

Probing Surface Chemistry at the Nanoscale Level

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A Nicolas mon amour,
pour m'avoir accompagnée et soutenue
tout le long de cette aventure
de l'autre côté de l'océan.

A mes parents,
pour leur amour indéfectible
et leurs encouragements constants.

Abstract

Studies of various nanostructured materials have gained considerable interest within the past several decades. This novel class of materials has opened up a new realm of possibilities, both for the fundamental comprehension of matter, but also for innovative applications. The size-dependent effect observed for these systems often lies in their interaction with the surrounding environment and understanding such interactions is the pivotal point for the investigations undertaken in this thesis. Three families of nanoparticles are analyzed: semiconductor quantum dots, metallic silver nanoparticles and rare-earth oxide nanomaterials.

The radical scavenging ability of cerium oxide nanoparticles (CeO_2) is quite controversial since they have been labeled as both oxidizing and antioxidant species for biological systems. Here, both aqueous and organic stabilized nanoparticles are examined in straightforward systems containing only one reactive oxygen species to ensure a controlled release. The apparent absence of their direct radical scavenging ability is demonstrated despite the ease at which CeO_2 nanoparticles generate stable surface Ce^{3+} clusters, which is used to explain the redox activity of these nanomaterials. On the contrary, CeO_2 nanoparticles are shown to have an indirect scavenging effect in Fenton reactions by annihilating the reactivity of Fe^{2+} salts.

Cadmium selenide quantum dots (CdSe QD) constitute another highly appealing family of nanocolloids in part due to their tunable, size-dependent luminescence across the visible spectrum. The effect of elemental sulfur treatment is investigated to overcome one of the main drawbacks of CdSe QD: low fluorescence quantum yield. Herein, we report a

constant and reproducible quantum yield of 15%. The effect of sulfur surface treatment is also assessed following the growth of a silica shell, as well as the response towards a solution quencher (4-amino-TEMPO). The sulfur treated QD is also tested for interaction with pyronin Y, a xanthene dye that offers potential energy and electron transfer applications with the QD. Interaction with the dye molecule is compared to results obtained with untreated quantum dots, as well as CdSe/ZnS core shell examples.

In another chapter of this thesis, the catalytic potential of silver nanoparticles is addressed for the grafting of polyhydrosiloxane polymer chains with various alkoxy groups. A simple one-pot synthesis is presented with silver salts and the polymer. the latter serves as a mild reducing agent and a stabilizing ligand, once silver nanoparticles are formed *in-situ*. We evaluate the conversion of silane into silyl ethers groups with the addition of several alcohols, whether primary, secondary or tertiary, and report the yields of grafting under the mildest conditions: room temperature, under air and atmospheric pressure.

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Abbreviations

AgNP	silver nanoparticles
AIBN	azo-bis(isobutyronitrile)
CB	conduction band
CeO ₂	cerium oxide (ceria) nanoparticles
DSL	dynamic light scattering
EMA	effective-mass approximation
FWHM	full width at half maximum
GC	gas chromatography
IC	internal conversion
IRF	instrument response factor
ISC	intersystem crossing
LED	light emitting diode
MB	methylene blue
MV	methyl viologen
NHE	normal hydrogen electrode
PAA	polyacrylic acid
PDMS	poly(dimethylsiloxane)
PIB	particle in a box
PMHC	2,2,5,7,8- pentamethyl-6-chromanol
PMHS	poly(methylhydrosiloxane)
PYY	pyronine Y
QD	quantum dot
RNA	ribonucleic acid
ROS	reactive oxygen species
S ₈	elemental sulfur

S_n	singlet excited state (S_0 : ground state)
SEM	scanning electron microscopy
SPB	surface plasmon band
SV	Stern-Volmer
S-K	Starnski-Krastanow
T_n	triplet excited state
TCD	thermal conductivity detector
TEM	tunneling electron microscopy
TEMPO	tetramethylpiperidine-1-oxyl
TEOS	tetraethyl orthosilicate
TOPO	tri-octylphosphine oxide
UVA	ultraviolet irradiation in the 315-400 nm region
UVB	ultraviolet irradiation in the 280-315 nm region
UVC	ultraviolet irradiation in the 100-280 nm region
VB	valence band
VR	vibrational relaxation
XPS	X-ray photoelectron spectroscopy
λ	wavelength ($-_{ex}$: excitation, $-_{em}$: emission, $-_{abs}$: absorption)
τ	lifetime
Φ	quantum yield ($-_F$: of fluorescence)

Chapter 1. Introduction to nanomaterials

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1.1 Why all this interest around nanomaterials?

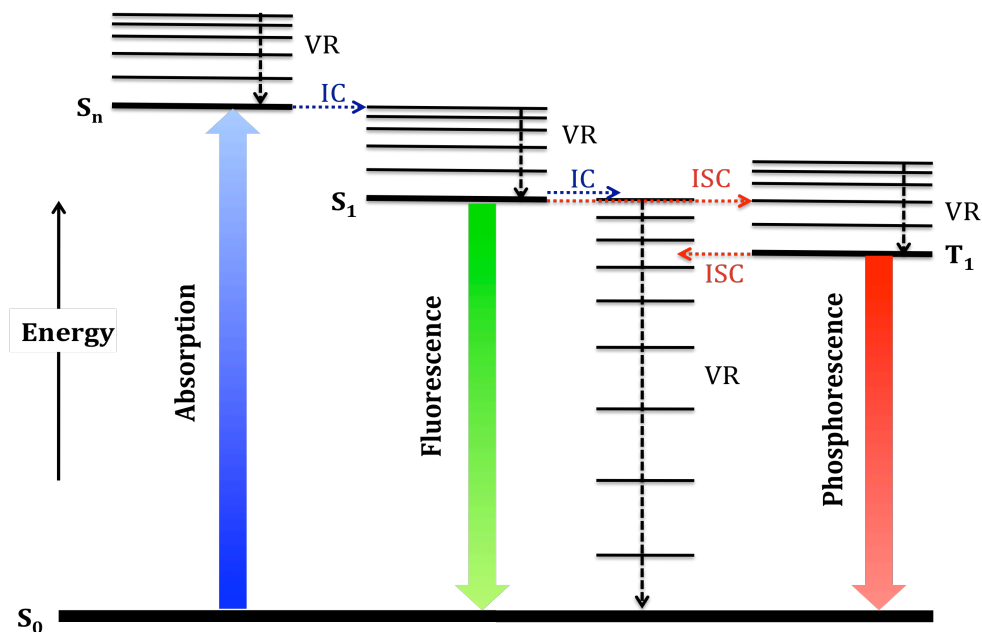
Nanotechnology is the use of nanoscience to create novel materials and systems that have new or enhanced behaviors for useful applications. Unfortunately, this concept is too often overlooked as the study of nanometer scale materials. The characteristics of these materials cannot just be a size factor, which is a regular material with one of its dimensions between 1 and 100 nm; there must be a specific size-dependent effect (the *nano-effect*) that appears when a critical size is reached. The Royal Society and the Royal Academy of Engineering eloquently define this:¹

“Nanoscience is the study of the phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale. Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nanometer scale”

Nanomaterials have brought a growing level of attention because of these size-dependent effects: mainly an increased relative surface area and the domination of quantum mechanics. The former effect usually results in improved chemical reactivity and can be useful in many areas, for example catalytic applications. The later effect plays an incremental role as the size of the material is reduced and can change its optical, magnetic or electrical properties.¹

I joined the Scaiano group at a turning point in its research focus. For this reason, I have studied different families of nanomaterials: semiconductors, metals and rare-earth oxides. For all of them, understanding the surface interaction with the environment was the driving force. Also, being in Dr. Scaiano's research group, a lot of the systems involved in

this doctoral thesis are photoactive. For a species to be active, it first needs to absorb light within the electromagnetic spectral range (270-2500 nm). The absorption of incident light results in an excited state, and its relaxation to the ground state can be either radiative or non-radiative. A radiative relaxation can either be defined as fluorescence or phosphorescence, depending on whether or not the relaxation involves a change of multiplicity (see Scheme 1. 1). This multiplicity is dictated by the relaxation from a singlet excited state. For fluorescence, the multiplicity of the transition does not change, making it spin-allowed, and it occurs rapidly with rate constants in the range of 10^6 s^{-1} to 10^{12} s^{-1} ; on average the lifetime is of the order of nanoseconds. Phosphorescence, on the other hand, requires a change of spin twice: first to reach the triplet excited state through intersystem crossing, and secondly to relax back to the ground state and recover the original multiplicity. All these factors contribute to slower phosphorescence relaxation times, with lifetimes in the millisecond to second range.



Scheme 1.1: Jablonski diagram for an optically active species. Full arrows represent radiative transitions, whereas dashed arrows represent non-radiative transitions (VR: vibrational relaxation, IC: internal conversion, ISC: intersystem crossing)

1.1.1 Particle-in-a-box: a top-down approach to quantum confinement

To understand the current interest in nanomaterials, one needs to appreciate the peculiar property they bear: quantum confinement. This phenomenon is based on the confined motion of free electrons within the material and results in discrete energy levels. A quick review of the particle-in-a-box model helps in understanding this behavior.

When considering a three-dimensional (3D) system like a bulk material containing N free electrons, those electrons are free to move along all three axes x , y and z . Whenever an orientation is finite, the free electrons are no longer able to move freely along this axis, creating a confinement in this direction. As an electron moves freely with a velocity $\vec{v} = (v_x,$

v_y, v_z), its energy is solely kinetic energy (Equation 1. 1, where m is the effective mass of electrons/holes in the crystal) since free electrons do not have potential energy ($V = 0$).²

$$E = \frac{1}{2} m \vec{v}^2$$

Equation 1. 1: *Electron kinetic energy expression*

However, for a particle in the solid state, the wavevector $\vec{k}$ is more often used than $\vec{v}$. Since both terms are proportional to the linear momentum $\vec{p}$ (Equation 1. 2), we obtain Equation 1. 3 where $k \propto \sqrt{E}$ is always true, and thus one always observes a parabolic dispersion relation of the energy states for free electrons as shown in Figure 1. 1.²

$$\vec{p} = m\vec{v} = \frac{h}{2\pi} \vec{k} = \hbar \vec{k}$$

Equation 1. 2: *Linear momentum expression*

$$E = \frac{1}{2} \frac{\hbar^2}{m} \vec{k}^2$$

Equation 1. 3: *Electron kinetic energy expression as a function of the wavevector k*

The calculation of the energy states is done by solving the Schrödinger equation under specific boundary conditions for the electrons; whether they move in infinite planes (case (a) where distance $d \rightarrow \infty$), or they are confined into a finite plane (case (b) where $d \rightarrow 0$). For a three-dimensional bulk material, the solution to the Schrödinger equation is given in Equation 1. 4:²

$$\Psi(x,y,z) = \Psi(x)\Psi(y)\Psi(z) = Ae^{ik_x x}e^{ik_y y}e^{ik_z z} \quad \text{with} \quad k_{x,y,z} = \pm n\Delta k = \pm n \frac{2\pi}{d_{x,y,z}}$$

Equation 1. 4: *Solution to the Schrödinger equation for a three-dimensional bulk material*

where n is an integer ($n = 0, 1, 2, 3$, etc.). Since $d_{x,y,z} \rightarrow \infty$ and $\Delta k \rightarrow 0$, the distance between each energy states will be very small and the distribution will be a quasi-continuum, as shown in Figure 1. 1 (a). For any other case where at least one direction is confined, the energy states in that plane are resolved by solving a one-dimensional (1D) Schrödinger equation for an electron trapped within a well of width d : this is the particle-in-a-box approach. The solution is represented in Equation 1. 5:²

$$E_n(k_{x,y,z}) = \nabla^2 \frac{k_{x,y,z}^2}{2m} = \frac{h^2 k_{x,y,z}^2}{8\pi^2 m} = \frac{h^2 n^2}{8md_{x,y,z}^2}$$

Equation 1. 5: *Energy expression of state ‘n’ along the finite direction x , y or z*

where n is an integer ($n = 1, 2, 3$, etc.) and where x or y or z is the finite direction. Since $d_{x,y,z} \rightarrow 0$ and $\Delta k \rightarrow \infty$, the thinner the width d , the larger the spacing between each allowed energy state, giving rise to discrete levels, as shown in Figure 1. 1 (b).

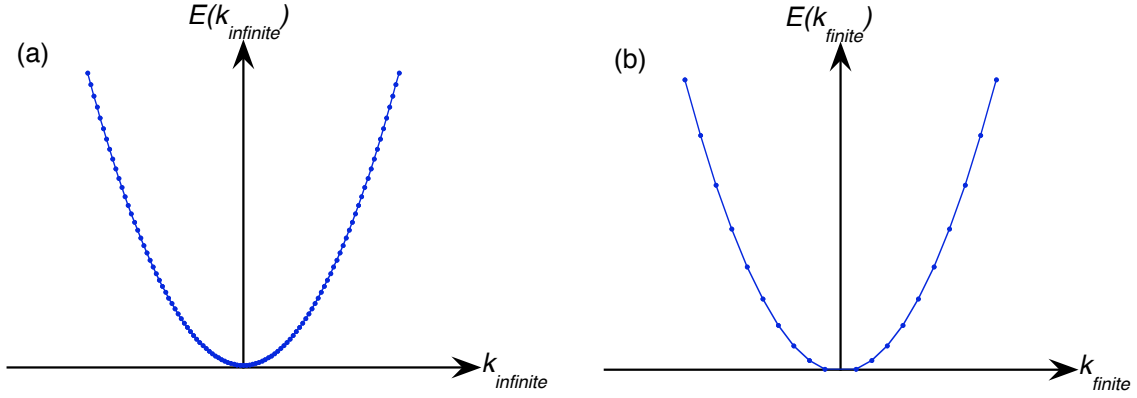


Figure 1.1: Dispersion relation of energy states for an electron (a) moving freely in an infinite direction or (b) restricted along a finite axis. Each state is represented with a point, putting emphasis on the quasi continuum of case (a) and the discrete distribution of case (b).

When assessing particle-in-a-box, the density of states D must also be considered. This value determines the number of states present between each allowed energy level ($E_n + \Delta E_n$) or the number of electrons with a wavenumber between k and $k + \Delta k$. Logically, any finite dimension in space will influence the density of states. Depending on the variable considered, D is defined as:²

$$D(k) = \frac{dN(k)}{dk} \quad \text{or} \quad D(E) = \frac{dN(E)}{dE} = \frac{dN(k)}{dk} \frac{dk}{dE}$$

Equation 1.6: Density of state expression as a function of the wavenumber k or the energy level E

where $N(k)$ is the total number of electrons with a wavenumber k within a material.² To keep it simple, we shall just look at proportionalities to understand the shapes taken by density of states for 3D, 2D, 1D and 0D materials respectively. When considering $N(k)$, a visualization

of the occupied space is helpful. For instance, a cube or a sphere for 3D materials, a sheet or a disc for 2D, a string for 1D and a dot for 0D systems. Since $k \propto \sqrt{E}$ is always true, based on Equation 1.6 we can conclude:

- for a 3D system: $N(k) \propto k^3$ so $D_{3D}(k) \propto k^2$ and $D_{3D}(E) \propto E \times \frac{1}{\sqrt{E}} = \sqrt{E}$
- for a 2D system: $N(k) \propto k^2$ so $D_{2D}(k) \propto k$ and $D_{2D}(E) \propto \sqrt{E} \times \frac{1}{\sqrt{E}} = 1$
- for a 1D system: $N(k) \propto k$ so $D_{1D}(k) \propto 1$ and $D_{1D}(E) \propto 1 \times \frac{1}{\sqrt{E}} = \frac{1}{\sqrt{E}}$
- for a 0D system: $N(k) \propto 1$ so $D_{0D}(k) \propto 0$ and $D_{0D}(E) \propto 0 \times \frac{1}{\sqrt{E}} = 0$

These proportionalities help us understand the shape of the curve between each allowed energy level shown in Figure 1.2. Therefore, in the 3D case the number of states rises as the square root of the energy between each energy level allowed along the x-axis. For a 2D system, the density of states is completely independent of the energy, resulting in a perfectly horizontal line. Any 1D material will have its number of states dropping, since they follow the inverse of the square root of the energy, as the energy falls back to the E_1 value. Finally a 0D dot, otherwise known as a completely quantum confined material, has no density of states in between each energy level. For this reason, three-dimensional nanomaterials are considered to have discrete electronic energy levels, which lead to specific properties that will be covered throughout this thesis.

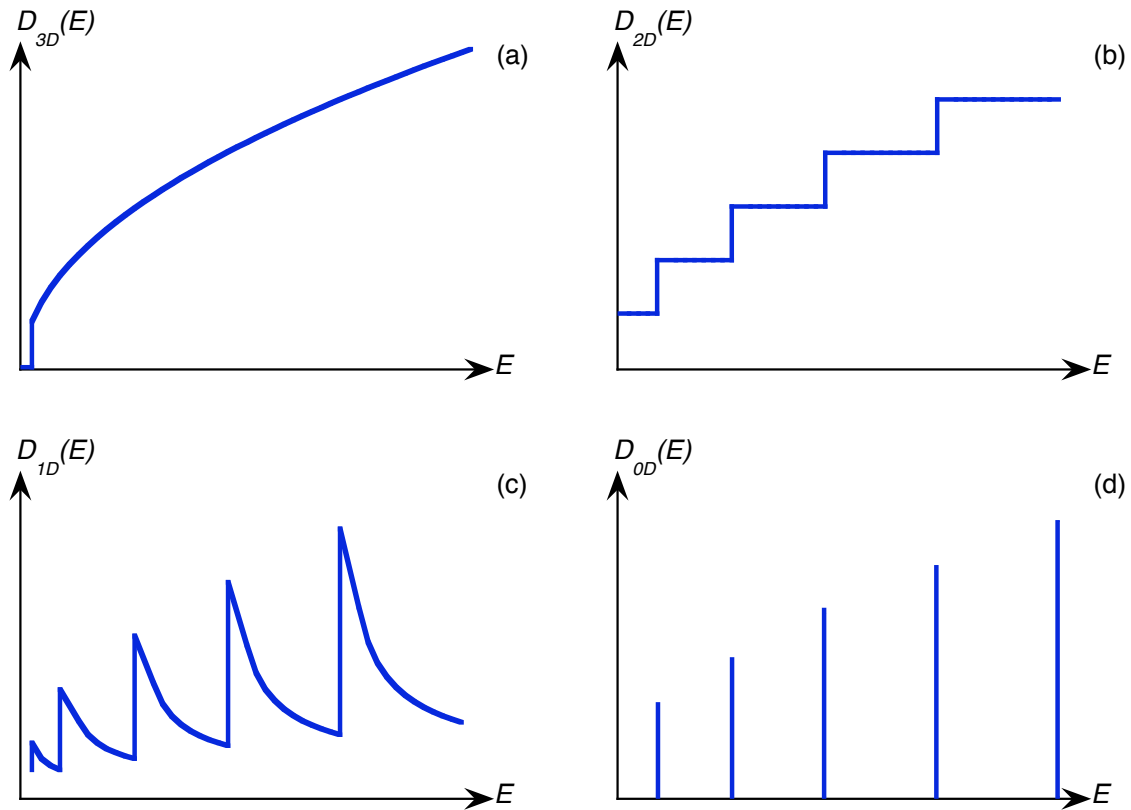
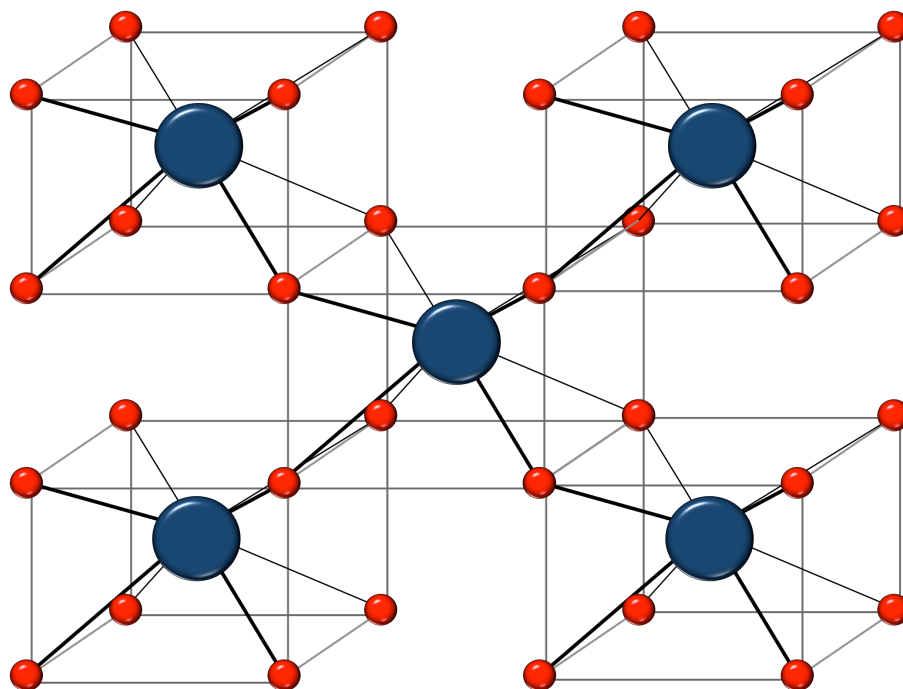


Figure 1.2: Density of states for (a) a three-dimensional, (b) a two-dimensional, (c) a one-dimensional and (d) a zero-dimensional free electron

1.2 Cerium oxide nanoparticles: some unique structural properties

Cerium dioxide (CeO_2 , also called ceria) is a rare-earth oxide that crystallizes in the fluorite structure with a face-centered cubic (fcc) unit cell. At the center of each fcc unit is a cerium cation coordinated to eight equivalent neighbor oxygen anions present at each corner of the cube as shown in Scheme 1.2:³



Scheme 1. 2: Representation of the fluorite cubic crystal structure for CeO_2 drawn with cerium ions (blue) at the center of eight oxygen ions (red)

The fluorite cubic centered structure, drawn in Scheme 1. 2 as a primitive array of cerium ions, highlights the presence of large vacant octahedral holes in the structure. This feature is what renders cerium oxide so interesting, as it strongly influences the movement of ions within the lattice defects.³

1.2.1 Cerium oxide defect structure and oxygen diffusion ability

Cerium has a $4f^25d^06s^2$ electron configuration and can exhibit both +3 and +4 oxidation states. Since thermodynamic data has confirmed how unstable cerium is in presence of oxygen, it logically forms Ce_2O_3 and CeO_2 species easily.³

Cerium oxide lattices can bear either intrinsic or extrinsic defects and, in reducing environments, the crystal is able to release oxygen from this lattice, leaving predominantly anion vacancy (O^{2-}) defects.⁴ This special property leads to an overall positively charged structure as a result of excess Ce^{4+} cations. One way for ceria to overcome this variation is by introducing two electrons for each oxygen anion released, reducing two Ce^{4+} to Ce^{3+} cations and enabling the crystal structure to remain stable.⁵ An oxygen-rich atmosphere will return the crystal structure back to its original Ce^{4+} content. Because the oxygen lattice is very mobile, oxygen can diffuse rapidly within the crystal, and cerium oxide is a favored support for catalysts whenever oxygen storage and release is required.

1.2.2 Nanoscale crystals: some applications

The ability of ceria to oscillate between its +4 and +3 oxidation state makes it an ideal candidate for any catalytic oxidation or reduction reactions. Depending on the conditions (temperature, external stimuli, pressure or oxygen content of the atmosphere), the defects that give rise to the catalytically active Ce_2O_3 species are found within the bulk of the material, but mostly at the surface.⁶

This particularity explains the vast interest given to cerium oxide nanoparticles when compared to their bulk counterparts. With a surface containing more oxygen vacancies and more adjacent Ce^{3+} ions, nanoparticles offer the advantage of an increased surface to bulk ratio, giving nanoceria its enhanced catalytic ability. Because of these very peculiar properties, cerium oxide nanoparticles have been widely used for commercial applications, such as catalytic converters for exhaust systems, sunscreens and solar cells, to name a few.⁷⁻⁹

1.3 Semiconductor quantum dots: the controllable nano-rainbow

A semiconductor quantum dot (QD) is an optically active three-dimensional nanoparticle confining the motion of charge carriers (electrons and holes) at the nanometer scale.

$$\lambda_{DB} = \frac{h}{\sqrt{2mk_B T}}$$

Equation 1. 7: De Broglie wavelength expression

This activity is measurable if the QD size is comparable to or smaller than the De Broglie wavelength λ_{DB} of the charge carriers within the particle, as can be seen in Equation 1. 7 where h and k_B are the Planck's and Boltzmann's constants, m the effective mass of electrons/holes in the semiconductor crystal and T the absolute temperature. The quantum confinement confers a discrete energy level structure that explains why QD are often nicknamed “artificial atoms” although they are composed of 10^3 - 10^5 atoms. The smallest distance that separates an electron cloud from a nucleus (or a hole) is given by its Bohr radius a . Thus, when considering a QD it is easier to depict it as a region whose size is comparable to, or smaller than, the exciton Bohr radius a as seen in Equation 1. 8, where ϵ_0 is the permittivity of free space, ϵ_r the relative permittivity of the medium, $\hbar$ the reduced Planck's constant, μ^* the electron/hole reduced effective mass and e the elementary charge. For example, the exciton Bohr radius of CdSe semiconductor is 5.6 nm.¹⁰

$$a = \frac{4\pi\epsilon_0\epsilon_r\hbar^2}{\mu^* e^2}$$

Equation 1.8: Exciton Bohr radius expression

Semiconductor QD were first mentioned in a solid matrix by Russian scientist Alexey Ekimov,¹¹ while the first colloidal experiments on QD were done by the American professor Louis E. Brus,¹² both in the early 1980s. The most studied nanocrystals are made of the II/VI group semiconductors (*e.g.*, CdSe or ZnS), but studies based on the III/V group semiconductors (*e.g.*, InP) are also developed.¹³

The fabrications of QD started in the late 1980s where the first approach was top-down. Various lithographic techniques (optical with laser beams, X-ray) permitted design of QD from quantum wells (QW) with very precise localization, however the etching process resulted in many surface defects. A new bottom-up approach was then developed for defect-poor QD that are deposited on a solid support: the Stranski-Krastanow (S-K) heteroepitaxial growth. These QD have been extensively produced and studied under the fundamental physics perspective due to their enhanced optical nonlinearity; this could have tremendous applications such as quantum computation or quantum cryptography.²

Quantum dots are at the frontier between molecules and bulk material. Molecules can be defined as small organizations with a limited amount of atoms, whereas bulk crystalline materials have a translational symmetry with such a large amount of atoms that they can be regarded as infinite. This explains why physicists regard QD as small crystals, whereas

chemists view them as large molecules. Either way, the quantum confinement that arises from this intermediate state is what renders QD interesting to both fields.

1.3.1 The consequence of quantum confinement for semiconductor nanoparticles

Semiconductor QD have very unique electronic properties influenced by their size that lies between the molecular and the bulk boundaries of a material. This results in optical properties that are strongly size-dependent and one can observe the luminescence of these nanoparticles, from red to blue as the mean diameter decreases (see Figure 1. 3). Many calculations have been attempted to account for the size-dependent transition. Some, such as Bawendi and Norris with the effective-mass approximation (EMA) approach,¹⁴ started from the molecular orbital standpoint until the QD size range was reached. Other theories consider the bulk three-dimensional (3D) material and gradually render each (x , y , z) orientation finite until a 0D or atom-like structure was obtained. This second approach is commonly called particle-in-a-box (PIB) or particle-in-a-sphere (PIS) and was discussed earlier in this chapter. Both approaches, whether bottom-up or top-down, draw the same conclusion: the energy gap between the valence band and the conduction band of a QD increases with decreasing size of the nanoparticle.

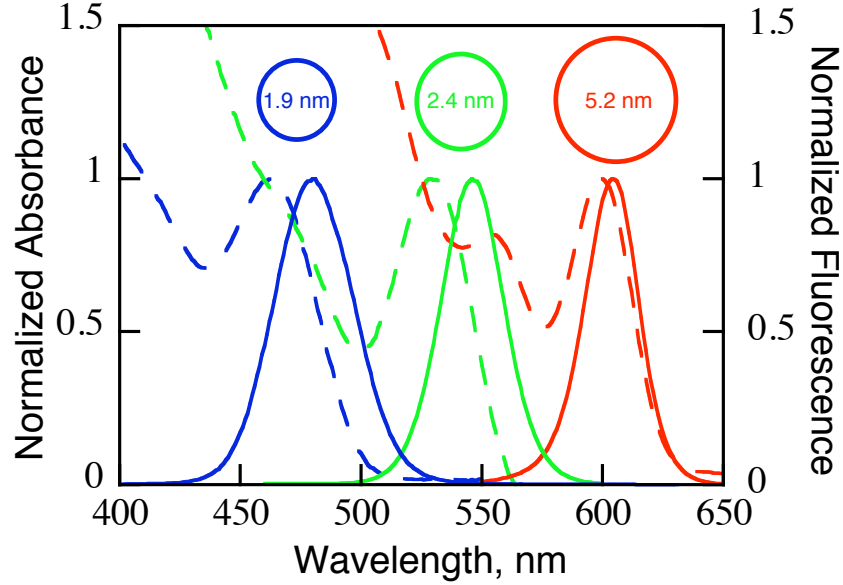


Figure 1.3: Normalized absorption (dashed lines) and fluorescence (full lines) spectra for commercial quantum dots Evidots® from Evident Technologies.

The growth of the band gap as the size of the nanocluster decreases finds its explanation in the solution to the particle-in-a-box Schrödinger equation (Equation 1. 5). Since $n = 0$ cannot be a solution, the ground state energy in confinement condition is $E_1 \neq 0$ (the first excited state being E_2), whereas $E_0 = 0$ is the lowest state in classical non-quantized directions. The band gap $E_g(QD)$ in the quantum dot, that corresponds to the generation of an electron-hole pair, has several contributions, including E_g from the bulk material, as can be seen in Equation 1. 9.²

$$E_g(QD) = E_g(bulk) + E_{Confinement} + E_{Coulomb}$$

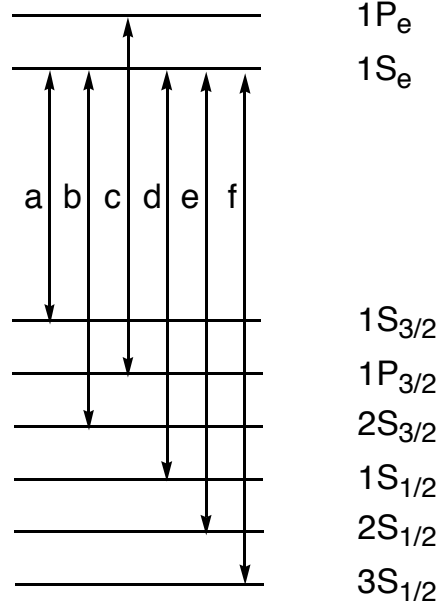
Equation 1.9: Size dependent energy band gap for a spherical semiconductor QD

The second contribution, $E_{\text{Confinement}} = \frac{h^2}{2md^2}$, corresponds to the lowest energy of a state confined in a diameter d : this is the confinement of the electron-hole pair. The third contribution $E_{\text{Coulomb}} = -1.8e^2 / 2\pi\epsilon\epsilon_0 d$, where ϵ is the dielectric constant of the semiconductor, is the Coulomb interaction taking into account the mutual attraction between the hole and the electron with a screening factor by the crystal.² Therefore, the band gap $E_g(QD)$ will effectively increase as d is getting smaller.

1.3.2 The dynamics of excitons in quantum dots: an enigma still under investigation

The PIB approach applied to semiconductor QD does not provide reasonable insights on some aspects of the dot such as the luminescence Stokes shift or the nature of the discrete excitonic transitions that can be observed in an absorption spectrum.¹⁵ To understand these, Bawendi and Norris have used the EMA approach to fit the data obtained through photoluminescence excitation spectroscopy.^{14, 16}

Norris and Bawendi have been able to assign from within the valence and conduction bands the main discrete electronic transitions (excitons).¹⁴ To do so, they used photoluminescence excitation spectroscopy at very low temperature (10 K) and compared the extracted data to the calculation of quantum dot transitions as a function of size. The first eight excitons were attributed due to a strong agreement with the theory and are widely accepted (see transitions based on reference 15 in Scheme 1. 3). The deeper transitions were more difficult to assign because the approximations made for the calculations, perfect spheres and cubic symmetry instead of hexagonal crystal lattice, could no longer be disregarded at this level of confinement.



Scheme 1.3: Energy level diagram with transitions assigned to specific excitonic states. Transitions (a), (b) and (c) are the strongest and most resolved, with (a) being the band edge or first excited state.¹⁵

For our measurements (room temperature and aerobic conditions) we now have a deeper understanding of the typical shape for a CdSe QD absorption spectrum. The first and sharpest peak is due to the first excited state $1S_{3/2}1S_e$, also called band edge transition as it has the lowest energy. This peak is often the only one considered to determine the size of CdSe QD since it corresponds to the band gap E_g . Although some homogeneities and a rather high temperature (293 K vs. 10 K) tend to broaden the absorption features and conceal the hot exciton transitions, one may also observe the two other predominant peaks, $2S_{3/2}1S_e$ and $1P_{3/2}1P_e$, at lower wavelength (higher energy). Also apparent is the overall increase in absorption as the energy increases. This change in absorption is due to the continuum-like nature of the underlying transitions. The spectrum from a typical, homemade sample presents some of these features (Figure 1.4).

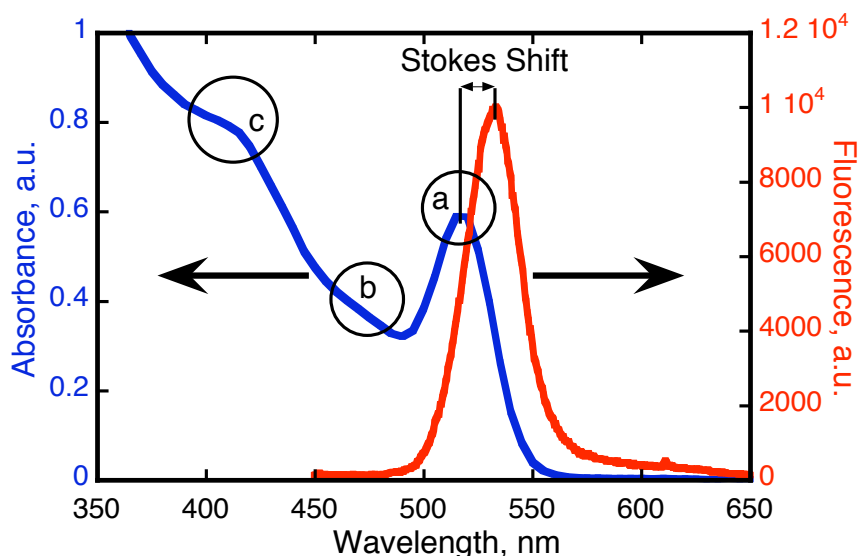


Figure 1. 4: Typical absorption and fluorescence ($\lambda_{ex} = 400$ nm) spectra of core CdSe QD in chloroform and stabilized by tri-octylphosphine oxide (TOPO) ligands. Excitons of interest in absorption spectrum are circled and labeled with the letter corresponding to their transition as shown in **Scheme 1. 3**. Stokes shift is also highlighted.

The corresponding fluorescence emission spectrum, also shown in Figure 1. 4, does not display multiple transition features like the absorption spectrum. Quantum dots follow the same rule as any other excited molecule having the ability to relax to its ground state through light emission. As stated by Kasha's rule, this photon may be absorbed at any higher electronic state, but will only emit from the lowest excited state, $1S_e$.¹⁷ This explains how a unique relatively sharp peak is observed, with a full width at half maximum (FWHM) that reflects the size distribution of the nanoparticles in a sample. For any FWHM below 25 nm, the sample is regarded as monodispersed (about 10% size distribution).¹⁸

One last characteristic of interest highlighted in Figure 1. 4 is the energy difference observed between the $1S_{3/2}1S_e$ exciton and the emission. This loss of energy in

semiconductor nanoparticles, called Stokes shift, is the result of their band edge exciton degeneracy splitting caused by the electron-hole exchange, their crystal field and their asymmetric shape (more prolate than spherical).¹⁹

1.3.3 The advantages and disadvantages of colloidal quantum dots from a chemistry perspective

Colloidal QD may be used for many purposes: fluorescent labeling, Förster resonance energy transfer (FRET), or energy conversion to name a few. Our group has focused on understanding their brightness, in other words, getting an optimum fluorescence quantum yield (Φ_F) for QD under various conditions. The many advantages and the drawbacks of CdSe QD are detailed under that perspective and compared to traditional organic dyes, such as fluorescein.

As seen in Figure 1. 3, QD have a broad absorption region combined with a relatively sharp and narrow emission. This specific property allows the simultaneous excitation of multiple sizes of QD with a single wavelength, an asset for multicolor labeling. Organic dyes on the other hand have discrete bands for their absorption, which renders them less versatile. Within an economical context, QD also have a better “photon investment return” than organic dyes where the molar absorption coefficients (ϵ) at the band edge transition are typically between 100,000 and 1,000,000 $M^{-1}cm^{-1}$ and organic dyes have ϵ anywhere between 25,000 and 250,000 $M^{-1}cm^{-1}$.²⁰ One drawback is the capacity of QD to relax from their excited state through fluorescence emission; for most applications in the visible spectrum region, many organic dyes have their fluorescence quantum yield Φ_F (the yield of excited state electrons that return to the ground state through a fluorescence pathway) at almost

unity. On the other hand, QD will have their $\Phi_F(QD)$ anywhere between 0.1 and 0.6 depending on their passivation and the environment. Indeed, low quantum yield has been attributed to the presence of surface traps (defects on the outer layer of the nanoparticle). These sites disrupt the electron/hole recombination, making it a non-radiative process. The typical approach for passivation of quantum dots, especially CdSe QD, is the growth of a semiconductor shell with a larger band gap than the core quantum dot (*e.g.*, a ZnS or a CdS shell for a CdSe core).²¹ This results in a red shift of the emission wavelength due to an enhanced delocalization of the carriers, but above all, it brings an improved quantum yield of fluorescence thanks to the surface vacancies and non-radiative recombination sites that are passivated.²¹ Moreover, as will be shown in Chapter 4, one given synthetic route for core quantum dots does not guarantee a reproducible behavior upon excitation.

For any *in-vivo* biological purposes, three factors have limited the evolution of QD as fluorescent labels: their size, their solubility in relevant media and their potential toxicity. Some semiconductors are made of cytotoxic elements such as cadmium. Leakage of these materials is highly detrimental, but can be prevented by addition of an inert layer. When this layer is silicon oxide, it can be further derivatized with proper ligands to ensure solubility and stability in typical biological media, such as buffers. This highlights the need for additional engineering since QD are usually synthesized in organic media. On the other hand a lot of organic dyes are readily available for these relevant media. Therefore, a QD that may be between 1 and 10 nm comes close to an actual 60 nm diameter when considering the additional shells and stabilizing agents.²⁰ This is significantly larger than fluorescent organic dyes that are in the sub-nanometer scale and, thus, must be accounted for whenever the labeling process involves cellular uptake.

When considering labeling applications, the stability of the label is essential. The tremendous success of semiconductor QD resides in their notably enhanced thermal and photochemical stabilities when compared to the vast majority of organic dyes for any long term imaging.²⁰ The resistance to photobleaching makes QD an ideal candidate for single molecule experiments where prolonged and high power irradiation is common.

These advances in technology highlighted one of the major drawbacks for QD: their tendency to blink. Blinking is a fluorescence intermittency event for a continuously excited QD, and can be defined as interrupted emission by dark states due to radiationless transitions.²² Nirmal *et al.* were the first ones to observe this phenomenon with distinctive on/off behavior on a single dot's fluorescence intensity at the microsecond scale.²³ Since then, blinking has been extensively studied, and its origin has been traced to the ionization of the core with an overall positive charging of the crystal: the trapping of a charge carrier (an electron or a hole) at the QD surface also known as *surface trap* would be induced.

1.4 Silver nanoparticles: novel properties of noble metal nanoclusters

Silver nanoparticles (AgNP) are noble metallic materials that have attracted an increased interest in the past, due to the unique chemical and physical properties arising from their small size. The small volume to big surface area ratio, combined with their size dependent optical and electronic properties, makes them potentially useful in areas such as catalysis, optics, or sensor applications.

1.4.1 Localized surface plasmon resonance: Mie's theory

Silver, like gold or copper, is a metal that typically displays a strong UV-visible absorption at the nanometer scale that does not exist for the bulk material. This light absorption by small metallic particles has been described by Mie's theory, developed for perfectly spherical gold nanoparticles.²⁴ Rather than a theory, Gustav Mie actually solved the Maxwell's equations for gold clusters with imposed boundaries based on the bulk dielectric functions and the nature of the surrounding medium. For a very fine distribution of colloidal spherical particles that are less than one-tenth of the incident light wavelength, the color of the solution is independent of the size, and the absorption coefficient is only proportional to the concentration of particles.²⁴ Based on this theory, the absorption is dominated by the dipole term, for particle sizes between 3 and 20 nm, and has an absorption coefficient α (in $\text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$) calculated from the following equation:²⁵

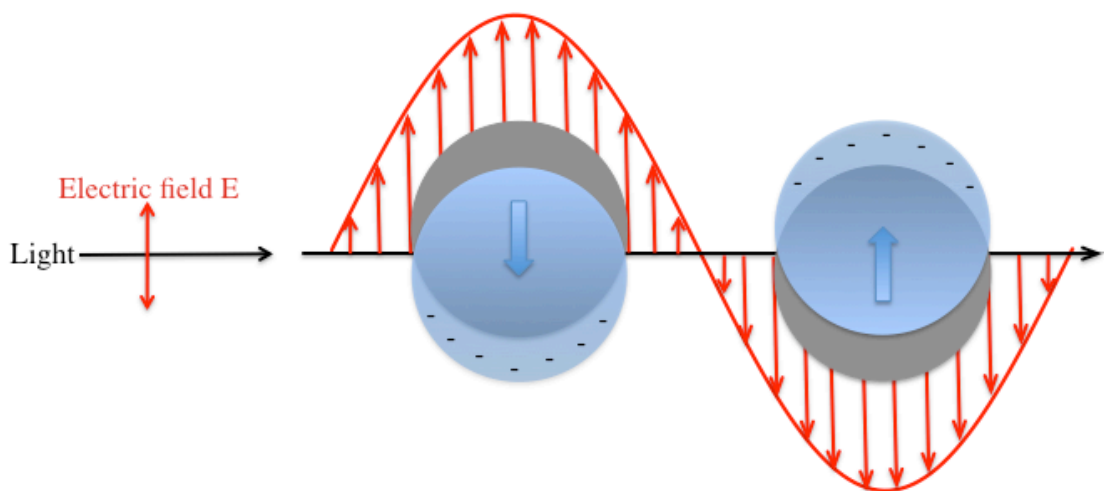
$$\alpha = \frac{18\pi}{\ln 10} \frac{10^5}{\lambda} \frac{M n_0^3}{\rho} \frac{\varepsilon_2}{(\varepsilon_1 + 2n_0^2)^2 + \varepsilon_2^2}$$

Equation 1. 10: Absorption coefficient of nanometer scale spherical metallic particles.

where λ is the wavelength of light (in nm), M and ρ are the molecular weight and density of the metal, n_0 is the refractive index of the solvent and ε_1 and ε_2 are the real and imaginary parts of the dielectric constant of the metal.

This absorption depends on the incident light frequency. The dipole excitation induces a counter-balancing positive polarization that leads to the collective oscillation for free electrons present in the conduction band.²⁵ Because of the confinement, the oscillation

occurs at the surface of the particle, whereas the density at the core remains constant as depicted in Scheme 1. 4. This overall dipole is called localized surface plasmon. Resonance with the incident light occurs at a wavelength where the real part of the metal dielectric constant, ϵ_l , is the exact opposite of twice the solvent dielectric constant, n_0^2 . In other words, when the term $(\epsilon_l + 2n_0^2)$ disappears from Equation 1. 10. This is depicted by a strong absorption band, usually in the visible region for noble metals: this is called localized surface plasmon band (or SPB for short).



Scheme 1. 4: Schematic representation of a localized surface plasmon resonance showing the oscillation on an electron cloud (blue) at the surface of the noble metal sphere (gray) as it enters in resonance with electric field frequency (red) of the incident light.

Mie's calculations were done assuming a perfectly spherical and finely distributed group of gold nanoparticles. The theory does not account for the influence of size and shape of the nanoclusters, although both have an influence on the position and the width of the SPB. Dormus and others attributed any deviation from this ideal model to the free path

effect.²⁶ Particles with a diameter smaller than their bulk mean free path (52 nm in the case of silver) would have their optical excitation influenced by the scattering of the free electron with the particle surface. Corrections are possible with computational methods such as finite-difference time domain (FDTD) and more often used discrete dipole approximation (DDA).²⁷

This surface plasmon resonance property allows an easy monitoring for the generation of metallic silver nanoparticle using UV-visible spectroscopy as will be demonstrated in Chapter 5.

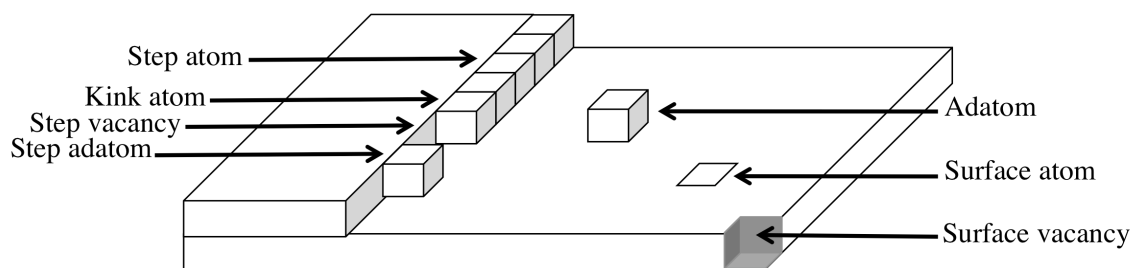
1.4.2 Applications for silver nanoparticles: the rise of nano-catalysis

Silver nanoclusters have been used in the past for many applications. In the ancient times and because of their property described in 1.4.1, silver nanoparticles were used as coloring agents in stained glass windows giving a bright rose color upon sun irradiation.²⁷ In more recent times, silver nanoparticles have displayed interesting electrochemical properties.²⁸ More prominently, silver nanomaterials have been utilized as anti-bacterial agents in a wide range of applications; for example in health industry, food storage or textile coatings.²⁹

The main interest of this thesis is in the use of silver nanoparticle systems for their catalytic activities. Silver nanoparticles can be used with photocatalytic approaches where a given system is excited with light centered at its surface plasmon band. The energy dissipation in presence of other molecules can occur through four main pathways: thermal transfer, electron transfer, hole transfer, or sensitization of an organic molecule towards its excited state (also called the antenna effect). Other members of the Scaiano research group

are currently examining this new and extremely promising photochemical reactivity of silver and other noble metal nanoparticles.^{30, 31}

Other catalytic reactivities for silver nanomaterials lie in the nature of the support itself. Being a nanocluster, a very high surface area to volume ratio is observed; therefore most Ag atoms are exposed and potentially reactive to the environment. An important aspect is the shape of the cluster, as it dictates the facets preferentially present. In typical transition metal nanoclusters having a catalytic activity (*e.g.* Pt, Pd or Ru), some facets are more responsive to organic molecule chemisorptions or physisorptions than others.³² The active sites at the surface are mostly located at the surface defects: kinks, adatoms, vacancies or steps are among the possible surface defects, as depicted below.³³



Scheme 1.5: Schematic of point defects using the TSK (terrace-step-kink) model portrayed on a simple cubic (100) crystal structure.

The stronger curvature, (spherical shape) found in smaller clusters, usually favors more defects and therefore more active sites for the catalytic reaction. In Chapter 5, it is the actual surface catalysis aspect of silver nanoclusters that is studied.

1.5 Outline of research presented

The work presented in this doctoral thesis focuses on the surface reactivity for colloidal nanocrystals when exposed to various environments. The ability of cerium oxide nanoparticles to scavenge radicals and present antioxidant properties is discussed in Chapter 3. Chapter 4 introduces the development of modified cadmium selenide core semiconductor quantum dots. These sulfur treated nanoparticles display improved behaviors towards various environmental stimuli. Metallic silver nanoparticles are also studied for the catalytic alcoholysis of polysiloxane polymers in new, mild reaction conditions. Chapter 6 will present a collaborative work on the interaction of a xanthene-type dye with various quantum dots. Finally, some conclusions, as well as future directions are presented in Chapter 7.

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2.1 Introduction

This chapter deals with the various techniques and instruments used throughout this thesis. The specific experimental details for each given study are given at the end of the corresponding chapter.

2.2 Steady-state and time-resolved spectroscopy

Throughout this thesis, optically active materials are studied; therefore UV-visible spectroscopy analysis is a preliminary study to most. Whenever a radiative relaxation occurs, both steady-state and time-resolved fluorescence measurements can be acquired. Here are summarized the typical experimental set-ups for such analyses.

2.2.1 UV-visible spectroscopy

The UV-visible absorption measurements were performed at room temperature on a CARY-50 or a CARY-100 spectrophotometer, both from Varian. For any typical measurement, a 1 cm by 1 cm rectangular quartz cuvette was filled with the chosen solvent to acquire a blank. The same cuvette was then filled with the diluted solution of interest and capped with a septum. The absorption spectra were all acquired in the 200-800 nm range (unless otherwise specified).

2.2.2 Fluorescence spectroscopy

The steady-state emission spectra were all recorded using the luminescence spectrophotometer from Photon Technology International. All samples were measured in a 1 cm by 1 cm quartz cell capped with a septum. The samples included in the same study were all optically matched at the excitation wavelength prior to fluorescence measurements.

2.2.3 Fluorescence lifetime

Time-resolved fluorescence decay spectra were acquired using the *EasyLife* lifetime spectrometer from Photon Technology International. The excitation source was a nanosecond pulsed LED, with a wavelength as close as possible to the excitation wavelength used for the steady-state fluorescence acquisition. Typically, a decay spectrum corresponds to the average time an excited state takes to return to its ground state: this is the fluorescence lifetime (τ_F), given in Equation 2.1:

$$\tau_F = \Phi_F \tau_{rad} = \frac{1}{k_{rad} + \sum k_{nr}}$$

Equation 2.1: *Fluorescence lifetime expression as a function of radiative and non-radiative relaxation rate constants*

where Φ_F is the fluorescence quantum yield, τ_{rad} the radiative lifetime, k_{rad} the radiative process rate constant ($\Phi_{rad}=k_{rad}^{-1}$), and k_{nr} any other non-radiative decay rate constant. The fluorescence decay $D(t)$ can be convoluted to a single-exponential function such as the one shown in Equation 2.2 with $n=1$, but more complicated systems (such as quantum dots in

Chapter 4) are usually better described by a sum of exponential functions ($n= 2$ or 3 in general).¹

$$D(t) = \sum_{i=1}^n a_i \cdot \exp\left(-\frac{t}{\tau_i}\right)$$

Equation 2.2: Fluorescence decay described as a sum of exponential functions

2.3 Size characterization techniques

2.3.1 Electron microscopy (EM)

Colloidal solutions of nanoparticles can be analyzed with both scanning electron microscopy (SEM) or transmission electron microscopy (TEM). All SEM and TEM images were acquired at the Centre for Catalysis Research and Innovation (CCRI, University of Ottawa). SEM images were obtained using a JEOL JSM-7500F Field Emission SEM in Transmission Electron Detector (TED) mode with a bright field and the following typical conditions:

- Accelerating voltage: 20 kV
- Emission current: 20 μ A
- Working distance: 8.0 mm

For the silver nanoparticle samples (Chapter 5), the differentiation between the metallic particles and their non-reduced salt counterparts was possible thanks to a retractable

backscattering detector (RBEI) used with COMPO reading mode; only metallic species appear illuminated.

TEM images were obtained using a JEOL JEM-2100F Field Emission TEM equipped with an ultrahigh-resolution pole piece operating at 200 kV. Dr Yun Liu acquired all the TEM images.

Prior to any electron microscope measurement, approximately 50 μL of sample was slowly deposited on either a copper or a gold grid coated with a carbon film (400 mesh for both) and left to dry under air. The grids were then placed overnight into an ultra-high vacuum system (Varian Turbo Mini Pumping station, typical $P=2.5\times 10^{-8}$ Torr) for a complete drying and to ensure that all volatile organic matter was removed.

2.3.2 Dynamic light scattering

The dynamic light scattering (DLS), also known as photon correlation spectroscopy or the quasi-elastic light scattering, also aided in the determination of nanoparticle size. This technique is based on the Brownian motion of particles randomly dispersed in a solvent as they collide with solvent molecules and scatter the light coming from an incident laser source.² This technique is size dependent, since bigger particles will have a much slower motion than smaller ones. Therefore, by measuring the fluctuations of the scattered light, one can obtain the speed at which particles are diffusing due to Brownian motion (called translational diffusion coefficient D) and link it to the hydrodynamic diameter d_H by using the Stokes-Einstein Equation 2.3:

$$d_H = \frac{kT}{3\pi\eta D}$$

Equation 2.3: *Stokes-Einstein equation*

where k is Boltzmann's constant, η is the viscosity and T the absolute temperature. Bigger particles will scatter more light than small particles, therefore, within a polydispersed sample, the conversion of intensity to volume is based on Mie's theory rather than Rayleigh scattering since the former allows the visualization of small particles (*e.g.*, 5 nm) present in the same sample as big particles (*e.g.*, 500 nm). This also means that this technique assumes perfectly spherical nanoparticles, which is not always the case for our samples, but is still a fair approximation.

Typically, a 500 μ L sample was diluted in 1.5 mL of an adequate solvent inside a 1 cm by 1 cm quartz high-precision cuvette. The DLS measurement was done using a Malvern Zetasizer Nano (ZEN3500) fitted with a 633 nm laser (DPSS, 50 mW) located in the CCRI. An average of four consecutive measurements was calculated for each sample to obtain the hydrodynamic diameter.

2.4 Elements analysis

2.4.1 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy was undertaken to study the surface of our various nanoparticles. Typically, a sample would be concentrated down if diluted or used as such,

then deposited on a clean silicon wafer and dried under mild vacuum overnight in a dessicator. The sample would then undergo further vacuum inside the XPS chamber for a couple of hours prior to the analysis. Mr. Alexander Mommers acquired all the XPS spectra on a Kratos analytical model Axis Ultra DLD, using monochromatic aluminum $K\alpha$ X-rays at a power of 140 watts.

2.4.2 Gas chromatography coupled to thermal conductivity detector (GC-TCD)

Analysis of all the gas samples generated in Chapter 4 (polysiloxane embedded silver nanoparticles interacting with alcohols) was obtained on the PerkinElmer Clarus 480 gas chromatograph in line with a thermal conductivity detector (TCD). The gases carried on argon are eluted along a packed column (9' Molecular Sieve 13X, 45/60 mesh, 1/8" SF) that separates all the light gases (O_2 , N_2 , CO , CH_4 , H_2 , etc.), in line with another column (7' HayeSep N, 60/80 mesh, 1/8" SF) that separates the heavier gases.

For a typical analysis, 2 mL of gas sample was manually injected for a 7-minute run, with the columns at a constant temperature of 60°C and the TDC at a constant temperature of 150°C. Argon gas was chosen instead of the standard helium carrier gas due to its improved sensitivity for hydrogen gas. The tradeoff was a low sensitivity for oxygen and nitrogen, which was not an issue in the present case, as these two molecules were solely present from the air in these systems. This analysis had mainly a qualitative purpose to identify the nature of the gas generated, since the quantitative data were obtained on the highly sensitive gas evolution apparatus (see description below).

2.4.3 Nuclear magnetic resonance

All the NMR spectra were acquired on the 400 MHz Bruker ADVANCE 400 NMR spectrometer equipped with an auto-sampler. Data were analyzed using the Bruker TOPSPIN NMR software.

2.5 Others

2.5.1 Gas evolution apparatus

For any reaction that involved gas generation or consumption (Chapters 3 & 5), the quantity involved was measured with an instrument built in-house and donated by Professor Ross Barclay (Mount Allison University, NB). The experimental theory behind the operation of this apparatus is detailed in the Master of Science thesis of Miss Vasilisa Filippenko.³ Briefly, a closed system composed of two Pyrex vessels connected through a pressure-sensitive membrane is immersed in a temperature-controlled water tank. A schematic representation can be seen in Figure 2. 1. The membrane is connected to a pressure transducer that converts any pressure difference between the two vessels into an electrical signal that is recorded both on a paper chart and electronically using a program developed in the Labview v8.5 software environment.

For a typical experiment, both the reference and the reaction vessel were filled with the proper solvent for an overnight equilibration at 30°C (unless otherwise stated). The cells were attached to a shaker to ensure a fast diffusion of gas at all times throughout the experiment. Prior to the actual measurement, both a calibration and a baseline were run. The

calibration consisted of the electrical signal conversion of a known volume of air injected to the system; this was carried out using three volumes (and an average of three runs), assuming that air is an ideal gas and applying the ideal gas law $PV=nRT$. The baseline, where both the reference and the reaction vessels contain the same reagents, was allowed to acquire for a minimum of 15-20 minutes. Finally the reagent that would trigger pressure change (usually an initiator) was injected in the reaction vessel, whereas the reference vessel would receive an equivalent volume of solvent only. Whenever light irradiation was required (H_2O_2 degradation in Chapter 3), the wooden front panel of the tank could be removed, exposing a glass window. A Luzchem EXPO panel with five UVA lamps was placed in front, facing the water tank, and was turned on to initiate the reaction.

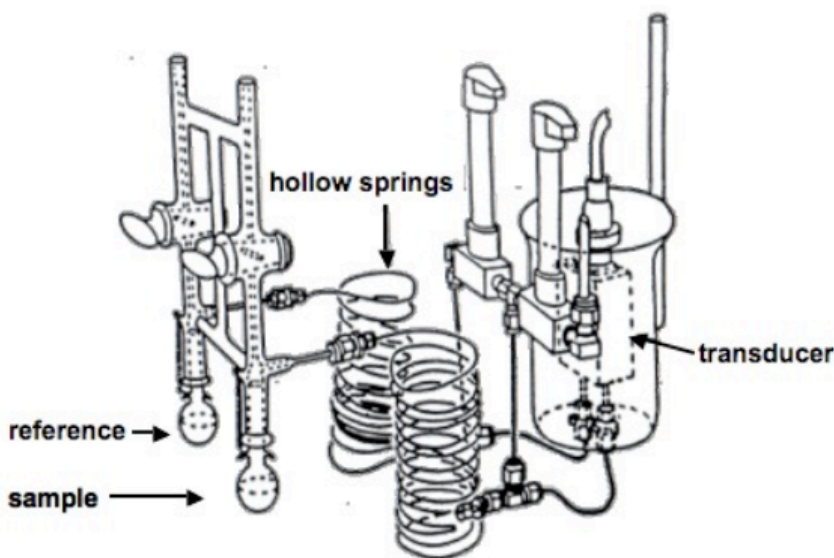


Figure 2.1: Schematic representation for the gas evolution apparatus showing the main parts of the instrument ³

2.5.2 Light exposition reactors

Irradiation experiments were carried out using two different apparatus: a LZC-4 photoreactor or an EXPO panel, both from Luzchem Research Inc., equipped with fluorescent tubes centered at various wavelengths (UVA, UVB, UVC, 420 nm and Visible).

Unless otherwise stated, all irradiation experiments occurred inside the photoreactor. Samples, transferred in quartz cuvettes capped with septa, were placed on a rotating carousel at the center of the reactor. Six fluorescent tubes of a given spectral region were connected on the sidewalls of the reactor. The EXPO panel was primarily used for light exposure within the gas evolution apparatus.

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3.1 Introduction

The consistently increasing usage of cerium oxide nanoparticles (also called ceria) has brought about concern regarding their human toxicity and environmental impact. In particular, there has been some controversy regarding their oxidant/antioxidant effect, mainly in biological systems.¹⁻⁵ Lin *et al.* have assessed the toxicity of cerium oxide nanoparticles in human lung cancer cells by showing that exposure to 20 nm particles induced oxidative stress as a result of high levels of reactive oxygen species (ROS).³ More recently, Park *et al.* have discussed cerium oxide nanoparticles' induced oxidative stress in cultured BEA-2B cells (derived from human bronchial epithelia normal cells) and showed that the initial size of the nanoparticles did not significantly affect the levels of ROS as cerium oxide would tend to aggregate upon uptake by the cells.⁴ On the other hand, cerium oxide nanoparticles were shown to offer some neuroprotection. Chen and coworkers demonstrated that exposing retinal neurons to hydrogen peroxide after incubation with 5 nm cerium oxide nanoparticles decreased the amount of intracellular H₂O₂-induced ROS.¹ Similarly, both Das *et al.* and Schubert *et al.* labeled cerium oxide nanoparticles as biologically active antioxidants that actively protect respectively spinal cord and hippocampal nerve cells from oxidative stress.^{2,5} Both the oxidant and antioxidant behaviors were attributed to the ability for cerium oxide to switch between its trivalent and its tetravalent states. A high Ce³⁺/Ce⁴⁺ ratio at the surface of cerium oxide nanoparticles translates to an increased amount of oxygen vacancies at the surface, which often leads to an improved catalytic activity.⁶

Most studies looking at the influence of cerium oxide on radical scavenging in biological systems are rather complicated. In fact, neurons and cells in general contain not

only the radical species and the added ceria solution, but also proteins, fatty acids and other enzymes with embedded metal salts. In most biological studies about the subject, hydrogen peroxide (H_2O_2) is the element added in large excess to the system to trigger the radical stress. All of these species may take part in either the formation or the scavenging of radical species. Iron, for example, is a powerful metal present in biological systems that can undertake redox catalytic cycles. Iron has the well-established ability to react with hydrogen peroxide to generate hydroxyl radicals through the “Fenton” reaction, much like copper, cobalt, vanadium and chromium.⁷ Although many enzymes (such as catalase) are able to catalytically convert hydrogen peroxide into less reactive products (H_2O and O_2), a high topical concentration of H_2O_2 and the presence of such metal salts in the system can lead to damaging ROS. Considering this, it is still unclear whether cerium oxide nanoparticles act as direct antioxidant or if they protect from oxidative stress by inhibiting a step in the pathway towards necrosis (premature cell death caused by external factors).

In this chapter, the antioxidant activity of water-soluble cerium oxide nanoparticles will be tested with the simplest system generating ROS: water and hydrogen peroxide. The radical species are generated *via* direct UVA irradiation or through a Fenton⁸ or Fenton-like reaction. Tracking the oxygen gas liberated in these reactions can be used to illustrate hydrogen peroxide degradation, with hydroxyl and hydroperoxyl radicals as the intermediate species.⁹ By comparing the rate of oxygen generation for each situation, ceria is shown to act more as a Fenton-like reagent itself once it has oxidized reactive Fe^{II} ions present in the reaction. The possible antioxidant activity of cerium oxide nanoparticles is also measured in an organic medium where a catalytic autooxidation of styrene takes place. As compared to 2,2,5,7,8- pentamethyl-6-chromanol (PMHC) (an organic soluble vitamin E analogue)

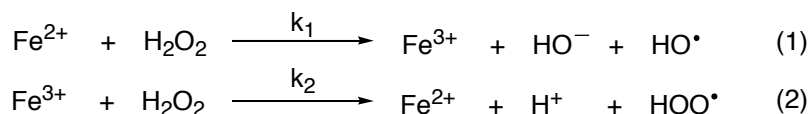
cerium oxide nanoparticles were found to barely have any ability to scavenge any radicals present in the reaction medium.

3.2 Results

3.2.1 Fenton and Fenton-like reactions with water soluble CeO₂

Oxygen generation due to the degradation of hydrogen peroxide is followed using the pressure-transducer system described in Chapter 2. Hydrogen peroxide was chosen as it is one of the simplest sources of reactive oxygen species and, therefore, has been the radical initiator of choice for most biological studies pertaining to antioxidant activity. The influence of cerium oxide addition on the gas generation rate and on the H₂O₂-degradation rate was examined.

First, a catalytic cycle based on iron salts was used to trigger the degradation of hydrogen peroxide (see Scheme 3. 1).



Scheme 3. 1: Iron catalyzed hydrogen peroxide degradation for the generation of highly reactive hydroxyl radicals (Fenton reaction)

Both Fe^{II} and Fe^{III} salts are individually used as catalysts to trigger the degradation of H_2O_2 . As can be seen in Figure 3. 1 and based on the notations used in Scheme 3. 1, the rates k_1 and k_2 for each degradation differ in the catalytic cycle. Upon addition of CeO_2 , both rates decreased; however complete quenching of the oxygen generation was not observed. Also, the baseline taken prior to adding hydrogen peroxide to the system showed that the oxygen generated in this experiment is only due to the degradation of the peroxide.

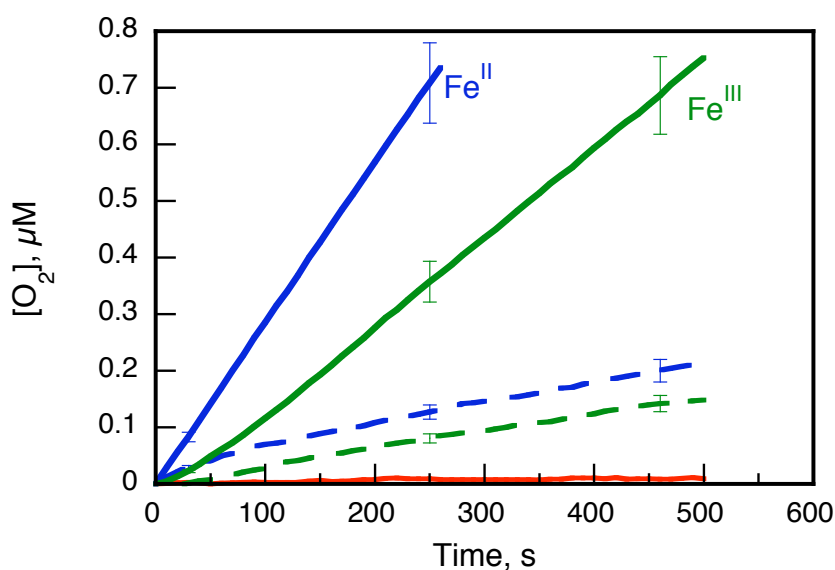


Figure 3. 1: Oxygen generation upon catalytic hydrogen peroxide degradation at 30°C. The baseline (in red) is run prior to H_2O_2 addition (3.25 M). Oxygen release is measured under Fenton (with $[\text{Fe}^{\text{II}}] = 5 \mu\text{M}$ in blue) and Fenton-like (with $[\text{Fe}^{\text{III}}] = 5 \mu\text{M}$ in green) conditions before (solid) and after (dashed) CeO_2 addition (0.5 mM).

The radical scavenging ability of cerium oxide was also examined through the photochemical degradation of H_2O_2 with UVA light. This also allows for determination of the degradation rate of H_2O_2 in the absence of iron salts. Firstly, the rate of degradation through UVA irradiation was slower than by the catalytic Fenton reaction (see Figure 3. 2,

blue traces). However, a decrease in O_2 generation was observed following CeO_2 addition, but the hydrogen peroxide degradation did not completely stop. Since the commercial cerium oxide is stabilized by polyacrylic acid (PAA), a control experiment was carried out where only the stabilizing agent was added, in the same concentration as the commercial sample. Figure 3. 2 (green traces) illustrates that the previously observed reduction in rate is mostly due to the polymer used to stabilize the nanoparticles:

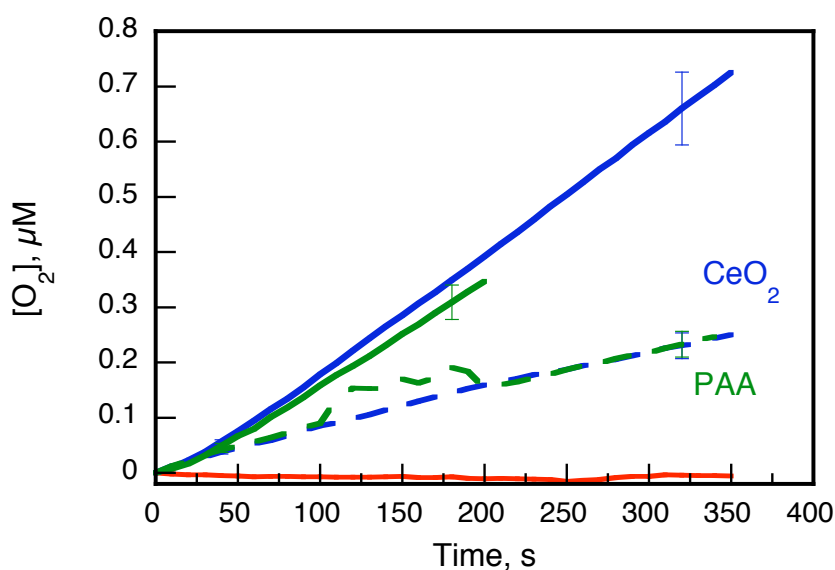


Figure 3. 2: Oxygen generation upon photochemical hydrogen peroxide degradation at 30°C. The baseline (in red) is run prior to H_2O_2 addition (3.25 M). Oxygen release is measured under UVA irradiation before (plain) and after (dashed) addition of CeO_2 (blue, 0.5 mM) or PAA (green, 1.9 g/L).

A final experiment was undertaken in the pressure-transducer apparatus, where H_2O_2 was diluted in water at 30°C and CeO_2 added in the absence of catalytic or photochemical H_2O_2 degradation initiators (Figure 3. 3). Although a small amount of oxygen generation is

observed due to the temperature of the system, it is upon addition of cerium oxide that the oxygen generation increases.

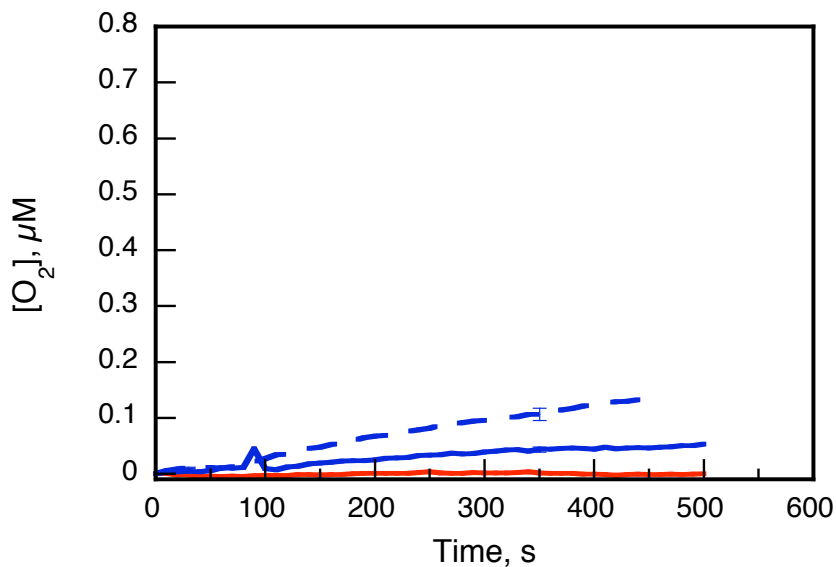


Figure 3.3: Control experiment with 3.25M of H_2O_2 (plain blue trace) followed by the addition of 0.5 mM of CeO_2 (dashed blue trace).

Note that all three figures (Figures 3. 1 - 3. 3) are plotted with the same scale to emphasize the differences in rates. Also, the concentrations of H_2O_2 and CeO_2 introduced for each experiment are kept constant to really compare the effect in various environments. These rates are all summarized in Figure 3. 4.

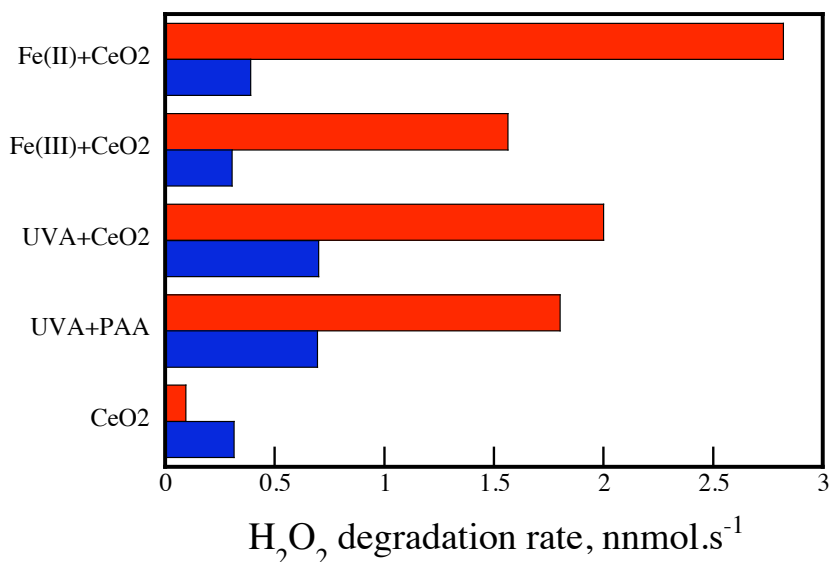


Figure 3. 4: Comparison of Hydrogen Peroxide (3.25 M) degradation rate before (red bar) and after (blue bar) injection of either Cerium Oxide or poly(acrylic acid) (PAA)^a under various conditions. (^a The CeO₂ solution used contains PAA in the same concentration as added in the “PAA-only” experiment)

The addition of cerium oxide does not lead to complete inhibition of oxygen generation, but rather to a significant decrease in the H_2O_2 degradation rate. In the Fenton and Fenton-like reactions, the injection of cerium oxide in both systems leads to a decrease of at least 80%. The degradation of hydrogen peroxide initiated through the use of UVA irradiation and in the absence of any other catalyst is reduced rather than completely inhibited upon addition of cerium oxide. The addition of the stabilizing agent PAA, instead of CeO₂ solution, under hydrogen peroxide UVA degradation is also highlighted. By comparing “UVA + CeO₂” and “UVA + PAA”, we can see that the majority of the decrease observed in the former case is due to the stabilizing agent alone. More surprisingly (as seen in Figure 3. 3) when neither a catalyst, nor light initiate the degradation of hydrogen

peroxide, the addition of cerium oxide alone leads to a marked increase in degradation reflected by the 233% increase of the rate.

3.2.2 Iron content in commercial CeO₂ solution

At this point, it is interesting to highlight that the rates for “Fe^(III) + CeO₂” and “CeO₂” after CeO₂ addition in Figure 3. 4 are the same. Unless fresh batches with MilliQ water are prepared prior to any experiment, it is extremely difficult to prevent the contamination of aqueous solutions with metal salts. The last results obtained in Figure 3. 4 (“CeO₂” alone) prompted the titration of the commercial solution of cerium oxide for ferric salt (Fe^{III}) using the method developed by Buettner and the catalytic degradation of ascorbic acid (see Experimental Section).¹⁰ This method is chosen over other colorimetric methods such as 1,10-phenanthroline addition because the later does not form a detectable colored complex with the traces amount of iron present. The calibration curve obtained and shown in the Experimental Section is used for Figure 3. 5, where a known volume of the commercial cerium oxide solution is added to ascorbic acid and its subsequent degradation is monitored through UV-visible absorbance.

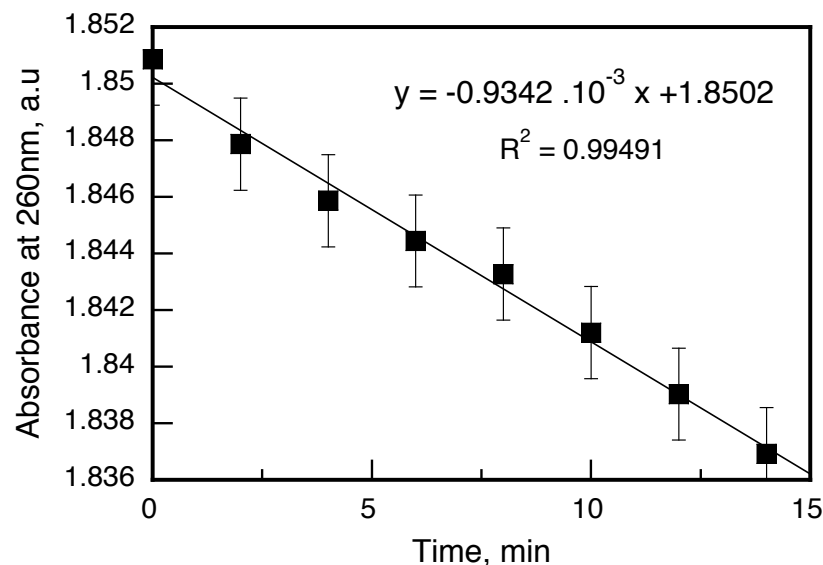


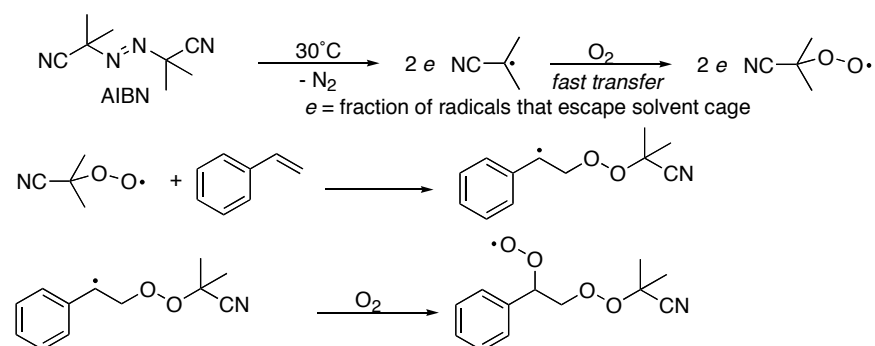
Figure 3.5: Absorbance decay of ascorbic acid at 260 nm after injection of a 50 μL cerium oxide solution aliquot (line: linear fit for the data).

The degradation rate, -0.93×10^{-3} a.u./min, was proportional to the slope in Figure 3.5 and corresponded to a concentration of Fe^{III} in the commercial stock solution of cerium oxide of 0.22 mM. Despite the significant amount of Fe^{III} present in the cerium oxide solution, the rate of oxygen generation listed in Figure 3.4 after addition of cerium oxide in “ CeO_2 ” is the same as the rate after addition of cerium oxide in entry 2, rather than before the addition where only Fe^{III} salt is present.

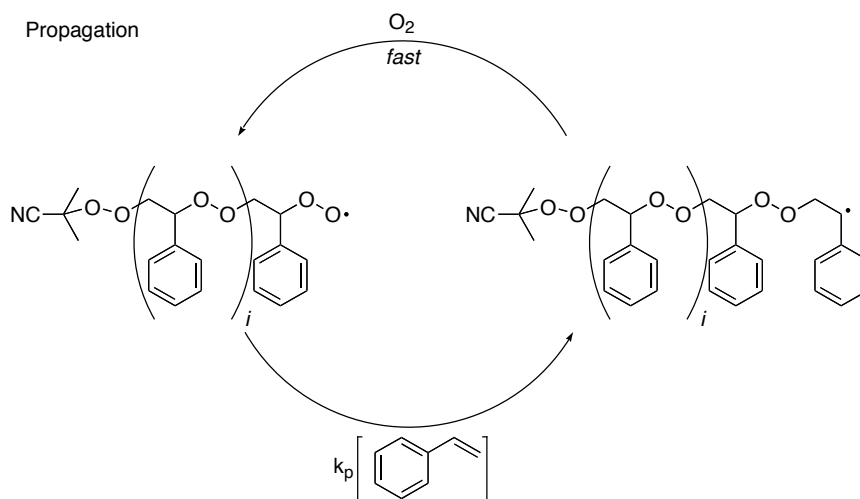
3.2.3 Polystyrene auto-oxidation with organic soluble CeO_2

An inhibited oxygen uptake (IOU) experiment was done with the auto-oxidation of pure styrene initiated by AIBN (see Scheme 3.2). This classic reaction is typically run in the Scaiano research group as a reference analysis for the antioxidant ability of an unknown molecule against a known antioxidant.^{11, 12}

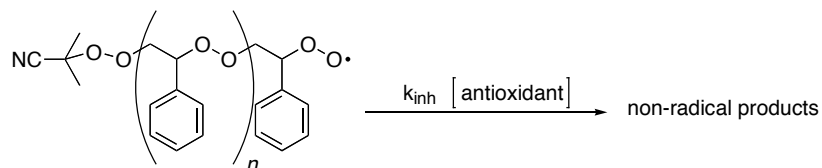
Initiation and first transfers



Propagation



Antioxidant termination



Scheme 3. 2: Initiation with AIBN followed by auto-oxidative chain polymerization of styrene. Only the antioxidant termination, of interest for this specific process, is presented.

This reaction leads to oxygen consumption illustrated by a negative slope in Figure 3. 6 (trace *a*, blue). Upon addition of PMHC, a known antioxidant capable of terminating two polymerization chains ($n=2$), we observe an inhibition of the oxygen uptake until the PMHC

was fully consumed (trace *b*, red). The antioxidant activity of cerium oxide in 1-tetradecene was tested using the same procedure.

First, when a concentration of cerium oxide comparable to [PMHC] was added, no inhibition was observed (trace *c*, orange). When a ten-times equivalent dose of CeO_2 was injected, a decrease in oxygen consumption was observed rather than an actual quenching of the auto-oxidation (trace *d*, green).

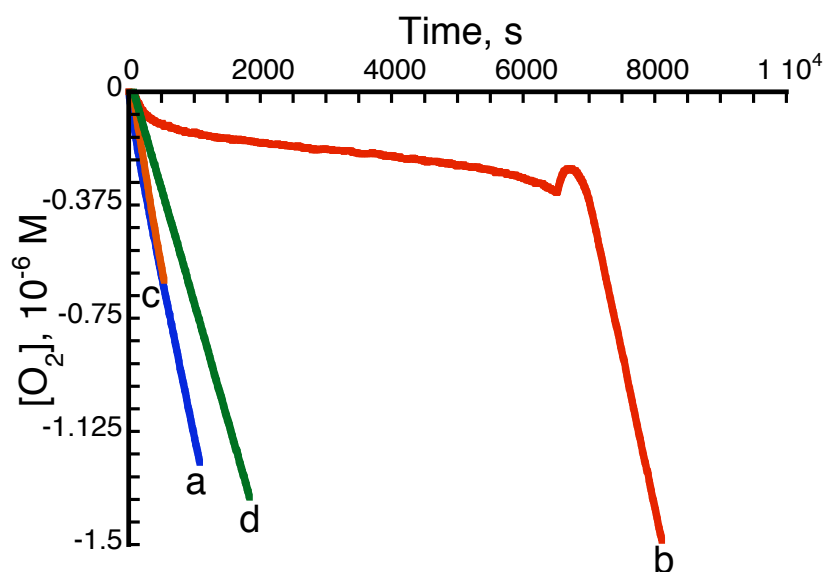


Figure 3. 6: Oxygen uptake curves for auto-oxidation of styrene ($\sim 2.6\text{ M}$) in chlorobenzene, initiated with azo-bis(isobutyronitrile) (AIBN, $\sim 18\text{ mM}$) at 30°C . Curve *a*: uninhibited oxygen uptake. Curve *b*: inhibited by 2,2,5,7,8-pentamethyl-6-hydroxychroman (PHMC), $\sim 4.5\text{ }\mu\text{M}$. Curve *c* and *d*: inhibited by Cerium Oxide ($5.3\text{ }\mu\text{M}$ and $51\text{ }\mu\text{M}$) in 1-tetradecene.

Given the small effect of traces *c* and *d* and given the viscosity and the nature of the cerium oxide solvent 1-tetradecene, a control experiment containing only the solvent and the stabilizing agent oleic acid (Figure 3. 7) was undertaken.

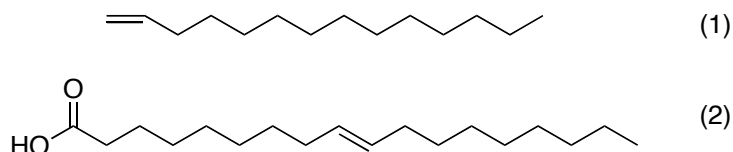


Figure 3. 7: Structures of the solvent 1-tetradecene (1) and the stabilizing agent oleic acid (2) used in the synthesis of organic CeO₂ nanoparticles.

As can be seen in Figure 3. 8, a superimposition of traces *c* and *d* with their control equivalents (in the absence of cerium oxide nanoparticles) gives traces with the same slopes. This clearly shows that the slight changes observed in Figure 3. 6 are mostly due to the solvent and stabilizing ligand rather than CeO₂ particles. Those changes observed could be due to a change of reactivity in the system that leads to a decreased rate of hydrogen abstraction due to the nature of the system itself.

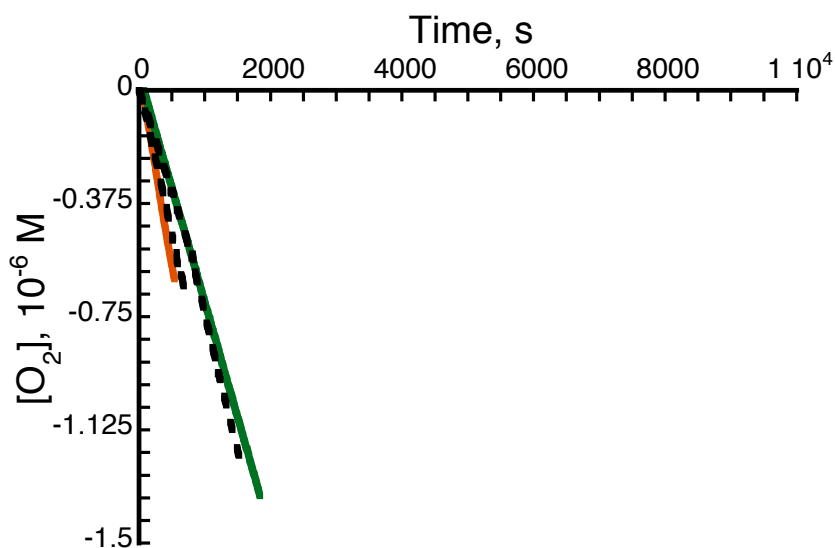


Figure 3. 8: Comparison of traces *c* (orange) and *d* (green) from **Figure 3. 6** with the same volume and concentration of solvent 1-tetradecene and stabilizing agent oleic acid (overlying dashed lines).

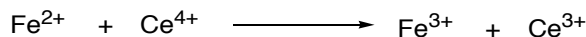
Discussion

For most examples of antioxidant activity, cell lines are systematically incubated with hydrogen peroxide to generate oxidative stress in the biological system. To get as close as possible to a biological system, an aqueous system is evaluated with the simplest ROS source available: hydrogen peroxide. Upon degradation, H_2O_2 yields one of the most reactive oxygen centered radical in biology; the hydroxyl radical ($\text{HO}\bullet$). Two routes are selected to generate this radical: iron salt catalysis and UVA light irradiation.

UVA irradiation allows the cleanest way to generate hydroxyl radicals. It is also a very mild release of the radicals, as only the tail of the H_2O_2 absorption band can be excited by UVA irradiation. This spectral region, however, was preferred to UVB irradiation for some control on the gas generation in this ultra-sensitive apparatus. Although the irradiation is done through a glass window and the incident light is greatly scattered by the water bath surrounding the reaction vessels, the main interest is in the relative quenching of H_2O_2 degradation before and after addition of cerium oxide; therefore the influence of light scattering is not considered. Upon irradiation some decrease in the degradation rate of H_2O_2 was observed (-67%) following addition of cerium oxide with most of this being attributed to the presence of polyacrylic acid (-61%). It is no surprise that a synthetic route will influence the reactivity of a nanoparticle, especially the stabilizing agent used, as it will control the availability of the surface to the reactants. Unfortunately, this stabilizer is often limited to the role of mediator rather than an active participant in the process and some polymers containing hydroxyl groups, such as dextran or polyacrylic acid, have the ability to trap radicals.³ The low scavenging action of cerium oxide nanoparticles has also been

attributed to acidic pH with a pH of 4 or less that usually leads to no antioxidant property. This has been attributed to the high concentration of $[H^+]$ that inhibits the regeneration of Ce^{3+} from Ce^{4+} .³ Our system however has a pH = 6.2, yet it shows no antioxidant activity.

When hydroxyl radicals are generated through Fenton (Fe^{II}) and Fenton-like (Fe^{III}) pathways, the addition of cerium oxide leads to an observable decrease in the degradation rate of hydrogen peroxide (-86% and -80%, respectively). We propose that a secondary reduction-oxidation occurs when both iron and cerium ions are present in the reaction mixture in (Scheme 3. 3). The standard electrode potentials ($E^\circ(Fe^{2+}/Fe^{3+})=0.77$ V and $E^\circ(Ce^{3+}/Ce^{4+})=1.44$ V) render this reaction highly favorable ($K > 10^{15}$).⁶ These constants were established for ions in a homogeneous solution, whereas the present system is heterogeneous comprising of CeO_2 nanoparticles. The nanoparticles used in this work are small in diameter (1-10 nm). Although they are not the same as dissolved ions, a similar behavior from the soluble cerium salt and the Ce^{4+} units at the surface of the nanoparticles can be assumed, with respect to the iron salts. The presence of cerium oxide prevents Fe^{II} from reacting with hydrogen peroxide through a Fenton pathways as it is rapidly oxidized to less reactive Fe^{III} .

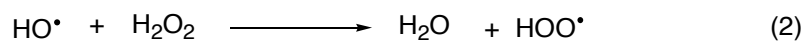
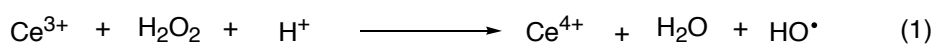


Scheme 3. 3: Reduction-Oxidation reaction between cerium oxide ions present at the surface of the nanoparticles and iron(II) salt present in solution

Once cerium oxide has hindered the Fenton reaction caused by the iron salt, an oxygen generation is still observed at a rate of ~0.3-0.4 nmol/s. These results imply that

some hydrogen peroxide degradation still occurs. Further, adding cerium oxide to a hydrogen peroxide solution that does not undergo degradation leads to an oxygen generation rate of 0.3 nmol/s after injection (Figure 3. 4). The presence of iron traces in the commercial cerium oxide solution could be an explanation for the increased rate. The volumes injected correspond to a concentration of $[\text{Fe}^{\text{III}} @ \text{FeBr}_3] = 5 \mu\text{M}$ from the iron bromide stock solution, compared to the concentration of $[\text{Fe}^{\text{III}} @ \text{CeO}_2] = 15 \mu\text{M}$ from the cerium oxide stock solution. This implies that after injection of CeO_2 , the concentration of iron salt in the system is $[\text{Fe}^{\text{III}}] = 20 \mu\text{M}$ for “ $\text{Fe}^{\text{(III)}} + \text{CeO}_2$ ” and $[\text{Fe}^{\text{III}}] = 15 \mu\text{M}$ for “ CeO_2 ” (Figure 3. 4). However, the rates are the same after the actual injection for both. This result shows that the impact on the degradation really is due to the cerium oxide nanoparticles themselves rather than the traces of iron that may be present.

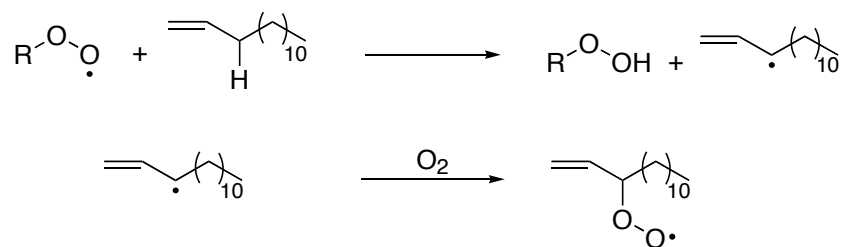
Supposing that ceria nanoparticles are a rare earth metal oxide capable of undergoing a catalytic cycle analogous to Fenton chemistry (see Scheme 3. 4), all subsequent degradation rates observed upon CeO_2 injection should be due only to cerium. This reactivity is most likely activated by cerium in its (+3) oxidation state present at the surface of the nanoparticles, as shown below in equation (1). The cycle closes with the reduction of the more stable Ce^{4+} back to Ce^{3+} due to reaction with a hydroperoxyl radical as shown in equation (3). A similar mechanism has been suggested previously for $\text{Ce}^{3+}/\text{Ce}^{4+}$ in solution.¹³



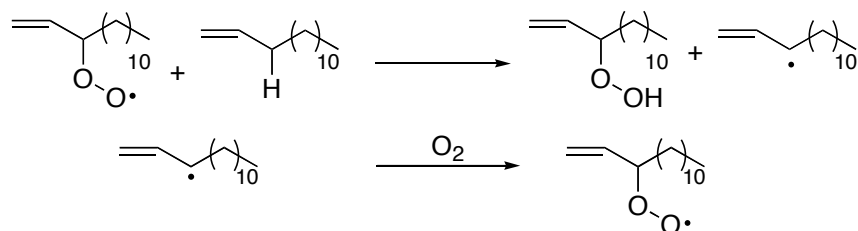
Scheme 3. 4: Cerium catalyzed hydrogen peroxide degradation analogous to Fenton/Haber Weiss pathways, where Ce^{3+} and Ce^{4+} refer to surface ions on the particle.

The inhibited oxygen uptake experiment done in chlorobenzene is a direct technique used to assess the antioxidant activity of a molecule by testing its ability to shut down the chain growth oxidation of polystyrene and, thus, the uptake of oxygen. If a molecule or a system has the ability to scavenge radicals much like PMHC (see Scheme 3. 6), a drastic decrease (or plateau) in oxygen uptake is observed. This plateau is not observed with cerium oxide additions, even when the concentration of cerium oxide is ten times higher than that of PMHC (Figure 3. 6, traces c and d). Both 1-tetradecene and oleic acid molecules possess allylic hydrogen atoms (respectively 2 and 4 atoms) that can be easily abstracted in a radical oxidative environment. The allylic radical can subsequently react with oxygen to create peroxide radical and a chain reaction, shown in Scheme 3. 5, can unfold.

Initiation and first transfer

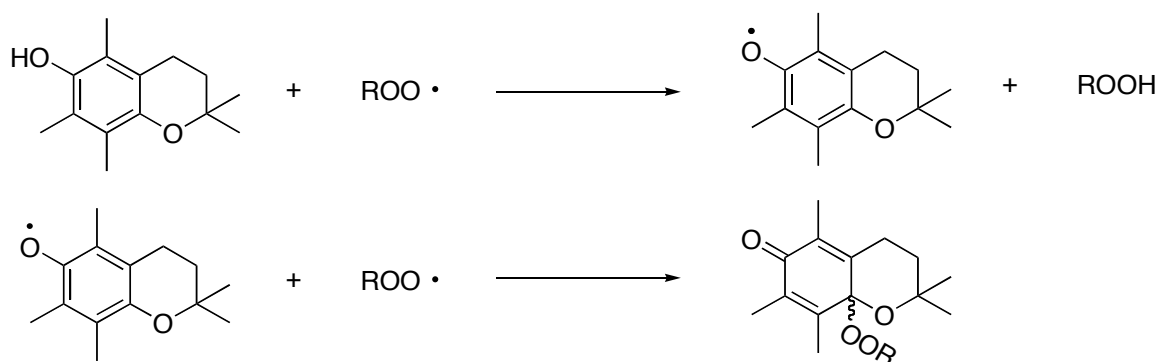


Propagation



Scheme 3. 5: Auto-oxidative chain reaction with a molecule (here 1-tetradecene) possessing an allylic hydrogen atom.

If this competing reaction was to occur upon injection of the 1-tetradecene / oleic acid mixture, an increased or unchanged rate of oxygen consumption would be observed in Figure 3. 8 as their concentrations were increased. Instead, the slight reduction in the oxygen uptake is attributed to the decreased rate at which the rate-determining hydrogen abstraction takes place, most likely due to a decrease of reactivity for the peroxy radical in this new solvent.



Scheme 3. 6: Reaction pathways illustrating the peroxy radical trapping ability of 2,2,5,7,8-pentamethyl-6-chromanol (PMHC).

This very simple and reproducible experiment is evidence that cerium oxide nanoparticles do not act as an antioxidant capable of terminating a chain reaction. Indeed cerium oxide nanoparticles in an organic, non-biological environment are not able to trap peroxy radicals like PMHC does.

All the claims of antioxidant activity from the cerium oxide nanoparticles are done with biological systems under extreme oxidative stress in the presence of high concentrations of H_2O_2 . This high excess of ROS leads to the unbalanced equilibrium where antioxidant enzymes such as catalase or glutathione peroxidase are no longer able to reduce free

hydrogen peroxide into harmless water and oxygen and some radicals generated are able to initiate the cell death due to necrosis.

3.3 Summary

In summary, we have shown that cerium oxide nanoparticles are redox active in part due to their ability to generate stable Ce^{3+} clusters at the nanoparticle surface. This ability does not make them a direct radical scavenger in organic medium when stabilized by oleic acid in tetradecene. Instead, cerium oxide has an indirect effect on radical scavenging wherever Fenton reactions take place, as it oxidizes the iron salt to its less reactive Fe^{III} form. The rate of oxygen generation for cerium oxide undergoing its own Fenton cycle with hydrogen peroxide is also observed. Even in the latter case, some of the effect on radical scavenging is due to the stabilizing ligand poly(acrylic acid). Both examples emphasize the importance of the stabilizing shell, mandatory for stable discrete CeO_2 nanoparticles, in the actual behavior of the nanocrystals.

The complicated reactivity of cerium oxide may help to explain the controversial results presented previously where cerium oxide was presented either as an antioxidant or as an oxidizing agent depending on the biological system used. Cerium oxide can either have a positive effect by inhibiting more reactive oxidants or a negative effect by being oxidizing itself, depending on the surroundings in the reaction medium.

Further study is required within a more complex system (*e.g.*, cells) as a better understanding on the mechanistic pathways of CeO_2 nanoparticles is now acquired.

3.4 Experimental

3.4.1 Materials

Cerium (III) chloride heptahydrate (99%), oleic acid (99%), 1-tetradecene (92%), sodium oleate (>99%), iron(III) bromide, iron(II) sulfate heptahydrate and hydrogen peroxide (solution 30 wt. % in water) were all purchased from Sigma and used as received. The aqueous suspension of cerium oxide (CeO_2) was purchased from Vivenano, stored at 4°C and used directly. Initiator azo-bis(isobutyronitrile), (AIBN, Sigma 98%), was used after re-crystallization from a dichloromethane/*n*-hexane/ethanol solvent mixture and stored at 4°C. Antioxidant 2,2,5,7,8- pentamethyl-6-chromanol (PMHC, Sigma 97%), was used after further purification by recrystallization from *n*-hexane/dichloromethane. Styrene (Sigma, 99%) was distilled to remove stabilizers by bulb-to-bulb vacuum distillation and filtered through a silica column (or aluminum oxide). Solvents ethanol, *n*-hexane and chlorobenzene were all purchased from Sigma (HPLC grade) and used directly. Milli-Q water (Millipore Corporation) was deionized in house and always used freshly collected.

3.4.2 Hydrogen peroxide degradation assays

Hydrogen peroxide degradation induces a gas generation (oxygen) that is followed in a sensitive pressure-transducer system. The pressure difference between the degradation of the hydrogen peroxide solution and that of a reference cell (same composition, minus the hydrogen peroxide) is measured. This difference is recorded in volts, read by a computer and converted to moles of oxygen by calibrating the apparatus with a known volume of gas.

Two main degradation routes are tested: 1) through Fenton reactions and 2) through UVA light exposure. Both pathways used commercially available aqueous cerium oxide dispersion.

For a typical Fenton reaction, the reference and sample cells are filled with water (1 mL) and either iron(III) bromide or iron(II) sulfate heptahydrate solutions (10 μ L, 5 μ M). The measurement starts upon addition of hydrogen peroxide (500 μ L, 3.25 M) to give the rate of oxygen generation. The effect of cerium oxide is measured by further adding its aqueous suspension to both cells of the system (up to 100 μ L, 86.2 mM concentration based on total cerium content). A control experiment containing only the stabilizing polymer poly(acrylic acid) (100 μ L, 1.9 g/L) in water is similarly undertaken by injecting the solution in both the reference and the reaction cells.

To undergo a photo-degradation, hydrogen peroxide diluted in water (2.5 mL, 1.96 M) is exposed to UVA irradiation (65 W/m²) and the effect of cerium oxide is measured by further adding its aqueous suspension to both cells of the system (up to 100 μ L, 52.2 mM). It is important to emphasize that for the photo-degradation path, the freshly collected MilliQ water is passed through Chelex[®] to remove any significant amount of iron.

3.4.3 Titration of ferric salt (Fe^{III}) in commercial aqueous solution of cerium oxide

To generate a calibration curve, a solution of ascorbic acid (0.4410 g, 0.1000 M) and a solution of iron(III) bromide (0.0052 g, 755 μ M) are both prepared in freshly collected MilliQ water (25 mL for each solution). The rate of degradation of ascorbic acid (3.5 μ L of the stock solution, 117 μ M) by Fe^{III} is followed by UV-Visible spectroscopy: the decrease of the absorbance peak at 260 nm is monitored for different initial concentrations of [FeBr₃] (up

to 10 μM). The calibration curve is obtained where the degradation rate is plotted against number of moles of Fe^{III} (see Figure 3. 9).

To determine the Fe^{III} content in the cerium oxide solution, a known volume (50 μL) is added to the fresh ascorbic acid solution and, under similar conditions used for the calibration, the degradation is observed with use of UV-visible absorbance spectroscopy. The degradation rate is determined and the corresponding concentration of Fe^{III} is obtained.

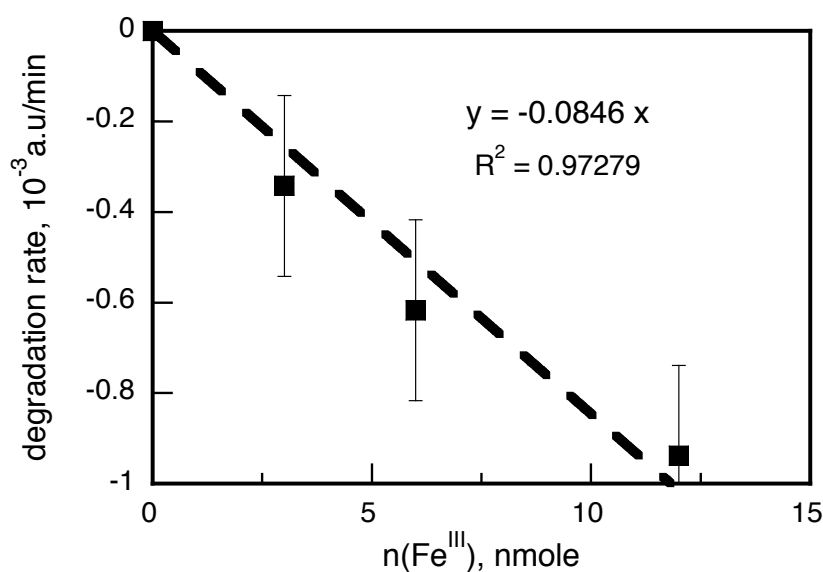


Figure 3. 9: Calibration curve for Fe^{III} content (Dashed line: linear fit of the data)

3.4.4 Cerium oxide synthesis in 1-tetradecene

The synthesis of CeO_2 in an organic solvent is a 2-step reaction.¹⁴ First a cerium-oleate complex is formed by reaction of cerium (III) chloride heptahydrate (5.0 g, 13.5 mM) with sodium oleate (12.2 g, 40.5 mM) in a solvent mixture (40 mL of ethanol, 30 mL of water and 70 mL of hexane) under reflux (70°C) for four hours. The extracted complex (0.42

g, 0.43 mM) is then dissolved in 80 mL of a high boiling point solvent, 1-tetradecene, with a slight excess of oleic acid (0.16 mL, 0.50 mM), then the system is put under reflux (250°C) for two hours under inert atmosphere. The cerium oxide obtained is further used as is in 1-tetradecene.

SEM analysis of the material shows an average particle size of 67 nm for the oleic acid-stabilized cerium oxide nanoparticles:

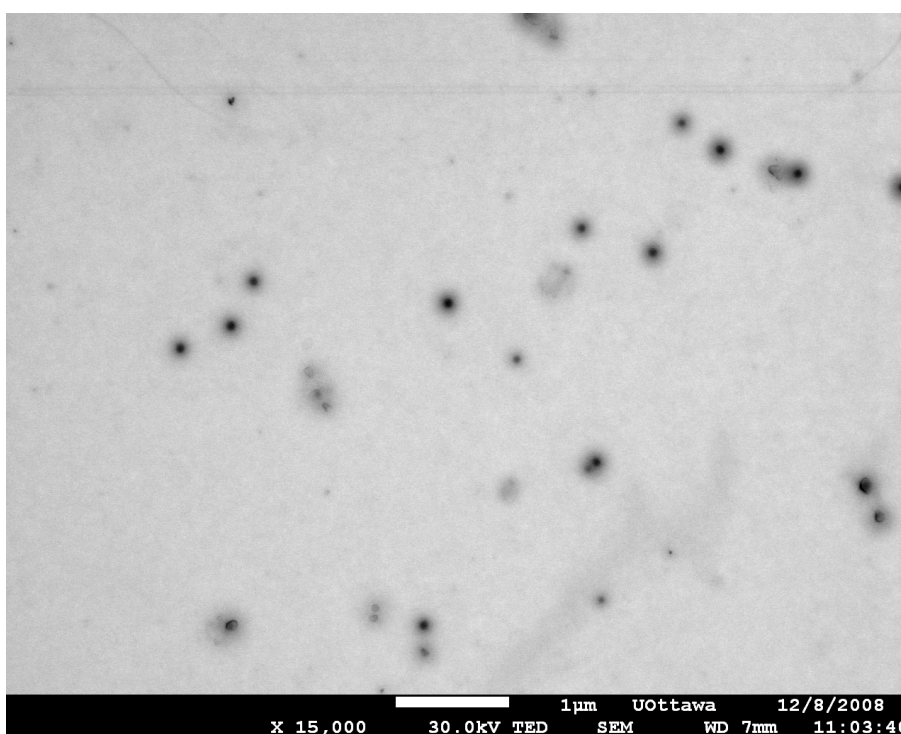


Figure 3. 10: Typical SEM acquisition image for cerium oxide nanoparticles in an organic solvent

3.4.5 Inhibited oxygen uptake (IOU) experiments

Typical inhibited oxygen-uptake (IOU) experiments have been explained previously.¹¹ In brief, 2.5 – 2.6 M styrene in chlorobenzene is auto-oxidized under air at

30°C. The AIBN initiator (18 mM) starts the auto-oxidation process. Pressure differences between this auto-oxidizing solution and that of a reference cell (same composition, minus the initiator) are measured by means of the same pressure transducer that was used for the hydrogen peroxide degradation assay. This particular auto-oxidation process was chosen because it has a known oxygen uptake rate.¹¹ The entire pressure-transducer system is placed in a water bath for a constant controllable temperature of 30°C.

To inhibit the oxygen uptake, PMHC, an efficient peroxy radical trap ($n=2$),¹¹ is compared to our home-made cerium oxide nanoparticles dispersed in 1-tetradecene. A control is also run with only 1-tetradecene and oleic acid, but without CeO₂ nanoparticles.

3.5 References

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4.1 Introduction

Colloidal quantum dots (QDs), in particular CdSe semiconductor quantum dots, are fairly easily synthesized and have a well defined luminescence across the visible spectrum dependent upon their size.^{1, 2} Despite their useful properties, core QDs have several drawbacks, such as blinking, luminescence quantum yields that depend on their “quality” (*i.e.*, subtle variations in their synthesis), age, air sensitivity, history of light exposure and other ambient conditions.

Numerous efforts have been focused on enhancement and stabilization of QD luminescence, as well as to minimize the leaking of Cd^{2+} ions into the surrounding environment, some of them with considerable success. For example, CdSe/ZnS “core-shell” QDs, containing a shell of ZnS, are quite stable and are readily available commercially.^{3, 4} Similarly, the fluorescence of QD can be stabilized with polymers containing amine ligands.⁵⁻⁷ A comparative study of core and core-shell CdSe QDs carried out in the Scaiano research group has shown that the presence of a shell greatly reduces CdSe QD sensitivity towards solution quenchers.⁸ This property is certainly desirable for simple label-type applications where a maximum fluorescence quantum yield is required, but it is a problem for the development of quantum dot-based sensors.

In this chapter, the effect of the treatment of CdSe QDs with cadmium oxide (CdO) as well as elemental chalcogens (selenium and sulfur) is shown, in the presence or absence of light exposure. In particular, treatment with elemental sulfur followed by UVA irradiation leads to a remarkable enhancement of QD luminescence and to QDs with improved luminescence stability. In addition, the luminescence quantum yields before and after

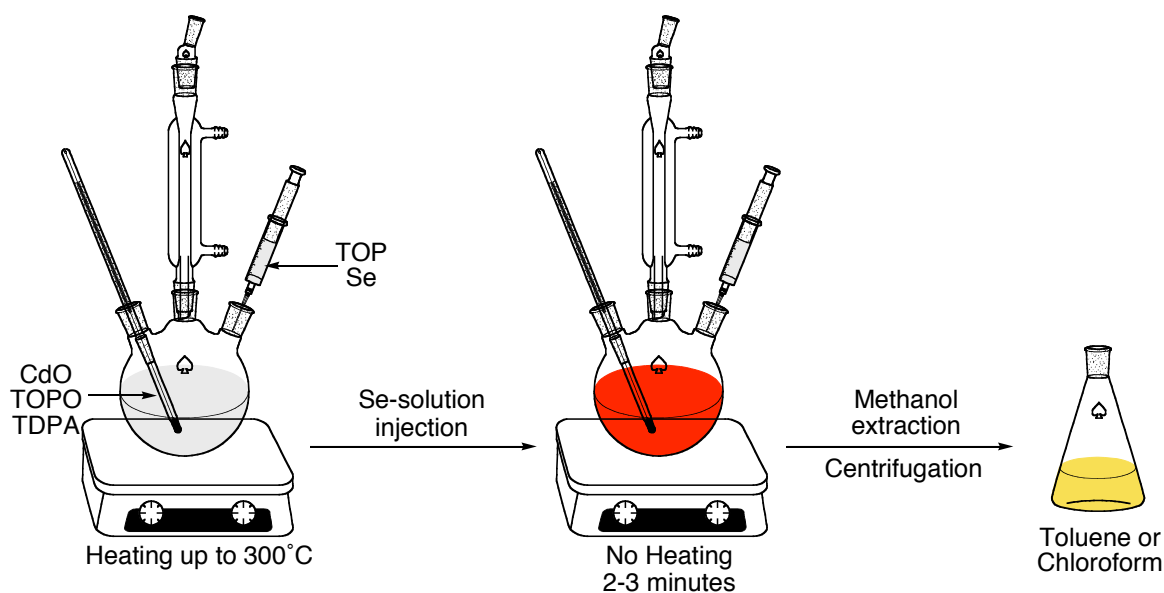
treatment were measured using emission standards with good spectral overlap with these QD samples. The usage of proper emission standards is a consideration that has been too often overlooked and possibly contributed to the large variability of fluorescence quantum yields in the literature.

Our studies will also show that the enhanced luminescence of sulfur-treated QDs is accompanied by an improved response to solution quenchers. This improvement is illustrated using 4-amino-TEMPO (4AT), a persistent free radical with excellent binding and quenching properties.⁹ This QD-4AT complex is studied for free radical sensor applications as the quenched fluorescence is partially restored when carbon-centered free radicals are trapped by the nitroxide moiety to form diamagnetic alkoxyamines.

CdSe QDs are usually synthesized in organic solvents. Their growth at high temperature enhances the dispersion and ensures a smooth, defect-less surface for a sharp and narrow full-width-at-half-maximum (FWHM) emission peak.⁴ Whenever stable aqueous suspensions are necessary, some direct synthetic approaches with water-soluble precursors are undertaken; however the resulting QDs tend to have lower quantum yield of fluorescence and a broad FWHM.¹⁰ Therefore, the most successful approach consists in growing the QDs in an organic environment and then to transfer into aqueous media through ligand exchange.^{11, 12} Unfortunately, this process frequently leads to a quantum yield drop. In the final part of this chapter, the effect of sulfur treatment is studied for further derivatization of core CdSe QDs with a silicon dioxide (SiO₂) shell.¹³

4.2 Results

For the studies discussed in this thesis small core QD (2.6 nm, $\lambda_{em} \sim 520$ nm) were selected and were prepared by the well-known trioctylphosphine oxide (TOPO)-method reported by Peng *et al.*¹ (Scheme 4. 1). The TOPO-coated QD were separated at relatively short times to prevent the formation of larger particles. Smaller QD are known to have more surface defects but also to be more sensitive to quenching by solutes, which is a desired property for our sensor application.^{8, 14} These particular QD are more challenging to stabilize, but ideal substrates for this work.



Scheme 4. 1: Synthetic route towards small, monodispersed CdSe quantum dots stabilized by TOPO

This study started with the evaluation of core CdSe QD under UVA irradiation. The fluorescence response shows large variations from one batch of QD to another. The first

objective was therefore to stabilize the core semiconductors without the addition of a ZnS shell that would later reduce their response to the environment.

4.2.1 Stabilization of core CdSe with cadmium oxide and elemental chalcogens

Previous theoretical and experimental work has shown that the poor fluorescent response of QD is often due to surface trap radiation-less transitions.¹⁵ Surface traps are usually adatoms, terraces or kinks. Thus, one approach to reduce traps is to provide Cd^{2+} or Se^{2-} ions to the already formed QD to help smooth the surface by satisfying bonding vacancies. These methodologies were carried out with cadmium oxide and elemental selenium, separately. Since both elements are largely insoluble in the organic solvents normally employed for QD studies, the treatment with them is a heterogeneous process (see Experimental Section). At the same time, it is easy to separate the chemicals once the treatment is complete, as the excess cadmium or selenium can be readily separated by filtration or centrifugation. Essentially, exposure of CdSe QD to cadmium oxide for several days has no significant effect on the emission regardless of whether the QD are irradiated with UVA light.

Conversely, treatment with elemental selenium has some effect on the corresponding luminescence. The luminescence enhancement with selenium followed by UVA excitation is qualitatively reproducible, with an example shown in Figure 4. 1.

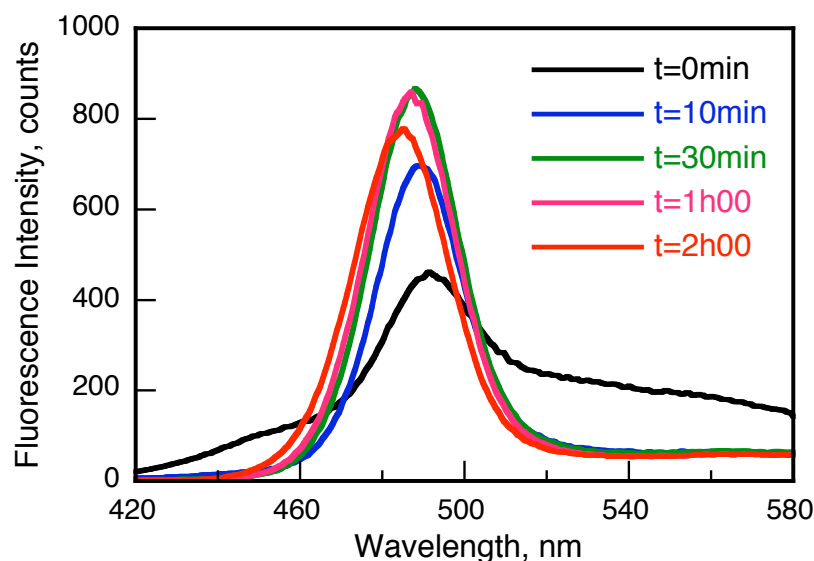


Figure 4.1: Luminescence enhancement after 1% selenium treatment followed by UVA exposure. Residual solid selenium was separated prior to UVA exposure.

With the limited success of elemental selenium exposure, elemental sulfur was considered a logical next step. Elemental sulfur holds many advantages, the first being that S_8 can be dissolved in many organic solvents, including chloroform, in the concentrations required for this work. Treatment with sulfur has little effect on QD fluorescence in the absence of light irradiation. If anything, it quenches the absorbance and the fluorescence intensities, an effect that has already been observed whenever monolayers of anionic chalcogens are added to core QD.^{16,17} A typical example of these changing optical properties is illustrated in Figure 4.2, where the aliquots are diluted in chloroform to have the same concentration. A higher absorbance and fluorescence can readily be observed for the sulfur treated aliquot. Moreover, the higher absorbance for QD_{S_8} at higher energy is due to more efficient underlying transitions as explained in Chapter 1.

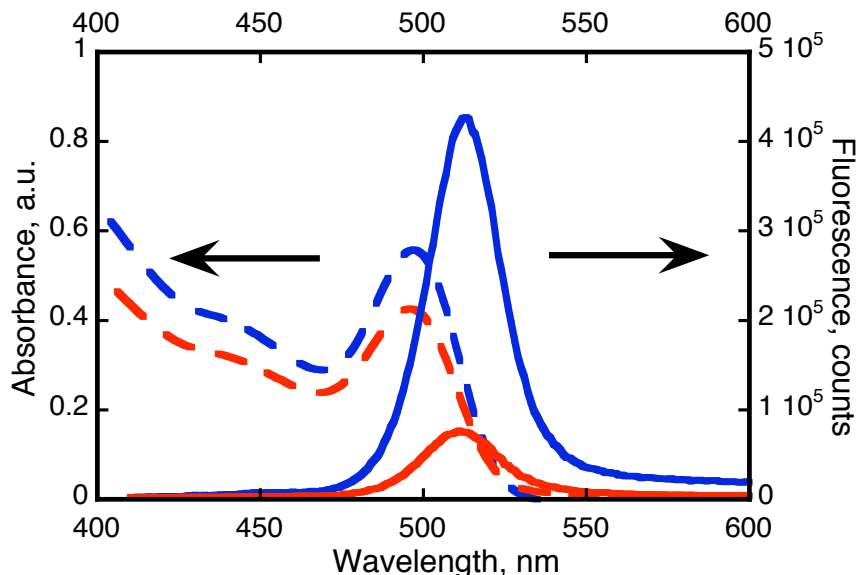
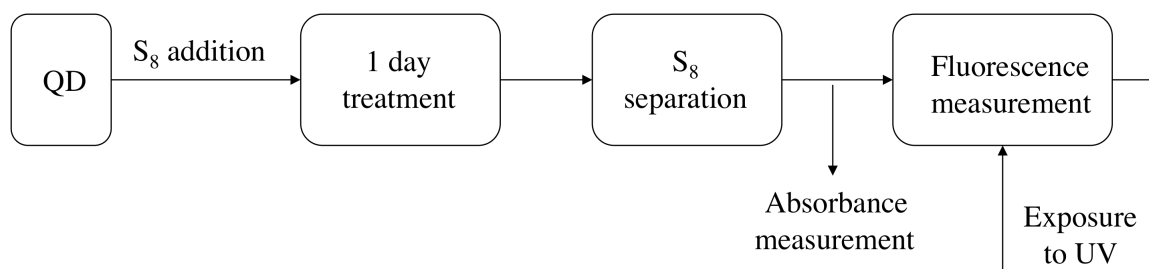


Figure 4. 2: Absorbance (dashed line) and Fluorescence (plain line) of a QD sample with (red) and without (blue) S_8 treatment, under air and prior to any light irradiation.

Due to the substantial luminescence enhancement and stabilization of the S_8 treated QD in comparison with selenium treated materials, all subsequent experiments were carried out comparing the untreated control quantum dots (QD) to the sulfur-treated quantum dots (QD_{S_8}), first without and then with irradiation ($QD(i)$ and $QD_{S_8}(i)$, respectively).

UVA exposure of QD_{S_8} leads to a large emission enhancement, with a final stabilization at a fluorescence quantum yield around 0.15 (Figure 4. 4). Figure 4. 3 shows a comparison of the response to photoexcitation of two samples differing only in that one of them has been pre-treated with S_8 . The actual pre-treatment lasts twenty-four hours, where the CdSe quantum dots are left in an environment containing an excess of elemental sulfur (QD_{S_8}). However, the sample irradiated does not contain free S_8 in solution, since the QD_{S_8} is extracted prior to any experimentation (see Scheme 4. 2).



Scheme 4. 2: Typical elemental sulfur treatment in chloroform followed by UVA light irradiation.

Shown in Figure 4. 3, the untreated sample QD has a steady decrease of luminescence coupled with a blue shift attributed to a constant degradation. The treated sample QD_{S₈}, on the other hand, has a significant increase in fluorescence. Specifically, QD_{S₈} after one hour of irradiation exhibits fifty-eight times more fluorescence than QD before any exposure. After two hours of irradiation, the same degradation as for QD was observed. Any blue shift of λ_{max} observed is attributed to a decrease of the quantum dots diameter.

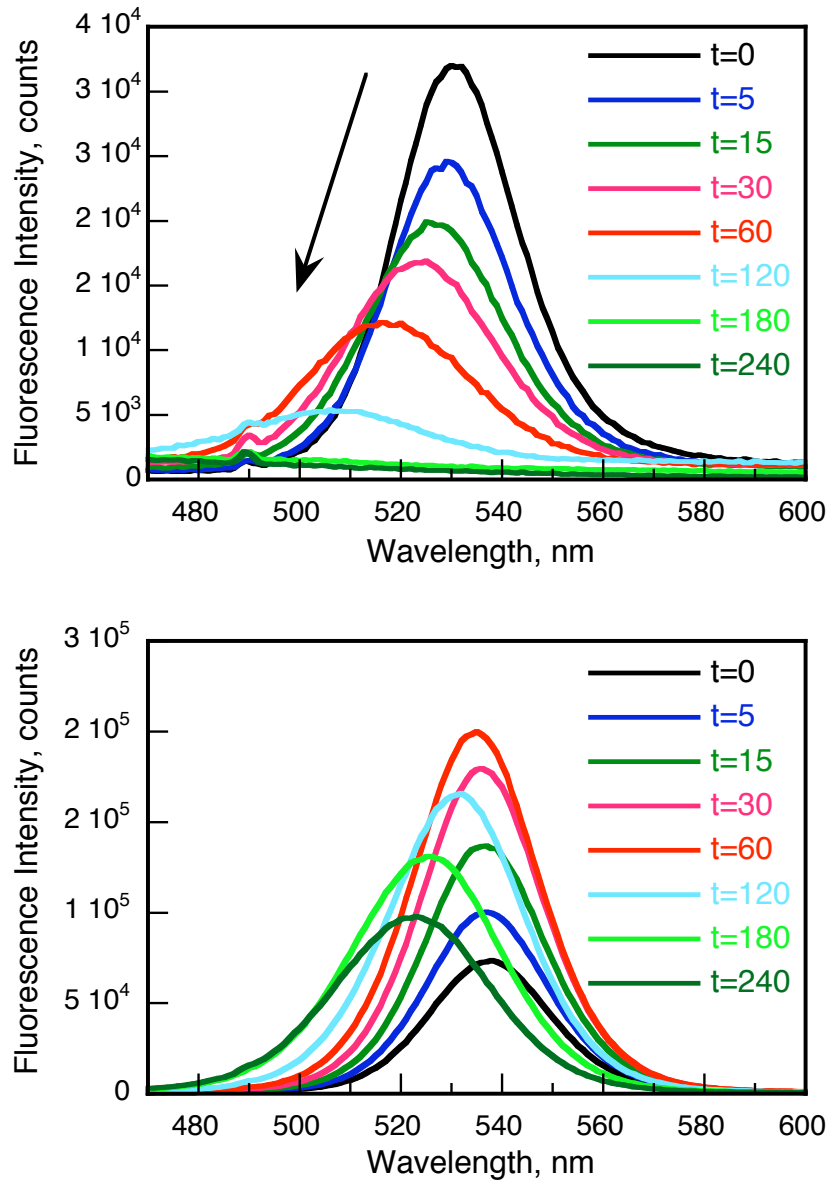


Figure 4.3: Luminescence behavior under UVA irradiation of CdSe QD(i) (top) and of CdSe QD_{ss}(i) (bottom) in chloroform and under air ($\lambda_{ex}=450$ nm). Note that the vertical scales are different for each panel to clearly see the trend. Times of UVA exposure are given in minutes

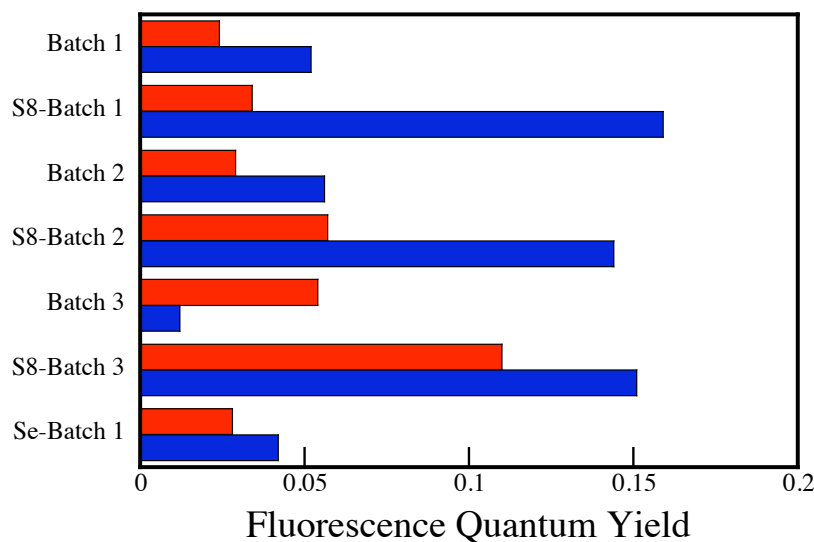


Figure 4. 4: Quantum yields for fluorescence emission before (red) and after (blue) UVA irradiation. The fluorescence reference compound is fluorescein.

Interestingly, several samples of $\text{QD}_{\text{S}_8}(i)$ all led to approximately the same final quantum yield (~ 0.15) after treatment and irradiation (see Figure 4. 4). Again, it is not uncommon for different batches of QD to show variable initial quantum yields, probably reflecting surface variations. Moreover, the irradiation of $\text{QD}(i)$ with UVA light does not automatically lead to fluorescence enhancement (see Control batch 3). Thus, it is important to note the reliable enhancement a sulfur treatment brings, regardless of the initial state of the QD batch. Also shown in Figure 4. 4, a comparison of Batch 1 treated with elemental sulfur against the treatment with elemental selenium. One can again appreciate the increased efficiency when using S_8 for being four times more effective than selenium.

All the samples that have been treated with elemental sulfur and kept in the dark under air display a more stable fluorescence emission than their untreated counterparts over

time. The QD_{S8} FWHM remains below 30 nm, a proof that these materials are fairly monodisperse.

Lifetime studies carried out at $\lambda_{\text{ex}} = 440$ nm reveal different behaviors for QD and QD_{S8} samples. The fluorescence decay of the $\text{QD}_{\text{S8}}(i)$ is rather stable under irradiation, whereas for $\text{QD}(i)$ fluorescence intensity drops dramatically (see Figure 4. 5 top). Each aliquot displayed two distributions of lifetimes: one around 11 ns and the other above 50 ns. Under irradiation, the fluorescence of the untreated aliquot is gradually weighted to the shortest lifetime (around 35 ns). In contrast, more of the fluorescence is gradually due to the longest lifetime for the $\text{QD}_{\text{S8}}(i)$ aliquot (see Figure 4. 5 bottom). This result is interesting, as faster lifetimes have been attributed to surface emitting states and slower lifetimes to more deeply confined states.¹⁵

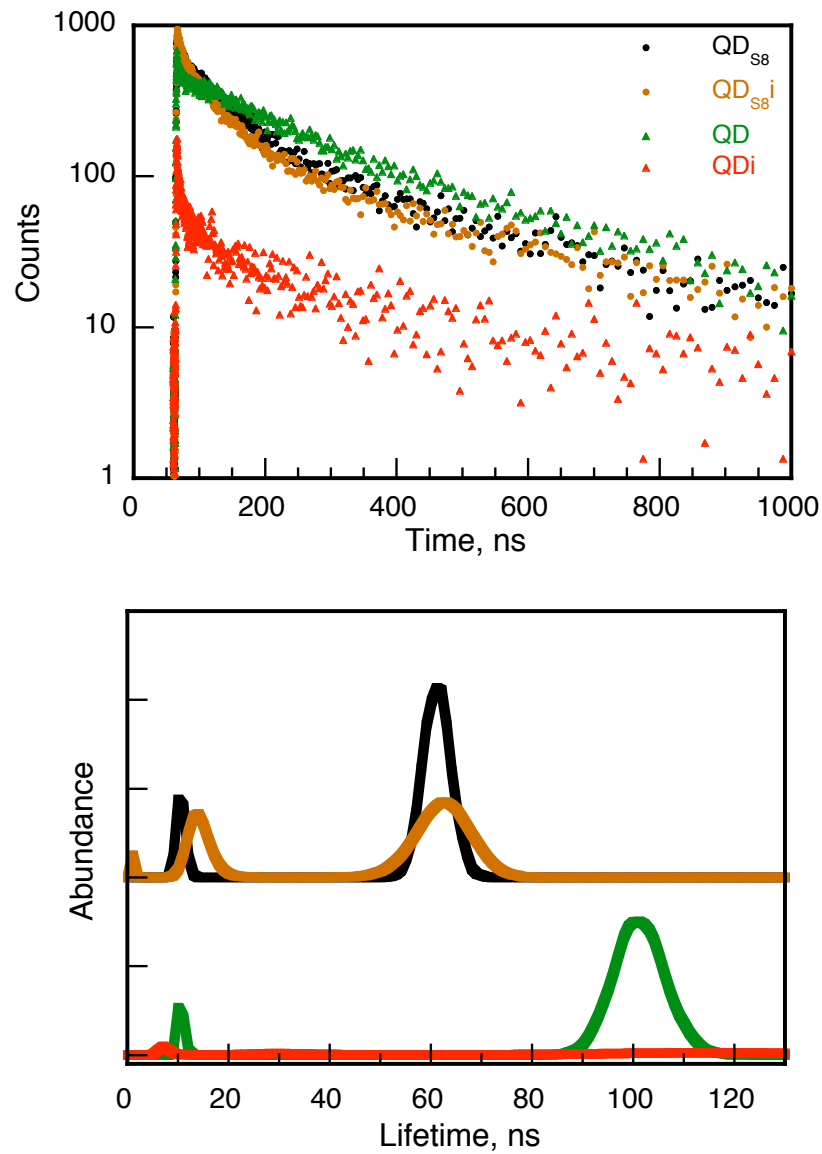
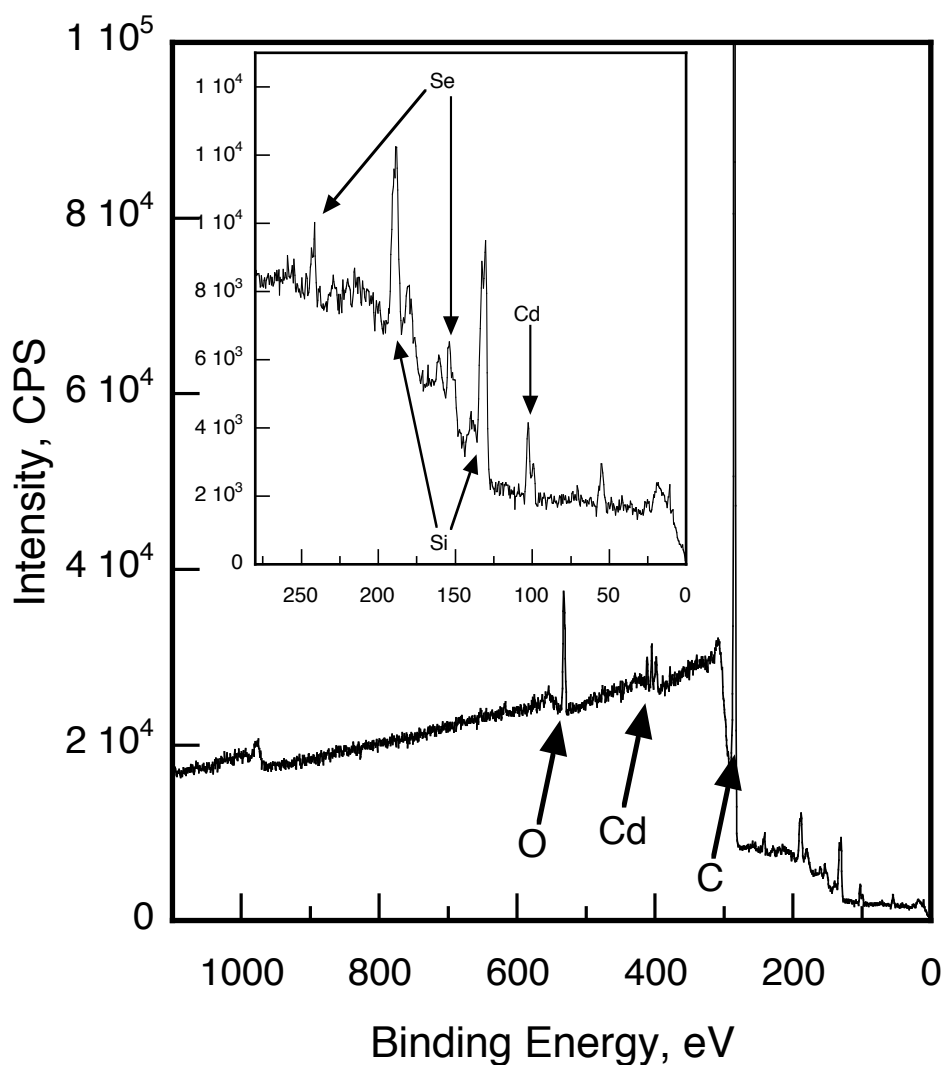


Figure 4. 5: Lifetime study. Top: Intensity decay of QD_{S8} , QD_{S8}^i , QD and QDi , quantum dots in chloroform before and after UVA irradiation (Note that the control was exposed for 75 minutes, while the more robust S_8 treated sample was exposed for 360 minutes). Log scale is used for a better visualization of the decays. Bottom: Lifetime distribution of each decay shown above.

4.2.2 Surface characterization after sulfur treatment

X-ray photoelectron spectroscopy (XPS) was run for both QD and QD_{ss}. XPS is a surface chemical analysis technique that investigates the elemental analysis at the surface of a deposited dry QD. This study confirms the presence of the sulfur at the surface of the treated quantum dots (see Figure 4. 6)



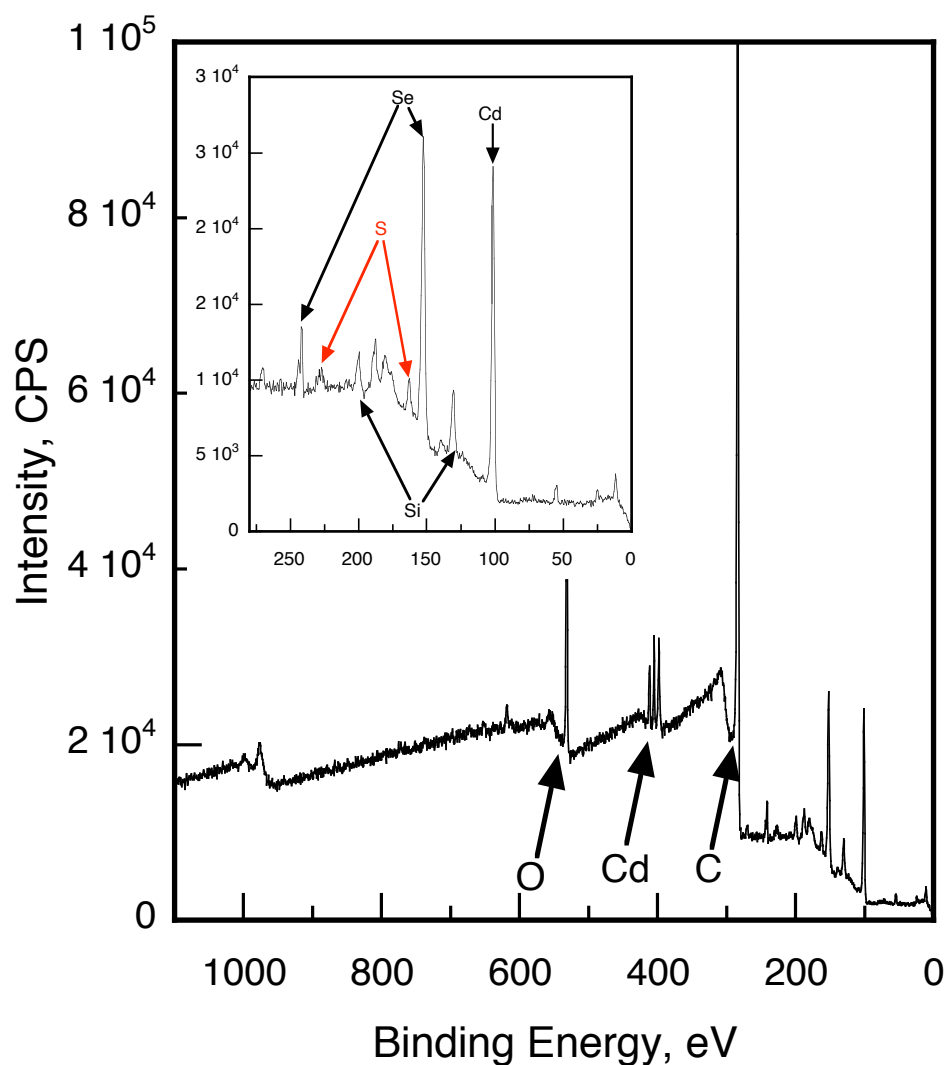


Figure 4. 6: X-ray photoelectron spectra of the untreated sample of QD (left) and the S_8 -treated sample (right). Peaks of interest are labeled. Inset: Zoom in of the region [0 eV ; 240 eV].

TEM images allow us to compare the size of QD and QD_{s8} particles. For all samples discussed in this work, TEM characterization illustrated little variation in the size of particles with and without treatment.

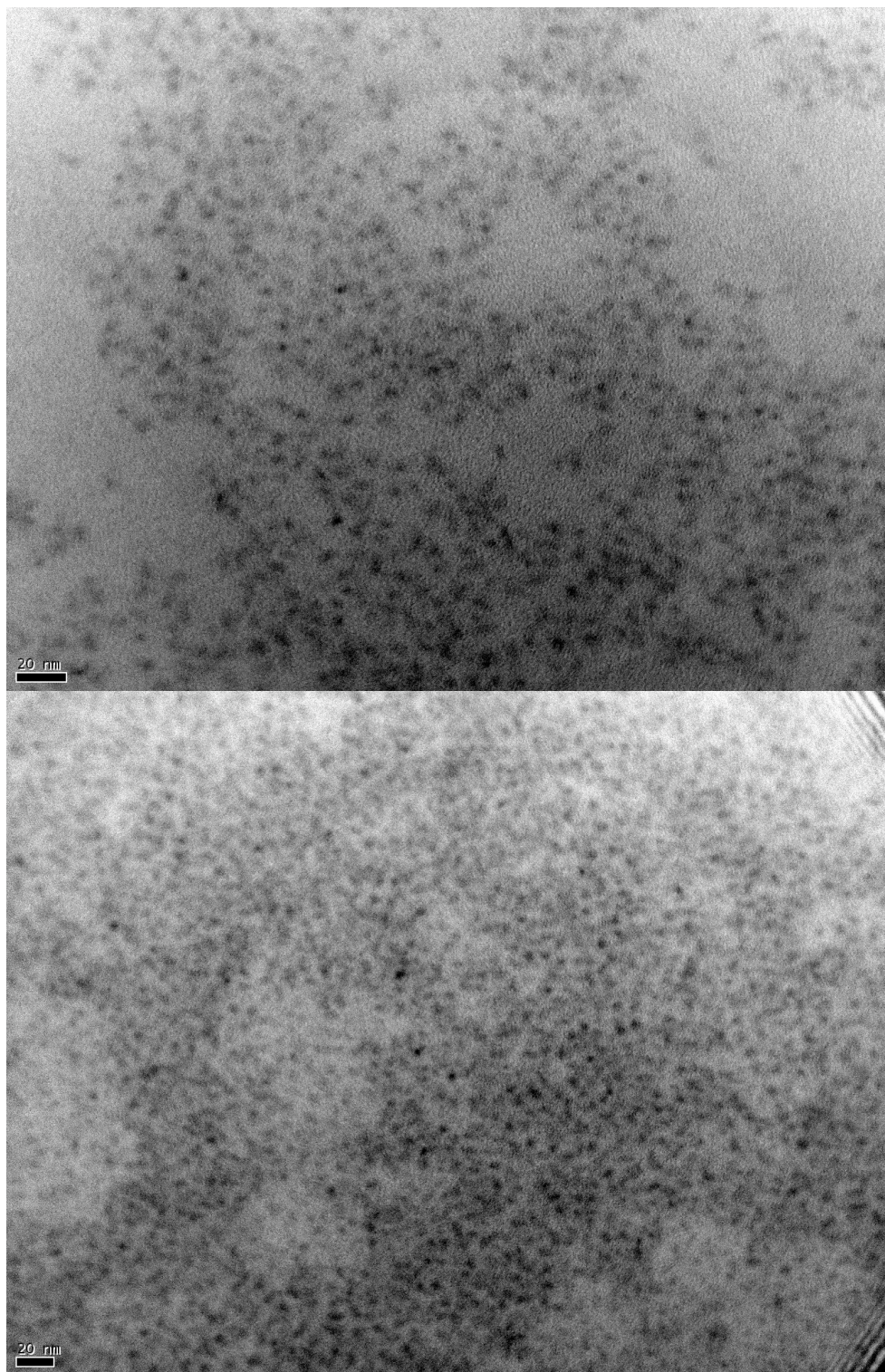


Figure 4.7: TEM acquisition CdSe quantum dots before (top) and after (bottom) sulfur treatment (size bar=20 nm)

4.2.3 Influence of the spectral region for irradiation

CdSe quantum dots absorb light at the characteristic λ_{max} visible band, but also, essentially, at all wavelengths in the ultraviolet region.¹⁸ In contrast, elemental sulfur has a very weak absorption in the visible, but a very significant one in the ultraviolet region, where irradiation is known to lead to sulfur oligomer intermediates such as S_3 and S_4 .¹⁹ In order to evaluate which spectral region was most effective for luminescence enhancement, samples that had undergone sulfur treatment and purification were divided into three aliquots, one irradiated with visible light, another one with 420 nm light, and the last with UVA light (see emission spectra of excitation sources in Figure 4. 8). Any enhancement of fluorescence with an irradiation in the visible region (whether broad irradiation or centered at 420 nm) would not be due to the direct photochemistry of elemental sulfur.

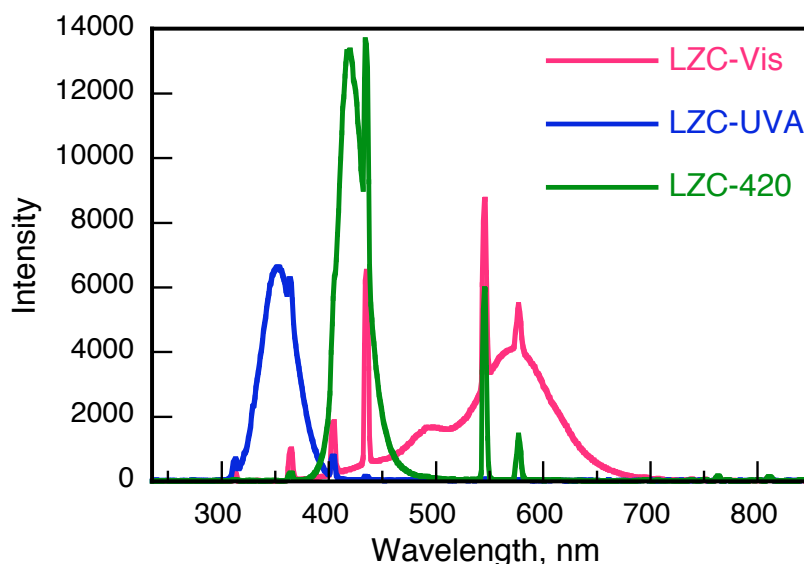


Figure 4. 8: Irradiance of the lamps used (in $\text{mW.m}^{-2}.\text{nm}^{-1}$) determined for 6 bulbs. These spectra were recorded in a LZC-1 Luzchem photoreactor. The total irradiance during the experiments was measured at the specific location where the samples were placed. (Courtesy of Luzchem Research, Inc).

All the aliquots displayed fluorescence enhancement following light treatment, but the aliquots under UVA and 420 nm lights showed a much faster and noteworthy enhancement when compared to visible light (see the effect after respective optimal irradiance in Figure 4. 9). Moreover the UVA irradiated aliquot displays a blue shift characteristic for a decrease of the average size of the QD.

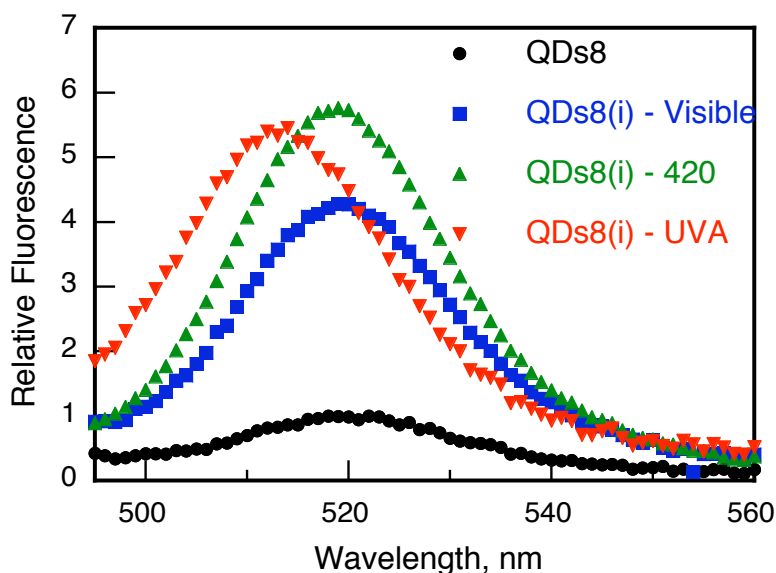


Figure 4. 9: Relative fluorescence enhancement for three aliquots of QD_{s8} against the normalized emission of the non-treated sample. Spectra are taken after one hour of visible, 420 nm or UVA light irradiation, respectively

In all the experiments, however, the number of light bulbs was matched (*e.g.*, 6 bulbs of a specific spectral region) rather than matched irradiance. For comparison purposes, it would be more accurate to look at the enhancement for each spectral region as a function of incident dose. To do so, the fluorescence enhancement is calculated as:

$$\text{Enhancement} = \frac{I_t - I_{t=0}}{I_{t=0}} - 1$$

Equation 4. 1: Fluorescence enhancement under light irradiation overtime

where I_t and $I_{t=0}$ are the emission intensities at time 't' and before irradiation, respectively.

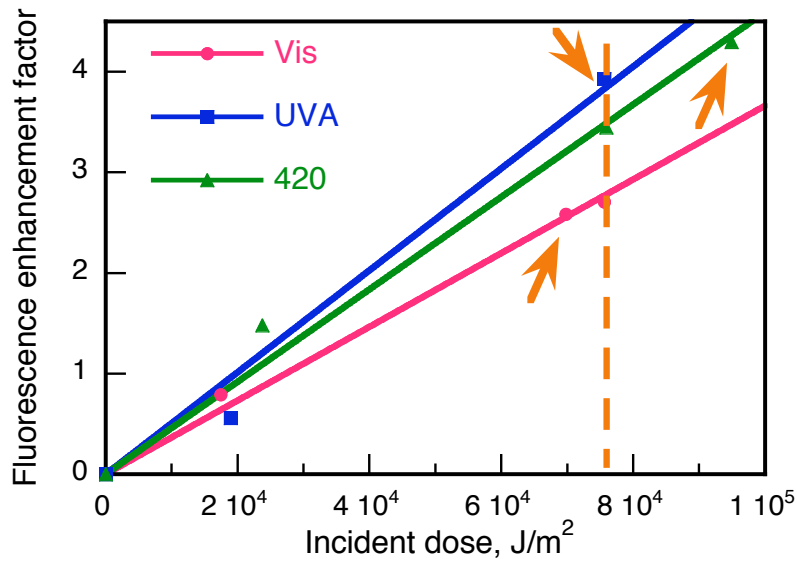


Figure 4. 10: Fluorescence enhancement for aliquots of the same S_8 treated sample as a function of exposure with 6 lamps of the type shown in **Figure 4. 8**. The orange arrows indicate the 1 hour exposure for each region, while the vertical dashed orange line compares the same dose as received in 1 hour when using UVA lamps.

Figure 4. 10 shows the corresponding plots and suggests that there are only minor differences between the efficiencies of the different lamps. Since QD absorb both in the visible and UV regions, this shows that fluorescence enhancement is caused mainly by the absorption from the QD. Since no elemental sulfur is present in solution, the tremendous enhancement is mainly due to S_8 bound onto the surface of the quantum dots that react to

photogenerate small sulfur oligomers such as S_4 and S_3 . These intermediates must then passivate the surface traps (defects) of the quantum dot and enable more efficient fluorescence. From this experiment we conclude that light irradiation is the dominant cause of enhancement of the QD fluorescence, not the S_8 treatment itself.

4.2.4 Response to solution quencher towards free radical sensor application

A sensor based on QD typically requires having a luminescence “on-off” switch ability. Hence, the first part in the development of such sensor is the surface derivatization towards a given selectivity, accompanied either with an enhancement or with a quenching of the luminescence in the process. With this rationale, a known solution quencher was tested, 4-amino-TEMPO.

Quenching studies on irradiated samples reveal that in spite of their higher luminescence, QD_{S8} are quenched more readily than QD; in fact, at high quencher concentrations QD_{S8} emission is comparable to that of QD (see Figure 4. 11). The corresponding quenching plots, for 4-amino-TEMPO (4AT) as a quencher, are shown in Figure 4. 12, and reveal a characteristic downward curvature.

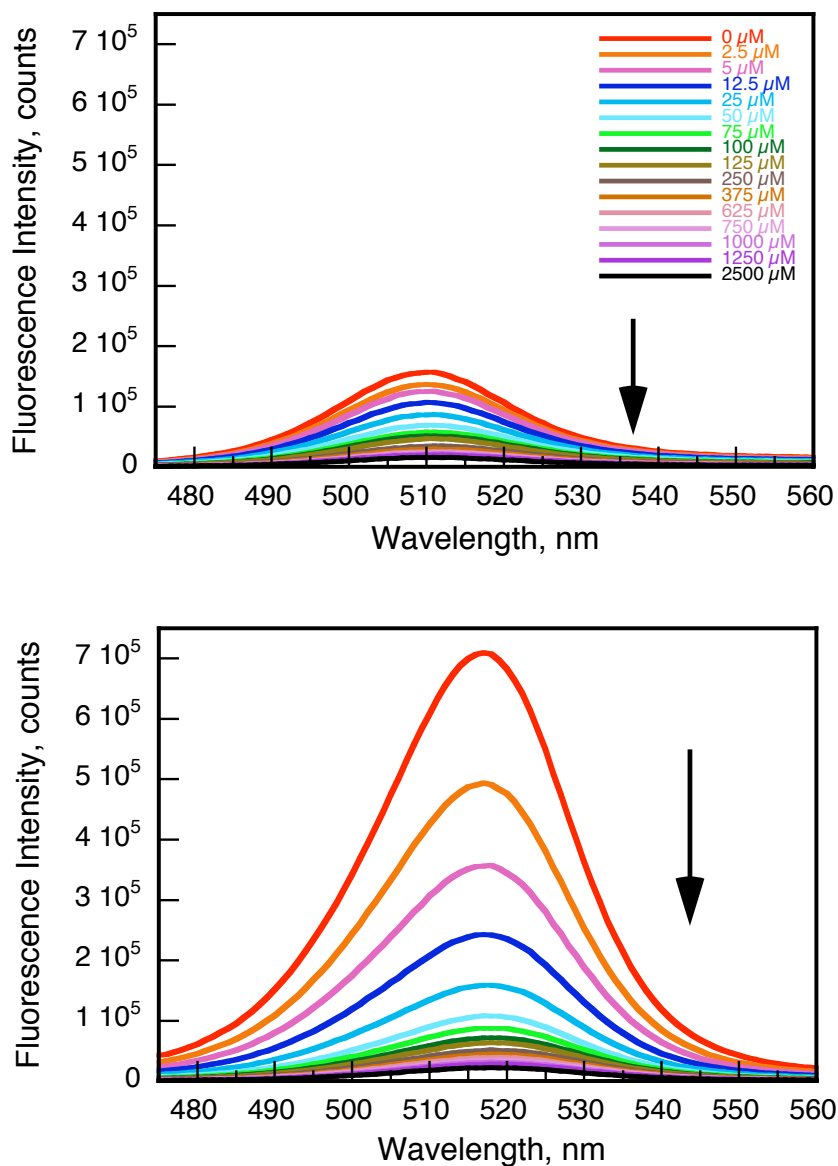


Figure 4.11: Quenching of the fluorescence of 8.0 μM solutions of $\text{QD}(i)$ (top) and $\text{QD}_{s8}(i)$ (bottom) by an increasing concentration of 4AT in chloroform. Same scale is applied to highlight the difference of intensity before quenching: 709,000 for $\text{QD}_{s8}(i)$ and 157,000 for $\text{QD}(i)$.

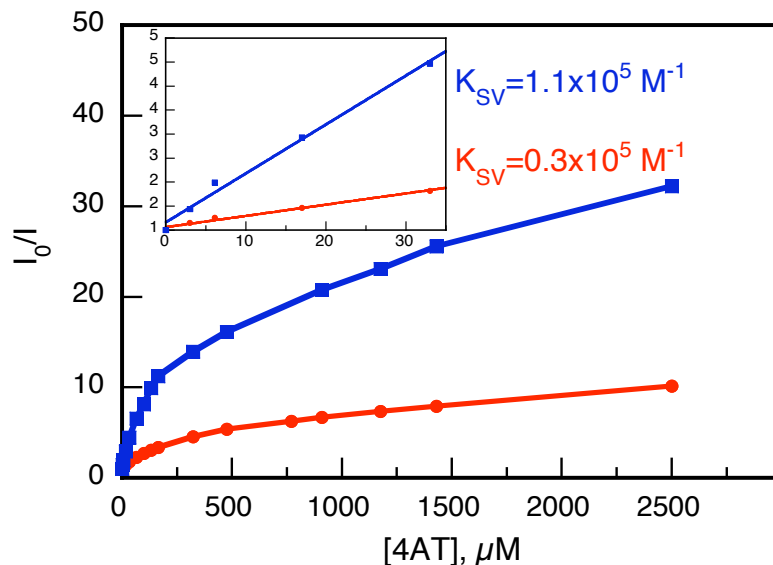
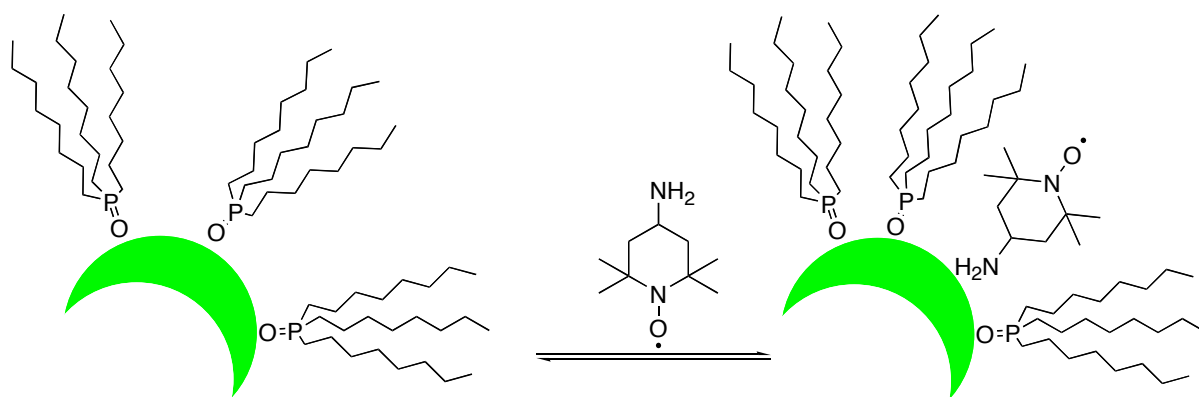


Figure 4. 12: Stern-Volmer quenching plots calculated from spectra recorded in **Figure 4. 11** with QD (red) and QD_{ss} (blue) (I = fluorescence intensity at 510 nm, I_0 = fluorescence intensity at 510 nm with no 4AT). Inset: expansion of the Stern-Volmer plots for low concentrations of 4AT, with the corresponding slopes K_{SV} .

A non-linear, downward curving Stern-Volmer plot (as observed here) is indicative of a more complex mechanism than static-only or dynamic-only quenching. This mechanism involves either a combination of sites with different accessibilities undergoing the same quenching or a combination of states with multiple lifetimes and reactivities. The quenching at low concentrations of 4AT is linear, as shown in the inset of Figure 4. 12, with a slope for the Stern-Volmer plots $K_{SV} = 0.3 \times 10^5 \text{ M}^{-1}$ and $K_{SV} = 1.1 \times 10^5 \text{ M}^{-1}$ for QD(*i*) and QD_{ss}(*i*), respectively. Such high values for K_{SV} could be due to a static quenching where the fluorophore and the quencher form a stable, non-fluorescent complex before the absorption of any photon.⁹ The slower quenching that is observed for higher concentrations of 4AT can be attributed to a decreased accessibility of the QD reactive sites: the first molecule of 4AT

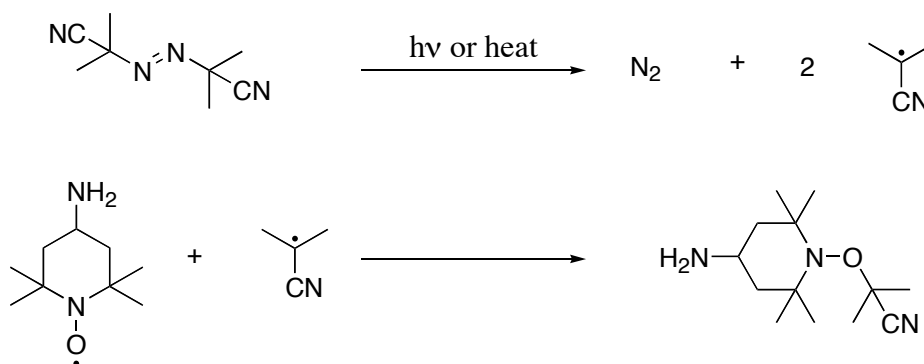
can easily intercalate in between the TOPO molecules, but it would render the intercalation of subsequent 4AT molecules more difficult (see Scheme 4. 3) as it would require the displacement of some TOPO ligands. This slower quenching can also be dynamic, due to collisions between the QDs and those 4AT molecules that remained in solution.



Scheme 4. 3: Intercalation of one molecule of 4-amino-TEMPO between two molecules of TOPO at the surface of a QD, leading to a tighter reorganization of the ligands.

Due to its nitroxide radical, 4AT is paramagnetic and the quenching on QD has been attributed to electron exchange interactions. The excited electron will transfer from the conduction band of the QD to the SOMO of 4AT and back to the valence band of the QD.¹⁴ One way to recover the fluorescence is to alienate the “electron shuttle” role played by 4AT. When the nitroxide radical traps a carbon-centered radical, it forms a diamagnetic alkoxyamine that is no longer able to quench the fluorophore.⁹ To test the fluorescence recovery, the 4AT-QD(*i*) and 4AT-QD_{s8}(*i*) complexes are put in presence with azo-bis-isobutyronitrile (AIBN), a known photochemical or thermal source of carbon-centered

radicals. Upon formation of the alkoxyamine shown in Scheme 4. 4, the QDs should be able to partially recover their fluorescence.



Scheme 4. 4: Formation of carbon-centered radicals by photochemical or thermal degradation of azo-bis-isobutylnitrile, followed by their trapping with 4-amino-TEMPO.

Figure 4. 13 is normalized to appreciate the percentage recovered for $\text{QD}(i)$ and $\text{QD}_{\text{ss}}(i)$, respectively. The concentrations selected, $[\text{QD}] = 8 \mu\text{M}$ and $[4\text{AT}] = 160 \mu\text{M}$, put the QD-4AT complexes in the linear Stern-Volmer plot area where mostly static quenching occurs. All the recovery experiments are done under air, even though the dissolved oxygen present is a drawback as it reacts readily with any carbon-centered radicals present within diffusion controlled limits.

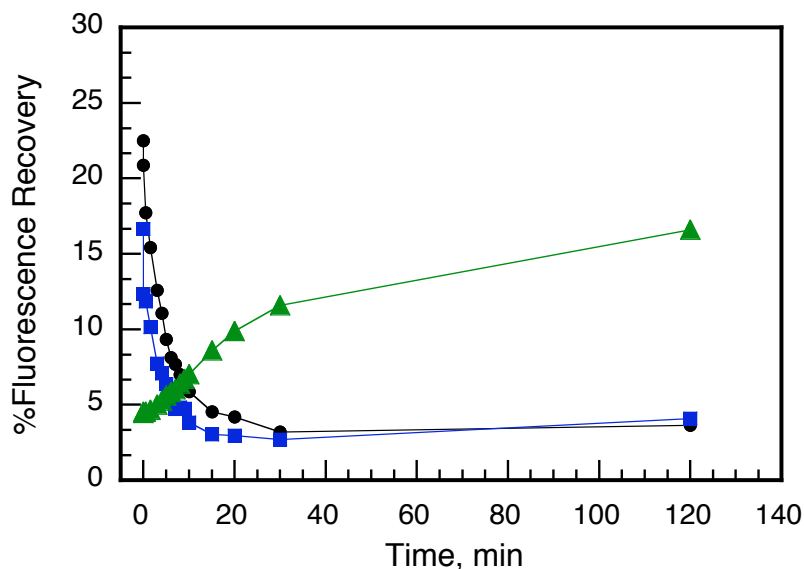


Figure 4.13: Fluorescence recovery upon addition of 160 μM of 4-amino-TEMPO to 8 μM solutions of QD (●), QD_{s8} (■) and QD_{s8}(i) (▲), followed by 48 mM of AIBN at 50°C.

For the AIBN to thermally degrade, a temperature of 50°C is chosen, but since the luminescence of QD is affected by temperature (fluorescence decreases upon increasing temperature), all the aliquots are left to equilibrate in a thermostated water bath for thirty minutes prior to any experiment. This practice ensures that no subsequent fluorescence decrease observed is due to thermal quenching of the quantum dots. The addition of AIBN followed by its slow release at 50°C does not induce a recovery for QD(i) but, rather, a further decrease of the fluorescence. The QD_{s8}(i) pre-fluorescent probe displays more promising results. The quenching with 4AT is followed by fluorescence recovery immediately upon addition of AIBN. Unfortunately, with a recovery of just 17% after two hours, the described system illustrated considerable limitations as a probe for carbon-centered free radicals. Interestingly, none the less, the same QD_{s8}-4AT complex taken

without irradiation and subjected to a similar carbon-centered radical treatment shows no fluorescence recovery over time. This behavior stresses even more the need for UVA irradiation after a sulfur treatment to obtain optimum results.

4.2.5 Silica shell growth

The effect of sulfur treatment with and without irradiation is assessed for silicon dioxide (SiO_2) shell growth. Such a shell makes any subsequent functionalization of the QD easier; especially for dispersion in aqueous solutions and possesses the double advantage of being chemically inert and optically transparent.

A microemulsion approach developed by Darbandi *et al.* was used¹³ (see Experimental Section) on QD, QD(*i*), QD_{s8} and QD_{s8}(*i*), respectively and the change in fluorescence is presented in Figure 4. 14.

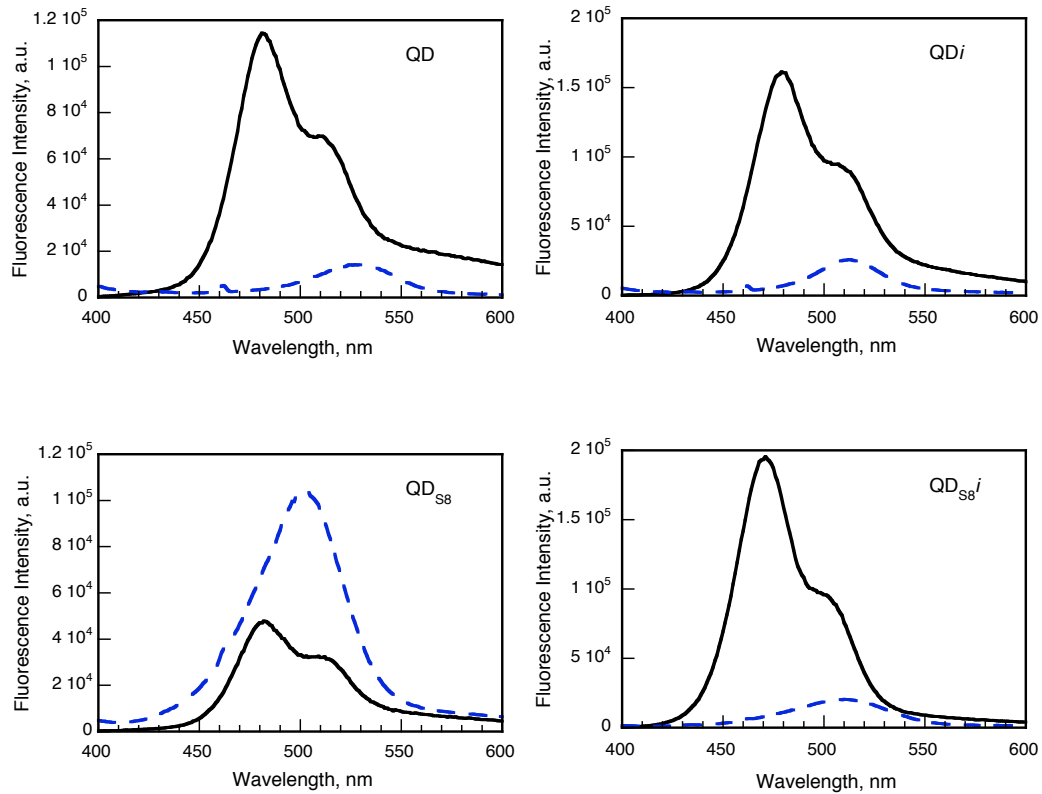


Figure 4. 14: Fluorescence change for 6 μM QD solutions before (plain black trace, in chloroform) and after (dashed blue trace, in water) SiO_2 encapsulation for QD, QD(*i*), QD_{S8} and QD_{S8}(*i*)

Two observations can arise from those plots. First, as QD, QD(*i*) and QD_{S8}(*i*) samples display an expected fluorescence quenching upon SiO_2 encapsulation, QD_{S8} is the only sample to actually exhibit a fluorescence enhancement after silica has been added. Secondly the example purposely shown here has poly-distribution after synthesis. One can, therefore, appreciate how all samples after encapsulation regain one size distribution, where the bigger particles are favored to the smaller ones.

4.3 Discussion

The luminescence behavior of core quantum dots under light irradiation can be quite inconsistent from one batch to another and even more so from one synthetic method to another. However, these results have shown that pre-treatment of CdSe QD with elemental sulfur followed by photoactivation leads to systematic enhancement of the fluorescence quantum yield. These experiments also reveal some details for the mechanism leading to fluorescence enhancement.

The first important aspect of this treatment is that it must be done with a chalcogen, either selenium or sulfur, as cadmium oxide has been demonstrated to not lead to any improvement. In fact, QD are synthesized in the presence of TOP and TOPO as stabilizing agents. The trioctylphosphine (TOP), also a soft Lewis base, will bind mostly to the soft acid surface cadmium cation Cd^{2+} . This usually results in cadmium-rich surfaces after a stoichiometric synthesis of the QD and, hence, a favored subsequent deposition of either selenium or sulfur.²⁰ Nevertheless sulfur is more efficient because of its solubility in organic solvents. Treatment with elemental sulfur and without light must lead to the deposition of short S_8 oligomers at the surface defects. This interaction is strong enough for the oligomers to remain on the surface after washing and resuspension of the TOPO-coated QD as revealed by XPS. From the weak magnitude of the signals, we suggest that the amount of sulfur coverage required for fluorescence enhancement is in fact quite low. However, this treatment by itself is not enough to cause a significant increase in the QD fluorescence and may occasionally lead to a decrease of the fluorescence quantum yield.

In order to achieve a significant enhancement of fluorescence (sometimes as much as 500% of the original none-treated sample), the sulfur-treated QD_{S8} needs to be photoactivated. This activation leads to the fastest luminescence enhancement when using UVA light where both the QD and S₈ absorb the most. However, by weighing the irradiation efficiency against the incident dose of light applied to the system (as done in Figure 4. 10), one notices how the enhancement occurs to a comparable extent using 420 nm centered light, where the QD have significant absorption, but where sulfur has none. Even visible light irradiation results in a fluorescence quantum yield increase, but to a lower extent, probably due to a smaller absorbed light dose. This would suggest that an electron transfer from the QD to S₈ does occur and leads to a significant activation of surface-bound sulfur. The proposal of an electron transfer process conclusively shows that the dosage of light on the system is crucial. Irradiation with visible light will take a longer exposure time than irradiation with UVA light, but overall the same result is obtainable.

The solution photochemistry of S₈ is known to yield at least S₃ and S₄ oligomers, most likely in their open forms.¹⁹ We assume that the same intermediates are formed from surface-bound S₈. These small oligomers of sulfur are most likely more reactive than S₈ itself and, since the irradiation is done under air, the observed enhancement is probably caused by their photo-oxidation. A photoexcited electron is transferred to the O₂ present in solution to generate a reactive O₂^{•-} that can oxidize S (and any Se) at the surface to yield sulfate SO₄²⁻ (and selenium dioxide SeO₂), or tetrathionate S₄O₆²⁻ that are short oligomers oxidized at the ends with oxidation state of +5. This produces a very thin oxide layer as shown in the emission data in Figure 4. 3, as well as TEM analysis, and suggests that for at least the first 30 minutes of irradiation this enhancement occurs without any significant decrease in QD

size. This production of an oxide layer also explains why prolonged irradiation leads to a blue shift of the emission maxima and a small decrease of the overall emission intensity which is attributed to surface etching and degradation. Overall, the sulfur treatment renders the QD more robust in the photo-oxidation process that allows them to minimize their surface defects. The lifetime experiments corroborate this trend where QD_{S8} displays a good stability whereas QD degrades fairly quickly under UVA irradiation.

Also interesting to note is that the behavior observed for treated quantum dots is quite reproducible from one batch to another. The fluorescence is always enhanced under UVA irradiation and the QD_{S8} are always more responsive to a solution quencher than core QD. The only factor that varies from batch to batch is the relative change between “before” and “after” manipulation. For example, a sample that already displayed good spectroscopic features (*i.e.*, an already high quantum yield of fluorescence) without treatment has a small enhancement, whereas a poor material shows spectacular improvement. Overall, all QD_{S8} samples have their final quantum yield of fluorescence stabilizing around the value 0.15. This observation supports the assumption that small oligomers of sulfur bind specifically to the surface traps (defects) of the QD and, hence, have more or less impact depending on the original amount of defects that were present on the surface of the QD.

The most common way to enhance QD luminescence while improving stability is to use a ‘shell’ of semiconductor materials with a larger band gap than the core material.³ For CdSe QD this is frequently achieved with a ZnS shell, this type of core-shell particles being readily available commercially. Earlier studies have shown that core-shell nanoparticles are less prone to solution quenching than core-only particles.⁸ For applications as fluorescent markers, it is clear that a robust nanoparticle with minimal response to environmental

quenchers would be best. On the other hand, for sensor development one would like a particle with good luminescence quantum yield and a very sensitive response to environmental quenchers. In terms of response to quenching, our study with 4AT highlighted that the following order seems to prevail: S_8 treated QD > core QD > core-shell QD. The S_8 treatment gives not only more luminescent QD, but also more sensitive QD to a solution quencher. This translates into a dark state at lower concentrations of 4AT and, overall, into a superior “on-off” switch compared to core QD.

When put in presence with AIBN, only $QD_{S_8}(i)$ shows some recovery; QD and QD_{S_8} both show further quenching upon addition of the carbon radical source. The $QD_{S_8}(i)$ system is rather robust since the experiment is carried out under air: thus 2 mM of dissolved O_2 in chloroform²¹ are in direct competition with 0.2 mM of 4AT to scavenge the carbon centered radicals generated by thermal decomposition of AIBN. Nevertheless, some slow recovery is observed. The most interesting observation comes from the comparison of $QD_{S_8}(i)$ with both QD and QD_{S_8} . For our system to be responsive and at optimal operation, it does require photoactivation. Although, in itself, this system still requires some improvement to have a faster and more dramatic response to carbon centered radicals, it is in comparison much better than the core QD counterpart.

Finally, the silica shell growth highlights another advantage of sulfur treatment, but at a different stage. Two main routes exist to grow a silica shell on a QD: the Stober method^{22, 23} and the reverse microemulsion method¹³. The latter approach has been preferred due to the polar ligand TOPO that stabilizes the QD studied. Indeed, a microemulsion allows a simple and straightforward encapsulation. The surfactant, Igepal® CO-720, is used to generate the microemulsion, and the phase transfer from cyclohexane is probably done with a ligand

exchange¹³ where TOPO is replaced by tetraethyl orthosilicate (TEOS). The actual silica shell is then formed by a base catalyzed hydrolysis of TEOS into silicic acid followed by its condensation into silica. Before the exchange occurs, the CdSe quantum dots observed have specifically at the surface (in addition to the TOPO ligand) nothing for QD, short S_8 oligomers for QD_{S_8} , a thin layer of selenium dioxide SeO_2 for QD_i , or a thin layer of sulfate SO_4^{2-} for $QD_{S_8}(i)$. Therefore, QD_{S_8} is the only aliquot that maintains an S_8 ligand, once all the TOPO has been displaced, that can later be utilized as a template to form a mesoporous silica shell. This extra spacing is sufficient to create a weaker surface interaction between the quantum dot and the silica shell. This diminishes the non-radiative recombination processes that could occur more for the three other aliquots that didn't have any ligand left on their surface other than the TEOS that replaced TOPO. It is also important to note that fluorescence enhancement through photoactivation is still possible after the silica shell has been added. Thus, the benefits that have been observed on the core system are maintained within the silicon dioxide shell. The narrowing of the FWHM observed in Figure 4. 14 is certainly due to the cleaning process: bigger particles favorably separated during the centrifugation step.

4.4 Summary

To maintain consistent properties for core quantum dots under light irradiation is difficult. Each lot will display a different emission intensity and blinking behavior and will be more or less prone to photo-degradation. Growing a shell with a larger band gap is a standard method to overcome those limitations; however, it is done at the expense of the quantum dots reactivity towards the environment. Whenever this asset is primordial, a treatment with elemental sulfur S_8 followed by irradiation in the UV-visible region, where the QD, rather than S_8 , absorbs light, is the solution. It leads to brighter and more robust quantum dots with a quantum yield that stabilizes around 15%. Recent studies have shown that the surface ligands (TOPO here) on CdSe QD do not follow the accepted L-type ligand model; instead they interact with the surface Cd^{2+} ions by forming X-type binding.²⁴ In light of this new model, further study would be required for a better understanding of the reactivity core QD must have when put in presence with short S_8 oligomers.

The development of a carbon-centered radical sensor is tested with 4AT and AIBN, and although the quenching step is very efficient, the degree of recovery is quite low and requires further improvement to be sustainable. However the $QD_{S_8}(i)$ -4AT complex is very promising as it displays significantly stronger response than the non-treated counterpart.

Another advantage of sulfur treatment is demonstrated for silica encapsulation whenever water solubility is sought. However a specific sequence must be respected to obtain the most robust system: treatment -> encapsulation -> light irradiation.

4.5 Experimental

4.5.1 Materials

Tetradecylphosphonic acid (TDPA) and tri-n-octylphosphine (TOP) were purchased from Alfa. Selenium powder 99.99%, cadmium oxide (CdO), tri-n-octylphosphine oxide (TOPO), sulfur 99.999%, 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-aminoTEMPO or 4AT), Igepal® CO-720 (Polyoxyethylene nonylphenyl ether), and tetraethyl orthosilicate 99.999%(TEOS) were purchased from Aldrich. Chloroform, cyclohexane, ethanol and methanol were all purchased from Fisher Scientific. 1-Propanol and 1-butanol OmniSolv were purchased from BDH Chemicals. All chemicals and solvents were used without further purification.

4.5.2 CdSe quantum dot synthesis

All reactions were performed in a 50 mL three-neck round-bottom flask under an argon atmosphere. The injection solutions were all freshly prepared just prior to injection. Typically, a mixture of CdO (0.0514 g, 0.40 mmol), TOPO (3.78 g, 9.77 mmol) and TDPA (0.223 g, 0.80 mmol) was heated to 300°C and then allowed to cool down to 270°C. A solution of Se (0.0410 g, 0.52 mmol) in TOP (2.4 mL) was swiftly injected into this hot solution. The temperature would then be allowed to drop to 250°C for the growth of CdSe nanocrystals. Once the desired size/color (approximately ~3 nm after two minutes) was reached, the hot solution was poured into cold methanol, and the unused starting materials were separated from the nanocrystals by repeated centrifugation/decantation cycles in

methanol. The final product was re-dispersed in chloroform and kept in the dark under air for measurement and further applications.

4.5.3 CdSe quantum dots characterization

The photochemical properties of each batch of QD were determined with absorption and emission spectroscopy. The average size and concentration of the quantum dots were obtained from UV-visible absorption and fluorescence measurements following the calibration reported by Yu *et al.*²⁵ The average size was determined using Equation 4. 2:

$$D = (1.6122 \times 10^{-9})\lambda_{em}^4 - (2.6575 \times 10^{-6})\lambda_{em}^3 + (1.6242 \times 10^{-3})\lambda_{em}^2 - 0.4277\lambda + 41.57$$

Equation 4. 2: Average QD diameter D (in nm)

where λ_{em} is the emission wavelength maximum of the quantum dots in solution. Then the concentration was derived using:

$$c = \frac{A}{l \times \varepsilon} = \frac{A}{l \times 5857(D)^{2.65}}$$

Equation 4. 3: Concentration of the colloidal QD solution

where ε [$\varepsilon = 5857(D)^{2.65}$] is the molar extinction coefficient, A the maximum absorbance and l the path length.

The full-width at half-maximum (FWHM) was used as an indicator of size distribution, where a FWHM < 30 nm indicates close to monodisperse samples.

4.5.4 CdSe quantum dot treatment with elemental sulfur (S_8)

Elemental sulfur was added to the chloroform solution of CdSe at an optimal weight percentage of 1% with respect to solvent. The solution was left to sit for twenty-four hours in the dark, under air. Since S_8 is fully dissolved in the solvent, the quantum dots were precipitated in methanol followed by centrifugation and extraction, following a procedure similar to that employed in the separation following synthesis (*vide supra*). This ensured that no excess sulfur remained in solution as residual S_8 could have a screening effect during the irradiation process. The treated and extracted QD were then re-dispersed in chloroform and kept in the dark under air for further experiments.

4.5.5 CdSe quantum dot treatment with cadmium oxide or with selenium

Cadmium oxide or elemental selenium was also added to the chloroform solution of CdSe QD at a weight percentage of 1%. With both elements being insoluble in the organic solvent, they were separated from the QD after twenty-four hours by centrifugation. The supernatant, composed of treated QD, was kept in the dark under air for further experiments.

4.5.6 CdSe quantum dots irradiation under UVA light

Quantum dots were irradiated with UVA lamps centered at 350 nm. Each quartz cell was placed in a photoreactor containing 6 lamps (corresponding to 48 Watt input power); these lamps deliver about 39 Watt/m² light with approximately 4% spectral contamination, mostly visible and UVB light. The effect of irradiation was followed by steady-state fluorescence measurements, and pursued until maximum fluorescence emission was reached.

4.5.7 Fluorescence Quantum Yield (Φ_F) calculation

In order to obtain meaningful quantum yields it is necessary to select an appropriate reference compound. To measure relative quantum yields this reference must have emission spectrum overlapping extensively with that of the QD, and have a suitable absorption so that reference and sample can be excited at the same wavelength. This may seem like a trivial set of conditions, however many exceptionally high quantum yields have been reported in the literature using an inadequate reference. In fact, most fluorescence spectrometers have poor spectral correction and if the sample and reference spectra do not overlap the yields measured can have very large errors as demonstrated in Figure 4. 15. Further, instruments used for steady state quantum yield measurements should not have gated detection (or the gates should be much longer than the relevant lifetimes).

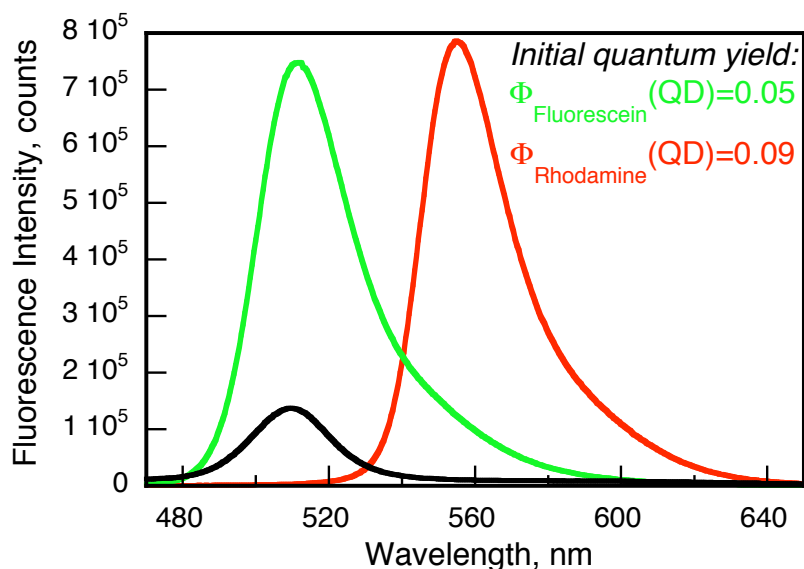


Figure 4. 15: Quantum yield of fluorescence calculation against two references: one with fluorescein having a good spectral overlap (green) versus rhodamine 6G, a poorly overlapping reference (red)

A dilute solution of QD was prepared in its solvent, such that its absorbance at the excitation wavelength (λ_{ex}) would be <0.10 ; as well as a diluted solution of the reference of comparable absorbance. Then an emission spectrum was recorded using this λ_{ex} and the quantum yield was obtained by:

$$\Phi_{QD} = \Phi_R \frac{A_{\text{fluo}QD}}{A_{\text{fluo}R}} \frac{\alpha_R}{\alpha_{QD}} \frac{\eta_{QD}^2}{\eta_R^2}$$

Equation 4. 4: *Quantum Yield of Fluorescence of QD*

where QD stands for quantum dot, R for reference, Φ are the quantum yields, A_{fluo} the area under the fluorescence peak, α the fraction of light absorbed, and η the refractive index of the solvents.

4.5.8 Fluorescence lifetimes

Each lifetime experiment was done with a class-I short-pulse LED matching as closely as possible the excitation wavelength of our sample (e.g., $\lambda_{\text{ex}} = 440$ nm). Long-pass cutoff filters were used after the sample cuvette to lower the spectral contamination of the decay signal (FEL 500 nm: transmits light from 500 nm and above). The samples' absorbance were matched at a low value of 0.21 at the excitation wavelength and the following conditions were used for the lifetime acquisitions:

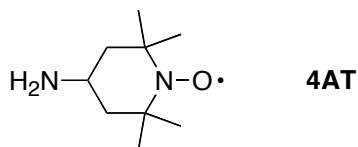
- $\lambda_{\text{ex}} = 440$ nm / $\lambda_{\text{em}} = 510$ nm;

- Start delay: 60 ns / End delay: 1000 ns

The fitting was performed with the ESM (Exponential Series Method) analysis program against the Instrument Response Function (IRF), as this fitting was done using Equation 2. 2 presented in Chapter 2. This way, the method recovers lifetime distribution without any *a priori* assumptions about their shapes and is ideal for complex systems such as quantum dots. The maximum amount of lifetimes (200) was entered to allow the most refined possible fitting, however, quantum dots always displayed a bi-exponential or tri-exponential decay.

4.5.9 Fluorescence quenching

Solutions of 4-amino TEMPO (4AT) were prepared in the solvent of study, in this case chloroform.



The stock solution was made at [4AT]= 10 mM to have an increase of concentration upon addition from 0 to 2500 μM . The treated (QD_{S8}) and non-treated (QD) CdSe QD solutions were diluted in chloroform to obtain a final concentration [QD]= 6 μM for both samples. Quenching data were analyzed as Stern-Volmer plots. A typical Stern-Volmer plot for simple systems follows Equation 4. 5:

$$\frac{\Phi_0}{\Phi} = \frac{I_0}{I} = 1 + K_{SV}[\text{quencher}]$$

Equation 4.5: Stern-Volmer equation for simple systems

where Φ_0 and Φ are the luminescence quantum yields in the absence and presence of quencher, and I_0 and I the corresponding experimental emission intensities, $K_{SV} = k_q \tau_0$ with k_q the bimolecular rate constant for quenching and τ_0 the fluorescence lifetime.

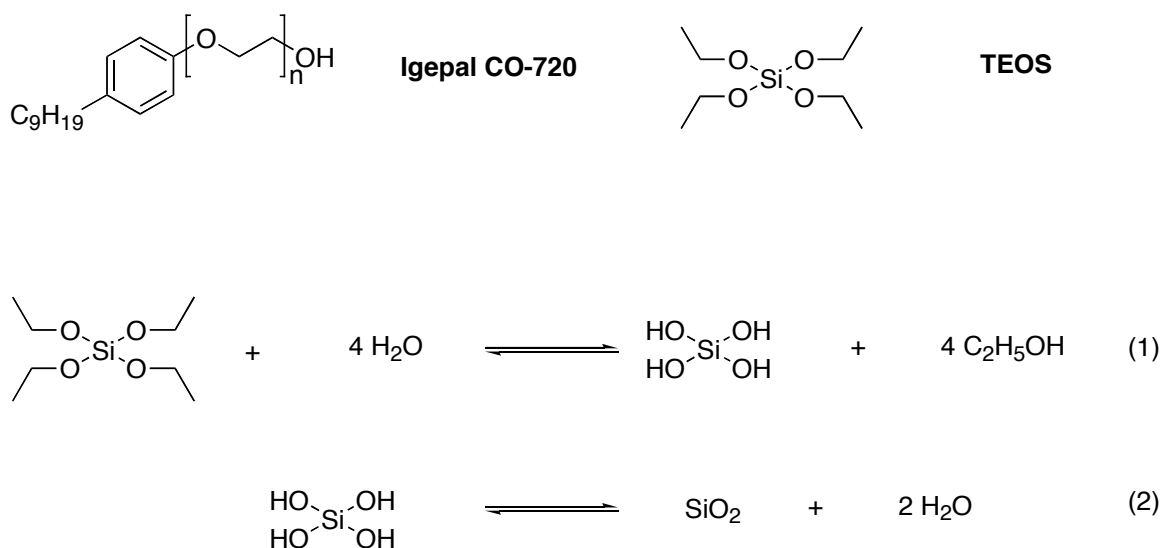
4.5.10 Radical-mediated fluorescence recovery

The previously formed QD-4AT complexes were tested as pre-fluorescent probes for carbon-centered free radicals: typically $[QD] = 8 \mu M$ and $[4AT] = 160 \mu M$ to have mostly a quenching located in the linear region of the Stern-Volmer plot. The complexes were left to equilibrate at $50^\circ C$, then 48 mM of freshly prepared AIBN were injected and the fluorescence variations were followed on the PTI fluorimeter.

4.5.11 Silica shell encapsulation via a microemulsion process

Typically 400 μL of stock solution for each QD (QD, QD(*i*), QD_{s8} or QD_{s8}(*i*)) was added to 10 mL of cyclohexane, 1.3 mL of Igepal® CO-720, and 80 μL of TEOS in a round-bottom flask under vigorous stirring for thirty minutes. After the microemulsion system was formed, 150 μL of ammonia aqueous solution (33 wt%) was added to initiate the polymerization, and each sample was left under stirring and under air for twenty-four hours. The mechanism for the formation of a silica polymer under basic catalysis is proposed in

Scheme 4. 5. Once the growth was complete, the encapsulated particles were precipitated using acetone and isolated by centrifugation (1200 rpm for fifteen minutes). The precipitate was washed in sequence with 1-butanol, 1-propanol and ethanol. Finally the clean precipitate was dispersed in 2 mL of Milli-Q water and stored in the dark, under air, for further analyzes.



Scheme 4. 5: Proposed mechanism for the formation of a silicon dioxide shell based on reference 13. (1): base catalyzed hydrolysis. (2): polymerization in alkaline solution by condensation and cross-linking

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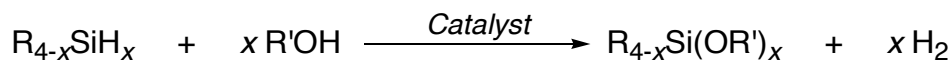
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5.1 Introduction

Noble metal nanoclusters have been extensively studied in the past years. Amongst them, silver nanometrials are of interest due to their wide range of applications, such as nanoelectronics, nanomedicine, surface enhanced Raman spectroscopy (SERS) and, especially, catalysis. Often deposited on supports, silver nanoclusters (AgNP) have been used for oxidation^{1, 2}, alkylation³ or Diels-Alder cycloaddition⁴ reactions, with all systems experiencing a higher reactivity combined with recyclability when compared to regular homogeneous catalysts.

Siloxane polymers have many interesting properties, such as good heat resistance, low toxicity, biocompatibility, high oxygen permeability, poor wettability, low surface tension, low melting point and glass transition temperatures, resistance to radiation and great electrical isolating properties to name a few.⁵ Therefore, it is a very interesting family of polymers. The hydrosiloxane polymer containing a transformable Si-H bond, are very attractive as they can be further derivatized for fine-tuning of chemical and physical properties of the new polymer. The formation of silicon-oxygen bond to form silyl ether groups in small hydrosilane molecules has been widely studied. The use of an alcohol or an alkoxide under acidic or basic conditions is favored because the only side product is hydrogen gas (see Scheme 5. 1).⁶ However, this reaction always requires a catalyst since alcohols are not basic enough and will not be sufficiently nucleophilic to attack the Si-H bond, which requires activation for a successful reaction.



Scheme 5.1: Typical route to silyl ethers from hydrosilanes and alcohols

The need for a catalyst would be even further justified when the formation of a silyl ether functionality is required on a hydrosiloxane polymer. The reactivity of the Si-H bonds on the backbone is significantly reduced by the steric hindrance coupled to a low solubility of the polymer in a given alcohol. Various approaches have been undertaken. Metal complexes such as H_2PtCl_4 have been added to the reaction mixture containing polysiloxane and an alcohol. The complexes underwent reduction to colloidal Pt^0 while grafting the silicon centers.⁵ Another route would pre-form Pd^0 nanoparticles in polymethylhydrosiloxane (PMHS), forming nanoconjugates that were stable and could be redispersed in a reaction mixture for the grafting⁷. For all of them, metals and metals salts of groups 8-10 were selected as catalysts, with a strong preference for the expensive palladium and platinum derivatives. Moreover, these systems would require either heating to reflux temperatures, inert atmosphere or long reaction time to obtain a quantitative conversion of the reactive Si-H bonds to Si-OR bonds.

In this chapter, we present an easy, one-pot synthesis method where polymethylhydrosiloxane (PMHS) acts as the reaction medium, the reducing agent⁸ and the stabilizing agent of the *in situ* formation of silver nanoparticles (AgNP). This polysiloxane has also the advantage of being inexpensive, easy to handle, stable, easy to remove and environmentally friendly.⁹ The Ag@PMHS nanoconjugate formed is the first group 11 metal derivative generated as a stable colloid that can undergo catalytic generation of hydrogen gas

through alcoholysis of the polyhydrosiloxane. Also, it is the first system that allows the reaction to take place in combined conditions, under air and at room temperature.

5.2 Results

5.2.1 Embedded silver nanoparticles synthesis

Silver nanoparticles (AgNP) are obtained from the reduction of a silver salt. Here silver nitrate was chosen as the precursor. Poly(methylhydro)siloxane is a stable siloxane polymer commonly used as a mild, environmentally friendly reducing agent.

When silver nitrate (AgNO_3) was suspended in polymethylhydrosiloxane (PMHS) under air and vigorous stirring, the solution quickly turned into a light yellow color, then slowly progressed to orange then light brown, generating the organosol of Ag@PHMS nanoconjugates. This reaction could be followed by UV-Visible absorption as shown in Figure 5. 1. A typical surface plasmon absorption band, characteristic of metallic silver nanoclusters, was observed at 420 nm.

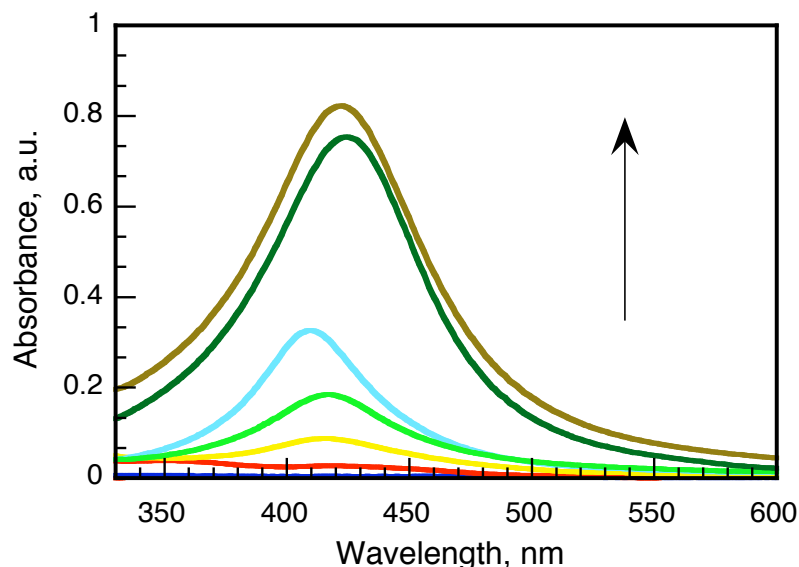


Figure 5. 1: UV-visible absorption spectra of Ag@PMHS showing the surface plasmon band growth over 48 hours.

The broad peak, as well as the brown color indicates the polydispersity of the system, which is expected with such a slow growth. However, a precise size analysis with more techniques is necessary. Both scanning electron microscopy (SEM) and dynamic light scattering (DLS) analyses were run. SEM images of the final sample (after a 48 hours growth) were acquired using both regular transmission mode (TED) and backscattering mode (COMPO). As can be seen in Figure 5. 2 (left), particles embedded within the polymer appear darker, however the organic matrix leads to rapid charging of the sample during acquisition, resulting in difficult distinction between the polymer matrix and the metallic nanoparticles. For this reason, backscattering acquisition of the same sample was preferred for the size distribution analysis, as only metallic species would appear brighter than the dark

background, as can be see in Figure 5. 2 (right). The mean size of those particles seems to be around 135 nm with a large size distribution (Figure 5. 2, bottom).

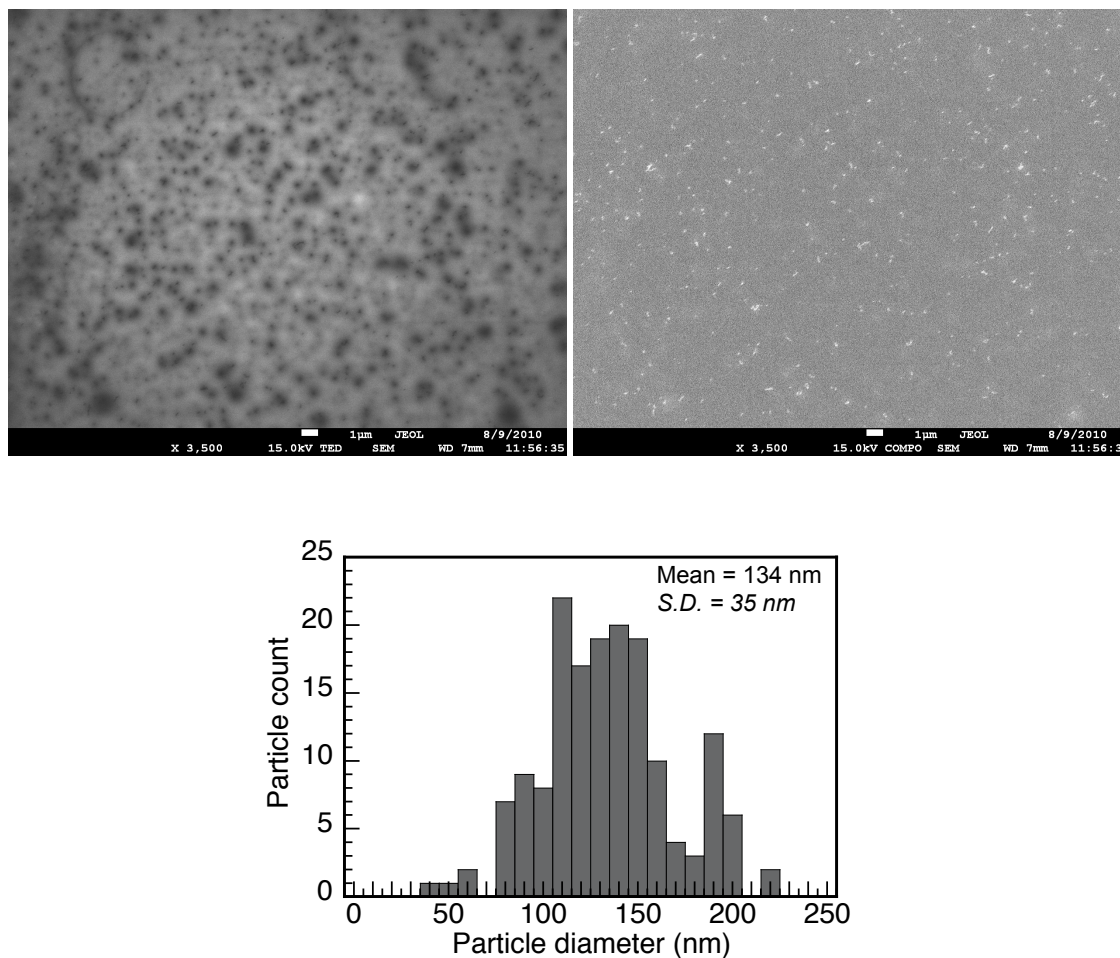


Figure 5.2: Scanning electron micrographs of Ag@PMHS using transmission (left) and backscattering (right) modes. Particle size distribution histogram for the above backscattered sample.

A higher magnification is not proposed here. Indeed, a closer look would show the big nanoparticles to actually be aggregates or chains of smaller nanoparticles wrapped around PMHS. However, no acquisition was possible, as charging of the organic layer

resulted in the electron beam burning the film, rendering image analyses impracticable. Therefore, the particle size distribution displayed in Figure 5. 2 actually corresponds to aggregates of silver nanoparticles along the polymer chains and arranged in a pearl-necklace fashion.

DLS studies allowed for a more accurate measurement of the embedded nanoparticles during growth. These values gave the hydrodynamic diameter of the colloidal suspension. This diameter not only includes the active metallic core, but also any outer layer stabilizing it. As Figure 5. 3 shows, the silver nanoparticles growth slowed down after 12 hours of reaction and, after 48 hours, were around 40 nm in diameter.

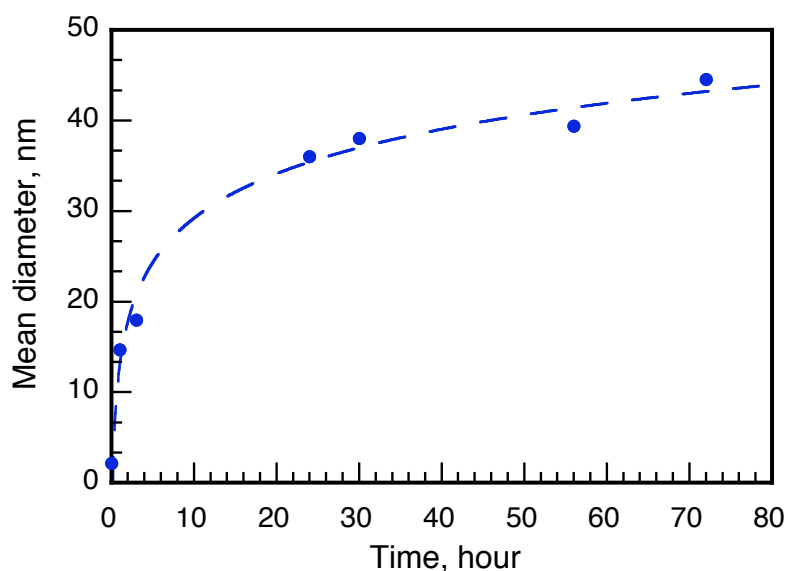


Figure 5. 3: Dynamic light scattering measurement of silver particles in PMHS, diluted in toluene prior to analysis. The logarithmic fit is used to guide the eye.

An X-ray photoelectron analysis (XPS) allowed for the study of the surface of the formed nanoconjugates. However, being a surface technique, XPS analysis proved difficult due to the polymer matrix encircling the particles. Only peaks from the polysiloxane were detected. After proper etching, a large portion of the polymer matrix was removed and silver nanoparticles were exposed for surface analysis. As can be seen in Figure 5. 4, the doublet that belongs to $\text{Ag}^{(0)}$ was clearly visible at 366 and 373 eV. Although a small tail is present on the left side of each peak, no actual peak corresponding to silver oxide species was observed.

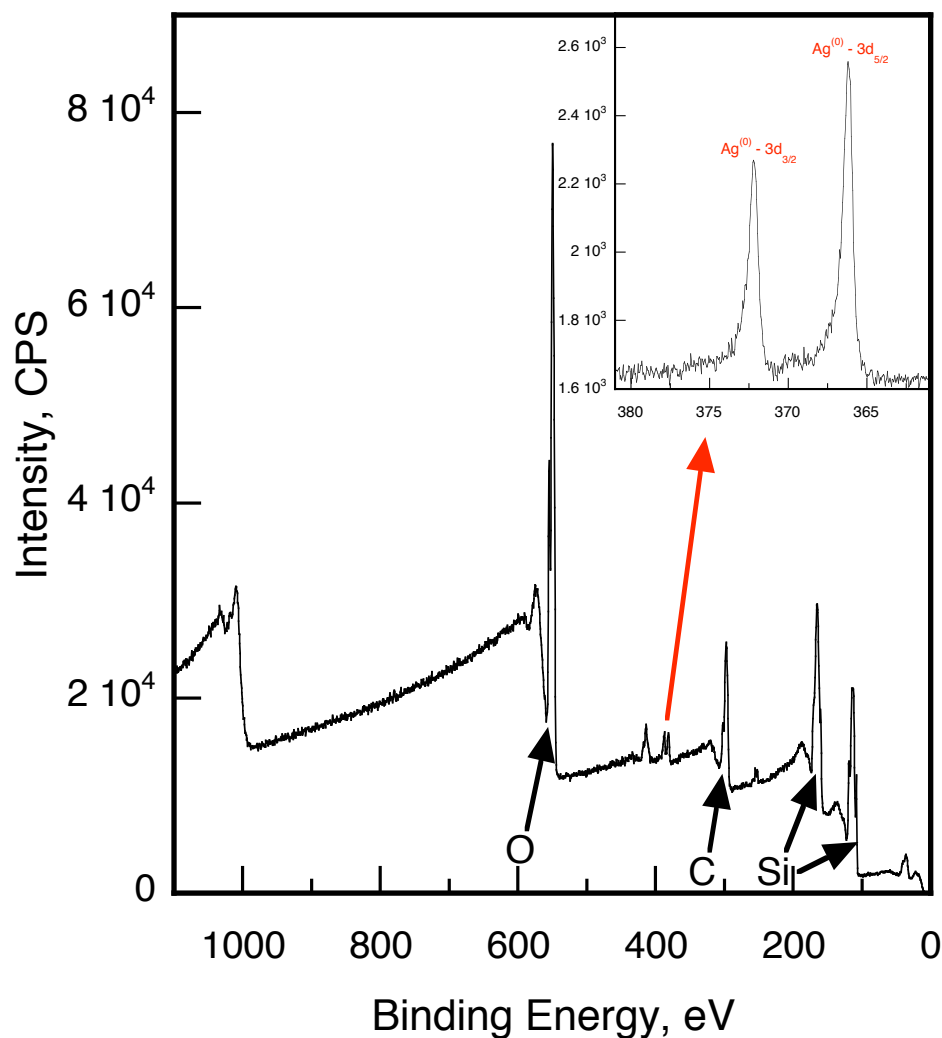


Figure 5. 4: XPS spectra of the silver nanoparticles in PMHS with a general scan and a scan centered at the $\text{Ag}^{(0)}$ doublet position (inset)

XPS analysis, coupled with UV-visible spectroscopy, was further proof that silver nitrate was fully reduced to $\text{Ag}^{(0)}$ and formed stable nanoparticles embedded within the polysiloxane matrix.

5.2.2 Polymer alcoholysis towards functional poly(methylalkoxy)siloxanes

When the AgNP@PMHS matrix, insoluble in aqueous media and alcohols, was put in the presence of an alcohol, a strong and continuous bubbling was observed. The kinetics of the gas generation, as well as the total amount of gas generated was measured in the *in-house* sensitive pressure-transducer system where the pressure induced by the gas generated in the sample cell against a reference cell was converted into a voltage.¹⁰ Figure 5. 5 shows a typical gas generation curve when adding AgNP@PHMS to methanol. A brief induction period (not visible here due to the short delay between the beginning of the reaction and the start of acquisition) was observed at the beginning of the reaction, probably due to the diffusion of methanol within the poly(methylhydrosiloxane) matrix to reach the interface between the silver surface and the stabilizing polymer. The reaction then accelerated at a rate of 2.6 mmol/h on a very short timescale, to produce 0.17 mmol of gas.

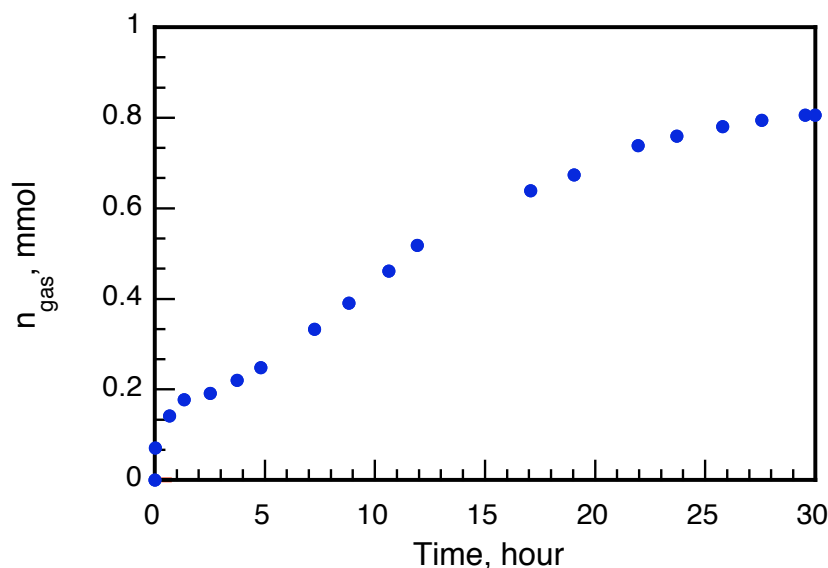


Figure 5.5: Gas generation kinetic for the reaction of methanol (2 mL, 50 mmol) over AgNP@PHMS (50 μ L, $n_{\text{Ag}}=23 \mu\text{mol}$, $n_{\text{PMHS}}=0.8 \text{ mmol}$) at 30 °C

Interestingly a slow down, or a second induction period was observed, followed by a slower generation of gas over the next 25 hours. Overall, 0.8 mmol of gas was generated from 23 μ mol of Ag and 0.8 mmol of PMHS, meaning that the reaction was conclusively catalytic in the presence of AgNP, whereas a perfectly stoichiometric amount of gas is generated when compared to the polymer Si-H content.

The nature of the gas generated needed to be identified to ensure an alcoholysis reaction was taking place, since the system used in Figure 5. 5 simply measured pressure difference. An aliquot of AgNP@PMHS (1 mL) was left to react with methanol (5 mL) in a closed vessel, under air. The strong bubbling would create a gas build-up above the reaction mixture. The gas sample was taken to a gas chromatograph equipped with a packed column and a universal thermal conductivity detector (TCD) and compared to the gas sample taken above a mixture of methanol and PMHS only.

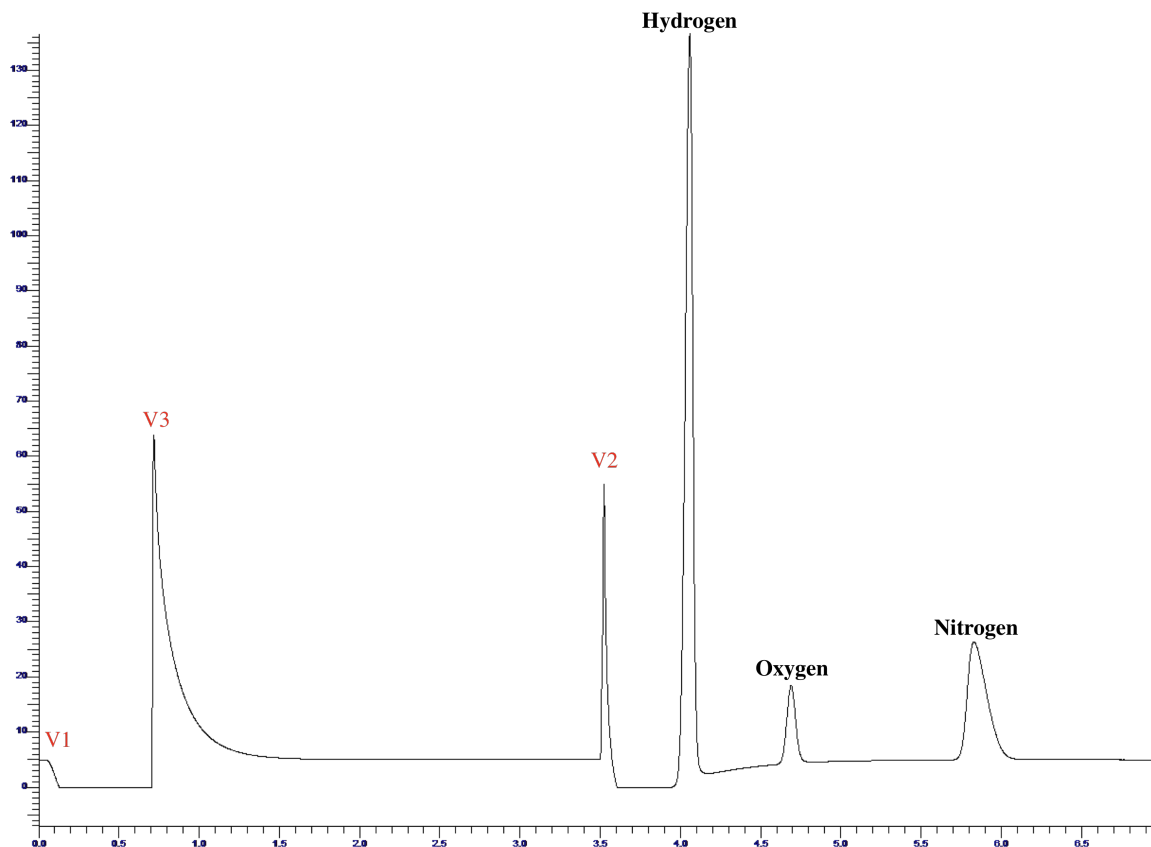


Figure 5. 6: GC-TCD chromatograph of a gas sample after reaction between AgNP@PHMS and methanol (V1, V2 and V3 represent valves closing)

Hydrogen, with a retention time of 3.97 min, was the only gas detected other than oxygen and nitrogen from air as shown in Figure 5. 6. Based on this experiment and Figure 5. 5, a stoichiometric amount of hydrogen was produced upon alcoholysis of the polymer chain with the corresponding alcohol.

The grafting was further confirmed with ^1H and ^{13}C NMR spectroscopy. The simplicity of the system did not require the time-consuming acquisition of ^{29}Si NMR, since the peaks corresponding to Si-H and Si-OCH₃ were clearly distinct in the ^1H NMR spectra.

In Figure 5. 7, were the grafting of PMHS with methanol was undertaken, the singlet at 4.7 ppm corresponding to the Si-H resonance disappeared completely and was replaced by a broader singlet at 3.4 ppm corresponding to the Si-O-CH₃ resonance.

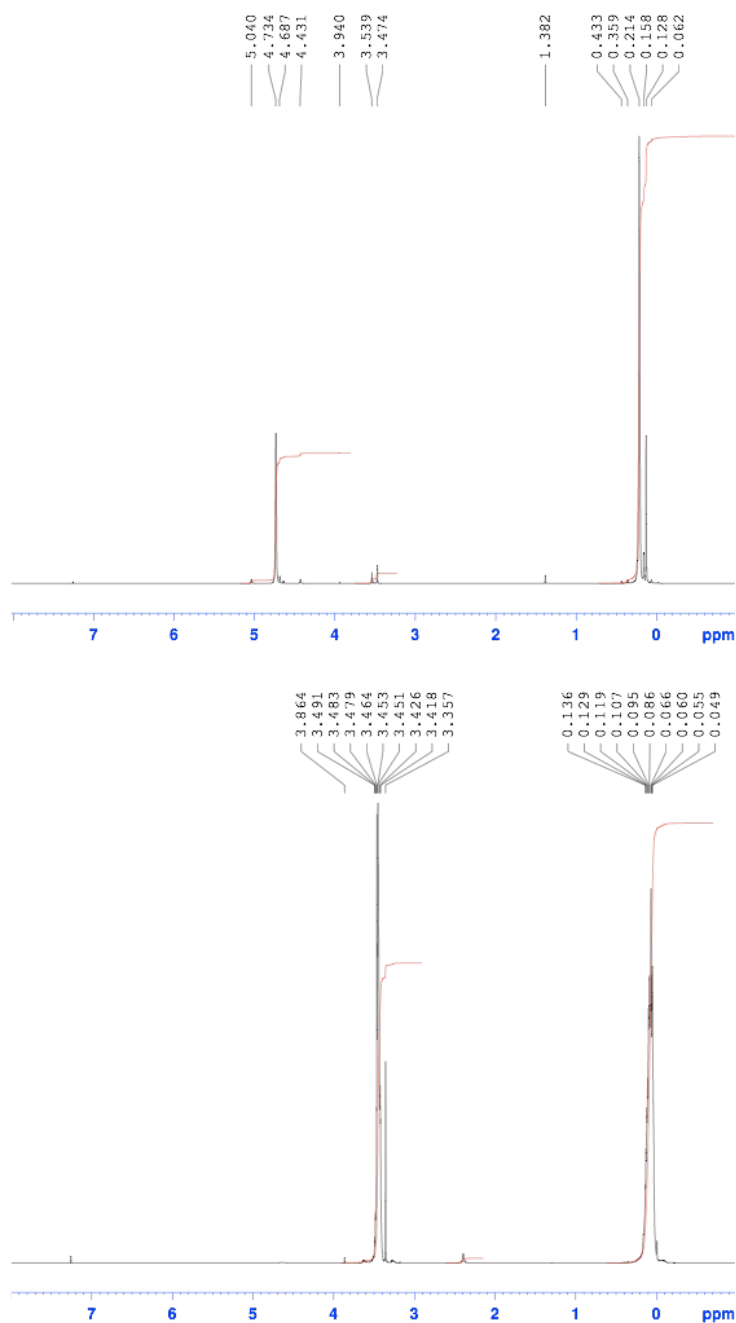


Figure 5. 7: ¹H NMR spectra of AgNP@PMHS in CDCl₃ before (top) and after (bottom) reaction with methanol.

This system is not limited to poly(methylhydrosiloxane) and methanol. Other polymers were tested, including poly(dimethylsiloxane) (PDMS) and poly(dimethylsiloxane-co-methylhydrosiloxane) (co-PDMS/PMHS). The former was not able to reduce the silver salts to silver particles (data not shown) and, therefore, further studies were terminated. The latter displayed the same behavior as PMHS as a result of its Si-H bonds. Moreover, other alcohols were used as precursors for the grafting of alkoxy groups to the polymer chains. GC-TCD measurements (see Annex) of the various systems after five minutes of reaction highlighted the difference in reactivity. ^1H NMR measurements (see Annex) confirmed the substitution on the Si-H backbone with the corresponding alkoxy groups. This is summarized in Table 5. 1: the yield of conversion to the corresponding silyl ether is presented after 24 hours of reaction rather than completion of the reaction to compare the alcohols' reactivity.

Table 5. 1: Product yields from AgNP@PHMS catalyzed reaction with various alcohols after 24 hours of reaction

Entry	Alcohol	Product	Yield (%)
1	CH ₃ OH	(CH ₃) ₃ SiO[(CH ₃ O)(Me)SiO] _n Si(CH ₃) ₃	27.2
2	CH ₃ CH ₂ OH	(CH ₃) ₃ SiO[(CH ₃ CH ₂ O)(Me)SiO] _n Si(CH ₃) ₃	17.1
3	CH ₃ CH ₂ CH ₂ OH	(CH ₃) ₃ SiO[(CH ₃ CH ₂ CH ₂ O)(Me)SiO] _n Si(CH ₃) ₃	23.7
4	(CH ₃) ₂ CHOH	(CH ₃) ₃ SiO[((CH ₃) ₂ CHO)(Me)SiO] _n Si(CH ₃) ₃	16.3
5	CH ₃ (CH ₂) ₂ CH ₂ OH	(CH ₃) ₃ SiO[(CH ₃ (CH ₂) ₃ O)(Me)SiO] _n Si(CH ₃) ₃	19.7
6	CH ₃ (CH ₂) ₃ CH ₂ OH	(CH ₃) ₃ SiO[(CH ₃ (CH ₂) ₄ O)(Me)SiO] _n Si(CH ₃) ₃	17.0
7	CH ₃ (CH ₂) ₆ CH ₂ OH	(CH ₃) ₃ SiO[(CH ₃ (CH ₂) ₇ O)(Me)SiO] _n Si(CH ₃) ₃	14.4
8	CH ₃ CH(CH ₃)CH ₂ OH	(CH ₃) ₃ SiO[(CH ₃ CH(CH ₃)CH ₂ O)(Me)SiO] _n Si(CH ₃) ₃	17.7
9	(CH ₃) ₃ COH	(CH ₃) ₃ SiO[((CH ₃) ₃ CO)(Me)SiO] _n Si(CH ₃) ₃	16.3
10	CF ₃ CH ₂ OH	(CH ₃) ₃ SiO[(CF ₃ CH ₂ O)(Me)SiO] _n Si(CH ₃) ₃	17.6
11	CH ₃ CH(OH)CH ₂ OH	(CH ₃) ₃ SiO[(CH ₃ CH(OH)CH ₂ O)(Me)SiO] _n Si(CH ₃) ₃	10.0

All the primary alcohols investigated in this study successfully underwent grafting, with methanol and *n*-propanol being the most efficient. Secondary and tertiary alcohols were also successfully grafted, but to a lower extent. The least effective grafting was with the diol (entry 11) although it did not present major steric hindrance, but it had two neighboring –OH groups.

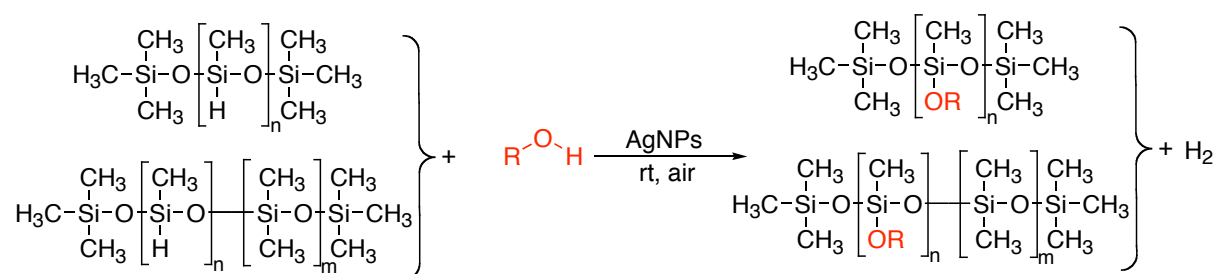
5.3 Discussion

The condensation of monomeric hydrosilanes and hydrosiloxanes through transition-metal catalysis is well studied. The controlled substitution is efficiently achieved with groups 8 to 10 transition metals or metals salts (typically Rh, Pd and Pt) that undergo an *in-situ* reduction during the process. The same selective conversion of the Si-H bonds present on the backbone of a polymeric chain is more complicated, due to the tendency of these bonds to undergo dehydrocoupling, rearrangement or backbone degradation.⁷ Also, the nature of the polymer limits the accessibility to Si-H bonds and reduces tremendously their reactivity. The catalytic grafting of PMHS through alcoholysis has been reported with palladium-polysiloxane nanocomposites or platinum divinyltetramethyldisiloxane complex, but required the use of an organic solvent, as well as heating and long reaction times.^{5,7}

Here, silver nitrate was chosen as the precursor for silver nanoclusters due to its low cost, its superior stability towards humidity when compared to other silver salts (*e.g.*, silver fluoroborate or silver perchlorate), and its stability to light. In addition, this salt is soluble in many solvents, making it the most versatile precursor for a mild reduction process. Using PMHS or co-PDMS/PMHS as the sole reducing agent lead to the very slow growth of silver nanoclusters. As shown in the DLS graph, the growth rate was significantly reduced after two days of reaction giving a stable particle size of 35-40 nm. A similar size range was obtained for PMHS reducing Pd(OAc)₂ salt.⁷ Given the length of PMHS, also used here to stabilize the silver nanoparticles, the hydrodynamic diameter measured through DLS should have been much larger than the one measured in Figure 5. 1. This is an indication that the long polymer chains tend to wrap around the nanocrystals as they are being formed. Such a

high degree of flexibility is expected from siloxane polymeric chains provided by the freedom of rotation around the Si-O bond present along the backbone.

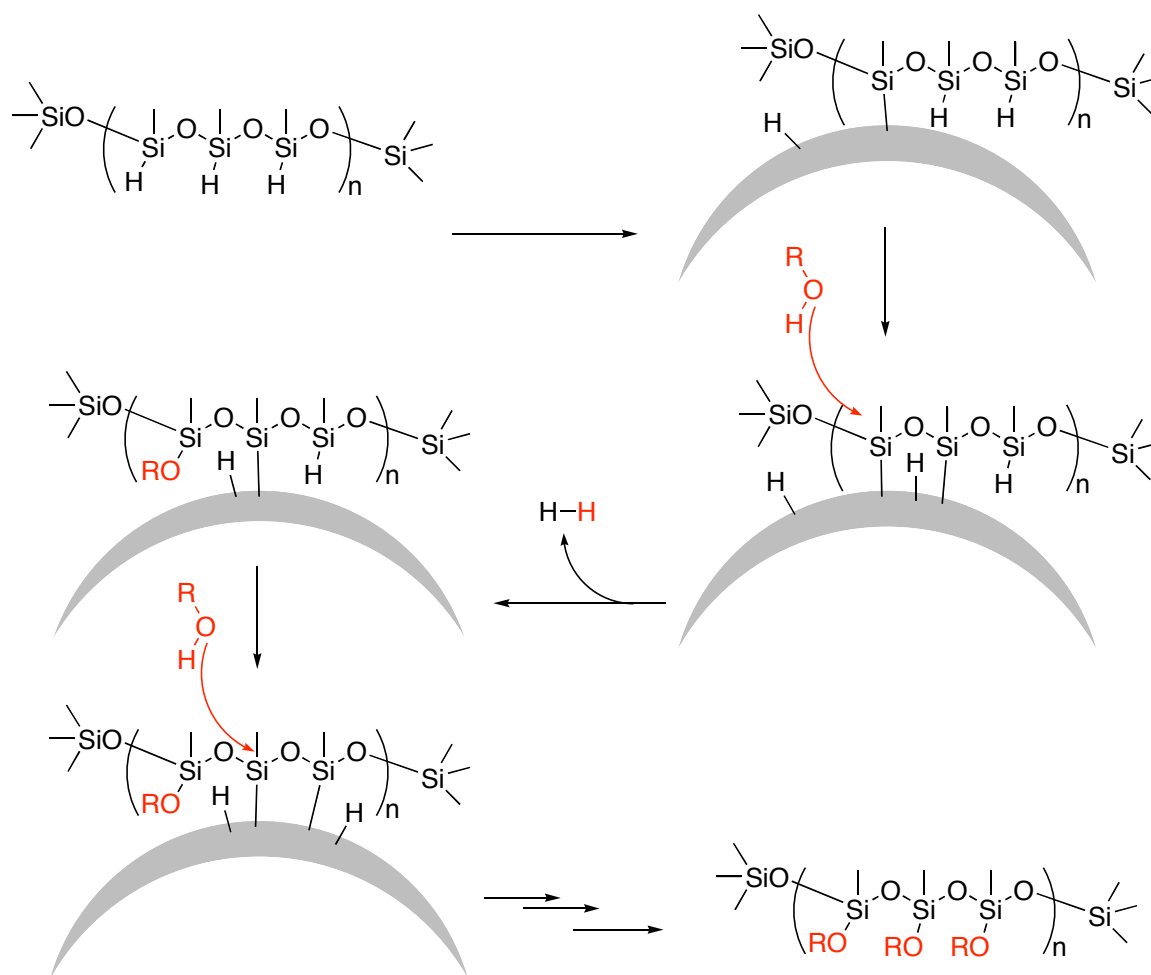
The generated nanoconjugates were stable yet reactive when put in the presence with an alcohol. The silver nanoparticles were stabilized by PHMS and were deeply confined within the polymer matrix as was shown by the XPS analysis. However, this stabilization must be steric, as the AgNP were, nevertheless, catalytically active. The reactivity of AgNP towards alcohol grafting on the polysiloxane backbone proved their surface was mostly unpassivated. With such a flexible system, it was anticipated and confirmed that it was not limited to poly(methylhydrosiloxane) combined with the small methanol molecule only. The prerequisite for the siloxane polymer is to possess Si-H bonds on its backbone or on the polymer side chains,⁶ both for the reducing ability and later for the grafting at this position. Therefore, the general reaction pathway for our system can be summarized in Scheme 5. 2.



Scheme 5. 2: Catalytic reaction pathway for the alcoholysis grafting of polyhydrosiloxane chains.

The proposed mechanism presented in Scheme 5. 3 for the catalytic grafting of PMHS on the surface of silver nanoparticles is based on the reactivity of the Si-H bond as

well as the behavior of disiloxanes with metal complexes.^{11, 12} Although the usual oxidative addition and reductive elimination sequence is accepted for homogeneous metal complex catalysts, it is reasonable to assume a similar behavior at the surface defect of heterogeneous silver nanoparticles.



Scheme 5.3: Proposed mechanism for the silver-catalyzed grafting of polyhydrosiloxane with an alcohol (here: methanol is used as the nucleophile).

The Si-H bond is activated on an active surface site (surface defect) of the silver nanocluster. This activation would occur during the growing process of the nanoparticles. Subsequently, the generation of a disiloxane cycle with the adjacent Si-OH bond occurs and is based on the reactivity with disiloxane metal complexes.¹¹ The nucleophilic attack that follows on one of the cyclic silicon atoms is possible due to the polarization of the former Si-H bond. An alcohol, usually one of mediocre nucleophilicity, is able to form the corresponding silyl ether while breaking the cycle. The adjacent Si atom that was part of the initial cycle is now able to form a new disiloxane cycle with a neighboring Si atom, activating both sites for a second nucleophilic attack. These consecutive steps can occur as long as Si-H bonds are available on the polymer backbone. However, the grafting reaction leads to the destabilization of AgNP. In fact, the alkoxy-substituted polysiloxane is no longer able to weakly bind to the surface defects, thus resulting in the precipitation of silver aggregates and allowing for facile separation of the catalyst from the modified polymer. These aggregates are much less reactive than the native AgNP, but the addition of a polyhydrosiloxane triggers the re-suspension of nanosize particles that are as reactive as the Ag@PMHS that were generated *in situ*.

5.4 Summary

A facile, one-pot synthesis of silver nanoclusters with polyhydrosiloxane polymers was presented. The polymer acted as both the mild reducing agent and the stabilizing ligand, with no additional solvent or heating being required. Moreover, this system is stable under ambient conditions, eliminating the need to handle in inert atmospheres. The obtained AgNP

were embedded within the polymer matrix, but weakly passivated, allowing them to be very reactive for any subsequent catalytic reaction.

The grafting of polyhydrosiloxane polymers was possible with a wide variety of monofunctional alcohols, with a preference for primary alcohols albeit the steric hindrance of the mixture. The catalytic reactions probably used the ability of disiloxane units with transition metal atoms to form cycles and thus activate the Si atoms for a nucleophilic attack by weakly acidic alcohols.

This is the first example of a system based on a group 10 metal, silver, that is able to support the catalytic conversion of silane groups into silyl ethers with exceptional yields.

5.5 Experimental

5.5.1 Materials

Silver nitrate powder 99.9% (AgNO_3) was purchased from Alfa Aesar. Poly(methylhydrosiloxane) (PMHS, $M_n=2,500$), poly(dimethylsiloxane-co-methylhydrosiloxane) trimethylsilyl terminated (co-PDMS/PMHS, 50-55% dimethylsiloxane, $M_n=950$) and poly(dimethylsiloxane) hydride terminated (PDMS, $M_n=17,500$) were all purchased from Sigma-Aldrich. Chloroform, ethanol and methanol were purchased from Fisher Scientific. The other alcohols were purchased from BDH Chemicals. All chemicals and solvents were used without further purification.

5.5.2 Polymer embedded silver nanoparticles synthesis

All reactions were performed in a 50 mL round-bottom flask under air. Typically, a mixture of AgNO_3 (400 mg, 2.35 mmol) and the desired polymer PMHS (5 mL, 78.5 mmol), PDMS (5 mL, 64.9 mmol) or co-PDMS/PMHS (5 mL, 52.1 mmol) is allowed to react at room temperature under a constant, vigorous stirring. The reaction is left to proceed with its slow reduction for 48 hours and aliquots are taken at regular intervals for sample size analyses. The final nanoconjugate system is kept in the dark under air for further applications.

5.5.3 Silver nanoparticle UV-visible characterization

The reduction of silver salts into silver nanoparticles gives rise to a surface plasmon band (SPB) at a characteristic wavelength for this material. The growth of SPB was followed by UV-visible spectroscopy. Typically, an aliquot (0.1 mL) from the nanoconjugate system

is dispersed in toluene (2.5 mL) and placed in a quartz cuvette for an absorption measurement. The diluted sample is preserved for further size analysis.

5.5.4 Silver particle size analyses

The same sample that was used for the UV-visible characterization (100 μ L aliquot + 2.5 mL toluene) was also analyzed through dynamic light scattering (DLS) to obtain the hydrodynamic diameter; that is, the actual diameter of the particle with any potential shell or ligand surrounding it. This technique gives a better idea of whether a thick shell of silver oxide surrounds the metallic particle, especially when compared to scanning electron microscopy (SEM) explained below. DLS also gives information on the stabilizing ligand, PMHS in the present case. A hydrodynamic diameter significantly larger than the particle size indicates a spread out ligand only anchored to the surface atoms at one point, whereas a slightly larger diameter indicates a ligand wrapping around the particle.

The DLS analysis is combined to SEM images acquisition. Typically, 40-50 μ L of the previously diluted sample was drop-casted on a copper grid coated with a carbon film and let to dry inside an ultra-high vacuum pump chamber for at least six hours. The grid was analyzed using both the transmission electron detector (TED) and the retractable backscattering detector (RBEI) modes to ensure all images acquired had metallic silver particles.

5.5.5 Alcoholysis grafting assays

The grafting of the alkoxy groups on the polysiloxane chains from the corresponding alcohol induces a gas generation that was followed in a sensitive pressure-transducer system.

The pressure difference between the catalytic grafting of poly(methylhydro)siloxane and that of a reference cell (same composition, minus the embedded silver nanoparticles) was measured. This difference was recorded in volts, read by a computer and converted to moles of hydrogen by calibrating the apparatus with a known volume of gas.

For a typical polysiloxane grafting, the reference and sample cells are filled with a chosen alcohol, usually methanol (2 mL, 25 M) and let to equilibrate at 30°C overnight. The measurement starts upon addition of AgNP@PMHS (50 μ L, 0.2×10^{-4} mol of Ag and 0.8×10^{-3} mol of polymer) in the sample cell, and PMHS alone (50 μ L, 0.8×10^{-3} mol) in the reference cell to give the rate of gas generation, as well as the total amount generated.

5.5.6 Gas analysis from alcoholysis grafting reaction

The nature of the gas generated in the grafting reaction was confirmed with a gas chromatography analysis combined with a thermal conductivity detector (GC-TCD). Typically, a 1 mL aliquot of AgNP@PMHS was added to a 5 mL alcohol sample in a flask sealed with a rubber septum. The system was left to react for a couple of minutes to create a gas build-up atop the liquid, then a gas sample was removed through the septum with an air tight syringe and directly injected into the GC-TCD.

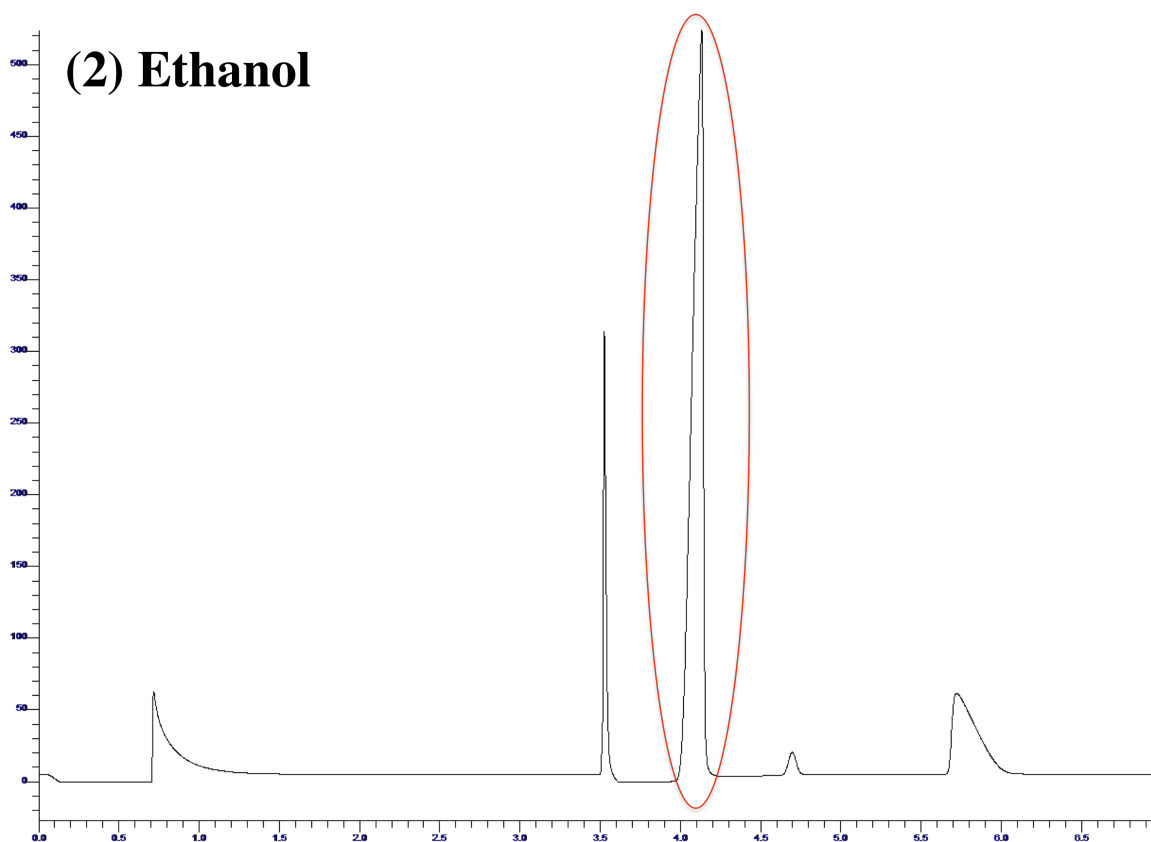
5.5.7 Polymer analysis from alcoholysis grafting reaction

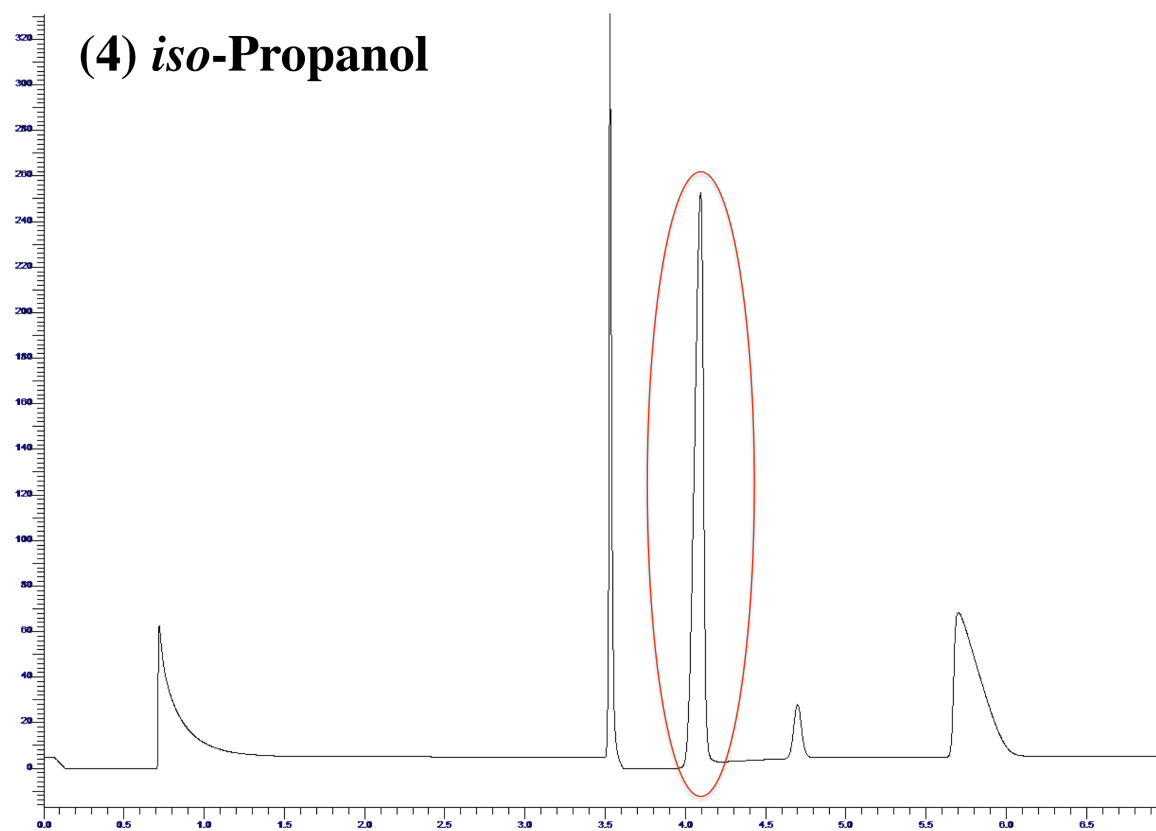
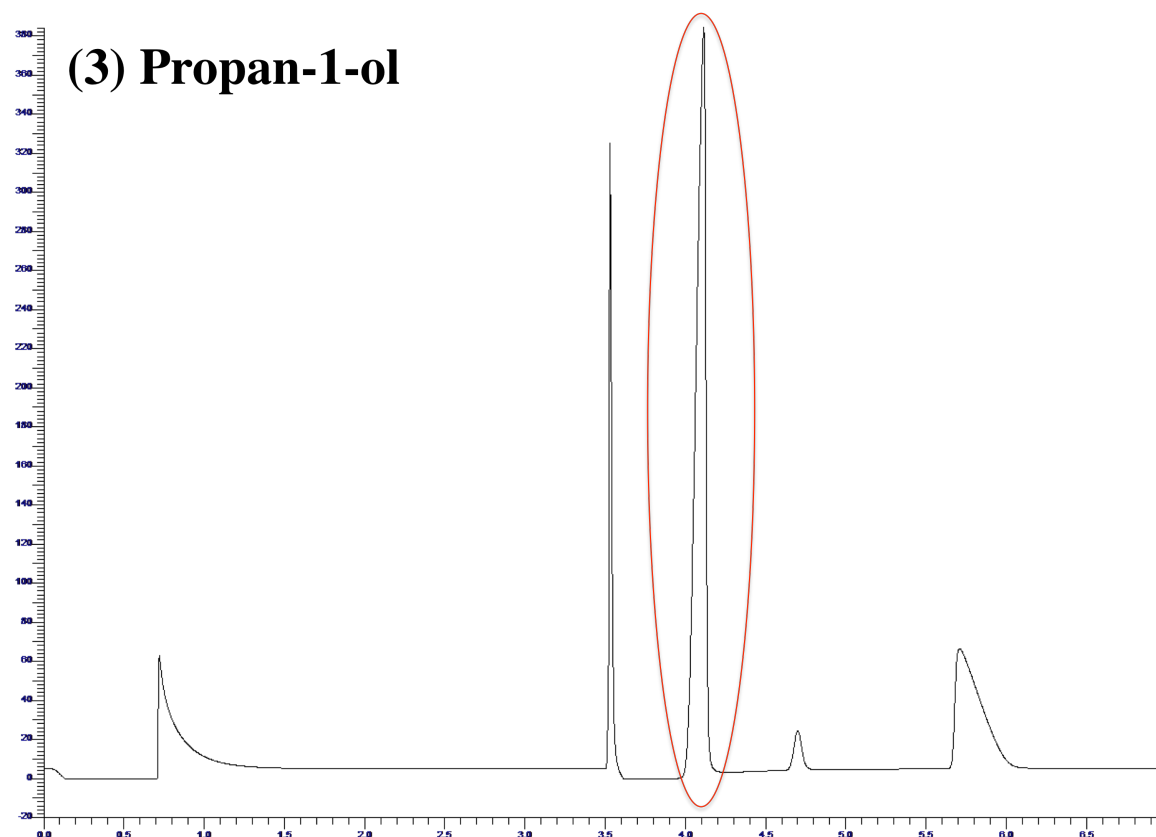
The yield of conversion for the Si-H bonds on the PMHS backbone was determined with ^1H and ^{13}C NMR. Typically, the reaction mixture used in 5.6.6 (1 mL AgNP@PMHS + 5 mL alcohol) was left to react to completion for 48 hours. Indeed, a strong bubbling of hydrogen could be observed for the first 4 or 5 hours, but the subsequent light degassing

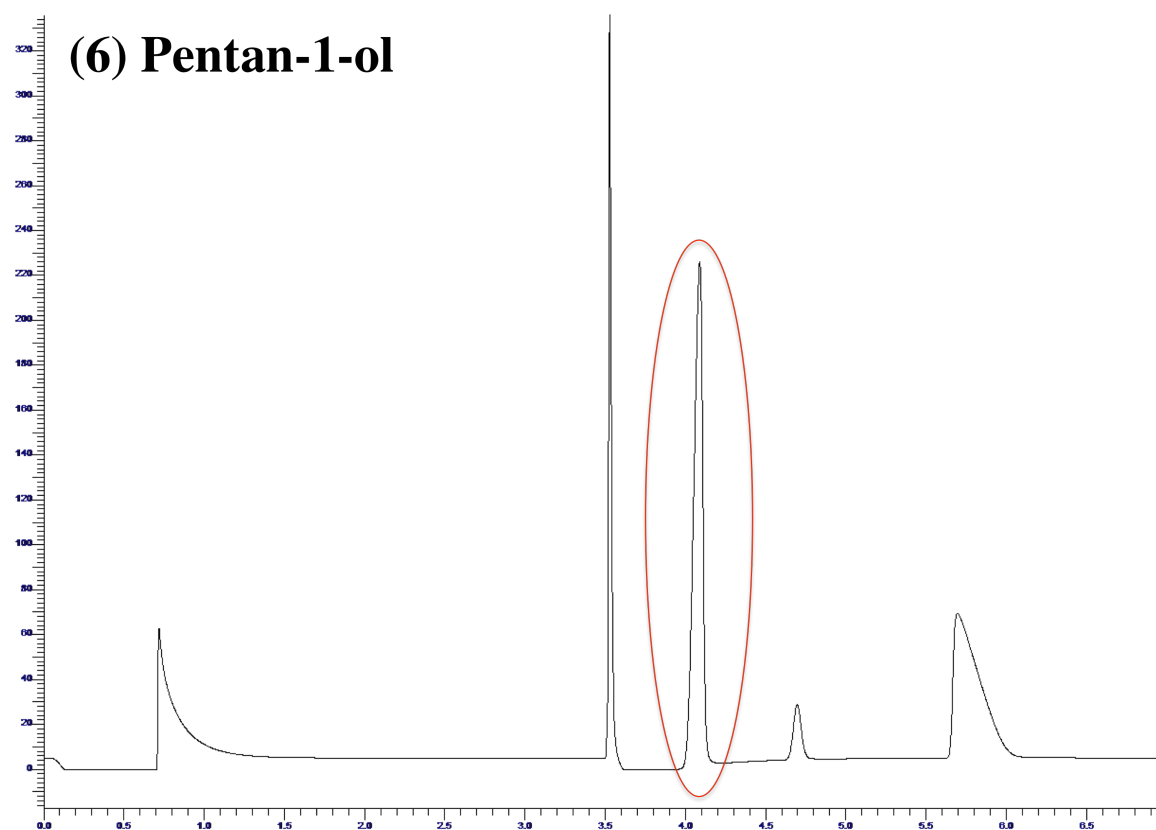
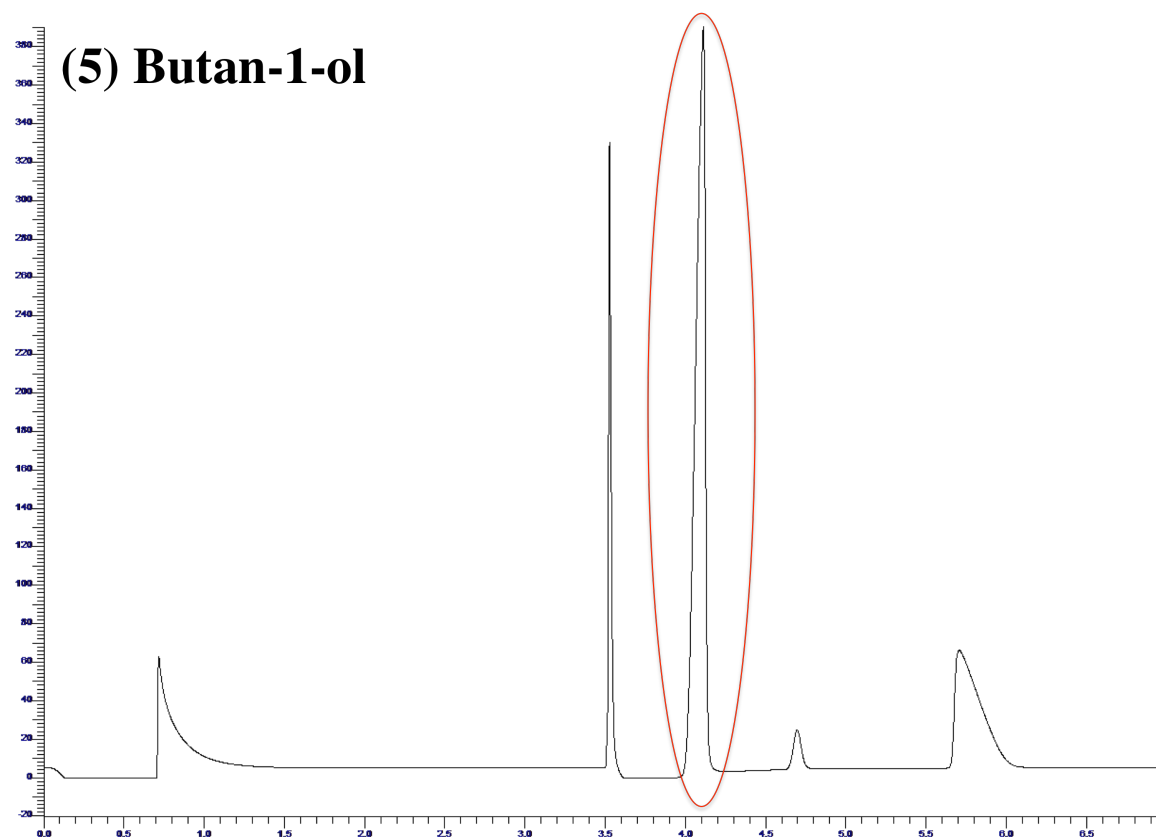
could be observed for over two days. Upon completion, the unreacted alcohol was removed by evaporation and the resulting polymer was re-suspended in deuterated chloroform. All the spectra were acquired on a 400 MHz Bruker spectrometer at room temperature.

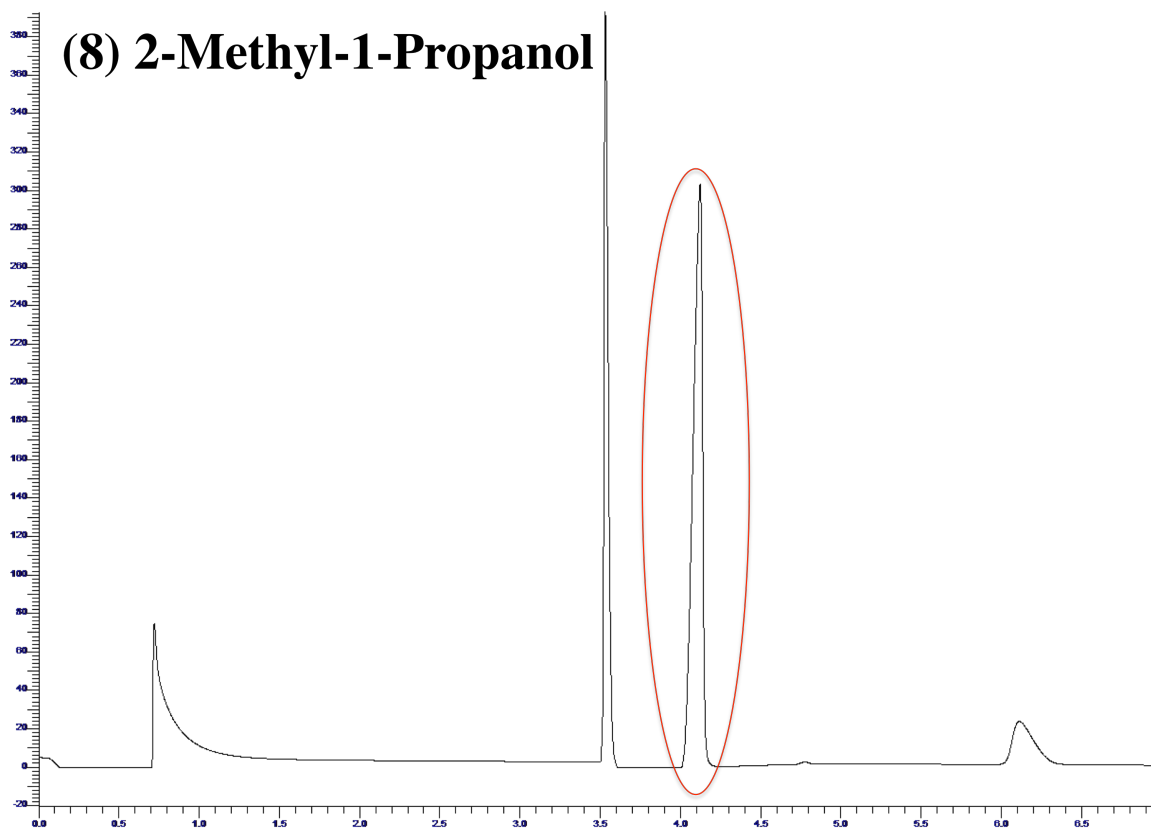
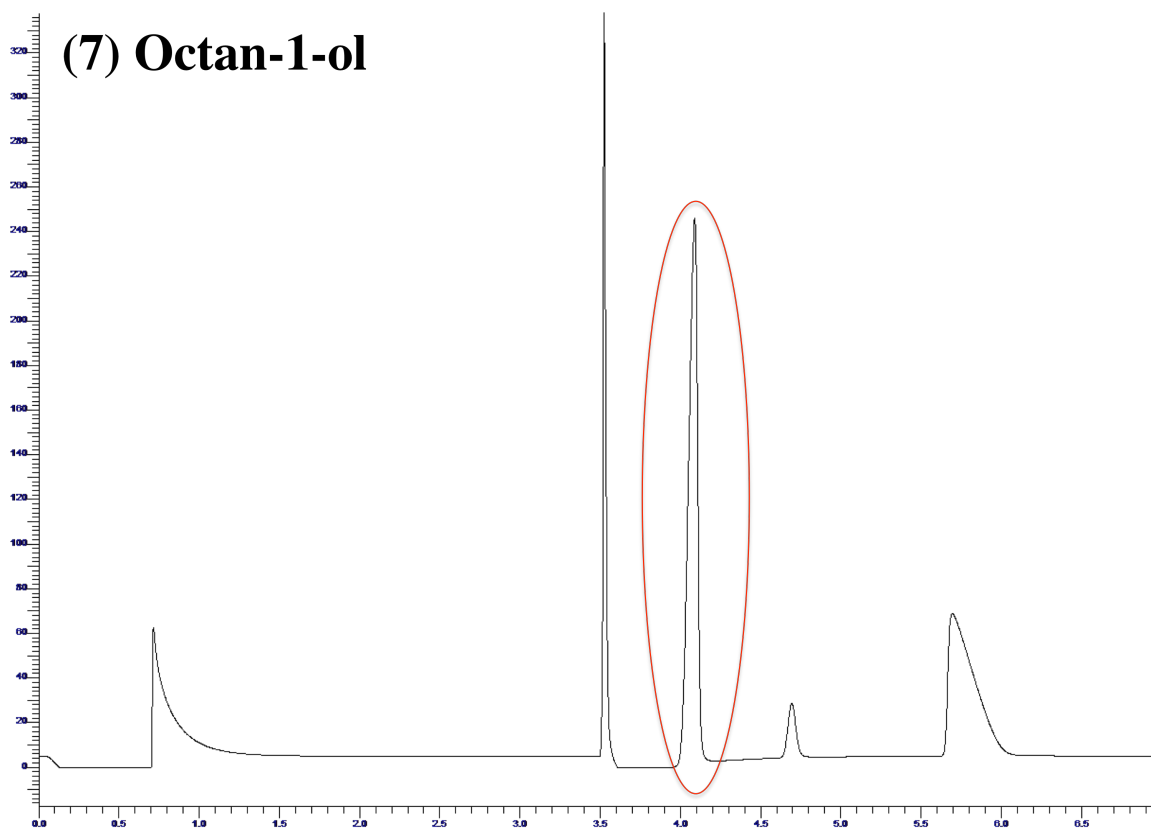
5.6 Annex

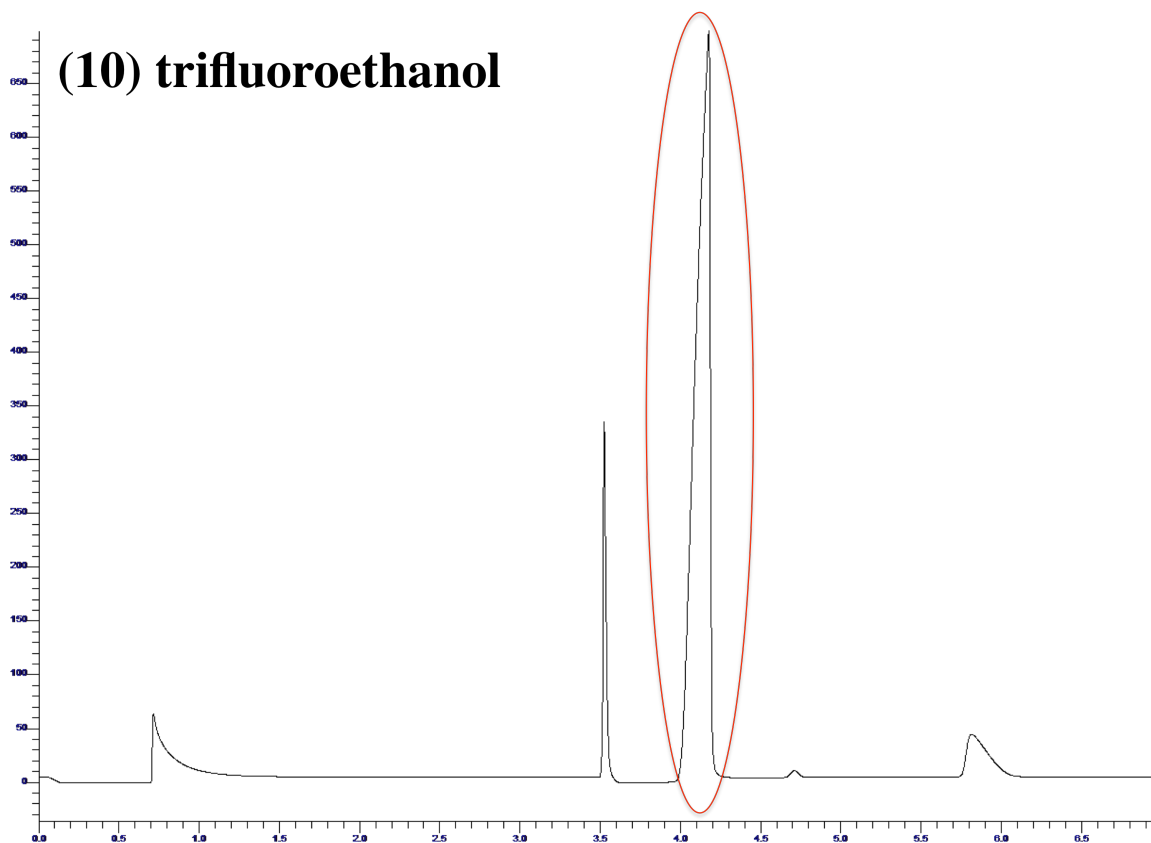
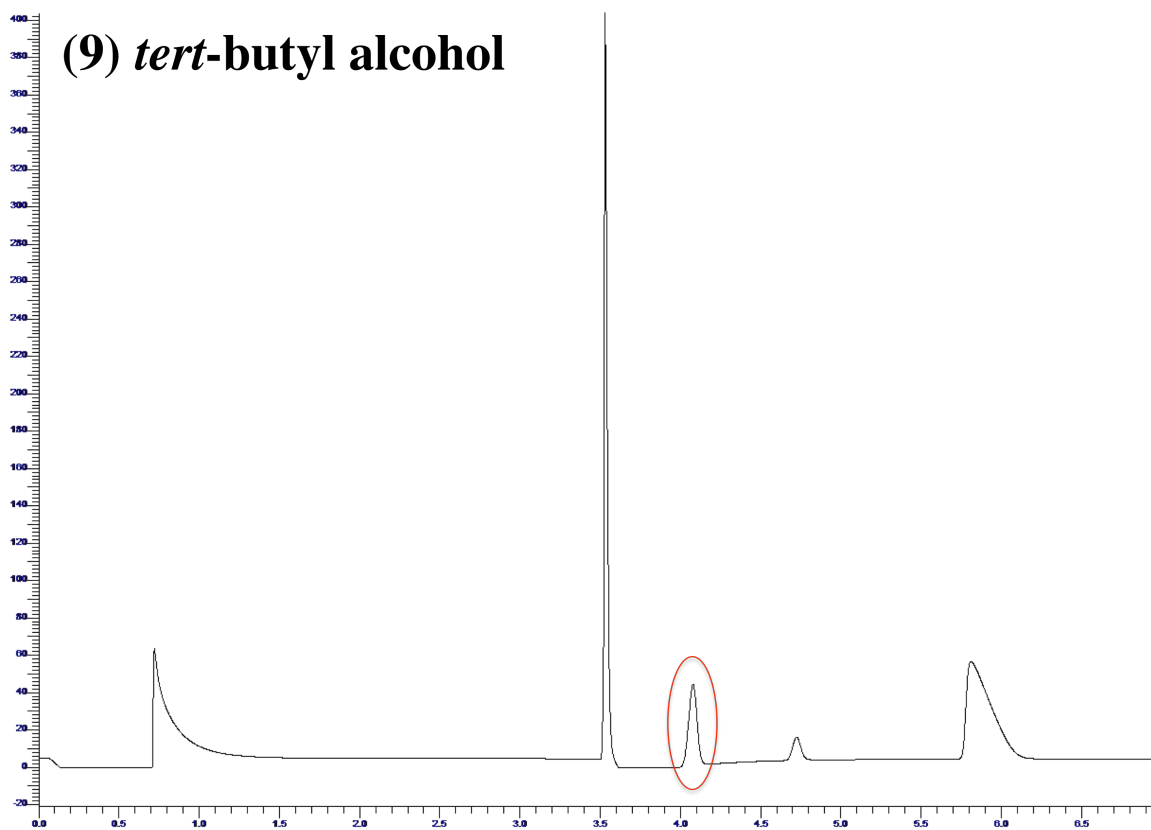
All GC-TCD and NMR graphs are presented for polymer grafting reactions with alcohol precursors other than methanol. The GC-TCD spectra all displayed peaks corresponding to oxygen (4.6 min) and nitrogen (5.9 min) since the reactions were performed under atmospheric conditions. All spectra displayed the hydrogen peak (4.1 min) after five minutes of reaction, with various reactivities as depicted by the intensity of the hydrogen peak. Since the peak retention times and the valves set-up were the same as in Figure 5. 6, they are not specified in the following spectra.

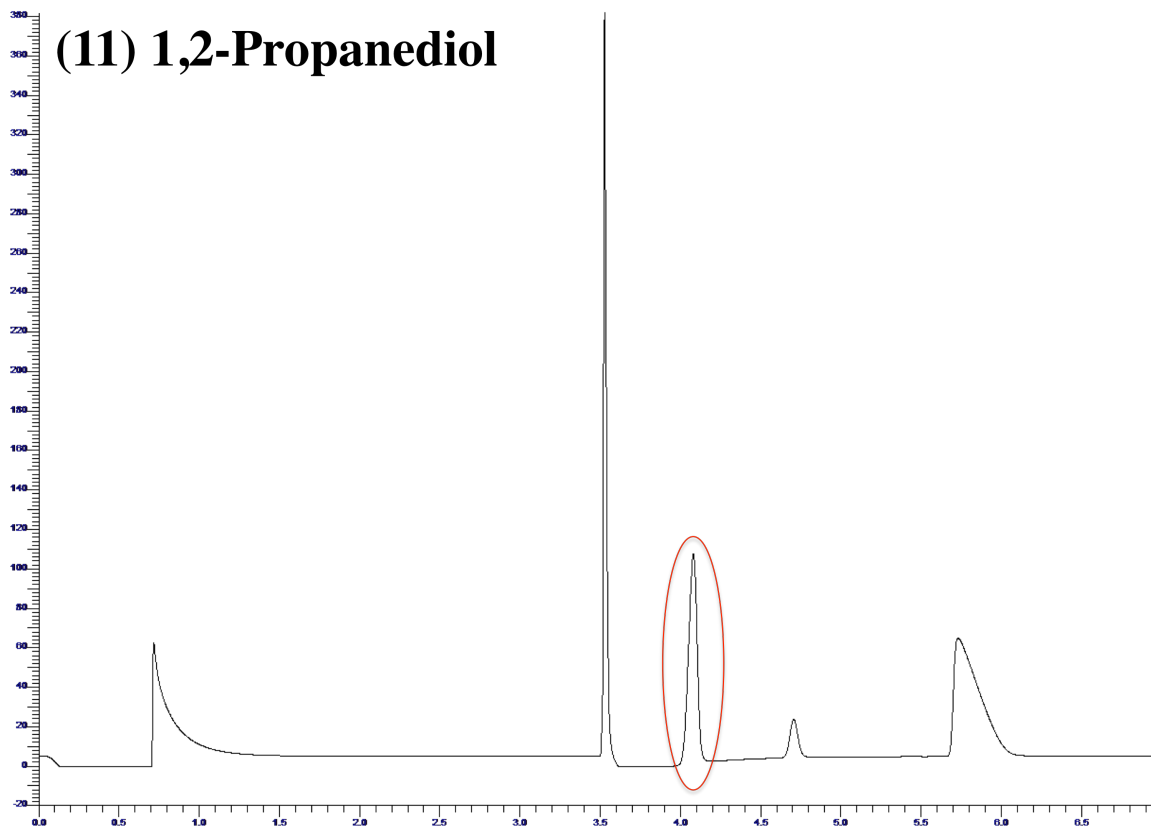




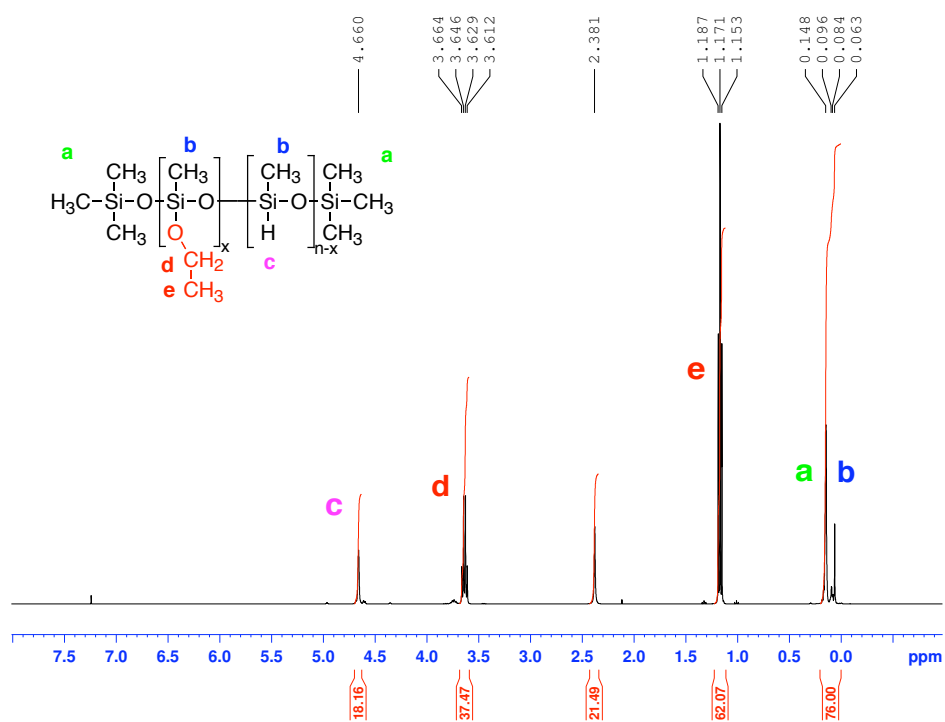
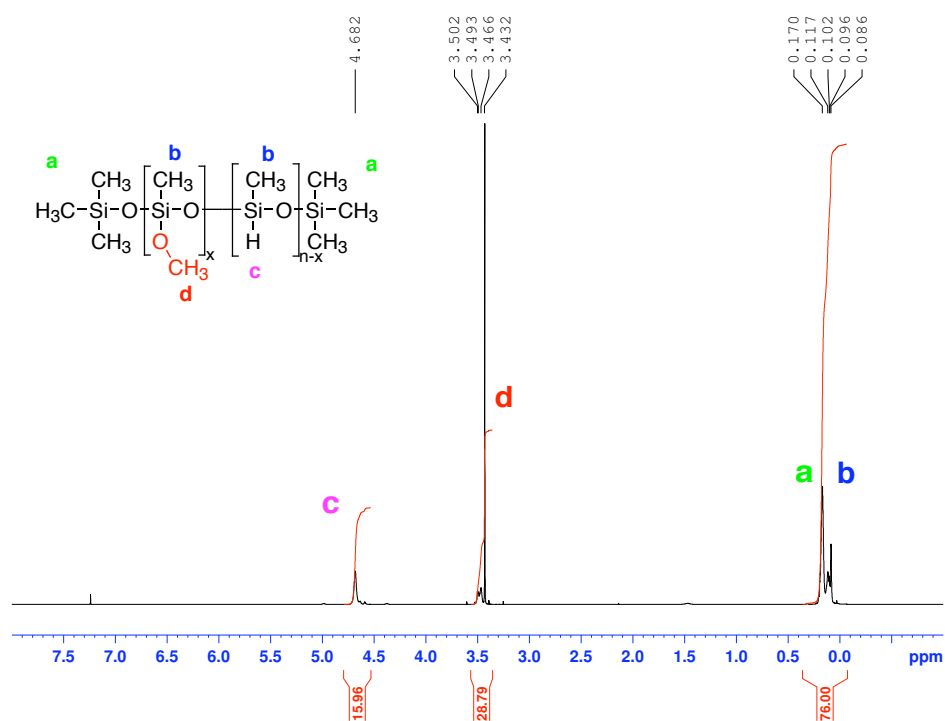


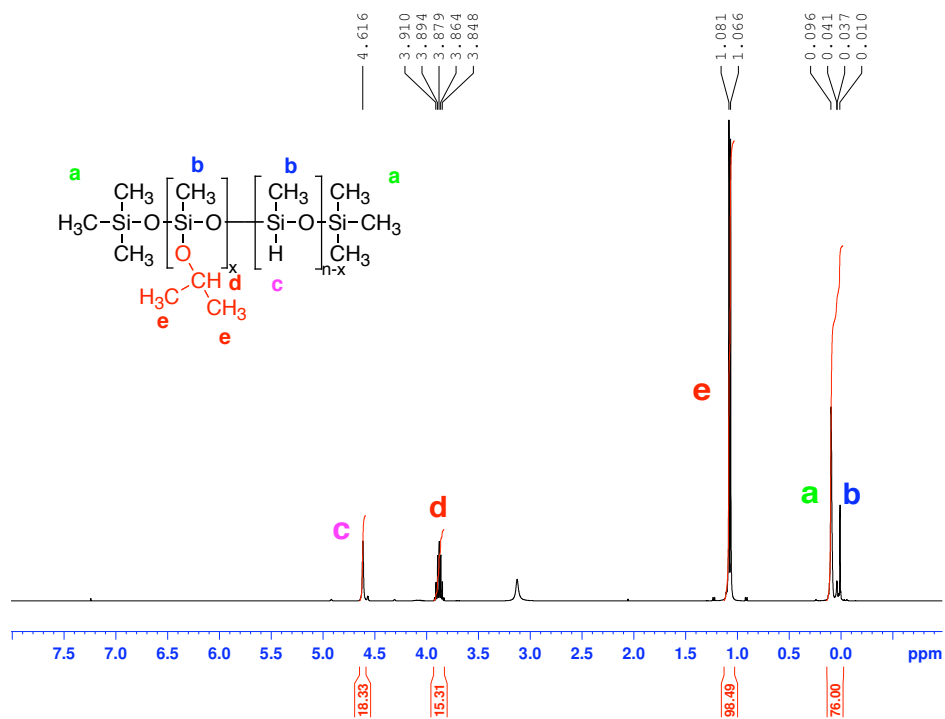
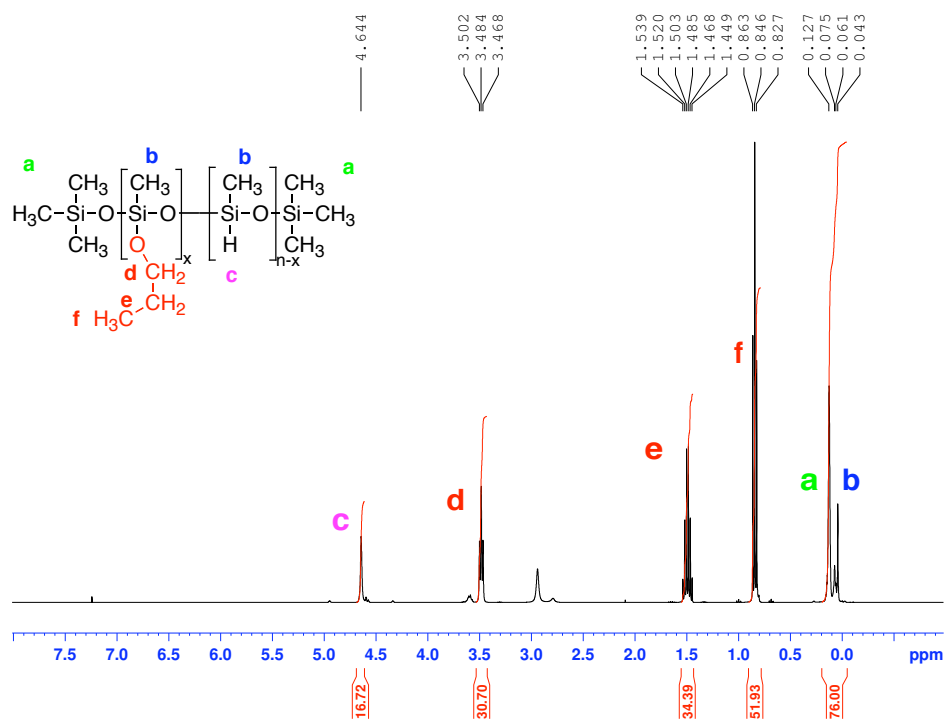


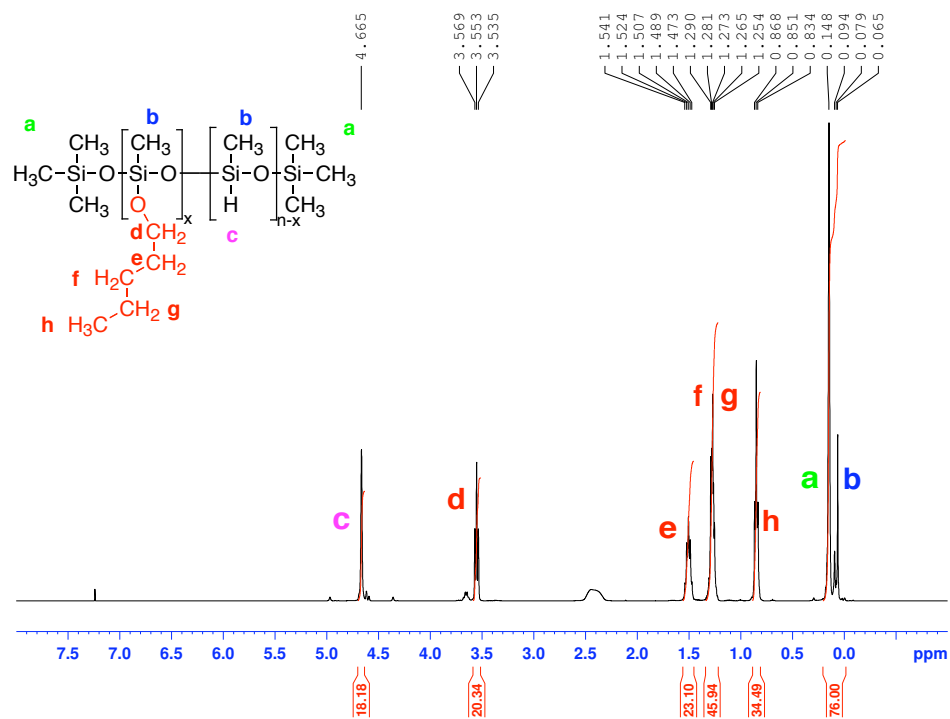
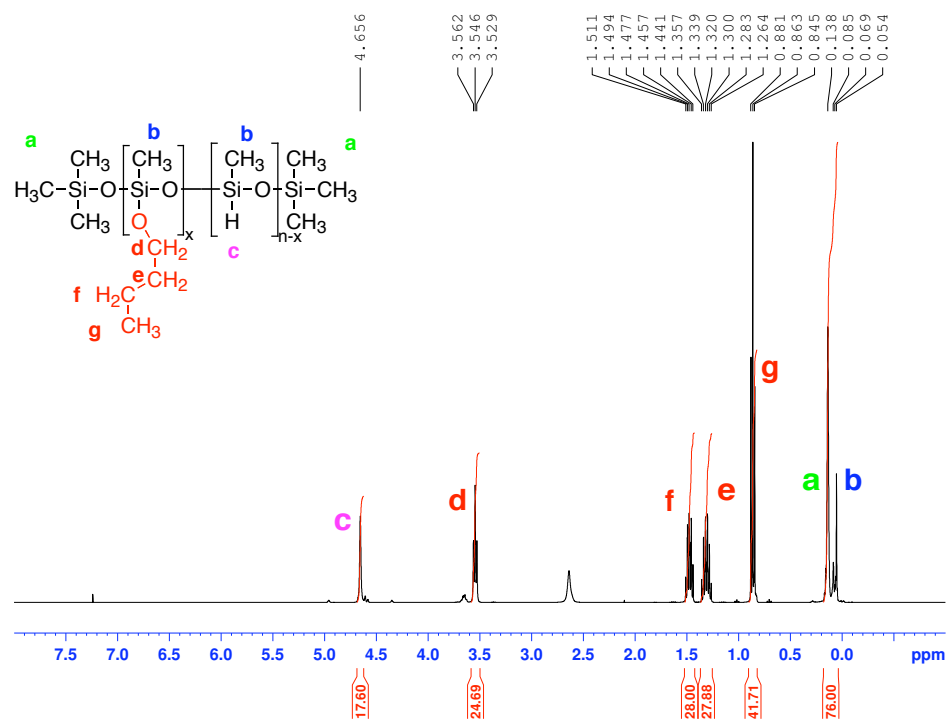


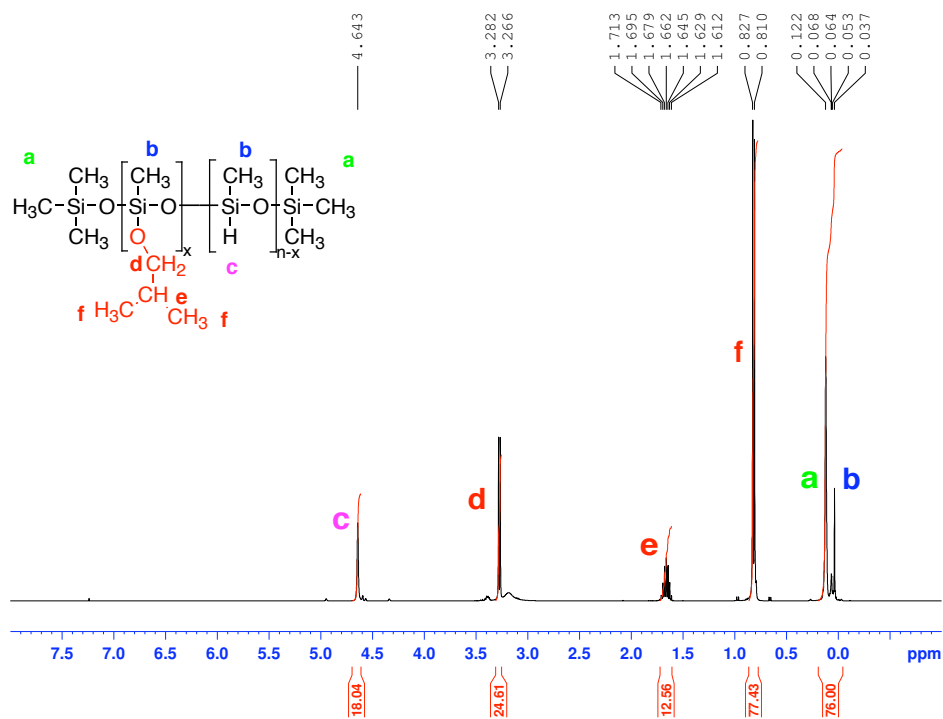
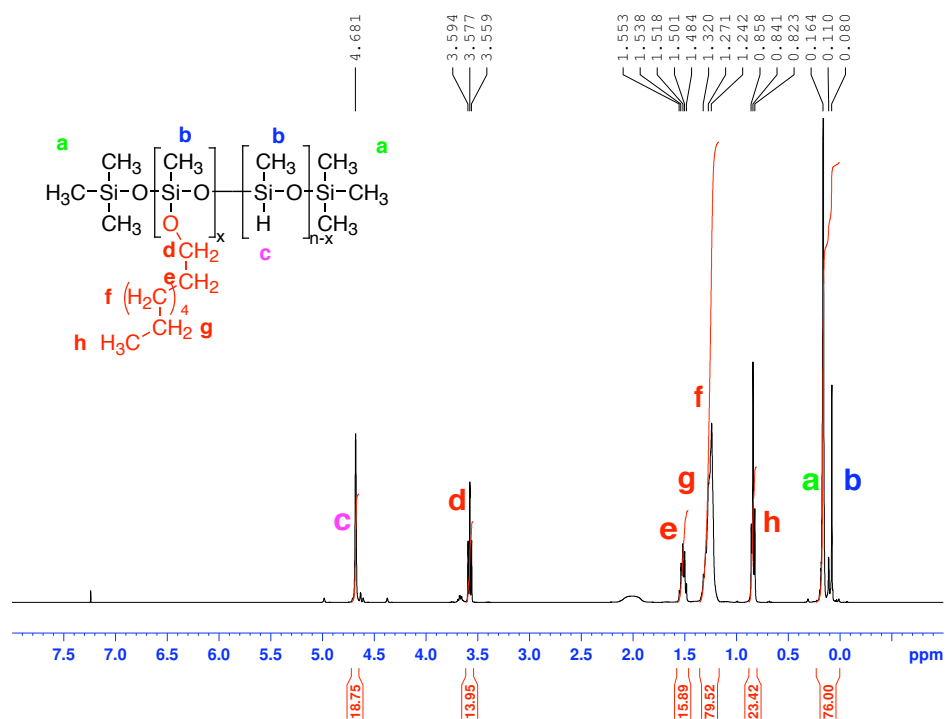


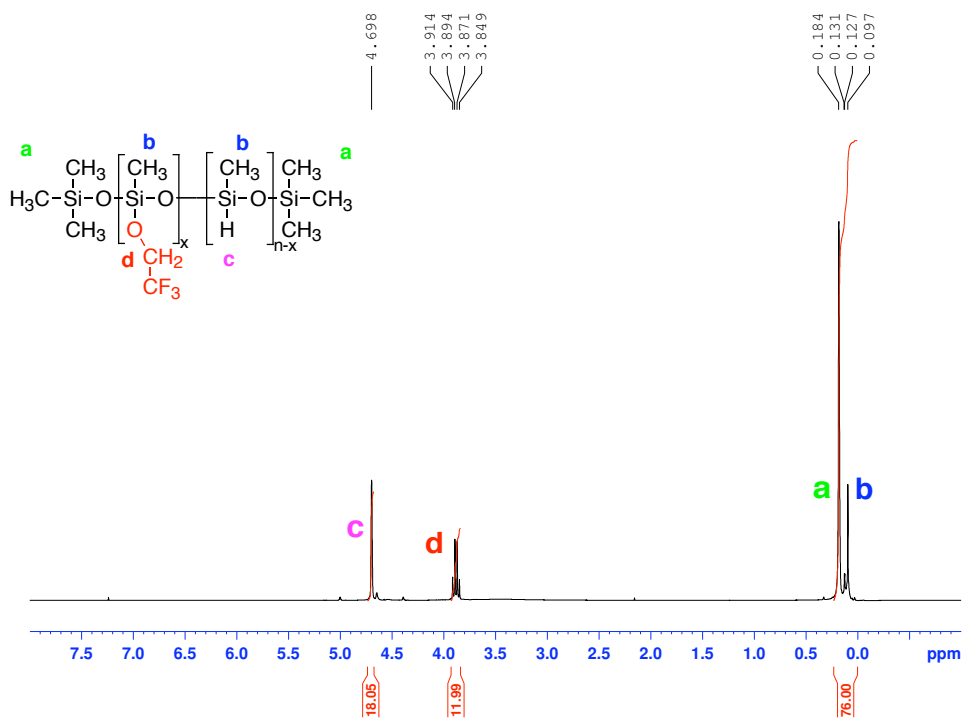
The ^1H NMR spectra correspond to the PMHS polymer, 24 hours after grafting of the corresponding alcohol and are done in CDCl_3 . The integrations are calibrated on the unreactive $-\text{CH}_3$ species of the polymer with an arbitrary value of 76,000.

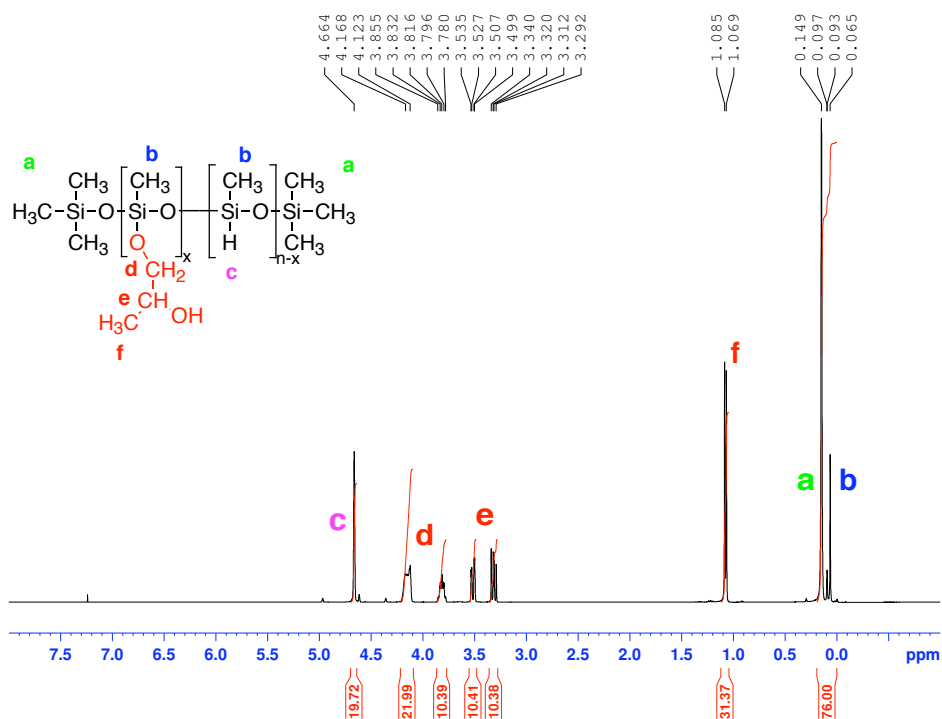












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Chapter 6. Pyronine Y interaction with CdSe quantum dots: the shell effect

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6.1 Introduction

As seen in Chapter 4, colloidal quantum dots (QD) are photoluminescent, semiconductor nanocrystals. Their relevance lies in their size-dependent optical properties due to quantum confinement behavior. Quantum dots also have several advantages when compared to small organic dyes, such as high photostability and high resistance to photobleaching.¹ The development of organic, as well as inorganic, materials at the nanometric scale into hybrid optoelectronic structures is a fundamental aspect to be taking into account for QD engineering.² The number of defect states on the QD surface determines their fluorescence efficiency (less defects leading to higher fluorescence) and influences their reactivity.^{3,4} Therefore, core QD (*e.g.*, CdTe, CdSe) have been functionalized with a variety of different inorganic layers or shells (*e.g.*, ZnS, chalcogenides)^{5, 6} to increase their luminescence efficiency and photostability by surface passivation.

The interaction of QD with organic molecules depends, to a large extent, on QD synthesis and their surface modification, as well as on the QD environment and it is far from being understood.^{5,7} In particular, QD-dye interactions have attracted considerable attention, and different fluorescence quenching mechanisms of the QD can take place according to the dye of interest. Quenching by energy transfer,^{3, 8-11} photo-induced electron transfer,¹² charge transfer¹³ processes or spatial extension of the exciton wave function¹⁴ have been reported. In particular, the understanding of electron transfer processes is crucial for photovoltaic applications, since it allows multiple exciton generation by charge carrier multiplication.¹⁴ For example, rhodamine B adsorbed onto CdS QD produces multiple exciton separations before the exciton-exciton annihilation process takes place.¹⁵ Similarly, methylene blue (MB)

adsorbed on CdSe QD promotes the exciton dissociation by electron transfer to the adsorbed dye in ~ 2 ps.¹⁶ Moreover, Matytilsky *et al.* have shown how methyl viologen (MV) adsorbed on a quantum dot surface, can dissociate up to four excitons by ultrafast electron transfer forming MV cation radical on the surface in less than 100 fs.¹⁴ Some other organometallic dyes,^{12, 17, 18} as well as organic molecules,¹⁹ have also demonstrated some electron accepting or carrying properties from or to the QD. Despite the well-detailed mechanistic studies, a systematic investigation of the influence of surface variation of the QD on the interaction with xanthene-type dyes remains unexplored.

To understand those interactions, pyronine Y, a xanthene dye largely employed to stain RNA in flow cytometry experiments, was selected.²⁰ The interactions were studied with four different CdSe QD capped with TOPO: one core-only example and three core-shell examples (ZnS or S₈) of different diameters. UV-visible, steady state and time resolved (ns) fluorescence studies were performed. Interestingly, the presence of a ZnS shell strongly affected the dye aggregation process and adsorption. Consequently, the QD fluorescence quenching efficiency of pyronine Y varied depending on the system studied. The rationale behind this quenching, whether due to energy or electron transfer, was also contemplated.

The work described in this chapter was part of a collaborative project with Professor Hermenegildo García from the Instituto de Tecnología Química at the Polytechnic University of Valencia in Spain.

6.2 Results

Pyronine Y (PYY) has a structure that differs from MB in the oxygen that replaces the sulfur (Figure 6. 1). Moreover, PYY tends to form dimers, even at low concentration, in both high polarity²¹ and low polarity²² solvents. This behavior will be considered upon interaction with various examples of quantum dots.

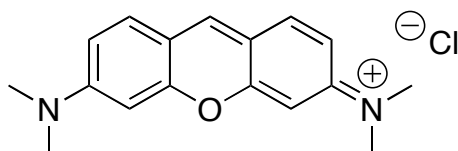


Figure 6. 1: Chemical structure of pyronine Y, a xanthene-type dye

Four examples of QD were selected to study how the size and/or the shell composition can affect the interaction between CdSe QD and PYY. The selection criteria of these materials merit some comments. Chapter 4 highlighted the differences between core QD and QD_{s8}. Moreover, expertise has been gained in the Scaiano research group on ZnS capped core-shells of various sizes for sensor applications. Therefore, it is crucial to understand the influence of a QD shell on the interaction with organic molecules, especially for sensor and photovoltaic applications. Our study compares two ZnS capped QD emitting in the blue and green respectively, as well as QD core with and without sulfur treatment, as summarized in Figure 6. 2.

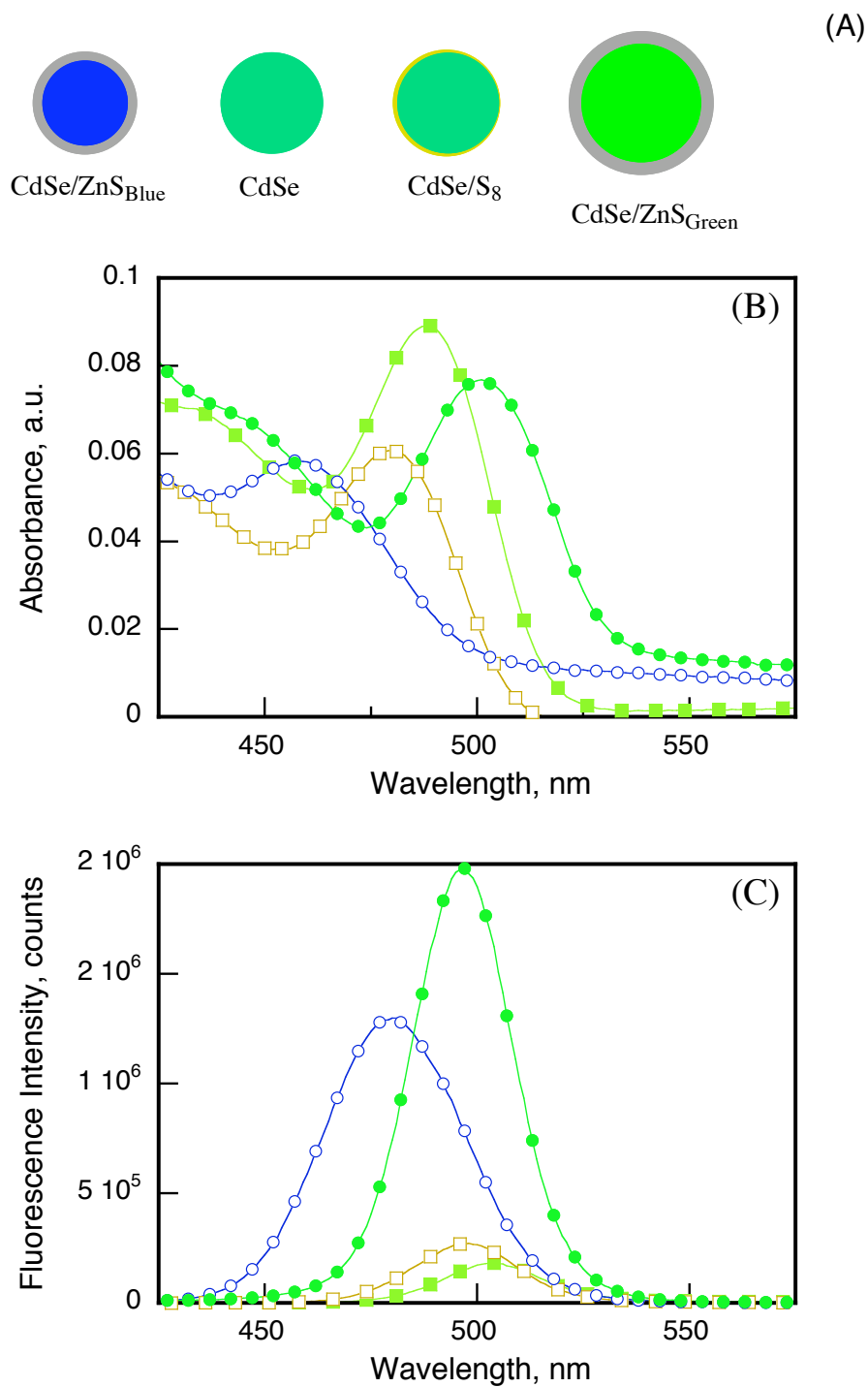


Figure 6. 2: (A) Schematic representation, (B) Absorption and (C) Emission (λ_{ex} : 350 nm) spectra of all four QD (1.4 μ M) in chloroform: (■) CdSe; (□) CdSe/S₈; (●) CdSe/ZnS_{Blue}; (○) CdSe/ZnS_{Green}

CdSe refers to core only QD whereas CdSe/S₈, CdSe/ZnS_{Blue} and CdSe/ZnS_{Green} are core/shell QD and the subscripts when the shell is ZnS refer to the QD emission color. Table 1 compiles the sizes, absorption (first exciton peak) and emission wavelength maxima as well as fluorescence quantum yields (Φ_F) for all the aforementioned QD.

Table 6. 1: Selected properties of CdSe quantum dots used in this study

QD	Size (nm) ^[a]	$\Phi_F^{[b]}$ / $\langle \tau_F \rangle$ (ns) ^[c]	$\lambda_{abs}, \lambda_{em}$ (nm) ^[d]
CdSe/ZnS _{Blue}	2.2	0.80 / 22.0	460, 480
CdSe	2.4	0.08 / 24.0	490, 509
CdSe/S ₈	2.4	0.09 / 27.2	483, 502
CdSe/ZnS _{Green}	2.5	0.63 / 21.0	500, 517

^[a] QD sizes were calculated with Equation 4. 2. ^[b] Φ_F were calculated using quinine hemisulfate as the standard. ^[c] $\langle \tau_F \rangle$ are the average lifetimes based on calculations with Equation 6. 1. ^[d] $\lambda_{abs}, \lambda_{em}$ are the respectively the maximum absorption and emission wavelengths.

6.2.1 Steady-State analyses of Pyronine Y interactions

Pyronine Y also displays absorption and emission spectra. Figure 6. 3 shows these spectra combined to those for the QD CdSe/ZnS_{Green} sample only (for simplification purposes). The PYY UV-visible spectrum in chloroform has an intense absorption band centered at 550 nm and a shoulder with a hypsochromic shift (~500 nm) that correspond to the monomer and dimer species respectively.²³

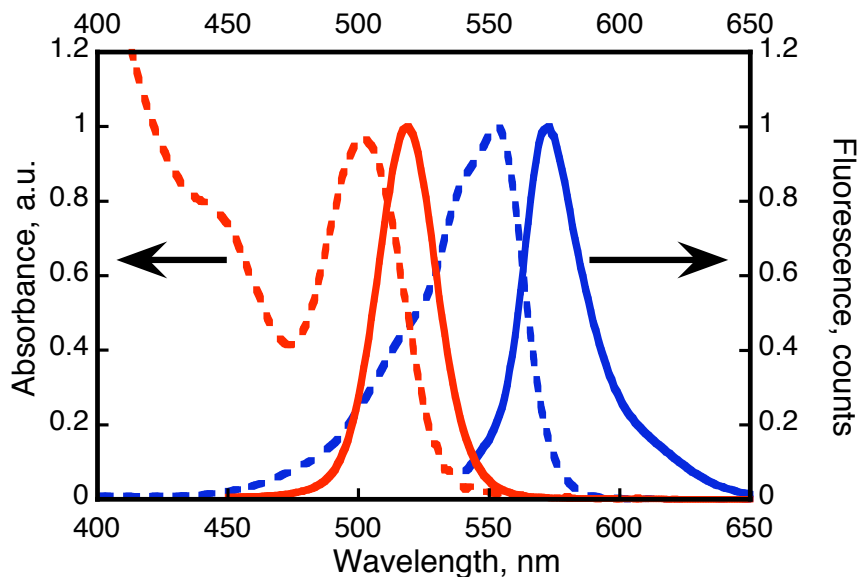


Figure 6.3: Normalized absorption (dashed lines) and emission (solid lines) spectra of CdSe/ZnS_{Green} QD (red) and PYY (blue) in chloroform ($\lambda_{ex} = 350$ nm)

Figure 6.3 clearly illustrates how the PYY absorption band overlaps with the CdSe/ZnS_{Green} emission, making our system ideal to favor energy transfer processes from the QD to PYY.

The co-existence of PYY monomers and dimers in QD-PYY mixtures was expected to affect the ratio and properties of these species differently based on the QD used. To allow some insight into the interaction of QD and PYY in the ground state, the dye absorptions at 550 and 500 nm were monitored over time upon PYY addition (see Figure 6.4) to each QD solution (all [QD] = 1.4 μ M).

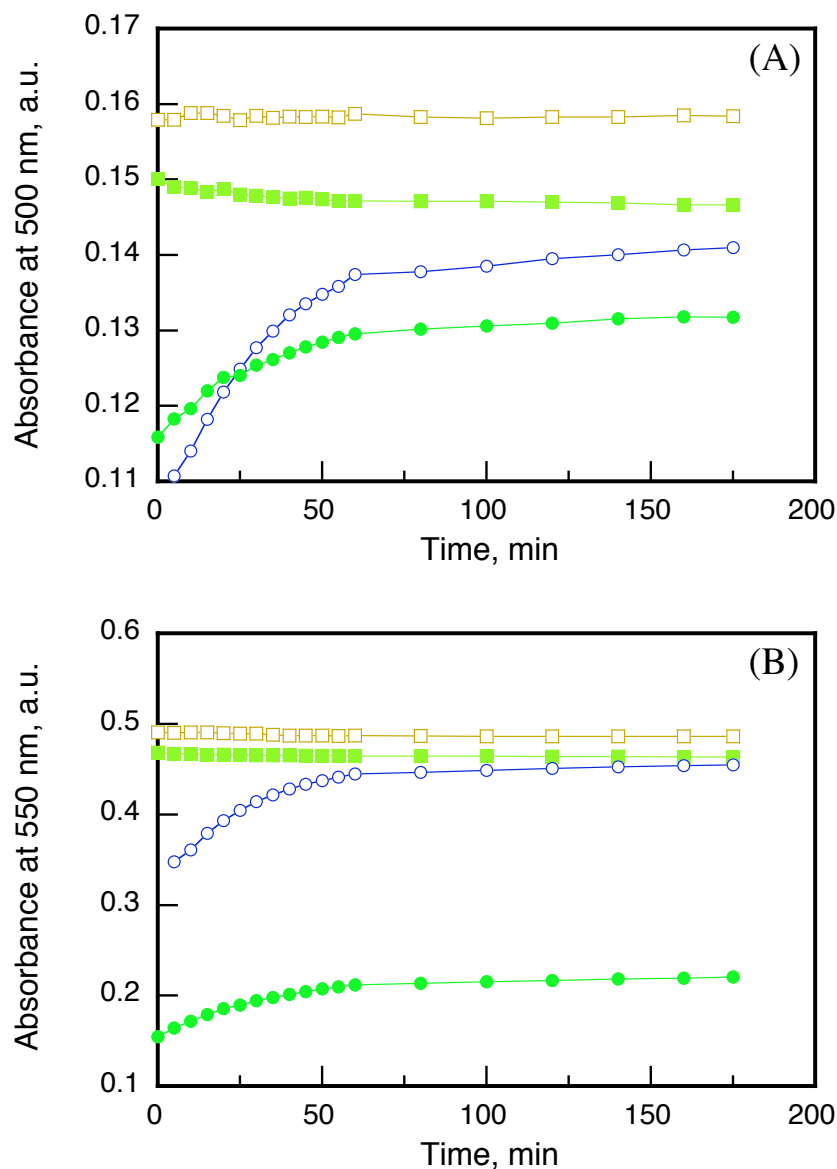


Figure 6.4: Changes in absorbance for pyronine Y (20 μM) in presence with each QD solution (1.4 μM) at (A) 500 nm and (b) 550 nm over time, in chloroform and at room temperature: (■) CdSe; (□) CdSe/S₈; (●) CdSe/ZnS_{Blue}; (○) CdSe/ZnS_{Green}

All the solutions remained clear and stable at the concentrations used for this study, but the absorbance value decreased for both core-shell QD samples at the reaction onset. However, both absorbances at 500 and 550 nm reach a plateau one hour after mixing. The

PYY spectrum remained unchanged for both CdSe and CdSe/S₈, with none of the initial decreases as observed for the core-shells.

To ensure equilibrium was reached in all four systems studied, all the subsequent experiments and analyses were performed after allowing the QD and PYY reagents to equilibrate overnight for complete stabilization.

The change in ratio between the PYY monomer (550 nm) and dimer (500 nm) was monitored as a function of PYY concentration for each variety of QD (Figure 6. 5).

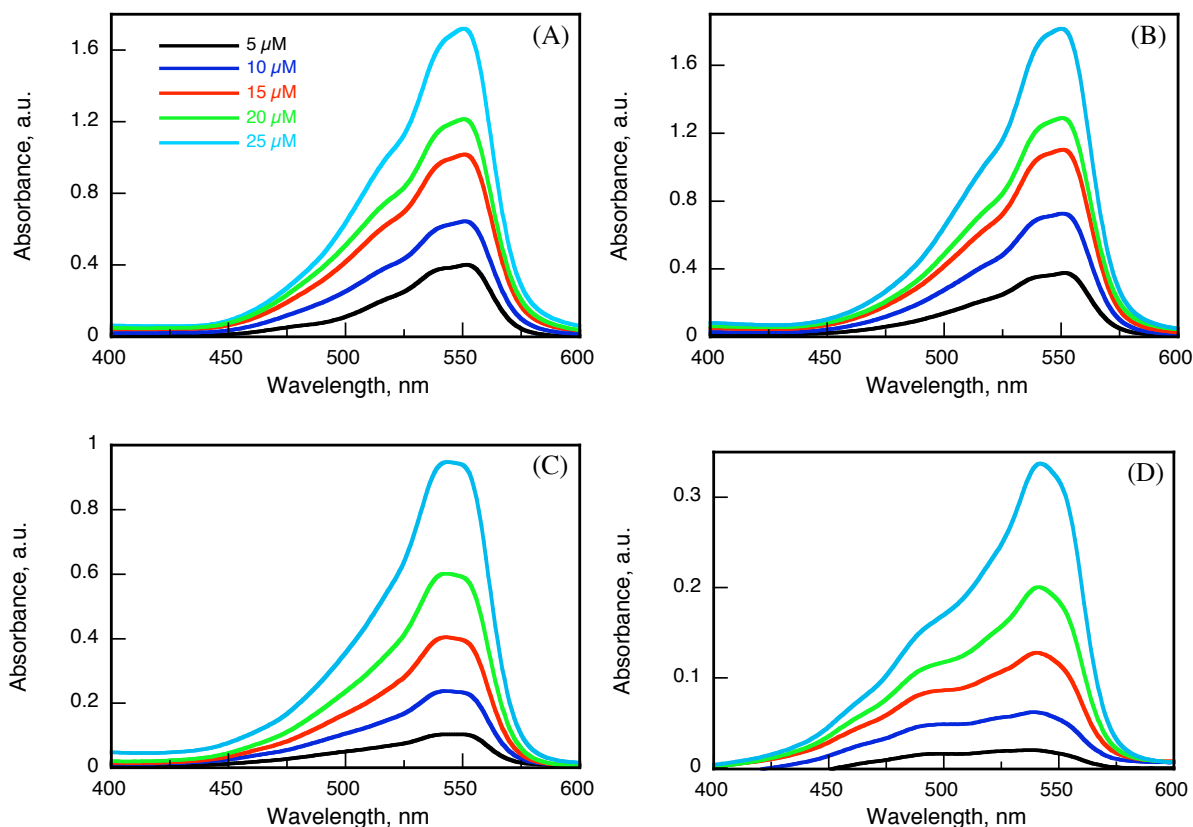


Figure 6. 5: Changes in absorption spectra upon incremental addition of pyronine Y dye of 5 μM , 10 μM , 15 μM , 20 μM and 25 μM in the presence of a 1.4 μM solution of (A) CdSe; (B) CdSe/S₈; (C) CdSe/ZnS_{Blue} and (D) CdSe/ZnS_{Green} (QD absorption has been subtracted in each case)

The ratio monomer/dimer increased for all samples but the core CdSe (Figure 6. 5 - A) as the concentration of PYY was increased.

FTIR measurements were carried out to help determine the placement of PYY with respect to the quantum dot surface (see Figure 6. 6). Using CdSe/ZnS_{Green} as an example, FTIR spectra confirmed the presence of PYY aggregates at the surface of the QD, with the band at 1050 cm⁻¹ (highlighted with an arrow) on the blue trace attributed to ether group overlaps.²⁴

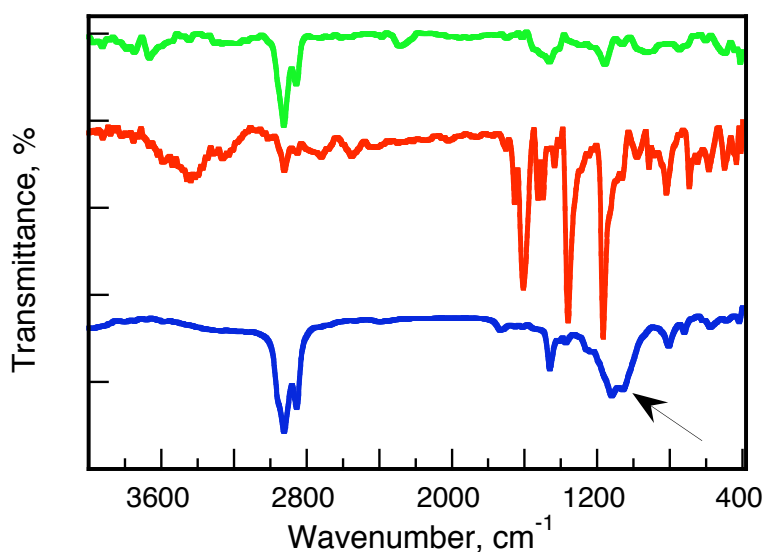


Figure 6. 6: FTIR spectra for CdSe/ZnS_{Green} alone (green trace), pyronine Y alone (red trace) and a mixture of the two after equilibration (blue trace)

As seen in the introduction and Chapter 4, quantum dots have a broader absorption window than most organic dyes. This property allows excitation of multiple sizes of QD at the same wavelength. Thus, steady state fluorescence could be undertaken with one single excitation at 350 nm to display the corresponding emissions showed in Figure 6. 2 (C). This

choice of wavelength also enables excitation far from the PYY absorption. The emission spectra were acquired for all QD-PYY systems with incremental increases in the concentration of PYY, as shown in Figure 6. 7. In all cases, QD emissions were quenched after PYY addition. A new emission peak attributed to PYY arose at 562 nm for all QD. This second peak had a bathochromic shifts at 573 nm when further PYY was added.

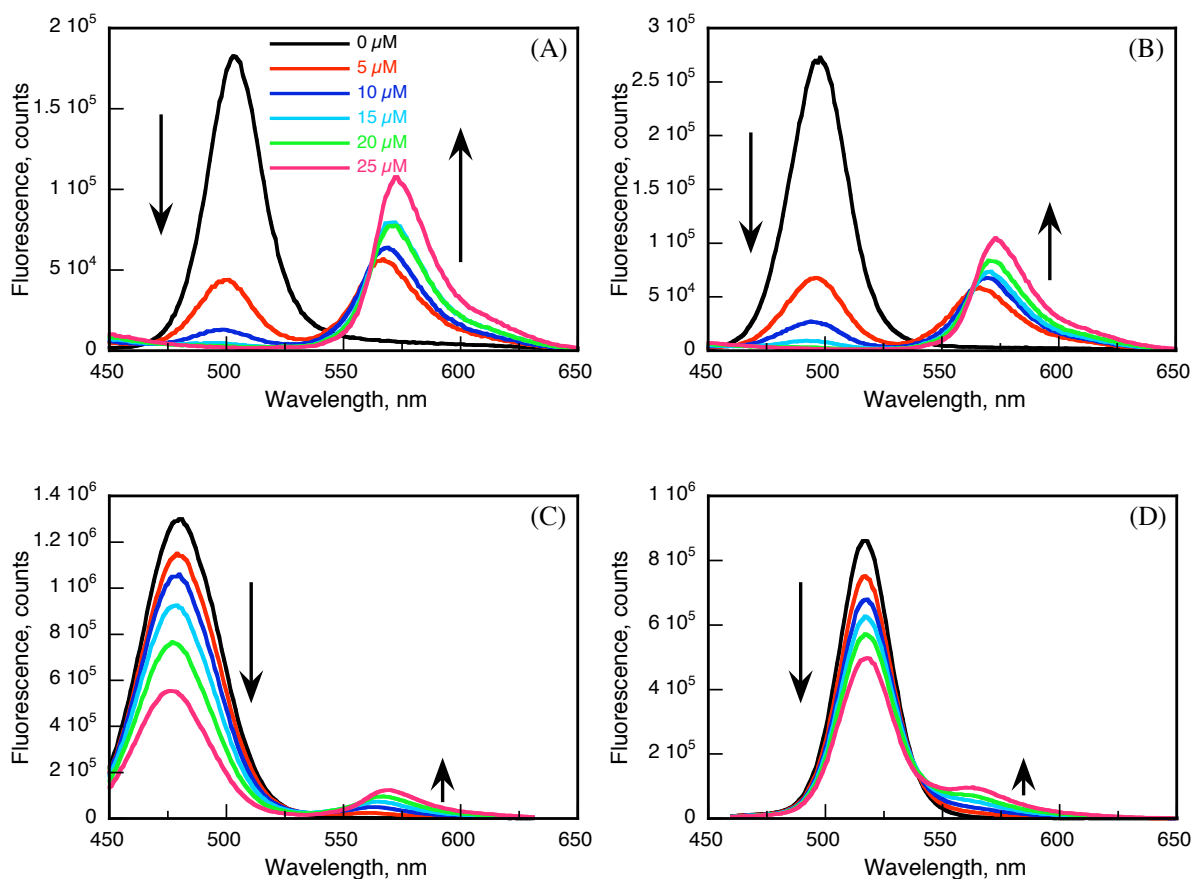


Figure 6. 7: Changes in the fluorescence emission spectra ($\lambda_{exc} = 350$ nm) corresponding to (A) CdSe; (B) CdSe/S₈; (C) CdSe/ZnS_{Blue} and (D) CdSe/ZnS_{Green}, obtained after the addition of different PYY concentration up to 25 mM. All measurements were carried out in chloroform at room temperature after previous equilibration of the samples for 12 hours in the dark

6.2.2 Time-resolved kinetic study of the quenching process

Time-resolved fluorescence experiments were also performed for all four QD samples in the presence of increasing concentrations of PYY. The fluorescence decay was observed after excitation at 350 nm to ensure that no component could be attributed to PYY emission. QD fluorescence decay lifetimes decreased for all QD after PYY addition (see Figure 6. 8).

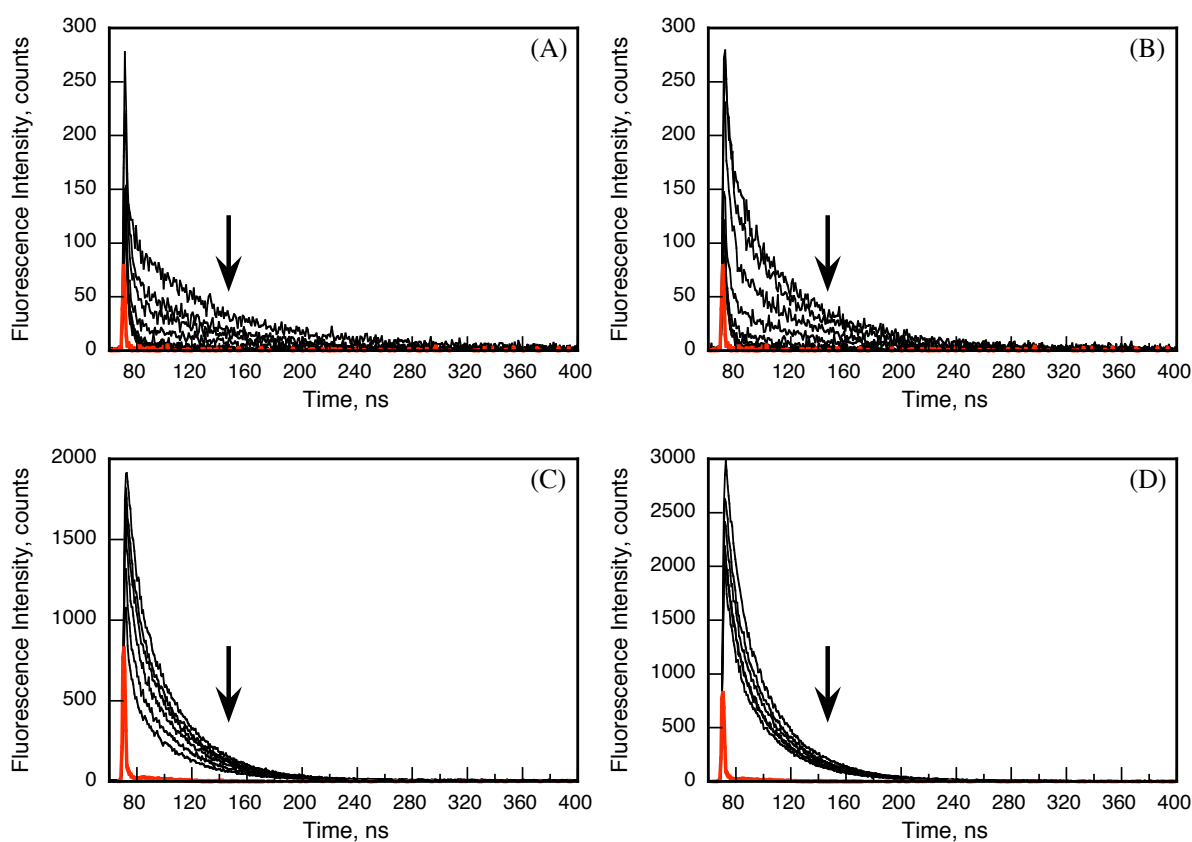


Figure 6. 8: Kinetic profiles for QD ($1.4 \mu\text{M}$) with increasing amounts of PYY (5 to $25 \mu\text{M}$) corresponding to (A) CdSe; (B) CdSe/S₈; (C) CdSe/ZnS_{Blue} and (D) CdSe/ZnS_{Green}, ($\lambda_{\text{exc}} = 350 \text{ nm}$). Red traces are IRF. All measurements were carried out in chloroform at room temperature after previous equilibration of the samples for 12 hours in the dark

Similarly to the approach used in Chapter 4, the emission decays were fitted with an ESM (Exponential Series Method) analysis, as quantum dots are complex systems. The decays fit well to bi-exponential kinetics.

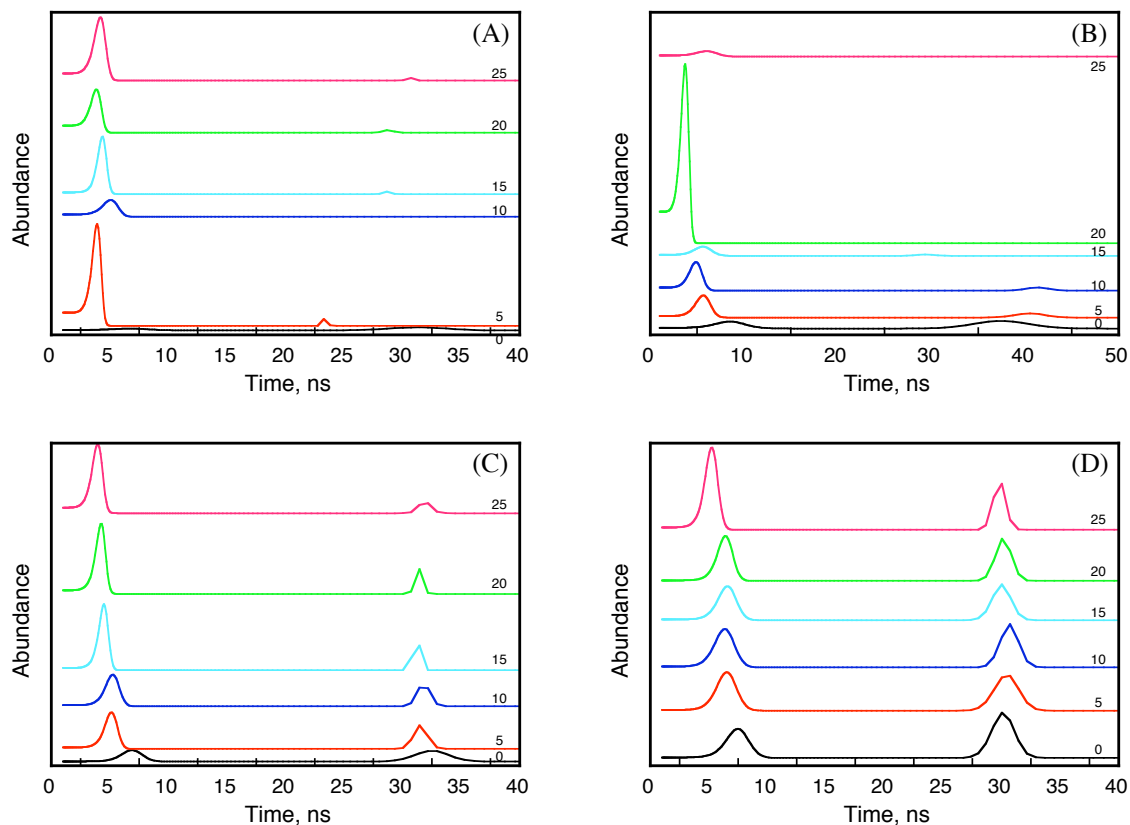


Figure 6.9: Lifetime distribution for (A) CdSe; (B) CdSe/S₈; (C) CdSe/ZnS_{Blue} and (D) CdSe/ZnS_{Green}, obtained for different PYY concentrations (specified on each trace, in μM)

The distribution of the lifetimes suggest that there is a mixture of static and dynamic quenching where the decay traces show both a decrease of intensity for the slower lifetime around 30 – 40 ns (static), and a shortening but increased contribution from the faster lifetime below 10 ns (dynamic). The intensity-averaged lifetimes for each system studied, based on the lifetimes (τ_1 and τ_2) and the pre-exponential factors (A_1 and A_2) from Figure 6.

9, are compiled in Table 6. 2. A global decrease of the lifetime is observed for all systems, in accordance with the quenching observed in Figure 6. 8.

Table 6. 2: *Intensity-average lifetime variation for each QD system upon increasing concentration of PYY*

$[PYY]$ (μM)	$\langle \tau_F(CdSe) \rangle$ (ns)	$\langle \tau_F(CdSe/S_8) \rangle$ (ns)	$\langle \tau_F(CdSe/ZnS_{Blue}) \rangle$ (ns)	$\langle \tau_F(CdSe/ZnS_{Green}) \rangle$ (ns)
0	24.0	27.2	22.0	21.0
5	13.1	10.9	15.5	19.1
10	10.4	9.9	15.2	18.4
15	5.0	8.6	11.6	18.3
20	5.0	3.7	9.7	17.9
25	4.7	n/a	8.1	13.8

To have a better understanding of the quenching modes for each system, the Stern-Volmer model is applied in Figure 6. 10.

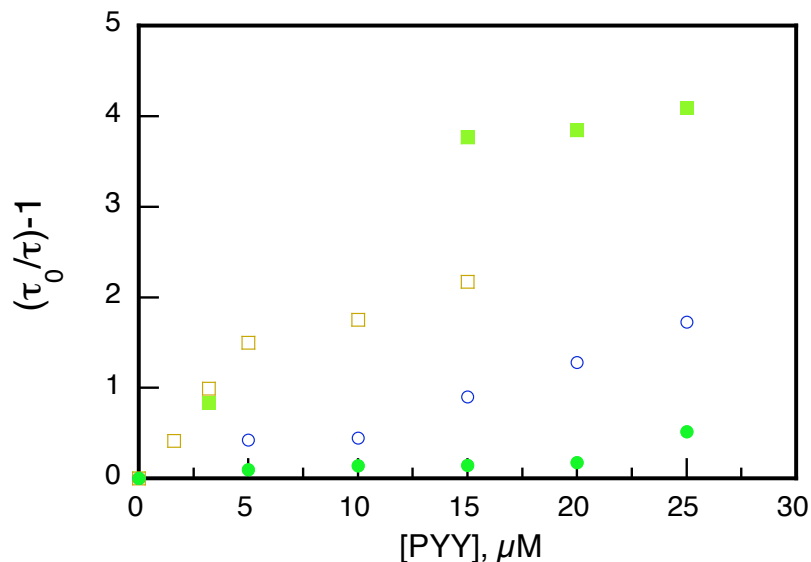


Figure 6.10: Stern-Volmer quenching plots based on the fluorescence lifetime of (■) CdSe; (□) CdSe/S₈; (●) CdSe/ZnS_{Blue}; and (○) CdSe/ZnS_{Green} with a fixed concentration of 1.4 μM

Both QD with a ZnS shell display a mild upward curvature. On the other hand, CdSe with and without sulfur treatment have an opposite downward curvature, showing the differences of quenching mode depending on the nature of the surface.

6.3 Discussion

From the data of Figure 6. 2, it is obvious that the presence of a shell around the QD increases luminescence efficiency as it protects the CdSe emitting core from interactions with the surroundings by decreasing the amount of surface states.^{25, 26} The nature of the QD surface surely affects its behavior when in presence with pyronine Y. One interesting property of PYY is its tendency to dimerize, even at low concentrations. However, this work

was carried out mostly in chloroform where the dimerization degree in non-polar media is small as compared with polar ones.²²

Upon addition of PYY to each QD solution, all the solutions remained clear and stable at the concentrations used for this study. However, the absorbance value decreased in all cases when compared to a solution of PYY alone. This decrease was especially marked for both ZnS core-shell samples, although an hour of equilibration was sufficient to recover some of this absorbance back. These results suggest that PYY is reduced on contact, supported by the loss of its characteristic pinkish colour.

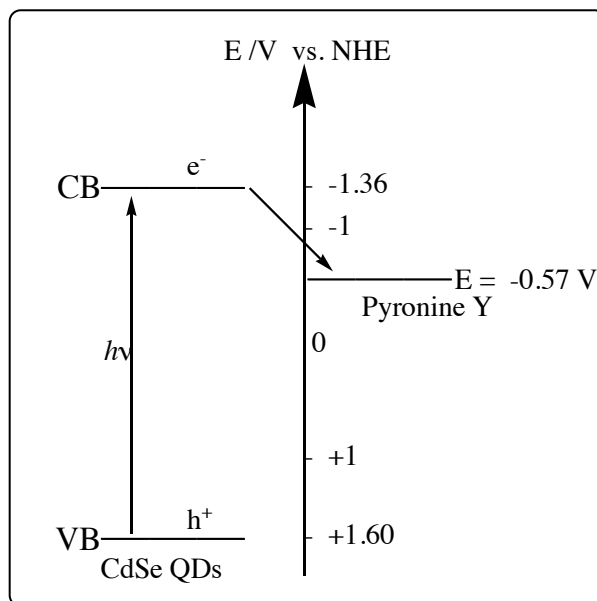
Figure 6. 5 illustrates the differences in PYY absorption for our four QD in the presence of an increasing PYY concentration (QD absorption has been subtracted in all cases). Although the two extinction maxima at 500 and 550 nm, corresponding to the dimer and the monomer of PYY, respectively, were not deconvoluted, the ratios display a higher percentage of dimers at lower concentrations. This observation, especially marked in the CdSe/ZnS_{Green} case, suggest that some initial physisorption of PYY occurs in solutions confirming that PYY molecules adsorb on to the QD surface, as previously observed for methylene blue, due to electrostatic attractive forces.²⁷ The formation of aggregates is confirmed through FTIR measurements

All the adsorbed PYY molecules cause some fluorescence quenching on the emission of each QD studied. As expected, the quenching by PYY on the QD is easier for CdSe having no shell or a very thin layer of sulfur due to the lower initial quantum yield of fluorescence Φ_F (Table 6. 1). QD quenching efficiency is shell and size-dependent, being stronger for smaller QD²⁸ since these nanomaterials have more surface trap states compared

to their larger counterparts.³ For QD with a comparable size, the presence of a ZnS shell leads to extended surface passivation; it enhances the quantum yield of emission (as seen in Table 6. 1), but it also slows down the QD fluorescence quenching of an adsorbed molecule.²⁹ Conversely, a small sulfur passivation also improves the quantum yield and stability of a core CdSe QD, but at the same time, improves its response to a solution quencher as already shown in Chapter 4 and as confirmed here with another type of molecule.

Each QD displays a bi-exponential distribution of lifetimes prior to any quenching process. The faster component has been attributed to emission from surface defect states, whereas the slower lifetime has been assigned to more deeply confined states.^{30, 31} Figure 6. 9 clearly illustrates these lifetime distributions showing the main effects of the quenching; a shortening of the fast component and a decrease of contribution from the slower one. At higher concentrations the signal is much weaker for both CdSe and CdSe/S₈, and the analysis less reproducible for these QD since their quantum yield of fluorescence is extremely low. These experiments demonstrate how all possible quenching pathways reduce the lifetime of excitons, but these pathways cannot be differentiated by the fluorescence measurement alone in our experimental time-scale.³²

The quenching process could be explained in terms of either an energy transfer mechanism from the QD to the PYY monomer/dimer producing an excited dye molecule, or in terms of an electron transfer from the QD conduction band (CB) to the unoccupied molecular orbitals of PYY, producing a reduced PYY and a hole in the QD (see Scheme 6. 1). A mixture of the two transfer modes is also possible given the properties of the donor (each QD) and the acceptor (pyronine Y).



Scheme 6. 1: Electron transfer mechanism from the conduction band (CB) of the QD to PYY leaving a hole in the valence band (VB). PYY has a redox wave potential at -0.57V vs. normal hydrogen electrode (NHE).³³ CB and VB positions are calculated based on $E_{\text{HOMO}} = -5.80\text{ eV}$ and $E_{\text{LUMO}} = -2.84\text{ eV}$ at vacuum level for an average particle diameter of 2.36 nm ³⁴⁻³⁶

The energy transfer from the quantum dots must take place in the vicinity of the surface, but as seen in Figure 6. 7, this is very inefficient despite the good spectral overlap between the QD emissions and PYY absorption. This downfall is likely due to the fact that mostly aggregates adsorb on the QD surface; although the monomeric form of PYY is highly fluorescent ($\Phi_{\text{F}}=0.76$), the H-type aggregates are non-fluorescent.³⁷ Therefore, even though an energy transfer certainly takes place, the measure of its efficiency is difficult.

The mixture of the two processes is confirmed with the Stern-Volmer style plots done for each sample's lifetime (τ) (see Figure 6. 10).³⁸ The Stern-Volmer plots for CdSe/ZnS_{blue} and CdSe/ZnS_{green} agree with a Perrin model approximation in which only the quencher molecules present within a certain sphere of action would quench the QD

emission.^{29, 39} The CdSe and CdSe/S₈ plots on the other hand show a downward curvature. This behavior has been attributed for other systems to a dynamic quenching with different accessibility of the emitting sites.⁴⁰ The dynamic fraction of our quenching is affected by the presence or not of a ZnS shell as more deeply confined states are more readily available when no shell is present. Those states, corresponding to the slower lifetime, are slowly quenched for the core-shell QD (see Figure 6. 9) but are almost immediately quenched for the core QD (Figure S8).

6.4 Summary

Pyronine Y interacted differently with each type of CdSe quantum dots (without a shell, or with a ZnS or sulfur shell). This process could be readily followed spectroscopically by UV-Visible and fluorescence (steady state and time resolved), providing important information about the shell role on the dye QD surface adsorption. Similarly, the presence of a shell affected the fluorescence quenching efficiency of the process as well as the supramolecular organization of dyes by adsorption on the QD surface. Therefore, PYY has shown a strong tendency to aggregate onto CdSe/ZnS_{green} surface whereas the absence of a ZnS shell diminishes or seems to avoid this dynamic of adsorption.

In this system, quenching can occur by a combination of energy transfer and electron transfer. The rationale for this quenching is that some PYY molecules adsorb on the surface of the QD, causing some static quenching for the surface emitting states. In addition some molecules of PYY undergo collisional quenching with both surface and deeply confined states, where the deeper states are more accessible when no ZnS shell is present.

Further studies employing faster time-resolution techniques are needed to fully understand the factors that control the pathways involved in those systems.

6.5 Experimental

6.5.1 Materials

Selenium powder 99.99%, cadmium oxide (CdO), tri-*n*-octylphosphine oxide (TOPO), sulfur 99.999%, pyronin Y Chloride (PYY > 99%) and quinine hemisulfate (purum for fluorescence >98%) were all purchased from Sigma-Aldrich. Ethanol (>99%) and chloroform (>99%) were purchased from Merck. All chemicals and solvents were used without further purification.

6.5.2 CdSe quantum dots selection

TOPO-capped blue and green emitting core-shell CdSe/ZnS quantum dots (QD) were purchased from Evident Technologies in toluene solution and used without further purification. Core CdSe and CdSe/S₈ (sulfur treated QD) were synthesized as reported in Chapter 4. Both the core and the sulfur treated QDs were irradiated under UVA light in a Luzchem LZC-4V photoreactor to obtain a matching fluorescence quantum yield between the two prior to any subsequent studies.

6.5.3 CdSe quantum dots characterization

The photophysical properties of each batch of QD were determined in a similar fashion than the one used in the experimental section of Chapter 4 (section 4.5.3).

Similarly, the fluorescence quantum yields Φ_F were calculated with the same approach used in Chapter 4, section 4.5.7. In this study, quinine hemisulfate was used as the

reference for all four QD samples. The PYY Φ_F in chloroform was calculated using the PYY Φ_F in water (0.46) as a reference.⁴¹

6.5.4 Fluorescence lifetimes

Each lifetime experiment was done with a class-I short-pulse LED with an excitation wavelength accommodating all of our samples (e.g., λ_{ex} = 350 nm). Long-pass cutoff filters were used after the sample cuvette to lower the spectral contamination of the decay signal similarly to the strategy applied in Chapter 4.

The intensity-average lifetime $\langle\tau_F\rangle$ was calculated using Equation 6. 1:

$$\langle\tau\rangle = \frac{(A_1 \times \tau_1 + A_2 \times \tau_2)}{(A_1 + A_2)}$$

Equation 6. 1: Intensity-average lifetime formula

where τ is the lifetime and A the pre-exponential factor.

6.5.5 Spectroscopic measurements

All spectroscopic measurements were performed in chloroform at room temperature. In a typical experiment, a solution of QD (1.4 μ M) was prepared in a precision quartz cuvette in the absence or in the presence of varying amounts of a 33 μ M PYY stock solution Ethanol/ CHCl_3 (1/99, v/v%) and chloroform such that the final volume added to each cuvette was 2 mL. The concentration of dye in the solution was calculated by using a molar extinction coefficient $\epsilon_{553\text{nm}} = 8.9 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ reported by Jakobsen *et al.*,²² for PYY in

ethanol/chloroform mixtures. Thus, the ratio between PYY/QD was varied by keeping constant the QD concentration. The solutions were prepared and kept in the dark for 12 hours before the measurements. For steady state fluorescence experiments, all samples were excited at 350 nm in order to minimize PYY absorption.

6.5.6 FTIR measurements

FTIR analysis was carried out on a BOMEM MB-100 spectrometer. For each measurement, a drop of CdSe/ZnS_{Green} QD solution, PYY solution, or a mixture of the two respectively was cast between two plates of sodium chloride (NaCl).

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7.1 Final comments

The work presented in this thesis highlights a portion of the wide variety of nanomaterials available today. These new materials have generated a novel interest due to the new array of properties specific to their size range, especially semiconductor quantum dots for their new optical, magnetic and electrical properties. However, this work illustrates that core quantum dots are very unstable particles, and tend to have a low quantum yield of fluorescence. Growing a ZnS shell has already been developed to overcome this drawback; unfortunately, it is also accompanied by a lower sensitivity to the surrounding environment. For the development of sensors or any hybrid materials, such as photovoltaic devices, the quantum dots presented in Chapter 4 offer more versatility. Indeed, we were able, with a simple sulfur treatment followed by photoactivation, to create modified core quantum dots that displayed an enhanced stability and a consistently higher quantum yield of fluorescence. Yet, these nanoparticles were capable of a superior response to external stimuli such as 4-amino-TEMPO. Chapter 6 also highlighted the higher quenching efficiency of a xanthene dye, pyronine Y, on the treated quantum dots. In fact, the absence of the ZnS shell prevented the PYY molecules from forming aggregates at the surface of the semiconductor.

Nanoparticles are also making their way into more biological applications and are both feared and praised. They are praised thanks to the new powerful hybrids that could be developed, such as precise drug delivery systems or accurate sensors. These new materials are also feared because of their unknown toxicity; their small size combined with their relative novelty renders predictions on their accumulation in the body difficult. In the wake of these contradictory claims, cerium oxide nanoparticles have been presented in the last

decade as both a potent antioxidant and a reactive oxygen species sensitizer for various cell types. Our studies in both organic and aqueous media were performed in much simpler systems that allowed highlighting the true interactions of cerium oxide. Rather than a direct antioxidant able to scavenge radicals being generated in its vicinity, cerium oxide was able to oxidize metal salts such as Fe^{II} into its less Fenton reactive form, Fe^{III} . This redox activity was still due to its ability to easily oscillate between its +4 and +3 oxidation states; however, it was not a direct antioxidant. Instead, cerium oxide nanoparticles were shown to lower the ability of metal salts to undergo damaging Fenton reaction within the cells.

One of the fastest growing fields in nanotechnology is catalysis. The main appeal is the improved per atom efficiency due to a higher surface area to total volume ratio. Many systems containing reduced metals such as Pt, Pd or Au have been exploited and Ag is no exception. However, Chapter 5 was the first account for the use of silver nanoparticles towards the grafting of alkoxy groups to polyhydrosiloxane polymers, making this system a more economical approach than the current Pd-based one. It was also an overall greener approach, as the reduction of silver salts did not require addition of extra reducing agents, and no solvent was required to undergo the grafting. The entire reaction was done in neat polymer.

Overall, the nature of the stabilizing agents used and the surface of the nanoparticle itself are key in understanding the reactivity. The chemistry happening at the surface of the system will be affected by the interaction with the environment, making it more or less prone to a favorable dynamic (molecules adsorption, reaction and then desorption). This field will strongly benefit in the future from instrumentation advancements allowing monitoring of a reaction at the sub-nanometer scale and sub-femtosecond scale.

7.2 Future directions

7.2.1 Interaction of semiconductor quantum dots with other organic dyes: energy / electron transfer mechanisms

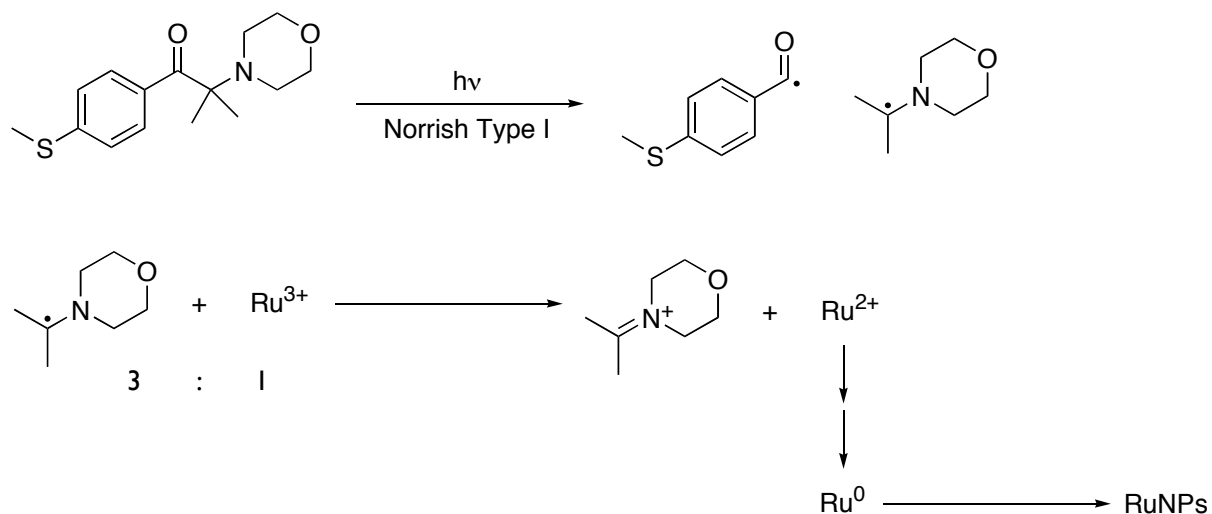
Semiconductor quantum dots are very interesting materials and are included in many hybrid systems. However, when put in presence with other photoactive species, a better understanding of their interaction is lacking. More precisely, it would be interesting to know whether QD undergo electron or energy transfer, or a combination of both as suspected in the system we studied. Since QD have a fluorescence lifetime of their surface state typically in the 10-20 ns range, a faster resolution technique such as a femtosecond laser flash photolysis instrument could be employed to monitor rapidly decaying excited states. Also, these studies would benefit from the single molecule fluorescence imaging techniques such as FLIM, allowing one to observe the kinetics of quenching at the nanoparticle level. Finally, other types of dyes and stains such as Eosin, with another mode of aggregation, could be tested.

7.2.2 Development of metallic nanoparticle systems for catalytic applications

Many types of metallic nanoparticles have been developed in the Scaiano research group, mostly through photochemical routes.¹ Amongst them, gold, silver and cobalt have recently been employed for various catalytic reactions by other members of the group. Another transition metal nanoparticle has been generated with a photochemical approach: ruthenium. A photoinitiator, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, commonly called Irgacure-907 (or I-907), irradiated at 300 nm would undergo a Norrish Type-I reaction and generate an α -aminoalkyl radical. This radical being a strong reducing

agent could then reduce a ruthenium salt until nanoparticles were formed, as depicted in

Scheme 7. 1:



Scheme 7. 1: Norrish Type-I reaction for I-907 (3 mM in acetonitrile) upon UVB irradiation. When put in presence with RuCl_3 (1 mM in acetonitrile), the α -aminoalkyl radical reduces Ru^{3+} salts to Ru^0 , then nanoparticles

The nanoparticles generated, as shown by the TEM images in Figure 7. 1, are extremely small and monodispersed, with an average size of 1.6 nm. With such a high surface area to volume ratio, this system could be potentially powerful in catalytic reactions.

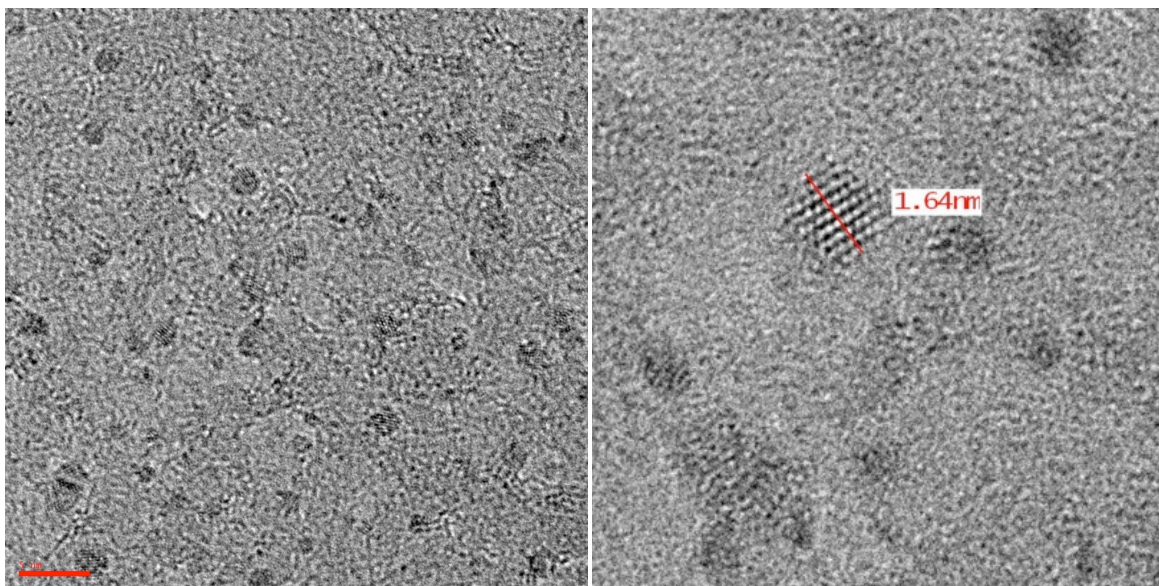
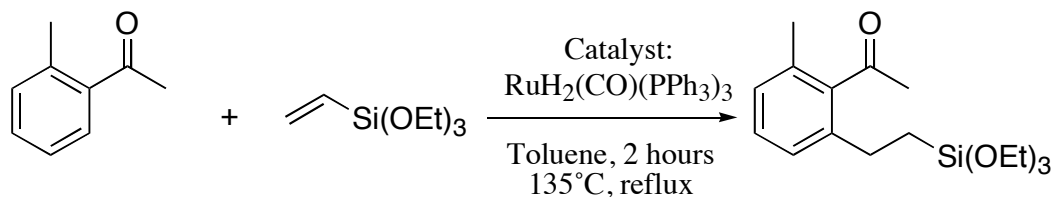


Figure 7.1: TEM images of ruthenium nanoparticles with a zoom (right) depicting a typical particle with its lattices in a hexagonal close-packed structure (bar = 5 nm)

An example of a reaction that would be interesting to attempt would be the Murai reaction, an olefin coupling reaction that currently uses ruthenium complex catalysts (as shown in Scheme 7. 2).^{2, 3} This reaction would be of interest because it has been suggested for the mechanism that ruthenium undergoes *in situ* reduction to form the real catalyst, that is ruthenium nanoparticles.⁴



Scheme 7.2: Murai catalytic reaction for the coupling of methylacetophenone with triethoxyvinylsilane, using a ruthenium complex²

7.3 Claims to original research

1. The reactivity of cerium oxide nanoparticles in presence with hydrogen peroxide was elucidated with different hydroxyl radical generation routes: iron salts and UVA irradiation. It was shown to have a significant effect on the radical generation when iron salts were used: it would slow down the Fenton reaction by oxidizing Fe^{II} into less reactive Fe^{III} species. This was the first proof of the indirect antioxidant ability of cerium oxide.
2. The absence of radical scavenging ability in an organic medium was proven for cerium oxide in tetradecene as it was unable to slow down the styrene autooxidation process to the corresponding polymer.
3. Core CdSe quantum dots stabilized by TOPO ligands in organic solvents were modified with elemental sulfur treatment. This treatment consisted in surface deposition followed by photoactivation of the surface bound S_8 oligomers, giving more stable and consistently more luminescent QD. These quantum dots were also proven to be more reactive to a solution quencher and to be more stable to further derivatization with a silica shell.
4. Silver nanoparticles embedded in polysiloxane matrices were developed with no addition of a reducing agent or the need for an organic solvent. These new systems were proven efficient for the alcoholysis of the Si-H bonds along the polymer chain.

5. The effect of a shell on the interaction of CdSe quantum dots with a xanthene-type dye was investigated by comparing core with sulfur treated and two sizes of CdSe/ZnS core-shell quantum dots. The presence of a ZnS shell was shown to favor the dye aggregation in a plane-to-plane stacking mode (H-type). Moreover, the quenching process was more efficient for the core and sulfur treated quantum dots, because of their surface states being more readily available for energy and electron transfers.

7.4 Publications

7.4.1 Publications resulting from work presented in this thesis

René-Boisneuf, L., Scaiano, J. C., Sensitivity versus Stability: Making Quantum Dots More Luminescent by Sulfur Photocuring without Compromising Sensor Response, *Chemistry of Materials*, **2008**, 20, 6638–6642.

René-Boisneuf, L., Maretti, L., Scaiano, J. C., Facile One-Pot synthesis of silver-polysiloxane nanoconjugates for catalytic alcoholysis, *in preparation*.

René-Boisneuf, L., Ingold, K. U., Scaiano, J. C., On the role of Cerium Oxide in the radical scavenging of reactive oxygen species, *in preparation*.

René-Boisneuf, L., Montes-Navajas, P., Alarcón, E., García, H., González-Béjar, M., Scaiano, J. C., Shell effect on the interaction between CdSe quantum dot with Pyronine Y, *in preparation*.

7.4.2 Publications resulting from work not presented in this thesis

Zang, M., **René-Boisneuf, L.**, Hu, Y., Moozeg, K., Hassan, Y., Scholes, G., Winnik, M., Preparation and Photo/Chemical-Activation of Wormlike Network Micelles of Core-shell Quantum Dots and Block Copolymer Hybrids, *Journal of Materials Chemistry*, **2011**, 21, 9692-9701

Scaiano, J. C., Netto-Ferreira, J. C., Alarcon, E., Billone, P., Bueno Alejo, C. J., Crites, C.-O. L., Decan, M., Fasciani, C., González-Béjar, M., Hallett-Tapley, G., Grenier, M., McGilvray, K. L., Pacioni, N. L., Pardoe, A., **René-Boisneuf, L.**, Schwartz-Narbonne, R., Silvero, M. J., Kevin G. Stamplecoskie, K. G., Wee, T.-L., Tuning plasmon transition and their applications in organic photochemistry, *Pure and Applied Chemistry*, **2011**, 83 (4), 913-930.

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