)

Colloidal lithography is a resist-free, low-cost, large-scale and repeatable nanofabrication technique. This technique combines bottom-up and top-down approaches which start with a monolayer of synthesized nanoparticles assembled on a target substrate followed by metal deposition. If the nanoparticles are too closely packed, the monolayer is exposed to RIE to shrink the colloidal sizes, before metal deposition. A hexagonal arrangement of metallic nanoholes can be created using this method. For instance, Xue *et al.* [101] developed an approach for fabricating graded plasmonic arrays of Ag nanowells with a geometric gradient.

In this approach, colloidal lithography combined with an inclined RIE process was used to produce graded plasmonic arrays, as shown in Figure 23.

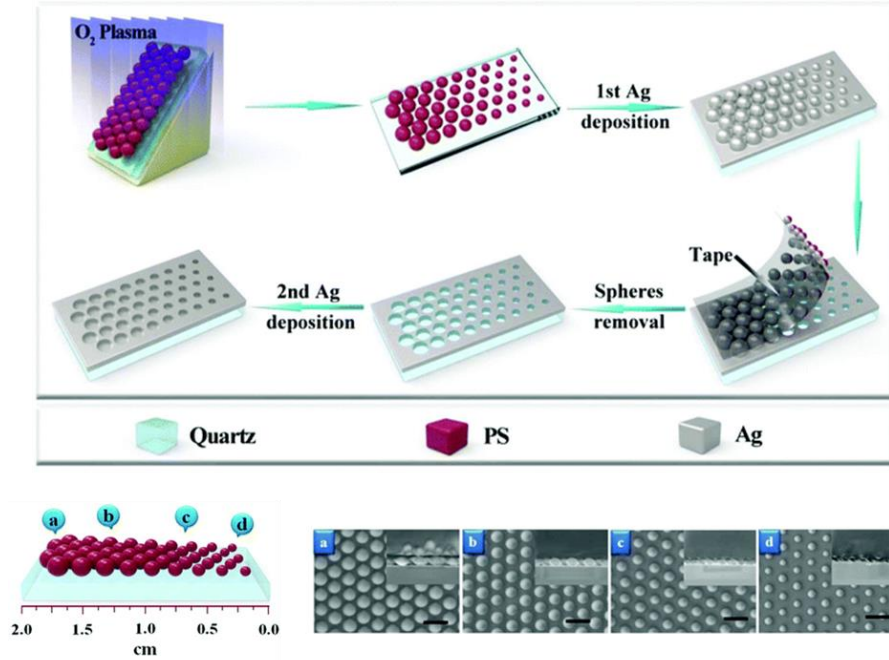


Figure 23 (Top panel) Schematic for the fabrication of Ag nanowell arrays with a geometric gradient, using the colloidal lithography combined with an inclined RIE process. (Bottom panel) The SEM images of the PS microsphere masks on different positions along the substrate. (The scale bars for SEM images are 1μm) [101].

B. Bottom-up nanofabrication

Bottom-up nanofabrication approaches are described as the construction of nanostructures by the self-assembly of atoms or molecules. The physical and chemical forces at the nanoscale level are responsible for the arrangement of atoms or molecules. Some bottom-up nanofabrication methods are discussed in this section.

a. Atomic layer deposition

Atomic layer deposition (ALD) is a thin-film deposition technique based on sequential self-terminating surface reactions of a gas phase precursor, which leads to forming extremely thin and high-quality films. The thickness of the film can be controlled at the atomic level. Figure

24 illustrates the operation of one ALD cycle of the TMA/H₂O process[102] (TMA is trimethylaluminium). Cao *et al.* [103] described an approach to fabricate AuNP / nanogap / AuNP structures for surface-enhanced Raman scattering (SERS) applications. This plasmonic structure was built using a combination of rapid thermal annealing (RTA), atomic layer deposition (ALD), and chemical etching, as shown in Figure 25. An Al₂O₃ layer deposited using the ALD technique was controlled on the nanometer scale, which resulted in precise tunability of the nanogap size between Au NPs. In another study, Whitney *et al.* [104] used ALD to deposit 1 to 600 monolayers of Al₂O₃ with ~ 1 Å thickness resolution on Ag nano triangles, in which the thickness of each Al₂O₃ monolayer was 1.1 Å. The performance of the Ag nano triangles was examined as an LSPR nanosensor by detecting Al₂O₃ film growth with atomic spatial resolution normal to the nanoparticle surface.

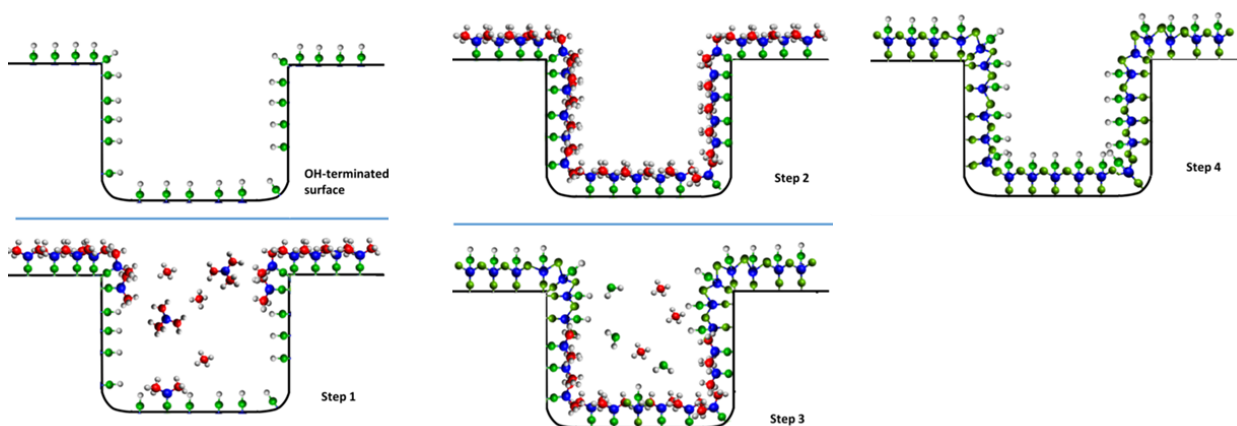


Figure 24 Schematic illustration of one ALD cycle of the TMA/H₂O process. Step 1: The first reactant A (TMA) reacts in a self-terminating way with the available functional groups on the OH-terminated surface. Step 2: The excess of reactant A (TMA) and the gaseous by-products (CH₄) are purged or pumped away. 3. Step 3: The second reactant B (H₂O) reacts in a self-terminating way with the adsorbed species (A) on the surface. 4. Step 4: The excess of reactant B (H₂O) and the gaseous by-products (CH₄) are purged or pumped away

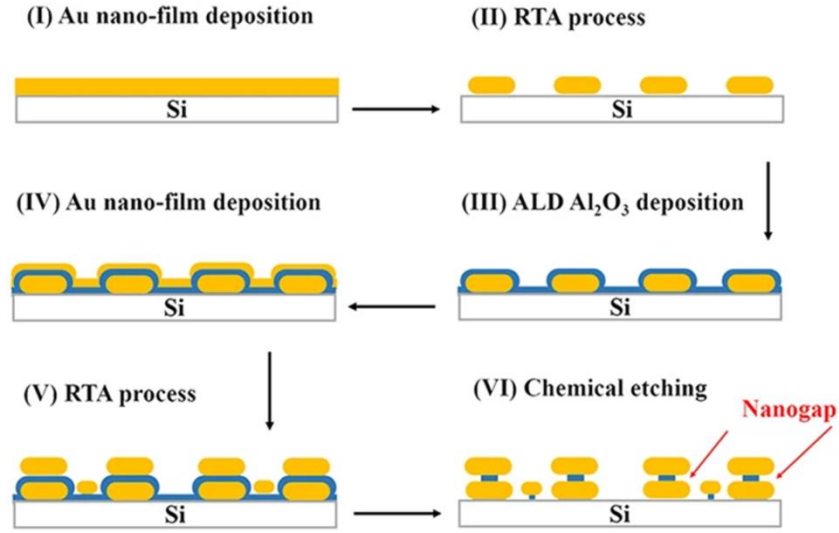


Figure 25 Schematic of the fabrication process of AuNP / nanogap / AuNP structure which consist of ALD technique (I) gold film is deposited on the substrate, using sputtering (II) Au NPs are fabricated using RTA process; (III) very thin Al_2O_3 layer is formed on Au NPs via ALD process; (IV, V) second thin Au film is deposited on the Al_2O_3 coated Au NPs, then RTA process is used to form a structure of AuNP / Al_2O_3 / AuNP; (VI) Al_2O_3 is partially etched to create the final AuNP / nanogap / AuNP structure [102].

b. Self-assembly

The organization of close-packed plasmonic NPs in lattices consisting of thousands of NPs provides control and tuning of optical properties due to surface plasmon coupling between neighboring NPs and forming hot spot in interparticle gaps. The optical properties of self-assembled nanostructures can be controlled by changing structural parameters such as the number of NPs in the cluster, direction of NP organization, inter-particle gaps, and the size and shape of the NPs. Solution-based self-assembly of metallic NPs could decrease the interparticle gap to 1 to 2 nm [105].

Different groups have used self-assembly to fabricate plasmonic nanostructures [106, 107]. For instance, Fan *et al.* [108] used self-assembly to fabricate clusters of metal-dielectric spheres, as shown in Figure 26. They measured the optical properties of the fabricated self-assembled clusters and demonstrated that their plasmonic properties could be tuned by changing the number of particles and also their position in the cluster. As schematically illustrated in Figure 26, the assembly of colloidal clusters involved several steps. The first step is the synthesis of

gold nanoshells, consisting of a metallic shell with a silica core. In the next step, a droplet of the particles placed on a hydrophobic substrate starts to dry slowly at room temperature. During the evaporation step, the droplet of particles breaks into smaller droplets, and nanoshells start to bundle together by capillary forces.

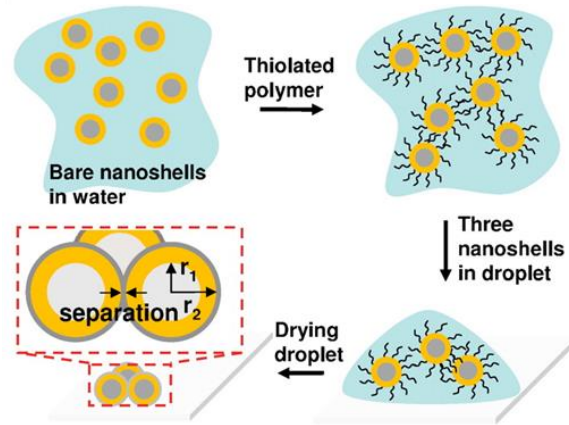


Figure 26 To assemble the clusters, nanoshells in aqueous solution is placed on a hydrophobic substrate and evaporated [108].

c. Sol–gel nanofabrication

Nanofabrication involving a sol-gel can be classified as a bottom-up method, and has been used for the fabrication of metallic nanostructures, especially ones involving the oxides of silicon (Si) and titanium (Ti). In this process, monomers are converted into a colloidal solution (called a *sol*), used as the precursor to start forming an integrated network (called *gel*) of nanoparticles, for instance. The sol-gel process is one of the important methods used for synthesis of nanoparticles. It has several advantages such as ultra-homogeneity and high purity, and it is a cost effective nanofabrication method [109]. Kumar *et al.* [110] used sol-gel methods to synthesize silver nanoparticles in titanasilicate matrix. Due to the excitation of LSPPs, the absorbance spectra of these silver nanoparticles exhibit a broad peak in the 380–410 nm range, which is suitable for solar cell applications.

Fano resonance

Unlike typical plasmonic resonances which are described by a symmetric Lorentzian line shape, Fano resonances with asymmetric profiles have been commonly observed in various fields of science and engineering such as atomic and solid-state physics [111, 112], electronic circuits [113], photonics, nonlinear optics [114], acoustic systems [115], and also atomic, nuclear, and hadronic systems [116]. The origin of a Fano resonance is usually described as the coherent interference of a continuum (or subradiant mode) acting as a background, with a localized (or superradiant) mode.

In general, this kind of asymmetric line shape is usually described by the famous Fano formula [117]:

$$I(\omega) = \frac{(q\gamma + \omega - \omega_0)^2}{(\omega - \omega_0)^2 + \gamma^2} \quad (10)$$

which can be simplified to:

$$I(E) = \frac{(\varepsilon + q)^2}{\varepsilon^2 + 1} \quad (11)$$

where ω is the frequency of the incident photon, ω_0 is the resonance frequency, q is the Fano asymmetry parameter, γ is the resonance linewidth, and ε is defined as $\varepsilon = (\omega - \omega_0)/\gamma$. The q parameter determines the degree of asymmetry in the Fano resonance and depends on the interference conditions between subradiant and superradiant modes. Fano profiles with different values of q , ranging from 0 to 3 are illustrated in Figure 27. For large $|q|$ ($|q| \gg 1$) the interference is dominated by the superradiant mode resulting in a Lorentzian peak on top of a weak background. Decreasing $|q|$ increases the asymmetry with $|q| = 1$ producing an asymmetric Fano-profile with a minimum adjacent to a maximum. As seen in Figure 27, when $|q| = 0$ the interference results in a spectral dip in the continuum.

Several models have been suggested to explain the physical nature of the Fano resonance intuitively. One useful model in this regard is the coupled oscillator model, where the modes of a system are treated as masses coupled by a spring [11].

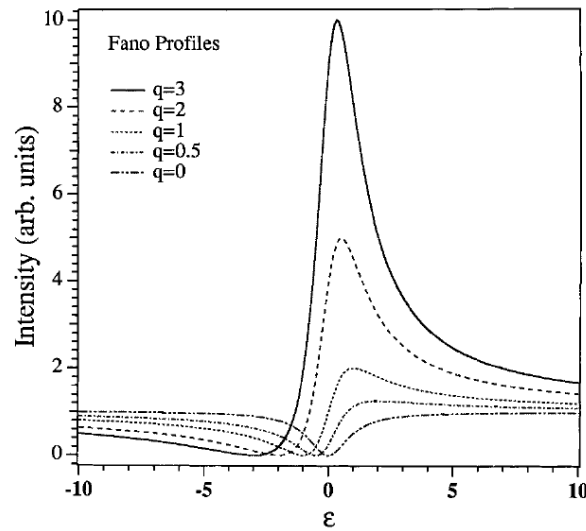


Figure 27 A schematic illustration of the line shape of a Fano resonance for various q -parameter [118].

A. History of Fano resonance

Ugo Fano [119] was the first to propose an explanation for the asymmetric line shape seen in some Rydberg spectral atomic lines. Rydberg spectral lines of materials is an essential diagnostic tool in physics, allowing scientists to investigate the properties of matter. For example, Bohr developed his model of atoms (the Bohr model) based on the Rydberg formula, which made a foundational contribution to understanding quantum theory. However, some Rydberg spectral atomic lines had an asymmetric line shape, which couldn't be explained at that time [120]. Fano described the origin of this asymmetric line shape based on the interference between a discrete excited state of an atom and a continuum sharing the same energy level [119]. He was the first person to give a theoretical explanation for the asymmetric line-shape seen in the scattering of electrons from helium [117]. His first paper included a derivation of the line shape formula, which was published in 1935 [119]. However, his second paper [117], published in 1961, became one of the most remarkable publications in the physics of the 20th century (with over 11,772 citations to date). His pioneering papers [117, 119, 121], in which he suggested a key new ingredient for radiation-matter interaction in atomic physics, made him one of the leading players in 20th century physics.

The first observed asymmetric lineshapes can be traced to the discovery made by Wood in 1902 [122] when he observed an unexpected narrow asymmetric resonance with rapid intensity variations in the diffracted spectra of a grating illuminated by a light source. It was termed an "*anomaly*" because the effect could not be explained using conventional grating theory [122, 123]. For the first time, Fano explained this asymmetric line shape, in a series of publications [124-127], suggesting that this anomaly could be associated with the excitation of a leaky surface wave along the grating. He showed that the Fano formula could fit the observed asymmetric line shape with reasonable accuracy, where the leaky mode can be considered as a discrete state and the incoming radiation as a continuum. So, the interference between the leaky mode and incoming light results in an asymmetric Fano line shape. This interference is similar to the interference phenomena observed in the absorption of Rydberg atoms, in which a leaky mode was associated with a discrete state and the incoming wave with a continuum.

This kind of asymmetric line profile has been observed in various systems and structures, and sometimes it is not easy to explain their origin. To provide a general explanation for the origin of the Fano line shape in various arrangements, a simple model of two coupled oscillators has been introduced [128]. It sheds light on the origin of the interference phenomena and makes it simple to understand the origin of the Fano profile in various systems in a unified way.

B. Origin of Fano resonance

a. Single oscillator

Usually, a resonance in the response of a system has a Lorentzian shape, and it is defined as the enhancement of a system response at a specific frequency in response to a driving force. It is usually referred as the resonant frequency or natural frequency (eigenmode) of the system. To explain the Lorentzian line shape of the resonance, the system is considered as a harmonic oscillator with periodic driving force. Then the following differential equation is used to describe its motion [11]:

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = \frac{1}{2} A (e^{+i\omega t} + e^{-i\omega t}) \quad (12)$$

where ω and ω_0 are the frequency of the external force and natural frequency of the oscillator in the absence of damping, respectively. γ is a frictional parameter (damping constant). The steady-state solution for equation (12) may be written as $x = x^+ + x^-$ where $x^\pm$ are solutions for the ‘positive’ and the ‘negative’ frequencies, respectively. So, the solution can be written as $x(t) = 2 \operatorname{Re} (x^+(t))$ where x^+ may be considered as the solution of the equation:

$$\ddot{x}^+ + \gamma \dot{x}^+ + \omega_0^2 x^+ = a e^{i\omega t} \quad (13)$$

in which $a = \frac{1}{2} A$, and x^+ can be expressed in the form of $x^+(t) = c(\omega) e^{i\omega t}$, in which $c(\omega)$ is [11]:

$$c(\omega) = \frac{a}{\omega_0^2 - \omega^2 + i\omega\gamma} \quad (14)$$

which can be expressed as $c(\omega) = |c(\omega)| e^{-i\varphi(\omega)}$, with

$$|c(\omega)| = \frac{a}{\sqrt{(\omega_0^2 - \omega^2)^2 + \omega^2 \gamma^2}}, \quad \varphi(\omega) = \tan^{-1} \left(\frac{\omega\gamma}{\omega_0^2 - \omega^2} \right) \quad (15)$$

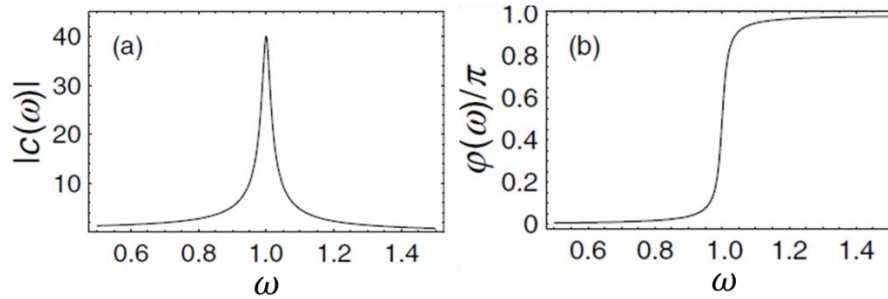


Figure 28 (a) The resonant line shape of the amplitude for the single oscillator. The driven frequency is in units of the natural frequency of the oscillator, ω_0 . (b) The phase jumps by π when the frequency passes through the resonance.

$|c(\omega)|$ and $\varphi(\omega)$ are plotted in Figure 28. Based on Figure 28 (b), when the frequency of the driving force is close to the natural frequency of the oscillator, $\omega = \omega_0$, a resonance in $|c(\omega)|$ occurs, which is the resonance in the oscillator response (x). Also, it is seen in Figure 28, that the phase of oscillator response increases from $\varphi = 0$ at $\omega = 0$ to $\varphi = \frac{\pi}{2}$ at $\omega = \omega_0$ (at

resonance) and to π for $\omega \rightarrow \infty$. So, if the oscillator and the external force are in phase for $\omega < \omega_0$, they will be out of phase for $\omega > \omega_0$ [11]. While the resonance in a variety of physical systems can be explained by the single oscillator model, some physical systems exhibit resonances with an asymmetric line shape, which is not possible to be described by this model.

b. Two coupled oscillators

Some physical systems show asymmetric line shapes in their responses, which can't be explained based on the single oscillator model. A simple model to describe these asymmetric features is a system of two weakly coupled harmonic oscillators, as illustrated in Figure 29(a), where an external force drives just one oscillator. As explained in the previous section, the equation of motion for each oscillator can be written as [11]:

$$\begin{aligned} \ddot{x}_1 + \gamma_1 \dot{x}_1 + \omega_0^2 x_1 + \gamma_{12} x_2 &= a_1 e^{i\omega t} \\ \ddot{x}_2 + \gamma_2 \dot{x}_2 + \omega_0^2 x_2 + \gamma_{12} x_1 &= 0 \end{aligned} \quad (16)$$

where γ_{12} is described as the coupling of the oscillators.

For the case of $a_1 = 0$, the normal modes of the oscillators can be reviewed. In this case, if the coupling is absent ($\gamma_{12} = 0$), the two free oscillators may move independently at their natural frequencies. However, when the oscillators are coupled, they have two normal modes (or eigenmodes). For the first normal mode, the two oscillators move in phase and swing back and forth together. For the second normal mode, they move out of phase, swinging in opposite directions.

To explain the meaning of eigenmodes for this system, assume that there is no friction between oscillators, $\gamma_1 = \gamma_2 = 0$. Then, the eigenmodes of the coupled oscillators can be written as

$$(\omega_1^2 - \omega^2)(\omega_2^2 - \omega^2) - \gamma_{12}^2 = 0 \quad (17)$$

For a weak coupling parameter ($\omega_2^2 - \omega_1^2 \gg \gamma_{12}$), the eigenfrequencies of this coupled system can be obtained from

$$\tilde{\omega}_1^2 \approx \omega_1^2 - \frac{\gamma_{12}^2}{\omega_2^2 - \omega_1^2} \quad \tilde{\omega}_2^2 \approx \omega_2^2 + \frac{\gamma_{12}^2}{\omega_2^2 - \omega_1^2} \quad (18)$$

It is seen that the eigenfrequencies of the coupled oscillators are slightly shifted from those of independent oscillators.

Now, we consider a more general case a_1 , γ_1 , γ_2 and γ_{12} are not equal to zero. After some manipulation, the steady-state solutions for the oscillators' displacement can be written in harmonic forms such that:

$$x_1(t) = c_1(\omega)e^{i\omega t}, \quad x_2(t) = c_2(\omega)e^{i\omega t} \quad (19)$$

where:

$$c_1(\omega) = \frac{(\omega_2^2 - \omega^2 + i\gamma_2\omega)}{(\omega_1^2 - \omega^2 + i\gamma_1\omega)(\omega_2^2 - \omega^2 + i\gamma_2\omega) - v_{12}^2} a_1 \quad (20)$$

$$c_2(\omega) = \frac{v_{12}}{(\omega_1^2 - \omega^2 + i\gamma_1\omega)(\omega_2^2 - \omega^2 + i\gamma_2\omega) - v_{12}^2} a_1 \quad (21)$$

and $c_1(\omega) = |c_1(\omega)|e^{-i\varphi_1(\omega)}$ and $c_2(\omega) = |c_2(\omega)|e^{-i\varphi_2(\omega)}$. So, the phase difference between the two oscillators can be given as:

$$\varphi_2 - \varphi_1 = \pi - \Delta; \quad (22)$$

where the extra phase shift Δ is:

$$\Delta = \tan^{-1} \left(\frac{\gamma_2 \omega}{\omega_2^2 - \omega^2} \right) \quad (23)$$

For simplicity, the case of negligible friction for the second oscillator is examined ($\gamma_2 = 0$). For this situation, the amplitude of the first oscillator versus the frequency of the external force is illustrated in Figure 29(b), for $\gamma_1 = 0.025$ and $\gamma_{12} = 0.1$. Two peaks appear, a symmetric one at $\omega = 1$ and an asymmetric one at $\omega = 1.21$. The location of these resonant peaks corresponds to

the real parts of the complex eigenfrequencies of the coupled oscillators, $\tilde{\omega}_1$ and $\tilde{\omega}_2$, which are correspond to the zero values for the denominator of equations (20) and (21).

Based on equation (20), the amplitude of the first oscillator (c_1) has two resonance peaks (symmetric and asymmetric line-shape, shown in Figure 29(a)) near the eigenfrequencies $\omega = \text{Re}[\tilde{\omega}_1] = 1$ and $\omega = \text{Re}[\tilde{\omega}_2] = 1.21$ and it vanishes at the zero-frequency $\omega = \omega_{\text{zero}} = 1.2$. This

frequency (ω_{zero}) appears just before the peak position at eigenfrequency, $\omega = \text{Re}[\tilde{\omega}_2] = 1.21$.

The adjacency of a minimum to a maximum causes the second mode resonance to be asymmetric. The physical meaning of this zero amplitude can be explained based on the phase difference between the two oscillators by examining Figure 29(c) and 29(d). Unlike the first resonance, the phases of the two coupled oscillators are changing differently around the second resonance. When the frequency of the external force is less than ω_{zero} ($\omega < \omega_{\text{zero}}$), the first and second oscillators experience almost the same phase shift with respect to the external force, so both are in phase. However, just before ω_{zero} , the phase of the first oscillator eventually drops by π , to ultimately become out of phase with respect to the second oscillator. So, the motion of the first oscillator is wholly dampened by the second oscillator, and zero amplitude is experienced by the first oscillator. This forms a dip right before the peak resonance at $\omega = 1.21$, at which the two oscillators are in phase again.

A zero amplitude right before the peak is the main characteristic of a Fano resonance, which describes its narrow and asymmetric line shape. In other words, the critical feature of the Fano resonance is the possibility of destructive interference, which results in its asymmetric line shape [129-132]. In the case of $\gamma_2 \neq 0$, the amplitudes of both oscillators at resonance become smaller as γ_2 increases (not shown here). Besides, ω_{zero} for the first oscillator shifts, and the amplitude at this frequency does not vanish but gains a minimal value [11].

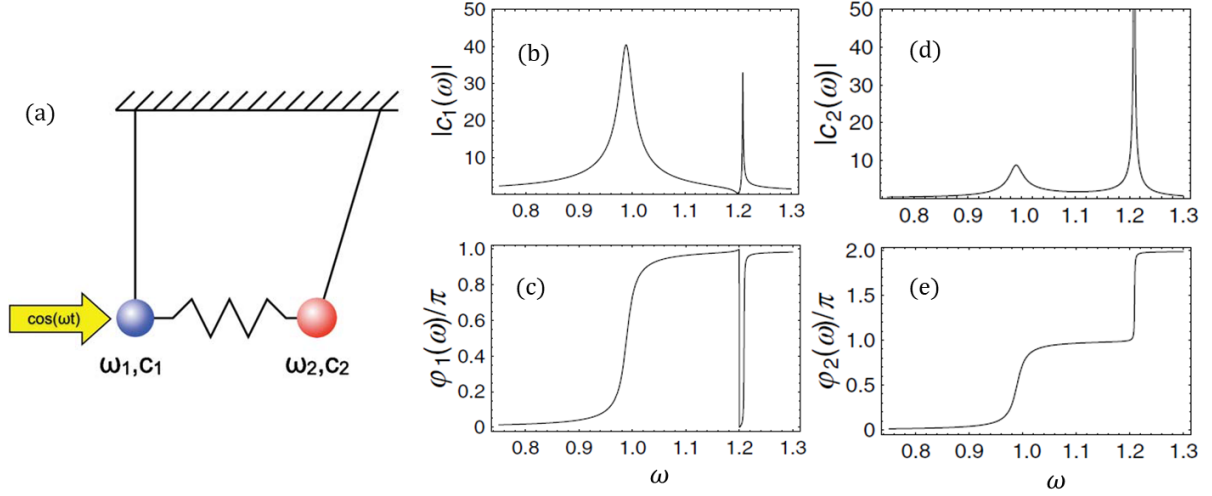


Figure 29 (a) Schematic view of two coupled oscillators with a driving force applied to the first one. The resonant behaviour of the amplitude of the (b) first oscillator and (d) second oscillator in two coupled oscillator system; where the frequency is in units of the natural frequency, ω_0 . There is a zero-amplitude at $\omega_{\text{zero}} = \omega_2 = 1.2$ for the first oscillator, which causes that this oscillator experiences an asymmetric lineshape near $\omega = 1.21$. The phase behaviour of the (c) first oscillator and (e) second oscillator amplitude have been provided, as well [11].

C. Plasmonic Fano resonance

Fano resonances in plasmonic structures are usually described based on coherent interference between superradiant and subradiant plasmon modes [133]. The superradiant mode has a finite dipole moments and can be excited by incident light. In contrast, the subradiant mode has an almost zero dipole moment, which hardly couples to incident light.

In other words, the Fano feature appears due to the coherent interference between a discrete (Lorentzian) mode and a spectrally broad continuum. Since the phase of the discrete mode changes rapidly with frequency around a resonance, while the continuum has a constant (or slowly changing) phase, there will be spectral locations of constructive and destructive interference on opposite sides of the resonance frequency. This is the main reason behind the formation of asymmetric Fano line-shape in plasmonic structures. Recently, Fano resonances have been found in various complex plasmonic nanoclusters [133, 134] such as pentamers [135], heptamers [136], nanodisks [137], and structures such as carbon nanotubes [138]. Fano resonances can be generated in plasmonic systems which have been engineered to support a

discrete subradiant dark mode and a broad superradiant one [133] . The key approach to observe a Fano resonance is to design a plasmonic geometry or a '*plasmonic molecule*' supporting simultaneous excitations of both types of modes. To do so, researchers have designed and studied different families of plasmonic nanostructures, such as asymmetric geometries, a NP near a metallic surface, periodic arrays of NPs, nanostructure clusters, and nanoparticles on a reflector.

a. Asymmetric geometries

Fano resonances have been detected and seen in a variety of physical systems. There are various ways to design a family of plasmonic nanostructures, called *plasmonic molecules*, to support Fano resonances. One of the conventional approaches is asymmetric, which forces the structure to support higher-order modes in addition to the dipole like mode. Generally, it is not easy to generate strong Fano resonances in a single plasmonic nanoparticle with high structural symmetry. That is why asymmetric plasmonic geometries have attracted significant attention for creating Fano resonances. The nonconcentric ring/disk cavity (NCRDC) arrangement [139] was one of the first asymmetric plasmonic structures, supporting a Fano resonance. As shown in Figure 30, asymmetric can be achieved by the displacement of the disk with respect to the center of the ring in a metallic disk-ring system. The plasmon resonances of this system are described in terms of the plasmon hybridization (PH) of the single ring and disk plasmon modes, which result in generating a new set of modes including symmetric and asymmetric ones [140]. The asymmetric one is a subradiant mode due to the opposite alignment of dipolar moments of the disk and ring. However, the symmetric one is superradiant, which strongly radiates because the dipolar plasmons of the disk and ring are in phase. The interference between these two modes results in a Fano resonance. Also, it has been shown that a non-concentric ring/disk cavity (NCRDC) can produce much more significant electromagnetic field enhancements than a concentric ring/disk cavity (CRDC).

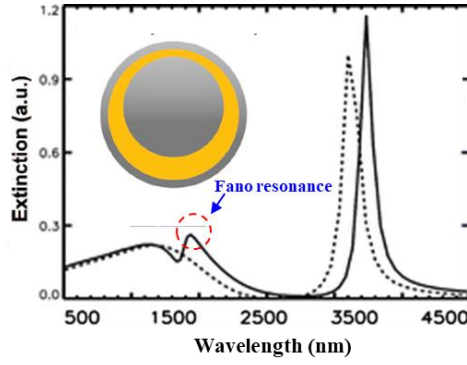


Figure 30 Extinction spectra for Ag centric ring/disk cavity (dashed lines) and Ag nonconcentric ring/disk cavity (solid lines) [140].

Panaro *et al.* [141] applied asymmetry to a nano-antenna dimer such that it may support a Fano resonance. In general, the aligned nanoantenna dimers promote an intense dipolar resonance (bright), but it can't support any dark modes, which is necessary for generating a Fano resonance. Panaro *et al.* [141] have shown that by tilting one arm of the dimer, consisting of the same length and width (see Figure 31(a)), symmetry is broken. This results in generating two new hybridized plasmon modes; an antibonding dark mode and a bright mode. Applying normally-incident light polarized parallel to the long axis of the non-tilted arm, experimental extinction spectra were obtained for various tilting angles between two dimers ($0^\circ < \delta < 90^\circ$), as illustrated in (Figure 31b). For $\delta < 70^\circ$, only a bonding peak exists, but a Fano dip starts to appear at shorter wavelengths for $\delta > 70^\circ$, as seen Figure 31 (b). This Fano dip is due to the interference of bonding and antibonding modes, which exist for the cases of $\delta > 70^\circ$.

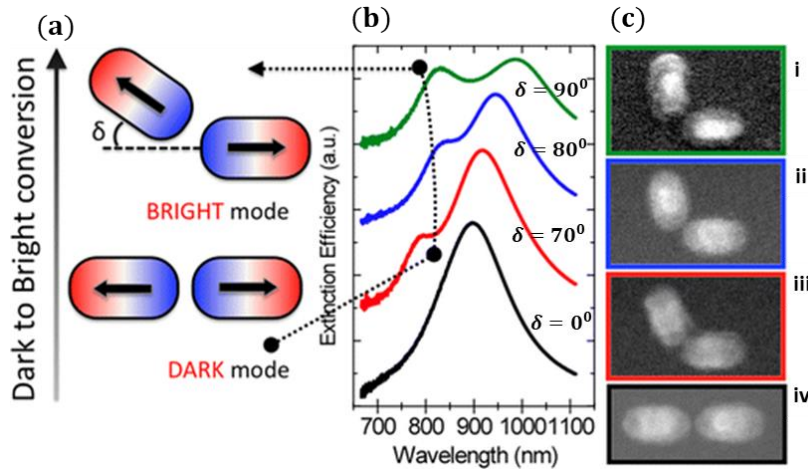


Figure 31 (a) Sketch of an aligned and a tilted nanoantenna dimer. (b) Experimental extinction spectra of the dimers for different tilting angle, δ . (c) SEM images of dimers for various tilting angles

0° (i), 70° (ii), 80° (iii), and 90° (iv) (single antenna sizes: length $l = 160$ nm, width $w = 80$ nm, height $h = 60$ nm, and interparticle gap is 5 nm) [141].

b. Periodic array of nanostructures

Arrays of metallic NPs may support collective optical excitations known as surface lattice resonances (SLRs). SLR can be supported in a plasmonic structure when NPs are positioned in an array with a lattice periodicity comparable to the wavelength of the incident light. By choosing the right combination of particle dimensions and material, and also the array periodicity, the scattered (diffracted) field arrived at each NP could be in phase with the plasmon resonance induced by the incident light. In this situation, the LSPP is reinforced, and then a new kind of resonance emerges, which is known as a surface lattice resonance (SLR) [142, 143]. This is an asymmetric Fano-like resonance which is sharper than the LSPP associated with the isolated single particle, and also is very sensitive to its surrounding environment [142, 144]. Figure 32(a), shows the extinction spectra for a single isolated NP (green line), and an array of NPs in a 480 nm square lattice (blue line). The extinction spectra of a 50 nm silver NP array of periodicity ranging from 200 to 700 nm, are provided in Figure 32(b).

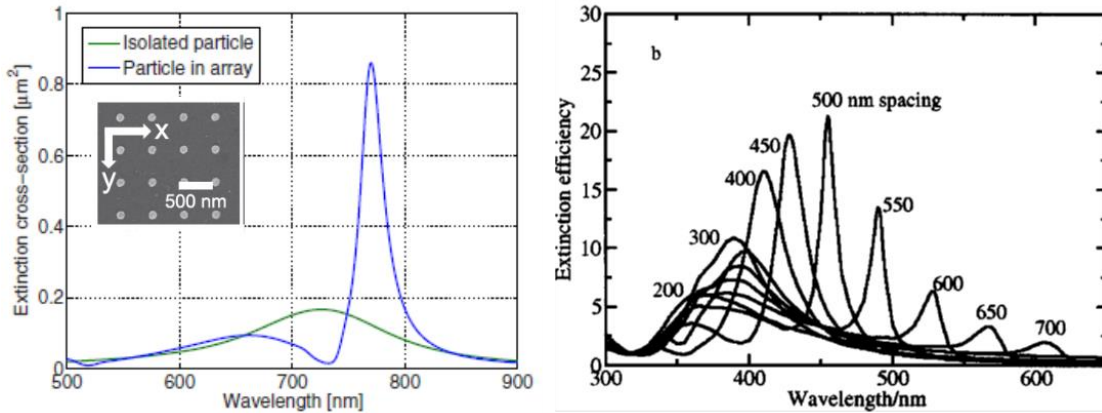


Figure 32 (a) Extinction spectra of a single isolated NP (green line) and a particle in a 480 nm square lattice (blue line). The NPs are silver disks with a diameter of 120 nm and a height of 30 nm embedded in a homogeneous medium ($n = 1.515$). (b) Extinction spectra of 50 nm silver NPs array of 400 particles with interparticle spacing (periodicity) ranging from 200 to 700 nm. The isolated particle spectrum is included for reference; it is evident that SLR is profound for specific periodicity, which is at $P=500$ nm, in this case [142].

Extraordinary optical transmission

A periodic array of plasmonic NPs or NHs can support Fano resonances due to excitations of SLRs, which occur for a specific periodicity. However, periodic arrays of subwavelength NHs exhibit another unusual behaviour discovered by Ebbesen *et al.* [58], who reported pioneering work on metallic nanohole arrays, demonstrating extraordinary optical transmission (EOT) with a Fano lineshape at specific wavelengths [58, 145]. Van der Molen *et al.* [146] explained that the mechanism behind the Fano resonance is the coupling between SPPs or LSPPs and light directly transmitted through the holes. Gao *et al.* [147] reported a theoretical and experimental study on periodic nanohole arrays in a thin gold film, as illustrated in Figure 33(a). They have shown that this subwavelength hole array exhibits EOT due to the coupling between SPPs and the light directly transmitted through the holes. They showed that the hybridization of a SPP-Bloch wave on one side of the film with a Wood's anomaly (WA) on the other side, leads to a narrow linewidth peak, which is very sensitive to the surrounding refractive index, and is suitable for sensing applications.

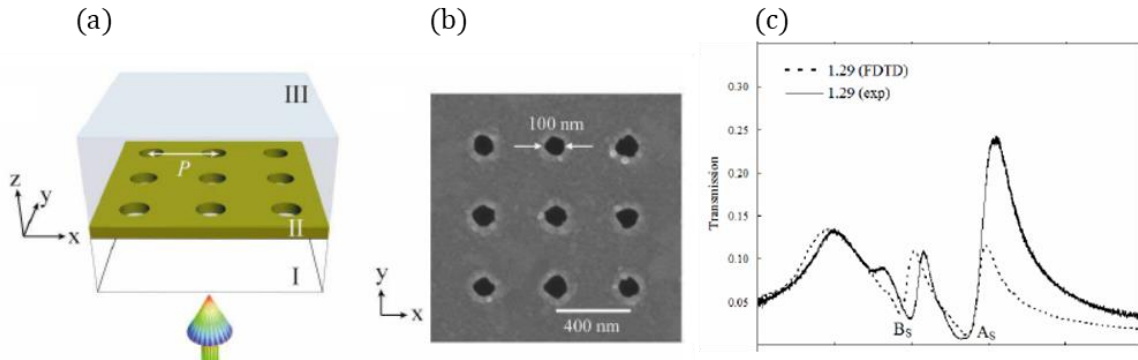


Figure 33 (a) Schematic of an array of nanohole on SiO₂ substrate (b) SEM image of the array (c) Finite-difference time-domain (FDTD) and experimental transmission spectra for $n_{III} = 1.29$ (n_{III} is the refractive index of the superstrate). This structure supports several Fano-shape resonances originating due to the coupling of SPR or LSPR and the light directly transmitted through the holes [148].

c. NP near a metallic surface

An interesting plasmonic structure supporting Fano resonances is the metal-film/nanoparticle system, which is a coupled system consisting of NPs on top of a metallic film with a dielectric spacer in between, as shown in Figure 34 (a). The primary mechanism behind the generation of

Fano resonances in this system is the coupling and plasmonic hybridization of LSPPs on the NPs with delocalized (propagating) SPP modes of the structure. The first experimental study on such a coupled system was reported by Holland and Hall [149], in which the reflectivity spectra of silver and gold island films deposited on a silver film were measured for spacers of various thickness. Maurer *et al.* [150] have published a review article focusing on coupled plasmonic NP/film systems, where NPs on top of the metal film are either isolated, random or ordered (periodic array of NPs). In addition, they discussed advances and the potential applications of such plasmonic coupled systems. In another study, Nicolas *et al.* [151] investigated and measured the response of a coupled AuNP metal film system consisting of an array of AuNPs on top of a 50 nm thick Au film, with a 6 nm thick SiO₂ spacer in between, as shown in Figure 34 (a), which supports Fano resonances. The originality of their work was in the simplicity of the designed structure. In this structure, the Au film operates as a mirror reflecting the white light which acts as the continuum. Interaction between the continuum and the localized gap mode in the 6 nm spacer results in a Fano resonance. They have shown that a Fano profile can be highly tunable by altering the NP diameters and the periodicity of the lattice. Also, they illustrated that increasing the incident angle of illumination, from 0° (normal incidence) up to 60° could result in decreasing the asymmetry of the Fano profile, as shown in Figure 34 (c). Finally, they examined the sensing performance of this coupled system by measuring the FOM, reporting a value of 3.8, the highest for a sensor of this type at this wavelength.

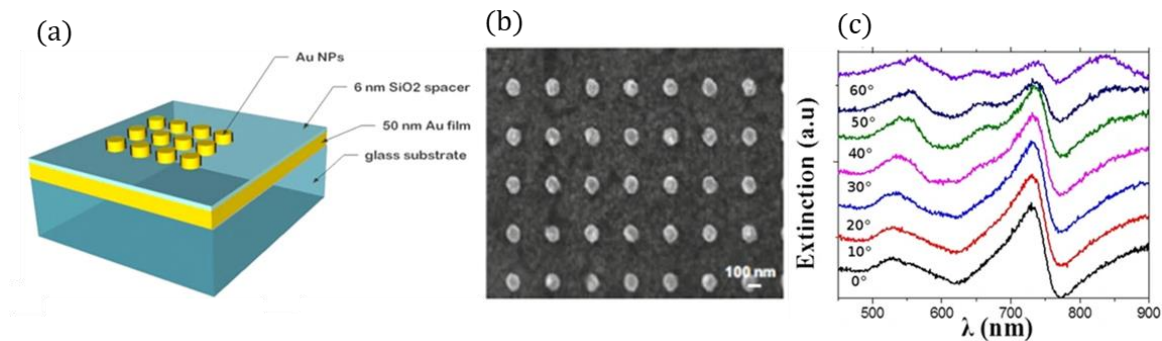


Figure 34 (a) Schematic of the coupled system of AuNPs on a 50-nm-thick Au film with a 6-nm-thick SiO₂ spacer. (b) SEM images of an array of AuNPs with a periodicity of 300 nm and diameters of 110 nm (c) Evolution of extinction spectra for a various incident angle of illumination for TE illumination [151].

In another study, Le *et al.* [152] examined the coupled system of a metallic nanoshell near a metallic film, as shown in Figure 35. They illustrated that this metallic nanoshell/film structure supports bonding and anti-bonding modes, that the coupling between these two modes results in strong Fano resonances with significant local field enhancements. The strength and the line width of the Fano resonances depend strongly on the aspect ratio of the nanoshell (the ratio of inner to outer radius) and the thickness of the film.

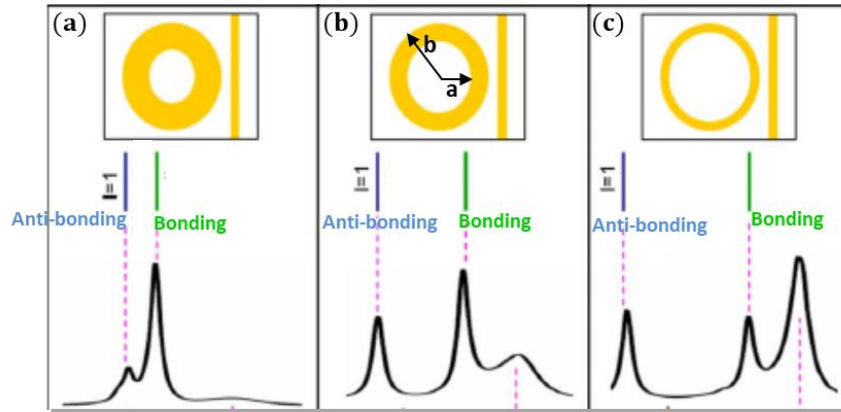


Figure 35 (a) Schematic of the nano shell-metallic film interaction with a different aspect ratio (a/b). The black curves show the absorption spectrum resulting from the plasmonic interaction between the nanoshell and the film.

d. Nanostructure clusters

One family of nanostructures exhibiting sharp Fano resonances is a finite cluster of plasmonic nanostructures. When two or more nano elements are located very close to each other, their plasmons can couple through near-field interactions and form a new set of hybridized collective plasmonic modes. A variety of plasmonic nanoclusters consisting of three [153], four [154], seven particles [108], and even more elements [155] have been studied, which exhibit Fano features when the near-field coupling between elements is sufficiently high. A dolman-type slab arrangement was one of the first plasmonic geometries investigated, supporting a Fano resonance in its transmission spectrum [156].

In this category, the heptamer arrangement of NPs has attracted significant attention. This symmetric NP cluster consists of a central particle surrounded by six nanoparticles [108, 157].

The collective plasmon modes of this arrangement are hybridized states formed by the interaction of the central particle LSPPs with the collective LSPPs of the surrounding six particles, as shown in Figure 36 (a). Two different modes, bonding and antibonding modes, form. For the bonding mode, the dipolar plasmons of all particles oscillate in-phase along the polarization direction of the incident light. So, it is a superradiant mode, resulting in a strong scattering due to the constructive interference of the particles' radiated fields. However, for the antibonding mode, the total dipolar plasmon of the surrounding NPs oscillates out of phase respect to the dipolar plasmon of the central particle. For a heptamer constructed of identical particles, the dipolar plasmon of the central particle and ring particles cancel each other out, leading to substantial destructive interference of their radiating fields. So, this subradiant plasmon mode weakly couples into the incident light, resulting in a sharp Fano resonance in the spectra, as illustrated in Figure 36(a–c).

Fan *et al.* [108] have investigated a self-assembled nanoshell heptamer. They reported observing Fano resonances in the scattering spectra, seen as a dip at $\lambda = 1490$ nm, as shown in Figure 36(a–c). Hentschel *et al.* [158] investigated the optical response of plasmonic hexamer and heptamer arrangements of planar disks, as shown in Figure 36 (d). They showed that decreasing the interparticle separation beyond 60 nm results in a pronounced Fano resonance, as illustrated in Figure 36 (f). The optical response of the hexamer exhibits a drastic change with respect to the heptamer, so the hexamer which has a missing central particle doesn't support any Fano resonance, as illustrated in Figure 36 (e).

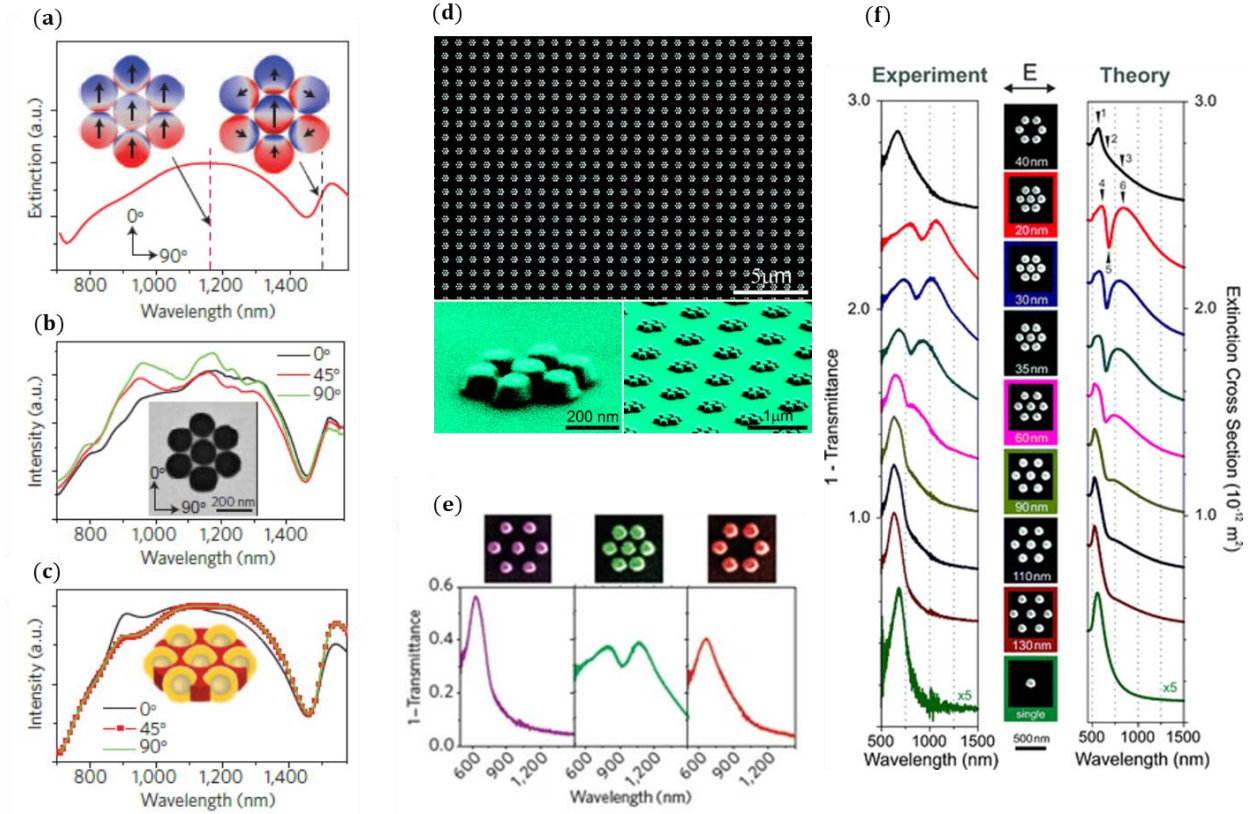


Figure 36 Fano resonances in plasmonic nanoparticle clusters. (a) calculated dipole amplitudes of the bonding and antibonding plasmon modes in a gold nanoshell heptamer[108]. (b) Measured and (c) calculated scattering spectra of a gold nanoshell heptamer [108]. (d) SEM images of the fabricated gold nanodisk heptamer. (Top) view of the sample, (bottom) enlarged views of the sample at a tilting angle of 70°. (e) and (f) Transmission spectra are showing that the heptamer supports a profound Fano resonance for small interparticle distances [108].

Bao *et al.* [155] numerically studied the optical properties of spherical silver nanoparticle clusters. They showed how the extinction spectra of the clusters evolve when the number of particles increases in the cluster. As seen in Figure 37(a), when the cluster is a heptamer, it exhibits a Fano resonance due to the interference between super- and subradiant collective cluster plasmon modes. For hexamer clusters composed of identical particles, the central particle has a larger dipole moment than the ring. So, the antibonding mode has a net total dipole moment, which means that it is no longer subradiant, and thus cannot contribute in generating a sharp Fano resonance, Figure 37(b) (left panel, first row). To overcome this problem, the size of the central particle was decreased to force the antibonding mode to become subradiant and generate a Fano dip (right panel, first row). For the octamer with

equally-sized particles (left panel, second row), the dipole moment of the ring is larger than the one of the central particle. Increasing the size of the central particle, the total net dipole moment could be zero. Then the antibonding mode becomes subradiant to create a sharp Fano dip (right panel, second row). The same idea can be applied to larger clusters, as shown in Figure 37 (b).

In another study [159], they used the plasmon hybridization approach and group theory to investigate the optical properties of a symmetric Ag heptamer oligomer placed on a glass substrate surrounded by dielectric media of different permittivity, as shown in Figure 38. The pronounced Fano resonance in its extinction spectrum is highly sensitive to the surrounding dielectric medium. Its calculated sensitivity was reported $\sim 515 \text{ nm/RIU}$, and its corresponding FoM was 10.6. This shows the great potential of this oligomer for sensing applications.

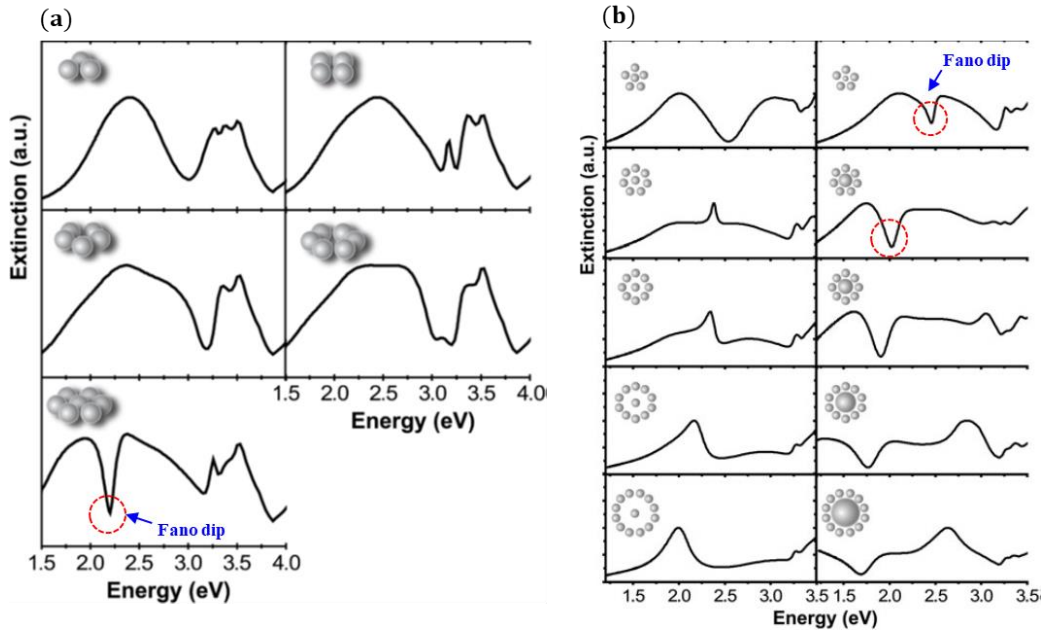


Figure 37 Calculated extinction spectra for different oligomers of silver nanospheres (a) showing the formation of Fano feature when the oligomer is a heptamer (b) illustrating that by changing the size of the central hole, the oligomer can support a Fano resonance. All peripheral particles have $R = 50 \text{ nm}$, and their interparticle gaps are 5 nm . The radius of the central particle is varying in the right panel to let the cluster have a zero net dipole moment for antibonding mode, and then support a Fano resonance.

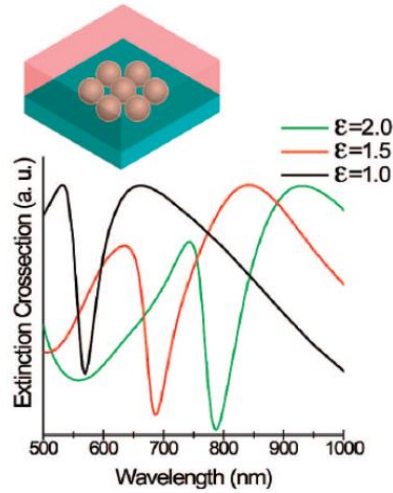


Figure 38 Extinction spectra of the Ag heptamer oligomer for surrounding media with different dielectric permittivity. The heptamer is composed of Ag sphere with radius = 50 nm and an interparticle gap of 5 nm. The glass substrate has a permittivity of 2.09.

While the origin of Fano resonances in plasmonic clusters is usually described as the interference of a bright and dark mode, some studies show that interference between two bright modes can lead to forming a Fano feature as well. For instance, a hybridized system composed of four interacting gold nanorods has been reported by Lovera *et al.* [154], and exhibits Fano resonances due to the interaction between bright modes only. As shown in Figure 39 (a), the structure consists of nanoantennas (yellow) coupled to two parallel nanorods (blue). The whole nanostructure is made of gold (different colors in Figure 39 (a) were used for clarity). As demonstrated in Figure 39 (b), the system exhibits a pronounced Fano resonance. The Fano resonance is highly tunable by changing the aspect ratio of the rods. Instead of using the conventional coupled oscillator (CCO) model [11], they developed an extended coupled oscillator model (ECO) for describing Fano interference in their system. They experimentally proved the tunability of the Fano resonance in this oligomer structure, Figure 40(a). With numerical calculations using a surface integral equation (SIE) method, they verified the accuracy of the ECO model, for a range of geometrical parameters, as illustrated in Figure 40 (a-c).

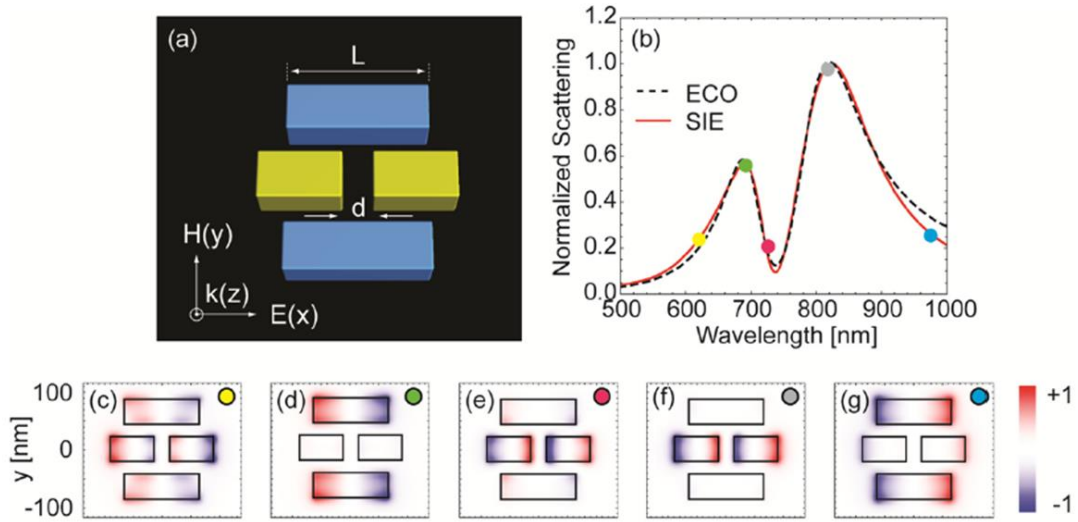


Figure 39 (a) Schematic of the oligomer structure consisting of a dipole antenna (yellow) and two nanorods (blue). The antenna has an arm length of 70 nm and a gap $d=25$ nm, and the other has an arm with a length of $L = 120$ nm. The whole system is made out of gold. (b) SIE simulation (solid red line) and ECO model fit (black dashed line) of the scattering spectrum for a structure. (c-g) The real part of the normal component of the electric field at some wavelengths illustrated in panel b [154].

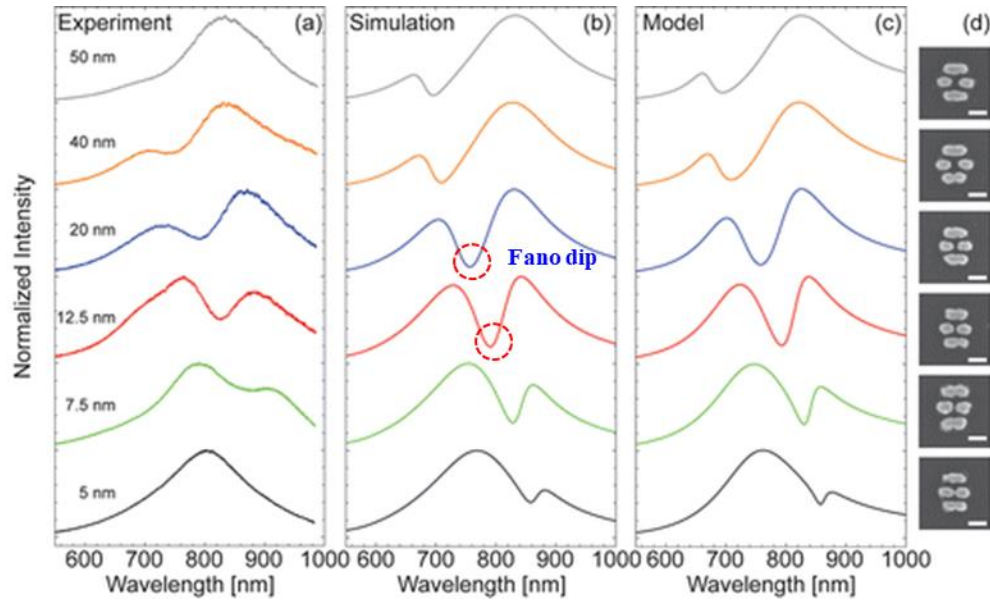


Figure 40 Scattering spectrum of the system (shown in Figure 39 (a)) (a) Dark-field experimental measurements, (b) SIE simulations, (c) ECO model simulation, and (d) SEM images of geometries with nanorods length $L = 120$ nm and varying antenna gap size from 5 to 50 nm (scale bar is 100 nm).

Complementary plasmonic structures, *nanohole oligomers*, are interesting due to their potential to support both LSPPs and propagating SPPs. In some cases, this kind of structure has been used to combine propagating SPPs with LSPP by hybridizing two modes to generate new ones [160]. Although great deal of attention has been paid to metallic nanoparticle clusters, the optical properties of their complementary structures – arrangement of nanoholes in a metallic film – remain mostly uninvestigated. Zhan *et al.* [161] have shown that a gold nanohole quadrumer, illustrated in Figure 41(a), can support two Fano resonances, arising from strong mode coupling between either two antiparallel dipolar modes or dipole–quadruple modes in the nanohole quadrumer. They used full-wave finite element modelling to study this structure numerically and they showed that the Fano linewidth and its spectral location can be engineered by adjusting the geometrical parameters of the nanohole cluster, including the nanohole diameter, film thickness and inter-hole separation, as shown in Figure 41(b). This nanohole quadrumer system exhibits a sensing figure of merit of up to 14.25, far exceeding the value achieved for nanoparticle clusters, at that time.

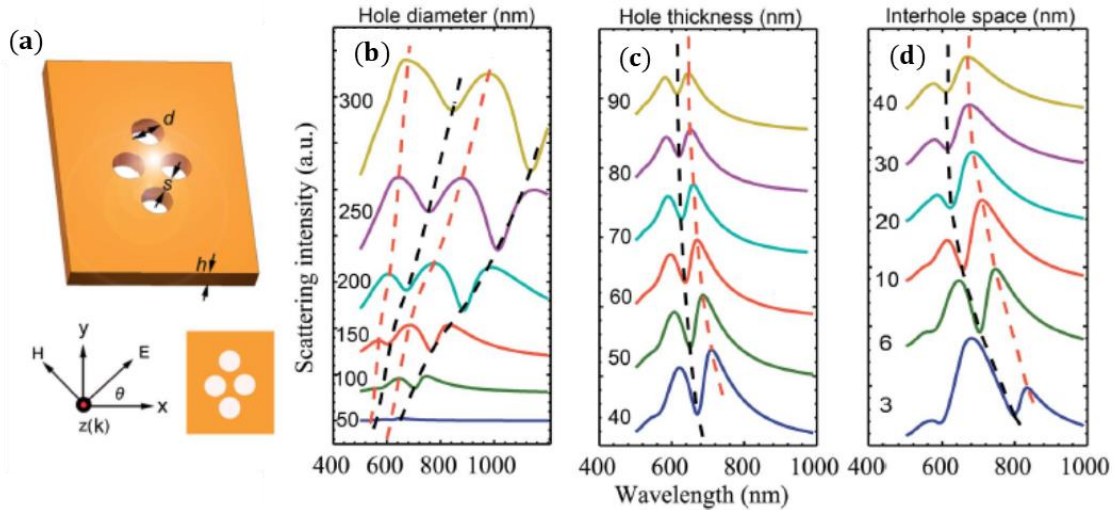


Figure 41 (a) Schematic of a quadrumer nanohole cluster in a gold film. (b) Scattering spectra of the cluster as a function of (b) hole diameter d (for $s = 6$ nm and $h = 30$ nm), (c) gold film thickness h (for $d = 100$ nm and $s = 30$ nm), and (d) inter hole distance s (for $d = 100$ nm and $h = 6$ nm). A y -polarized normal incidence field illuminates the whole system. Dashed lines indicate the positions of the dark modes (black) and bright modes (brick red).

e. Nanoparticles on reflecting dielectric

Fano resonances have been reported in a variety of plasmonic structures in which the hybridization between the plasmon modes of structure elements generates a new set of superradiant and subradiant modes. Usually, the interaction between these two new modes leads to the formation of a Fano feature in the optical response of the structure. Svedendahl *et al.* [162] proposed a different type of plasmonic structure consisting of layers of uncoupled gold nanodisks on a glass substrate, as illustrated in Figure 42(a). They measured reflectance spectra as a function of incidence angle and found highly asymmetric line shapes fitting very well with the Fano formula, shown in Figure 42. Unlike conventional Fano resonances, which form due to two plasmonic hybridized modes, here the Fano feature was described as originating from the interference between the LSPPs of the gold nanodisks and a “white” continuum caused by the interface reflection.

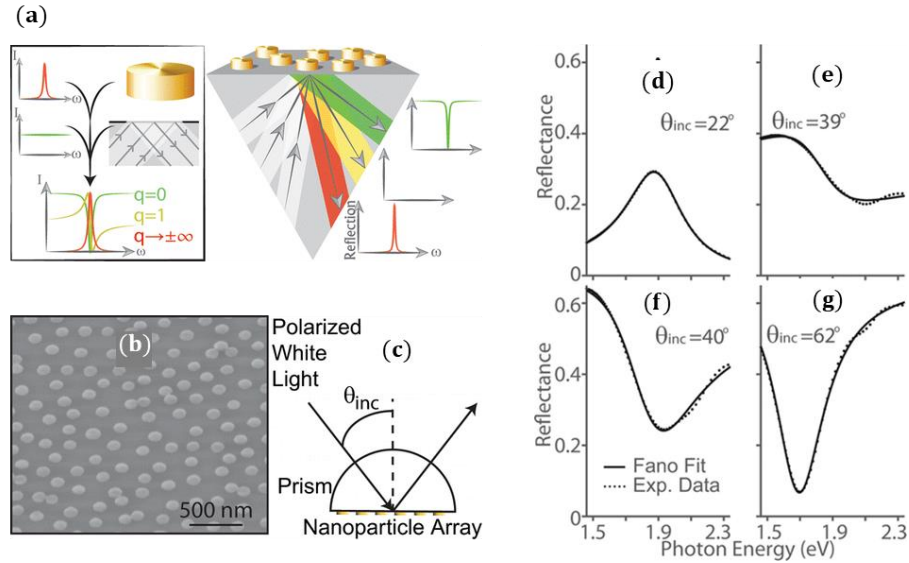


Figure 42 (a) Schematic of gold nanodisks on glass showing Fano interference due to the interaction between localized plasmons and an interface reflection. (b) SEM image of gold nanodisks on glass (c) schematic of the experimental measurement configuration. (d-g) Reflectance spectra for various incident angles. The asymmetric line-shapes is seen for angles close to the critical angle of the glass_–air interface, $\theta_c = 41.1^\circ$. Dotted lines correspond to experimental data, and solid lines are the Fano formula fits [162].

2. Ordered gold nanoparticle arrays on glass and their characterization.

A. Summary

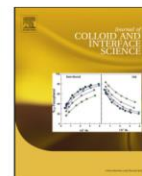
A novel method to fabricate hexagonal arrays of AuNPs was developed, in which diblock copolymer self-assembly followed by seeding growth was used to produce ordered AuNP arrays on SiO₂ substrates. First, diblock copolymer self-assembly was used to create AuNP seeds with various mean diameters, and centre-to-centre inter-particle spacings, by changing the molar ratio of the gold precursor to pyridine unit. Then the AuNP seeds with a mean diameter of ~ 10.0 nm and inter-particle spacing of ~ 62 nm were put in a growing chemical solution with the gold precursor, in which AuNPs gradually enlarged. The AuNP size and inter-particle spacing were managed by controlling the growth time and the concentration of the growth solution. Eventually, the AuNP seeds were grown to mean diameters of ~ 25.7 and ~ 33.0 nm, while simultaneously the edge-to-edge inter-particle spacing shrunk to ~ 37 and ~ 29 nm, respectively. Theoretical study and numerical simulations were carried out, and the results were compared with the experimental data to determine the arrays' characteristics, such as the size, pattern of NP arrays and spectral position of the LSPR. The bulk sensitivity was also calculated and measured to examine the structure for biosensing applications.

B. Contribution

The results provided in this chapter were published as an article in the *Journal of Colloid and Interface Science*. Jie Yuan designed and built the experimental setup; she performed the fabrication and obtained the experimental measurements; she wrote the experimental part of the manuscript. I performed the theoretical and numerical studies; I wrote the theoretical parts of the manuscript, and contributed to the interpretation of the results. Shan Zou contributed to the design, the analysis of the results and revised the manuscript. Dr. Berini contributed to the interpretation of the results and revised the manuscript.

C. Article

The published article follows verbatim.



Editor's Choice

Ordered gold nanoparticle arrays on glass and their characterization

Jie Yuan^{a,b}, Akram Hajebifard^c, Christeen George^{a,b}, Pierre Berini^{c,d,*}, Shan Zou^{a,*}^a National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada^b Department of Chemical and Biological Engineering, University of Ottawa, 161 Louis Pasteur, Ottawa, Ontario K1N 6N5, Canada^c Department of Physics, University of Ottawa, 150 Louis Pasteur, Ottawa, Ontario K1N 6N5, Canada^d School of Electrical Engineering and Computer Science, University of Ottawa, 800 King Edward, Ottawa, Ontario K1N 6N5, Canada

ARTICLE INFO

Article history:

Received 16 May 2013

Accepted 29 July 2013

Available online 12 August 2013

Keywords:

Gold nanoparticles (AuNPs)

Localized surface plasmon resonance (LSPR)

Self-assembly

Diblock copolymer

Seeding growth

ABSTRACT

Using self-assembly of block copolymer micelle loaded metal precursors, combined with a seeding growth route, we have developed a novel approach to create ordered metal nanoparticle (NP) arrays of controllable size over large areas ($\sim 80 \text{ mm}^2$) on solid substrates. Atomic force microscopy (AFM), UV–Vis extinction spectrophotometry, and theoretical simulations were systematically carried out to determine the size and pattern of NP arrays, and locate the localized surface plasmon resonance (LSPR) peak. By tuning the molar ratios of precursors, hexagonal arrays of AuNPs of mean heights of $5.2 \pm 0.6 \text{ nm}$, $8.3 \pm 1.7 \text{ nm}$, and $10.0 \pm 2.1 \text{ nm}$ were obtained by self-assembly of poly(styrene-*b*-2-vinyl pyridine) micelle-loaded gold salt on glass. Further seeding growth was then used to enlarge the AuNPs to heights of 25.7 and 33 nm and decrease the edge-to-edge inter-particle spacing. The optical response of AuNP arrays was determined by measuring and computing their absorbance spectra as a function of the cover medium refractive index over the range from 1 to 1.55; the measured spectra agree very well with the computations. The resonance wavelength red-shifts as the medium refractive index increases and the bulk sensitivity of the arrays increases with increasing AuNP size. When the edge-to-edge inter-particle spacing decreased to $\sim 50 \text{ nm}$, coupling of adjacent AuNPs became apparent, as a shoulder which developed in the spectra. Also, the AuNPs were found to be embedded in the substrate glass by about $\sim 20\text{--}30\%$, as determined by comparing the experimental and computed bulk sensitivities. The fabrication technique devised is suitable for low-cost mass-manufacturing of large area arrays of ordered high-quality AuNPs on a substrate for biosensor or other applications.

Crown Copyright © 2013 Published by Elsevier Inc. All rights reserved.

1. Introduction

The unique chemical, optical and electro-kinetic properties of gold nanoparticles (AuNPs), which are size- and shape-dependent, have been widely used in catalysts, solar energy harvesting, and sensing applications [1–5]. Although e-beam lithography or focused ion beam milling are commonly used to fabricate metallic nano-structures, the serial nature of these processes and their high costs are limiting. There is a pressing need for controlled solution-based nanoparticle fabrication methods applicable to large-area samples or substrates. Efforts have been expended in this direction but it remains challenging to create ordered metal NP arrays of controlled particle size and controlled spacing between particles. Using alkyl chain length (ligand-) controlled AuNP spacing, Lin

and others have demonstrated the possibility to prepare AuNP super-lattices by controlling solvent evaporation [6–8]. However, this approach limits the spacing of AuNPs to $\sim 3 \text{ nm}$ due to difficulties in the synthesis of longer alkyl chain lengths [9]. DNA-based routes extended the AuNP spacing to 20 nm [10–16], but unfortunately, it is difficult to produce a continuous super-lattice sheet of AuNPs over a large area [12,16]. Möller et al. introduced the method of using diblock copolymer micelles to load metal precursors and form NP arrays on solid supports [17]. For example, AuCl_4^- ions bind tightly to protonated pyridine units in the core of micelles so that the micelle structure served as nanoreactors and carriers of AuNPs [4,17–26]. This solution-based approach can yield NPs of uniform size (narrow size distribution), and is a simple and cost-friendly NP fabrication method [18,23,27].

Localized surface plasmon resonances (LSPRs) are charge density oscillations on metal NPs excited by light. They are sensitive to the optical properties of the surrounding environment. Metal NPs can scatter or absorb incident light. Extinction, the summation of absorption and scattering, is an optical property that characterizes metal NPs, particularly extinction spectra which reveal the location of LSPRs. According to the Mie theory [28], for metal NPs with a

* Corresponding authors at: School of Electrical Engineering and Computer Science, University of Ottawa, 800 King Edward, Ottawa, Ontario K1N 6N5, Canada. (P. Berini), National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada (S. Zou).

E-mail addresses: berini@eecs.uottawa.ca (P. Berini), shan.zou@nrc-cnrc.gc.ca (S. Zou).

diameter much smaller than the exciting wavelength, the extinction, absorption and scattering cross-sections are given by [29]

$$C_{\text{ext}} = C_{\text{abs}} + C_{\text{scat}} \quad (1)$$

$$C_{\text{abs}} = k \text{Im}(\alpha) = 4\pi R^3 \left(\frac{2\pi}{\lambda_0} \right) \left(\frac{3\varepsilon_2 \varepsilon_d^{3/2}}{|\varepsilon_1 + 2\varepsilon_d|^2 + \varepsilon_2^2} \right) \quad (2)$$

$$C_{\text{scat}} = \frac{1}{6\pi} k^4 |\alpha|^2 = \frac{8\pi R^6}{3} \left(\frac{2\pi}{\lambda_0} \right)^4 \varepsilon_d^2 \left(\frac{|\varepsilon_1 - \varepsilon_d|^2 + \varepsilon_2^2}{|\varepsilon_1 + 2\varepsilon_d|^2 + \varepsilon_2^2} \right) \quad (3)$$

$$\alpha = 4\pi R^3 \left(\frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \right) \quad (4)$$

where k is the wavenumber of the incident light, λ_0 is the free-space wavelength, R is the radius of the nanoparticle, ε_d is the dielectric constant of the surrounding medium, and $\varepsilon_m = \varepsilon_1 + i\varepsilon_2$ is the dielectric constant of the metal ($e^{-j\omega t}$ time-harmonic form implied). For a good plasmonic metal ($\varepsilon_2 \ll \varepsilon_1$) the extinction is largest at the wavelength where $\varepsilon_1 = -2\varepsilon_d$, $k = 2\pi\sqrt{\varepsilon_d}/\lambda_0$ for the case of the dipolar (bright) LSPR; we denote this wavelength as λ_{LSPR} . While λ_{LSPR} is mainly determined by the real part of the metal dielectric constant, the strength and width of the extinction, absorption and scattering spectra are determined mainly by the imaginary part of the dielectric constant, see Eqs. (1)–(3). For small NPs of diameter in the range of 10–30 nm, absorption dominates [30,31].

Several key factors are essential in characterizing metal NP arrays. First of all, λ_{LSPR} depends on the refractive index of the NP's surrounding medium, including the substrate, cover medium and any adsorbed species [1,3,32–39]. Secondly, when two or several AuNPs are deposited closely enough, inter-particle coupling is not negligible [40–46]. Depending on the orientation of AuNP arrays, the LSPR is polarization sensitive, and both red-shifts and blue-shifts can be achieved with increasing cover index [42]. Lastly, bandstructure effects can become more prevalent in the optical properties of AuNPs if they can be organized on the atomic scale [47]. In general, most of these characteristics can be enhanced significantly and utilized effectively if the AuNPs are organized in accurate and organized arrays [48].

Here, we report a simple fabrication method to generate hexagonal ordered AuNP arrays on glass cover slip substrates using self-assembly combined with seeding growth approach. As shown in Scheme 1, hexagonal patterned gold salt loaded poly(styrene-*b*-2-vinyl pyridine) (PS-*b*-P2VP) micelles are spin-coated on

substrates, and the polymer shell is removed by oxygen plasma etching. Arrays of AuNPs with 5 to 10 nm in size were created on glass substrates forming “seeds”, from which larger AuNPs were grown chemically. Series of AuNP sizes with controlled inter-particle spacing were obtained over large areas on glass substrates. The absorbance spectra of AuNP arrays on glass were characterized by UV–Vis spectroscopy. The influence of size, inter-particle spacing, surrounding permittivity (substrate and cover medium), and AuNP embedding ratio into the substrate are discussed. Also, the influence of the ionic strength and charge density of the micelle solution were considered.

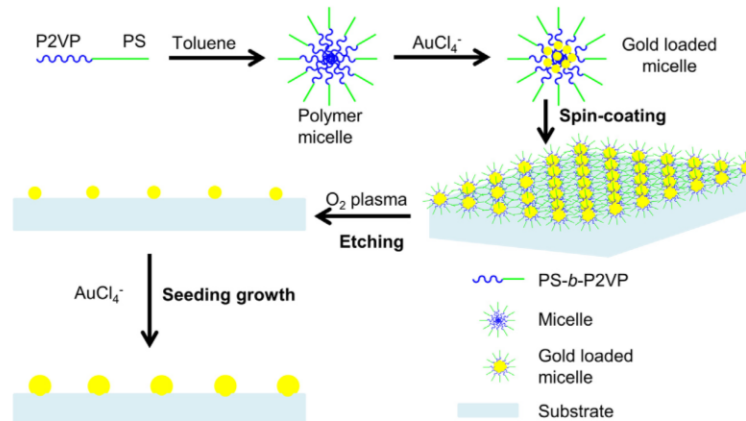
2. Materials and methods

2.1. Chemicals

Diblock copolymer poly(styrene(48.5k)-*b*-2-vinyl pyridine(70k)) (PS-*b*-P2VP, Polymer Source Inc., Montreal, QC, Canada) was used as purchased. Gold(III) chloride hydrate (99.999%) (HAuCl₄) and hydroxylamine hydrochloride (NH₂OH·HCl) were both purchased from Sigma–Aldrich Canada Ltd. (Oakville, ON, Canada), and used as received. 25 mm (78.5 mm²) premium glass cover slip substrates were purchased from Fisher Scientific (Ottawa, ON, Canada). 45 × 12.5 × 3.5 mm³ quartz cuvettes were purchased from Hellma Canada Ltd. (Concord, ON, Canada). HPLC grade methanol, dichloromethane, heptane, 99% ethanol, chloroform and *o*-dichlorobenzene were purchased from EMD Chemicals Inc. (Gibbstown, NJ, USA), Greenfield Ethanol Inc. (Brampton, ON, Canada), Caledon Laboratories Ltd. (Georgetown, ON, Canada) and Sigma–Aldrich Inc. (St. Louis, MO, USA). ACS grade toluene (Fisher Scientific, Fair Lawn, NJ, USA) was purified using an Innovative Technology Pure Solv. Device (activated alumina column containing a copper catalyst and molecular sieves). Milli-Q water deionized to a resistivity of 18 MΩ cm was used in all of the experiments.

2.2. Combined self-assembly and seeding growth methods

Patterned AuNP arrays on glass cover slips were prepared by the self-assembly of diblock copolymer micelle loaded gold salt [17,25,26,48,49]. Briefly, 5 mg/mL diblock copolymer micelle solution was prepared in dry toluene by vigorous stirring. Gold precursor (HAuCl₄) was added to the micelle solution at a molar ratio of 0.1, 0.2, 0.3, 0.4 and 0.5 per pyridine unit. The gold loaded micelle



Scheme 1. Processes of forming ordered hexagonal AuNP arrays on glass substrates: combining the self-assembly of diblock copolymer micelle loaded gold precursors with the seeding growth method.

solution was stirred overnight and spin-coated on clean glass cover slips at 2000 rpm (SPIN COATER, Chemat Scientific, Northridge, CA, USA). The polymer was removed by 15 min treatment in an oxygen plasma etcher (PlannerEcher IIA, Technics Inc., San Jose, CA). Hexagonal patterned AuNP arrays were formed and may be partially embedded into the glass cover slip substrates [48]. The ordered AuNP arrays served as seeds for further seeding growth processes [50–58]. The pre-seeded samples were put in a growing solution with 0.24 mM gold precursor in a container. 5 mM hydroxylamine hydrochloride (NH_2OH) solution was dropped into the container with pre-seeded AuNP array on glass at 1 drop per second until the final concentration reached 0.5 mM. After 15 and 30 min, a homogenous cherry-red film appeared on the side of the glass slide bearing the AuNP seed array. The other side of the glass was covered by tape in order to avoid AuCl_4^- stains. The samples were washed thoroughly with MQ water. By controlling the growth time and the concentration of the growth solution, the AuNP size and edge-to-edge inter-particle spacing are controlled.

2.3. Size measurement of gold precursor loaded PS-*b*-P2VP micelles in toluene

The diblock copolymer micelle diameters were evaluated by dynamic light scattering (DLS) (Nano Zetasizer, Malvern Instrument Ltd, Worcestershire, United Kingdom). The sample was diluted to 0.1 mg/mL in toluene and filled in a PSC115-Glass cuvette of square aperture. All of the data were obtained at 25 °C.

2.4. Characterization of patterned AuNP arrays on glass

The height and inter-particle spacing of patterned AuNP arrays on glass were measured by an AFM (Nanowizard II BioAFM, JPK Instruments, Berlin, Germany) mounted on an Olympus IX81 inverted confocal microscope. Silicon cantilevers and tips (NSC14, MikroMasch, Estonia) were used to image all samples in intermittent contact mode. At least five locations on each sample were tested. Absorbance spectra measurements were carried out using a Varian Cary 5000 UV–VIS–NIR spectrometer (Varian Inc., AC, USA). For each measurement, the AuNP arrays on glass were immersed in each solvent sequentially while the surface of the AuNP arrays was kept perpendicular to the optical source. Multiple measurements were taken for each sample to ensure the reproducibility of the measurements. The absorbance spectrum of the AuNP arrays on glass was measured in each solvent in turn commencing with the solvent having the lowest refractive index. After each measurement, the substrate and the cuvette were rinsed in turn with methanol, ethanol and water, and then dried with nitrogen. This step was repeated several times to completely remove the previous solvent.

Two sets of solvents with different refractive index ranges were chosen. One set of six solvents provides refractive indices from 1.3284 to 1.4458, as listed in Table 1. The other set of six solvents were prepared by mixing toluene and *o*-dichlorobenzene at different volume ratios (Table 1). The refractive index of the toluene/*o*-dichlorobenzene binary mixture was estimated via Eq. (5) and all solvents were verified by prism-coupling techniques using a Metricon Model 2010 (Metricon Corporation, Pennington, NJ, USA).

$$n_{\text{mix}} = \frac{n_{\text{D-Toluene}} \times V_{\text{Toluene}} + n_{\text{D-Dichlorobenzene}} \times V_{\text{Dichlorobenzene}}}{V_{\text{Toluene}} + V_{\text{Dichlorobenzene}}} \quad (5)$$

The differences between the estimated values (n_D) and the measured values for all solvents (n_D^*) in Table 1 were less than 0.4%. Thus, the refractive index of the toluene/*o*-dichlorobenzene binary mixture was properly evaluated by Eq. (5). The stability of AuNP arrays on glass was verified in various solvents, such as ethanol (3 days), water (7 days), detergent aqueous solution (1 day),

Table 1

Refractive indices of toluene/*o*-dichlorobenzene binary mixtures and six other solvents used.

Toluene and <i>o</i> -Dichlorobenzene mixture	Refractive index of binary mixture (n_D)	Refractive index of binary mixture (n_D^*)
T/D 1:0	1.4969	1.49112
T/D 3:7	1.5133	1.51094
T/D 1:1	1.5242	1.52198
T/D 7:3	1.5351	1.53541
T/D 1:9	1.5460	1.54191
T/D 0:1	1.5514	1.54580
Solvents	Refractive index (n_D)	Refractive index (n_D^*)
Methanol	1.3284	1.32598
Water	1.3330	1.32724
Ethanol	1.3614	1.35922
Heptane	1.3876	1.38781
Dichloromethane	1.4241	1.41850
Chloroform	1.4458	1.44265

Note: The n_D was estimated by assuming that the refractive index of the binary mixture is proportional to the volume ratio of the two components for the toluene and *o*-dichlorobenzene binary mixture. For solvents, it was evaluated by the ratio of the velocity of light (sodium D line) in air to the velocity of light in the solvent at 20 °C (provided by Burdick & Jackson). The n_D^* was experimental measurement by using Metricon Model 2010. T/D represents the volume ratio of the two components in the mixture.

dichloromethane (3 h), piranha solution (H_2O_2 (30%): H_2SO_4 (97%) 1:4(vol), 5 min), and saturated potassium hydroxide in ethanol (15 wt%, 5 min). The arrays remained stable for further experiments.

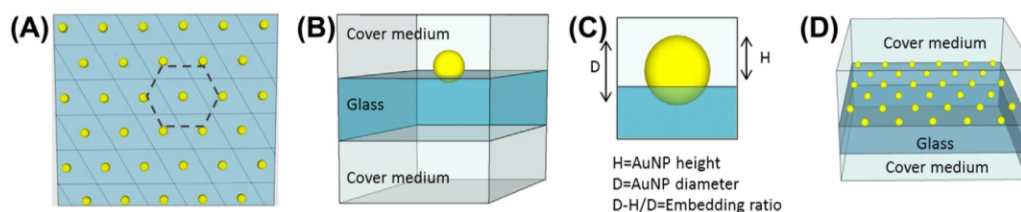
2.5. Computations

The calculations were carried out using the RF module of COMSOL finite element software. The modeling was defined as following: the unit cell is illuminated by a plane-polarized electromagnetic wave from the top (Scheme 2), and absorbance is calculated as the optical response of the sample. An x-polarized wave strikes the unit cell and propagates through the medium along the unit cell. A surface integral on the *z* component of the time averaged pointing vector is used to calculate transmittance and then absorbance. The following equation is applied for the calculation of the absorbance (as measured):

$$A = -\log\left(\frac{T}{T_0}\right) \quad (6)$$

where *A* is the absorbance, and *T* and *T*₀ are used to denote the transmittance with and without the nanoparticle in the unit cell, respectively. The absorbance is computed over the spectral range corresponding to a free space wavelength of 400–700 nm.

Computations have been done for AuNPs with a height of 10 nm, and 25.7 nm. The 33 nm one was modeled as an oblate spheroid having a ratio of major to minor axes of 1.06. The longitudinal diameter along the glass-superstrate interface is 35 nm and the transverse one is 33 nm. The edge-to-edge inter-particle spacing used was 52, 46 and 29 nm, for the 10, 25.7 and 33 nm NPs, respectively. In all cases, an AuNP array is assumed to involve an infinite number of particles with the same shape and center to center inter-particle distance. Since the geometrical properties of the NPs fluctuate particle to particle, the averaged geometrical properties of the experimental sample were chosen. AuNPs fabricated on the glass have a quasi-hexagonal pattern, as shown in Scheme 2(A) and (D). This kind of pattern can be made by repeating a parallelogram-shape unit cell with equal sides representing center to center inter-particle spacing, as shown in Scheme 2(A).



Scheme 2. (A) Model of an AuNP array fabricated on a glass substrate; the array pattern is hexagonal. (B) Simulated parallelepiped unit cell includes a glass-supported AuNP bounded by cover media. (C) An AuNP embedded into the surface of the glass slide. (D) AuNP arrays on a glass substrate exhibited a quasi-hexagonal pattern.

To take advantage of the structural symmetry, only one unit cell including one NP is modeled, as shown in Scheme 2(B). Scattering boundary conditions are applied to the top and bottom of the unit cell to define an incident wave with boundaries having no physical reflections into the cell. Periodic boundary conditions have been applied to the rest of the boundaries.

Different mesh densities have been tested to assess convergence of the analysis. The optimum discretization was chosen to be 0.8 nm within the NP domain and in its vicinity, and 3 nm within the rest of the domain. Since the skin depth for gold (~ 25 nm) over the spectral range of interest is of the order of the particle diameter, the mesh density within the entire gold domain was taken as 0.8 nm.

2.6. Calculated optical properties

The optical properties of the materials used in the computations were taken as the frequency-dependent complex refractive index (permittivity) measured over the wavelengths of interest for glass [59], gold [60,61], and some of our solvents [62–64], such as methanol, water, ethanol, heptane, chloroform and toluene. Cubic spline interpolation functions were applied to determine the materials' refractive index at specific wavelengths of interest where data are not available. For other solvents a wavelength-independent refractive index at the sodium D line ($\lambda = 589$ nm) was chosen for the whole spectra range. Refractive index values of 1.4241, 1.5514, 1.5132, 1.5241, 1.5351, and 1.5459 were used for dichloromethane, o-dichlorobenzene, T/D 3:7, T/D 1:1, T/D 7:3, T/D 1:9 respectively.

3. Results and discussion

3.1. Self-assembly controlled formation of AuNP seed arrays

Atomic force microscopy (AFM) height images of representative AuNP seed arrays formed with 0.1, 0.2 and 0.5 mol ratio of gold precursor per pyridine unit are shown in Fig. 1. Correspondingly, the mean heights of AuNPs were 5.2 ± 0.6 , 8.3 ± 1.7 , and 10.0 ± 2.1 nm, respectively. Fast Fourier transformed (FFT) images are shown as insets to the AFM topography images in Fig. 1. The AFM height images although limited in area are typical of the distribution of particles over the full area of the glass substrate (~ 80 mm²). Ordered hexagonal patterns were obtained when the standard deviation of height distribution was controlled to within ± 0.6 nm; as the deviation increased, the hexagonal patterns degraded slightly (as shown in Fig. 1(B) and (C)). When the gold precursor loading ratio (in short, the loading ratio) increased, the center-to-center distance (D) varied. The distance initially increased from 80 ± 8 to 88 ± 9 nm as the loading ratio increased from 0.1 to 0.2 mol/pyridine unit (Fig. 1(A) and (B)), then as the loading ratio increased to 0.5 mol/pyridine unit, the D decreased to 62 ± 11 nm as shown in Fig. 1(C).

3.2. Micelle sizes and inter-particle spacings of AuNPs

In order to understand the non-linear relation between the inter-particle spacing and the loading ratio per pyridine unit, the diameter of PS-P2VP micelles in toluene was evaluated by dynamic light scattering (DLS). Fig. 2 shows that the micelle diameter was 83 nm with the loading ratio of 0.1 mol per pyridine unit, then expanded to 91 nm as the loading ratio increased to 0.2 mol per pyridine unit, and reached a maximum of 94 nm as the loading ratio increased to 0.3. However, further increasing the loading ratio led to a decrease in micelle diameter; as the ratio increased to 0.4 and 0.5, the micelle diameter decreased to 84 and 67 nm, respectively. This finding is partially supported by other studies which showed that increasing the loading ratio would only cause a marginal expansion of the micelle [23]. We propose the following that may lead to micelle shrinkage at a high loading ratio.

Once the gold precursors accumulate in the core area of micelles where is enriched in P2VP blocks, the salt will alter the interaction between the polymer chains locally, as well as between the polymer and solvent. In toluene, the accumulation of gold salt enhances the unfavorable interaction between P2VP core and the solvent (thus with the PS corona), resulting in collapses of PS chains and the shrunk of corona (PS) thickness. At the same time, due to the favorable interaction between the P2VP blocks and the gold salt, the core of micelles may expand. At a low loading ratio, the influence of the gold precursor on the PS corona is not as significant as on the P2VP, such that the micelle diameter expands slightly. When further increasing the loading ratio the core-shell structure changes accordingly. When micelles with larger core covered by thinner layer of PS shell were formed, their structures are not as stable as the micelles with lower loading ratios of gold precursors.

In Fig. 2, the micelle diameters measured in toluene by DLS coincides with the AuNP inter-particle spacing on the substrate. This is not surprising because the gold-loaded micelles in solution were spun on the substrate surface and the inter-particle spacing is dominantly controlled by the micelle diameter. During solvent evaporation, the surface tension causes a monolayer of micelles formed onto the substrate surface, thus preserving the inter-particle spacing after the sample was dried.

Absorbance spectra of AuNP seed arrays on glass with the mean height of 10.0 ± 2.1 nm were measured for cover media (solutions) of refractive index ranging from 1 to 1.5514, as shown in Fig. 3(A). The spectra were offset along the y-axis for clarity except for the one measured in air. The λ_{LSPR} is observed to increase with the cover medium refractive index, i.e., the resonances red-shift with increasing index. There was no shoulder apparent in the absorbance spectra; thus, coupling between different AuNPs was negligible (the inter-particle spacing here was 62 ± 11 nm) [41,65]. Arrays of seed AuNPs of different sizes are compared in Fig. 3(B). The λ_{LSPR} of the arrays, measured with a cover medium of refractive index 1.3876, shifted from 524 to 527 nm, then to 532 nm, as the AuNP mean heights increased from 5.2 ± 0.6 to 8.3 ± 1.7 nm and

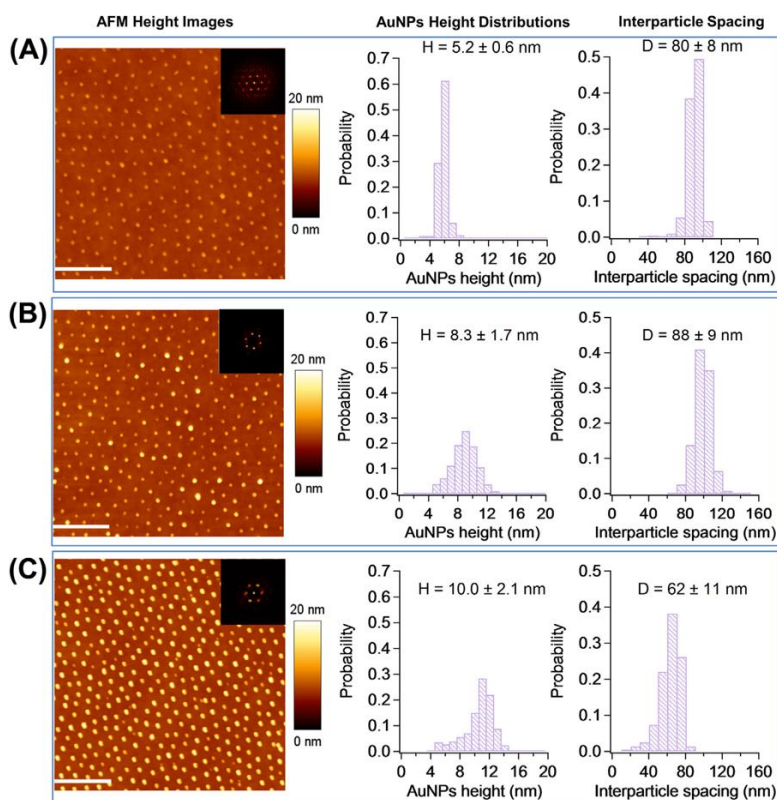


Fig. 1. Representative patterned AuNP (seed) arrays with different heights and center-to-center distances of the nearest neighbor. AuNP array samples with height distribution (H) and center to center distance (D) determined from AFM topography images: H of 5.2 ± 0.6 nm and D of 80 ± 8 nm (A); H of 8.3 ± 1.7 nm and D of 88 ± 9 nm (B); H of 10.0 ± 2.1 nm and D of 62 ± 11 nm (C). Insets to AFM height images are the fast Fourier transformed images of the corresponding height images. Scale bars on AFM images are 350 nm; the numbers of counted particles in each panel are in the order of 350–800.

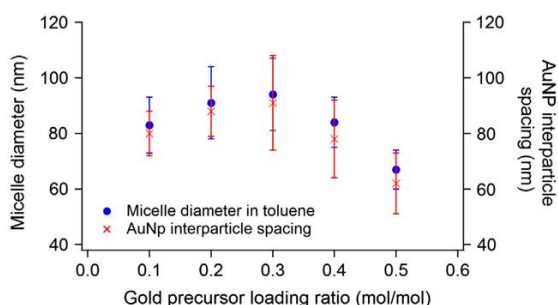


Fig. 2. Comparison between micelle diameters in toluene and the inter-particle spacings of AuNPs on glass.

then to 10.0 ± 2.1 nm, respectively. Thus λ_{LSPR} is sensitive to AuNP size (height), as well as to the cover medium refractive index [36].

3.3. Seeding growth to enlarge the size of AuNPs on hexagonal seed arrays

In order to better understand the influences of AuNP size, inter-particle spacing and surrounding medium refractive index, absorbance measurements were obtained on enlarged AuNP arrays prepared using our self-assembly and seeding growth approaches. Samples were prepared by using AuNP seed arrays with the mean

height of 10 nm and center-to-center inter-particle spacing of 62 nm followed by chemically seeding growth. As observed from the AFM images in Fig. 4, the grown AuNP mean heights are 25.7 ± 2.7 nm (A), and 33.0 ± 4.4 nm (B) and the edge-to-edge inter-particle spacings are 46 and 29 nm, respectively.

λ_{LSPR} increases more with increasing cover medium refractive index for the samples with larger AuNPs. In addition, as the AuNP size increases, and the edge-to-edge inter-particle spacing decreases, coupling between AuNPs becomes observable in the measured absorbance: as noted from Fig. 4(B), in addition to the main λ_{LSPR} , a clear shoulder appears at a longer wavelength (~ 650 – 670 nm) in the absorbance spectrum for the case of air as the cover medium (the inter-particle spacing is less than 5 times of the AuNP radius) [66]. Interestingly, when the cover medium refractive index increases, the shoulder disappears (in addition to red-shifting λ_{LSPR}), indicating weaker coupling between particles. It is known that λ_{LSPR} and particle coupling are highly depended on the refractive index of the medium [67]. In this case the fields are increasingly confined to the AuNPs as the medium refractive index increases leading to less coupling.

3.4. Computations

It is worth to notice that in Figs. 1 and 4, the applied forces (i.e., imaging parameters) were controlled at the minimum to preserve the AuNP patterns while the AFM tip was scanning across the samples. Surprisingly, when changing the imaging mode to contact mode and increasing the imaging setpoint values

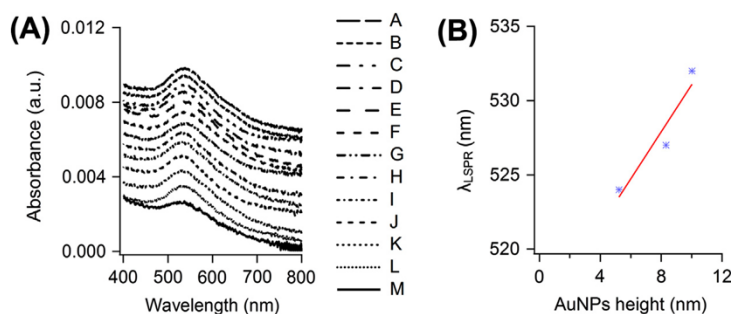


Fig. 3. (A) Measured absorbance spectra on representative AuNP (seed) arrays of height 10.0 ± 2.1 nm on glass for cover media (solutions) of refractive index ranging from 1.5514 to 1 (See Table 1 for details). A, *o*-dichlorobenzene; B, T/D 1:9; C, T/D 3:7; D, T/D 1:1; E, T/D 7:3; F, toluene; G, chloroform; H, dichloromethane; I, heptane; J, ethanol; K, MilliQ water; L, methanol; M, air. T/D represents the binary mixture of toluene and *o*-dichlorobenzene by volume ratio. Spectra are off-set along the y-axis for clarity by 0.0002 a.u. (B) λ_{LSPR} of AuNP seed arrays in heptane ($n = 1.3876$) showing a positive linear relation to AuNP heights.

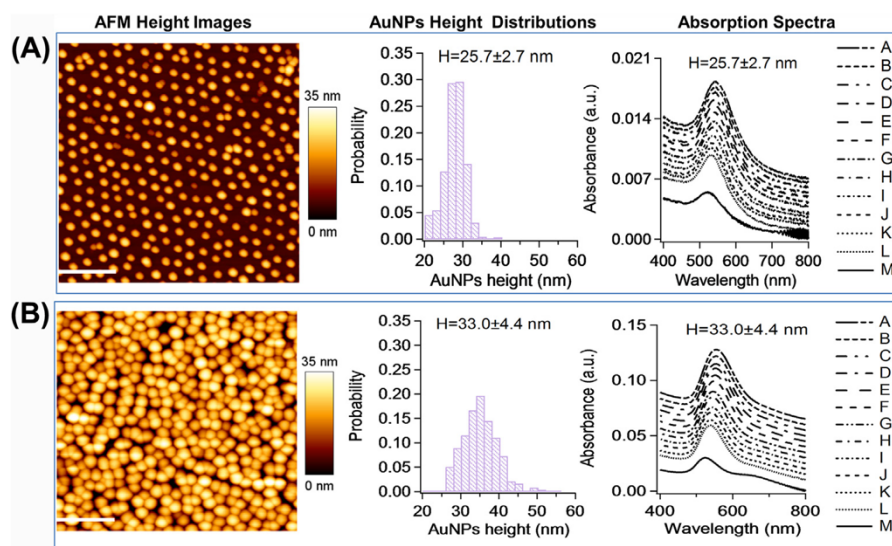


Fig. 4. Representative AuNP arrays of different heights after seeding growth and measured absorbance spectra for different cover media. (A) AuNP array with height distribution (H) of 25.7 ± 2.7 nm; (B) AuNP array with H of 33.0 ± 4.4 nm. The scale bars are 350 nm in the AFM images, and the numbers of counted particles in each panel are in the order of 350–800. Spectra are off-set along the y-axis for clarity by 0.0002 a.u. A, *o*-dichlorobenzene; B, T/D 1:9; C, T/D 3:7; D, T/D 1:1; E, T/D 7:3; F, toluene; G, chloroform; H, dichloromethane; I, heptane; J, ethanol; K, MilliQ water; L, methanol; M, air. T/D represents the binary mixture of toluene and *o*-dichlorobenzene by volume ratio (see Table 1 for details).

to applied forces of 15–20 nN, the hexagonal AuNP array patterns were retained after 7 days soaking in aqueous solution. The hexagonal patterns also survived from multiple peels of scotch tape. So it is reasonable to speculate that the particles are embedded slightly into the glass slide. Thus, absorbance computations for AuNPs on/embedded into glass cover slips were carried out to help understand and interpret the experimental results. The AuNP arrays form a quasi-hexagonal pattern made of a repeated parallelogram unit cell, as shown in Scheme 2. To take advantage of the structural symmetry, only one unit cell including one AuNP was modeled using periodic boundary conditions on lateral walls and absorbing boundary conditions above and below. Scheme 2(C) shows an AuNP embedded into the glass surface and defines the embedding ratio. The structure was excited by a plane wave incident from the top and the absorbance was computed (Scheme 2(D)).

As Boreman et al. [68] have shown, there is a combination of data from Palik [61] and Johnston and Christy [60] (JC) which

forms the best set for nanostructures made of gold. In this set of data the imaginary part of the dielectric constant is taken from JC, and its real part taken as a mixture of data from JC and Palik. Palik's data is used over the spectral range of 400–500 nm, and JC's data is applied above 500 nm. In addition, the optical properties of gold were corrected for the nanoparticle sizes of interest (Fig. 5) [69,70]. Utilizing this set of data in the computations leads to a good agreement between numerical and experimental results in terms of λ_{LSPR} .

Fig. 5 illustrates how the optical properties of AuNPs depend on their radius. As seen in the plots $-Im\{\epsilon_{Au}\}$, the negative imaginary part of the gold dielectric constant decreased with increased particle radius. However, $-Re\{\epsilon_{Au}\}$, the negative real part of the gold dielectric constant, increases with particle radius. In addition, it is obvious from Fig. 5 that the optical properties of smaller AuNPs are more size-dependent than the bigger ones. This fact results in having broader experimental absorbance spectra than the computations for small AuNPs.

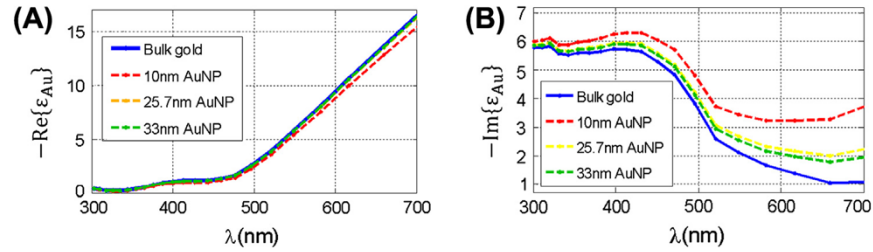


Fig. 5. Size-dependent real part (A) and imaginary part (B) of the gold dielectric constant.

Fig. 6(A)–(C) show the computed spectra of AuNP arrays with mean heights of 10, 25.7 and 33 nm, respectively, as the cover medium refractive index varied from 1 to 1.5514. The computations agree well with the experimental results as observed via comparisons with the measured spectra of Figs. 3 and 4, and as summarized in Fig. 6(D)–(F) which plot the measured and computed λ_{LSPR} versus the cover medium refractive index. A red shift from 521 to 539 nm for 10 nm AuNPs, from 522 to 544.5 nm for 25.7 nm AuNPs, and from 525.5 to 553 nm for 33 nm AuNPs, is achieved over the full range of indices. Thus, λ_{LSPR} is strongly dependent on the refractive index of the cover medium, which is a well-known characteristic of metal nanoparticles [35,69,71–74]. The origin of this dependence comes from the LSPR condition, $\epsilon_1 = -2\epsilon_d$. Since the negative real part of the dielectric constant of gold increases with wavelength in the visible range [60,61], an increase in the surrounding medium's dielectric constant causes λ_{LSPR} to red-shift. From Fig. 6(D)–(F) we also note that increasing the AuNP size and shrinking the inter-particle spacing red-shift λ_{LSPR} due to increasing electromagnetic retardation in larger particles [71,75]. Therefore, not only is λ_{LSPR} sensitive to the cover medium refractive index, but also to the AuNP size.

As noted from the spectra of Figs. 3 and 4 (measured) and Fig. 6(A)–(C) (computed), the peak absorbance increases with

increasing cover medium refractive index. This is expected in part from Mie theory, as Eq. (2) shows that the absorption cross-section increases with the (homogeneous) background refractive index. This is also apparent from computations of the heat loss distribution for 10 nm AuNPs bounded by cover media of different refractive indices, revealing increasing heat loss with increasing index, see Fig. 7).

3.5. Optical properties of the AuNP arrays

As observed from the measurements (Figs. 3 and 4) and computations (Fig. 6), the absorbance peak also increases with AuNP size. This is consistent with the literature [76] and expected theoretically (Eqs. (2), (3)). In air, for 10 nm AuNP arrays, the measured absorbance peak is 2.65×10^{-3} (Fig. 2(A)); for 25.7 nm AuNP arrays, the absorbance peak increases to 5×10^{-3} (Fig. 4(A)); and for 33 nm AuNP arrays, the absorbance peak reaches 0.03 (Fig. 4(B)). This trend is verified in the computations (Fig. 6(A)–(C)), although the value of the peak absorbance agrees only to within a factor of ~ 3 .

The distribution in inter-particle spacing and size of the AuNPs is thought to cause the discrepancy between the experimental and computed absorbance – the measured absorbance peaks are

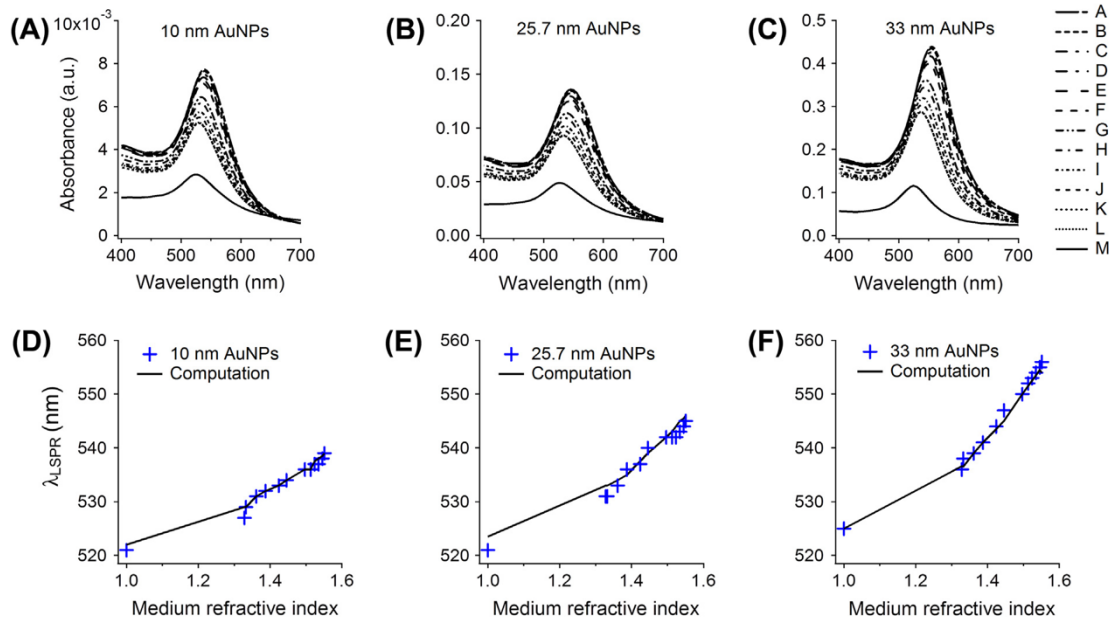


Fig. 6. (A)–(C): Computed absorbance spectra of AuNP arrays with mean heights of 10 nm (A), 25.7 nm (B) and 33 nm (C) for various cover media: A, *o*-dichlorobenzene; B, T/D 1:9; C, T/D 3:7; D, T/D 1:1; E, T/D 7:3; F, toluene; G, chloroform; H, dichloromethane; I, heptane; J, ethanol; K, MilliQ water; L, methanol; M, air. T/D represents the binary cover medium refractive index for AuNP arrays with mean heights of 10 nm (D), 25.7 nm (E), and 33 nm (F).

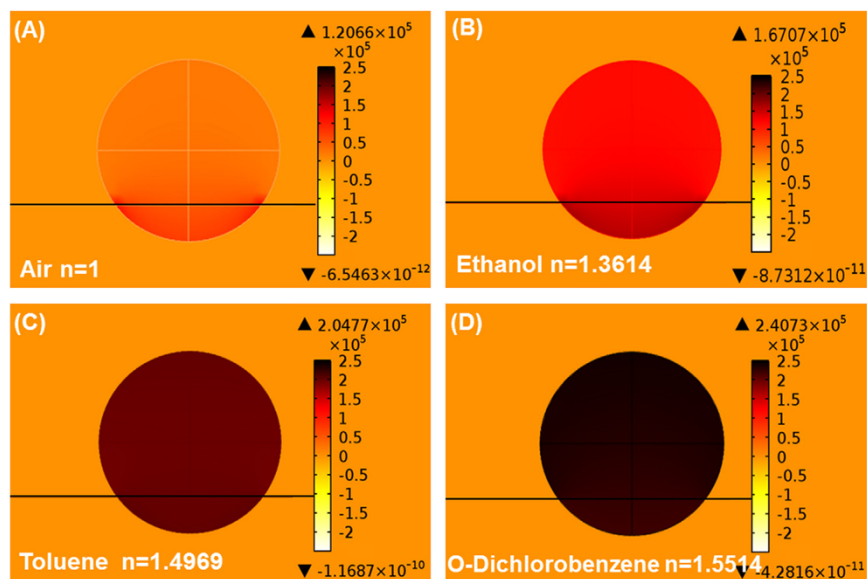


Fig. 7. Computed heat loss distribution at λ_{LSPR} for a 10 nm AuNP surrounded by (A) air, (B) ethanol, (C) toluene and (D) *o*-dichlorobenzene. Increasing cover medium refractive index leads to raising heat loss in AuNPs.

consistently lower than the computed ones. In the computations, the radius and spacing are invariant over the array as periodic boundary conditions are applied, whereas these quantities are distributed in the experimental samples (Figs. 1(C), 4(A) and (B)). The optical parameters of gold deviate from bulk values in very small particles (see Fig. 5), so the size distribution results in a distribution of optical parameters across the array. Because the largest deviations occur for the smallest diameters, the 10 nm AuNPs show the largest discrepancy between experimental and computed results. However, the deviations between the computed and measured λ_{LSPR} were no more than 1 nm, except for the case of water, which might be due to the influences of ionic strength and charge density which alter the LSPR fields.

Absorbance spectra of AuNPs on glass were affected by ion concentration, as shown in Fig. 8(A). MilliQ water and PBS buffer were served as the bulk surroundings without/with ions, respectively. In water, the λ_{LSPR} was at 529.4 nm; in PBS buffer, the λ_{LSPR} of the same sample was shifted to 533.3 nm. (PBS buffer contains 1.544 mM $[K^+]$, 157.881 mM $[Na^+]$, 1.544 mM $[H_2PO_4^-]$, and 2.709 mM $[HPO_4^{2-}]$). The refractive index is 1.33137 for MilliQ water and 1.33324 for PBS buffer. When the proton concentration

is increased, which is represented by pH value of the solution, the positive charge density in solution cannot be negligible to electric field distribution of AuNPs. A patterned AuNP array on glass with a mean height of 25 nm was tested in PBS buffer solutions with different pH, as shown in Fig. 8(B) and (C). The correlation between the λ_{LSPR} position and proton concentration indicates that the λ_{LSPR} position is shifted to longer wavelength when the proton concentration is close to neutral. Herein, proton concentration has a negative effect of absorbance spectra. Also, this effect is diminished by the ion effect in our experiments. Hence, when AuNPs presented in a saline buffer surroundings, the overall behavior of the absorbance is still red-shift.

3.6. Bulk sensitivity

As the refractive index of the cover medium increases to values that are comparable with the index of the glass substrate, the LSPR fields become increasingly symmetrical, which leads to an increased bulk sensitivity for arrays with a cover medium of higher refractive index.

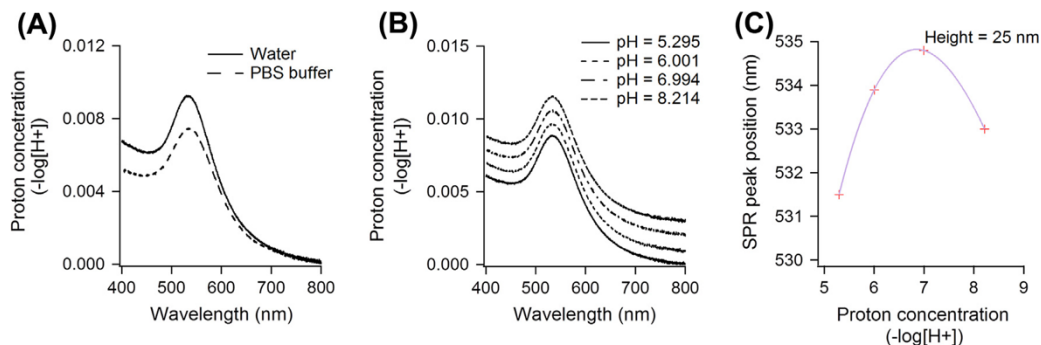


Fig. 8. Absorbance spectra of AuNPs on glass affected by ion concentration (A); proton concentration (B); and the correlation between λ_{LSPR} position and proton concentration in bulk surrounding (C).

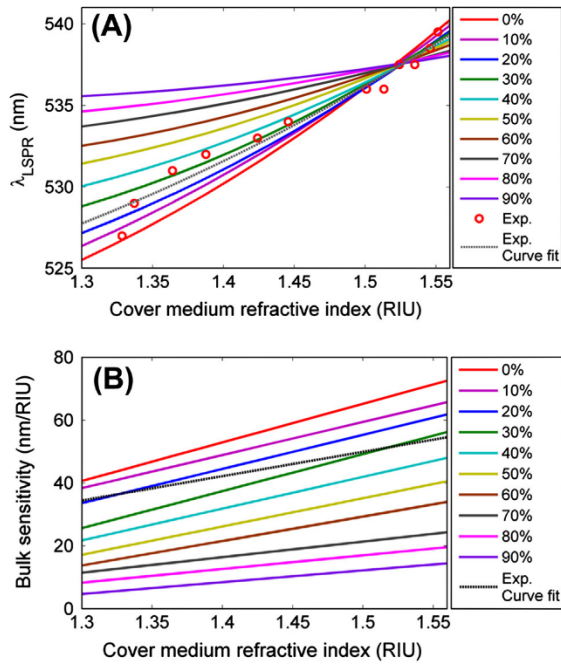


Fig. 9. (A) λ_{LSPR} and (B) bulk sensitivity versus cover medium refractive index for 10 nm AuNPs of different embedding ratios. The red circles and gray dashed curve correspond to the experimental results.

Comparing our λ_{LSPR} (Fig. 6(D)–(F)) to those of similar-sized AuNPs suspended in the same solvent [49,77,78] reveals that our λ_{LSPR} are ~ 10 nm larger. The reason for this is that our AuNPs are on (or embedded a few nanometers into) a glass surface, thus causing a distortion in the fields of the dipolar resonant mode when covered with a low-index medium – the fields are thus different from those of a suspension of AuNPs in a homogeneous medium. In this situation, ε_d in Eqs. (1)–(3) could be considered as an “effective” dielectric constant which may reasonably be assumed as the mean value of the glass and cover medium dielectric constants. Therefore, fulfillment of the LSPR condition, $\varepsilon_1 = -2\varepsilon_d$ in Eqs. (1)–(3), is achieved at a longer wavelength, explaining the red-shift in our λ_{LSPR} relative to other work [79].

From Fig. 6(D)–(F) we notice that as the AuNP height increases from 10 to 25.7 then to 33.0 nm, λ_{LSPR} red-shifts more with increasing cover medium refractive index. The sensitivity of λ_{LSPR} to the cover medium refractive index ($\Delta\lambda/\Delta n$) over the range of 1.3284–1.5514 is on average about 43.4, 54.4 and 85.0 nm/RIU for the 10, 25.7 and 33 nm arrays, respectively. Thus, the sensitivity is proportional to AuNP size.

Increasing the embedding ratio decreases the bulk sensitivity, as observed for the 10 nm AuNP array in Fig. 9. The more the

AuNPs are embedded into the glass, the less their surfaces are exposed to the cover medium, resulting in less sensitivity. Comparing the computed with the experimental λ_{LSPR} and bulk sensitivities (Fig. 9) reveals that the AuNPs are embedded into the glass surface by $\sim 20\%$ to 30% .

The bulk sensitivity also depends on the cover medium refractive index, partly because the AuNPs are bounded asymmetrically (glass and cover medium). Fields penetrate more into the medium with the higher refractive index which is glass in this case. As the refractive index of the cover medium increases, approaching that of the glass, the fields become symmetrically distributed, penetrating more into the cover medium, as shown in Fig. 10. Distributions of the Ex field component on the resonance for 10 nm AuNPs bounded to glass below. Consequently, higher bulk sensitivity and a larger field enhancement are achieved in a higher refractive index cover medium.

4. Concluding remarks

In conclusion, we have presented a novel fabrication method for producing patterned AuNP arrays on large-area glass substrates by combining seeding growth with diblock copolymer self-assembly. The method provides a new approach to tune the AuNP size and edge-to-edge inter-particle spacing while preserving the AuNP ordering. Diblock copolymer self-assembly provided AuNP seeds with mean heights of 5.2 ± 0.6 , 8.3 ± 1.7 and 10.0 ± 2.1 nm, and center-to-center inter-particle spacings of 80 ± 8 , 88 ± 9 and 62 ± 11 nm by varying the molar ratio of the gold precursor to pyridine unit. The samples with 10.0 ± 2.1 nm AuNP seeds were treated by chemical growth methods to enlarge their sizes to mean heights of 25.7 ± 2.7 and 33.0 ± 4.4 nm, while simultaneously reducing the edge-to-edge inter-particle spacing to 37 and 29 nm, respectively. The properties of several AuNP arrays on glass were fully characterized, including their size, edge-to-edge inter-particle spacing, optical spectral properties and LSPR wavelength, bulk refractive index sensitivity, and embedding ratio. Optical modeling results agree well with the experimental results and allowed deduction of the embedding ratio of the AuNPs into the glass surface. The fabrication method is easy to apply and yields uniform, large-area ($\sim 80 \text{ mm}^2$), ordered arrays of AuNPs of controllable size and inter-particle spacing.

Acknowledgments

We thank Dr. Maohui Chen, Dr. Zygmunt Jakubek and Dr. Zhengfang Lu for technical supports, and Anthony Olivieri and Ewa Lisicka-Skrzek for assistance with the Metricon measurements. This work was partially supported by the National Sciences and Engineering Research Council (NSERC) of Canada through the Strategic Network BiopSys.

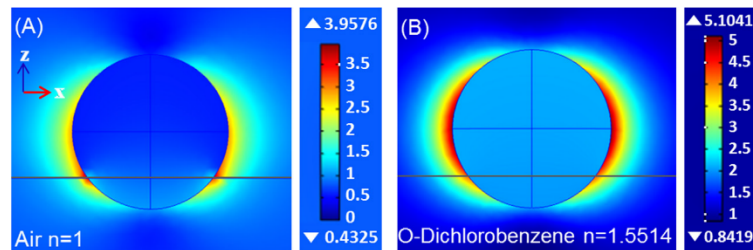


Fig. 10. Distribution of the Ex field component on resonance for 10 nm AuNPs bounded by glass below; (A) air, and (B) o-dichlorobenzene were set as the cover medium, respectively. An embedding ratio of 20% was assumed.

References

- [1] K.C. Vernon, A.M. Funston, C. Novo, D.E. Gomez, P. Mulvaney, T.J. Davis, *Nano Lett.* 10 (2010) 2080.
- [2] A. Lopatynskiy, O. Lopatynska, V. Chegel, *Semicond. Phys. Quantum Electron. Optoelectron.* 14 (2011) 114.
- [3] T.J. Davis, D.E. Gomez, K.C. Vernon, *Phys. Rev. B* 81 (2010) 045432.
- [4] D. Li, J.Y. Lee, D.H. Kim, *J. Colloid Interface Sci.* 354 (2011) 585.
- [5] H.M. Kim, S.M. Jin, S.K. Lee, M.-G. Kim, Y.-B. Shin, *Sensors* 9 (2009) 2334.
- [6] J. He, P. Kanjanaboos, N.L. Frazer, A. Weis, X.-M. Lin, H.M. Jaeger, *Small* 6 (2010) 1449.
- [7] X.M. Lin, H.M. Jaeger, C.M. Sorensen, K.J. Klabunde, *J. Phys. Chem. B* 105 (2001) 3353.
- [8] E. Rabani, D.R. Reichman, P.L. Geissler, L.E. Brus, *Nature* 426 (2003) 271.
- [9] J.E. Martin, J.P. Wilcoxon, J. Odinek, P. Provencio, *J. Phys. Chem. B* 104 (2000) 9475.
- [10] A.P. Alivisatos, K.P. Johnsson, X.G. Peng, T.E. Wilson, C.J. Loweth, M.P. Bruchez, P.G. Schultz, *Nature* 382 (1996) 609.
- [11] W. Cheng, M.J. Campolongo, J.J. Cha, S.J. Tan, C.C. Umbach, D.A. Muller, D. Luo, *Nat. Mater.* 8 (2009) 519.
- [12] C.A. Mirkin, R.L. Letsinger, R.C. Mucic, J.J. Storhoff, *Nature* 382 (1996) 607.
- [13] D. Nykypanchuk, M.M. Maye, D. van der Lelie, O. Gang, *Nature* 451 (2008) 549.
- [14] S.Y. Park, A.K.R. Lytton-Jean, B. Lee, S. Weigand, G.C. Schatz, C.A. Mirkin, *Nature* 451 (2008) 553.
- [15] J.P. Zhang, Y. Liu, Y.G. Ke, H. Yan, *Nano Lett.* 6 (2006) 248.
- [16] J. Zheng, P.E. Constantinou, C. Micheel, A.P. Alivisatos, R.A. Kiehl, N.C. Seeman, *Nano Lett.* 6 (2006) 1502.
- [17] J.P. Spatz, A. Roescher, M. Moller, *Adv. Mater.* 8 (1996) 337.
- [18] R. Glass, M. Moller, J.P. Spatz, *Nanotechnology* 14 (2003) 1153.
- [19] J.P. Spatz, T. Herzog, S. Mossmer, P. Ziemann, M. Moller, *Adv. Mater.* 11 (1999) 149.
- [20] J.P. Spatz, S. Mossmer, C. Hartmann, M. Moller, T. Herzog, M. Krieger, H.G. Boyen, P. Ziemann, B. Kabis, *Langmuir* 16 (2000) 407.
- [21] S. Zou, R. Hong, T. Emrick, G.C. Walker, *Langmuir* 23 (2007) 1612.
- [22] X. Li, H. Yang, L. Xu, X. Fu, H. Guo, X. Zhang, *Macromol. Chem. Phys.* 211 (2010) 297.
- [23] T. Lohmueller, D. Aydin, M. Schwieder, C. Morhard, I. Louban, C. Pacholski, J.P. Spatz, *Biointerphases* 6 (2011) MR1.
- [24] S. Mossmer, J.P. Spatz, M. Moller, T. Aberle, J. Schmidt, W. Burchard, *Macromolecules* 33 (2000) 4791.
- [25] S. Papp, L. Korosi, B. Gool, T. Dederichs, P. Mela, M. Moller, I. Dekany, *J. Therm. Anal. Calorim.* 101 (2010) 865.
- [26] S.T. Selvan, J.P. Spatz, H.A. Klok, M. Moller, *Adv. Mater.* 10 (1998) 132.
- [27] R. Glass, M. Arnold, E.A. Cavalcanti-Adam, J. Blummel, C. Haferkemper, C. Dodd, J.P. Spatz, *New J. Phys.* 6 (2004) 101.
- [28] G. Mie, *Ann. Phys. (Leipzig)* 25 (1908) 377.
- [29] L.M. Liz-Marzán, *Mater. Today* 7 (2004) 26.
- [30] D. Boyer, P. Tamarat, A. Maali, B. Lounis, M. Orrit, *Science* 297 (2002) 1160.
- [31] P.K. Jain, K.S. Lee, I.H. El-Sayed, M.A. El-Sayed, *J. Phys. Chem. B* 110 (2006) 7238.
- [32] J.N. Anker, W.P. Hall, O. Lyandres, N.C. Shah, J. Zhao, R.P. van Duyne, *Nat. Mater.* 7 (2008) 442.
- [33] H. Chen, X. Kou, Z. Yang, W. Ni, J. Wang, *Langmuir* 24 (2008) 5233.
- [34] D. Eck, C.A. Helm, N.J. Wagner, K.A. Vaynberg, *Langmuir* 17 (2001) 957.
- [35] K.L. Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, *J. Phys. Chem. B* 107 (2003) 668.
- [36] M.W. Knight, Y. Wu, J.B. Lassiter, P. Nordlander, N.J. Halas, *Nano Lett.* 9 (2009) 2188.
- [37] A.I. Kuznetsov, A.B. Evlyukhin, M.R. Goncalves, C. Reinhardt, A. Koroleva, M.L. Arnedillo, R. Kiyari, O. Marti, B.N. Chichkov, *ACS Nano* 5 (2011) 4843.
- [38] J.B. Lassiter, M.W. Knight, N.A. Mirin, N.J. Halas, *Nano Lett.* 9 (2009) 4326.
- [39] N. Nath, A. Chilkoti, *Anal. Chem.* 74 (2002) 504.
- [40] Y.W.C. Cao, R.C. Jin, C.A. Mirkin, *Science* 297 (2002) 1536.
- [41] T.J. Davis, K.C. Vernon, D.E. Gomez, *Phys. Rev. B* 79 (2009) 155423.
- [42] W. Rechberger, A. Hohenau, A. Leitner, J.R. Krenn, B. Lamprecht, F.R. Aussenegg, *Opt. Commun.* 220 (2003) 137.
- [43] S. Schultz, D.R. Smith, J.J. Mock, D.A. Schultz, *Proc. Natl. Acad. Sci. USA* 97 (2000) 996.
- [44] I.E. Sendrou, S.F.L. Mertens, D.J. Schiffrin, *Phys. Chem. Chem. Phys.* 8 (2006) 1430.
- [45] K.H. Su, Q.H. Wei, X. Zhang, J.J. Mock, D.R. Smith, S. Schultz, *Nano Lett.* 3 (2003) 1087.
- [46] P.K. Jain, W. Huang, M.A. El-Sayed, *Nano Lett.* 7 (2007) 2080.
- [47] S.L. Altmann, *Band Theory of Solids: An Introduction from the Point of View of Symmetry*, Oxford University Press, New York, 1991.
- [48] G. Kastle, H.G. Boyen, F. Weigl, G. Lengel, T. Herzog, P. Ziemann, S. Riethmüller, O. Mayer, C. Hartmann, J.P. Spatz, M. Moller, M. Ozawa, F. Banhart, M.G. Garnier, P. Oelhafen, *Adv. Funct. Mater.* 13 (2003) 853.
- [49] S. Link, M.A. El-Sayed, *J. Phys. Chem. B* 103 (1999) 4212.
- [50] K.R. Brown, M.J. Natan, *Langmuir* 14 (1998) 726.
- [51] K.R. Brown, D.G. Walter, M.J. Natan, *Chem. Mater.* 12 (2000) 306.
- [52] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, *J. Chem. Soc. Chem. Commun.* (1994) 801.
- [53] A. Henglein, *Langmuir* 15 (1999) 6738.
- [54] N.R. Jana, L. Gearheart, C.J. Murphy, *Langmuir* 17 (2001) 6782.
- [55] M.N. Martin, J.I. Basham, P. Chando, S.-K. Eah, *Langmuir* 26 (2010) 7410.
- [56] J. Rodríguez-Fernández, J. Pérez-Juste, F. J. G. de Abajo, L.M. Liz-Marzán, *Langmuir* 22 (2006) 7007.
- [57] J. Turkevich, P.C. Stevenson, J. Hillier, *Discuss. Faraday Soc.*, 11 (1951) 55.
- [58] C. Ziegler, A. Eychmüller, *J. Phys. Chem. C* 115 (2011) 4502.
- [59] http://www.us.schott.com/advanced_optics/english/products/optical-materials/thin-glass/cover-glass-d-263-m/index.html.
- [60] P.B. Johnson, R.W. Christy, *Phys. Rev. B* 6 (1972) 4370.
- [61] E.D. Palik, *Handbook of Optical Constants of Solids*, Academic Press, Boston, 1997.
- [62] J. Rheims, J. Koser, T. Wriedt, *Meas. Sci. Technol.* 8 (1997) 601.
- [63] A. Samoc, *J. Appl. Phys.* 94 (2003) 6167.
- [64] D.J. Segelstein, *The Complex Refractive Index of Water*, Thesis, University of Missouri, Kansas City, 1981.
- [65] V. Myroshnychenko, J. Rodríguez-Fernández, I. Pastoriza-Santos, A.M. Funston, C. Novo, P. Mulvaney, L.M. Liz-Marzán, F.J.G. de Abajo, *Chem. Soc. Rev.* 37 (2008) 1792.
- [66] M. Quinten, U. Kreibig, *Appl. Opt.* 32 (1993) 6173.
- [67] B.C. Sih, M.O. Wolf, *J. Phys. Chem. B* 110 (2006) 22298.
- [68] G.D. Boreman, T. Johnson, A.C. Jones, S.-H. Oh, R.L. Olmon, M.B. Raschke, D. Shelton, B. Slovick, *Broadband Electrical Permittivity of Gold for Plasmonics and Nano-Optics Applications*, IEEE, New York, 2011.
- [69] S. Underwood, P. Mulvaney, *Langmuir* 10 (1994) 3427.
- [70] U. Kreibig, *J. Phys. F: Met. Phys.* 4 (1974) 999.
- [71] P.K. Jain, X. Huang, I.H. El-Sayed, M.A. El-Sayed, *Acc. Chem. Res.* 41 (2008) 1578.
- [72] U. Kreibig, M. Volmer, *Optical Properties of Metal Clusters*, Springer Verlag, Berlin, 1995.
- [73] S. Link, M.A. El-Sayed, *Int. Rev. Phys. Chem.* 19 (2000) 409.
- [74] W.P. McConnell, J.P. Novak, L.C. Brousseau, R.R. Fuieler, R.C. Tenent, D.L. Feldheim, *J. Phys. Chem. B* 104 (2000) 8925.
- [75] C.F. Bohren, D.R. Huffman, *Absorption and Scattering by Small Particles*, Wiley, New York, 1983.
- [76] W. Huang, W. Qian, M.A. El-Sayed, Y. Ding, Z.L. Wang, *J. Phys. Chem. C* 111 (2007) 10751.
- [77] M.A.K. Abdelhalim, M.M. Mady, M.M. Ghannam, *J. Nanomed. Nanotechnol.* 3 (2012) 1000133.
- [78] S. Link, M.A. El-Sayed, *J. Phys. Chem. B* 103 (1999) 8410.
- [79] M.D. Malinsky, K.L. Kelly, G.C. Schatz, R.P. van Duyne, *J. Am. Chem. Soc.* 123 (2001) 1471.

3. Plasmonic Fano interference produced by gold nano-disks on a dielectric Bragg stack

A. Summary

A dielectric-plasmonic system consisting of arrays of gold nano-disks (AuNDs) supported by a Bragg stack was studied theoretically and numerically. The reflectance spectra of this plasmonic array exhibit Fano features, forming due to the interference between LSPPs on the AuNDs and the reflection spectrum of the Bragg stack. Fitting the computed data with the Fano lineshape formula, the Fano parameters of resonances were obtained. Fano resonances exhibit linewidths of ~ 9 nm, which is much narrower than the nano-disk LSPP bandwidth (~ 80 nm) and the Bragg reflection bandwidth (~ 100 nm). These narrow resonances are potentially attractive for sensing applications. To examine the structure as a plasmonic sensor, bulk sensitivities and FOM values were calculated. Bulk sensitivities up to ~ 52 nm/RIU were obtained, and FOM of 4 (RIU)^{-1} was achieved.

B. Contribution

The results provided in this chapter were published as an article in the *Journal of Applied Physics*. I proposed and designed the structure; I performed theoretical and numerical studies; I generated and interpreted the results, and wrote the manuscript. Dr. Berini contributed to the interpretation of the results and revised the manuscript.

C. Article

The published article follows verbatim.



Plasmonic Fano interference produced by gold nano-disks on a dielectric Bragg stack

Akram Hajebifard and Pierre Berini

Citation: *Journal of Applied Physics* **118**, 093107 (2015); doi: 10.1063/1.4930090

View online: <http://dx.doi.org/10.1063/1.4930090>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/118/9?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Multiple Fano interferences in a plasmonic metamolecule consisting of asymmetric metallic nanodimers](#)

J. Appl. Phys. **117**, 023118 (2015); 10.1063/1.4905619

[Ultraviolet surface plasmon-mediated low temperature hydrazine decomposition](#)

Appl. Phys. Lett. **106**, 023102 (2015); 10.1063/1.4905593

[Effective light concentration in gold short nanosphere chain on platinum mirror for surface-enhanced Raman scattering](#)

Appl. Phys. Lett. **105**, 121114 (2014); 10.1063/1.4896688

[Tuning multiple Fano and plasmon resonances in rectangle grid quasi-3D plasmonic-photonic nanostructures](#)

Appl. Phys. Lett. **103**, 053117 (2013); 10.1063/1.4817398

[Surface plasmon resonance in nanostructured metal films under the Kretschmann configuration](#)

J. Appl. Phys. **106**, 124314 (2009); 10.1063/1.3273359

A promotional banner for AIP Photonics. The background is a vibrant red with a bright yellow sunburst effect emanating from the top right. On the left, the text 'AIP | APL Photonics' is written in white. Below it, a larger white text reads 'APL Photonics is pleased to announce Benjamin Eggleton as its Editor-in-Chief'. On the right side of the banner, there is a small, square, black-and-white portrait of Benjamin Eggleton, a man with a beard and short hair, wearing a suit and tie.



Plasmonic Fano interference produced by gold nano-disks on a dielectric Bragg stack

Akram Hajebifard^{1,a)} and Pierre Berini^{1,2,3}

¹Department of Physics, University of Ottawa, Ottawa K1N 6N5, Canada

²School of Electrical Engineering and Computer Science, University of Ottawa, Ottawa K1N 6N5, Canada

³Centre for Research in Photonics at the University of Ottawa, Ottawa K1N 6N5, Canada

(Received 24 June 2015; accepted 24 August 2015; published online 4 September 2015)

Fano interference is predicted in a structure consisting of a periodic array of uncoupled gold nano-disks (AuNDs) supported by a Bragg stack. The phenomenon occurs due to resonant interference between the reflection spectrum of the Bragg stack and localized surface plasmon resonances (LSPRs) on the AuNDs. Fitting the computational results to the Fano lineshape formula yields the Fano parameters of the resonances including their linewidth. One of the most important advantages of the structure is that the linewidth of the Fano resonances (~ 9 nm) is much narrower than the bandwidth of the LSPR nano-disks (~ 80 nm) and the reflection bandwidth of the Bragg stack on which the disks are supported (~ 100 nm). The narrow Fano linewidth and the ease with which they can be interrogated using perpendicularly incident light makes the structure attractive for biosensing applications. The bulk sensitivities and figure of merit of Fano resonances in a proposed design are 44 nm/RIU (redshift) and -52 nm/RIU (blueshift), and ~ 4 RIU⁻¹, respectively. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4930090>]

I. INTRODUCTION

For many years, the symmetric Lorentzian formula was the only expression used to describe a resonance, but it cannot describe the asymmetric lineshape resonance originating from the interference of several independent resonances of differing origin. In 1961, Fano¹ discovered a new kind of resonance (bearing his name), exhibiting an asymmetric lineshape. Its origin fundamentally is due to the coupling of resonances at the resonator level, often occurring as a narrow Lorentzian resonance couples with a broader spectral continuum. Fano resonances have been reported in different types of plasmonic structures such as metamaterials,^{2,3} clusters,^{4,5} single multi-surface nanoparticles,^{6,7} and periodic structures.^{8–11} In most of these works, the Fano resonance is based on strong near-field coupling between constituents of the structure. This strong coupling happens when the inter-particle gap is very small,^{12–14} which poses fabrication and application challenges. Therefore, structures producing Fano resonances without the need for inter-particle near-field coupling are desirable. Recently, the reflectance from glass-supported gold nano-disks (AuNDs) has been demonstrated to produce Fano interference, due to the interaction of the nanoparticles' Lorentzian scattering and reflection from the underlying glass surface;¹⁰ in this structure, there was no need for near-field coupling between nano-particles, which allowed them to be separated far from each other in the array. Here, we introduce a structure consisting of an array of uncoupled AuNDs on a planar Bragg stack (Fig. 1(a)), which exhibits narrow Fano resonances in its reflectance spectrum. The Fano resonances originate from near-field interaction between the dipolar localized surface plasmon

resonance (LSPR) of the AuNDs and the reflection spectrum of the Bragg stack, are much narrower (~ 9 to 12 nm) than the bandwidth of either constituent responses, and are very sensitive to the geometry of the structure and the local refractive index. Illumination of the structure is via a normally incident plane wave that renders the structure simple and easy to use. Also, due to the geometrical symmetry of the structure about the surface normal, its optical response is independent of the orientation of the in-plane polarization of the incident light. Thus, there is no need for polarization control, conferring another advantage to the structure. Since no near-field coupling between particles is required to produce the Fano resonances, the AuNDs can be spread far enough from each other to facilitate fabrication. Another advantage is the observation of reflectance (or transmittance) spectra that are more convenient to observe than scattering and extinction spectra as are normally measured in comparable studies.¹⁵ These advantages, and the narrow lineshape of the Fano resonance, make the structure attractive for sensing applications.

II. PROPOSED STRUCTURE

In this work, the diameter and height of the gold nano-disks are assumed to be $D = 120$ nm and $h = 20$ nm, respectively, letting them have a LSPR near 675 nm, which is a good wavelength for biosensing applications. This array of disks is supported by a quarter-wave stack, as shown in Fig. 1(a), consisting of 13 pairs of alternating layers of two different dielectric materials of refractive index $n_1 = 1.5$ and $n_2 = 1.7$ and thickness $a = \lambda_B/(4n_1)$ and $b = \lambda_B/(4n_2)$, where λ_B is the Bragg wavelength of the stack. The chosen parameters for the stack produce λ_B around the nano-disks' LSPR, which is needed to generate Fano resonances. Also, 13 pairs of layers are required at a minimum to produce a smooth

^{a)}Author to whom correspondence should be addressed. Electronic mail:

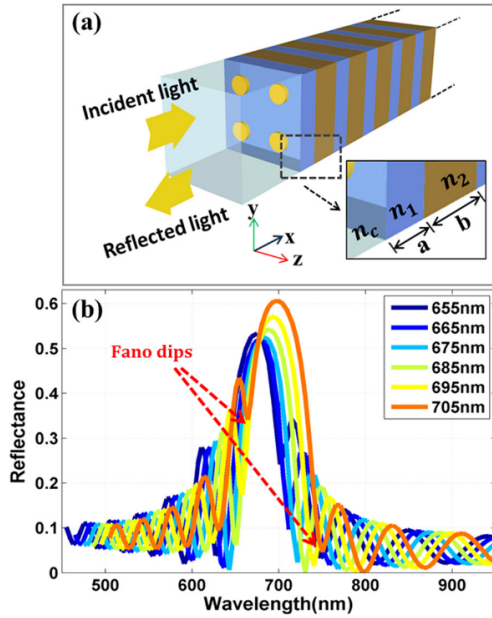


FIG. 1. (a) Schematic of an array of gold nano-disks on a dielectric Bragg stack (AuNDs-Bragg). (b) Reflectance spectra of the structure as λ_B ranges from 655 to 705 nm; dashed arrows point to the Fano interferences (computed using the FEM (COMSOL)). Air was assumed as the bounding medium ($n_c = 1$).

spectral response for the stack over its stop-band. The bounding medium has a refractive index n_c and is taken as either air or water.

Identical AuNDs are assumed to be arranged in a square lattice with a 285 nm center-to-center inter-disk separation as an infinite array in the y-z plane. So, there is a well-defined long-range periodicity, and since $D/2 = \Lambda/4.75$, where D is the disks' diameter and Λ the lattice constant, there is a lack of particle near-field coupling, which makes it possible to consider the response of the AuND array as the response of an isolated particle.^{14,16} To compute the reflectance spectra and fields of the AuNDs-Bragg reflector, the structure was modeled using a commercial (COMSOL) implementation of the finite element method (FEM) solving the vector wave equations for the E and H fields throughout the structure, subject to the applicable boundary conditions, and the applied source fields (if any). In our case, we compute the electromagnetic (EM) response of the structure of interest upon excitation by a plane wave source. The AuNDs are modelled accurately (boundaries and material properties), as is the Bragg stack, so all near-field effects are properly taken into account. Taking advantage of the structural symmetry of our model, only one unit cell incorporating one AuND has been simulated. To do so, periodic boundary conditions were applied on the lateral walls and absorbing boundary conditions on the front and back walls. The structure was then illuminated by a y-polarized electromagnetic wave perpendicularly incident onto the face of the structure where the AuNDs are present

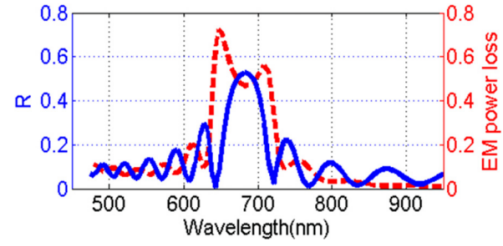


FIG. 2. Reflectance (solid blue curve) and electromagnetic power loss of an AuND (dashed red curve) for the case of $\lambda_B = 675$ nm (computed using the FEM (COMSOL)). The loss is maximized at wavelengths corresponding to the Fano dips.

(Fig. 1(a)). The reflectance was then calculated as the optical response of the structure.

III. FANO RESONANCES

Fig. 1(b) shows the reflectance spectra (computed using the FEM) of the AuNDs-Bragg reflector with air as the bounding medium, as λ_B is varied from 655 to 705 nm by changing the thicknesses a and b of the dielectric layers. Compared to a simple Bragg reflector (without AuNDs),¹⁷ two Fano resonances are observed in the reflectance spectra of the AuNDs-Bragg structure as two unusual dips close to the peak reflectance, indicated by the dashed arrows in Fig. 1(b). At the position of these dips, the AuNDs strongly absorb incident light that would otherwise be reflected (more on this below—Fig. 2). The depth and location of these Fano dips vary with λ_B . For example, in the results of Fig. 1(b), the left-side Fano dip has a shallow depth for $\lambda_B = 705$ nm, but deepens with decreasing λ_B until reaching a maximum depth at $\lambda_B = 675$ nm, and then becomes shallow again as λ_B decreases further. It is shown below that both dips in the spectra can be described by the Fano lineshape formula expressed as^{1,18}

$$I_F(\omega) = A_F \frac{(q\gamma + \omega - \omega_0)^2}{(\omega - \omega_0)^2 + \gamma^2} + B_F. \quad (1)$$

In the above, ω_0 is the resonance frequency, γ is the resonance bandwidth, q is the Fano asymmetry parameter, A_F is the resonance amplitude, and B_F is a background term. In order to find the best fit, A_F and B_F were taken as $A \times R(\omega)$ and $B \times R(\omega)$, respectively, where A and B are constants and $R(\omega)$ is the reflectance of the Bragg stack without AuNDs.

A. Origin of the Fano resonances

The Fano resonance has generally been considered in quantum systems, but it can also be explained as an electromagnetic interference phenomenon in classical optics.^{19–21} In nanoplasmonics, the underlying physics of Fano resonances are usually explained by considering a physical arrangement involving two coupled resonators.^{18,22–24} In this arrangement, the first resonator can be viewed, effectively, as being driven by two coupled fields, one being the incident field and the other being the near-field of the second

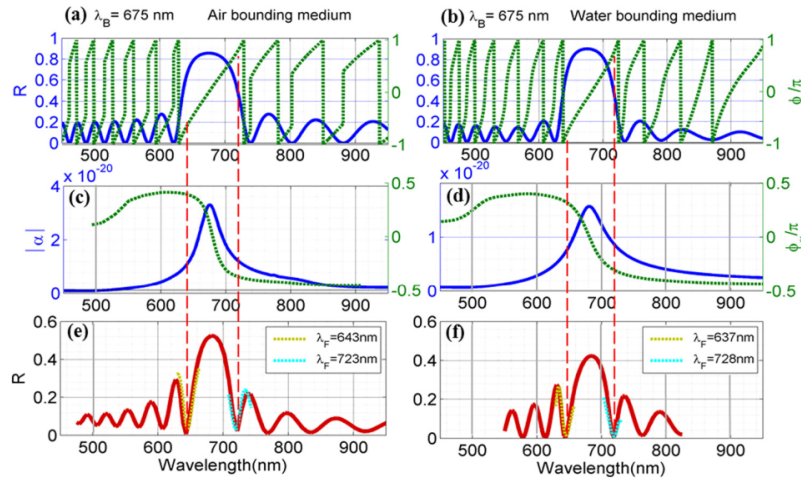


FIG. 3. (a) and (b) Reflectance (blue solid curve) and phase (green dashed curve) spectra for a 13-period bare Bragg stack with alternating refractive indices $n_1 = 1.5$ and $n_2 = 1.7$ and $\lambda_B = 675$ nm, with (a) air and (b) water as the bounding medium. (c) and (d) Polarizability magnitude (blue solid curve) and phase (green dashed curve) spectra of an AuND of thickness $h = 20$ nm and radius (c) $r = 60$ nm on an air-glass interface and (d) $r = 45$ nm on a water-glass interface. (e) and (f) Reflectance spectra of AuNDs-Bragg reflectors with (e) air and (f) water as the bounding medium of the AuNDs. The dashed yellow and cyan curves are best-fit Fano formulae. The red vertical dashed lines indicate the Fano resonances' spectral positions and mark the corresponding phases of the AuND polarizability and bare Bragg stack reflection coefficient. Figs. 3(a) and 3(b) have been calculated using the TMM, (c) and (d) using analytic formulae, (e) and (f) using the FEM (COMSOL).

resonator. A Fano dip is produced in the wavelength response of the system (at the Fano wavelength) due to the destructive interference of resonances from the external field and the second oscillator, which occurs when the two driving fields are out of phase. Fano resonances in a physically different arrangement, where only one resonator is present but placed near a reflecting surface (e.g., a glass-air interface), can be explained fundamentally in the same way, as a single resonator driven by two coupled fields.^{10,25} Thus, although the physical arrangements are different, the basis underlying Fano resonance in plasmonic nanostructures is the same (i.e., a Fano resonance appears when a resonator is driven by two coupled fields of differing phase).

Our AuND-Bragg system is analogous to the latter arrangement, in that an AuND is driven by the incident field directly and by the near-fields reflected from the Bragg stack. Fano resonances are induced on the AuND because at specific wavelengths these driving fields are out of phase (more on this below—see Fig. 3). On a Fano resonance, the reflectance drops (Fano dips) and enhanced absorption are expected.²⁶ Fig. 2 plots the electromagnetic power loss of a AuND on a Bragg stack (air as the bounding medium), which is observed to maximize at wavelengths associated with the Fano dips, further corroborating our interpretation. The EM power loss is calculated based on the following equation:

$$P_L = \frac{1}{2} \omega \int_V (\mu |\vec{H}|^2 + \varepsilon |\vec{E}|^2) dv + \frac{1}{2} \sigma \int_V |\vec{E}|^2 dv, \quad (2)$$

where μ , ε , and σ are the gold permeability, permittivity, and conductivity, respectively. The integral is over the volume (V) of an AuND on a Bragg stack.

B. Coupled driving fields

In the following, it is explained how we can anticipate the position of the two Fano resonances by considering the independent responses of the two constituent elements, which build up the whole structure. We follow Chang and Solgaard²⁷ who have interpreted the Fano resonance seen in their structure's response by taking into account the interference between light reflected from a Bragg waveguide and the end facet and Svedendahl and Kall¹⁰ who have used a similar approach for explaining Fano resonances seen in the reflectance spectrum of their structure.

To this end, two columns of plots are provided in Fig. 3, where air ($n_c = 1$) and water ($n_c = 1.32$)²⁸ have been used as the bounding medium in the left and right column plots, respectively. For a better comparison between these two cases, the LSPR of the AuNDs in each case has been set to ~ 675 nm by choosing AuNDs' radii of 60 and 45 nm for air and water, respectively, and also the inter-disk distances have been selected large enough (4.75 times the disk radius) to minimize near-field coupling between the particles. The Bragg reflector remains the same in both cases and its center wavelength is $\lambda_B = 675$ nm.

Spectra of the reflectance, R , and phase of the reflection coefficient, ϕ_r , of bare Bragg reflectors having $\lambda_B = 675$ with air and water as the bounding medium are shown in Figs. 3(a) and 3(b), respectively. The electromagnetic field scattered by the AuNDs is proportional to the polarizability of the NDs,²⁹ so their polarizability spectrum is plotted in Figs. 3(c) and 3(d). In addition, the reflectance spectra of the AuNDs-Bragg reflector are given in Figs. 3(e) and 3(f).

To compute the reflection coefficient of the bare Bragg stack, shown in Figs. 3(a) and 3(b), the transfer-matrix

method (TMM) was used because it is much more efficient than FEM modelling¹⁷

$$r_N = \frac{M_{21}}{M_{11}}, \quad (3)$$

$$M = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} = D_s^{-1} [D_1 P_1 D_1^{-1} D_2 P_2 D_2^{-1}]^N D_0, \quad (3a)$$

$$D_i = \begin{bmatrix} 1 & 1 \\ n_i & -n_i \end{bmatrix} \quad \text{and} \quad P_i = \begin{bmatrix} e^{i\varphi_i} & 1 \\ 1 & e^{-i\varphi_i} \end{bmatrix}, \quad (3b)$$

where r_N is the reflection coefficient of a stack with N pairs of alternating layers, D_i is the transition matrix, P_i is the matrix for light propagation through a layer with refractive index n_i , D_s is the transition matrix for the bounding medium, and $\varphi_1 = 2\pi n_1 a/\lambda$ and $\varphi_2 = 2\pi n_2 b/\lambda$. To compute the polarizability of the AuNDs, plotted in Figs. 3(c) and 3(d), the AuNDs were modeled as oblate spheroids, with polarizability in the quasistatic limit written as^{30,31}

$$\alpha = \frac{4\pi r^2 h}{3} \frac{\varepsilon_{\text{eff}}(\varepsilon_m(\lambda) - \varepsilon_{\text{eff}})}{\varepsilon_{\text{eff}} + L(\varepsilon_m(\lambda) - \varepsilon_{\text{eff}})}, \quad (4)$$

where $\varepsilon_m(\lambda)$ is the wavelength-dependent dielectric function of gold³² and ε_{eff} is the effective dielectric response of the surrounding medium (both are relative permittivities), L is the geometric depolarization factor, and r and h are the long and short axes of the spheroid, respectively. For the case of AuNDs, r and h are taken as the radius and height. For spheroid with radii 60 and 45 nm, the geometric depolarization factor is $L \approx 0.1077$ and 0.1355 , respectively.^{30,33} Here, for calculation of the AuNDs' polarizability in the array, the spectrum of the array is considered similar to that of an isolated one because of the large inter-disk spacing, which results in a lack of near-field coupling.¹⁴ The reflectance spectra of the full AuNDs-Bragg reflector structure, plotted in Figs. 3(e) and 3(f), were computed rigorously using the FEM (COMSOL).

As mentioned before, to anticipate the position of the Fano dips, the interference between the responses of the individual constituent elements, a bare Bragg stack and independent AuNDs, must be considered. As shown in Figs. 3(a)–3(d), both constituent responses vary in phase and magnitude as a function of wavelength, and this is the main reason behind the unusual spectral behaviour and formation of Fano interferences in the reflection bandwidth of the AuNDs-Bragg reflector. The phase of the Bragg stack's reflection coefficient (φ_r) varies from about $-\pi$ to π (Figs. 3(a) and 3(b)), while the phase of the AuNDs' polarizability (φ_x) varies from about $-\pi/2$ to $\pi/2$ (Figs. 3(c) and 3(d)). For reference, red vertical dashed lines have been added to indicate the Fano resonances' spectral position and to mark the corresponding phases of the two component responses (AuNDs and bare Bragg stack). It is clear that Fano resonances occur when $|\varphi_r - \varphi_x| \approx \pi$. This condition is met at $\lambda_{F1} = 643$ nm and $\lambda_{F2} = 723$ nm for air as the bounding medium (left panels of Fig. 3) and at $\lambda_{F3} = 637$ nm and $\lambda_{F4} = 728$ nm for water as the bounding medium (right panels of Fig. 3).

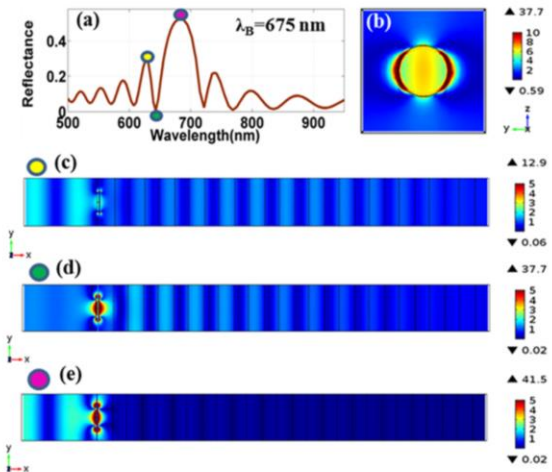


FIG. 4. (a) Reflectance spectrum of the AuNDs-Bragg structure with $\lambda_B = 675$ nm. Markers indicate the wavelengths at which the fields have been computed in (c)–(e). (b) Field distribution in the yz plane at 643 nm. (c), (d), and (e) Field distribution in xy plane at three wavelengths corresponding to the colored circles plotted on the reflectance spectrum of part (a): 627 nm—yellow circle; 643 nm—green circle; 675 nm—pink circle. The color bar range has been selected to be between (b) 0 and 10 and (c)–(e) 0 and 5 to show the field enhancement more clearly. Computations carried out using the FEM (COMSOL).

C. Fit to Fano lineshape formula

Both dips in the spectrum of an AuNDs-Bragg structure can be described by the Fano lineshape formula. We have fit Eq. (1) to the data presented in Figs. 3(e) and 3(f), as shown by the dashed yellow and cyan curves. The fitting region for each was limited to the region of the spectrum over which the Fano resonance occurs. The Fano parameters (A , B , q , $\Delta\lambda$, and λ_{F1}) were deduced by manually fitting the computed responses to Eq. (1); Table I summarizes the Fano parameters obtained (since the computed responses are in the form of wavelength spectra, the resonance wavelength $\lambda_F = 2\pi c/\omega_0$ and the resonance wavelength bandwidth $\Delta\lambda = \gamma(\lambda_F)^2/2\pi c$ are reported instead of ω_0 and γ). The bandwidth of the Fano resonances (~ 9 to 12 nm) seen in the reflectance spectra is much narrower than the constituent resonances of the AuNDs (LSPR bandwidth ~ 55 nm for air and 80 nm for water as the bounding medium)³¹ and of the Bragg stack (bandwidth ~ 100 nm).

D. Field distributions

Fig. 4 shows the y component of electric field (E_y) distributed throughout the structure at three different wavelengths: $\lambda_1 = 627$ nm (yellow circle), $\lambda_{F1} = 643$ nm (green

TABLE I. Fano parameters of the resonances of Figs. 3(e) and 3(f).

I	λ_{F1} (nm)	A	B	q	$\Delta\lambda$ (nm)
1	643	0.9	0.06	0.2	12
2	723	0.85	0.06	0.3	12
3	637	0.65	0.02	0.8	10
4	728	0.65	0.02	0.9	9

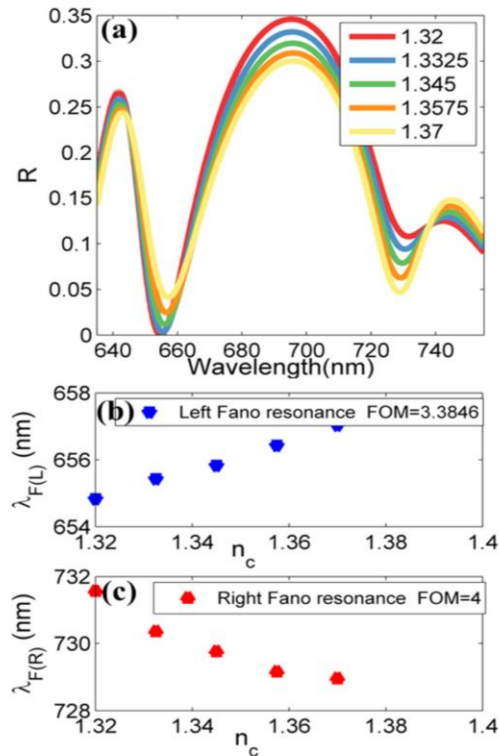


FIG. 5. (a) Evolution of the reflectance spectra vs. the refractive index of the bounding medium (n_c). (b) and (c) Shifts of the left Fano dip ($\lambda_{F(L)}$) and right Fano dip ($\lambda_{F(R)}$) vs. the index of the bounding medium (n_c). Computations carried out using the FEM (COMSOL).

circle), and $\lambda_B = 675$ nm (pink circle) for air as the bounding medium. Since the electric field of the incident plane wave is 1 V/m, the figures show directly the field enhancement, and as seen in Fig. 4(b), there is a strong field enhancement around the AuNDs, which is desirable for sensing applications. Also, as observed in Figs. 4(c) and 4(e), the incident field is reflected by the structure at these wavelengths, more so at λ_B , as expected. However, strong fields are trapped in the structure at the Fano resonance wavelength, λ_{F1} (Fig. 4(d)), which is consistent with maximum absorption on Fano resonances, as discussed relative to Fig. 2.

IV. BULK SENSITIVITY

To characterize the performance of a structure for sensing, two parameters can be considered: the bulk refractive index sensitivity and the FOM (figure of merit). To find the bulk sensitivity, the refractive index of the medium bounding the AuNDs was changed from $n_c = 1.32$ (pure water) to $n_c = 1.37$ (e.g., water mixed with glycerol); Fig. 5(a) presents the evolution of the reflectance spectra vs. the refractive index of the bounding medium, and Figs. 5(b) and 5(c) show the shifts of the Fano dips vs. the index of the bounding medium. As observed in these figures, there is a redshift and a blueshift in the left and right Fano dips, respectively. Bulk sensitivity that is defined as a resonant wavelength shift vs.

the refractive index change ($\partial\lambda_F/\partial n_c$) was calculated and is 44 and -52 nm/RIU for the first and second Fano resonances, respectively. These sensitivities are comparable to arrays of gold nanoshells,³⁴ gold nanorods,³⁵ and similar AuND arrays on glass³⁶ or even nano-spheres on glass.³⁷ However, the overall performance for sensing depends on the spectral width of the resonance as well, which is significantly narrower in this work. The narrowband response allows for an accurate measurement of small shifts in the resonance wavelength caused by changes in the refractive index of the bounding medium. The FOM was defined to compare the overall performance of sensing structures, as the ratio of the resonance wavelength shift per unit refractive index change, divided by the spectral width of the resonance.³⁸ The spectral width is taken as the wavelength difference between the Fano dip and the peak before the dip,⁶ because a Fano resonance usually has an asymmetric line shape, and the full width at half maximum is often not appropriate. The resulting FOM for the first and second Fano resonances is 3.4 and 4 (RIU)⁻¹, respectively, which is high compared to arrays of gold nanoshells (Au/SiO₂)³⁴ ($\lambda_{\text{peak}} = 770$ nm; FoM = 0.9), gold nanorods³⁵ ($\lambda_{\text{peak}} = 720$ nm; FoM = 1.3), AuNDs³⁶ ($\lambda_{\text{peak}} = 700$ nm; FoM = 2), and gold nano-bipyramids³⁹ ($\lambda_{\text{peak}} = 680$ nm; FoM = 4.5).

V. CONCLUSIONS

To summarize, we have shown that the reflectance spectra of an array of AuNDs on a dielectric Bragg stack exhibit Fano resonances. This phenomenon can be explained as interference between LSPRs on the AuNDs and the reflection spectrum of the Bragg stack. We have characterized the proposed structure and modelled the observed interference using the Fano lineshape formula by fitting to the computed responses. One important advantage of the proposed structure is that the linewidth of the Fano resonances (~ 9 nm) is much narrower than the nano-disk LSPR bandwidth (~ 80 nm) and the Bragg reflection bandwidth (~ 100 nm), which makes the structure potentially attractive for sensing applications. Sensing calculations were performed and bulk sensitivities of 44 and -52 nm/RIU for the first and second Fano resonances were calculated; the former was observed to redshift, while the latter was observed to blueshift with increasing bounding medium index. Also, a FOM of 4 (RIU)⁻¹ was recorded for the second resonance, which is high compared to other sensors including gold nanoparticle arrays operating at an almost similar resonance wavelength.

¹U. Fano, *Phys. Rev.* **124**(6), 1866–1878 (1961).

²N. Liu, T. Weiss, M. Mesch, L. Langguth, U. Eigenthaler, M. Hirscher, C. Soennichsen, and H. Giessen, *Nano Lett.* **10**(4), 1103–1107 (2010).

³N. Papasimakis, Y. H. Fu, V. A. Fedotov, S. L. Prosvirnin, D. P. Tsai, and N. I. Zheludev, *Appl. Phys. Lett.* **94**(21), 211902 (2009).

⁴J. A. Fan, C. Wu, K. Bao, J. Bao, R. Bardhan, N. J. Halas, V. N. Manoharan, P. Nordlander, G. Shvets, and F. Capasso, *Science* **328**(5982), 1135–1138 (2010).

⁵K. Thyagarajan, J. Butet, and O. J. F. Martin, *Nano Lett.* **13**(4), 1847–1851 (2013).

⁶F. Hao, Y. Sonnefraud, P. Van Dorpe, S. A. Maier, N. J. Halas, and P. Nordlander, *Nano Lett.* **8**(11), 3983–3988 (2008).

⁷J. B. Lassiter, H. Sobhani, J. A. Fan, J. Kundu, F. Capasso, P. Nordlander, and N. J. Halas, *Nano Lett.* **10**(8), 3184–3189 (2010).

- ⁸A. Christ, T. Zentgraf, J. Kuhl, S. G. Tikhodeev, N. A. Gippius, and H. Giessen, *Phys. Rev. B* **70**(12), 125113 (2004).
- ⁹A. Christ, S. G. Tikhodeev, N. A. Gippius, J. Kuhl, and H. Giessen, *Phys. Rev. Lett.* **91**(18), 183901 (2003).
- ¹⁰M. Svedendahl and M. Kall, *ACS Nano* **6**(8), 7533–7539 (2012).
- ¹¹I. Baryakhtar, Y. Demidenko, and V. Lozovski, *J. Opt. Soc. Am. B* **30**(4), 1022–1026 (2013).
- ¹²M. Hentschel, M. Saliba, R. Vogelgesang, H. Giessen, A. P. Alivisatos, and N. Liu, *Nano Lett.* **10**(7), 2721–2726 (2010).
- ¹³F. Hao, P. Nordlander, Y. Sonnefraud, P. Van Dorpe, and S. A. Maier, *ACS Nano* **3**(3), 643–652 (2009).
- ¹⁴Y. Zhen, K. H. Fung, and C. T. Chan, *Phys. Rev. B* **78**(3), 035419 (2008).
- ¹⁵B. Luk'yanchuk, N. I. Zheludev, S. A. Maier, N. J. Halas, P. Nordlander, H. Giessen, and C. T. Chong, *Nature Mater.* **9**(9), 707–715 (2010).
- ¹⁶D. S. Citrin, *Nano Lett.* **4**(9), 1561–1565 (2004).
- ¹⁷A. Yariv and P. Yeh, *Optical Electronics in Modern Communications*, 6th ed. (Oxford University Press, 2007).
- ¹⁸B. Gallinet, A. Lovera, T. Siegfried, H. Sigg, and O. J. F. Martin, "Fano resonant plasmonic systems: Functioning principles and applications," *AIP Conf. Proc.* **1475**, 18 (2012).
- ¹⁹M. Sarrazin, J. P. Vigneron, and J. M. Vigoureux, *Phys. Rev. B* **67**(8), 085415 (2003).
- ²⁰H. T. Lee and A. W. Poon, *Opt. Lett.* **29**(1), 5–7 (2004).
- ²¹M. V. Rybin, A. B. Khanikaev, M. Inoue, K. B. Samusev, M. J. Steel, G. Yushin, and M. F. Limonov, *Phys. Rev. Lett.* **103**(2), 023901 (2009).
- ²²B. Gallinet and O. J. F. Martin, *ACS Nano* **5**(11), 8999–9008 (2011).
- ²³W. Zhao, D. Ju, and Y. Jiang, *Plasmonics* **10**(2), 469–474 (2015).
- ²⁴A. E. Miroshnichenko, S. Flach, and Y. S. Kivshar, *Rev. Mod. Phys.* **82**(3), 2257–2298 (2010).
- ²⁵M. Svedendahl, P. Johansson, and M. Kall, *Nano Lett.* **13**(7), 3053–3058 (2013).
- ²⁶D. Cai, Y. Huang, W. Wang, W. Ji, J. Chen, Z. Chen, and S. Liu, *J. Phys. Chem. C* **119**(8), 4252–4260 (2015).
- ²⁷C. Chang and O. Solgaard, *Opt. Express* **21**(22), 27209–27218 (2013).
- ²⁸D. J. Segelstein, "The complex refractive index of water," M.S. thesis (University of Missouri, Kansas City, MO, 1981).
- ²⁹A. V. D. Meindert, "Nonlinear-optical studies of single gold nanoparticles," Ph.D. thesis (Leiden University, City of Leiden, 2007).
- ³⁰C. F. Bohren and D. R. Huffman, *Absorption and Scattering by Small Particles* (Wiley, New York, 1983).
- ³¹I. Zoric, M. Zach, B. Kasemo, and C. Langhammer, *ACS Nano* **5**(4), 2535–2546 (2011).
- ³²P. B. Johnson and R. W. Christy, *Phys. Rev. B* **6**(12), 4370–4379 (1972).
- ³³P. Hanarp, M. Kall, and D. S. Sutherland, *J. Phys. Chem. B* **107**(24), 5768–5772 (2003).
- ³⁴F. Tam, C. Moran, and N. J. Halas, *J. Phys. Chem. B* **108**(45), 17290–17294 (2004).
- ³⁵K. M. Mayer, S. Lee, H. Liao, B. C. Rostro, A. Fuentes, P. T. Scully, C. L. Nehl, and J. H. Hafner, *ACS Nano* **2**(4), 687–692 (2008).
- ³⁶M. Svedendahl, S. Chen, A. Dmitriev, and M. Kall, *Nano Lett.* **9**(12), 4428–4433 (2009).
- ³⁷J. Yuan, A. Hajebifard, C. George, P. Berini, and S. Zou, *J. Colloid Interface Sci.* **410**, 1–10 (2013).
- ³⁸L. J. Sherry, S. H. Chang, G. C. Schatz, R. P. Van Duyne, B. J. Wiley, and Y. N. Xia, *Nano Lett.* **5**(10), 2034–2038 (2005).
- ³⁹J. Burgin, M. Liu, and P. Guyot-Sionnest, *J. Phys. Chem. C* **112**(49), 19279–19282 (2008).

D. Corrigendum

- The first sentence above Eq. (4) should read:
 - *The AuNDs with a diameter of 120 nm and a height of 20 nm are small enough to behave in the quasistatic limit [163]. To compute the polarizability of the AuNDs, plotted in Figs. 3(c) and 3(d), the AuNDs were modeled as oblate spheroids, with their polarizability in the quasistatic limit written as.*
 - *In Eq. 2, the permittivity and permeability should be their imaginary parts only.*

4. Fano resonances in gold heptamer nano-hole arrays

A. Summary

A comprehensive theoretical and numerical study was performed on the optical properties of arrays of heptamer-arranged nanoholes (HNH). Several pronounced Fano resonances appear in the optical response due to various phenomena such as LSPP excitations, diffractive effects, propagating SPP excitations, and WA waves. To understand the mechanism behind the generation of Fano resonances, near-field distributions associated with each resonance were provided, as well as the effects of changing the structural parameters, such as periodicity, metal thickness, inter-hole gap and central hole radius. To examine the structure as a biosensor, bulk sensitivity, FoM and surface sensitivity were calculated. The highest bulk (400 nm/RIU) and surface (2 nm/nm) sensitivities were calculated for LSPP Fano resonances, while the highest FoM (24.5 RIU^{-1}) was achieved for the WA-SPPs Fano resonance. In comparison with the single nanohole arrays, this structure exhibits an improvement in the bulk sensitivity and FoM values.

B. Contribution

The results provided in this chapter were published as an article in the journal *Optics Express*. I proposed and designed the structure; I performed theoretical and numerical studies; I generated and interpreted the results and wrote the manuscript. Dr. Berini contributed to the interpretation of the results and revised the manuscript.

C. Article

The published article follows verbatim.



Fano resonances in plasmonic heptamer nano-hole arrays

AKRAM HAJEBIFARD¹ AND PIERRE BERINI^{1,2,3,*}

¹Department of Physics, University of Ottawa, Ottawa K1N 6N5, Canada

²School of Electrical Engineering and Computer Sci., University of Ottawa, Ottawa K1N 6N5, Canada

³Centre for Research in Photonics at the University of Ottawa, Ottawa K1N 6N5, Canada

*berini@eecs.uottawa.ca

Abstract: The optical properties of gold heptamer nanohole arrays have been investigated theoretically and numerically. This structure support pronounced Fano resonances with high transmittance (~50%) and narrow bandwidths (down to 12 nm). The Fano features arise from the interference between light directly transmitted through the holes, and light indirectly scattered through the excitation of localized surface plasmon polaritons (LSPPs), propagating surface plasmon polaritons (SPPs), or/and waves related to Wood's anomaly (WA). The mechanisms behind the generation of these resonances are revealed by observing near-field distributions, altering the structural parameters and applying the Bloch wave model. Furthermore, it is shown that Fano resonances associated with LSPPs exhibit high surface (2 nm/nm) and bulk sensitivities (400 nm/RIU). However, the highest figure of merit (~24 RIU⁻¹) occurs for a Fano resonance involving a WA and SPP mode.

© 2017 Optical Society of America

OCIS codes: (240.6680) Surface plasmons; (250.5403) Plasmonics; (280.4788) Optical sensing and sensors.

References and links

1. A. Otto, "Excitation of nonradiative surface plasma waves in silver by method of frustrated total reflection," *Z. Phys. A: Hadrons Nucl.* **216**(4), 398–410 (1968).
2. C. Wu, A. B. Khanikaev, R. Adato, N. Arju, A. A. Yanik, H. Altug, and G. Shvets, "Fano-resonant asymmetric metamaterials for ultrasensitive spectroscopy and identification of molecular monolayers," *Nat. Mater.* **11**(1), 69–75 (2011).
3. A. E. Cetin and H. Altug, "Fano resonant ring/disk plasmonic nanocavities on conducting substrates for advanced biosensing," *ACS Nano* **6**(11), 9989–9995 (2012).
4. N. A. Mirin, K. Bao, and P. Nordlander, "Fano resonances in plasmonic nanoparticle aggregates," *J. Phys. Chem. A* **113**(16), 4028–4034 (2009).
5. N. Liu, T. Weiss, M. Mesch, L. Langguth, U. Eigenthaler, M. Hirscher, C. Sönnichsen, and H. Giessen, "Planar metamaterial analogue of electromagnetically induced transparency for plasmonic sensing," *Nano Lett.* **10**(4), 1103–1107 (2010).
6. N. Verellen, Y. Sonnefraud, H. Sobhani, F. Hao, V. V. Moshchalkov, P. V. Dorpe, P. Nordlander, and S. A. Maier, "Fano resonances in individual coherent plasmonic nanocavities," *Nano Lett.* **9**(4), 1663–1667 (2009).
7. B. Gallinet and O. J. F. Martin, "Influence of electromagnetic interactions on the line shape of plasmonic Fano resonances," *ACS Nano* **5**(11), 8999–9008 (2011).
8. N. Papasimakis, Y. H. Fu, V. A. Fedotov, S. L. Prosvirnin, D. P. Tsai, and N. I. Zheludev, "Metamaterial with polarization and direction insensitive resonant transmission response mimicking electromagnetically induced transparency," *Appl. Phys. Lett.* **94**(21), 211902 (2009).
9. J. A. Fan, C. Wu, K. Bao, J. Bao, R. Bardhan, N. J. Halas, V. N. Manoharan, P. Nordlander, G. Shvets, and F. Capasso, "Self-assembled plasmonic nanoparticle clusters," *Science* **328**(5982), 1135–1138 (2010).
10. K. Thyagarajan, J. Butet, and O. J. F. Martin, "Augmenting second harmonic generation using Fano resonances in plasmonic systems," *Nano Lett.* **13**(4), 1847–1851 (2013).
11. F. Hao, Y. Sonnefraud, P. Van Dorpe, S. A. Maier, N. J. Halas, and P. Nordlander, "Symmetry breaking in plasmonic nanocavities: subradiant LSPR sensing and a tunable Fano resonance," *Nano Lett.* **8**(11), 3983–3988 (2008).
12. J. B. Lassiter, H. Sobhani, J. A. Fan, J. Kundu, F. Capasso, P. Nordlander, and N. J. Halas, "Fano resonances in plasmonic nanoclusters: geometrical and chemical tunability," *Nano Lett.* **10**(8), 3184–3189 (2010).
13. A. Christ, T. Zentgraf, J. Kuhl, S. Tikhodeev, N. Gippius, and H. Giessen, "Optical properties of planar metallic photonic crystal structures: Experiment and theory," *Phys. Rev. B* **70**(12), 125113 (2004).
14. A. Hajebifard and P. Berini, "Plasmonic Fano interference produced by gold nano-disks on a dielectric Bragg stack," *J. Appl. Phys.* **118**(9), 093107 (2015).

15. A. Christ, S. G. Tikhodeev, N. A. Gippius, J. Kuhl, and H. Giessen, "Waveguide-plasmon polaritons: strong coupling of photonic and electronic resonances in a metallic photonic crystal slab," *Phys. Rev. Lett.* **91**(18), 183901 (2003).
16. M. Svedendahl and M. Käll, "Fano interference between localized plasmons and interface reflections," *ACS Nano* **6**(8), 7533–7539 (2012).
17. I. Baryakhtar, Y. Demidenko, and V. Lozovski, "Interaction between localized-on-nanoparticles plasmon polaritons and surface plasmon polaritons," *J. Opt. Soc. Am. B* **30**(4), 1022–1026 (2013).
18. A. Artar, A. A. Yanik, and H. Altug, "Directional double Fano resonances in plasmonic hetero-oligomers," *Nano Lett.* **11**(9), 3694–3700 (2011).
19. G. F. Walsh and L. Dal Negro, "Enhanced second harmonic generation by photonic-plasmonic Fano-type coupling in nanoplasmonic arrays," *Nano Lett.* **13**(7), 3111–3117 (2013).
20. R. Near, C. Tabor, J. Duan, R. Pachter, and M. El-Sayed, "Pronounced effects of anisotropy on plasmonic properties of nanorings fabricated by electron beam lithography," *Nano Lett.* **12**(4), 2158–2164 (2012).
21. S. N. Sheikholeslami, A. García-Etxarri, and J. A. Dionne, "Controlling the interplay of electric and magnetic modes via Fano-like plasmon resonances," *Nano Lett.* **11**(9), 3927–3934 (2011).
22. J. A. Fan, K. Bao, C. Wu, J. Bao, R. Bardhan, N. J. Halas, V. N. Manoharan, G. Shvets, P. Nordlander, and F. Capasso, "Fano-like interference in self-assembled plasmonic quadrumer clusters," *Nano Lett.* **10**(11), 4680–4685 (2010).
23. J. A. Fan, Y. He, K. Bao, C. Wu, J. Bao, N. B. Schade, V. N. Manoharan, G. Shvets, P. Nordlander, D. R. Liu, and F. Capasso, "DNA-enabled self-assembly of plasmonic nanoclusters," *Nano Lett.* **11**(11), 4859–4864 (2011).
24. Y. Cui, J. Zhou, V. A. Tamma, and W. Park, "Dynamic tuning and symmetry lowering of Fano resonance in plasmonic nanostructure," *ACS Nano* **6**(3), 2385–2393 (2012).
25. M. Hentschel, M. Saliba, R. Vogelgesang, H. Giessen, A. P. Alivisatos, and N. Liu, "Transition from isolated to collective modes in plasmonic oligomers," *Nano Lett.* **10**(7), 2721–2726 (2010).
26. P. Alonso-Gonzalez, M. Schnell, P. Sarriugarte, H. Sobhani, C. Wu, N. Arju, A. Khanikaev, F. Golmar, P. Albella, L. Arzubia, F. Casanova, L. E. Hueso, P. Nordlander, G. Shvets, and R. Hillenbrand, "Real-space mapping of Fano interference in plasmonic metamolecules," *Nano Lett.* **11**(9), 3922–3926 (2011).
27. N. Liu, S. Kaiser, and H. Giessen, "Magnetoinductive and electroinductive coupling in plasmonic metamaterial molecules," *Adv. Mater.* **20**(23), 4521–4525 (2008).
28. J. Ye, F. Wen, H. Sobhani, J. B. Lassiter, P. Van Dorpe, P. Nordlander, and N. J. Halas, "Plasmonic nanoclusters: near field properties of the Fano resonance interrogated with SERS," *Nano Lett.* **12**(3), 1660–1667 (2012).
29. Z. Liu and J. Ye, "Highly controllable double Fano resonances in plasmonic metasurfaces," *Nanoscale* **8**(40), 17665–17674 (2016).
30. M. Alavirad, S. S. Mousavi, L. Roy, and P. Berini, "Schottky-contact plasmonic dipole rectenna concept for biosensing," *Opt. Express* **21**(4), 4328–4347 (2013).
31. R. Gordon, D. Sinton, K. L. Kavanagh, and A. G. Brolo, "A new generation of sensors based on extraordinary optical transmission," *Acc. Chem. Res.* **41**(8), 1049–1057 (2008).
32. L. Pang, G. M. Hwang, B. Slutsky, and Y. Fainman, "Spectral sensitivity of two-dimensional nanohole array surface plasmon polariton resonance sensor," *Appl. Phys. Lett.* **91**(12), 123112 (2007).
33. A. Lesuffleur, H. Im, N. C. Lindquist, K. S. Lim, and S.-H. Oh, "Laser-illuminated nanohole arrays for multiplex plasmonic microarray sensing," *Opt. Express* **16**(1), 219–224 (2008).
34. C. J. Alleyne, A. G. Kirk, R. C. McPhedran, N.-A. P. Nicorovici, and D. Maystre, "Enhanced SPR sensitivity using periodic metallic structures," *Opt. Express* **15**(13), 8163–8169 (2007).
35. Y. Zhan, D. Y. Lei, X. Li, and S. A. Maier, "Plasmonic Fano resonances in nanohole quadrumers for ultra-sensitive refractive index sensing," *Nanoscale* **6**(9), 4705–4715 (2014).
36. J. He, P. Ding, J. Wang, C. Fan, and E. Liang, "Double Fano-type resonances in heptamer-hole array transmission spectra with high refractive index sensing," *J. Mod. Opt.* **62**(15), 1241–1247 (2015).
37. S. H. Chang, S. Gray, and G. Schatz, "Surface plasmon generation and light transmission by isolated nanoholes and arrays of nanoholes in thin metal films," *Opt. Express* **13**(8), 3150–3165 (2005).
38. C. Genet, M. van Exter, and J. Woerdman, "Fano-type interpretation of red shifts and red tails in hole array transmission spectra," *Opt. Commun.* **225**(4–6), 331–336 (2003).
39. E. D. Palik, *Handbook of Optical Constants of Solids*, No. Book, Whole (Academic, 1997).
40. W. L. Barnes, W. A. Murray, J. Dintinger, E. Devaux, and T. W. Ebbesen, "Surface plasmon polaritons and their role in the enhanced transmission of light through periodic arrays of subwavelength holes in a metal film," *Phys. Rev. Lett.* **92**(10), 107401 (2004).
41. A. Hessel and A. A. Oliner, "A new theory of wood's anomalies on optical gratings," *Appl. Opt.* **4**(10), 1275–1297 (1965).
42. Z. Ruan and M. Qiu, "Enhanced transmission through periodic arrays of subwavelength holes: the role of localized waveguide resonances," *Phys. Rev. Lett.* **96**(23), 233901 (2006).
43. H. F. Ghaemi, T. Thio, D. E. Grupp, T. W. Ebbesen, and H. J. Lezec, "Surface plasmons enhance optical transmission through subwavelength holes," *Phys. Rev. B* **58**(11), 6779–6782 (1998).
44. J. A. Fan, C. Wu, K. Bao, J. Bao, R. Bardhan, N. J. Halas, V. N. Manoharan, P. Nordlander, G. Shvets, and F. Capasso, "Self-assembled plasmonic nanoparticle clusters," *Science* **328**(5982), 1135–1138 (2010).

45. M. Hentschel, T. Weiss, S. Bagheri, and H. Giessen, "Babinet to the half: coupling of solid and inverse plasmonic structures," *Nano Lett.* **13**(9), 4428–4433 (2013).
46. J. J. Burke, G. I. Stegeman, and T. Tamir, "Surface-polariton-like waves guided by thin, lossy metal films," *Phys. Rev. B Condens. Matter* **33**(8), 5186–5201 (1986).
47. P. Berini, "Plasmon-polariton waves guided by thin lossy metal films of finite width: Bound modes of asymmetric structures," *Phys. Rev. B* **63**(12), 125417 (2001).
48. J. M. McMahon, J. Henzie, T. W. Odom, G. C. Schatz, and S. K. Gray, "Tailoring the sensing capabilities of nanohole arrays in gold films with Rayleigh anomaly-surface plasmon polaritons," *Opt. Express* **15**(26), 18119–18129 (2007).
49. J. M. Steele, C. E. Moran, A. Lee, C. M. Aguirre, and N. J. Halas, "Metallodielectric gratings with subwavelength slots: Optical properties," *Phys. Rev. B* **68**(20), 205103 (2003).
50. T. Rindzevicius, Y. Alaverdyan, B. Sepulveda, T. Pakizeh, M. Kall, R. Hillenbrand, J. Aizpurua, and F. J. Garcia de Abajo, "Nanohole plasmons in optically thin gold films," *J. Phys. Chem. C* **111**(3), 1207–1212 (2007).
51. Y. Chu and K. B. Crozier, "Experimental study of the interaction between localized and propagating surface plasmons," *Opt. Lett.* **34**(3), 244–246 (2009).
52. N. Papanikolaou, "Optical properties of metallic nanoparticle arrays on a thin metallic film," *Phys. Rev. B* **75**, 235426 (2007).
53. T. Ohno, C. Wadell, S. Inagaki, J. Shi, Y. Nakamura, S. Matsushita, and T. Sannomiya, "Hole-size tuning and sensing performance of hexagonal plasmonic nanohole arrays," *Opt. Mater. Express* **6**(5), 1594–1603 (2016).
54. T. Sannomiya, O. Scholder, K. Jefimovs, C. Hafner, and A. B. Dahlin, "Investigation of plasmon resonances in metal films with nanohole arrays for biosensing applications," *Small* **7**(12), 1653–1663 (2011).
55. S. Zhang, L. Chen, Y. Huang, and H. Xu, "Reduced linewidth multipolar plasmon resonances in metal nanorods and related applications," *Nanoscale* **5**(15), 6985–6991 (2013).
56. H. Gao, J. M. McMahon, M. H. Lee, J. Henzie, S. K. Gray, G. C. Schatz, and T. W. Odom, "Rayleigh anomaly-surface plasmon polariton resonances in palladium and gold subwavelength hole arrays," *Opt. Express* **17**(4), 2334–2340 (2009).
57. G. A. Cervantes Tellez, S. Hassan, R. N. Tait, P. Berini, and R. Gordon, "Atomically flat symmetric elliptical nanohole arrays in a gold film for ultrasensitive refractive index sensing," *Lab Chip* **13**(13), 2541–2546 (2013).
58. A. E. Cetin, D. Etezadi, B. C. Galarreta, M. P. Busson, Y. Eksioglu, and H. Altug, "Plasmonic nanohole arrays on a robust hybrid substrate for highly sensitive label-free biosensing," *ACS Photonics* **2**(8), 1167–1174 (2015).
59. A. Hajiaboli, M. Kahrizi, and T. Vo-Van, "Optical behaviour of thick gold and silver films with periodic circular nanohole arrays," *J. Phys. - Appl. Phys. (Berl.)* **45**, 485105 (2012).

1. Introduction

Compared to the symmetric Lorentzian lineshape supported in various nanostructures [1], asymmetric Fano resonances in plasmonic structures have recently attracted intense attention [2,3] due to their remarkable characteristics such as a narrow asymmetric line-shape, strong electromagnetic field enhancement, light confinement to the nanometer scale, and high spectral sensitivity to changes in the local dielectric environment [1,4–6]. In plasmonic structures, Fano resonances originate from the interference between light directly coupled to a bright mode (continuum), and light indirectly coupled to a dark mode (subradiant) excited via near-field interactions with the bright mode [7]. A Fano peak is a consequence of constructive interference between such modes, whereas a Fano dip arises as the two modes interfere destructively such as when the dark mode is out of phase with respect to the continuum. Taking advantage of this principle, different types of plasmonic structures, such as metamaterials [5,8], clusters [9,10], single and multi-surface nanoparticles [11,12] and periodic structures [13–17] have been proposed and studied, seeking Fano resonances in their spectral responses. Structures generating pronounced Fano resonances include assemblies of plasmonic nanoparticles, such as dimers [18–20], trimers [21], quadrumers [22], pentamers [23] and heptamers [10,24–26], where various parameters such as inter-particle separation and particle size can be tuned, but also symmetry can be broken, to tailor the characteristics of Fano resonances.

Unlike plasmonic nanoparticle assemblies, far less attention has been paid to complementary structures - arrangement of metallic nanoholes - which are also expected to support Fano resonances [5,27]. We show that arrangements of nanoholes in metal films produce more complex spectral responses because the structure supports many excitations, including localised surface plasmon polaritons (LSPPs) in the vicinity of holes, and propagating surface plasmon polaritons (SPPs) or Wood's anomaly (WA) waves excited on

the metal film that also interact with the holes. In comparison with complementary structures, the increased number of modes in metallic nanohole assemblies suggests broadband interrogation to track multiple resonances, resulting in improvement of the detection limit and measurement accuracy. Also, the increased number of resonances, and the ability to independently tune the position of SPP and LSPP resonances (both providing near-field enhancement) is favorable for double-resonance SERS applications, where simultaneous enhancement at both the excitation and Stokes wavelengths is needed [28,29].

In addition, compared to complementary structures where interconnections between nanoantennas are required for, *e.g.*, optoelectronic applications, the continuity of the metallic layer in the nanohole arrangements can be useful for producing, *e.g.*, resonant Schottky contacts [30]. Finally, nanohole arrays as biosensors allow for a high degree of multiplexing, parallel optical detection, and the ability to integrate microfluidics [31–34]. Recently, some research has been focused on plasmonic nanohole clusters, such as individual nanohole quadrumers [35], and arrays of heptamer-arranged nanoholes [36], but this area of study remains largely unexplored. The purpose of this paper is to investigate the optical properties of arrays of heptamer-arranged nanoholes (HNH) in detail, offer physical interpretations for the generation of Fano resonances in such arrays, and consider their application to biosensors. Heptamer-arranged nanoholes form a plasmonic oligomer consisting of one nanohole surrounded by six others forming a high packing density arrangement of nanoholes, which produces many hot spot areas between neighboring elements. Also the high spatial symmetry of HNH simplifies polarization alignments and facilitates interrogation.

We numerically study arrays of HNH drilled into a thin gold film on a SiO_2 substrate covered by different superstrate media, which renders the structure asymmetric and rich in excitations and spectral features. We also investigate in detail the effects caused by changing the geometrical parameters, including periodicity, metal thickness, inter-hole distance and the radius of the central hole in the heptamer, and we connect the numerical results to an analytical Bloch wave model. The sensitivity of the Fano features to small changes in the refractive index (RI) of the superstrate medium makes the structure a potential candidate for chemical and biological sensors. We thus also examine the device for use as a biosensor by calculating the bulk sensitivity, the Figure of Merit (FoM) and the surface sensitivity. We find that the proposed structure supports pronounced Fano resonances in the near infrared (NIR) range of the optical spectrum. Four types of modes, consisting of LSPPs and propagating symmetric SPP (SPP_s), asymmetric SPP (SPP_a) and WA waves play essential roles in the formation of Fano resonances. The Fano resonances arise from the interference between the light transmitted directly through the holes (continuum) and the light indirectly scattered due the excitation of these four types of modes [37,38].

2. Proposed structure and numerical model

Figure 1 shows schematically the structure under study, which is an array of HNH in a thin Au film supported by a SiO_2 substrate and covered by a dielectric medium (several considered). The geometrical parameters including the metal thickness (t), inter-hole gap (G), periodicity of the array ($P = P_y = P_z$), and diameter of the central hole (D_c) are varied, but the diameter of holes on the outer ring (D) remains fixed. Transmittance (T), reflectance (R) and absorptance ($A = 1 - R - T$) spectra are calculated as the response of the structure, because each might be useful based on the potential applications of the system. For instance, the absorptance is required for SERS and Schottky contact photodetector applications [28,30], whereas the transmittance and reflectance are useful for biosensing applications [31]. Throughout the paper, absorptance peaks are used to identify the position of resonances. To compute the spectra and the associated electromagnetic fields, the structure was modeled using a commercial (COMSOL) implementation of the finite element method (FEM), solving the vector wave equations for the E and H field vectors throughout the structure, subject to the applicable boundary conditions, and the applied source fields. The structure was meshed

using tetrahedral mesh elements with a resolution between 5 and 12 nm in the gold film, while the mesh size was increased gradually away from the gold film with a maximum mesh element size of 100 nm. Taking advantage of the structural symmetry, only one unit cell incorporating one heptamer arrangement of nanoholes was modelled. To do so, periodic boundary conditions were applied on the lateral walls and absorbing boundary conditions on the front and back walls. The structure was then illuminated by y- and z-polarized electromagnetic waves perpendicularly incident onto the structure from the substrate side. The optical properties of the materials were taken as the wavelength-dependent complex refractive index measured over the range of interest for SiO₂ [39] and Au [40]. Cubic spline interpolation functions were applied to determine the refractive indices at some wavelengths of interest where data were not available.

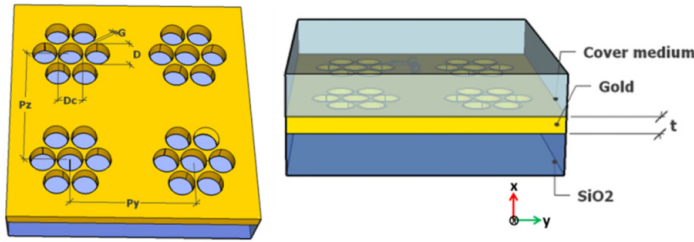


Fig. 1. Schematic of an HNH array on a SiO₂ substrate, and covered by a superstrate medium. The geometrical parameters include, metal thickness (t), inter-hole gap (G), periodicity of the array ($P = P_y = P_z$), and the diameter of the central holes (D_c) and of the surrounding holes (D).

3. Results and discussions

Considering the HNH array as a grating of lattice constant $P = P_y = P_z$ illuminated by light incident at an angle θ , the light gains additional momentum given by $|G_y| = |G_z| = 2\pi/P$, which can excite propagating SPP modes (Bloch waves) on the metal film following the Bragg coupling condition [41]:

$$K_{spp} = K_0 \sin \theta + S_y G_y + S_z G_z \quad (1)$$

In addition to SPP modes guided by the metal film, the grating effect of the HNH array can launch WA waves, which are associated with light diffracted parallel to the surface of the structure, excited under the following condition [37,41]:

$$K_{WA} = K_0 \sin \theta + W_y G_y + W_z G_z \quad (2)$$

In the above, k_0 , k_{spp} ($= k_0 n_{spp}$) and k_{WA} ($= k_0 n_d$) are the wavenumbers of free-space, of the SPP mode (symmetric or asymmetric) excited and guided by the thin metal film, and of WA waves, respectively. n_d is the refractive index of the medium in which the WA wave travels, n_{spp} is the effective mode index of an SPP mode, which is defined as $n_{spp} = \beta/k_0$ and $\beta = \beta' + i\beta''$ is the propagation constant of the mode. The integer index pairs (S_y, S_z) and (W_y, W_z) denote the diffraction order and are included in our nomenclature; for example, $SPP_a(1,0)$ and $SPP_s(1,1)$ refer to the asymmetric SPP propagating along the y axis, and the symmetric SPP along the diagonal to the y and z axes, respectively. For the case of normal incidence, Eqs. (1) and (2) can be rewritten as follows, in terms of the SPP wavelengths (λ_{spp}) and WA wavelengths (λ_{WA}) [42,43]:

$$\lambda_{spp} = \frac{P}{(S_y^2 + S_z^2)^{1/2}} n_{spp} \quad (3)$$

$$\lambda_{WA} = \frac{P}{(W_y^2 + W_z^2)^{1/2}} n_d \quad (4)$$

Equations (1)-(4) are approximate for our HNH arrays, because they hold for small perturbations whereas our arrays produce strong perturbations. The array of HNH not only operates as a diffraction grating to excite SPP modes supported by the metal film, or WA waves in either the substrate or superstrate, but it can also support LSPP resonances within the cluster of holes. A cluster of plasmonic nanoholes (or nanoparticles) can support coupled plasmon modes which are combinations of the plasmon modes supported by each constituent hole (nanoparticle) for sufficiently small inter-hole (inter-particle) separations [8,44]. It is expected that the HNH structure supports some Fano features arising from the interference between light directly transmitted through the holes, and light indirectly scattered through the excitation of LSPPs, propagating SPPs, or/and waves related to Wood's anomaly (WA).

3.1 Optical responses of HNH array

The optical responses of a HNH array, for both y- (black line) and z-(red line) linearly-polarized incident light, are shown in Fig. 2, which illustrates several Fano features. The HNH array includes holes with diameters of $D = D_c = 100$ nm and inter-hole distances of $G = 10$ nm in a gold film of thickness $t = 60$ nm, supported by SiO_2 substrate and covered by a dielectric material of refractive index $n_s = 1.33$. The periodicity was set to $P = P_y = P_z = 480$ nm, and the wavelength varied from 630 nm to 1000 nm. As shown in Fig. 2(b), the structure supports four Fano resonances for y-polarized incident light (black curve), at $\lambda_{1y} = 644$ nm, $\lambda_{2y} = 700$ nm, $\lambda_{3y} = 780$ nm and $\lambda_{4y} = 884$ nm, denoted as $\text{SPP}_a(1,1)$, $\text{WA-SPP}_s(1,0)$, $\text{SPP}_a(1,0)$ and LSPP_1 , respectively.

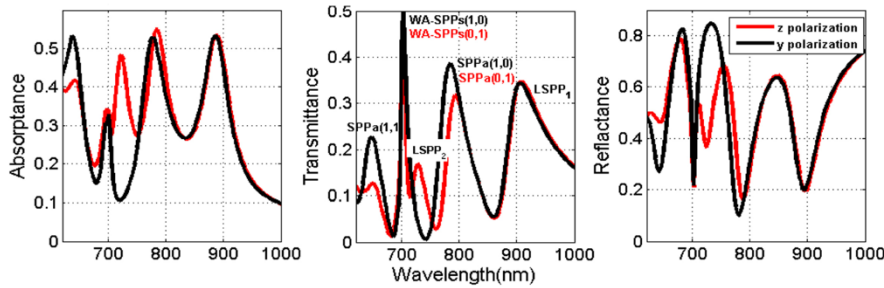


Fig. 2. Optical response of an array of HNH, for y-polarized (black curves) and z-polarized (red curves) incident light. The structure supports several Fano resonances denoted as $\text{SPP}_a(1,1)$, WA-SPP_s , LSPP_2 , $\text{SPP}_a(1,0)$ and LSPP_1 .

Also it supports five Fano resonances for z-polarized incident light (red curve), at $\lambda_{1z} = 642$ nm, $\lambda_{2z} = 698$ nm, $\lambda_{3z} = 721$ nm, $\lambda_{4z} = 785$ nm and $\lambda_{5z} = 886$ nm, denoted as $\text{SPP}_a(1,1)$, $\text{WA-SPP}_s(1,0)$, LSPP_2 , $\text{SPP}_a(1,0)$ and LSPP_1 , respectively. The physical mechanisms behind the formation of these resonances can be revealed by observing near electromagnetic field distributions, by changing the geometrical parameters of the structure, and also by considering the Bloch wave model.

3.2 Electromagnetic near-field distributions

To understand the mechanism behind the generation of each Fano resonance in the HNH array, electric and magnetic near-field distributions in a unit cell were computed at the spectral position of the resonances. The electric field amplitude of the incident wave was set to 1 V/m, so the electric field plots show directly the field enhancement. The electric field intensity ($|E|$), the x-component (perpendicular) of electric field (E_x), the x component of

magnetic field (H_x), and the y or z component of magnetic field (H_y or H_z) are shown in Fig. 3, for y-polarized incident light, and in Fig. 4, for z-polarized incident light. According to the Babinet's principle, resonances in a complementary structure are associated with the magnetic moment [45] which is revealed by H_x field distributions in this structure. Also, based on this principle, H_y or H_z magnetic field profiles can be provided to illustrate the propagating and localized surface plasmons. Based on the electromagnetic near-field distributions, the Fano resonances can be categorized as LSPP Fano resonances or propagating SPP Fano resonances.

3.2.1 LSPP Fano resonance

The near-field distribution of $|E|$, of the Fano resonances at $\lambda_{4y} = 884\text{nm}$ and $\lambda_{5z} = 886\text{ nm}$, shown in Figs. 3 (a4) and 4 (a5), reveals that the corresponding fields are strongly localized to the center of the unit cell, which is a typical feature of a LSPP mode. A dipolar pattern in the HNH structure is seen in the H_x field distribution provided in Figs. 3(d4) and 4(d5). Based on the H_x distribution, this LSPP mode, which is called LSPP₁, arises from anti-bonding hybridization between the central and surrounding ring holes, in which the central hole shows a notable magnetic dipole oscillating out of phase with respect to the dipole of the six surrounding holes, forming an antibonding coupled plasmon mode. A higher order LSPP mode, LSPP₂, which is excited by a z-polarized incident field, and occurring at $\lambda_{3z} = 721\text{ nm}$, shows a strong $|E|$ field localization near to the surrounding holes of the unit cell. Based on the corresponding H_x field distribution shown in Fig. 4(d3), LSPP₂ mode arises from the hybridization between the magnetic multipolar plasmon of the central hole and the magnetic dipolar plasmon of the six surrounding holes.

3.2.2 Propagating SPP Fano resonances

In a thick metal film, two independent single-interface SPP modes can be supported on opposite sides. However in the case of a thin metal film, these two SPP modes are coupled to each other, forming one lower energy symmetric supermode (often termed the sb mode [46] denoted herein as SPP_s) and one higher energy asymmetric supermode (often termed the ab mode, denoted herein as SPP_a). In terms of field distribution, both of them show a maximum $|E|$ at the metal-dielectric interfaces and decay exponentially away. In the case of the symmetric mode, the transverse electric field (E_x here) doesn't go through zero inside the metal film so this field component doesn't change in sign from one interface to the other. Conversely, E_x for the asymmetric mode goes through zero inside the metal film and changes sign from one interface to the other [47].

(i) SPP_a(1,0) and SPP_a(0,1): For the resonances at $\lambda_{3y} = 780\text{ nm}$ and $\lambda_{4z} = 785\text{ nm}$ (Fig. 2), the electric field distributions, plotted in Figs. 3 (a3) and 3(b3), and in Figs. 4(a4) and 4(b4) reveal the characteristics of an asymmetric SPP propagating along the metal film. The corresponding H_z field distribution shown in Fig. 3(e3) and H_y field distributions in Fig. 4 (e4) show the propagation of the SPP_a mode in the y direction for the y polarized incident light, and z direction for the z polarized incident light, respectively. Conclusively, these resonances are termed SPP_a(1,0) and SPP_a(0,1).

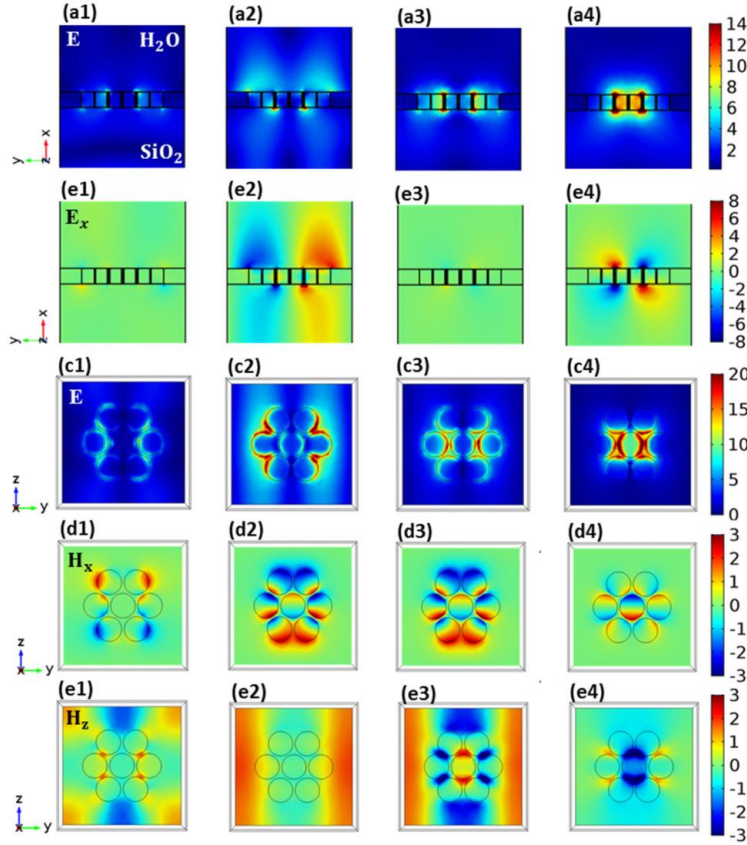


Fig. 3. Near-field distribution of $|E|$ at (a1) λ_{1y} , (a2) λ_{2y} , (a3) λ_{3y} and (a4) λ_{4y} , and near-field distribution of E_x at (b1) λ_{1y} , (b2) λ_{2y} , (b3) λ_{3y} and (b4) λ_{4y} , along the xy plane passing through the center of a unit cell. Near-field distribution of $|E|$ at (c1) λ_{1y} , (c2) λ_{2y} , (c3) λ_{3y} and (c4) λ_{4y} , near-field distribution of H_x at (d1) λ_{1y} , (d2) λ_{2y} , (d3) λ_{3y} and (d4) λ_{4y} , and near-field distribution of H_z at (e1) λ_{1y} , (e2) λ_{2y} , (e3) λ_{3y} and (e4) λ_{4y} , along the yz plane at the Au/cover interface. All fields were computed for y -polarized incident light on resonance where $\lambda_{1y} = 644$ nm, $\lambda_{2y} = 700$ nm, $\lambda_{3y} = 780$ nm, and $\lambda_{4y} = 884$ nm (cf. Figure 2).

(ii) $WA-SPP_s(1,0)$ and $WA-SPP_s(0,1)$: The narrowest resonances occur at $\lambda_{2y} = 700$ nm and $\lambda_{2z} = 699$ nm and are due to the coupling of a WA wave on one side of the metal film with the SPP_s mode [48]. The electric field distributions, plotted in Figs. 3 (b2) and 4(b2), reveal the excitation of the symmetric SPP mode, and also the excitation of WA waves in the SiO_2 as an extended plane wave propagating parallel to the metal film [49]. The corresponding field distributions of H_z , shown in Fig. 3(e2) and H_y shown in Fig. 4(e2), show the propagation of the $WA-SPP_s$ mode in the y direction for the y polarized incident light, and z direction for the z polarized incident light, respectively. Conclusively, these resonances are labelled $WA-SPP_s(1,0)$ and $WA-SPP_s(0,1)$.

(iii) $SPP_a(1,1)$: The shortest wavelength resonances observed, at $\lambda_{1y} = 644$ nm and $\lambda_{2z} = 642$ nm, are due to the excitation of the asymmetric SPP mode along the (1,1) direction. The electric field distributions, plotted in Figs. 3 (a1) and 3(b1), and in Figs. 4(a1) and 4(b1), reveal the excitation of this mode. Furthermore, the corresponding H_z shown in Fig. 3 (e1)

and H_y shown in Fig. 4 (e1) exhibit a diagonal standing wave pattern due to the propagation of the $SPP_{\text{a}}(1,1)$, corresponding to a second order diffraction.

The near-field distribution of $|E|$ on the yz plane at the cover/Au interface is shown in row c of Figs. 3 and 4, showing the electric field enhancement and hot spots that are useful for SERS applications. The highest field enhancement (up to 29) is localized near the central hole of the HNH and observed for the LSPR mode (Figs. 3(c4) and 4(c5)).

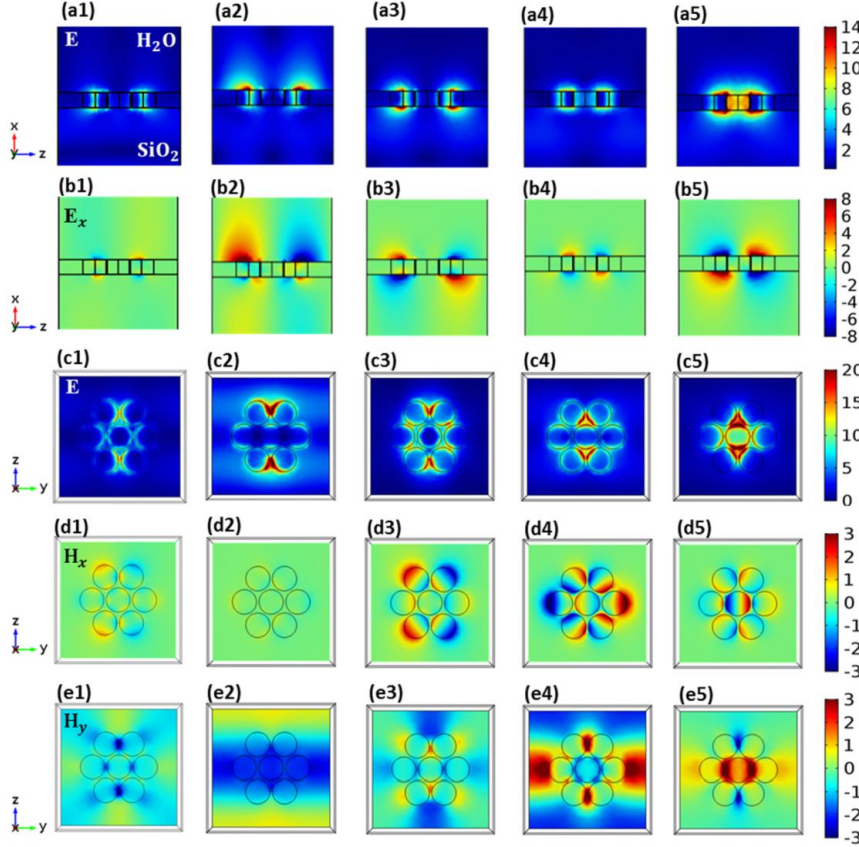


Fig. 4. Near field distribution of $|E|$ at (a1) λ_{12s} (a2) λ_{22s} (a3) λ_{32s} (a4) λ_{4z} and (a5) λ_{52s} and near field distribution of E_x at (b1) λ_{12s} (b2) λ_{22s} (b3) λ_{32s} (b4) λ_{4z} and (b5) λ_{52s} along the xz plane passing through the center of a unit cell. Near-field distribution of $|E|$ at (c1) λ_{12s} (c2) λ_{22s} (c3) λ_{32s} (c4) λ_{4z} and (c5) λ_{52s} , near-field distribution of H_x at (d1) λ_{12s} (d2) λ_{22s} (d3) λ_{32s} (d4) λ_{4z} and (d5) λ_{52s} , and near-field distribution of H_y at (e1) λ_{12s} (e2) λ_{22s} (e3) λ_{32s} (e4) λ_{4z} and (e5) λ_{52s} along the yz plane at the Au/cover interface. All fields were computed for z -polarized incident light on resonance where $\lambda_{1z} = 642$ nm, $\lambda_{2z} = 698$ nm, $\lambda_{3z} = 721$ nm, $\lambda_{4z} = 785$ nm, and $\lambda_{5z} = 886$ nm (cf. Fig. 2).

According to the electric and magnetic near-field distributions in Fig. 3-Fig. 4, the Fano resonances can be categorized as resonances related to the excitation of LSPs - fields are strongly localized about the heptamer, SPPs - fields propagate along the metal-dielectric interfaces (E_x is asymmetric), and WA-SPPs - fields also propagate, revealing the excitation of the SPPs and WA on opposite sides of metal film, along with coupling of these waves (E_x is symmetric).

3.3 Geometrical and dielectric parameters

3.3.1 Geometrical parameters

Changing the geometrical parameters of the system and observing the evolution of the Fano resonances provides further insight into their nature and formation. Here, for simplicity, we consider only the case of y-polarized incident light. The dependences of the spectra on the periodicity ($440 < P < 520$ nm), the central hole's diameter ($40 < D_c < 100$ nm), the inter-hole separation ($10 < G < 30$ nm) and the thickness of the metal film ($30 < t < 60$ nm) are plotted in Figs. 5(a)-5(d), respectively. In Fig. 5, the Fano resonances associated with the LSPP₁, and the propagating SPP_a(1,0) and WA-SPP_s(1,0) modes are indicated by yellow, black and red dashed lines on the absorptance spectra, respectively. The SPP-related Fano resonances are not only sensitive to the array periodicity P , but also to the metal thickness t and the full size of the aperture (which depends on D_c and G in our case) presented by the holes [47,50]. The LSPP_s-Fano resonance depends primarily on the HNH parameters.

(i) SPP_a(1,0): The resonance red-shifts with increasing pitch P , as anticipated by Eq. (3), and observed in Fig. 5(a). Increasing t decreases the effective index (n_{eff}) of the SPP_a mode, which based on Eq. (3) causes the associated Fano resonance to blue-shift, as observed in Fig. 5(d). However, as shown in Fig. 5(b), changing D_c has little effect on the position of this resonance - the blue shift for the specific case of $D_c = 80$ nm is due to the merging and strong coupling with the LSPP₁ Fano resonance, resulting in a repulsive behavior between these two resonances [51,52]. Conversely, increasing G from 10 to 30 nm results in increasing the full size of the aperture from 320 to 360 nm, leading to a blue-shift in the resonance [53,54].

(ii) WA-SPP_s(1,0): This Fano resonance involves the SPP_s coupled to a WA wave. The constituent WA wave is mainly influenced by the periodicity P , following Eq. (4), but the constituent SPP_s mode is influenced by the same factors as the SPP_a mode (the periodicity P following Eq. (3), the film thickness t and the full size of the aperture). The resonance red-shifts with increasing pitch P , as anticipated by Eqs. (3) and (4), as observed in Fig. 5(a). Increasing t from 30 to 60 nm (range of t over which the WA-SPP can exist) [48], increases the effective index (n_{eff}) of the constituent SPP_s mode, which based on Eq. (3), causes the associated Fano resonance to red-shift, as observed in Fig. 5(d) (opposite direction to the SPP_a(1,0) resonance). Changing D_c has little effect on the resonance, as observed in Fig. 5(b), whereas increasing G increases the full size of the aperture, leading to a blue-shift in the resonance as observed in Fig. 5(c). The shift is in the same direction as the SPP_a(1,0) mode but is weaker due to the lower confinement of the SPP_s mode to the metal film.

(iii) LSPP₁: The Fano resonance associated with the LSPP₁ is dependant primarily on the size of the holes D_c and the separation between holes G , but not much on the periodicity P as observed in Fig. 5. Unlike the SPP_a and WA-SPP_s Fano resonances, the LSPP₁ resonance arises from the anti-bonding hybridization between the central and surrounding holes, so it is affected strongly by the geometry of these features but not much by the pitch as observed in Fig. 5(a). This resonance exhibits a significant red shift of ~200 nm by increasing D_c from 40 to 100 nm. Meanwhile, increasing G shifts the resonance towards the blue, as observed in Fig. 5(c). The LSPP₁ is also sensitive to the metal thickness as changing the latter from $t = 30$ to 60 nm causes a blue-shift.

In summary, we observe the evolution of the Fano resonances with changes in the structural parameters of the system in Fig. 5, which helps elucidate their character. As predicted by Eqs. (3) and (4), this figure illustrates that the WA-SPP and SPP-related Fano resonances are sensitive to the array periodicity P , however, the LSPP-related Fano resonances are not. In addition, as expected, the LSPP Fano resonance is affected strongly by the central hole's diameter, whereas changing this parameter doesn't affect the other resonances. As seen in Fig. 5(d), increasing the metal thickness decreases and increases the effective index of the SPP_a and SPP_s mode, respectively, producing a blue-shift in the resonance associated with the former and a red-shift for the latter.

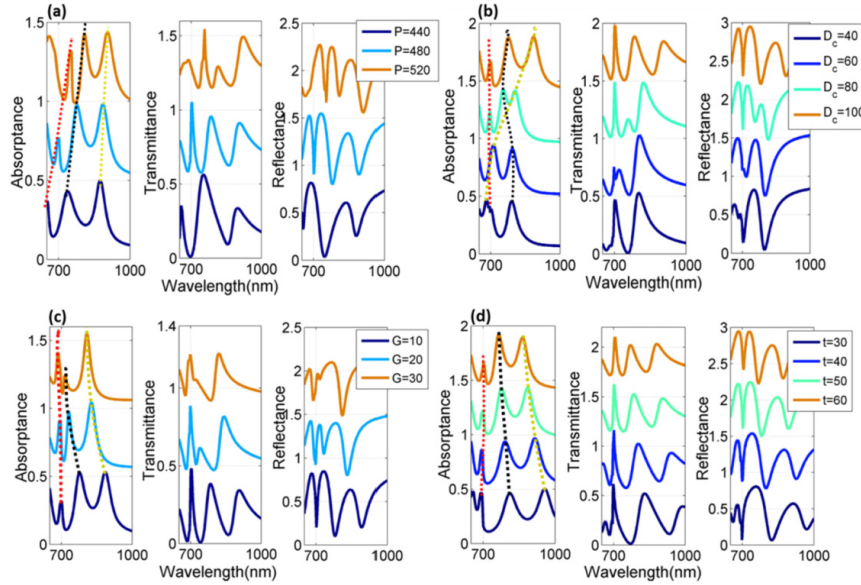


Fig. 5. Optical responses of the HNH arrays for the geometrical parameters of: (a) $D = D_c = 100$ nm, $G = 10$ nm, $t = 60$ nm and various P ; (b) $D = 100$ nm, $G = 10$ nm, $t = 60$ nm, $P = 480$ nm, and various D_c ; (c) $D = D_c = 100$ nm, $t = 60$ nm, $P = 480$ nm, and various G ; (d) $D = D_c = 100$ nm, $G = 10$ nm, $P = 480$ nm, and various t . Spectra in (a)-(d) are offset vertically for clarity. The Fano resonances associated with the LSP_{11} , and the propagating SPP_a and $WA-SPP_s$ modes are indicated by yellow, black and red dashed lines, respectively.

3.3.2 Dielectric parameters

The dependence of the Fano resonances on the refractive index of the cover medium n_s is plotted in Fig. 6 (a). This figure shows the optical responses of an array of HNH with the geometrical parameters $D = D_c = 100$ nm, $G = 10$ nm, $t = 60$ nm, and $P = 480$ nm, sandwiched between SiO_2 as the substrate and a medium of $1.33 < n_s < 1.49$ as the cover. As observed in the transmittance spectra shown in Fig. 6 (b), all resonances are sensitive to n_s and they all shift to longer wavelengths as n_s increases. In this figure, the resonances are identified as $SPP_a(1,1)$, $SPP_s(1,0)$, $WA-SPP_s(1,0)$, $SPP_a(1,0)$ and LSP_{11} . The narrowest resonance, $WA-SPP_s(1,0)$ (tracked by red arrows), experiences a rapid rise and narrowing with decreasing n_s . This rapid change is the direct result of a more effective coupling between the $WA(1,0)$ in SiO_2 and the $SPP_s(1,0)$ localized along the Au/cover interface. According to Eq. (4), the first diffraction order of the WA wave in SiO_2 , $WA(1,0)$, occurs at $\lambda = 697$ nm. By increasing n_s , the spectral position of the $SPP_s(1,0)$ mode moves away from $WA(1,0)$, so the coupling between these two waves decreases, which results in increased damping of this resonance for $n_s > 1.41$. For higher n_s , the coupled $WA-SPP_s(1,0)$ excitation no longer exists, so the $SPP_s(1,0)$ mode becomes independent (tracked by pink arrows).

3.4 Bloch wave model

More insight on the generation of the Fano resonances can be gained by using Eqs. (1)-(4), along with modal results, to anticipate the spectral position of the resonances associated with propagating SPP modes. As mentioned earlier, a thin metal film supports two bound coupled modes termed the symmetric SPP (SPP_s) and asymmetric SPP (SPP_a). In Fig. 7 (a), the effective index of SPP_a (dash-dot lines) and SPP_s (dash lines) modes are plotted as a function of wavelength for a gold film 60 nm thick, while n_s increases from 1.33 to 1.49. Inserting the

calculated effective indices in Eqs. (1) and (3), with $P = 480$ nm, the grating dispersion relation for the SPP_a (dash-dot blue) and SPP_s (dash blue) modes are plotted in Fig. 7(b) for the specific case of $n_s = 1.41$. At normal incidence ($k = 0$), the dispersion curves anticipate the excitation of the SPP_s mode at $\lambda = 698$ nm and of the SPP_a mode at $\lambda = 745$ nm. This is in reasonably good agreement with the results of Fig. 6, where these resonances occur at $\lambda = 725$ nm and $\lambda = 800$ nm, respectively, ~ 25 and ~ 50 nm away from what the dispersion curve anticipates - the origin of the discrepancies is that the HNH array is not a weak perturbation for which Eqs. (1) and (3) hold.

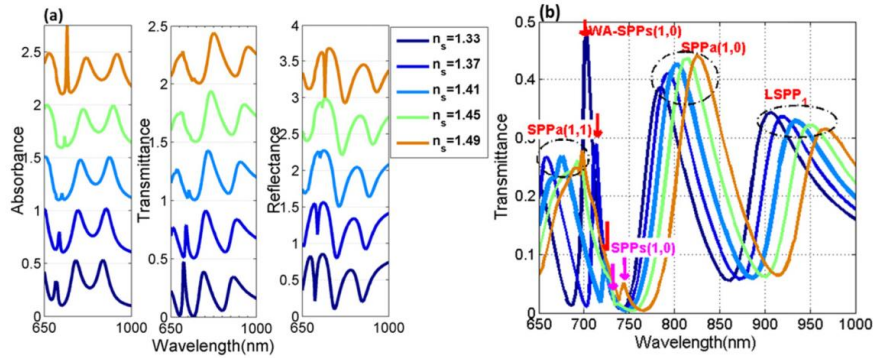


Fig. 6. (a) Optical responses of the HNH array for various cover medium's refractive index. Spectra are offset vertically for clarity. (b) Superimposed transmittance spectra of the array highlighting the shift in the $LSPR_s$, $SPP_s(1,0)$, $SPP_s(1,1)$ Fano resonances and the evolution of the $WA-SPP_s(1,0)$ and $SPP_s(1,0)$ Fano resonances (red and pink arrows, respectively).

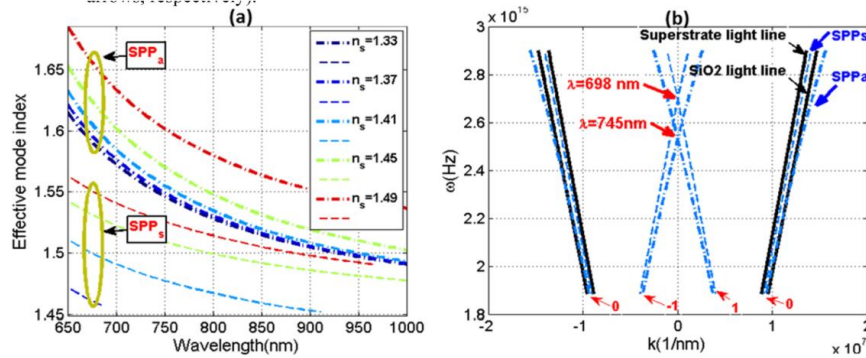


Fig. 7. (a) Effective index vs. wavelength for the SPP_a (dash-dot) and SPP_s (dash) modes on an Au film of $t = 60$ nm with n_s varying from 1.33 to 1.49. (b) Grating dispersion of the SPP_a (blue dash-dot) and SPP_s (blue dash) modes for $n_s = 1.41$ and $P = 480$ nm. The solid black lines are the light lines in SiO_2 and in the cover medium ($n_s = 1.41$). At normal incidence ($k = 0$), the dispersion curves anticipate the excitation of the SPP_s mode at $\lambda = 698$ nm and of the SPP_a mode at $\lambda = 745$ nm. The dispersion curves for the $-1, 0, +1$ diffraction orders are also shown on the figure.

3.5 Sensing performance

As shown in Fig. 6, the Fano resonances of the HNH array are very sensitive to n_s which suggests application of the structure to refractive index sensing, particularly biochemical sensing. To characterize the sensing performance of a structure, the refractive index sensitivity (bulk sensitivity - BS), figure of merit (FoM) and surface sensitivity (SS) were

calculated. The bulk sensitivity is defined as the shift in a resonant wavelength relative to the change in the refractive index of the cover medium and the FoM is defined as the bulk sensitivity divided by the spectral linewidth. Following conventions in previous work [11,16,22,55], the spectral linewidth for an asymmetric resonance like a Fano resonance is taken as the wavelength difference between the Fano dip and the adjacent peak. The surface sensitivity is defined as the shift in λ_{res} relative to the change in the adlayer thickness (a), for an adlayer growing at the Au/cover interface. In the following, these sensitivities were calculated for an HNH array having $D = D_c = 100$ nm, $G = 10$ nm, $t = 60$ nm, $P = 480$ nm, assuming SiO_2 as the substrate and a cover medium of refractive index $n_s = 1.33$ (e.g., H_2O). Results were obtained for both y- and z- polarized incident light.

3.5.1 Bulk sensitivity

Figure 8 (a) shows how the Fano resonances in the transmitted spectrum red-shift with small changes in cover refractive index ($\Delta n_s = 0.01$) for the case of y-polarized incident light. The wavelength shift relative to the nominal resonance wavelength of the modes at $n_s = 1.33$ is plotted vs. the cover refractive index in Fig. 8 (b). As indicated on this figure, the LSPP_1 , $\text{SPP}_s(1,0)$ and $\text{WA-SPP}_s(1,0)$ Fano resonances produce bulk sensitivities of 400, 200 and 250 nm/RIU, respectively, while their FoM values are 4.71, 3.78 and 23.8 RIU^{-1} , respectively. The LSPP_1 Fano resonance produces the largest bulk sensitivity because the electromagnetic field of this mode is highly localized to the holes, where the sensing medium penetrates. In addition, the $\text{WA-SPP}_s(1,0)$ Fano resonance exhibits the highest FoM because it has the sharpest resonance. For z-polarized incident light, the evolution of the Fano resonances is plotted in Figs. 9 (a), and 9 (b) shows the shift in resonance wavelength with respect to their nominal values at $n_s = 1.33$ vs. the cover refractive index. The bulk sensitivity and FoM associated with each Fano resonance is also given.

Compared to studies on arrays of individual nanoholes of similar geometry as our HNH, the HNH array provides improved bulk sensitivity and FoM values [48,56,57], and a higher transmittance ($\sim 50\%$) [40,48,58,59], resulting in higher intensity signals at the detector, improvement of signal to noise ratio, and limit of detection. Complementary structures - arrays of heptamer-arranged nanoparticles (HNP) - can only support LSPP_1 Fano resonances due to the absence of a waveguide and propagating modes, so spectra are not as rich in features. Our arrays of HNH compare well to arrays of HNP of similar dimensions. For instance, arrays of Au heptamer nano-disks with $G = 15$ nm, $D = D_c = 128$ nm and $t = 30$ nm, produce a bulk sensitivity of 428 nm/RIU and FoM of 5.1 RIU^{-1} [12], which corresponds to nearly the same performance as our HNH structures. For arrays of Ag heptamer nano-spheres with $G = 5$ nm and $D = D_c = 100$ nm on SiO_2 , the LSPP_1 Fano resonance produces a bulk sensitivity of 514 nm/RIU and FoM of 10.6 RIU^{-1} [4], which are higher than our values for the HNH structure. The better bulk sensitivity is due to an inter-particle distance that is smaller than in our HNH and to the sensing medium being air rather than water. Also their spheres are made of Ag which has better optical parameters than Au (the former is reactive).

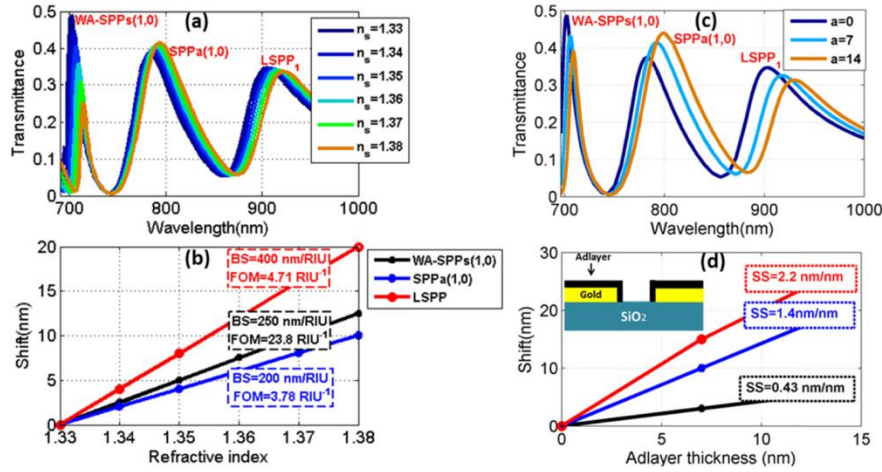


Fig. 8. Transmittance spectra of the HNH array illuminated with a y-polarized incident light, (a) while n_s changing. (b) Shift in the resonance wavelengths with respect to their nominal values at $n_s = 1.33$ vs. the superstrate refractive index. The bulk sensitivity (BS) and FoM for each Fano resonance has been provided on the figure. (c) Transmittance spectra of the same HNH array as the thickness of an adlayer grows from zero to 14 nm. (d) Shift in the resonance wavelengths with respect to their nominal values for the case of no adlayer vs. the adlayer thickness. The surface sensitivity (SS) for each resonance has been provided on the figure. The inset to part (d) shows a sketch of the adlayer (black) assumed to form on the structure.

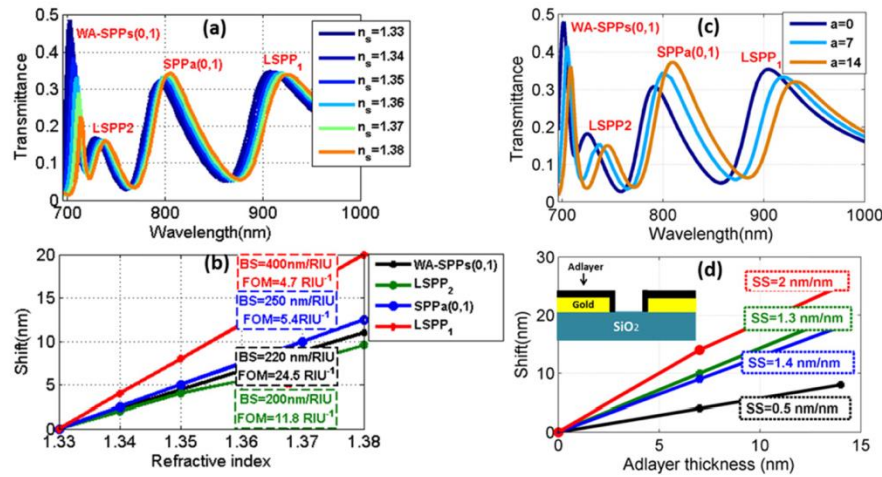


Fig. 9. Transmittance spectra of the HNH array illuminated with a z-polarized incident light, (a) while n_s changing. (b) Shift in the resonance wavelengths with respect to their nominal values at $n_s = 1.33$ vs. the superstrate refractive index. The bulk sensitivity (BS) and FoM for each resonance has been provided on the figure. (c) Transmittance spectra of the same HNH array as the thickness of an adlayer grows from zero to 14 nm. (d) Shift in the resonance wavelengths with respect to their nominal values for the case of no adlayer vs. the adlayer thickness. The surface sensitivity (SS) for each resonance has been provided on the figure. The inset to part (d) shows a sketch of the adlayer (black) assumed to form on the structure.

3.5.2 Surface sensitivity

Figure 8 (c) reveals how the Fano resonances red-shift with small changes in the adlayer thickness a ($\Delta a = 7\text{ nm}$) for the case of y-polarized incident light. In a biosensing experiment the metal surface in contact with an aqueous sensing solution (cover) would be functionalized chemically to react selectively with a target analyte. As analyte binds, an adlayer of refractive index greater than the sensing solution forms, which shifts the resonance wavelengths. Here, the adlayer formation is modeled as a uniform dielectric layer of refractive index $n_{\text{ad}} = 1.5$ (which is typical of biochemical matter), growing from a thickness of $a = 0$ to 14 nm (in steps of 7 nm , due to discretization constraints), representing the accumulation of biomaterial on the gold surface, as sketched in the inset of Fig. 8 (d). As illustrated in Figs. 8 (c) and 8(d), increasing the adlayer thickness causes the resonances to red-shift, which results in surface sensitivities of 0.43 , 1.43 and 2 nm/nm for the $\text{WA-SPP}_s(1,0)$, $\text{SPP}_a(1,0)$ and LSPP_1 Fano resonances, respectively. The highest surface sensitivity is produced by the LSPP_1 Fano resonance, because it has the highest field enhancement and confinement near the adlayer, compared to the other resonances. The $\text{WA-SPP}_s(1,0)$ produces the lowest sensitivity because SPP_s modes (excited at Au/cover medium interface) exhibit the lowest field confinement to the interface, so less overlap with the adlayer. For z-polarized incident light, the evolution of the Fano resonances with small changes in the adlayer thickness is given in Figs. 9 (c), and 9 (d) shows the shift in the resonance wavelength with respect to their nominal values at $a = 0$ vs. the adlayer thickness. The surface sensitivity of each Fano resonance is also given.

4. Conclusions

In conclusion, we have studied theoretically and numerically the optical properties of arrays of heptamer arranged nanoholes in detail. The optical responses are influenced by various phenomena, such as LSPP excitations, diffractive effects, the excitation of propagating SPP modes on the metal film and of WA waves in either media, resulting in the formation of several pronounced Fano resonances, producing high transmittance ($\sim 50\%$) over the wavelength range investigated (630 to 1000 nm). To understand the physical mechanism behind the generation of each Fano resonance, electromagnetic near-field distributions were computed and presented, along with the effects of varying the geometrical parameters, such as the periodicity, metal thickness, inter-hole distance and diameter of the central hole. In addition, the grating dispersion equation was combined with modal computations of the symmetric and asymmetric SPP modes supported by the metal film (SPP_s , SPP_a) to further elucidate the origin of the resonances. We examined the structure for use as a biosensor by calculating the bulk and surfaces sensitivities, and FoM. The highest bulk (400 nm/RIU) and surface (2 nm/nm) sensitivities are produced by LSPP Fano resonances, whereas the highest FoM (24.5 RIU^{-1}) is obtained for the WA-SPP_s Fano resonance. Compared to the single nanohole arrays, this structure provides us with an improved bulk sensitivity, FoM values [$48, 56, 57$], and a higher transmittance ($\sim 50\%$) [$40, 48, 58, 59$], while compared to its complementary structure, it shows a comparable sensitivity and FoM values [4]. However the spectrum of the HNH array is rich in features, which allows for a broadband interrogation and then improvement of the detection limit and measurement accuracy.

Funding

Natural Sciences and Engineering Research Council of Canada (NSERC) RGPIN-2016-04197; University of Ottawa Stephen Odoyok Memorial Scholarship (01476).

Acknowledgements

We would like to acknowledge the Centre for Advanced Computing (CAC), Queen's University, for the computational support, and also CMC Microsystems for the provision of COMSOL software that facilitated this research.

5. Helium focused ion beam direct milling of plasmonic heptamer-arranged nanohole (HNH) arrays

A. Summary

The fabrication of plasmonic HNH arrays using a HeFIB direct milling process is described in detail. HeFIB milling was used to directly mill arrays of 20×20 HNHs in a 55-nm-thick Au film, on a SiO₂ substrate. Each HNH consisted of a central hole surrounded by six holes, each 100 nm in diameter and separated by 15 nm edge-to-edge. The periodicity of the array was set to be 480 nm. HeFIB direct milling created high-quality HNHs with sharp edges, while there was minimal milled material redistribution. Due to the low milling rates, a drift correction scheme was necessary to counter instrument drift for writing large areas (arrays of 20×20 HNHs). The optical transmittance response of fabricated HNH arrays was measured confirming the existence of LSPP resonances on the HNHs.

B. Contribution

The results provided in this chapter were published as an article in the journal *Nanophotonics*. I designed and built the experimental setup; I generated the numerical results and performed the experimental measurements. I contributed to writing the manuscript and the interpretation of the results. Dr. Choloong Hahn (a post-doctoral fellow in Prof. Berini's group) performed the fabrication and co-wrote the manuscript. He also assisted in the design and construction of the experimental setup and contributed to interpretation of the results. Dr. Berini contributed to interpretation of the results, and revised the manuscript.

C. Article

The published article follows verbatim.

Research article

Choloong Hahn, Akram Hajebifard and Pierre Berini*

Helium focused ion beam direct milling of plasmonic heptamer-arranged nanohole arrays

<https://doi.org/10.1515/nanoph-2019-0385>

Received September 24, 2019; revised November 5, 2019; accepted November 9, 2019

Abstract: We fabricate plasmonic heptamer-arranged nanohole (HNH) arrays by helium (He) focused ion beam (HeFIB) milling, which is a resist-free, maskless, direct-write method. The small He⁺ beam spot size and high milling resolution achieved by the gas field-ionization source used in our HeFIB allows the milling of high aspect ratio (4:1) nanoscale features in metal, such as HNHs incorporating 15 nm walls of high verticality between holes in a 55-nm-thick gold film. Drifts encountered during the HeFIB milling of large arrays, due to sample stage vibrations or He beam instability, were compensated by a drift correction technique based on *in situ* He ion imaging of alignment features. Our drift correction technique yielded 20 nm maximum dislocation of HNHs, with 6.9 and 4.6 nm average dislocations along the horizontal and vertical directions, respectively. The measured optical resonance spectra of the fabricated plasmonic HNH arrays are presented to support the fabrication technique. Defects associated with HeFIB milling are also discussed.

Keywords: focused ion beam; helium ion microscopy; nanofabrication; plasmonics.

1 Introduction

Nanofabrication technologies have attracted great interest due to the possibilities of opening new functionalities by structuring materials at the nanoscale or creating devices of extremely small size. One of the most common and popular approaches to nanofabrication consists of using electron beam lithography (EBL), which can cover feature sizes from the microscales to the nanoscales by overlay or using complementary beam parameters [1]. Various photonic devices have been successfully realized with EBL, including plasmonic distributed feedback lasers [2], non-Hermitian photonic devices [3], and plasmonic nanoantennas to enhance high harmonic generation [4]. FIB milling using gallium (Ga) ions is also a very common approach to nanofabrication [5–7]. However, it is limited in resolution and may produce significant material redeposition and undesired implantation of ions into the substrate [8].

The development of gas field-ionization source technology allows helium (He) to be used as the ion beam. An HeFIB can have a beam spot size of less than 0.5 nm [9] and a direct milling resolution of 3.5 nm [10] due to the atomically defined metal tip used to form the He beam and the small de Broglie wavelength of He ions. Unlike liquid metal ion sources, such as Ga, He ions are pulled by high extraction voltages from a sharp, atomically defined metal tip, so they have a higher axial directionality, enabling high aspect ratio features to be defined by HeFIB direct milling [11, 12]. In addition, He ions produce less contamination by unintentional implantation, as He is a noble gas, and it has a high propensity to diffuse out of materials [13]. HeFIB milling is also more controllable due to the slow milling rate caused in part by the low atomic weight of He, making HeFIB milling more suitable for the controlled milling of sub-20 nm features [14]. Although a novel technique, HeFIB milling has already been applied to nanofabrication in several materials, such as graphene [15, 16], silicon nitride [17], and Au [18], including the fabrication of plasmonic antennas with partially loaded nanogaps [19].

Arrays of nanoholes in a metal film produce field enhancement and resonances that can be tuned over

*Corresponding author: Pierre Berini, School of Electrical Engineering and Computer Science, University of Ottawa, Ottawa K1N6N5, Canada; Center for Research in Photonics, University of Ottawa, Ottawa K1N6N5, Canada; and Department of Physics, University of Ottawa, Ottawa, Ottawa K1N6N5, Canada, e-mail: pberini@uottawa.ca

Choloong Hahn: School of Electrical Engineering and Computer Science, University of Ottawa, Ottawa K1N6N5, Canada; and Center for Research in Photonics, University of Ottawa, Ottawa K1N6N5, Canada. <https://orcid.org/0000-0003-3213-345X>

Akram Hajebifard: Center for Research in Photonics, University of Ottawa, Ottawa K1N6N5, Canada; and Department of Physics, University of Ottawa, Ottawa, Ottawa K1N6N5, Canada

a wide spectral range, motivating applications in, for example, surface-enhanced Raman scattering [20] and optical biosensors [21, 22]. Heptamer-arranged nanoholes (HNHs) are hexagonal close-packed arrangements of seven nanoholes in a metal film, inspired by complementary arrangements of metal nanoparticles [23]. Arrays of HNHs in a metal film are very interesting for their highly complex, rich spectral responses and pronounced Fano resonances involving propagating surface plasmon polaritons (SPPs), localized SPPs (LSPPs), and Wood's anomaly (WA) waves [24]. However, the fabrication of HNH arrays in a metal film is very challenging due to the small distance between the holes required for close-packing (10–15 nm) and the commensurate need for high verticality sidewalls in a 30- to 60-nm-thick metal film [24]; that is, nanoscale features with a 4:1 aspect ratio are required. Here, we report novel techniques developed using HeFIB milling of an Au film to form high-quality arrays of HNHs and demonstrate the operation of the arrays via optical measurements.

2 Fabrication

A unit cell of the HNH array of interest in this paper is illustrated in Figure 1A. An HNH arrangement consists of seven close-packed nanoholes in an Au film on an SiO_2 substrate. The geometrical parameters, including the diameter of each nanohole (D), the interhole separation (G), the periodicity of the array (P), and the thickness of the Au film (T), are chosen according to the desired spectral range of the resonances. Here, we chose $D=100$ nm, $G=15$ nm, $P=480$ nm, and $T=55$ nm for application in the

near-infrared spectral region [24]. Figure 1B shows the He ion microscope (HIM) images in tilted (54°) and top views of HNHs in a 55-nm-thick Au film taken after direct milling via HeFIB. The quality of the structures is evidently high: sharp edges are observed, the sidewalls are rather vertical, no milled material seems to be redeposited, and the dimensions achieved are accurate. A benefit of the HeFIB is that the same He ion source can be used for *in situ* microscopy and imaging via the detection of secondary electrons by simply adjusting the dose delivered to the sample. However, He microscopy is a destructive imaging method even at low He doses, so exposure to the He beam should be minimized to protect the sample surface from undesired damage.

For direct HeFIB milling, an SiO_2 substrate (fused silica) was coated by a 0.3-nm-thick layer of Cr as an adhesion layer followed by a 55-nm-thick Au layer. The Au layer was deposited by thermal evaporation at a rate of $0.5 \text{ \AA s}^{-1}$, whereas the Cr layer was deposited by electron beam evaporation at a rate of $0.1 \text{ \AA s}^{-1}$. All layers were deposited sequentially without breaking vacuum using an Angstrom NEXDEP evaporator. No protective layer on the Au surface was used in this process. Our Au deposition process targeted 60 nm in thickness, but we achieved 55 nm as measured by atomic force microscopy on a witness sample.

The prepared layered stacks were milled to create 20×20 arrays of HNHs using an HeFIB system (Zeiss Orion NanoFab) controlled using the nanopatterning and visualization engine (NPVE). In direct milling, the final structure is ready for use immediately after milling without any subsequent wet processes. An HIM image of an Au HNH array fabricated by direct HeFIB milling is shown in Figure 2A.

The He ion beam was prepared in an He gas pressure of 5×10^{-6} Torr using a $10 \text{ }\mu\text{m}$ aperture diameter and a spot

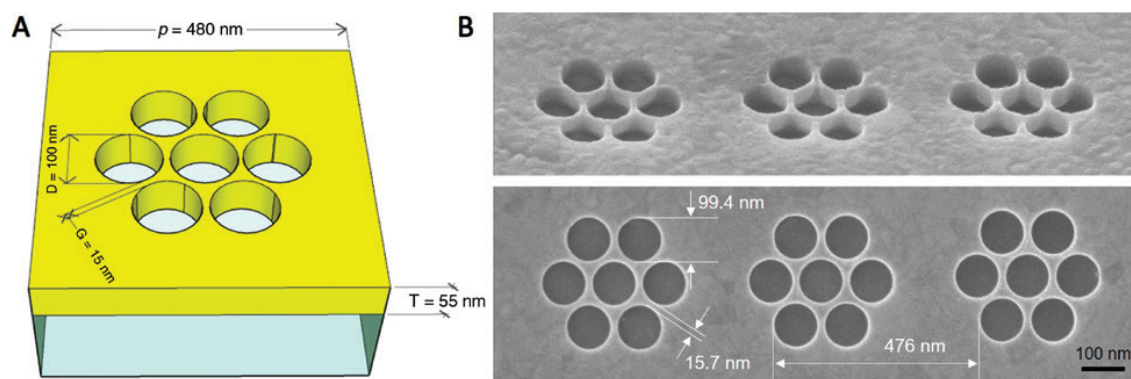


Figure 1: HNH array in an Au film.

(A) Schematic of the HNH design with the target dimensions. The Au film (yellow) is 55 nm thick and is supported by an SiO_2 (fused silica) substrate (light blue). (B) HIM images of HNHs fabricated via direct HeFIB milling. Top, 54° tilted view; bottom, top view.

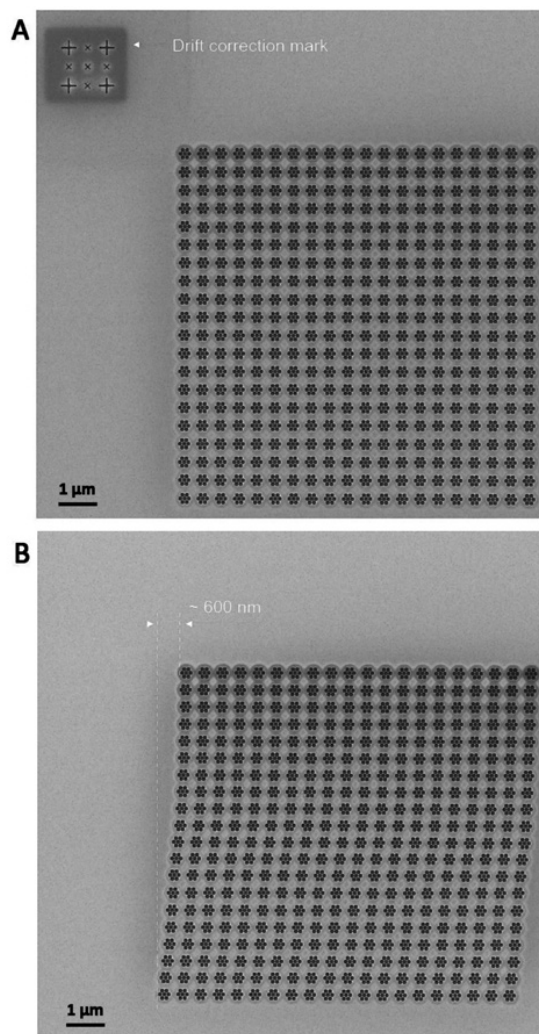


Figure 2: HIM images of 20×20 arrays of Au HNHs. (A) Array fabricated with drift correction. (B) Array fabricated without drift correction.

control parameter of 3.5, which resulted in a 10 pA He ion beam current using a 25 keV acceleration voltage. Here, the spot control parameter refers to the setting on the condenser lens, which focuses the beam through the aperture and affects the directionality of the beam. A single HNH was milled via a double-serpentine exposure method with 1 μ s dwell time, 0.25 nm pixel spacing, and several repeats to achieve the target dose. Double-serpentine exposure is applied as in a serpentine scan; however, instead of going back to the first dwell point once the first frame is completed, the same pattern is scanned but in the reverse direction. In this manner, the horizontal and vertical refresh times are ignored, yielding efficient patterning in time. The layout for

a single HNH was prepared as a single shape by the union of seven circles to ensure that all holes would be exposed within one iteration. Clearing doses to the substrate were initially estimated by *in situ* endpoint detection and subsequently confirmed by measured optical responses (discussed below). The clearing doses were found to be 10 nC μ m⁻² for the 55-nm-thick Au layer in the direct HeFIB milling process. Endpoint detection is a built-in function of NPVE, which captures live intensity images via secondary electron emission during milling. This is useful for the initial estimation of the clearing dose of each layer and is rather accurate especially when the milled material changes from conductive to insulating or vice versa.

He ions have low atomic weight, which leads to advantages in HeFIB milling such as the ability to define very fine features with a high degree of control over the milling process. However, a drawback is that the sputtering yield of an HeFIB process can be very low, leading to long milling times. For instance, the fabrication of a 20×20 array of HNHs requires a writing time of about 3 h. Our HeFIB system drifts over such a period of time, due to either stage drift or beam instability, resulting in skewed arrays. For this reason, drift correction was applied after the completion of every five HNH structures by imaging predefined features, calculating the drift from the image, and compensating in subsequent millings. The drift correction mechanism is a built-in function of the NPVE software used for HeFIB patterning. Here, we used several premilled crosses as shown in Figure 2A (top left) for drift correction. Figure 2B shows an HIM image of a 20×20 HNH array milled without drift correction, revealing that about 600 nm of lateral drift occurred during milling of the array. Figure 2A shows an image of an array written with drift correction, which effectively compensated for instrument drift.

We used a combination of several crosses of different sizes and shapes as the drift correction marks for better recognition and placed them $\sim 3 \mu$ m away from the top left corner of the HNH array. This location was chosen far enough to avoid any damage to the array while exposing the drift correction marks to He ions during imaging yet close enough to avoid any mechanical stage movement by keeping the marks within the small field of view required to ensure high-resolution milling. As the drift correction is based on a destructive imaging method (He ion irradiation), the number of corrections allowed while milling one array is limited and dependent on the imaging parameters used. Also, there is a trade-off between the frequency and the accuracy of drift correction because high-resolution imaging is more destructive. Here, we achieved a maximum dislocation of HNHs of less than 20 nm for

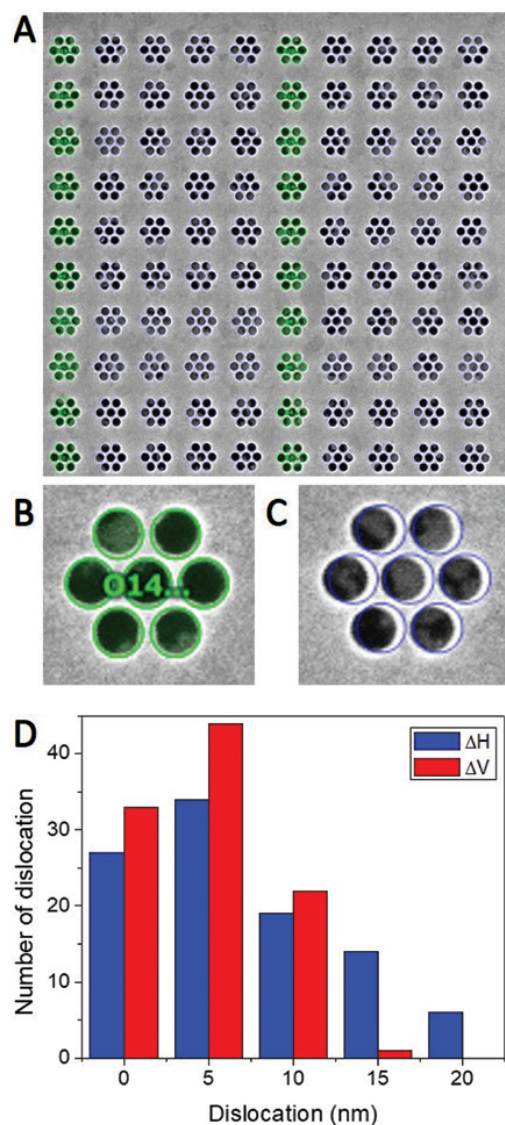


Figure 3: Dislocation of HNHs with drift correction. (A) HIM image of fabricated HNH array overlapped with the patterning layout. Digital zoomed-in image of a single HNH for (B) $\Delta H = \Delta V = 0$ and (C) $\Delta H = 20$ nm and $\Delta V = 5$ nm. (D) Distribution of dislocations in the horizontal (ΔH) and vertical (ΔV) directions for each HNH in an array.

most of the fabricated arrays using a 6.3 nm pixel spacing and 1 μ s dwell time while imaging for drift correction. We avoided the destruction of the predefined correction marks, although Figure 2A reveals a shallow milled-out area around the marks due to repeated imaging.

The dislocations of each HNH fabricated with drift correction was measured from an HIM image of the fabricated HNHs overlapped with the layout pattern, as shown

in Figure 3A. The blue and green colored circles are the layout pattern, and the green circles with an object label indicate the location in the array where the drift correction was applied. To collect enough HNHs for statistical analysis, we used an image of a 10×10 array at 1024×1024 pixel resolution, which results in a 5 nm pixel spacing. Figure 3B and C shows the digital zoomed-in images of Figure 3A as examples of a single HNH without dislocation and of one with horizontal dislocation ($\Delta H = 20$ nm) and vertical dislocation ($\Delta V = 5$ nm), respectively. The dislocations measured in Figure 3A are plotted in Figure 3D as the number of dislocations. The average dislocations in both directions are obtained as $\Delta H_{AVE} = 6.9$ nm and $\Delta V_{AVE} = 4.6$ nm with 20 and 15 nm maximum horizontal and vertical dislocations, respectively.

3 Discussion

The optical transmittance response was measured for several fabricated plasmonic HNH arrays. A tunable Ti:sapphire laser (SpectraPhysics) was used as the light source that delivers a highly coherent continuous-wave (CW) output ranging from 700 to 980 nm. With the assistance of a custom microscope operating in the visible range and integrated into the optical path, a vertically polarized light beam was focused onto the sample surface to a 10 μ m spot size and positioned at the center of an HNH array. The power spectral response of the sample was measured in transmission relative to a reference power (for noise suppression) followed by the response of the set-up without the sample also relative to a reference power, and the transmittance of the sample was taken as the ratio of these power spectral responses.

The measured optical transmittance spectra of HNH arrays fabricated with doses of 8, 10, and 12 nC μ m⁻² are given in Figure 4A–C, respectively. The corresponding scanning electron microscopy (SEM) image of the array associated with the black response in each plot is also given. The array fabricated with a dose of 10 nC μ m⁻², which is the clearing dose estimated by endpoint detection, produces a clear resonance spectrum as shown in Figure 4B (black solid curve). The optical transmittance of an HNH array with the same structural parameters as the fabricated one was calculated for vertical linearly polarized incident light, as shown in Figure 5A. As discussed in our previous work [24], an HNH array can support several excitations, including propagating SPPs due to the periodicity of the array, LSPs resonating on HNHs, and WA waves. Unlike our previous work [24], where the HNH array had $G = 10$ nm and was covered by a dielectric material of refractive index $n_s = 1.33$, here we have

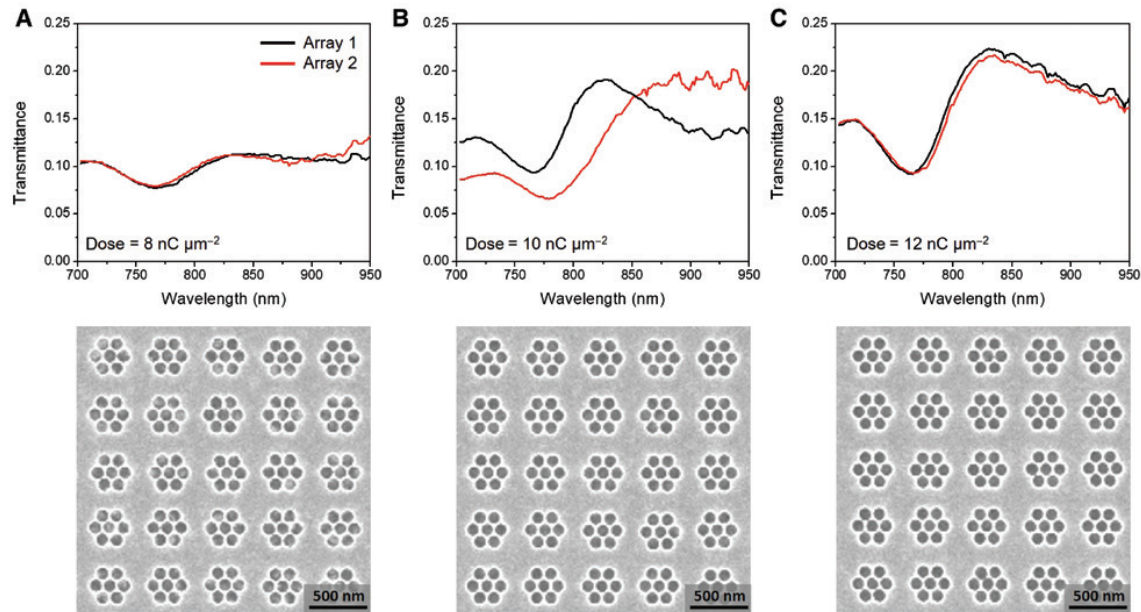


Figure 4: Optical transmittance responses (top) and SEM images (bottom) of HNH arrays fabricated by direct HeFIB milling at the milling dose of (A) $8 \text{ nC } \mu\text{m}^{-2}$, (B) $10 \text{ nC } \mu\text{m}^{-2}$, and (C) $12 \text{ nC } \mu\text{m}^{-2}$. The black and red curves are measurements for repeated fabrication iterations.

$G=15 \text{ nm}$ and $n_s=1$. Increasing G and decreasing the superstrate refractive index n_s result in a blue shift of the resonant wavelengths. Here, the LSPP and SPP peaks in the transmittance spectrum occur at 810 and 710 nm, respectively, which are blue shifted from 905 and 782 nm (respectively) in comparison to our previous work. The WA-SPP resonance no longer exists in the present system because the condition to support this resonance is no longer satisfied when the array is covered by air. As observed in Figure 4A, the second resonance peak, corresponding to LSPPs ($\sim 810 \text{ nm}$), disappears at the lower dose because the nanoholes are not milled out completely through the Au layer, so they cannot support strong LSPP resonances. This is also observed in the SEM image of Figure 4A (bottom), which shows the residual material at the bottom of the nanoholes. Increasing the milling dose from $8 \text{ nC } \mu\text{m}^{-2}$ (Figure 4A) to $10 \text{ nC } \mu\text{m}^{-2}$ (Figure 4B), results in an array of nanoholes, which does not have any Au residue in the holes and thus produces a profound LSPP resonance in its optical transmittance response ($\sim 810 \text{ nm}$). By increasing the dose to $12 \text{ nC } \mu\text{m}^{-2}$ (Figure 4C), the broadening of the LSPP resonance is observed, which implies breaking or degradation in the metal walls between nanoholes, although this is not clearly recognizable in the SEM image.

The black and red curves in Figure 4 correspond to the optical transmittance responses of two different arrays fabricated with identical parameters. The overlap

in their optical responses is indicative of the repeatability of the HeFIB direct milling process. Good repeatability is observed in the case of the arrays of Figure 4A and C. However, the red and black curves in Figure 4B do not coincide well. For the array corresponding to the red curve in Figure 4B, our drift correction scheme failed as can be appreciated from the He microscope image of this array taken immediately after milling, as shown in Figure 5B. In Figure 5B, we overlap the layout in blue on the image to show the mismatch between the layout and the fabricated array (the poor quality of this image is intended to protect the fabricated array from damage caused by He ion beam imaging). Our drift correction scheme can occasionally fail if low-quality imaging is carried out during drift correction, which rarely happened over many milling trials. As mentioned earlier, there is a trade-off between imaging quality for drift correction and the number of allowed drift correction steps. Due to this limitation, we achieved about 80% production yield of HNH arrays.

An alternative approach to FIB milling is metal-assisted FIB (MA-FIB) milling, which uses a metallic protective layer on top of the target layer [25]. The main purpose of using a protective layer in MA-FIB milling is to prevent blunt edges and protect the device surface against redeposition of milled material onto the surface. It is shown in the images in Figure 1B that direct HeFIB milling of an Au film produces nanoholes with sharp edges and

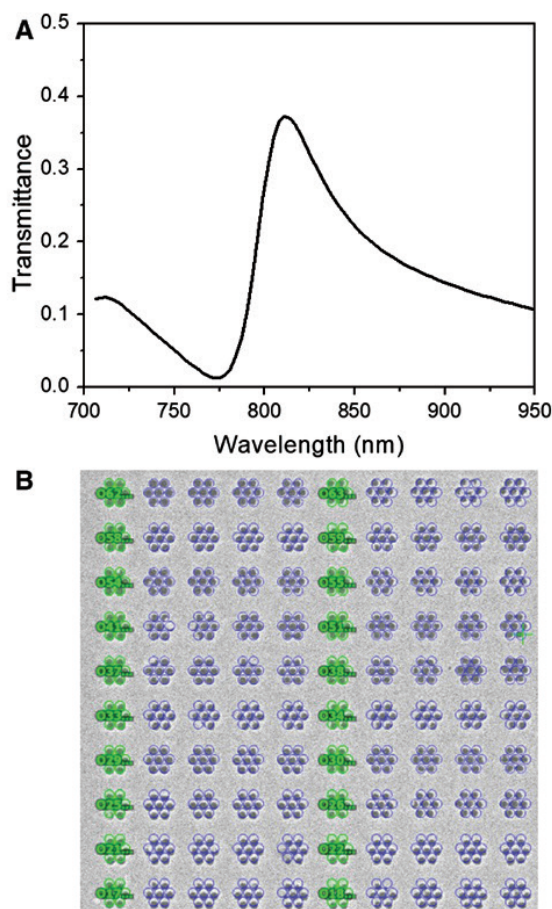


Figure 5: Theoretical calculation and drift correction failure. (A) Theoretical optical transmittance response of an HNH array. (B) HIM image overlapped with layout pattern, indicating drift correction failure.

dimensions that are very close to target. This is due to the high directionality of the He ion beam used for machining. Also, no major redeposition of milled material can be observed in these images likely due to the low sputtering yield of light He ions. Therefore, although useful in milling with heavier ions (e.g. Ga), a protective layer seems unnecessary for HeFIB milling, especially under the conditions explored herein.

4 Conclusions

In summary, we presented the fabrication of plasmonic HNH arrays using an HeFIB direct milling process. A drift correction scheme based on periodic He imaging of alignment

marks was also devised and demonstrated to be very effective in countering instrument drift. Arrays of 20×20 HNHs were successfully fabricated via direct milling HeFIB, in a 55-nm-thick Au layer, on an SiO_2 substrate, where each HNH consisted of seven close-packed holes, each 100 nm in diameter and separated by 15 nm edge-to-edge; high aspect ratio nanoscale features (4:1) were therefore achieved. Direct milling HeFIB produces high-quality HNHs with sharp edges and no milled material redeposition due to the high directionality and light atomic mass of He ions. The use of a protective layer was therefore deemed unnecessary under the milling conditions applied. The optical transmittance response of fabricated HNH arrays confirmed the proper operation of the structures in the near-infrared, with SPP resonances localized to HNHs being evident. Direct HeFIB milling yields high-quality nanostructures with minimal milled material redeposition, but the milling rates are low, so a drift correction scheme is necessary to counter instrument drift if large milled areas are required. The technique also involves minimal solvent and material contact and has the potential to be applied broadly to the investigation of plasmonic nanohole and nanoparticle arrays of different shapes and arrangements.

References

- [1] Fong NR, Berini P, Tait N. Fabrication of long-range surface plasmon hydrogen sensors on Cytop membranes integrating grating couplers. *J Vac Sci Technol B* 2015;33:021201.
- [2] Karami Keshmarzi E, Tait RN, Berini P. Single-mode surface plasmon distributed feedback lasers. *Nanoscale* 2018;10:5914–22.
- [3] Yoon JW, Choi Y, Hahn C, et al. Time-asymmetric loop around an exceptional point over the full optical communications band. *Nature* 2018;562:86–90.
- [4] Vampa G, Ghamsari BG, Siadat Mousavi S, et al. Plasmon-enhanced high-harmonic generation from silicon. *Nat Phys* 2017;13:659–62.
- [5] Tseng AA. Recent developments in nanofabrication using focused ion beams. *Small* 2005;1:924–39.
- [6] Vesseur EJR, De Abajo FJG, Polman A. Modal decomposition of surface plasmon whispering gallery resonators. *Nano Lett* 2009;9:3147–50.
- [7] Lanyon YH, De Marzi G, Watson YE, et al. Fabrication of nanopore array electrodes by focused ion beam milling. *Anal Chem* 2007;79:3048–55.
- [8] Ocelic N, Hillenbrand R. Subwavelength-scale tailoring of surface phonon polaritons by focused ion-beam implantation. *Nat Mater* 2004;3:606–9.
- [9] Marshall MM, Yang J, Hall AR. Direct and transmission milling of suspended silicon nitride membranes with a focused helium ion beam. *Scanning* 2012;34:101–6.
- [10] Scholder O, Jefimovs K, Shorubalko I, Hafner C, Senhauser U, Bona G-L. Helium focused ion beam fabricated

- plasmonic antennas with sub-5 nm gaps. *Nanotechnology* 2013;24:395301.
- [11] Seniutinas G, Gervinskas G, Anguita J, Hakobyan D, Brasselet E, Juodkazis S. Nano-proximity direct ion beam writing. *Nano-fabrication* 2015;2:54–62.
- [12] Scipioni L, Ferranti DC, Smentkowski VS, Potyrailo RA. Fabrication and initial characterization of ultrahigh aspect ratio vias in gold using the helium ion microscope. *J Vac Sci Technol B* 2010;28:C6P18–23.
- [13] Kollmann H, Piao X, Esmann M, et al. Toward plasmonics with nanometer precision: Nonlinear optics of helium-ion milled gold nanoantennas. *Nano Lett* 2014;14:4778–84.
- [14] Wang Y, Boden SA, Bagnall DM, Rutt HN, De Groot CH. Helium ion beam milling to create a nano-structured domain wall magnetoresistance spin valve. *Nanotechnology* 2012;23:395302.
- [15] Lemme MC, Bell DC, Williams JR, et al. Etching of graphene devices with a helium ion beam. *ACS Nano* 2009;3:2674–6.
- [16] Kalhor N, Boden SA, Mizuta H. Sub-10 nm patterning by focused He-ion beam milling for fabrication of downscaled graphene nano devices. *Microelectron Eng* 2014;114:70–7.
- [17] Emmrich D, Beyer A, Nadzeyka A, et al. Nanopore fabrication and characterization by helium ion microscopy. *Appl Phys Lett* 2016;108:163103.
- [18] Melli M, Polyakov A, Gargas D, et al. Reaching the theoretical resonance quality factor limit in coaxial plasmonic nanoresonators fabricated by helium ion lithography. *Nano Lett* 2013;13:2687–91.
- [19] Wang Y, Abb M, Boden SA, et al. Ultrafast nonlinear control of progressively loaded, single plasmonic nanoantennas fabricated using helium ion milling. *Nano Lett* 2013;13:5647–53.
- [20] Liu Z, Ye J. Highly controllable double Fano resonances in plasmonic metasurfaces. *Nanoscale* 2016;8:17665–74.
- [21] Brolo AG, Gordon R, Leathem B, Kavanagh KL. Surface plasmon sensor based on the enhanced light transmission through arrays of nanoholes in gold films. *Langmuir* 2004;20:4813–5.
- [22] Lesuffleur A, Im H, Lindquist NC, Lim KS, Oh SH. Laser-illuminated nanohole arrays for multiplex plasmonic microarray sensing. *Opt Express* 2008;16:219–24.
- [23] Ye J, Wen F, Sobhani H, et al. Plasmonic nanoclusters: near field properties of the Fano resonance interrogated with SERS. *Nano Lett* 2012;12:1660–7.
- [24] Hajebifard A, Berini P. Fano resonances in plasmonic heptamer nano-hole arrays. *Opt Express* 2017;25:18566–80.
- [25] Kannegulla A, Cheng L. Metal assisted focused-ion beam nanopatterning. *Nanotechnology* 2016;27:36LT01.

6. Optical response and Fano resonances in arrays of plasmonic heptamer-arranged nanoholes

A. Summary

We investigated, theoretically and experimentally, the optical properties of plasmonic heptamer nanohole (HNHs) arrays. He FIB milling was used to write arrays of HNHs by milling directly through a 55 nm thick Au film on a SiO₂ substrate. We demonstrated that the fabricated arrays support various excitations including LSPPs and propagating SPPs and Wood's anomaly waves, which are seen as resonances in transmittance spectra over the wavelength range of interest (600 to 1100 nm). The structure was examined for use in sensing applications by measuring and computing the bulk sensitivity of the resonant modes with respect to changes in the refractive index of the cover medium. The modes were all found to red-shift with increasing index. Due to providing the highest near-field enhancement, the resonance associated with the LSPP₁ mode exhibits the largest sensitivity, as expected based on numerical results. The computations of bulk sensitivity are in excellent agreement with experiment. The transmittance spectra of arrays of 20×20 HNH, fabricated with different He ion doses, have also been measured. The resonances start to appear for a He dose of 5 nCμm⁻² and they become increasingly stronger with increasing dose. A dose of 10 nCμm⁻² was found as clearing dose, which fully clears the holes in our 55 nm thick Au film.

B. Contribution

I modelled and designed the structures; I performed theoretical and numerical studies; I designed and built the experimental setup; I completed the experimental measurements and interpreted the results; I wrote the manuscript. Choloong Hahn performed the fabrication; he contributed to designing the experimental setup and interpretation of the results. Hamid Suleman (a visiting student in Prof. Berini's group), helped to develop and build the experimental setup. Dr. Berini contributed to interpretation of the results and revised the manuscript.

C. Article

The manuscript presented in this section is going to be submitted for publications.

Experimental observation of Fano resonances involving magnetic multipoles in nanohole oligomers in a gold film

Akram Hajebifard^{1,2,*}, Choloong Hahn^{2,3}, Hamid Suleman⁴, and Pierre Berini^{1,2,3,*}

¹*Department of Physics, University of Ottawa, Ottawa K1N 6N5, Canada*

²*Centre for Research in Photonics at the University of Ottawa, Ottawa K1N 6N5, Canada*

³*School of Electrical Engineering and Computer Sci., University of Ottawa, Ottawa K1N 6N5, Canada*

⁴*Max Planck Institute for the Science of Light, Staudtstr. 2, D-91058 Erlangen, Germany*

Keywords

Plasmonics, nanoholes, oligomers, magnetic multipoles, Fano, biosensor

Abstract

The optical properties of nanohole oligomers in a gold film have been investigated experimentally and theoretically. Helium focused ion beam milling was used to create arrays of heptamer-arranged nanoholes (HNH) in a 55 nm thick gold film on a fused silica substrate. The holes are slightly elliptical about a nominal diameter of 100 nm and are separated by 15 nm Au regions ("bridges") to form close-packed heptamer arrangements. Optical responses of the fabricated arrays are reported as measured and computed transmittance spectra, which show various Fano resonances due to different excitations on the structure, such as surface plasmon polaritons localised to the HNH, propagating surface plasmon polaritons, and waves associated with Wood's anomaly. All resonances observed involve the coupling (bonding and anti-bonding) of magnetic dipoles within the holes of HNH, and in some cases of magnetic multipoles (hexapoles) within the central hole. The sensing performance was investigated by measuring the bulk sensitivity of the resonances (up to 380 nmRIU⁻¹), anticipating application to biosensing. The evolution of the resonances with respect to the He ion dose delivered to the sample during milling was also measured. A clearing He ion dose of 10 nCμm⁻² was required to completely mill holes in our 55 nm thick gold film.

Introduction

The manipulation of electromagnetic surface waves using nano-structures is a prominent research area with applications in diverse fields such as biosensing,¹⁻³ nonlinear optics,⁴⁻⁶ quantum optics,^{7,8} and optoelectronics.⁹ Plasmonic nanostructures play a critical role in this context because they make it possible to control and manipulate optical energy at the subwavelength scale. Dielectric structures are diffraction-limited but metallic structures which support surface plasmon-polariton (SPP) waves or resonant modes are not.¹⁰

Resonant SPP modes on metal nanostructures can be excited efficiently by incident light, resulting in profound resonant features in, e.g., transmittance and reflectance responses. While the symmetric

Lorentzian lineshape is commonly observed in the optical response of plasmonic nanostructures,¹¹ asymmetric Fano resonances have also been reported in several plasmonic systems.^{12,13} Recently, much attention has been devoted to creating and exploiting such resonances in metallic nanostructures, motivated by their remarkable characteristics, such as nm-scale confinement of light, high local field enhancement, and high spectral sensitivity to changes in the local dielectric environment.

Various types of nanoplasmonic Fano resonant structures have been proposed and studied, including metamaterial concepts,^{14,15} clusters,^{1,16} single and multi-surface nanoparticles,¹⁷ and periodic structures.¹⁸ Structures made of deterministic arrangements of plasmonic nanoparticles (oligomers), such as dimers,¹⁹⁻²¹ trimers,²² quadrumers,²³ pentamers²⁴ and heptamers^{16,25,26} are interesting due to the diverse spectral responses and near-field distributions that are present in such arrangements. Importantly, the characteristics of the resonances in such systems can be tuned by tailoring structural parameters such as inter-particle separation, particle dimensions, and particle arrangement²⁷⁻²⁹ using a suitable nanofabrication process.

Though plasmonic nanoparticle oligomers have been extensively studied, the optical response of complementary structures – nanohole arrangements (clusters or oligomers) – has remained largely unexplored, with studies limited to investigation via numerical modelling.^{30,31} Following Babinet's principle,^{32,33} one may expect nanohole arrangements to support resonant SPP modes localised to the nanoholes with field configurations complementary to those in nanoparticle arrangements. This is only partially correct, and only qualitatively so. Babinet's principle applies to structures implemented from infinitesimally thin perfect conductors. Metals at optical and near-infrared wavelengths are not perfect conductors, and realistic nanostructures are fabricated in metals of finite thickness, so neither condition for the application of Babinet's principle are strictly met.

Furthermore, at optical and near-infrared wavelengths, a thin metal film is a waveguide that supports propagating SPP modes (symmetric and asymmetric) in the plane. Also Wood's anomaly (WA) waves may be supported along metal films. These propagating surface waves can be excited by periodicity in arrays of nanoholes, and along with resonant SPP modes localised to arrangements of nanoholes, leads to optical responses that are very rich in resonances.³⁴ In contrast, surface waves are not supported in nanoparticle arrangements on a substrate. Thus, Babinet's principle may be applied to relate complementary plasmonic nanostructures at optical wavelengths, but only qualitatively (metals are imperfect conductors and of finite thickness), and only for resonant SPP modes localised to the nanohole arrangements. Focussed investigation is required to rigorously unravel the optical response of complex arrangements of nanoholes.

Heptamer-arranged nanoholes (HNH) are clusters consisting of a central circular nanohole surrounded by six others, forming a highly-packed arrangement of coupled nanoholes. In a thin metal film HNH produce strong electric fields in defined areas between neighboring holes (hot spots), and strong magnetic fields within the holes.³⁴ The magnetic fields within the holes exhibit multipolar distributions.³² The electric field enhancement, localised on the nanometer scale, renders HNH highly sensitive to local refractive index changes and to small changes in geometrical parameters. The heptamer arrangement is motivated by the fact that it achieves hexagonal close-packing, which (along with face-centered cubic) produces the highest packing density possible for circular (spherical) features.

There are two main approaches for fabricating nanoholes which can be classified as resist-based and resist-free approaches. In the former, nanostructures are fabricated using techniques such as metal etching or lift-off, where features are defined lithographically using ultra-violet lithography,³⁵ interference lithography,³⁶ electron beam lithography³⁷ or nanoimprint lithography.³⁸ In resist-free approaches, nanoscale patterns in a metal film are produced using, *e.g.*, colloidal lithography,³⁷ or Focused Ion Beam (FIB) milling^{37,39,40} which employs a focused beam of ions to directly remove metal. This fabrication method provides good to excellent nanoscale resolution, particularly if Helium ions are used.⁴¹

Building on previous theoretical and fabrication work,^{34,41} we report here the experimental characterization of heptamer-arranged nanoholes (HNH) perforated in a thin Au film using He-FIB milling. We confirm experimentally the existence of resonances associated with SPP modes localised to nanohole arrangements, and resonances associated with symmetric and asymmetric SPP modes and WA waves propagating in the plane of the metal film. All of the modes observed involve magnetic multipoles. We determine experimentally the sensitivity of these resonances to small changes in the cover refractive index, anticipating application to biosensing. The evolution of measured spectra with fabrication process parameters is investigated. We also report theoretical results extending heptamer arrangements from circular holes to elliptical holes and compare our calculations with experiment.

Theoretical

Model

Elliptical HNH consist of a hexagonal arrangement of close-packed and identical elliptical holes, perforated in a gold film, as shown in Fig. 1(a) in top view, and Fig. 2(b) in isometric view. The geometrical parameters include the thickness of the Au film (t), the inter-hole “bridge” (G), the dimensions of the elliptical holes (D_x and D_y), and the periodicity of the array (P_x and P_y). The Au film is supported by a fused SiO_2 substrate and assumed covered by a fluid of refractive index n_s near that of water. Anticipating the experimental section, we are interested in the transmittance of HNH arrays that can support resonances in the red to near-infrared spectral regions, *i.e.*, from 600 to 1100 nm. The nominal parameters of $t = 55$ nm, $G = 15$ nm, $D_x = D_y = 100$ nm, and $P_x = P_y = 480$ nm fulfill this condition. The nominal diameter of the nanoholes ($D_x = D_y = 100$ nm) is such that only “extraordinary optical transmission” is expected.⁴²

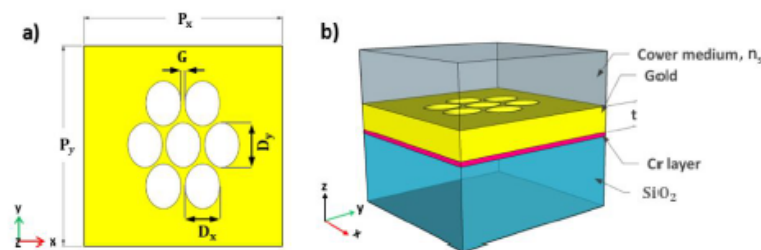


Fig. 1. (a) Top view and (b) 3D view of a unit cell of heptamer-arranged elliptical nanoholes (elliptical HNH). A gold layer of thickness t (yellow) is deposited on a Cr adhesion layer (red) on a fused SiO_2 substrate (dark blue). A fluid of refractive index n_s is used as a cover medium (light blue).

A commercial implementation of the finite element method (FEM) was used to model our HNH array. Taking advantage of the periodicity, a unit cell containing a single HNH was modelled. Periodic boundary conditions were applied on the lateral walls and a Perfectly Matched Layer (PML) was applied along the top and bottom of the structure to eliminate any reflections due to the Perfect Electric Conductor (PEC) boundary conditions applied to terminate the domain, as illustrated in Fig. 2(a). Two ports were defined between the PML and its adjacent domain: active port 1 and passive port 2. The first port is used to illuminate the structure with a plane wave and the second one to calculate the transmittance (T).

In each domain, the mesh was constrained to have a maximum element size of one-sixth of the wavelength in the medium. Specifically, the structure was meshed with a spatial resolution between 5 and 12 nm within the gold film, and the mesh size was allowed to increase gradually away from the gold film to a maximum size of 100 nm. Since a periodic boundary condition was used on the lateral walls, the adjacent regions were meshed identically to avoid interpolation errors across the periodic boundaries. First, we created the mesh on a lateral wall and copied this mesh to the opposite wall. Then, all domains except the PML regions were meshed by triangular elements. The PMLs were meshed using a swept mesh of at least five elements across. Fig. 2(b) shows our meshing strategy.

The optical properties of SiO_2 and Au were taken as their wavelength-dependent complex refractive index measured over the spectral range of interest (SiO_2 ⁴³ and Au⁴⁴). Cubic spline interpolation functions were applied to determine a refractive index at a wavelength of interest where data were not available. The Cr adhesion layer was not included in the model. The refractive index of the cover medium was set to $n_s = 1.3$, neglecting dispersion and absorption in this medium.

Illuminating the structure with a plane-wave source of electric field strength 1 V/m, the transmittance was calculated over the wavelength range of 625 to 1100 nm, for the x- and y-polarizations.

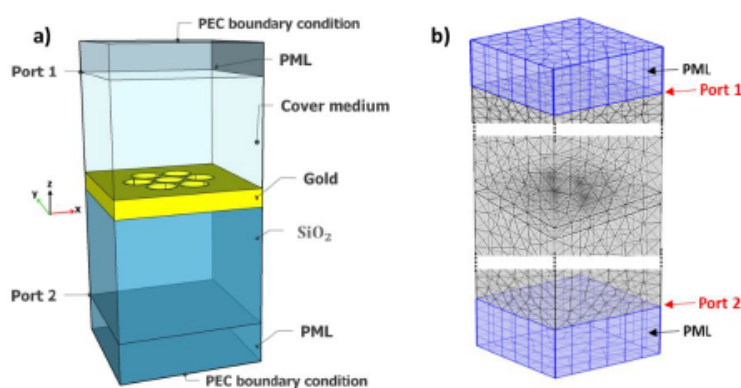


Fig. 2. (a) Schematic of the HNH model adopted in the simulations. Periodic boundary conditions are applied along the lateral walls, PMLs are applied along the two ends of the domain, active port 1 and passive port 2 are located on the interior faces of the PMLs, and PEC boundary conditions are applied along the exterior faces of the PMLs. (b) Meshing strategy.

Numerical Results

Anticipating the experimental section, we investigate here the evolution of the transmittance as the shape of the holes is perturbed from circular to elliptical by changing the diameters D_x or D_y . Figs. 3(a) and 3(b) summarise the results for $D_x > D_y = 100$ nm for x- and y-polarised incidence, respectively; whereas Figs. 3(c) and 3(d) summarise the results for $D_y > D_x = 100$ nm and the same incident polarizations. The resonances labelled LSPP₁ and LSPP₂ comprise SPPs localised to the HNH (first and second order modes).³⁴ Those labelled SPP_a comprise the strongly confined asymmetric surface plasmon mode propagating in the plane of the film,⁴⁵ coupled to the incident beam by the periodicity of the array (P_x, P_y).³⁴ Those labelled WA-SPP_s comprise the less confined symmetric surface plasmon mode⁴⁵ coupled to Wood's Anomaly waves propagating in the plane of the film, also excited by the incident beam through the periodicity of the array.³⁴ Thus, enhanced transmission occurs at particular wavelengths due to excitations associated with LSPP resonances, or the resonant excitation of propagating SPP modes or waves related to WA (the latter have no counterpart in the complementary nanoparticle structure).

Resonances in nanohole structures are conveniently described by observing their magnetic moment,³² which is revealed in this structure by the distribution of the H_z field. Near-field distributions of $\text{Re}\{H_z\}$ taken over the xy plane located 1 nm above the metal film (in the cover medium), corresponding to each resonance in Figs. 3(a) and 3(b), are plotted along the top of the figure; the near-field distributions of the resonances in Figs. 3(c) and 3(d) are similar. These field distributions are normalised to the incident magnetic field and thus may be viewed as the magnetic field enhancement. The fields of the WA-SPP_s resonances are less confined to the metal film compared to those of the other resonances, and thus are plotted with their own colour scale for clarity. All resonances exhibit dipolar distributions of $\text{Re}\{H_z\}$ over the nanoholes, but the WA-SPP_s and LSPP₂ resonances also exhibit hexapolar distributions over the central hole for illumination in the y-polarisation - the insets to Fig. 3(b) show expanded views of these two distributions. (These hexapolar distributions should not be confused with multipolar excitations that can exist in a large diameter hole due to waveguide modes propagating along the hole.⁴⁶) Furthermore, based on these field distributions, all resonances are observed to involve a degree of "anti-bonding" hybridization between the central and surrounding holes, where the central hole shows a magnetic field distribution that is out of phase with respect to the magnetic field in some of the surrounding holes. Hybridization into coupled modes involving a degree of anti-bonding is a hallmark of a Fano resonance.

We note from Fig. 3 (b) that small changes in D_x ($\Delta D_x = 6$ nm) cause a significant shift in the LSPP₁ resonance ($\Delta\lambda \sim 35$ nm) when the array is illuminated with y-polarised light. Similarly, as noted from Fig. 3(c) where D_y is perturbed ($\Delta D_y = 6$ nm), the LSPP₁ resonance shifts by a similar amount ($\Delta\lambda \sim 35$ nm) for x-polarised incident light. These shifts in resonance are very large considering the relatively small perturbation applied (6% of the hole diameter).

It may seem initially surprising that aligning the major axis of the elliptical holes in the HNH along the incident polarisation (Fig. 3(a) and Fig. 3(d)) does not have as strong an effect as aligning the major axis orthogonally to the incident polarisation (Fig. 3(b) and Fig. 3(c)). An explanation of this behaviour is found by inspecting the distributions of $\text{Re}\{H_z\}$ given along the top of Fig. 3. For the SPP_a and LSPP₁ resonances (which are most affected by the ellipticity), we note that a strong dipole-like magnetic field distribution, oriented perpendicular to the incident polarization, forms

within the holes of the HNH. Thus, enlarging the axis of the holes along the incident polarization, has no significant effect on the magnetic dipoles within the holes, so the resonances remain essentially unchanged. However, enlarging the axis of the holes perpendicular to the incident polarization strongly affects the magnetic dipoles, causing a significant redshift in the spectral position of these resonances. Resonances with lower confinement interact less strongly with the holes of the HNH, and are comparatively unaffected by the ellipticity (*e.g.*, WA-SPP₂).

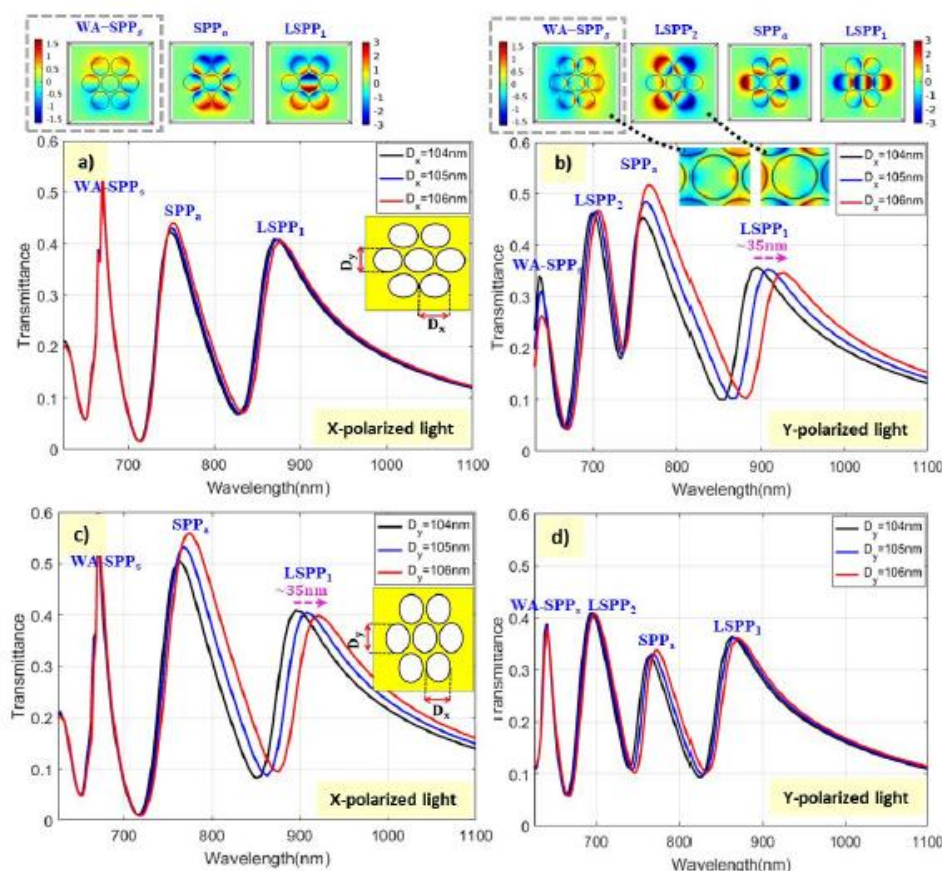


Fig. 3. Computed optical transmittance of an infinite array of elliptical HNH with structural parameters $t = 55$ nm, $G = 15$ nm, $P_x = P_y = 480$ nm, $D_y = 100$ nm and varying D_x for (a) x-polarised and (b) y-polarised incident light. Transmittance of the same array but for varying D_y and $D_x = 100$ nm for (c) x-polarised and (d) y-polarised incident light. The refractive index of the cover medium was set to $n_s = 1.3$ in all cases. The near-field distribution of $\text{Re}\{H_z\}$ over the xy plane 1 nm above the metal film, normalised to the magnetic field of the incident plane wave (magnetic field enhancement), is plotted along the top for each resonance in (a) and (b). The fields of the WA-SPP₂ resonances are plotted on a separate colour scale. The fields of the WA-SPP₂ and LSPP₂ resonances are shown in expanded view around the central hole as insets to part (b). Anticipating the experimental section, the following dimensions were used in the computation of the field plots: $t = 55$ nm, $G = 15$ nm, $D_x = 104$ nm, $D_y = 100$ nm, $P_x = 460$ nm, $P_y = 438$ nm. The near-field distributions for cases (c) and (d) are similar (qualitatively).

Experimental

Fabrication

Following ⁴¹, a helium focused ion beam (He-FIB) system (Zeiss Orion NanoFab) was used to directly mill through a 55 nm thick gold film to form high-quality arrays of 20×20 HNH for a total of 400 HNH, spanning an area of about 10×10 μm^2 . Drift correction was applied in writing an array by periodically imaging a reference feature. To prepare the sample, a 0.3 nm thick adhesion layer of Cr was deposited on a fused silica substrate using electron beam evaporation at a rate of 0.1 $\text{\AA s}^{-1}$. This was followed by gold deposition using thermal evaporation at a rate of 0.5 $\text{\AA s}^{-1}$. The gold layer thickness obtained was 55 nm based on AFM imaging on the fabricated sample. A 2 nm thick layer of SiO_2 followed by a 19 nm thick layer of Al were deposited on top of the gold film as protective layers against material redistribution during milling. The next step consisted of using the He-FIB system to directly mill the sample to create arrays of 20×20 HNHs in the gold film. The layers of Al and SiO_2 were then removed via chemical etching through brief TMAH and HF dips, respectively. (It is also possible to directly mill the Au layer without protective layers. ⁴¹)

Fig. 4(a) shows a helium ion microscope (HIM) image of a fabricated array of HNH, targeting the following structural parameters: $t = 55$ nm, $G = 15$ nm, $D_x = D_y = 100$ nm, and $P_x = P_y = 480$ nm. The realised arrays are generally close to the targeted ones. However, we hypothesise a slight ellipticity in the shape of the holes (as discussed below), and there are discrepancies in the periodicity, as determined by measuring the distance between HNH nearest neighbours along the x and y directions of a fabricated array. The distances between nearest neighbours, denoted Δx and Δy and defined on Fig. 4(c), were determined for all HNH in the array using an image processing technique, and are plotted as a histogram in Fig. 4(b). The mean values of the distances were then determined as $P_x = 458$ nm and $P_y = 438$ nm, and their standard deviations as 4 and 12 nm, respectively. The difference between the mean values of the realised periods ($P_x = 458$ nm, $P_y = 438$ nm) and the target ($P_x = P_y = 480$ nm) is attributed to instrument drift during fabrication and the imperfect nature of our compensation scheme. ⁴¹

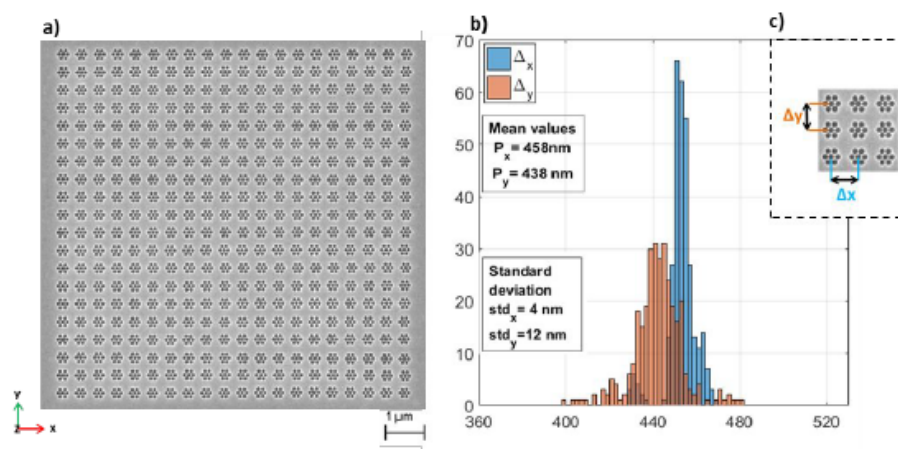


Fig. 4. (a) HIM image of a fabricated array of 20×20 HNH (10×10 μm^2 , 400 HNH). The target structural parameters were $t = 55$ nm, $G = 15$ nm, $D_x = D_y = 100$ nm, and $P_x = P_y = 480$ nm. (b)

Histogram of the measured Δx and Δy . (c) Expanded view of the array illustrating the definition of Δx and Δy , as the distances between nearest HNH neighbours in x and y directions, respectively.

Optical setup

All experiments were carried out at room temperature, using the experimental setup illustrated in Fig. 5. This setup has two main arms, one of them operates as a microscope, and the other serves as a measurement arm. The microscope arm, which is used for monitoring and scanning across the HNH arrays, consists of a white light source (halogen illuminator), two flipping mirrors (PF10-03-P01, Thorlabs), an objective lens (100 $\times$ /0.75 Epiplan, Zeiss), a screen, an adjustable iris (SM1D25, Thorlabs), a CMOS microscope camera (MU300, AmScope), and the device under test (DUT). The DUT has a machined area of $\sim 900 \mu\text{m}^2$ which includes seven arrays, each comprised of 20×20 HNH and surrounded by four crossed-shaped milled markers to facilitate identification (a microscope image is given in Fig. 5(a)). In this microscope arm, the white light is reflected by the first flipping mirror (FM₁) to illuminate the DUT which is mounted on an x-y-z stage to facilitate translation. Transmitted light from the DUT passes through the 100 $\times$ objective to generate a magnified picture of a machined area on the screen, as shown in Fig. 5(b). The transmitted light is then passed through the iris whose opening is adjusted to confine the field of view so that it just passes the light associated with one array. After passing through the iris, the light is reflected by the second flipping mirror (FM₂) towards the camera, which is used to view the image of the machined area. Such imaging, in conjunction with the translation stage, is used to find the array of interest. After finding the array, the iris is closed stepwise, as shown in Fig. 5(c), to block light transmitted from areas surrounding the array (thus minimizing noise). After adjusting the iris, the mirrors are flipped, enabling the measurement arm to become active.

The measurement arm includes a supercontinuum white light laser (EXR-15, NKT Photonics), two mirrors (PF10-03-P01, Thorlabs), a neutral-density filter (5215 Dual ND Filter Wheel, Newport), a linear polariser (LPNIR100-MP2, Thorlabs), the DUT, the 100 $\times$ objective, the adjustable iris, a 20 $\times$ objective (M-20 $\times$ microscope objective, Newport), and an optical spectrometer (OSM2-400VIS/NIR, Newport). The supercontinuum laser produces pulses at a 11.1 MHz repetition rate with spectral content over the wavelength range of 390-2400 nm in a collimated beam. The ND filter is inserted in the optical path to control the incident power, and two mirrors are used to reflect the beam onto the polariser and then the DUT. After illuminating the DUT, light passes through the 100 $\times$ objective, iris, and 20 $\times$ objective to be focused and coupled into an optical fibre connected to the optical spectrometer for analysis.

Since the supercontinuum laser is a class 4 laser, it has a risk of severe skin and eye injury. Eyewear with an appropriate optical density should be used during laser operation, and any contact between the skin and the beam, or its reflections should be avoided.

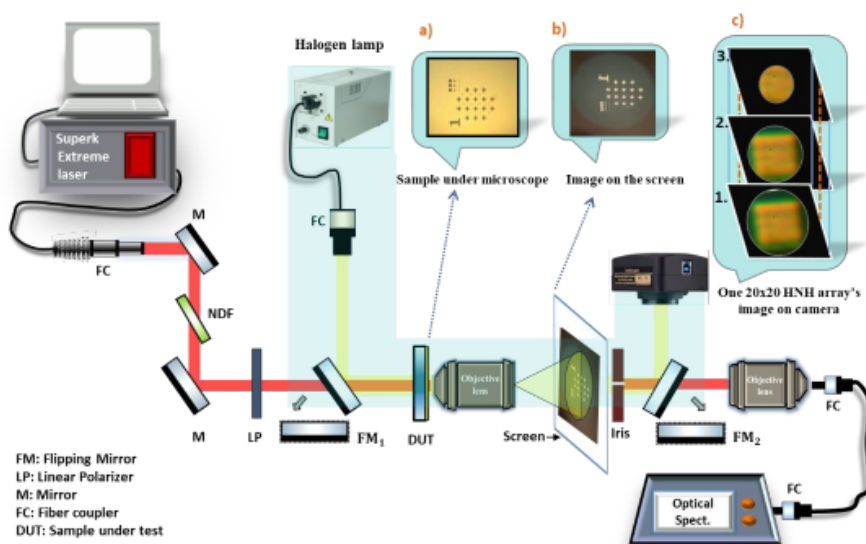


Fig. 5. The experimental setup includes two main arms: the microscope arm (yellow light path with a blue background), and the measurement arm (red light path). The microscope arm includes a halogen white light source, two flipping mirrors (FM₁ and FM₂), a 100× objective, a screen, an adjustable iris and a camera. The measurement arm includes a supercontinuum source, two mirrors (M), a neutral-density filter (NDF), a linear polariser (LP), a 100× objective, an adjustable iris, a 20× objective, and an optical spectrometer. (a) Optical microscope image of the machined area of a sample (~900 μm²) containing seven arrays, each comprised of 20×20 HNH and surrounded by four crossed-shaped milled markers to facilitate identification. (b) Magnified image of the machined area on the screen. (c) Iris is closed step by step to eliminate light transmitted from areas away from the array of interest.

Spectral responses

The measured optical transmittance of a fabricated array (Fig. 4(a)), covered sequentially with different oils of refractive index $n_s = 1.3$, 1.35 or 1.40 (Cargille oil,⁴⁷ Series AAA and AA), are given in Fig. 6 for x- and y-polarised incident light. The oils used as the cover medium were sufficiently viscous to hold on the vertically-oriented DUT. Prior to measurement with each oil, the sample was cleaned in several steps including sonication in Isopropyl Alcohol (IPA), then in de-ionised water, followed by UV ozone cleaning for 15 min.

The power spectral responses of the set-up with and without the DUT were measured and the DUT transmittance taken as the ratio of these two measurements. The measured transmittances of the structure involves several resonances, denoted WA-SPP_s, SPP_a and LSPP₁ for x-polarised incident light (Fig. 6(a)), and WA-SPP_s, LSPP₂, SPP_a and LSPP₁ for y-polarised incident light (Fig. 6(b)).

The computed transmittance spectra for an array of HNH with holes that are slightly elliptical ($D_x = 104$ nm and $D_y = 100$ nm), and arranged in the average periods determined through imaging ($P_x = 458$ nm, $P_y = 438$ nm, Fig. 4(b)), are shown in Fig. 7. This case produces the best agreement with the experimental results, suggesting that the fabricated nanoholes are slightly elliptical. A slight

ellipticity (4% in this case) is not evident even under high-magnification HIM imaging. The correspondence in the peaks and valleys between the measured and computed responses serve to identify the resonances in the experimental case. Recalling the field plots along the top of Fig. 3, we note that the resonances involve the coupling of magnetic dipoles within the holes of an HNH, as well as coupling to a magnetic hexapole within the central hole for the WA-SPP_s and LSPP₂ resonances under y-polarised excitation.

The resonances in the experimental spectra (Fig. 6) are weaker than in the computed ones (Fig. 7), which is attributed to fabrication imperfections and some factors which have not been taken into account in the modelling. For instance, Cr, which serves as the adhesion layer in the experimental structures is not included in the computations because it is a very thin film (0.3 nm), likely islandised and possibly oxidised, and difficult to model realistically. However, the Cr layer can increase the loss associated with the resonances, particularly those that involve propagating SPP and WA waves, localised to the metal/dielectric interfaces. The roughness along the top of the fabricated structures is low but also not modelled. Furthermore, the top surface of the Au layer may bear residual SiO₂ or Al from the protection layers (Al can react with Au forming an intermetallic compound), which may affect the optical performance, and is also not modelled.

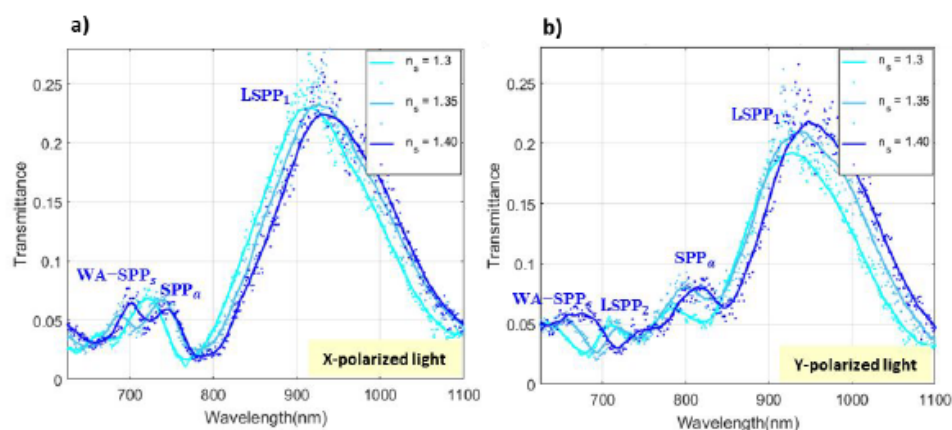


Fig. 6. Measured transmittances of an array of 20×20 HNH (as in Fig. 4(a)) covered with oils of different refractive index, $n_s = 1.3, 1.35$ or 1.45 , for (a) x-polarised and (b) y-polarised incident light. The dots correspond to the raw measurements and the solid curves a moving average best fit.

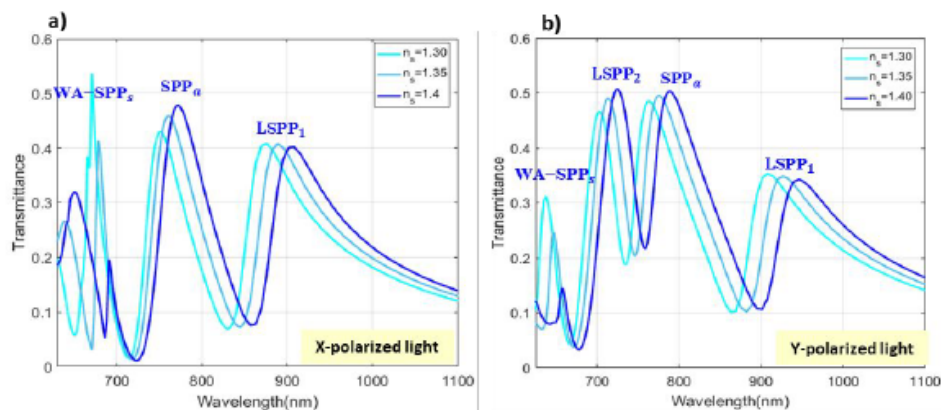


Fig. 7. Computed transmittances of an infinite array of HNH covered with media of different refractive index, $n_s = 1.3, 1.35$ or 1.45 , for (a) x-polarised and (b) y-polarised incident light. The following dimensions were used: $t = 55$ nm, $G = 15$ nm, $P_x = 458$ nm, $P_y = 438$ nm, $D_x = 104$ nm, $D_y = 100$ nm. Plots of $\text{Re}\{H_z\}$ for each resonance were shown along the top of Fig. 3 for the case $n_s = 1.3$.

Bulk sensitivity

The bulk sensitivity of the structure is defined as the shift in resonant wavelengths with respect to changes in the refractive index of the cover medium, $\partial\lambda_r/\partial n_s$. All resonances were observed to redshift with increasing n_s , via the application of oils of different refractive index, as noted in Fig. 6. The measured and computed shifts in resonant wavelength ($\Delta\lambda_r$) relative to the nominal resonant wavelength at $n_s = 1.3$ are plotted vs. n_s in Fig. 8 for all resonances observed in Figs. 6 and 7. The measured bulk sensitivity associated with each resonance is also noted on the figures.

As indicated in Fig. 8(a), the resonances associated with the LSPP_1 , SPP_a and WA-SPP_s modes have bulk sensitivities of 380, 200 and 260 nmRIU^{-1} under x-polarised incident light. For y-polarised light, bulk sensitivities of 370, 260, 200 and 220 nmRIU^{-1} are measured for the resonances associated with the LSPP_1 , SPP_a , LSPP_2 and WA-SPP_s modes, respectively, as noted in Fig. 8(b). For both polarisations, the largest bulk sensitivity is measured for the LSPP_1 mode, as expected because it produces the strongest field enhancement.³² The computed wavelength shifts and bulk sensitivities of each resonance are in good agreement with the experimental ones.

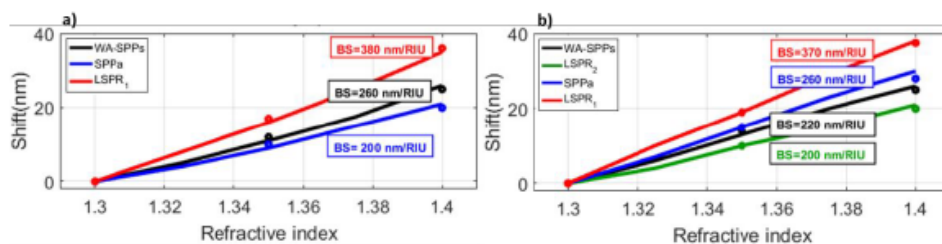


Fig. 8. Shift in the resonant wavelength of each resonance observed in Figs. 6 and 7, relative to their nominal values at $n_s = 1.3$, vs. the cover medium refractive index n_s . The experimental shifts (Fig. 6) are denoted as the solid dots, and the theoretical shifts (Fig. 7) are plotted as the solid curves. The

measured bulk sensitivity (BS) is noted on the plots for all cases. (a) x-polarised incident light and (b) y-polarised incident light.

Hole depth

We studied the effect of the He ion dose on the fabrication of the holes via measured optical responses of fabricated samples. Specifically, seven arrays of 20×20 HNH were fabricated with doses ranging from 5 to 17 $\text{nC}\mu\text{m}^{-2}$. The ion dose is defined as the amount of charge (nC) deposited by He ions per unit area (μm^{-2}). To fabricate an array with the desired dose, every HNH in the array was milled using a double-serpentine exposure method with a 1 μs dwell time, 0.25 nm pixel spacing, and repeats until the target dose was achieved.⁴¹ The evolution of the transmittance spectra of the HNH arrays with increasing dose is given in Fig. 9, for x- and y-polarised light.

Applying different doses results in holes of different depth. As shown in Fig. 9, when the dose is as low as 5 $\text{nC}\mu\text{m}^{-2}$, the response of the array is almost featureless, resembling that of a planar gold film with no holes. Increasing the dose beyond 5 $\text{nC}\mu\text{m}^{-2}$ produces holes of gradually increasing depth, sufficient to support resonances. The resonant wavelength of the LSPP_1 mode is noted to blue-shift with increasing dose beyond 10 $\text{nC}\mu\text{m}^{-2}$ and its full-width at half-maximum (FWHM) of 185 nm increases slightly. The optical measurements suggest that a dose near 10 $\text{nC}\mu\text{m}^{-2}$ was required to fully clear holes in the 55 nm thick Au layer (clearing dose).

Our He-FIB system is equipped with a camera for secondary electron imaging, capable of capturing in-situ images during the milling process. This capability is useful to identify the clearing dose by monitoring changes in the intensity of the images. The images changed abruptly when the milled material changed from conductive (gold) to insulating (SiO_2), confirming that the clearing dose was 10 $\text{nC}\mu\text{m}^{-2}$. The array fabricated with this dose was used in the measurements reported in this paper (Figs. 6 and 8). Increasing the dose beyond the clearing dose damages the HNH, particularly the narrow "bridges" (of width G) between the holes. As shown in the top left SEM insets of Fig. 9(a), increasing the dose from 10 $\text{nC}\mu\text{m}^{-2}$ to 15 $\text{nC}\mu\text{m}^{-2}$ has partially destroyed the bridges between the holes.

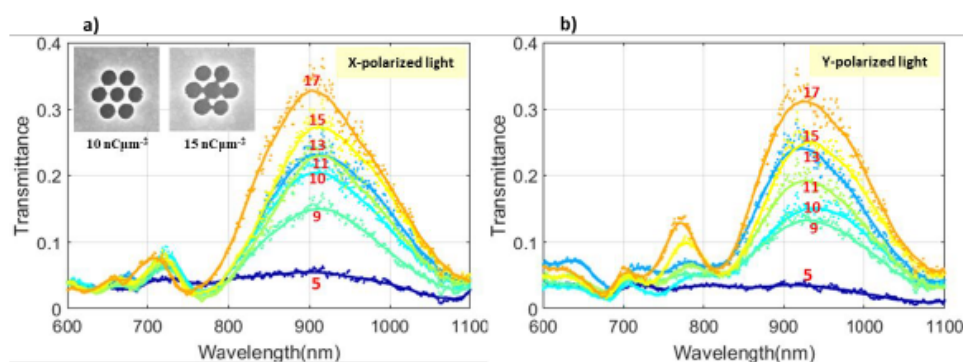


Fig. 9. Measured optical transmittance responses of arrays of 20×20 HNHs milled with different He doses; (a) x-polarised and (b) y-polarised incident light. The spectra are labeled in red according to the dose applied ($\text{nC}\mu\text{m}^{-2}$). The dots correspond to the raw measurements and the solid curves a moving average best fit. Top left insets of panel (a): SEM images of HNHs fabricated via direct HeFIB milling when the dose was set to 10 $\text{nC}\mu\text{m}^{-2}$ and 15 $\text{nC}\mu\text{m}^{-2}$.

Summary and conclusions

We have theoretically and experimentally investigated the optical properties of arrays of plasmonic HNH fabricated by direct He-FIB milling of a 55 nm thick Au film on a SiO₂ substrate. We demonstrate experimentally that the fabricated arrays support various excitations involving LSPPs and propagating SPPs and Wood's anomaly waves, which manifest as resonances in transmittance spectra over the wavelength range of interest (600 to 1100 nm). All resonances observed involve the coupling (bonding and anti-bonding) of magnetic dipoles within the holes of an HNH, and in some cases, involving a magnetic hexapole within the central hole (WA-SPP₁ and LSPP₂ under y-polarised excitation). By comparing the measured transmittance spectra with computed ones, we determine that the holes of the HNH have a slightly elliptical shape ($D_x = 104$ nm, $D_y = 100$ nm), rather than circular ($D_x = D_y = 100$ nm) as targeted. This slight change in D_x from target, unobservable under high-resolution HIM imaging, is responsible for a significant shift of $\Delta\lambda \sim 35$ nm in the resonance of the LSPP₁ mode of the fabricated array relative to the case with circular holes. Also, the HNH periodicities along the x and y axes in the fabricated array were found to vary slightly about average values ($P_x = 458$ nm, $P_y = 438$ nm), both differing from target ($P_x = P_y = 480$ nm), likely due to instrument drift during fabrication. The structures were also examined for use in sensing applications by measuring and computing the bulk sensitivity of the resonant modes to changes in the refractive index of the cover medium. All modes were found to redshift with increasing index. The resonance associated with the LSPP₁ mode has the largest sensitivity, as it also produces the largest near-field enhancement. The computations of bulk sensitivity are in excellent agreement with experiment. The transmittance spectra of arrays of 20×20 HNH, fabricated with different He ion doses, have also been measured. The resonances start to appear for a He dose of 5 nCμm⁻² and they become increasingly stronger with increasing dose. A dose of 10 nCμm⁻² was found to be necessary to fully clear the holes in our 55 nm thick Au film.

Funding

Department of National Defense of Canada (CFPMN1-040-Carleton); Natural Sciences and Engineering Research Council of Canada.

Acknowledgements

The authors are grateful to the Innovation for Defence Excellence and Security (IDEaS) Program of the Department of National Defence of Canada for financial support (CFPMN1-040-Carleton University). Also, they acknowledge the Centre for Advanced Computing (CAC), Queen's University, for the computational support that facilitated this research.

Disclosures

The authors declare that there are no conflicts of interest related to this article.

References

- 1 Fan, J. A. *et al.* Self-Assembled Plasmonic Nanoparticle Clusters. *Science* **328**, 1135-1138 (2010).
- 2 Rodrigo, D. *et al.* Mid-infrared plasmonic biosensing with graphene. *Science* **349**, 165-168 (2015).

- 3 Gordon, R., Sinton, D., Kavanagh, K. L. & Brolo, A. G. A new generation of sensors based on extraordinary optical transmission. *Accounts of Chemical Research* **41**, 1049-1057 (2008).
- 4 Danckwerts, M. & Novotny, L. Optical frequency mixing at coupled gold nanoparticles. *Physical Review Letters* **98** (2007).
- 5 Smirnova, D. & Kivshar, Y. S. Multipolar nonlinear nanophotonics. *Optica* **3**, 1241-1255 (2016).
- 6 Lesuffleur, A., Kumar, L. K. S. & Gordon, R. Enhanced second harmonic generation from nanoscale double-hole arrays in a gold film. *Applied Physics Letters* **88** (2006).
- 7 Chang, D. E., Sorensen, A. S., Hemmer, P. R. & Lukin, M. D. Quantum optics with surface plasmons. *Physical Review Letters* **97** (2006).
- 8 Fakonas, J. S., Lee, H., Kelaita, Y. A. & Atwater, H. A. Two-plasmon quantum interference. *Nature Photonics* **8**, 317-320 (2014).
- 9 Mak, K. F. & Shan, J. Photonics and optoelectronics of 2D semiconductor transition metal dichalcogenides. *Nature Photonics* **10**, 216-226 (2016).
- 10 Pitarke, J. M., Silkin, V. M., Chulkov, E. V. & Echenique, P. M. Theory of surface plasmons and surface-plasmon polaritons. *Reports on Progress in Physics* **70**, 1-87 (2007).
- 11 Otto, A. Excitation of nonradiative surface plasma waves in silver by the method of frustrated total reflection. *Zeitschrift Fur Physik* **216**, 398-& (1968).
- 12 Wu, C. H. *et al.* Fano-resonant asymmetric metamaterials for ultrasensitive spectroscopy and identification of molecular monolayers. *Nature Materials* **11**, 69-75 (2012).
- 13 Limonov, M. F., Rybin, M. V., Poddubny, A. N. & Kivshar, Y. S. Fano resonances in photonics. *Nature Photonics* **11**, 543-554 (2017).
- 14 Liu, N. *et al.* Planar Metamaterial Analogue of Electromagnetically Induced Transparency for Plasmonic Sensing. *Nano Letters* **10**, 1103-1107 (2010).
- 15 Kelly, C. *et al.* Controlling Metamaterial Transparency with Superchiral Fields. *Acs Photonics* **5**, 535-543 (2018).
- 16 Thyagarajan, K., Butet, J. & Martin, O. J. F. Augmenting Second Harmonic Generation Using Fano Resonances in Plasmonic Systems. *Nano Letters* **13**, 1847-1851 (2013).
- 17 Hao, F. *et al.* Symmetry Breaking in Plasmonic Nanocavities: Subradiant LSPR Sensing and a Tunable Fano Resonance. *Nano Letters* **8**, 3983-3988 (2008).
- 18 Baryakhtar, I., Demidenko, Y. & Lozovski, V. Interaction between localized-on-nanoparticles plasmon polaritons and surface plasmon polaritons. *Journal of the Optical Society of America B-Optical Physics* **30**, 1022-1026 (2013).
- 19 Artar, A., Yanik, A. A. & Altug, H. Directional Double Fano Resonances in Plasmonic Hetero-Oligomers. *Nano Letters* **11**, 3694-3700 (2011).

- 20 Walsh, G. F. & Dal Negro, L. Enhanced Second Harmonic Generation by Photonic-Plasmonic Fano-Type Coupling in Nanoplasmonic Arrays. *Nano Letters* **13**, 3111-3117 (2013).
- 21 Near, R., Tabor, C., Duan, J. S., Pachter, R. & El-Sayed, M. Pronounced Effects of Anisotropy on Plasmonic Properties of Nanorings Fabricated by Electron Beam Lithography. *Nano Letters* **12**, 2158-2164 (2012).
- 22 Sheikholeslami, S. N., Garcia-Etxarri, A. & Dionne, J. A. Controlling the Interplay of Electric and Magnetic Modes via Fano-like Plasmon Resonances. *Nano Letters* **11**, 3927-3934 (2011).
- 23 Fan, J. A. *et al.* Fano-like Interference in Self-Assembled Plasmonic Quadrumer Clusters. *Nano Letters* **10**, 4680-4685 (2010).
- 24 Fan, J. A. *et al.* DNA-Enabled Self-Assembly of Plasmonic Nanoclusters. *Nano Letters* **11**, 4859-4864 (2011).
- 25 Cui, Y. H., Zhou, J. H., Tamma, V. A. & Park, W. Dynamic Tuning and Symmetry Lowering of Fano Resonance in Plasmonic Nanostructure. *Acs Nano* **6**, 2385-2393 (2012).
- 26 Hentschel, M. *et al.* Transition from Isolated to Collective Modes in Plasmonic Oligomers. *Nano Letters* **10**, 2721-2726 (2010).
- 27 Fofang, N. T., Grady, N. K., Fan, Z. Y., Govorov, A. O. & Halas, N. J. Plexciton Dynamics: Exciton-Plasmon Coupling in a J-Aggregate-Au Nanoshell Complex Provides a Mechanism for Nonlinearity. *Nano Letters* **11**, 1556-1560 (2011).
- 28 Lassiter, J. B. *et al.* Fano Resonances in Plasmonic Nanoclusters: Geometrical and Chemical Tunability. *Nano Letters* **10**, 3184-3189 (2010).
- 29 Fang, Z. Y. *et al.* Removing a Wedge from a Metallic Nanodisk Reveals a Fano Resonance. *Nano Letters* **11**, 4475-4479 (2011).
- 30 Zhan, Y. H., Lei, D. Y., Li, X. F. & Maier, S. A. Plasmonic Fano resonances in nanohole quadrumers for ultra-sensitive refractive index sensing. *Nanoscale* **6**, 4705-4715 (2014).
- 31 He, J. N., Ding, P., Wang, J. Q., Fan, C. Z. & Liang, E. J. Double Fano-type resonances in heptamer-hole array transmission spectra with high refractive index sensing. *Journal of Modern Optics* **62**, 1241-1247 (2015).
- 32 Hentschel, M., Weiss, T., Bagheri, S. & Giessen, H. Babinet to the Half: Coupling of Solid and Inverse Plasmonic Structures. *Nano Letters* **13**, 4428-4433 (2013).
- 33 Horak, M. *et al.* Limits of Babinet's principle for solid and hollow plasmonic antennas. *Scientific Reports* **9** (2019).
- 34 Hajebifard, A. & Berini, P. Fano resonances in plasmonic heptamer nano-hole arrays. *Optics Express* **25**, 18566-18580 (2017).
- 35 Seisyan, R. P. Nanolithography in microelectronics: A review. *Technical Physics* **56**, 1061-1073 (2011).

- 36 Lu, C. & Lipson, R. H. Interference lithography: a powerful tool for fabricating periodic structures. *Laser & Photonics Reviews* **4**, 568-580 (2010).
- 37 Prasad, A., Choi, J., Jia, Z., Park, S. & Gartia, M. R. Nanohole array plasmonic biosensors: Emerging point-of-care applications. *Biosensors & Bioelectronics* **130**, 185-203 (2019).
- 38 Escobedo, C. On-chip nanohole array based sensing: a review. *Lab on a Chip* **13**, 2445-2463 (2013).
- 39 Brolo, A. G., Gordon, R., Leathem, B. & Kavanagh, K. L. Surface plasmon sensor based on the enhanced light transmission through arrays of nanoholes in gold films. *Langmuir* **20**, 4813-4815 (2004).
- 40 Tellez, G. A. C., Hassan, S., Tait, R. N., Berini, P. & Gordon, R. Atomically flat symmetric elliptical nanohole arrays in a gold film for ultrasensitive refractive index sensing. *Lab on a Chip* **13**, 2541-2546 (2013).
- 41 Hahn, C., Hajebifard, A. & Berini, P. Helium focused ion beam direct milling of plasmonic heptamer-arranged nanohole arrays. *Nanophotonics* **9**, 393-399 (2020).
- 42 Garcia-Vidal, F. J., Martin-Moreno, L., Ebbesen, T. W. & Kuipers, L. Light passing through subwavelength apertures. *Reviews of Modern Physics* **82**, 729-787 (2010).
- 43 Palik, E. D. *Handbook of Optical Constants of Solids*. (Academic Press, New York, 1985).
- 44 Yakubovsky, D. I., Arsenin, A. V., Stebunov, Y. V., Fedyanin, D. Y. & Volkov, V. S. Optical constants and structural properties of thin gold films. *Optics Express* **25**, 25574-25587 (2017).
- 45 Berini, P. Long-range surface plasmon polaritons. *Advances in Optics and Photonics* **1**, 484-588 (2009).
- 46 Nishida, M., Hatakenaka, N. & Kadoya, Y. Multipole surface plasmons in metallic nanohole arrays. *Physical Review B* **91** (2015).
- 47 Cargille-Sacher Laboratories Inc., <https://www.cargille.com/>, Accessed June 2020.

7. Conclusions and future work

A. Concluding remarks

In chapter 3, a new Bottom-up fabrication method was developed for producing patterned AuNP arrays of controllable size over large areas on SiO₂ substrates. This approach utilizes a *seeding growth technique combined with a self-assembly of block copolymer micelle loaded with metal precursors* to create ordered arrays of gold nanoparticles with the desired size. It was shown that this novel nanofabrication method offers a new approach to tune the AuNP size and inter-particle spacing while preserving their order. Diblock copolymer self-assembly was used to create AuNP seeds with mean diameters of ~ 5.2 , 8.3 and 10.0 nm, and centre-to-centre inter-particle spacings of ~ 80 , 88 and 62 nm by changing the molar ratio of the gold precursor to pyridine unit. The AuNP seeds with a mean diameter of ~ 10.0 nm were put in a growing chemical solution with the gold precursor in the container. By controlling the growth time and the concentration of the growth solution, the AuNP size and inter-particle spacing were controlled. So, the AuNP seeds were enlarged to mean diameters of ~ 25.7 and 33.0 nm, while simultaneously reducing the edge-to-edge inter-particle spacing to ~ 37 and 29 nm, respectively. Theoretical study and numerical simulations were carried out to determine the size and pattern of NP arrays and predict the LSPP peak. Besides, the bulk sensitivity was calculated and measured to examine the structure for biosensing applications. Unlike conventional top-down approaches, such as E-beam lithography which are expensive and time-consuming, this novel nanofabrication technique is promising for low-cost mass-production of high-quality AuNPs in large-area arrays.

In chapter 4, a metallic-dielectric plasmonic geometry has been studied seeking for Fano resonance in its response. This structure consisted of a *periodic array of gold nano-disks (AuNDs) supported by a Bragg stack*. It was determined that the structure exhibits Fano resonances in its reflectance spectrum. In most nanoplasmonic geometries, the Fano resonance occurs due to the strong near-field coupling between elements of the structure. This happens when the interparticle distances are minimal, which introduces fabrication challenges. However, in the proposed structure, AuNDs on a Bragg stack, no near-field coupling between AuNDs is needed to generate the Fano resonances. So, the AuNDs can be spread far enough

from each other to facilitate fabrication. The origin of the Fano resonances was explained based on the coherent interference between the reflection spectrum of the Bragg stack and the LSPPs on the AuNDs. Fano parameters were deduced by fitting the computational data to the Fano formula. The sensitivity of the system was investigated by calculating bulk sensitivities and the FOM of Fano resonances. The linewidth of the Fano resonances was ~ 9 nm which is much smaller than that of the Bragg stack ~ 100 nm and the LSPR for AuNDs ~ 80 nm. Bulk sensitivities of 44 nm/RIU and a FOM of 4 (RIU)⁻¹ were found, which are high compared to other sensors consisting of AuNPs arrays and operating in almost the same spectral range.

One family of plasmonic nanostructures which supports sharp Fano features is the NP cluster. When two or more plasmonic nano elements are tightly packed, their plasmons couple through near-field interactions, and generate a new set of hybridized plasmon modes. Various plasmonic nanoclusters consisting of two and even more elements have been designed and investigated, seeking for Fano features in their optical responses. In the category of NPs cluster, the heptamer arrangement of NPs has attracted significant attention. This symmetric cluster of NPs consists of a central particle surrounded by six equivalent particles. The interaction between the central particle plasmon and the plasmon of six surrounding particles forms a new set of hybridized plasmons: bonding and antibonding plasmon modes. The complementary structure of heptamer NPs arrangement - heptamer nanohole arrangement - behaves in the same way. However, the complementary structure is more attractive due to its potential to support more excitations such as propagating SPPs, LSPPs, and also woods anomaly (WA). Fano features in the periodic array of HNH arrangement arise due to the interference between the light directly transmitted through the holes, and the light indirectly scattered via the excitation of LSPPs, SPPs, or/and WA waves. In chapter 5, we explained, in detail, how direct milling HeFIB was used to write arrays of 20×20 HNHs in a 55-nm-thick Au film, on a SiO₂ substrate. Each HNH consisted of seven close-packed holes, with a diameter of 100 nm and edge-to-edge inter hole distance of 15 nm.

In chapters 6 and 7, we studied the optical responses of the fabricated gold HNH arrays, numerically and experimentally. The mechanism behind the formation of Fano resonances was explained by observing electromagnetic near-field distribution, and also varying the geometrical parameters, such as the periodicity, metal thickness, inter-hole distance and

diameter of the central hole. The structure was examined for use as a biosensor by providing the bulk sensitivity, surface sensitivity and FOM values for the Fano resonances. The highest bulk (~ 400 nm/RIU) and surface (2 nm/nm) sensitivities were obtained for LSPP Fano resonances, while the highest FoM (24.5 RIU^{-1}) belonged to the WA-SPPs Fano resonance.

List of articles published in refereed journals throughout this PhD are listed below:

- J. Yuan, A. Hajebifard, C. George, P. Berini, and S. Zou, "Ordered gold nanoparticle arrays on glass and their characterization," Journal of Colloid and Interface Science, vol. 410, pp. 1-10, Nov 15 2013, doi: 10.1016/j.jcis.2013.07.070.
- Hajebifard and P. Berini, "Plasmonic Fano interference produced by gold nano-disks on a dielectric Bragg stack," Journal of Applied Physics, vol. 118, no. 9, Sep 7 2015, Art no. 093107, doi: 10.1063/1.4930090.
- A. Hajebifard and P. Berini, "Fano resonances in plasmonic heptamer nanohole arrays," Optics Express, vol. 25, no. 16, pp. 18566-18580, Aug 2017, doi: 10.1364/oe.25.018566.
- C. Hahn, A. Hajebifard, and P. Berini, "Helium focused ion beam direct milling of plasmonic heptamer-arranged nanohole arrays," Nanophotonics, vol. 9, no. 2, pp. 393-399, Feb 2020, doi: 10.1515/nanoph-2019-0385.
- A. Hajebifard, C. Hahn, H. Suleman, Pierre Berini, "Optical response and Fano resonances in arrays of plasmonic heptamer-arranged nanoholes", to be submitted for publication.

List of articles published in refereed conferences throughout this PhD are listed below:

- A. Hajebifard, P. Berini, "Triple Fano resonances in plasmonic heptamer nanohole arrays: Symmetric and asymmetric structures," 2018 International Applied Computational Electromagnetics Society Symposium (Aces), China, 2018 2018.
- A. Hajebifard, P. Berini, and Ieee, "Fano resonances in gold heptamer nano-hole arrays," 2017 Photonics North, Ottawa, Canada, 2017 2017.

- A. Hajebifard, J. Yuan, S. Zou, and P. Berini, "Analysis of Localized Surface Plasmon Resonance in Glass-supported Gold Nanoparticles with a Hexagonal Pattern," in Photonics North Conference, Ottawa, CANADA, 2013

B. Future work

Further exploration of the structures discussed in this thesis would be warranted, as summarized below.

- **Gold HNH array on the tip of a photonic crystal fibre**

Due to its unique geometrical structure, photonic crystal fibres (PCFs) exhibit unique characteristics and capabilities making them potentially interesting for sensing applications. A PCF is usually made of a single material and characterized by a solid core surrounded by a microscopic air hole cladding running along the entire length of the fibre. Optical fibre-based sensors are attractive, due to their compact nature, flexibility in their design, network compatibility, and also the ability for remote and *in situ* measurements. To take advantage of the unique characteristics and capabilities of PCFs, we proposed fabricating an array of HNH on a thin gold film deposited on the tip of a PCF, to be structured as a nanoplasmonic sensor. This structure has been already fabricated and tested. The helium focused ion beam (He FIB) system (Zeiss Orion NanoFab) was used to directly mill through a 60 nm thick gold film on the tip of the fibre, to form high-quality arrays of 20×20 HNHs (spanning an area of about 10×10 μm^2). The supercontinuum laser operating over the wavelength range of 390-2400 nm was used as the light source. A 40× objective was used to launch incident light into the other facet of the PCF fibre. After travelling along the fibre, the light exits from the metallic HNH written on the other tip of the PCF. A 20× objective was used to couple the output light into an optical fibre connected to the Optical spectrometer for analysis. So, the optical transmittance of the array covered sequentially with different fluids of refractive index $n_s = 1.3, 1.35$ or 1.40 were measured. Using those data, the sensitivity of Fano resonances to the refractive index variations of the surrounding medium can be calculated. These results will be prepared as a manuscript for publication (outside the scope of this thesis). Subsequent work would explore the use of such fibres in biosensing applications involving complex fluids (*e.g.*, blood, urine).

- **Gold HNH array for Surface-enhanced Raman applications**

Surface-enhanced Raman scattering (SERS) is an optical spectroscopy technique, in which the localized surface plasmon facilitates the field enhancement mechanism of SERS. Raman scattering is a weak phenomenon because Raman scattering cross-sections are typically very small compared to the cross-section of other optical processes, such as fluorescence. This limits the usage of Raman scattering in applications. This problem can be overcome through surface-enhanced Raman scattering (SERS), in which the Raman signal is enhanced by locating the molecules on the "hot spots" of plasmonic nanostructures. A variety of plasmonic geometries have been designed to improve the capabilities of SERS. We are expecting that the gold HNH array structure can be used as a promising platform for SERS applications. Exciting electromagnetic hot spots associated with various Fano resonances in the metal surface can facilitate ultra-sensitive, subwavelength SERS detection. Numerical studies have been performed to characterize the HNH array for SERS applications. Based on the calculations, some designs with specific geometrical parameters have been proposed and fabricated using FIB milling technique. Next steps involve performing a set of measurements to examine experimentally the SERS performance of the structure.

References

- [1] B. A. Prabowo, A. Purwidyantri, and K. C. Liu, "Surface Plasmon Resonance Optical Sensor: A Review on Light Source Technology," *Biosensors-Basel*, vol. 8, no. 3, Sep 2018, Art no. 80, doi: 10.3390/bios8030080.
- [2] G. Kumar and P. K. Sarswat *Interaction of Surface Plasmon Polaritons with Nanomaterials*. Springer, 2016.
- [3] P. Drude, "Zur Elektronentheorie der Metalle," *Ann. Phys*, pp. 566-613, 1900.
- [4] E. T. Arakawa, M. W. Williams, R. N. Hamm, and R. H. Ritchie, "Effect of Damping on Surface Plasmon Dispersion," *Physical Review Letters*, vol. 31, no. 18, pp. 1127-1129, 1973, doi: 10.1103/PhysRevLett.31.1127.
- [5] N. T. H. University and MaNLab. "Surface Plasmon resonance." (accessed 2020).
- [6] J. J. Mock, R. T. Hill, A. Degiron, S. Zauscher, A. Chilkoti, and D. R. Smith, "Distance-dependent plasmon resonant coupling between a gold nanoparticle and gold film," *Nano Letters*, vol. 8, no. 8, pp. 2245-2252, Aug 2008, doi: 10.1021/nl080872f.
- [7] C. F. Bohren and D. R. Huffman, *Absorption and scattering of light by small particles*. Wiley-VCH Verlag GmbH, 1998.
- [8] K. M. Mayer and J. H. Hafner, "Localized Surface Plasmon Resonance Sensors," *Chemical Reviews*, vol. 111, no. 6, pp. 3828-3857, Jun 2011, doi: 10.1021/cr100313v.
- [9] C. Hahn, A. Hajebifard, and P. Berini, "Helium focused ion beam direct milling of plasmonic heptamer-arranged nanohole arrays," *Nanophotonics*, vol. 9, no. 2, pp. 393-399, Feb 2020, doi: 10.1515/nanoph-2019-0385.
- [10] M. Ananth *et al.*, "Creating Nanohole Arrays with the Helium Ion Microscope," in *Conference on Scanning Microscopies 2011 - Advanced Microscopy Technologies for Defense, Homeland Security, Forensic, Life, Environmental, and Industrial Sciences*, Orlando, FL, Apr 26-28 2011, vol. 8036, in Proceedings of SPIE, 2011, doi: 10.1117/12.887497. [Online]. Available: <Go to ISI>://WOS:000292651000015
- [11] Y. S. Joe, A. M. Satanin, and C. S. Kim, "Classical analogy of Fano resonances," *Physica Scripta*, vol. 74, no. 2, pp. 259-266, Aug 2006, doi: 10.1088/0031-8949/74/2/020.
- [12] Y. Sonnefraud *et al.*, "Experimental Realization of Subradiant, Superradiant, and Fano Resonances in Ring/Disk Plasmonic Nanocavities," *Acs Nano*, vol. 4, no. 3, pp. 1664-1670, Mar 2010, doi: 10.1021/nn901580r.
- [13] M. Wang, M. Cao, X. Chen, and N. Gu, "Subradiant Plasmon Modes in Multilayer Metal-Dielectric Nanoshells," *Journal of Physical Chemistry C*, vol. 115, no. 43, pp. 20920-20925, Nov 2011, doi: 10.1021/jp205736d.
- [14] A. Artar, A. A. Yanik, and H. Altug, "Directional Double Fano Resonances in Plasmonic Hetero-Oligomers," *Nano Letters*, vol. 11, no. 9, pp. 3694-3700, Sep 2011, doi: 10.1021/nl201677h.
- [15] J. A. Fan *et al.*, "Fano-like Interference in Self-Assembled Plasmonic Quadramer Clusters," *Nano Letters*, vol. 10, no. 11, pp. 4680-4685, Nov 2010, doi: 10.1021/nl1029732.
- [16] N. M. Ashcroft, N. David, *Solid State Physics* Brooks Cole, 1976.
- [17] H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*. Springer, 1988.
- [18] Kretschm.E and H. Raether, "RADIATIVE DECAY OF NON RADIATIVE SURFACE PLASMONS EXCITED BY LIGHT," *Zeitschrift Fur Naturforschung Part a-Astrophysik*

- Physik Und Physikalische Chemie*, vol. A 23, no. 12, pp. 2135-&, 1968, doi: 10.1515/zna-1968-1247.
- [19] E. D. Palik, *Handbook of Optical Constants of Solids*. Academic Press, New York, 1985.
 - [20] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters*. Springer, 1999.
 - [21] J. M. Pitarke, V. M. Silkin, E. V. Chulkov, and P. M. Echenique, "Theory of surface plasmons and surface-plasmon polaritons," *Reports on Progress in Physics*, vol. 70, no. 1, pp. 1-87, Jan 2007, doi: 10.1088/0034-4885/70/1/r01.
 - [22] S. A. Maier *Plasmonics: Fundamentals and Applications*. Springer-Verlag, 2007, pp. 21–34.
 - [23] A. Maradudin, J. R. Sambles, and W. L. Barnes, *Modern Plasmonics*. Elsevier Science, 2014.
 - [24] M. L. Brongersma and P. G. Kik *Surface Plasmon Nanophotonics*. Springer, 2007.
 - [25] V. M. Agranovich and D. L. Mills, *Electromagnetic Waves at Surfaces and Interfaces*. North-Holland Publishing Company, 1982.
 - [26] R. Schasfoort, A. B M Tudos , and J, "Handbook of Surface Plasmon Resonance," ed: Royal Society of Chemistry, 2008.
 - [27] W. L. Barnes, "Particle plasmons: Why shape matters," *American Journal of Physics*, vol. 84, no. 8, pp. 593-601, Aug 2016, doi: 10.1119/1.4948402.
 - [28] H. C. Wang, "Plasmonic refractive index sensing using strongly coupled metal nanoantennas: nonlocal limitations," *Scientific Reports*, vol. 8, Jun 2018, Art no. 9589, doi: 10.1038/s41598-018-28011-x.
 - [29] K. Sokolov, G. Chumanov, and T. M. Cotton, "Enhancement of molecular fluorescence near the surface of colloidal metal films," *Analytical Chemistry*, vol. 70, no. 18, pp. 3898-3905, Sep 1998, doi: 10.1021/ac9712310.
 - [30] J. F. Li, C. Y. Li, and R. F. Aroca, "Plasmon-enhanced fluorescence spectroscopy," *Chemical Society Reviews*, vol. 46, no. 13, pp. 3962-3979, Jul 2017, doi: 10.1039/c7cs00169j.
 - [31] C. Y. Chen and E. Burstein, "GIANT RAMAN-SCATTERING BY MOLECULES AT METAL-ISLAND FILMS," *Physical Review Letters*, vol. 45, no. 15, pp. 1287-1291, 1980, doi: 10.1103/PhysRevLett.45.1287.
 - [32] S. Y. Wu, Y. Shen, and C. J. Jin, "Surface-enhanced Raman scattering induced by the coupling of the guided mode with localized surface plasmon resonances," *Nanoscale*, vol. 11, no. 30, pp. 14164-14173, Aug 2019, doi: 10.1039/c9nr02831e.
 - [33] S. Unser, I. Bruzas, J. He, and L. Sagle, "Localized Surface Plasmon Resonance Biosensing: Current Challenges and Approaches," *Sensors*, vol. 15, no. 7, pp. 15684-15716, Jul 2015, doi: 10.3390/s150715684.
 - [34] M. M. Alvarez, J. T. Khoury, T. G. Schaaff, M. N. Shafigullin, I. Vezmar, and R. L. Whetten, "Optical absorption spectra of nanocrystal gold molecules," *Journal of Physical Chemistry B*, vol. 101, no. 19, pp. 3706-3712, May 1997, doi: 10.1021/jp962922n.
 - [35] M. Kanehara, H. Koike, T. Yoshinaga, and T. Teranishi, "Indium Tin Oxide Nanoparticles with Compositionally Tunable Surface Plasmon Resonance Frequencies in the Near-IR Region," *Journal of the American Chemical Society*, vol. 131, no. 49, pp. 17736-17737, Dec 2009, doi: 10.1021/ja9064415.
 - [36] J. M. Luther, P. K. Jain, T. Ewers, and A. P. Alivisatos, "Localized surface plasmon resonances arising from free carriers in doped quantum dots," *Nature Materials*, vol. 10, no. 5, pp. 361-366, May 2011, doi: 10.1038/nmat3004.

- [37] F. Hao, P. Nordlander, M. T. Burnett, and S. A. Maier, "Enhanced tunability and linewidth sharpening of plasmon resonances in hybridized metallic ring/disk nanocavities," *Physical Review B*, vol. 76, no. 24, Dec 2007, Art no. 245417, doi: 10.1103/PhysRevB.76.245417.
- [38] J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao, and R. P. Van Duyne, "Biosensing with plasmonic nanosensors," *Nature Materials*, vol. 7, no. 6, pp. 442-453, Jun 2008, doi: 10.1038/nmat2162.
- [39] A. G. Brolo, "Plasmonics for future biosensors," *Nature Photonics*, vol. 6, no. 11, pp. 709-713, Nov 2012, doi: 10.1038/nphoton.2012.266.
- [40] S. W. Zeng *et al.*, "Graphene-Gold Metasurface Architectures for Ultrasensitive Plasmonic Biosensing," *Advanced Materials*, vol. 27, no. 40, pp. 6163-6169, Oct 2015, doi: 10.1002/adma.201501754.
- [41] A. G. Brolo, R. Gordon, B. Leathem, and K. L. Kavanagh, "Surface plasmon sensor based on the enhanced light transmission through arrays of nanoholes in gold films," *Langmuir*, vol. 20, no. 12, pp. 4813-4815, Jun 2004, doi: 10.1021/la0493621.
- [42] Y. Iwasaki, T. Horiuchi, and O. Niwa, "Detection of electrochemical enzymatic reactions by surface plasmon resonance measurement," *Analytical Chemistry*, vol. 73, no. 7, pp. 1595-1598, Apr 2001, doi: 10.1021/ac0012851.
- [43] J. Homola, S. S. Yee, and G. Gauglitz, "Surface plasmon resonance sensors: review," *Sensors and Actuators B-Chemical*, vol. 54, no. 1-2, pp. 3-15, Jan 1999, doi: 10.1016/s0925-4005(98)00321-9.
- [44] K. V. Sreekanth, S. W. Zeng, K. T. Yong, and T. Yu, "Sensitivity enhanced biosensor using graphene-based one-dimensional photonic crystal," *Sensors and Actuators B-Chemical*, vol. 182, pp. 424-428, Jun 2013, doi: 10.1016/j.snb.2013.03.039.
- [45] J. Homola, *Surface Plasmon Resonance Based Sensors*. Springer, 2006.
- [46] H. W. Gao, J. Henzie, M. H. Lee, and T. W. Odom, "Screening plasmonic materials using pyramidal gratings," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 105, no. 51, pp. 20146-20151, Dec 2008, doi: 10.1073/pnas.0809034105.
- [47] Y. Lee, S. J. Kim, H. Park, and B. Lee, "Metamaterials and Metasurfaces for Sensor Applications," *Sensors*, vol. 17, no. 8, Aug 2017, Art no. 1726, doi: 10.3390/s17081726.
- [48] K. V. Sreekanth *et al.*, "Enhancing the Angular Sensitivity of Plasmonic Sensors Using Hyperbolic Metamaterials," *Advanced Optical Materials*, vol. 4, no. 11, pp. 1767-1772, Nov 2016, doi: 10.1002/adom.201600448.
- [49] W. Brullot, "Development, synthesis and characterization of multifunctional nanomaterials," Université de Namur, 2014.
- [50] M. Loos "Carbon Nanotube Reinforced Composites," ed: Elsevier, 2014, pp. 1-36.
- [51] D. Bohm and D. Pines, "A Collective Description of Electron Interactions . I. Magnetic Interactions," *Physical Review*, vol. 82, no. 5, pp. 625-634, 1951, doi: 10.1103/PhysRev.82.625.
- [52] W. L. Barnes, A. Dereux, and T. W. Ebbesen, "Surface plasmon subwavelength optics," *Nature*, vol. 424, no. 6950, pp. 824-830, Aug 14 2003, doi: 10.1038/nature01937.
- [53] A. E. Kryukov, Y. K. Kim, and J. B. Ketterson, "Surface plasmon scanning near-field optical microscopy," *Journal of Applied Physics*, vol. 82, no. 11, pp. 5411-5415, Dec 1997, doi: 10.1063/1.365568.

- [54] J. Ye *et al.*, "Plasmonic Nanoclusters: Near Field Properties of the Fano Resonance Interrogated with SERS," *Nano Letters*, vol. 12, no. 3, pp. 1660-1667, Mar 2012, doi: 10.1021/nl3000453.
- [55] C. Sonnichsen *et al.*, "Drastic reduction of plasmon damping in gold nanorods," *Physical Review Letters*, vol. 88, no. 7, Feb 2002, Art no. 077402, doi: 10.1103/PhysRevLett.88.077402.
- [56] S. J. Oldenburg, J. B. Jackson, S. L. Westcott, and N. J. Halas, "Infrared extinction properties of gold nanoshells," *Applied Physics Letters*, vol. 75, no. 19, pp. 2897-2899, Nov 1999, doi: 10.1063/1.125183.
- [57] J. Aizpurua, P. Hanarp, D. S. Sutherland, M. Kall, G. W. Bryant, and F. J. G. de Abajo, "Optical properties of gold nanorings," *Physical Review Letters*, vol. 90, no. 5, Feb 2003, Art no. 057401, doi: 10.1103/PhysRevLett.90.057401.
- [58] T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio, and P. A. Wolff, "Extraordinary optical transmission through sub-wavelength hole arrays," *Nature*, vol. 391, no. 6668, pp. 667-669, Feb 1998, doi: 10.1038/35570.
- [59] E. Altewischer, M. P. van Exter, and J. P. Woerdman, "Plasmon-assisted transmission of entangled photons," *Nature*, vol. 418, no. 6895, pp. 304-306, Jul 2002, doi: 10.1038/nature00869.
- [60] B. J. Wiley, S. H. Im, Z. Y. Li, J. McLellan, A. Siekkinen, and Y. N. Xia, "Maneuvering the surface plasmon resonance of silver nanostructures through shape-controlled synthesis," *Journal of Physical Chemistry B*, vol. 110, no. 32, pp. 15666-15675, Aug 2006, doi: 10.1021/jp0608628.
- [61] D. Radziuk and H. Moehwald, "Prospects for plasmonic hot spots in single molecule SERS towards the chemical imaging of live cells," *Physical Chemistry Chemical Physics*, vol. 17, no. 33, pp. 21072-21093, 2015, doi: 10.1039/c4cp04946b.
- [62] J. Q. Liu, "Plasmonic dispersion engineering based on the interaction between the dark mode and PSPs mode," *Journal of Physics D-Applied Physics*, vol. 47, no. 43, Oct 2014, Art no. 435301, doi: 10.1088/0022-3727/47/43/435301.
- [63] H. K. Yu, Y. S. Peng, Y. Yang, and Z. Y. Li, "Plasmon-enhanced light-matter interactions and applications," *Npj Computational Materials*, vol. 5, Apr 2019, Art no. 45, doi: 10.1038/s41524-019-0184-1.
- [64] E. Hao and G. C. Schatz, "Electromagnetic fields around silver nanoparticles and dimers," *Journal of Chemical Physics*, vol. 120, no. 1, pp. 357-366, Jan 2004, doi: 10.1063/1.1629280.
- [65] S. J. Barrow, A. M. Funston, D. E. Gomez, T. J. Davis, and P. Mulvaney, "Surface Plasmon Resonances in Strongly Coupled Gold Nanosphere Chains from Monomer to Hexamer," *Nano Letters*, vol. 11, no. 10, pp. 4180-4187, Oct 2011, doi: 10.1021/nl202080a.
- [66] H. X. Xu, J. Aizpurua, M. Kall, and P. Apell, "Electromagnetic contributions to single-molecule sensitivity in surface-enhanced Raman scattering," *Physical Review E*, vol. 62, no. 3, pp. 4318-4324, Sep 2000, doi: 10.1103/PhysRevE.62.4318.
- [67] S. Kasani, K. Curtin, and N. Q. Wu, "A review of 2D and 3D plasmonic nanostructure array patterns: fabrication, tight management and sensing applications," *Nanophotonics*, vol. 8, no. 12, pp. 2065-2089, Dec 2019, doi: 10.1515/nanoph-2019-0158.

- [68] A. Prasad, J. Choi, Z. Jia, S. Park, and M. R. Gartia, "Nanohole array plasmonic biosensors: Emerging point-of-care applications," *Biosensors & Bioelectronics*, vol. 130, pp. 185-203, Apr 2019, doi: 10.1016/j.bios.2019.01.037.
- [69] A. E. Cetin, D. Etezadi, B. C. Galarreta, M. P. Busson, Y. Eksioglu, and H. Altug, "Plasmonic Nanohole Arrays on a Robust Hybrid Substrate for Highly Sensitive Label-Free Biosensing," *Acs Photonics*, vol. 2, no. 8, pp. 1167-1174, Aug 2015, doi: 10.1021/acsp Photonics.5b00242.
- [70] A. E. Cetin *et al.*, "Plasmonic Sensor Could Enable Label-Free DNA Sequencing," *Acs Sensors*, vol. 3, no. 3, pp. 561-568, Mar 2018, doi: 10.1021/acssensors.7b00957.
- [71] Z. Zeng *et al.*, "Protein Trapping in Plasmonic Nanoslit and Nanoledge Cavities: The Behavior and Sensing," *Analytical Chemistry*, vol. 89, no. 10, pp. 5221-5229, May 2017, doi: 10.1021/acs.analchem.6b04493.
- [72] A. E. Grigorescu and C. W. Hagen, "Resists for sub-20-nm electron beam lithography with a focus on HSQ: state of the art," *Nanotechnology*, vol. 20, no. 29, Jul 2009, Art no. 292001, doi: 10.1088/0957-4484/20/29/292001.
- [73] S. Kumar, S. Cherukulappurath, T. W. Johnson, and S. H. Oh, "Millimeter-Sized Suspended Plasmonic Nanohole Arrays for Surface-Tension-Driven Flow-Through SERS," *Chemistry of Materials*, vol. 26, no. 22, pp. 6523-6530, Nov 2014, doi: 10.1021/cm5031848.
- [74] T. A. Green, "Gold etching for microfabrication," *Gold Bulletin*, vol. 47, no. 3, pp. 205-216, 2014, doi: 10.1007/s13404-014-0143-z.
- [75] M. Köhler, "Encyclopedia of Microfluidics and Nanofluidics," ed: Springer, 2008.
- [76] N. C. Lindquist, P. Nagpal, K. M. McPeak, D. J. Norris, and S. H. Oh, "Engineering metallic nanostructures for plasmonics and nanophotonics," *Reports on Progress in Physics*, vol. 75, no. 3, Mar 2012, Art no. 036501, doi: 10.1088/0034-4885/75/3/036501.
- [77] S. P. Lyman, J. L. Jackel, and P. L. Liu, "LIFT-OFF OF THICK METAL LAYERS USING MULTILAYER RESIST," *Journal of Vacuum Science & Technology*, vol. 19, no. 4, pp. 1325-1328, 1981, doi: 10.1116/1.571269.
- [78] J. Barnett, U. Plachetka, C. Nowak, and H. Wackerbarth, "Highly periodic Au nano-disc arrays for plasmon-resonant SERS structures on fused silica using UV-NIL based double-layer lift-off process," *Microelectronic Engineering*, vol. 172, pp. 45-48, Mar 2017, doi: 10.1016/j.mee.2017.02.020.
- [79] C. Hahn *et al.*, "Nanofabrication of plasmonic structures on insulating substrates by resist-on-metal bilayer lift-off," *Nanotechnology*, vol. 30, no. 5, Feb 2019, Art no. 054003, doi: 10.1088/1361-6528/aaefd6.
- [80] A. A. Yanik *et al.*, "Seeing protein monolayers with naked eye through plasmonic Fano resonances," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 108, no. 29, pp. 11784-11789, Jul 2011, doi: 10.1073/pnas.1101910108.
- [81] A. A. Yanik, M. Huang, A. Artar, T. Y. Chang, and H. Altug, "Integrated nanoplasmonic-nanofluidic biosensors with targeted delivery of analytes," *Applied Physics Letters*, vol. 96, no. 2, Jan 2010, Art no. 021101, doi: 10.1063/1.3290633.
- [82] R. P. Seisyan, "Nanolithography in microelectronics: A review," *Technical Physics*, vol. 56, no. 8, pp. 1061-1073, Aug 2011, doi: 10.1134/s1063784211080214.
- [83] M. Soler, A. Belushkin, A. Cavallini, C. Kebbi-Beghdadi, G. Greub, and H. Altug, "Multiplexed nanoplasmonic biosensor for one-step simultaneous detection of Chlamydia

- trachomatis and Neisseria gonorrhoeae in urine," *Biosensors & Bioelectronics*, vol. 94, pp. 560-567, Aug 2017, doi: 10.1016/j.bios.2017.03.047.
- [84] C. Lu and R. H. Lipson, "Interference lithography: a powerful tool for fabricating periodic structures," *Laser & Photonics Reviews*, vol. 4, no. 4, pp. 568-580, Jul 2010, doi: 10.1002/lpor.200810061.
- [85] J. H. Seo *et al.*, "Nanopatterning by Laser Interference Lithography: Applications to Optical Devices," *Journal of Nanoscience and Nanotechnology*, vol. 14, no. 2, pp. 1521-1532, Feb 2014, doi: 10.1166/jnn.2014.9199.
- [86] V. Auzelyte *et al.*, "Extreme ultraviolet interference lithography at the Paul Scherrer Institut," *Journal of Micro-Nanolithography Mems and Moems*, vol. 8, no. 2, Apr-Jun 2009, Art no. 021204, doi: 10.1117/1.3116559.
- [87] N. Mojarad, J. Gobrecht, and Y. Ekinici, "Interference lithography at EUV and soft X-ray wavelengths: Principles, methods, and applications," *Microelectronic Engineering*, vol. 143, pp. 55-63, Aug 2015, doi: 10.1016/j.mee.2015.03.047.
- [88] A. S. Gangnaik, Y. M. Georgiev, and J. D. Holmes, "New Generation Electron Beam Resists: A Review," *Chemistry of Materials*, vol. 29, no. 5, pp. 1898-1917, Mar 2017, doi: 10.1021/acs.chemmater.6b03483.
- [89] R. Gillibert, J. Q. Huang, Y. Zhang, W. L. Fu, and M. L. de la Chapelle, "Explosive detection by Surface Enhanced Raman Scattering," *Trac-Trends in Analytical Chemistry*, vol. 105, pp. 166-172, Aug 2018, doi: 10.1016/j.trac.2018.03.018.
- [90] M. C. Traub, W. Longsine, and V. N. Truskett, "Advances in Nanoimprint Lithography," *Annual Review of Chemical and Biomolecular Engineering*, Vol 7, vol. 7, pp. 583-604, 2016, doi: 10.1146/annurev-chembioeng-080615-034635.
- [91] S. Y. Chou, P. R. Krauss, and P. J. Renstrom, "Nanoimprint lithography," *Journal of Vacuum Science & Technology B*, vol. 14, no. 6, pp. 4129-4133, Nov-Dec 1996, doi: 10.1116/1.588605.
- [92] M. Khoury and D. K. Ferry, "Effect of molecular weight on poly(methyl methacrylate) resolution," *Journal of Vacuum Science & Technology B*, vol. 14, no. 1, pp. 75-79, Jan-Feb 1996, doi: 10.1116/1.588437.
- [93] H. J. Qi *et al.*, "Large-area gold nanohole arrays fabricated by one-step method for surface plasmon resonance biochemical sensing," *Science China-Life Sciences*, vol. 61, no. 4, pp. 476-482, Apr 2018, doi: 10.1007/s11427-017-9270-x.
- [94] T. I. Wong *et al.*, "High throughput and high yield nanofabrication of precisely designed gold nanohole arrays for fluorescence enhanced detection of biomarkers," *Lab on a Chip*, vol. 13, no. 12, pp. 2405-2413, 2013, doi: 10.1039/c3lc41396a.
- [95] H. Lee and G. Y. Jung, "Full wafer scale near zero residual nano-imprinting lithography using UV curable monomer solution," *Microelectronic Engineering*, vol. 77, no. 1, pp. 42-47, Jan 2005, doi: 10.1016/j.mee.2004.08.008.
- [96] Y. F. Chen, "Applications of nanoimprint lithography/hot embossing: a review," *Applied Physics a-Materials Science & Processing*, vol. 121, no. 2, pp. 451-465, Nov 2015, doi: 10.1007/s00339-015-9071-x.
- [97] E. J. R. Vesseur, F. J. G. de Abajo, and A. Polman, "Modal Decomposition of Surface-Plasmon Whispering Gallery Resonators," *Nano Letters*, vol. 9, no. 9, pp. 3147-3150, Sep 2009, doi: 10.1021/nl9012826.

- [98] Y. H. Lanyon *et al.*, "Fabrication of nanopore array electrodes by focused ion beam milling," *Analytical Chemistry*, vol. 79, no. 8, pp. 3048-3055, Apr 2007, doi: 10.1021/ac061878x.
- [99] N. Ocelic and R. Hillenbrand, "Subwavelength-scale tailoring of surface phonon polaritons by focused ion-beam implantation," *Nature Materials*, vol. 3, no. 9, pp. 606-609, Sep 2004, doi: 10.1038/nmat1194.
- [100] Y. Chen *et al.*, "Rapid Focused Ion Beam Milling Based Fabrication of Plasmonic Nanoparticles and Assemblies via "Sketch and Peel" Strategy," *Acs Nano*, vol. 10, no. 12, pp. 11228-11236, Dec 2016, doi: 10.1021/acsnano.6b06290.
- [101] P. Xue *et al.*, "Graded nanowell arrays: a fine plasmonic "library" with an adjustable spectral range," *Nanoscale*, vol. 9, no. 20, pp. 6724-6733, May 28 2017, doi: 10.1039/c7nr01505d.
- [102] V. Cremers, R. L. Puurunen, and J. Dendooven, "Conformality in atomic layer deposition: Current status overview of analysis and modelling," *Applied Physics Reviews*, vol. 6, no. 2, Jun 2019, Art no. 021302, doi: 10.1063/1.5060967.
- [103] Y. Q. Cao *et al.*, "Atomic-Layer-Deposition Assisted Formation of Wafer-Scale Double-Layer Metal Nanoparticles with Tunable Nanogap for Surface-Enhanced Raman Scattering," *Scientific Reports*, vol. 7, Jul 2017, Art no. 5161, doi: 10.1038/s41598-017-05533-4.
- [104] A. V. Whitney *et al.*, "Localized surface plasmon resonance nanosensor: A high-resolution distance-dependence study using atomic layer deposition," *Journal of Physical Chemistry B*, vol. 109, no. 43, pp. 20522-20528, Nov 2005, doi: 10.1021/jp0540656.
- [105] A. Klinkova, R. M. Choueiri, and E. Kumacheva, "Self-assembled plasmonic nanostructures," *Chemical Society Reviews*, vol. 43, no. 11, pp. 3976-3991, 2014, doi: 10.1039/c3cs60341e.
- [106] H. Kitching, M. J. Shiers, A. J. Kenyon, and I. P. Parkin, "Self-assembly of metallic nanoparticles into one dimensional arrays," *Journal of Materials Chemistry A*, vol. 1, no. 24, pp. 6985-6999, 2013, doi: 10.1039/c3ta00089c.
- [107] Y. Weizmann, "Surface encoding of nanoparticles for self-assembly and plasmonic bioapplications," *Abstracts of Papers of the American Chemical Society*, vol. 256, Aug 2018.
- [108] J. A. Fan *et al.*, "Self-Assembled Plasmonic Nanoparticle Clusters," *Science*, vol. 328, no. 5982, pp. 1135-1138, May 2010, doi: 10.1126/science.1187949.
- [109] G. De *et al.*, "Silver nanocrystals in silica by sol-gel processing," *Journal of Non-Crystalline Solids*, vol. 194, no. 3, pp. 225-234, Feb 1996, doi: 10.1016/0022-3093(91)00511-f.
- [110] K. V. A. Kumar, A. Balu, A. Ramachandran, N. V. Unnikrishnan, and N. B. Selvaraj, "Sol-gel synthesized plasmonic nanoparticles and their integration into dye sensitized solar cells," *Applied Surface Science*, vol. 491, pp. 670-674, Oct 2019, doi: 10.1016/j.apsusc.2019.05.344.
- [111] O. Ujsaghy, J. Kroha, L. Szunyogh, and A. Zawadowski, "Theory of the Fano resonance in the STM tunneling density of states due to a single Kondo impurity," *Physical Review Letters*, vol. 85, no. 12, pp. 2557-2560, Sep 2000, doi: 10.1103/PhysRevLett.85.2557.
- [112] A. C. Johnson, C. M. Marcus, M. P. Hanson, and A. C. Gossard, "Coulomb-modified Fano resonance in a one-lead quantum dot," *Physical Review Letters*, vol. 93, no. 10, Sep 2004, Art no. 106803, doi: 10.1103/PhysRevLett.93.106803.

- [113] A. Attaran *et al.*, "Circuit Model of Fano Resonance on Tetramers, Pentamers, and Broken Symmetry Pentamers," *Plasmonics*, vol. 9, no. 6, pp. 1303-1313, Dec 2014, doi: 10.1007/s11468-014-9743-y.
- [114] J. Butet and O. J. F. Martin, "Fano resonances in the nonlinear optical response of coupled plasmonic nanostructures," *Optics Express*, vol. 22, no. 24, pp. 29693-29707, Dec 2014, doi: 10.1364/oe.22.029693.
- [115] F. Zangeneh-Nejad and R. Fleury, "Topological Fano Resonances," *Physical Review Letters*, vol. 122, no. 1, Jan 2019, Art no. 014301, doi: 10.1103/PhysRevLett.122.014301.
- [116] S. E. A. Orrigo *et al.*, "Core excited Fano-resonances in exotic nuclei," *Physics Letters B*, vol. 633, no. 4-5, pp. 469-473, Feb 2006, doi: 10.1016/j.physletb.2005.12.046.
- [117] U. Fano, "EFFECTS OF CONFIGURATION INTERACTION ON INTENSITIES AND PHASE SHIFTS," *Physical Review*, vol. 124, no. 6, pp. 1866-&, 1961, doi: 10.1103/PhysRev.124.1866.
- [118] N. Martensson *et al.*, "Coherent and incoherent processes in resonant photoemission," *Applied Physics a-Materials Science & Processing*, vol. 65, no. 2, pp. 159-167, Aug 1997, doi: 10.1007/s003390050559.
- [119] U. Fano, "Sullo spettro di assorbimento dei gas nobilipresso il limite dello spettro d'arco," *Nuovo Cimento*, vol. 12, pp. 154-161, 1935.
- [120] H. Beutler, "Über Absorptionsserien von Argon, Krypton und Xenon zu Termen zwischen den beiden Ionisierungsgrenzen 2P_{3/2}/0 und 2P_{1/2}/0
" *Zeitschrift für Physik* volume, vol. 93, pp. 177-196, 1935.
- [121] U. Fano, "CITATION CLASSICS - EFFECTS OF CONFIGURATION INTERACTION ON INTENSITIES AND PHASE-SHIFTS," *Current Contents*, no. 27, pp. 8-8, 1977.
- [122] R. W. Wood, "On a remarkable case of uneven distribution of light in a diffraction grating spectrum," *Philosophical Magazine*, vol. 4, no. 19-24, pp. 396-402, Jul-Dec 1902, doi: 10.1080/14786440209462857.
- [123] R. W. Wood, "Anomalous diffraction gratings," *Physical Review*, vol. 48, no. 12, pp. 928-936, Dec 1935, doi: 10.1103/PhysRev.48.928.
- [124] U. Fano, "Some theoretical considerations on anomalous diffraction gratings," *Physical Review*, vol. 50, no. 6, pp. 573-573, Sep 1936, doi: 10.1103/PhysRev.50.573.
- [125] U. Fano, "On the anomalous diffraction gratings II," *Physical Review*, vol. 51, no. 4, pp. 288-288, Feb 1937, doi: 10.1103/PhysRev.51.288.
- [126] U. Fano, "Zur theorie der intensitätsanomalien der beugung," *Annalen der Physik* vol. 424, pp. 393-443, 1938.
- [127] U. Fano, "The theory of anomalous diffraction gratings and of quasi-stationary waves on metallic surfaces (Sommerfeld's waves)," *Journal of the Optical Society of America*, vol. 31, no. 3, pp. 213-222, Mar 1941, doi: 10.1364/josa.31.000213.
- [128] A. E. Miroshnichenko, S. Flach, and Y. S. Kivshar, "Fano resonances in nanoscale structures," *Reviews of Modern Physics*, vol. 82, no. 3, pp. 2257-2298, Aug 2010, doi: 10.1103/RevModPhys.82.2257.
- [129] G. Piao, R. A. Lewis, and P. Fisher, "FANO RESONANCES IN THE ABSORPTION-SPECTRUM OF SINGLY IONIZED ZINC IN GERMANIUM," *Solid State Communications*, vol. 75, no. 10, pp. 835-838, Sep 1990, doi: 10.1016/0038-1098(90)90761-y.

- [130] J. U. Nockel and A. D. Stone, "RESONANCE LINE-SHAPES IN QUASI-ONE-DIMENSIONAL SCATTERING," *Physical Review B*, vol. 50, no. 23, pp. 17415-17432, Dec 1994, doi: 10.1103/PhysRevB.50.17415.
- [131] S. Lee and B. Kim, "Direct evaluation of the asymmetry parameters for isolated resonances," *Journal of Physics B-Atomic Molecular and Optical Physics*, vol. 33, no. 17, pp. 3441-3448, Sep 2000, doi: 10.1088/0953-4075/33/17/321.
- [132] A. R. P. Rau, "Perspectives on the Fano resonance formula," *Physica Scripta*, vol. 69, no. 1, pp. C10-C13, Jan 2004, doi: 10.1238/Physica.Regular.069a00C10.
- [133] B. Luk'yanchuk *et al.*, "The Fano resonance in plasmonic nanostructures and metamaterials," *Nature Materials*, vol. 9, no. 9, pp. 707-715, Sep 2010, doi: 10.1038/nmat2810.
- [134] Z. J. Yang, Z. H. Hao, H. Q. Lin, and Q. Q. Wang, "Plasmonic Fano resonances in metallic nanorod complexes," *Nanoscale*, vol. 6, no. 10, pp. 4985-4997, 2014, doi: 10.1039/c3nr06502b.
- [135] S. D. Emami *et al.*, "Fano Resonance on Plasmonic Nanostructures," *3rd International Conference on Photonics 2012 (Icp 2012)*, pp. 149-153, 2012.
- [136] M. Frimmer, T. Coenen, and A. F. Koenderink, "Signature of a Fano Resonance in a Plasmonic Metamolecule's Local Density of Optical States," *Physical Review Letters*, vol. 108, no. 7, Feb 2012, Art no. 077404, doi: 10.1103/PhysRevLett.108.077404.
- [137] Z. Y. Fang, J. Y. Cai, Z. B. Yan, P. Nordlander, N. J. Halas, and X. Zhu, "Removing a Wedge from a Metallic Nanodisk Reveals a Fano Resonance," *Nano Letters*, vol. 11, no. 10, pp. 4475-4479, Oct 2011, doi: 10.1021/nl202804y.
- [138] J. Kim *et al.*, "Fano resonance in crossed carbon nanotubes," *Physical Review Letters*, vol. 90, no. 16, Apr 2003, Art no. 166403, doi: 10.1103/PhysRevLett.90.166403.
- [139] F. Hao, P. Nordlander, Y. Sonnefraud, P. Van Dorpe, and S. A. Maier, "Tunability of Subradiant Dipolar and Fano-Type Plasmon Resonances in Metallic Ring/Disk Cavities: Implications for Nanoscale Optical Sensing," *Acs Nano*, vol. 3, no. 3, pp. 643-652, Mar 2009, doi: 10.1021/nn900012r.
- [140] F. Hao, Y. Sonnefraud, P. Van Dorpe, S. A. Maier, N. J. Halas, and P. Nordlander, "Symmetry Breaking in Plasmonic Nanocavities: Subradiant LSPR Sensing and a Tunable Fano Resonance," *Nano Letters*, vol. 8, no. 11, pp. 3983-3988, Nov 2008, doi: 10.1021/nl802509r.
- [141] S. Panaro *et al.*, "Dark to Bright Mode Conversion on Dipolar Nanoantennas: A Symmetry-Breaking Approach," *Acs Photonics*, vol. 1, no. 4, pp. 310-314, Apr 2014, doi: 10.1021/ph500044w.
- [142] S. L. Zou, N. Janel, and G. C. Schatz, "Silver nanoparticle array structures that produce remarkably narrow plasmon lineshapes," *Journal of Chemical Physics*, vol. 120, no. 23, pp. 10871-10875, Jun 2004, doi: 10.1063/1.1760740.
- [143] L. L. Zhao, K. L. Kelly, and G. C. Schatz, "The extinction spectra of silver nanoparticle arrays: Influence of array structure on plasmon resonance wavelength and width," *Journal of Physical Chemistry B*, vol. 107, no. 30, pp. 7343-7350, Jul 2003, doi: 10.1021/jp034235j.
- [144] K. T. Carron, W. Fluhr, M. Meier, A. Wokaun, and H. W. Lehmann, "RESONANCES OF TWO-DIMENSIONAL PARTICLE GRATINGS IN SURFACE-ENHANCED RAMAN-SCATTERING," *Journal of the Optical Society of America B-Optical Physics*, vol. 3, no. 3, pp. 430-440, Mar 1986, doi: 10.1364/josab.3.000430.

- [145] S. H. Chang, S. K. Gray, and G. C. Schatz, "Surface plasmon generation and light transmission by isolated nanoholes and arrays of nanoholes in thin metal films," *Optics Express*, vol. 13, no. 8, pp. 3150-3165, Apr 2005, doi: 10.1364/opex.13.003150.
- [146] K. L. van der Molen, K. J. Klein Koerkamp, S. Enoch, F. B. Segerink, N. F. van Hulst, and L. Kuipers, "Role of shape and localized resonances in extraordinary transmission through periodic arrays of subwavelength holes: Experiment and theory," *Physical Review B*, vol. 72, no. 4, Jul 2005, Art no. 045421, doi: 10.1103/PhysRevB.72.045421.
- [147] H. Gao *et al.*, "Rayleigh anomaly-surface plasmon polariton resonances in palladium and gold subwavelength hole arrays," *Optics Express*, vol. 17, no. 4, pp. 2334-2340, Feb 2009, doi: 10.1364/oe.17.002334.
- [148] J. M. McMahon, J. Henzie, T. W. Odom, G. C. Schatz, and S. K. Gray, "Tailoring the sensing capabilities of nanohole arrays in gold films with Rayleigh anomaly-surface plasmon polaritons," *Optics Express*, vol. 15, no. 26, pp. 18119-18129, Dec 2007, doi: 10.1364/oe.15.018119.
- [149] W. R. Holland and D. G. Hall, "SURFACE-PLASMON DISPERSION-RELATION - SHIFTS INDUCED BY THE INTERACTION WITH LOCALIZED PLASMA RESONANCES," *Physical Review B*, vol. 27, no. 12, pp. 7765-7768, 1983, doi: 10.1103/PhysRevB.27.7765.
- [150] T. Maurer, P. M. Adam, and G. Leveque, "Coupling between plasmonic films and nanostructures: from basics to applications," *Nanophotonics*, vol. 4, no. 3, pp. 361-382, Oct 2015, doi: 10.1515/nanoph-2014-0015.
- [151] R. Nicolas *et al.*, "Plasmonic mode interferences and Fano resonances in Metal-Insulator-Metal nanostructured interface," *Scientific Reports*, vol. 5, Sep 2015, Art no. 14419, doi: 10.1038/srep14419.
- [152] F. Le, N. Z. Lwin, N. J. Halas, and P. Nordlander, "Plasmonic interactions between a metallic nanoshell and a thin metallic film," *Physical Review B*, vol. 76, no. 16, Oct 2007, Art no. 165410, doi: 10.1103/PhysRevB.76.165410.
- [153] N. Verellen *et al.*, "Fano Resonances in Individual Coherent Plasmonic Nanocavities," *Nano Letters*, vol. 9, no. 4, pp. 1663-1667, Apr 2009, doi: 10.1021/nl9001876.
- [154] A. Lovera, B. Gallinet, P. Nordlander, and O. J. F. Martin, "Mechanisms of Fano Resonances in Coupled Plasmonic Systems," *Acs Nano*, vol. 7, no. 5, pp. 4527-4536, May 2013, doi: 10.1021/nn401175j.
- [155] K. Bao, N. A. Mirin, and P. Nordlander, "Fano resonances in planar silver nanosphere clusters," *Applied Physics a-Materials Science & Processing*, vol. 100, no. 2, pp. 333-339, Aug 2010, doi: 10.1007/s00339-010-5861-3.
- [156] S. Zhang, D. A. Genov, Y. Wang, M. Liu, and X. Zhang, "Plasmon-induced transparency in metamaterials," *Physical Review Letters*, vol. 101, no. 4, Jul 2008, Art no. 047401, doi: 10.1103/PhysRevLett.101.047401.
- [157] J. B. Lassiter *et al.*, "Fano Resonances in Plasmonic Nanoclusters: Geometrical and Chemical Tunability," *Nano Letters*, vol. 10, no. 8, pp. 3184-3189, Aug 2010, doi: 10.1021/nl102108u.
- [158] M. Hentschel, M. Saliba, R. Vogelgesang, H. Giessen, A. P. Alivisatos, and N. Liu, "Transition from Isolated to Collective Modes in Plasmonic Oligomers," *Nano Letters*, vol. 10, no. 7, pp. 2721-2726, Jul 2010, doi: 10.1021/nl101938p.

- [159] N. A. Mirin, K. Bao, and P. Nordlander, "Fano Resonances in Plasmonic Nanoparticle Aggregates," *Journal of Physical Chemistry A*, vol. 113, no. 16, pp. 4028-4034, Apr 23 2009, doi: 10.1021/jp810411q.
- [160] R. Mohammadi, M. Ochs, A. Andrieu-Brunsen, and N. Vogel, "Effect of Asymmetry on Plasmon Hybridization and Sensing Capacities of Hole-Disk Arrays," *Journal of Physical Chemistry C*, vol. 124, no. 4, pp. 2609-2618, Jan 2020, doi: 10.1021/acs.jpcc.9b10229.
- [161] Y. H. Zhan, D. Y. Lei, X. F. Li, and S. A. Maier, "Plasmonic Fano resonances in nanohole quadrumers for ultra-sensitive refractive index sensing," *Nanoscale*, vol. 6, no. 9, pp. 4705-4715, 2014, doi: 10.1039/c3nr06024a.
- [162] M. Svedendahl and M. Kall, "Fano Interference between Localized Plasmons and Interface Reflections," *Acs Nano*, vol. 6, no. 8, pp. 7533-7539, Aug 2012, doi: 10.1021/nn302879j.
- [163] I. Zoric, M. Zach, B. Kasemo, and C. Langhammer, "Gold, Platinum, and Aluminum Nanodisk Plasmons: Material Independence, Subradiance, and Damping Mechanisms," *Acs Nano*, vol. 5, no. 4, pp. 2535-2546, Apr 2011, doi: 10.1021/nn102166t.