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*CONTROLLED SYNTHESIS OF
NANOPARTICLES AND COMPOSITES VIA
SPUTTERING IN LIQUID*



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SUMMARY

Nature challenges scientists, and many of the secrets behind its perfection lie in the nanoscale regime. This study aims at improving the understanding of the behavior of nanoparticles and nanoclusters synthesized using a sputtering into liquid. This synthesis method is important in terms of simplicity of the process and high purity of the samples: nanoparticles and nanoclusters are generated in the vacuum, without using reducing agent and toxic solvents. The design of their characteristics, composition and size, can then be controlled by using appropriate sputtering conditions and by choosing the sputtering media wisely. The dissertation presents and discusses the use of the above mentioned synthesis method for the production of nanoparticles-polymer hybrid materials. The study on the chemico-physical stability/transformation and optical properties of the nanoparticles was performed, as understanding about stability and nanoparticle behavior in determinate ambient conditions is of fundamental importance for future applications and safety.

Titanium dioxide, TiO_2 , nanoparticles (NPs) are important wide-bandgap materials used as UV-active photo-catalysts and various optical applications such as a UV block material in sunscreens, or to increase the refractive index of thin films and polymers. Besides, stoichiometric titanium monoxide, TiO , with narrow bandgap and strong visible-light absorption can be used for energy harvesting or catalyst applications towards the visible region. Therefore, the preparation of titanium oxides with control of its oxidation state offers a facile way to modify the optical properties of hybrid materials that contain titanium oxide NPs. It is still a challenge to use chemical methods for synthesizing clean titanium oxides of very small size (1–10 nm) with controlled composition dispersed in polymers since the decomposition of titanium complexes can result in various undesired titanium oxide phases and re-dispersion of pre-made NPs can cause agglomeration. My study proposed sputtering of Ti in liquid under controlled atmospheric conditions (oxygen content) for the direct synthesis of different titanium oxides embedded in liquid monomer and resin. Pentaerythritol ethoxylate (PEEL) with low vapor pressure was chosen as liquid substrate to obtain uniform dispersions of titanium oxide NPs. Titanium oxide (TiO_x , $x = 1, 2$) NPs with diameters of 4 nm with a controlled composition by adjusting the sputtering atmosphere were successfully prepared. Furthermore, as the electronic structure of the TiO_x NPs can change depending on the particle size, crystallinity and degree of oxidation, we were able to modify the optical properties of PEEL and the resin by embedding TiO_x NPs in the matrix. The enhancement of

the refractive index with high transparency and low dispersion of a resin containing TiO_2 NPs was observed. In addition, PEEL and resin containing TiO NPs were produced with strong visible absorption. This synthetic approach was demonstrated promising for the advanced preparation of highly pure TiO_x NPs for various applications in optical devices, energy conversion, and light harvesting in the UV-visible region.

Inorganic fluorescent probes and inorganic fluorescent-polymer hybrid composites are in the centre of much attention over the past few years. Many methods to stabilize metallic nanoclusters have been developed, trying to obtain highly versatile optical properties. Metallic nanoparticles, when in small enough in size, start showing discrete energy levels, and size-dependent properties, giving them a great advantages in terms of versatility. Gold and silver nanoclusters have been widely studied due to their non-toxic, higher stability and high photoluminescence emission extinction. In this study we describe the synthesis of, cheaper and more abundant, copper metallic photoluminescent nanoclusters using the sputtering method into a polyethylene glycol 600 (PEG) and mercaptoundecanoic acid (MUA), as well into pentaerythritol tetrakis(3-mercaptopropionate) (PEMP). The liquid media were chosen for their different amount of thiol moieties to cap the copper nanoclusters. We obtained stable nanoparticles with a size of 1.6 ± 0.2 nm in case of PEG-MUA mixture, showing luminescence emission at 440 nm. In case of sputtering into the thiol rich liquid (PEMP), a different behavior appears: at first the product shows similar photoluminescence properties with an emission at 440 nm; with time though, the high amount of sulfur slowly is ripped away from the capping, and the nanoparticles turn into copper sulfide with luminescence emission at 630 nm. The formation of copper sulfide is caused by the presence of an oxide shell of copper and the reaction of this oxide shell with the thiol rich capping moiety. This mechanism allows for producing nanoclusters whose optical properties vary as a function of their composition via sputtering in a controlled atmosphere and a liquid medium. In addition, this shows the importance of the choice of the liquid medium for this technique, as well as the versatility it has.

It was found in the above study that the transformation of copper nanoparticles into copper sulfide occurs over a couple of weeks timespan after sputtering. Therefore we've been developed another method to make the transformation go faster. Considering the way copper sulfide forms, which is mediated by the presence of copper oxide and the conversion of oxide to sulfide, we proposed that the usage of UV-light, irradiated on as-synthesized copper nanocluster dispersions, can provide energy to accelerate the reaction. In this way we

obtained photoluminescent copper sulfide nanoclusters in only few hours under UV-light irradiation at room temperature. The reaction speeded up to 50 times compared with a normal formation of copper sulfide by the previously investigated storage method. The results are impressive and contribute a feasible way to produce highly emitting copper sulfide nanoclusters well dispersed in monomers. Furthermore, the finding helps understanding the transformation of copper nanoclusters in rich thiol capping moiety environment obtained via sputtering methods.

The studies presented in this thesis contribute with different approaches to nanoparticles synthesis, for uniform, well dispersed, and highly pure nanoclusters with controlled compositions in liquid via sputtering. The understanding of the formation mechanism of nanocluster in relation to the liquid medium and the sputtering atmosphere is valuable for research in this field.

Key words: Magnetron Sputtering, Photoluminescence Nanoclusters, Titanium Oxide, Copper Nanoclusters

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Thanks to all the friends who made my life in Japan beautiful.

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Sample	Sputtering time (min)			Relative index increase (10^{-3})
	Blue ^a	Green ^b	Total	
PEEL	0	0	0	0
1	60	0	60	12.2
2	60	60	120	8.8
3	60	120	180	7.6
4	0	120	120	-4.5
5	30	30	60	4.1
6	30	60	90	3.6
7*	0	90	90	NA
8*	0	180	180	NA

^acathode voltage 310 V, ^bcathode voltage 265 V, *for SAXS measurement

Table 2.2. Average sputtering rates for blue and green plasma sputtering as calculated by measuring the thickness of sputtered films by SEM.

Sputtering rate [nm/min]	
Blue plasma	29 ± 10
Green plasma	63 ± 10

Table 3.1. XPS results for Cu samples sputtered into PEMP and stored for various amount of time. The discrepancy in the binding energy of Cu is due to the big charge effect caused by the great amount of thiol moieties in excess. The Modified Auger parameter is not affected by such energy shifts.

Sample	Modified Auger parameter for Cu (eV)	XPS binding energy of Cu2p 3/2 (eV)	XPS binding energy of S2p 3/2 (eV)
As-synthesized	1848.4	934.2	165.1
3 days storage	1848.3	934.7	165.0
8 days storage	1848.5	934.4	164.7
Ref. Cu (0)	1851.2 $\pm$ 0.2	932.6 $\pm$ 0.2	
Ref. Cu (I)	1849.4 $\pm$ 0.4	932.4 $\pm$ 0.2	
Ref. C-S-H			163.8 $\pm$ 0.4
Ref. Cu ₂ S	1849.8 $\pm$ 0.2	932.5 $\pm$ 0.2	161.9 $\pm$ 0.4
Ref. CuS	1850.2 $\pm$ 0.3	932.2 $\pm$ 0.2	162.1 $\pm$ 0.6

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Sample	Binding energy Cu2p 3/2 (eV)	FWHM (eV)	Cu LMM Auger Kinetic energy (eV)	Modified Auger parameter for Cu (eV)
As-sputtered	933.9	1.5	917.9	1851.8
Few nm etch	932.3	0.8	918.7	1851.0
	932.7	0.9	917.2	1849.9
Strong etch	932.3	0.8	918.7	1851.0
	932.7	0.9	917.2	1849.9

Table 3.3. Typical copper binding energy values depending on its oxidation state, and compound. Source: xpsfitting.com, an XPS web database.

Compound	Cu 2p _{3/2} (eV)	Std. Dev. (+/- eV)	FWHM, 10 eV Pass Energy	FWHM, 20 eV Pass Energy	Modified Auger Parameter	Std. Dev. (+/- eV)
Cu(0)	932.63 a)	0.025 b)	0.79	0.83	1851.24	0.025 b)
Cu(I) Oxide	932.18	0.12	0.88	0.98	1849.17	0.03
Cu(II) Oxide d)	933.76	0.11	3.00	3.00	1851.33	0.05
Cu(II) Hydroxide d)	934.67	0.02	2.74	2.85	1850.92	0.09

b) As defined by Kratos calibration procedure

c) GL(90) peak-shape

d) Shake-up peaks are present (see Figure 1 for shape)

Table 4.1. XPS data results for the Cu and S 2p 3/2 binding energy for the various samples

Sample	XPS binding energy of Cu 2p 3/2 (eV)	XPS binding energy of S 2p 3/2, purple curve (eV)	XPS binding energy of S 2p 3/2, green curve (eV)	XPS binding energy of S 2p 3/2, orange curve (eV)
1.00g MUA	933.3	163.9	162.4	
0.21g MUA	932.9		162.5	160.9
0.10g MUA	932.9		162.4	161.2
Ref. Cu(0)	932.6 ± 0.2			
Ref. Cu(I) oxide	932.4 ± 0.2			
Ref. C-S-H		163.8 ± 0.4		
Ref. Cu ₂ S	932.5 ± 0.2	161.9 ± 0.4		
Ref. CuS	932.2 ± 0.2	162.1 ± 0.6		

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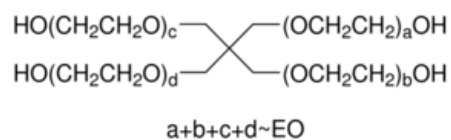


Figure 2.1. Molecular structure of Pentaerythritol ethoxylate.

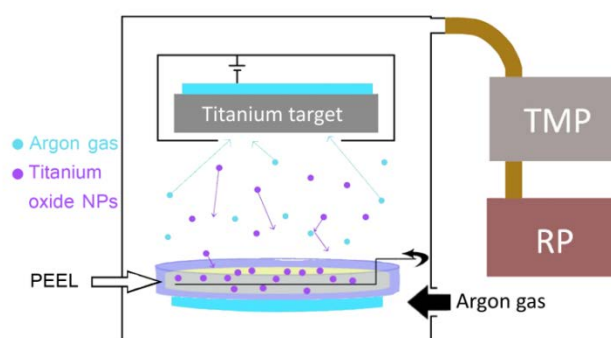


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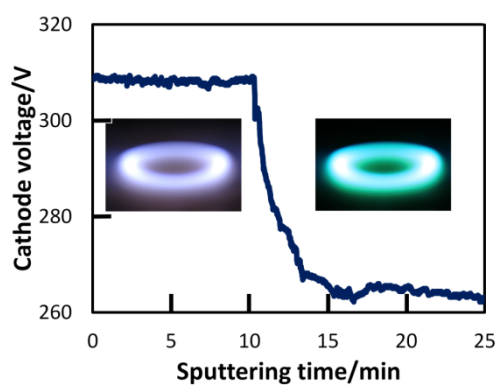


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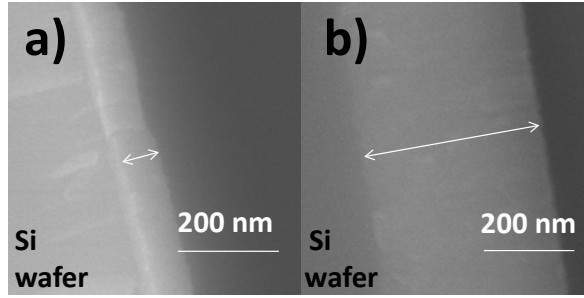


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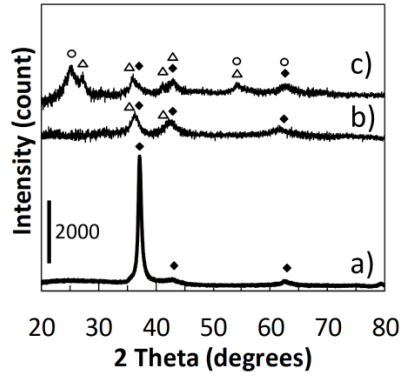


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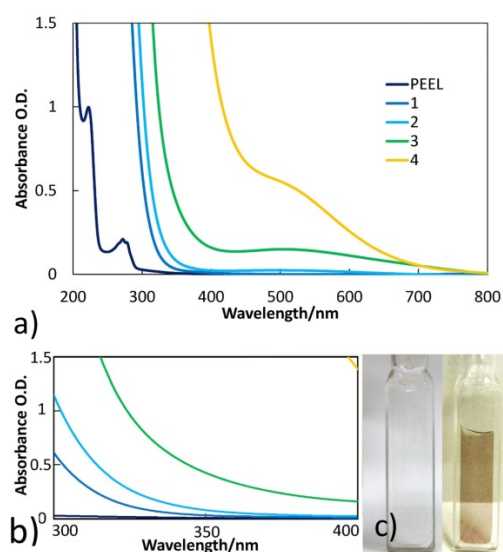


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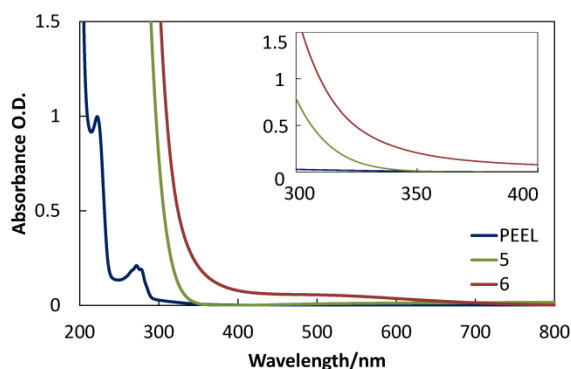


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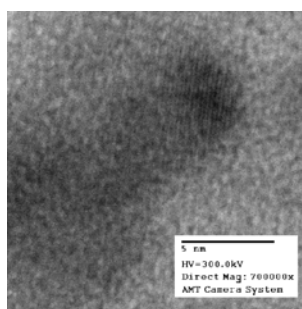


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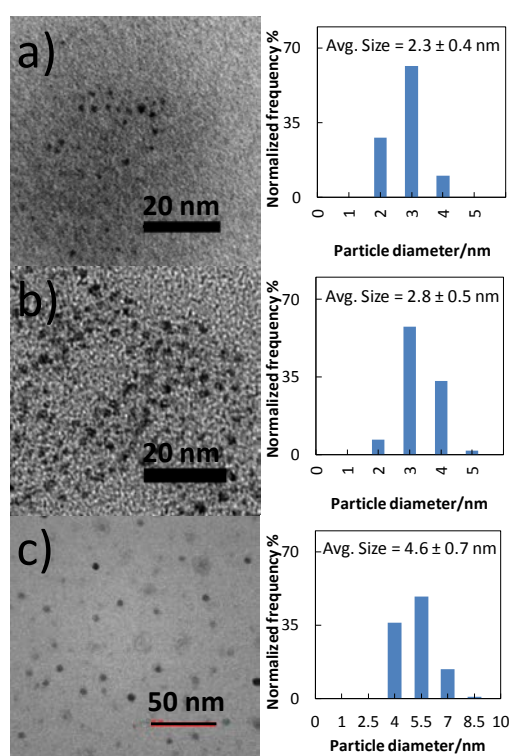


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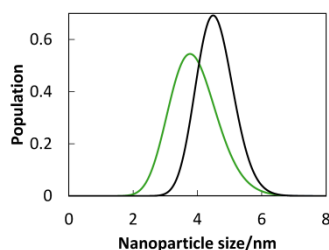


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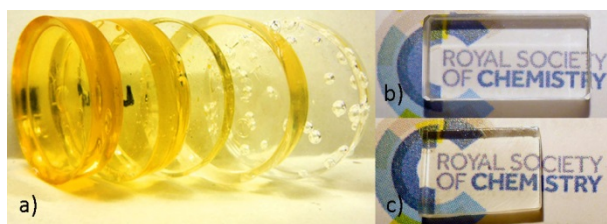


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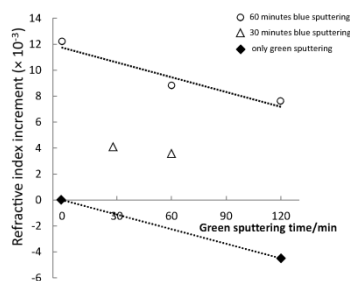


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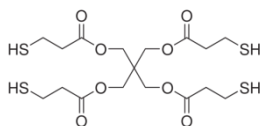


Figure 3.1. Molecular structure of pentaerythritol tetrakis (3-mercaptopropionate).

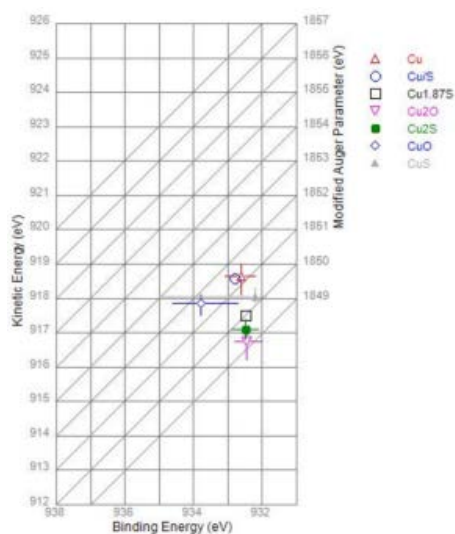


Figure 3.2. Wagner plot for copper compounds to show how the Auger parameters vary with different oxidation state.

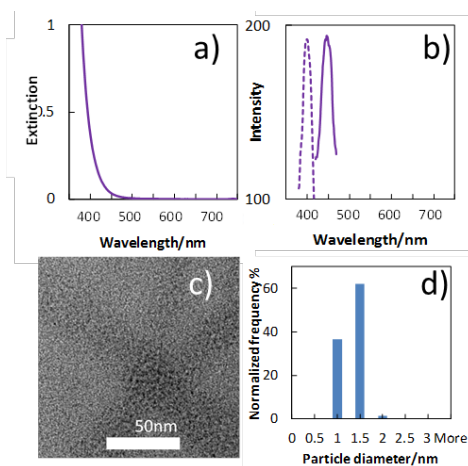


Figure 3.3. UV-Vis spectrum (a), photoluminescence spectra (b), TEM image (c), and size distribution (d) of the as-synthesized copper nanoclusters dispersed in PEMP. Dashed and solid curves in b correspond to excitation and emission spectra, respectively.

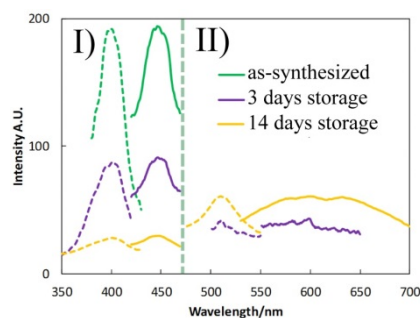


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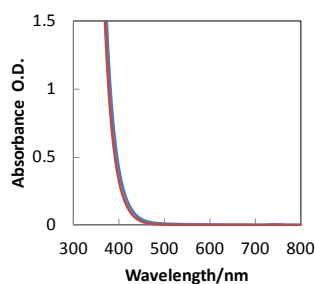


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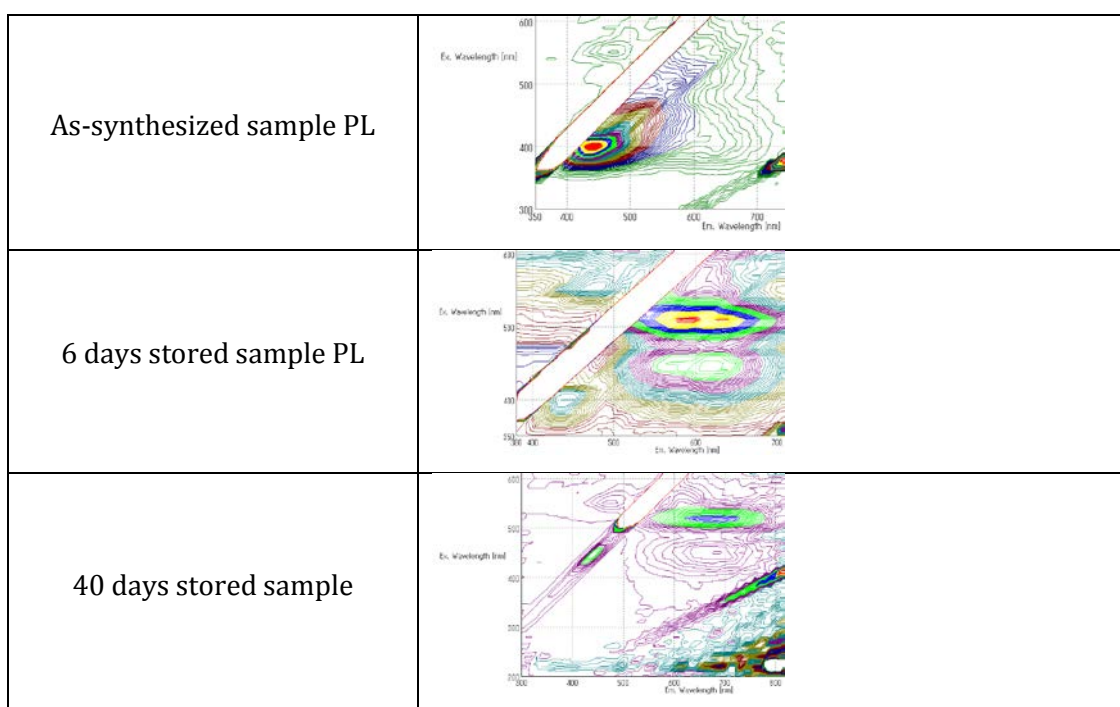


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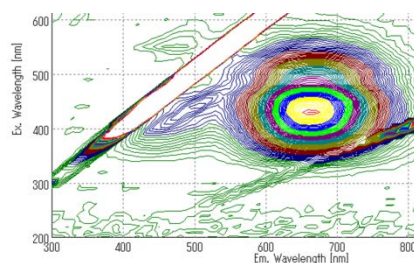


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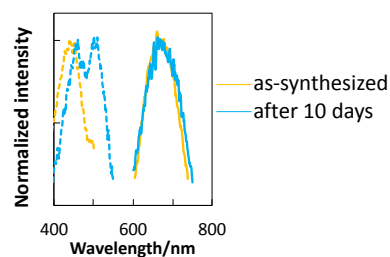


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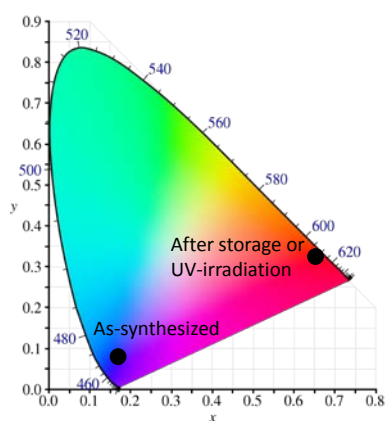


Figure 3.9. Graphical scheme showing the position of the emitted photoluminescence in a CIE 1931 color space.

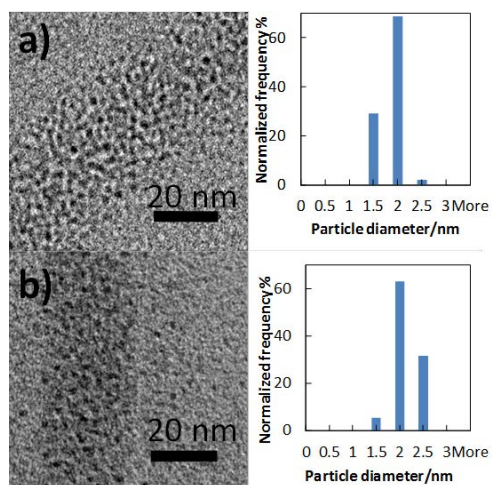


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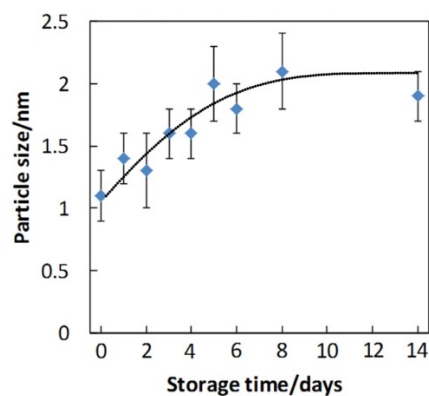


Figure 3.11. Particle growth with time as observed by TEM. Particles grow for the first few days after synthesis, to reach their final stable size just below 2.0 nm diameter.

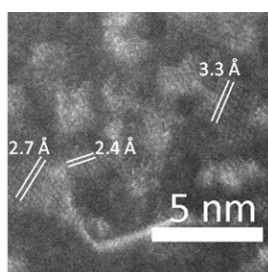


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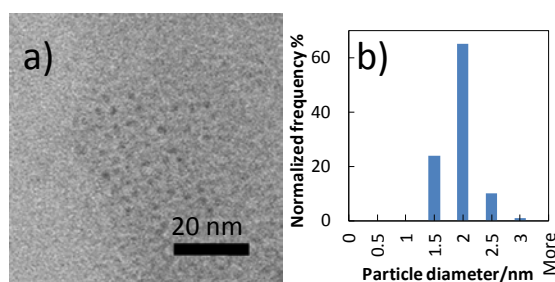


Figure 3.13. TEM image (a) and particle size distribution (b) for a sample sputtered into PEMP under air instead of Ar. The average particle size is 1.7 ± 0.3 nm.

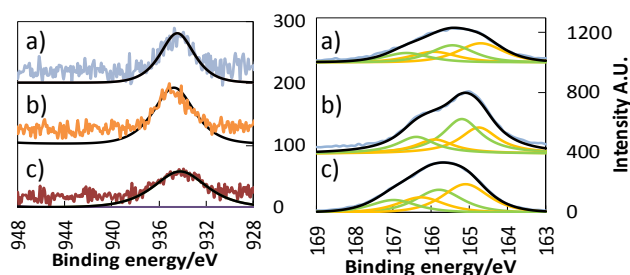


Figure 3.14. Narrow scan XPS spectra of Cu 2p and S 2p for as-synthesized nanoclusters in PEMP. The samples were stored for a) 8 days and b) 3 days, whereas c) is the XPS for an as-synthesized sample.

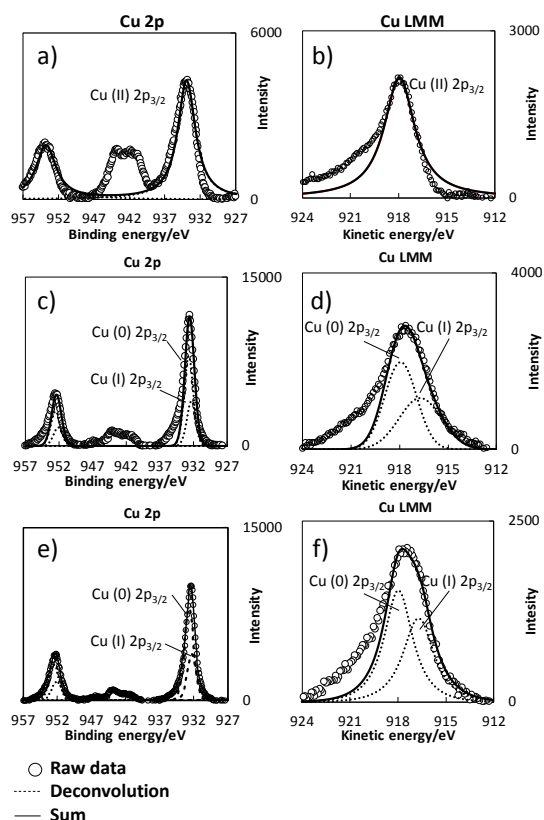


Figure 3.15. XPS depth profile of a sample sputtered onto a silicon grid in air. From the top, as-synthesized film (a,b), after a few nanometers etching (c,d), and after few tens of nanometers etching (e,f). The presence of Cu(I) and Cu(0) can be deduced by deconvoluting the Auger peak and calculating the modified Auger parameter. For as-sputtered material, CuO was detected, in fact there are clear secondary peaks between 940 and 950, that are caused by Cu^{2+} . After etching, the Cu(II) component decreases in intensity, while Cu and Cu(I) components appear. Tables 3.2 and 3.3 explain the results.

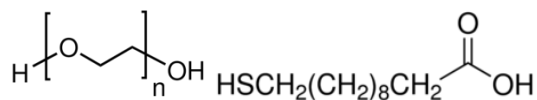


Figure 4.1. Molecular structure of polyethylene glycol (left) and of 11-mercaptoundecanoic acid (right).

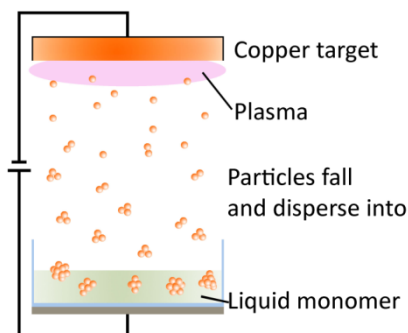


Figure 4.2. Schematic representation of the sputtering mechanism into liquid.

(Same as 3.2)

Figure 4.3. Wagner plot for copper compounds to show how the Auger parameters vary with different oxidation state.

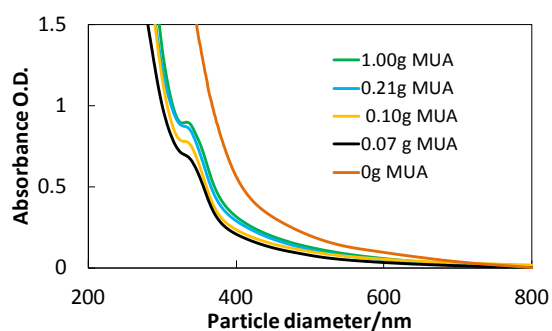


Figure 4.4. UV-Visible spectra for the sputtered copper nanoclusters dispersed in PEG and MUA. The amount of MUA was varied between 0 (only PEG) and 1.00 g.

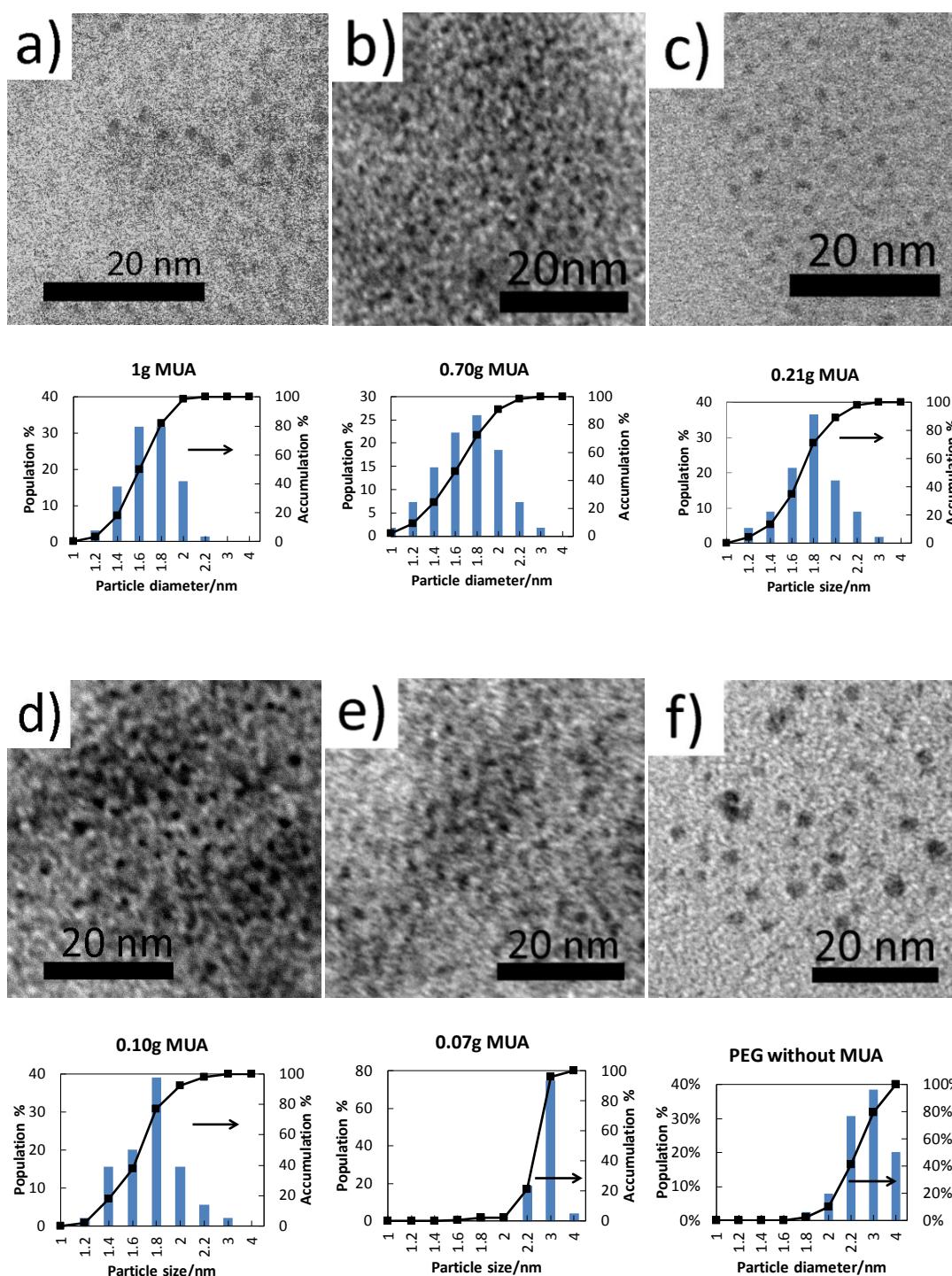


Figure 4.5. TEM images of the sputtered samples with the amount of MUA (a) 1.00 g, (b) 0.70 g, (c) 0.21 g, (d) 0.1, (e) 0.07 g, and (f) 0 g, and relative particle size distribution.

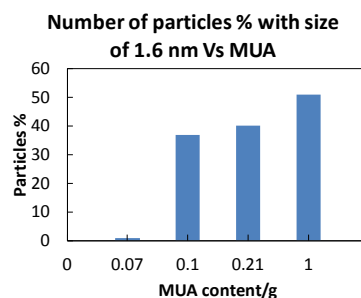


Figure 4.6. The graph shows the fraction of nanoclusters with size of and less than 1.6 nm plotted versus the amount of MUA used.

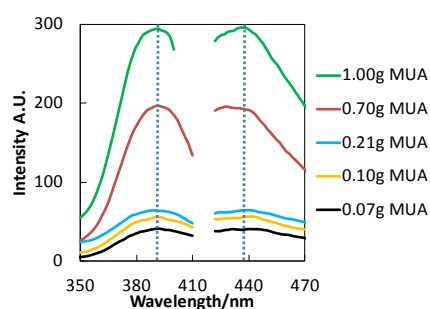


Figure 4.7. PL spectra for samples sputtered at various MUA amounts (0.07-1.00 g).

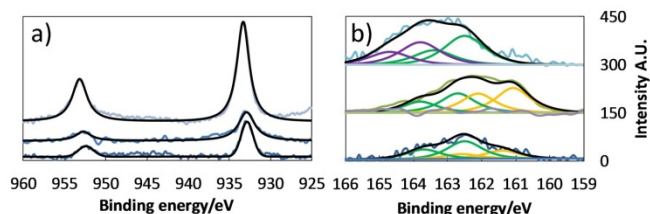


Figure 4.8. Narrow scan XPS spectra of Cu 2p (a) and S 2p (b) for nanoclusters prepared using 1.00, 0.21 and 0.10 g of MUA in PEG from top to bottom, respectively. The light blue and black curve are the raw and sum spectra, respectively. S 2p spectra were deconvoluted into two components labelled with purple, green, and orange for different states of S.

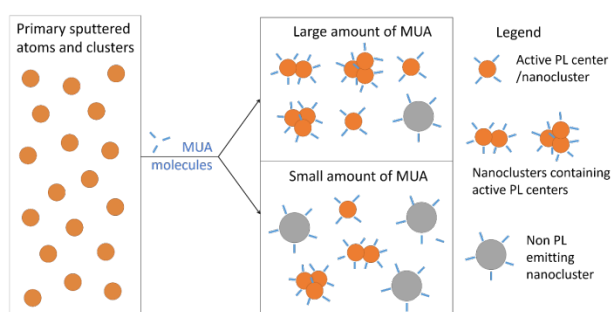


Figure 4.9. Formation mechanism of copper nanoclusters in relation to the MUA amount.

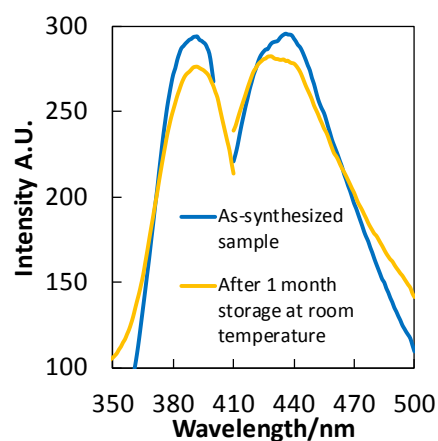


Figure 4.10. Evolution of the photoluminescence intensity over time. A sample containing 1 g of MUA was stored at room temperature for 30 days, and PL was measured again. The intensity decreased only slightly.

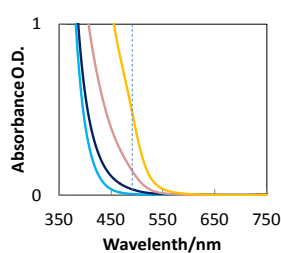


Figure 5.1. UV-visible absorbance of an as-synthesized sample, and the one of the same sample after being irradiated by UV-light for 2 h (blue line), 4 h (pink line) and 6 h (orange line). The formation of an absorption peak at 480 nm, whose position is indicated by a dotted line, becomes gradually evident.

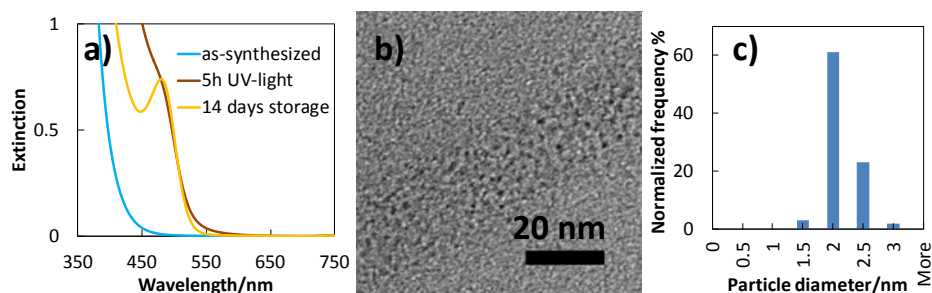


Figure 5.2. (a) Comparison of UV-Visible absorbance for an as-synthesized sample, a 14 days stored one, and another one irradiated for 5 hours under 365 nm UV-light. (b) TEM image of the UV-irradiated sample, and its relative size distribution (c). The average particle diameter is of 1.9 ± 0.3 nm.

(Same as Figure 3.11)

Figure 5.3. Particle growth with time as observed by TEM. Particles grow for the first few days after synthesis, to reach their final stable size just below 2.0 nm diameter.

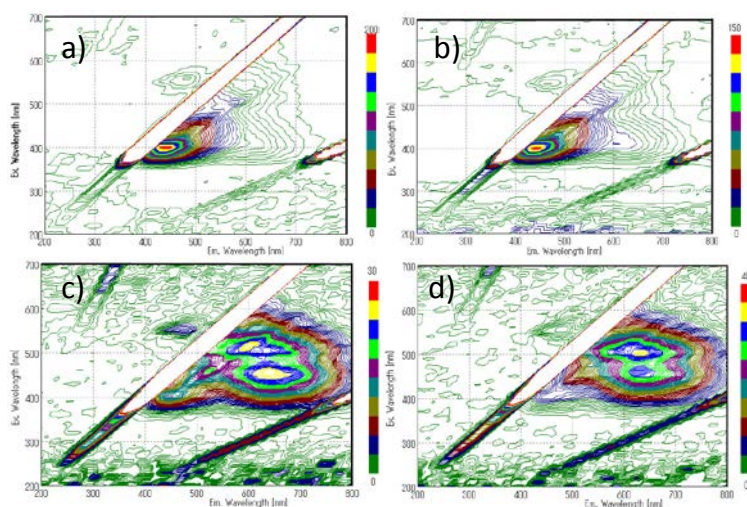


Figure 5.4. From (a) to (d) it's shown the evolution of the photoluminescence of copper nanoclusters under UV-light irradiation: PL mapping images were taken at intervals of 2 hours of UV-light irradiation. Gradually the initial PL at 445 nm disappears, to leave a final product that emits light at 630 nm wavelength.

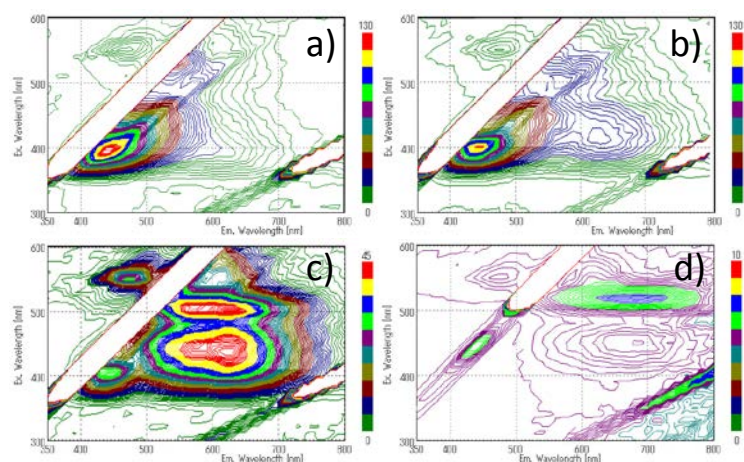


Figure 5.5. As a comparison, from (a) to (d) it's shown the evolution of the photoluminescence of copper nanoclusters with storage time at room temperature in the dark. a) as-synthesized sample, b) after 3 days of storage, c) after 14 days of storage, and after 40 days of storage d).

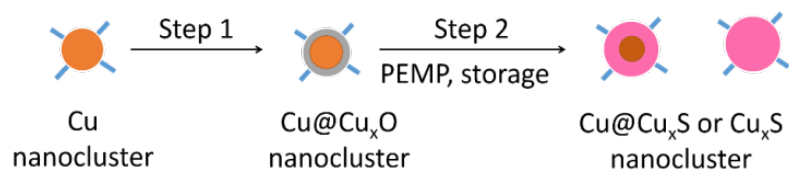


Figure 5.6. Formation mechanism of copper sulfide nanoclusters from copper nanoclusters in PEMP.

1 INTRODUCTION

1.1 Nanoparticles

Inorganic nanoparticles have been a breakthrough in modern science, as they allowed the production of materials showing the most disparate properties. In fact, when a material assumes sizes below 100 nanometers, it shows different characteristics compared to its bulk or microparticle equivalent. The reason for such changes lies in the fact that as the materials gets smaller, or change shape to have at least one dimension in the nanometer range (thin films) the surface to volume ratio increases sharply. Surfaces can be considered as discontinuities of the lattice: the atoms that lie on them will be bound to the material in a different way compared to the atoms in the bulk, therefore exhibiting a different behavior. Nanoparticles' quantum-scaled dimensions are the cause of much of their catalytic, optical and electronic properties, therefore tailoring size, shape and composition of the nanoparticles has been one of the primary concerns for researchers over the last few decades.

Metal and metallic complexes nanoparticles show very strong photoluminescence properties, that can be used in light harvesting for renewable energy applications, and if their surface is properly modified, can be used for bioimaging, or medical treatments. Easily tunable luminescent properties of quantum dots can be used by the electronic industry. Inorganic particles can be also used to modify the mechanical properties of materials, from bulk metals, to polymers, as they allow the control of the tensile (Young's modulus) and impact strength. Metal nanoparticles inks, in particular copper, are being researched for the fabrication of printed low cost electronics. Nanoparticles with a high refractive index are

being studied for the improvement of the optical properties of glasses and plastics; in case of a particularly small particle size, nanoparticle dispersions can become transparent to visible light, allowing the synthesis of hybrid materials. Nanoparticles are also widely used as catalysts (often paired with porous microstructures), as their large surface allow a much better efficiency compared to bulk materials.

1.2 Nanoparticles' synthesis

Nanoparticles may be synthesized using many different methods, and the number of them is increasing day by day. These processes can be classified into physical (dry) and chemical (wet) methods. Both ways allow the production of nanoparticles with a broad range of materials, shapes and sizes. Another common classification of the synthetic methods is the top-down bottom-up parameter, that classifies nanoparticles' production methods depending on the way the particles form: if breaking a bulk into nanometer-sized pieces, or if making atoms agglomerate (usually in solutions). Depending on the application of one particular nanoparticle, one synthetic method might be more suitable than others in crafting the desired product. Other big concerns nowadays are the environmental impact of the synthesis^[1] and the disposal of the waste produced during particle synthesis, as well as the impact of the nanoparticles themselves.

It is towards the scope of this work focusing on one particular range of products, which is the organic-inorganic nanocomposite material. Such materials are usually composed of a polymeric matrix, which encapsulates inorganic nanoparticles, protecting them from aggregation or deterioration. Over the last couple of decades many research groups around the world have been studying inorganic nanoparticles for the fabrication of such compound materials, using metals (eg. Au, Ag, Cu, Pt) oxides (eg. ZnO, TiO₂, CuO) and other compounds (eg. SiO₂, CdTe, SiC, CdS).

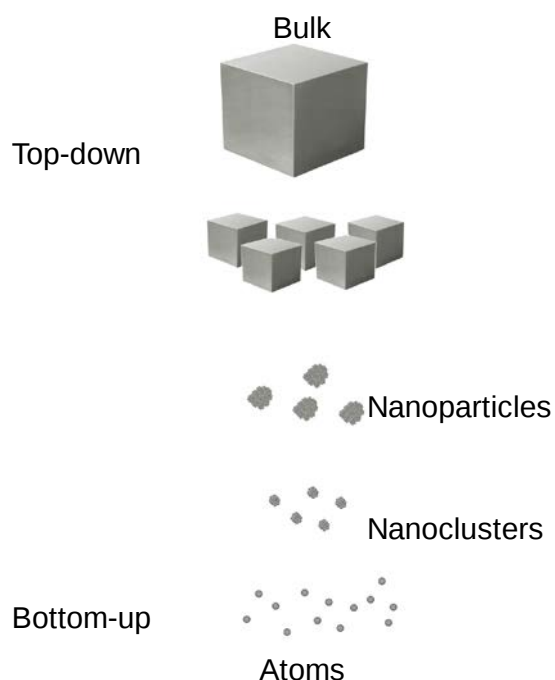


Figure 1.1. Schematic illustration of Top-down and Bottom-up processes.

1.2.1 Bottom-up methods

Bottom up processes are all those in which the starting point in the synthesis of nanostructure are single atoms. Those smallest units are then put together during the process, and stabilized to have the desired shape and size. Here a list of very commonly used bottom-up processes for the synthesis of inorganic nanoparticles.^[I]

1.2.1.1 Sol-gel processes

The sol-gel processing of nanoparticles is based on the slow formation of a network by dissolving a polymer in an aqueous or non-aqueous medium, into which nanoparticles form. The process has been used already for the synthesis of many kinds of nanocomposites with aluminum, titanium, silicon oxides just to mention few examples.^[II]

The peculiar conditions under which the synthesis occurs provide the opportunity of synthesizing materials like no other technique, with control over both composition and morphology of the products.

1.2.1.2 Chemical reduction

This bottom-up process is at the very basic for the synthesis of nanoparticles, as it's at the core of nanoparticle industrial production. It involves the reduction of metal salts in solution containing one or multiple protective agents. The freed metal atoms are then bound to the protective agent to form nanoparticles or nanotubes: by tuning the agents in the solution it is possible to synthesize nanoparticles with specific geometries and compositions, with a high level of crystallinity.

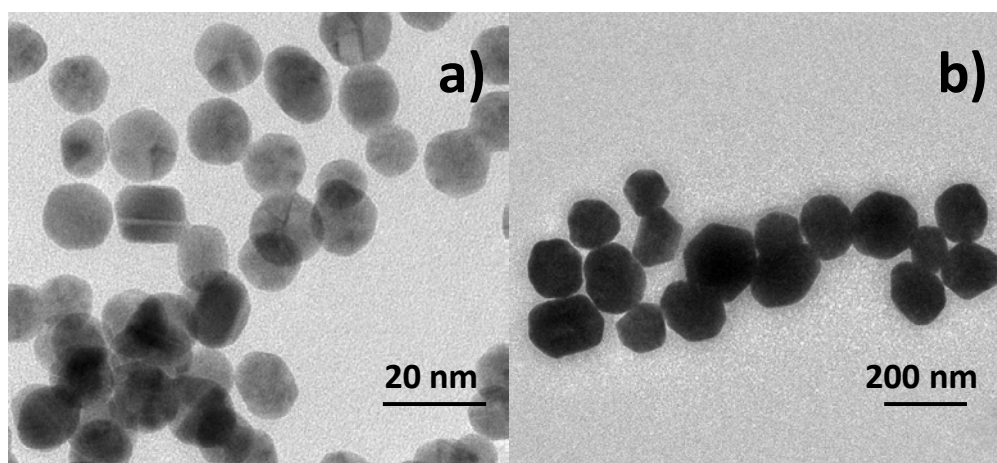


Figure 1.2 Example of chemical reduction synthesis for colloidal gold nanoparticles. Size and shape control is possible using various capping agents. a) Shows spherical nanoparticles used as seed for the synthesis of the bigger NPs shown in figure b).



Figure 1.3 Illustration of the seeded growth of Au NPs, from 12 nm (left) to 120 nm in diameter (right), as described by Bastus et al.^[111]

1.2.1.3 Reverse micelle process

Micelles are aggregates of molecules that form when surfactants are dispersed into water. In aqueous environments, micelles form with the hydrophilic part of the molecule towards the solution. The reverse micelle process involves instead non-polar solvents, to form micelles oriented inside out. In this situation, the amount of water can be used to determine the size of the micelles, which will host the reaction.

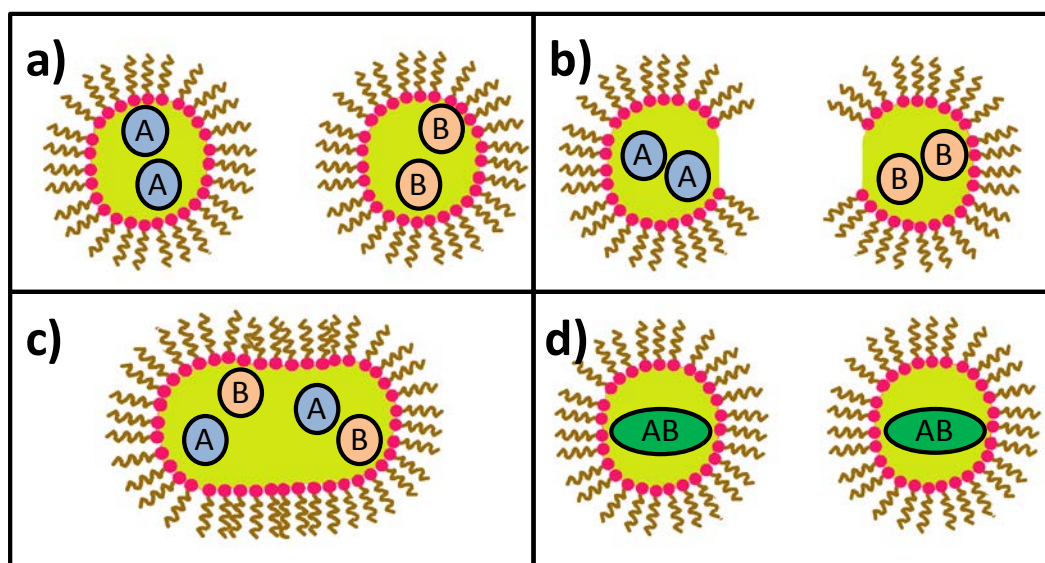


Fig. 1.4 Stages of the nanosilver particles formation in reverse micelles. ^[v]

1.2.2 Top-down methods

Top-down processes are synthetic methods in which nanostructures are generated starting from big chunks of material, bulk. They usually are methods during which the breaking down of bulk materials occur, usually are dry physical methods. The vacuum techniques used for the synthesis of nanomaterials, such as sputtering, laser ablation, thermal vapor decomposition are all top-down methods. Here below a list of commonly used top-down techniques.

1.2.2.1 Laser initiated processes

Lasers have been used to synthesize nanoparticles in different methods. As a top-down technique, laser ablation, consists in etching a metallic plate submerged in a solution with a strong laser: nanoparticles form and are dispersed in the solution. Another method would be using strong laser to reduce metal precursors in solution containing a protective agent, allowing the synthesis of nanoparticles without recurring to chemicals as reducing agents in the solution.

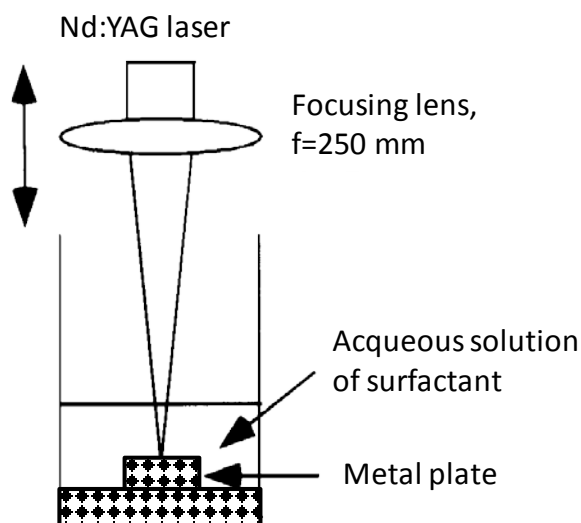


Figure 1.5 Schematic diagram of the experimental apparatus for a laser ablation experiment, for the synthesis of silver nanoparticles.^[VI]

1.2.2.2 Vapor deposition

By vapor deposition techniques it can be referred to a group of techniques that uses vaporized material to synthesize nanoparticles. There are many variants of such techniques, as they have been designed for many different purposes, but they all share the fact that are dry techniques: nanoparticles do not form in a gel or solution. We can distinguish two main groups: chemical vapor deposition (CVD)^[VII] and physical vapor deposition (PVD). CVD are those techniques that use mixtures of gases and vaporized inorganic materials to have a reaction in the gas phase (eg. flame pyrolysis, plasma enhanced CVD). PVD are instead techniques that rely on the condensation of vaporized inorganic materials (eg. electron beam PVD, sputtering).

1.2.2.3 Sputtering technique

Sputtering is a PVD technique that has been widely used over the past 40 years, mainly for the fabrication of thin films. One of the biggest advantages of this technique is that it allows the formation of highly pure and uniform thin films, and it has been developed for sputtering both metal (DC sputtering) and semiconductors (RF sputtering). In recent years the technique has been used also to create nanostructures^[VIII, IX], and nanoparticles^[X-XIII].

The technique for sputtering thin films consists in bombarding a metallic plate (target) with ions, usually Ar^+ , then allowing the materials to be etched away and deposit onto the desired surface. In order to do so, in a vacuum chamber, at a pressure usually between 0.1 and 10 Pa, a potential difference is applied between the anode (sample) and the cathode (target). The applied voltage accelerates the positive ions that will go to impact on the negatively charged cathode. The kinetic energy carried by the ions transfers to the target material: there is enough energy to eject atoms and small clusters, which are spread in the sputtering chamber. Due to the small size and light weight of the sputtered material, having the right pressure is a key factor for a successful sputtering: with too high pressure cathode discharge may occur, whereas if the pressure is too low, the sputtering rate will be decrease due to the low amount of ions in the chamber. Plasmas are electrically neutral, which means that the number of positive and negative ions is the same. Electrons are pushed by the electric field towards the anode, and used to excite the gas, feeding the plasma. It is common to have magnets installed in sputtering devices; a magnetic field normal to the surface of the target makes the electron move towards the anode on a spiral path, as charged particles are affected by magnetic fields following the Lorentz equation.

$$\vec{F} = q(\vec{E} + \vec{v} \times \vec{B})$$

Equation 1.1 Lorentz's equation: the force ($\vec{F}$) acting on a charged particle in an electromagnetic field is the sum of two components. One given by the scalar product of the charge q multiplied to the electric field ($\vec{E}$), whereas the other is given by the cross product between the particle's speed ($\vec{v}$) and the magnetic field ($\vec{B}$), times the charge q .

A spiral trajectory increases the path for charged particles between anode and cathode, therefore increasing the chance of impact against unexcited gas molecules, creating denser plasma. Every time an ion hits the surface of the metallic plate with sufficient energy, some atoms are ejected, and its charge is transferred to the cathode; thus current is one of the main parameters to control the sputtering rate.

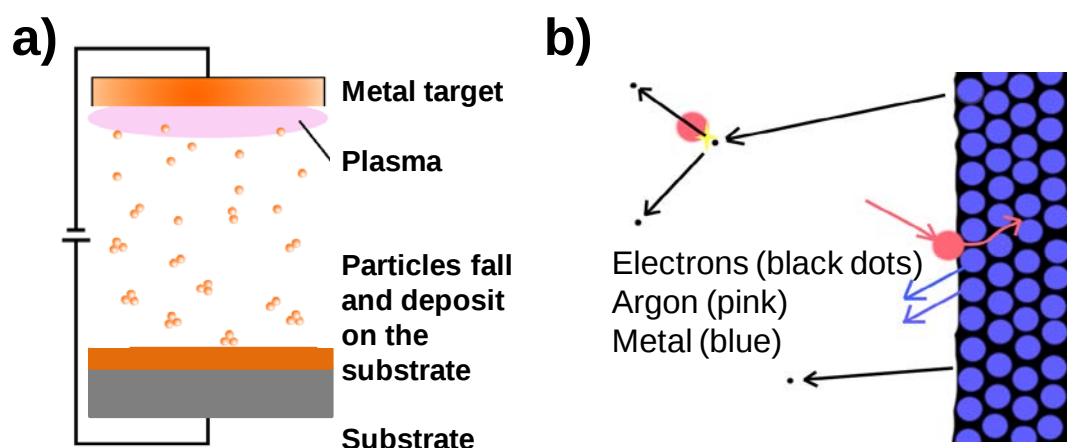


Figure 1.6 Schematic representation of a typical DC magnetron sputtering device a), and the physical process b).^[XIV]

1.2.3 Sputtering into liquids

Early experiments in which nanoparticles were deposited onto silicon oils^[XIV,XV] and ionic liquids^[X,XII,XIV] suggested the possibility of generating nanoparticles directly into a medium, using a top-down processes. Following the concept, over the last few years, sputtering techniques have been developed for the synthesis of nanoparticles, by sputtering into low vapor pressure liquids.^[XI, XIII, XVI, XVII] The physics of the sputtering process is the same as for when creating thin films, the only difference is that the substrate on which is being sputtered is not made of a solid material. Only liquids with low enough vapor pressure can be used for this technique, as if too much evaporation occurs, both the plasma and the attached . If the liquid has a low enough surface tension, the sputtered material won't form a thin film, but will be dispersed into the liquid instead. At this point, are the characteristics of the liquid to define the fate of the material: if the liquid has moieties that could connect to the sputtered atoms and nanoclusters, then functionalized stable nanoparticles can form. In case this doesn't happen, then the liquid will have only a steric hindrance to particle growth.

Sputtering into liquid is a quite versatile technique for the synthesis of nanoclusters and nanoparticles, as it allows the usage of a quite broad range of materials as sputtering target, plus, by choosing the monomer (dispersing medium) in a smart way, it's possible to functionalize the nanoparticles and attain control over the particle composition and size. Sputtering is a vacuum technique that uses ionized gas to detach atoms and clusters from a chosen metal target, meaning that also controlling the composition of the gas present in the

sputtering chamber can be an effective way to control nanoparticle composition and formation mechanism.

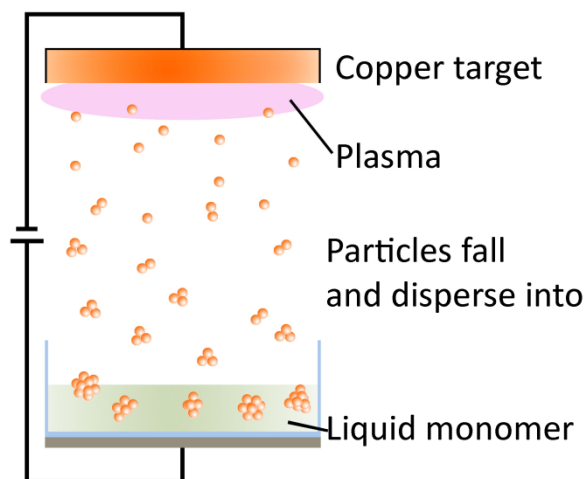


Figure 1.10 Schematic representation of a sputtering process into liquid.

1.2.4 Photoluminescent nanoparticles and sputtering

Metal nanoclusters (NCs) can be defined as isolated particles composed by two to one hundred atoms. Particles in this size show peculiar optophysical properties due to the discretization of their energy states caused by their size. In case of metal nanoclusters, among other properties, a very strong, size dependent, photoluminescence appear. Fluorescent materials used in the past were mostly made of organic dyes or semiconductor quantum dots (QDs), which presented some problems such as low photostability in case of the dyes, and toxicity in the case of semiconductor QDs. Metallic NCs can replace old materials for most applications, thanks to their very small size, high stability and the possibility to modify their surface properties to fit with the applications.

Since 1924 Policard's work,^[XVIII] photoluminescent materials have been used for imaging of organic tissues (bioimaging). A lot of research has been going on to improve the quality and intensity of the fluorescence, aiming at the production of biocompatible materials which have high absorbance, high quantum yield, narrow emission and large Stokes shift.

Sputter metal into liquid is a technique that allows the synthesis of extremely fine and well dispersed nanoparticles, whose size and composition depends on the sputtering conditions (temperature, current, sputtering target to sample distance, atmosphere in the chamber, etc...) as well as the capping liquid used. With this method nanoclusters exhibiting

photoluminescence have been synthesized, and improvements of the technique for better control over the sputtered nanoclusters are, to date, an open research field.

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2 PREPARATION OF TiO_x NANOPARTICLE-DISPERSED OPTICAL RESIN VIA SPUTTERING ONTO LIQUID

2.1 Introduction

Manipulation of macroscopic properties of materials is something scientist have been working on for decades, for all sort of applications. The higher the versatility of the material is, the greater the chances of producing technological breakthroughs are. One sector that has seen great development in recent years, is the production of composite inorganic-organic hybrid materials, particularly in the case of nanoparticles (NPs) embedded into polymers. Polymers themselves can show a broad range of properties depending on their structural units, but they can be controlled and tuned by dispersing nanoparticles into their matrix. This NPs-incorporated materials have been produced through various methods¹⁻⁶, for many different purposes^{1,4,7-11}.

When it comes to synthesize nanoparticles into a polymer matrix, many approaches are possible, as explained briefly in chapter 1. Depending on the final purpose of the experiment, one synthetic approach could be advantageous over others: in case of high refractive index (RI) optical nanocomposites, it is important to have no leftover by-products into the matrix, as they'd disturb both the optical properties and hinder the RI. Therefore, a direct preparation of pure and well dispersed NPs without need of post-purification is of

considerable interest. With recent developments in sputtering techniques, it is now possible to sputter directly into liquid media, and obtain pure NPs-organic hybrid materials. This technique for the synthesis of nanocomposite materials, which in recent years became a quite active research field, allowed the synthesis of nanoparticles with controlled composition and particle size in a single step process, such as the recently-reported synthesis of photoluminescent metal NPs via sputtering in various liquid media.¹²⁻²¹

Titanium oxides are important wide-bandgap semiconductor materials, used as UV-active photocatalysts, and have many applications as UV-block material in sunscreens. Titanium oxides are also well known for being one of the highest refractive index oxides, and for this property it has been used to increase the refractive index of thin films^{7,22} and polymers.^{7,9} Modification of the electronic structure of TiO₂ via doping or introducing oxygen defects can narrow the bandgap and extend its energy harvesting applications towards the visible region.²³ The one stoichiometric TiO can also be used for this purpose.²³ Composition (oxidation state) and particle size control allow the use of titanium oxide nanoparticles for tuning the optical properties of hybrid materials containing such particles. In fact, dispersing nanoparticles in polymers is a very simple and effective way to modify the macroscopic properties of materials.

Despite the fact that conventional chemical synthesis can produce TiO₂ NPs, to the best of our knowledge very small (1–10 nm in diameter) and clean TiO₂ NPs dispersed in polymers for use in advanced optical applications have not yet been reported. It is still a challenge to use chemical methods for synthesizing titanium oxides with controlled composition since the decomposition of titanium complexes can result in various undesired TiO₂ phases. Finally, previously reported fabrications of hybrid films or polymers containing titanium or titanium oxides NPs featured multi-step processes that are complicated and often produce products with a greater presence of contaminations.^{4,7,8,9,22,24} With its having many advantages over more traditional chemical synthesis in terms of purity and composition control with regards to oxidation state, we posit that direct sputtering of Ti under controlled atmospheric conditions could be a valuable technique for the synthesis of different titanium oxides.

2.1.1 Aim of this chapter

In this chapter we aim at the synthesis of a nanocomposite material containing titanium oxide nanoparticles. A transparent resin containing titanium oxide nanoparticles (NPs) is prepared using a molten matrix sputtering (MMS) technique. The low vapour

pressure of the liquid, pentaerythritol ethoxylate (PEEL) substrate permits the use of this vacuum technique directly with liquid PEEL under stirring conditions in order to obtain uniform dispersions of NPs. We found that it is possible to synthesize titanium oxide NPs with diameters of less than 5 nm with a controlled composition by simply adjusting the sputtering atmosphere. Furthermore, as the electronic structure of the TiO_x NPs changes depending on the particle size, crystallinity and degree of oxidation, we were able to modify the optical properties of PEEL and the resin by embedding TiO_x NPs in the matrix. The enhancement of the refractive index of a resin containing TiO_2 NPs was also demonstrated. This synthetic method is promising for the advanced preparation of high purity TiO_x NPs without using a reducing agent and leaving by-products for various applications in optical devices, energy conversion, and light harvesting in the UV visible region.

2.2 Experimental section

2.2.1 Materials

Pentaerythritol ethoxylate (3/4 EO/OH) (PEEL, $\text{C}[\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}]_4$), whose molecular structure is shown in figure 2.1, with an average molecular weight of $270 \text{ g}\cdot\text{mol}^{-1}$ was purchased from Sigma-Aldrich. *m*-Xylene diisocyanate (*m*-XDI) was purchased from TCI, Japan. Titanium 99.5% pure sputtering target (50 mm diameter, 3 mm thick) was purchased from Nilaco, Japan. All materials were used as received.

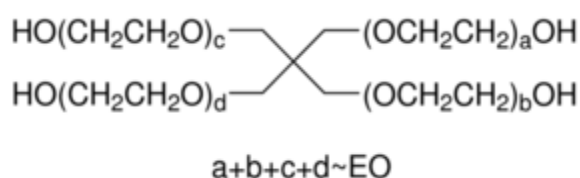


Figure 2.1. Molecular structure of Pentaerythritol ethoxylate.

2.2.2 Synthesis by sputtering

A magnetron sputtering device was modified in order to be better suited for the synthesis of nanoparticles dispersed in liquid samples (Figure 2.2). A mechanical stirring device was installed in the sputtering chamber. A turbo molecular pump / oil rotary pump system and a gas purging system equipped to the sputtering device were used to control the vacuum level and atmosphere inside the sputtering chamber. A cooling system was installed

to avoid overheating of the target and a temperature control device was used to maintain the PEEL at a constant temperature during the experiments.

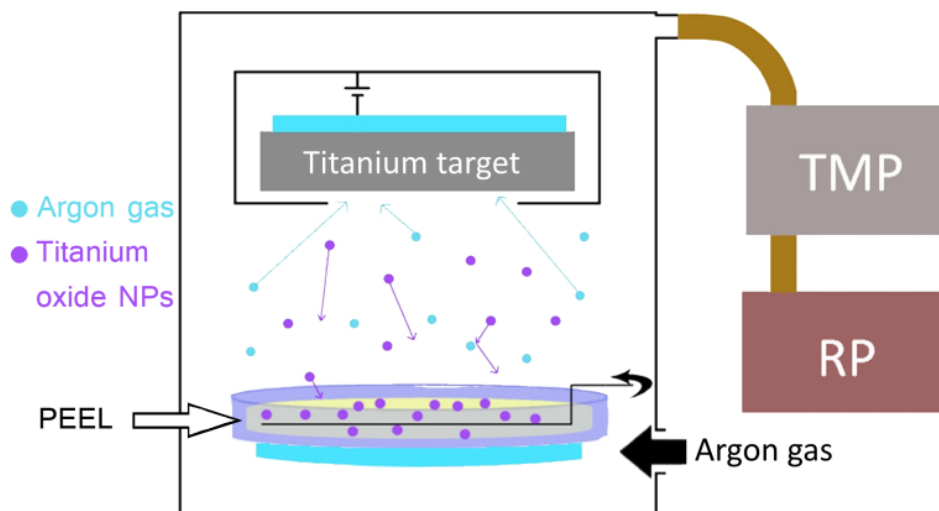


Figure 2.2. Schematic diagram of the sputtering device, and its stirring mechanism.

2.2.3 Preparation of titanium oxide NPs dispersed in PEEL

PEEL was dried under vacuum at 125 °C in order to eliminate dissolved gases and volatile molecules. 2.5 g of PEEL were then placed in a glass petri dish with an inner surface area of 5.7 cm², and inserted in the sputtering chamber. The surface of the liquid PEEL was positioned 60 mm below the Ti sputtering target, and PEEL was stirred at a constant 60 rpm. At least 10 cycles of evacuation (up to $\sim 10^{-2}$ Pa) and injection of Ar gas (up to 2.0 Pa) were performed in the chamber. After this repeated purging and re-filling, the pressure of the chamber was then adjusted to 2.0 Pa with Ar flow and the sputtering was initiated, generating and trapping the NPs in the liquid PEEL.

During sputtering, Ar gas was introduced into the chamber in order to change the sputtering atmosphere. With sputtering time, the sputtering atmosphere changed as indicated by a change in cathode voltage (Figure 2.3) from 310 to 265 V, which corresponded to the colour of the plasma changing from blue to green. Hereafter, we use the color (“blue” and “green”) of plasma to refer to the sputtering mode.

The total sputtering time was modified for each sample from 1 to 3 h (divided in intervals in order to avoid extreme overheating of the sputtering target and to select the sputtering plasma conditions), with a sputtering current of 400 mA and the atmosphere

inside the sputtering chamber was varied in order to control the oxidation states of the synthesized titanium oxide NPs. More detailed reaction conditions are given in Table 2.1.

Table 2.1. Sputtering time of Ti into PEEL for the preparation of samples and corresponding refractive index increments of the obtained samples.

Sample	Sputtering time (min)			Relative index increse (10^{-3})
	Blue ^a	Green ^b	Total	
PEEL	0	0	0	0
1	60	0	60	12.2
2	60	60	120	8.8
3	60	120	180	7.6
4	0	120	120	-4.5
5	30	30	60	4.1
6	30	60	90	3.6
7*	0	90	90	NA
8*	0	180	180	NA

^acathode voltage 310 V, ^bcathode voltage 265 V, *for SAXS measurement

2.2.4 Preparation of titanium oxide NPs embedded urethane resin

PEEL with dispersed TiO₂ NPs and *m*-XDI were mixed under vacuum at 1:2 molar ratio. The polymerization occurred through the formation of urethane linkages. During this process, the TiO₂ NPs acted as a catalyst and accelerated the polymerization. Because polymerization is an exothermic process, an increase in the reaction speed causes an increase in the temperature. An ice bath was used to cool the reaction in order to prevent the formation of bubbles in the polymer. The liquid was then poured in a mould where it rapidly solidified, and was then heated in an oven for 6 h at a maximum temperature of 130 °C. After the polymers were cooled to room temperature, the final titanium oxide-containing rigid resins were obtained.

2.2.5 Characterization

UV-Vis spectra of liquid samples were obtained using a PerkinElmer Lambda 750 spectrophotometer immediately after sputtering. Fused quartz flat cuvettes with optical path of 10 and 1 mm were used to perform the measurement.

Transmission electron microscopy (TEM) measurements were performed using a TEM Hitachi H-9500 (acceleration voltage of 300 kV) and a JEOL JEM-ARF200F (200 kV). TEM samples of sputtered NPs dispersed in PEEL were prepared by adding a drop of NP-containing PEEL on a carbon-coated Cu grid, which was then dipped into dried ethanol for 40 min. Other TEM observations were conducted on directly sputtered NPs mounted onto carbon-coated TEM grids, which were prepared by placing grids next to a vessel containing PEEL for a few seconds. Similar sputtering parameters were used as they used when sputtering onto PEEL.

Refractive indices of the NP-embedded resins with parallelepiped shape ($5 \times 7 \times 15$ mm) adequately polished on two sides was measured using an Abbe refractometer Atago DR-M4 at a wavelength of 589 nm (Na D line).

X-ray diffraction (XRD) measurements were performed on a Miniflex II diffractometer (Rigaku).

Small-angle X-ray scattering (SAXS) measurements were performed at the Photon Factory of the High Energy Accelerator Research Organization on the BL-6A beam line, in order to estimate the size distribution of Ti oxide NPs dispersed in PEEL. The detector used was PILATUS, at a distance of 2040 mm from the sample. The incident X-ray wavelength used was 0.150 nm, incident on a 0.3 mm thick sample for 60 s.

The cathode voltage was measured using a Graphtech midi Logger GL220 directly connected to the sputtering head while sputtering.

2.3 Results and discussion

2.3.1 Formation of different titanium oxides via sputtering in controlled atmosphere

The composition of the sputtered material is strongly related to the atmosphere in the sputtering chamber, as reported by Dreesen et al.²⁸ In their study, by controlling the oxygen flow rate into the sputtering chamber, they were able to sputter a film of metallic titanium and its oxides with low oxidation states when the O₂ flow was below a certain threshold, but they otherwise sputtered titanium dioxide.²⁸ This threshold was indicated by a change in the cathode voltage, which was constant at a high oxygen flow rate but diminished as the oxygen flow rate was decreased. This result suggests that the cathode voltage can be used as an

indirect but quantitative indicator for the atmosphere inside the sputtering chamber: a high oxygen atmosphere corresponds to the formation of TiO_2 , and a low oxygen one corresponds to the formation of titanium and titanium oxides with lower oxidation state. In the present study, we introduced only Ar into the sputtering chamber after pump-purging, leading a reduced oxygen content in the atmosphere inside the chamber with prolonged sputtering time.

We recorded the drop of the cathode-voltage from 310 V (high O_2) to 265 V (low O_2), as well as the change of the plasma colour from blue to green with an increase in the sputtering time (Figure 2.3).

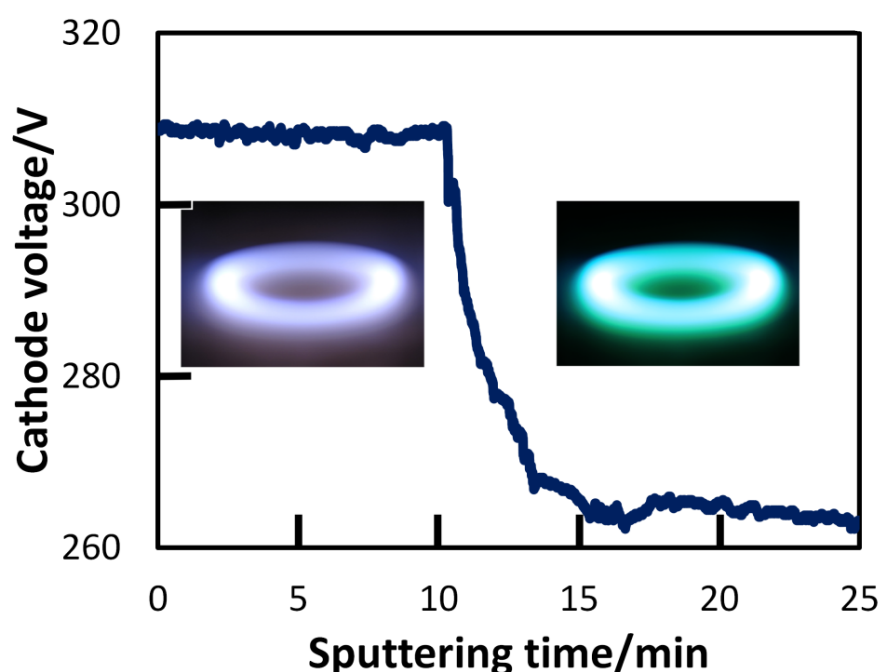


Figure 2.3. Typical cathode voltage curve that accompanies the change between the two sputtering modes: blue sputtering on the left, and green sputtering on the right.

A change in the atmosphere within the chamber from a high oxygen atmosphere to a lower one can lead to the formation of different surface oxides on the sputtering target. The change in target surface materials from titanium oxides with high oxidation state to titanium oxide with lower oxidation state is thought to be the reason for a drop in the cathode voltage. This also results in a change of the sputtered species that is reflected also by a variation in the plasma colour, from blue to green. Therefore, looking at these two parameters, we could

control the atmosphere of the sputtering chamber in order to synthesize TiO_x NPs of different oxidation states from TiO to TiO_2 and to prepare monomer liquids and NP-containing resins with tunable optical properties.

Then, considering about the differences among the two sputtering modes, we calculated the sputtering speed for high and low oxygen concentration within the chamber, by measuring a sputtered thin film deposited on a Si wafer in the two conditions. Figure 2.4 shows the thin films as observed using a scanning electron microscope (SEM).

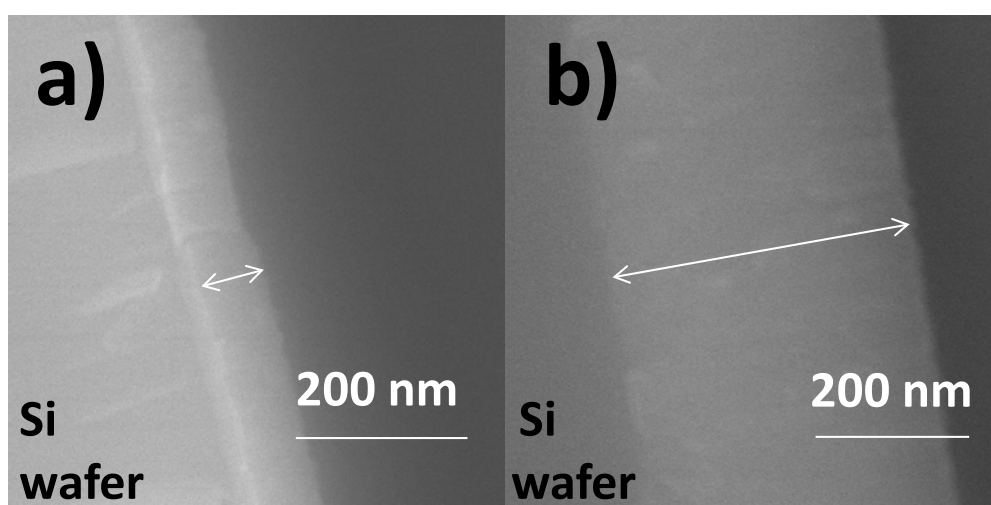


Figure 2.4. SEM images of thin films sputtered in a) high oxygen, and b) low oxygen conditions.

Table 2.2. Average sputtering rates for blue and green plasma sputtering as calculated by measuring the thickness of sputtered films by SEM.

	Sputtering rate [nm/min]
Blue plasma	29 ± 10
Green plasma	63 ± 10

The formation of TiO_2 and TiO under different sputtering atmosphere was confirmed by XRD measurements for the NP thin film produced under green and blue plasma sputtering conditions (Figure 2.5). Green-plasma sputtering produced a neat TiO film ((111),

(200), (220) and (222) crystal planes of TiO in the order from left to right, as shown in Figure 2.5a), whereas under blue plasma sputtering, while only peaks corresponding to the TiO phase were detected, they have significantly weaker intensities to the high background (Figure 2.5b).

This indicates that the TiO₂ and/oxygen deficient TiO₂ NPs generated via blue plasma sputtering are either too small (note that by measuring the thickness of the films formed under blue and green plasma sputtering for a certain time, it was found that the blue plasma sputtering rate was lower than that of the green plasma sputtering, as shown in Table 2.1) or amorphous in nature, as often reported for room temperature TiO₂ formation.²⁸⁻³⁰

In fact, after annealing at 500 °C for 2 h under N₂, in addition to the XRD peaks of TiO, signals related to TiO₂ are evident at 25.2° and 54.8° for the anatase phase and peaks at 27.4°, 36.1°, and 54.3° in 2θ for the rutile phase (Figure 2.5c), as a result of either the growth of small crystalline NPs or the crystallization of the amorphous NPs.

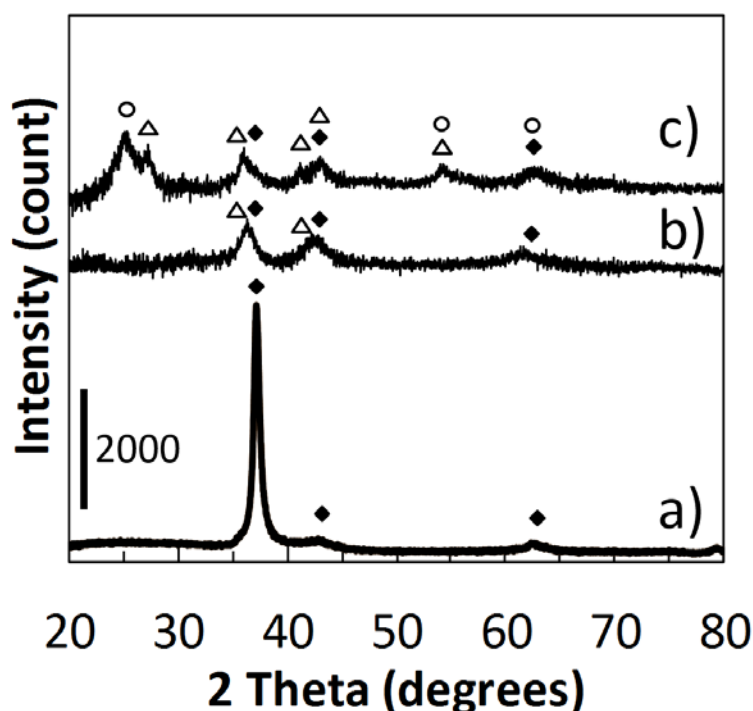


Figure 2.5. XRD patterns of samples obtained via (a) green plasma sputtering; (b) blue plasma sputtering; (c) corresponds to sample (b) after annealing at 500 °C for 2 h under N₂. TiO (JCPDS: 00-008-0117) is noted with solid diamond (◆). Tetragonal anatase TiO₂ (JCPDS: 01-071-1168) and rutile TiO₂ (JCPDS: 00-021-1276) are noted with open circles (○) and triangles (Δ), respectively.

As the gradual change from blue to green plasma sputtering occurred, some intermediate TiO_x ($1 < x < 2$) NPs could be expected in samples that underwent blue plasma sputtering. In order to simplify our analysis, we assume two distinct sputtering modes corresponding to blue- and green-plasma sputtering.

2.3.2 Optical properties of PEEL containing titanium oxide NPs synthesized in different plasma conditions

Various PEEL samples containing titanium oxide NPs were prepared under green-plasma sputtering, blue-plasma sputtering, and mixed blue- and green-plasma sputtering to examine their tuneable optical properties. Detailed experimental conditions are given in Table 2.1.

Blue-plasma sputtered samples demonstrate high transparency with respects to visible light, and a strong absorbance in the UV region when compared to pure PEEL, which does not show a high absorbance in that region (Figure 2.6a). Absorption in the UV region is strong in all the blue-plasma sputtering related samples, an expected behaviour for composites containing titanium oxide NPs.³¹ In the case of samples that underwent some green-plasma sputtering, a broad absorption centred at 520 nm appears in the visible region (e.g. samples 3 and 4 as shown in Figure 2.6). Similar phenomenon is also observed for samples 5 and 6 that underwent 30 min blue-plasma sputtering and different green-plasma sputtering times (Figure 2.6). It is noted that as the green-plasma sputtering time increases, the absorbance intensity centred at 520 nm increases and the samples become noticeable darker (Figure 2.6c). The absorption centred at 520 nm is assigned to TiO NPs, as reported elsewhere.²³ Furthermore, the red shift in UV-Vis absorption (Figures 2.6a,b and 2.7) as a function of the green-plasma sputtering time (for samples obtained in mixed blue- and green-plasma sputtering) is an indication that these samples are dispersions of mixed TiO_2 , TiO and TiO_x ($1 < x < 2$). These results can be explained due to the gradual lack of oxygen in the chamber as the plasma atmosphere changes, resulting in the sputtering mode shift from blue to green. As a result, green-plasma sputtering did not allow for a complete oxidation of metallic titanium into its most stable oxide (TiO_2), instead forming the monoxide or TiO_x . This finding is consistent with the XRD results discussed above. The visible absorption obtained from the sample containing TiO NPs under green-plasma sputtering conditions

allows the use of titanium oxides for energy conversion and harvesting in not only UV light, but also in the visible spectrum.

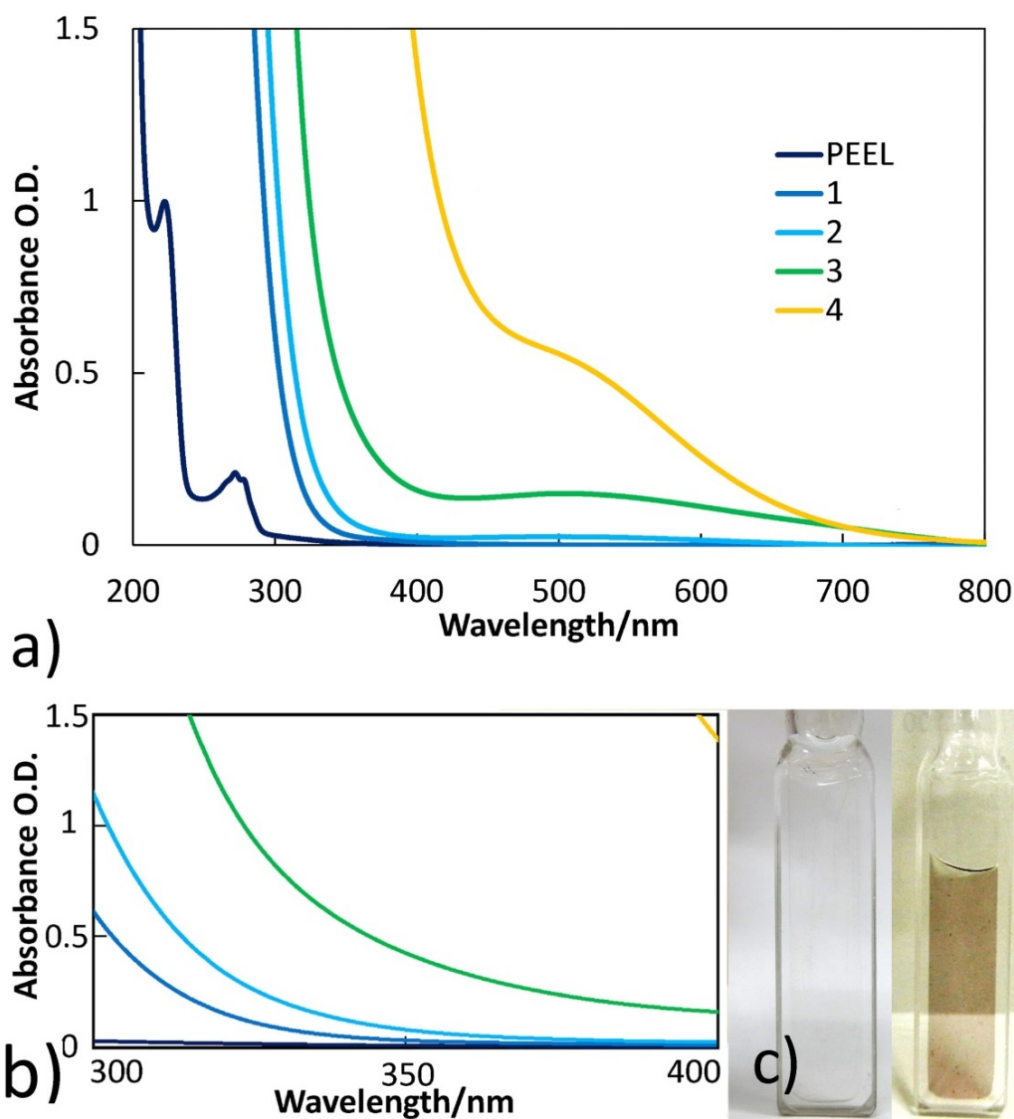


Figure 2.6. (a) UV-Vis spectra of NP-containing PEEL after 60 min of blue plasma sputtering and 0, 60, or 120 min of green plasma sputtering (samples 1, 2 and 3, respectively), and after only 120 min of green plasma sputtering (sample 4). (b) The enlarged UV-Vis spectra for region from 300 to 400 nm. (c) Photograph of sample 1 and 3 under room light right after synthesis.

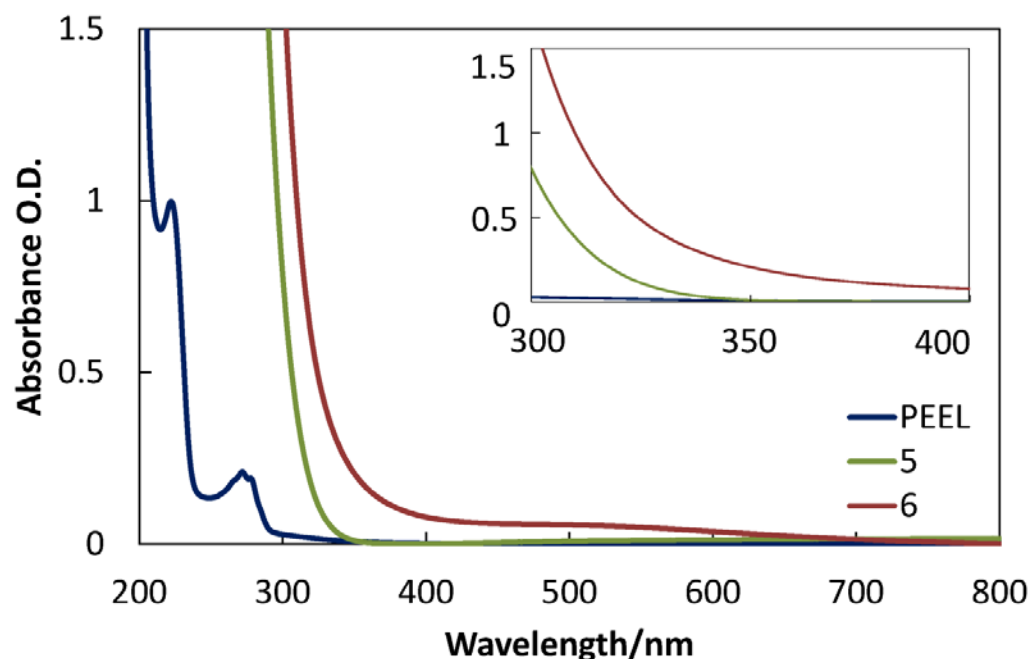


Figure 2.7. UV-Vis spectra of PEEL, and the 30 minutes blue-plasma sputtered samples that underwent to also 30 and 60 minutes of green-plasma sputtering for sample 5 and 6 (also see Table 2.1), respectively.

2.3.3 Size of titanium oxide NPs in PEEL

TEM was used for characterization of the sputtered samples, and it allowed a measurement of the sputtered nanoparticles' size (Figure 2.8, 2.8a,b). Images of the samples sputtered into PEEL in blue- and green-plasma for 1 h are shown in Figures 2.9a and 2.9b. NPs obtained in blue-plasma sputtering have a slightly smaller size (2.3 ± 0.4 nm) than that in green-plasma sputtering (2.8 ± 0.5 nm), according to the lower sputtering rate in the blue-plasma condition. Titanium dioxide crystalline structure was also observed via TEM (Figure 2.8). A large number of NPs were clearly observed for directly deposited titanium oxide NPs on TEM grids after 15 s sputtering (Figure 2.9c). For this case, clear images of NPs could be seen, and the average particle size is 4.6 ± 0.7 nm with quite uniform size over the whole area of the sample. In order to obtain a more precise size measurement of the NPs dispersed in liquid PEEL and a rough estimation of the particle size evolution for long time sputtering, we performed measurements using SAXS. The results shown in Figure 2.10 were obtained from liquid samples 7 and 8 produced by sputtering of titanium for 90 and 180 min in green-

plasma conditions. A long sputtering time and green-plasma sputtering were chosen, as it is known to have a higher sputtering rate than blue-plasma sputtering.^{28,32}

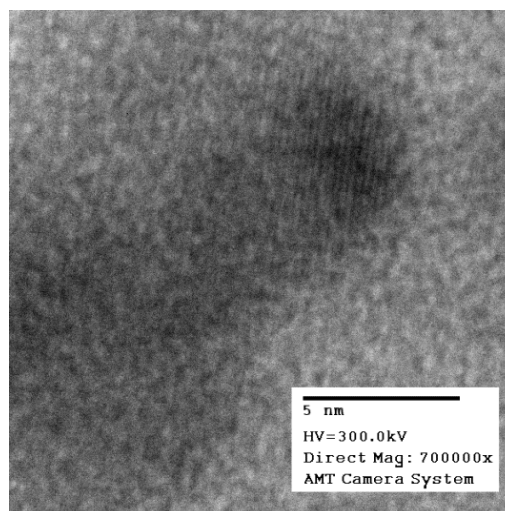


Figure 2.8. TEM image taken from a sample sputtered in blue-plasma condition for 30 minutes at 400 mA.

This experiment allowed us to get information about the maximal particle size in our samples. It can be noted that as the sputtering time is increased, the particle size increased slightly from 3.8 ± 0.6 nm (sample 7) to 4.4 ± 0.6 nm (sample 8), close to the size of the observed particles sputtered directly onto a carbon-coated TEM grid (4.6 ± 0.7 nm). This result strongly indicates that the titanium oxide NPs dispersed in PEEL were less than 5 nm in diameter, without aggregation during synthesis.

In summary, controlling the atmosphere of the sputtering chamber via monitoring the cathode voltage and plasma colour allows to control of the degree of oxidation for the obtained TiO_x NPs dispersed in PEEL. In all samples, uniform and well dispersed TiO_x NPs of less than 5 nm were achieved. The main product in blue-plasma sputtering conditions was TiO_2 (some oxygen deficient TiO_2 particles were also obtained) which do not affect the transparency of the NP-containing PEEL, while the green-plasma sputtering conditions yielded primarily TiO particles, which cause the NP dispersions to become coloured with high visible absorption.

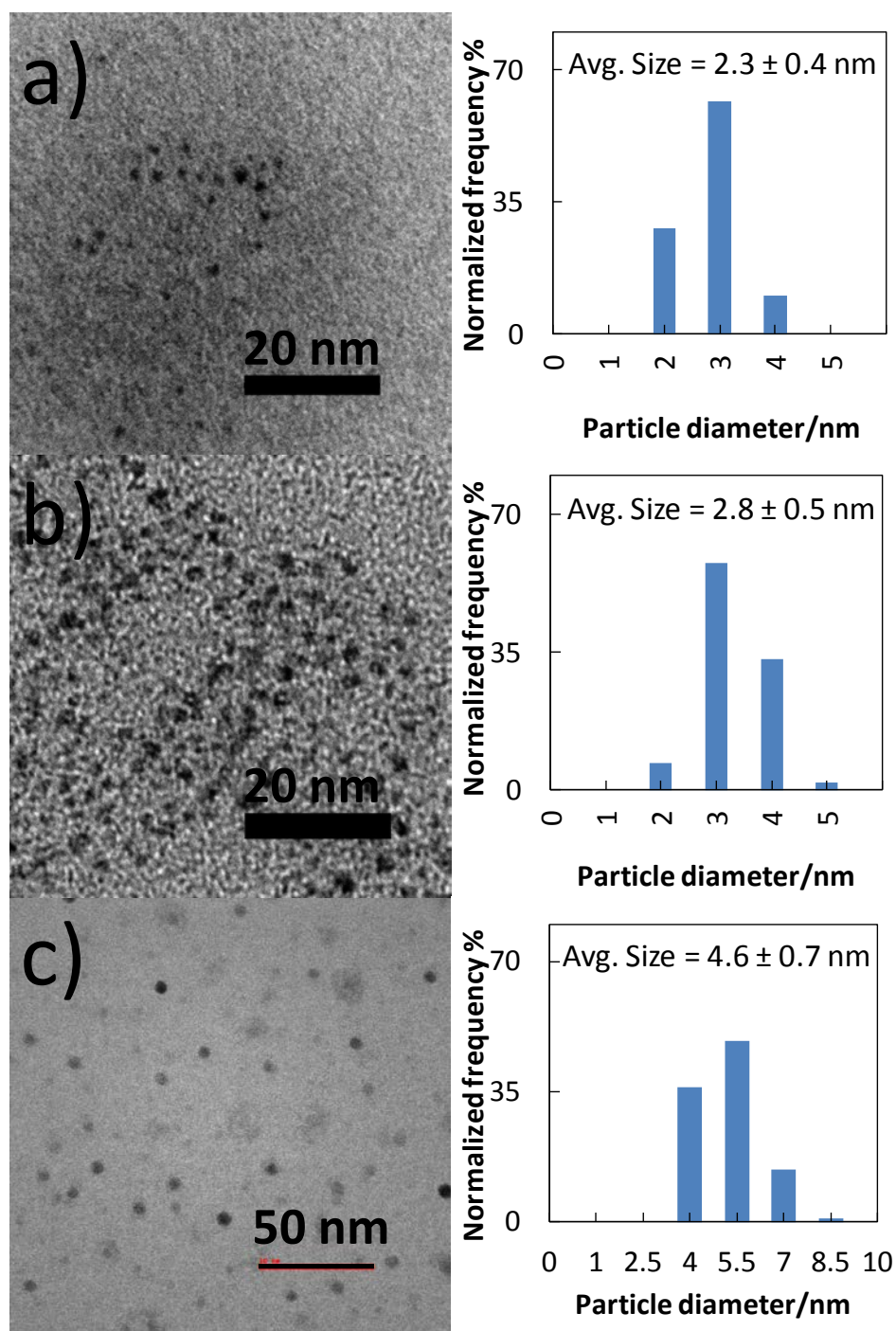


Figure 2.9. TEM images and size distribution of titanium oxide NPs dispersed in PEEL obtained via (a) blue-plasma and (b) green-plasma sputtering for 1 h. (c) TEM images the size distribution of the obtained titanium oxide NPs by sputtering directly on the TEM grid under green-plasma conditions.

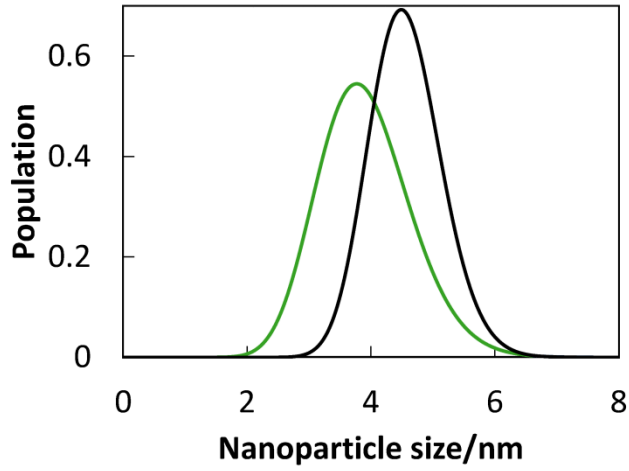


Figure 2.10. Particle size distribution of samples 7 (green) and 8 (black), as measured by SAXS.

2.3.4 Refractive index increment, colour and transparency of TiO_x NPs embedded in resin

As shown above, the sizes of the dispersed TiO_x NPs are one or two orders of magnitude smaller than the wavelengths of light in the visible region. This allows for negligible visible light scattering (Equation 2.1).²⁶ Therefore, the preparation of highly transparent resins from PEEL containing TiO_x NPs can be achieved. Figure 2.11 shows a series of resins exhibiting a high transparency; these resins are made from samples prepared in blue and green plasma. Moreover, owing to non-visible-light-absorption of TiO₂ NPs and their small sizes, the colourlessness and transparency of the resin made from sample 1 (60 min blue-plasma sputtering, Figure 2.11c) is comparable with that of resin made from pure PEEL (Figure 2.11b).

$$Q_{sca} = \frac{8}{3} \left| \frac{n^2 - 1}{n^2 + 2} \right|^2 \left(\frac{4\pi a}{\lambda} \right)^4$$

Equation 2.1. Represents the scattering probability (Q_{sca}) of a photon with wavelength λ passing through a nanoparticle of radius a . As the radius becomes smaller than the light wavelength, the scattering probability drops with a power of four dependence.

$$n = \sqrt{\sum_i n_i^2 V_i}$$

Equation 2.2. Gives an approximation of the refractive index (n) of composite compounds, starting from the refractive indices (n_i) of each component (i) and its corresponding volume fraction (V_i).

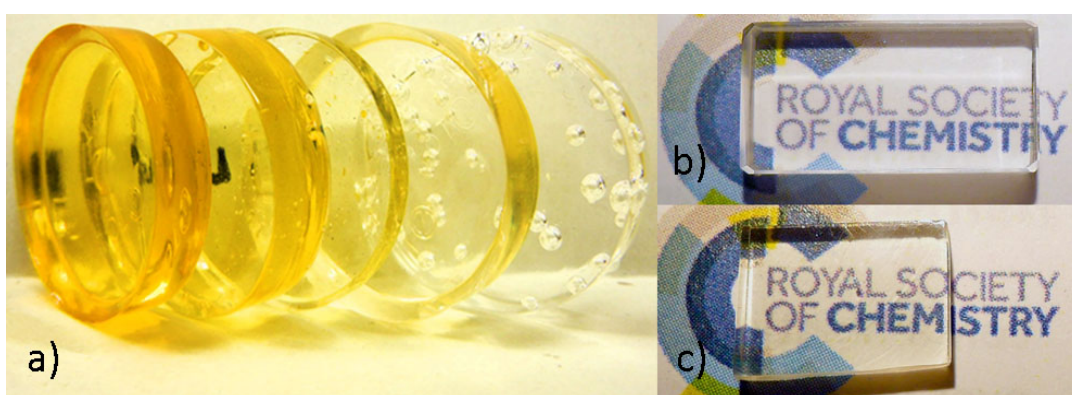


Figure 2.11. Photograph of the resins, with green sputtering time decreasing from left (120 minutes) to right (no green sputtering)(a), and pictures of resins made from pure PEEL (b) and from sample 1 (c).

Because addition of high refractive index particles, e.g. TiO_2 , into low refractive index polymer can improve the refractive index of the composite (Equation 2.2), we investigate the refractive index of various resins made using titanium oxide NPs dispersed in PEEL. The results in Figure 2.12 show the effect of titanium oxide NPs on the refractive index of the resin. Each dot represents the difference between the refractive indices of a NP-embedded urethane resin sample and of the pure resin. A positive value indicates an enhancement of the refractive index. The resin made from pure PEEL has a refractive index of 1.5586 ± 0.0005 , which increased to 1.5708 ± 0.0005 after 60 min of blue-plasma sputtering in optimal conditions (sample 1), corresponding to a refractive index increase of 0.0122 ± 0.0005 . Small increases on this scale were observed in all samples in relation to blue-plasma sputtering time. The increase in the refractive index is, at a constant sputtering rate, proportional to the blue plasma sputtering time, while inversely proportional to the green-

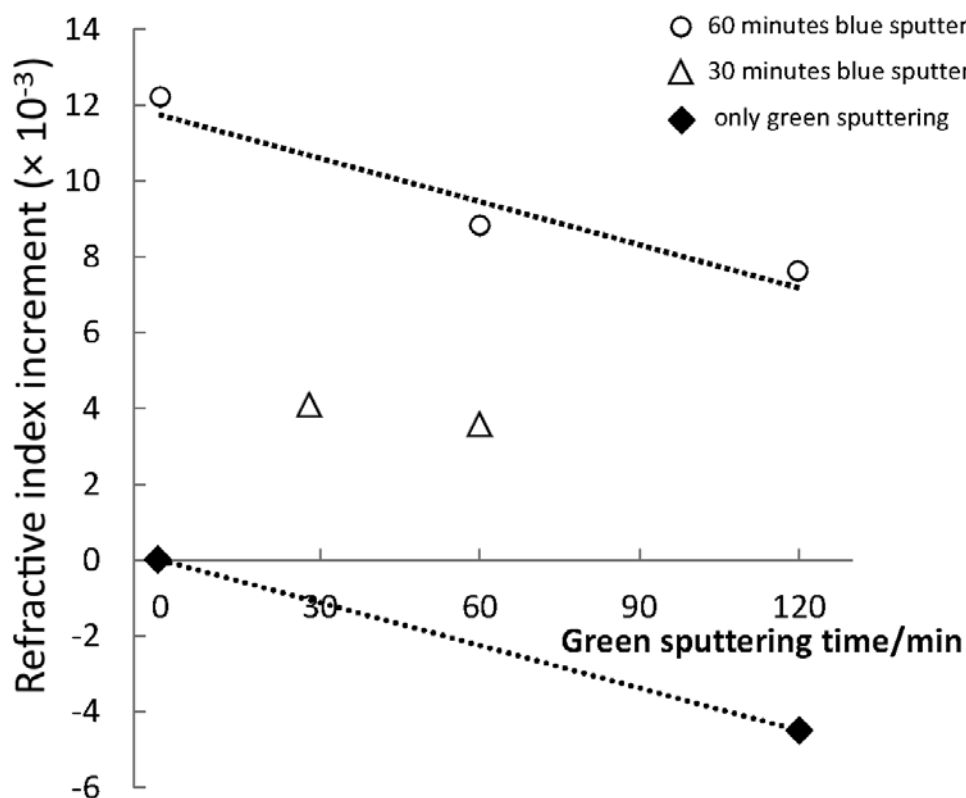


Figure 2.12. Refractive index changes of each sample after sputtering along with the effect of blue and green-plasma sputtering time. Each symbol corresponds to a set of experiments with blue-plasma sputtering time of 0, 30, and 60 min, in which the green-plasma sputtering time has been varied.

plasma sputtering time. Furthermore, this increment-to-TiO₂ ratio was in agreement with previously published results pertaining to other hybrid materials containing titanium dioxide.^{9,22}

As an extreme case, a sample that underwent only green-plasma sputtering (120 min, sample 4) showed a negative change in refractive index compared to that of pure resin. The results for mixed sputtering modes show how the blue and green plasma sputtering compete against each other in terms of increasing the refractive index of the composite materials. In particular, the refractive index measurements clearly demonstrate the importance of the TiO₂ formation process, as only blue-plasma sputtering can produce high index NPs. This demonstrates that the conditions for increasing the refractive index of low vapour pressure compounds involve TiO₂ formation during blue plasma sputtering.

In blue-plasma sputtering conditions the NPs are formed by etching the TiO₂ thin film that continuously regenerates on the titanium plate surface. On the other hand, when there is little oxygen in the atmosphere, atomic clusters of titanium and some titanium monoxide NPs get detached, which are subsequently oxidized to form a uniform TiO film. For each sample the

$$\nu = \frac{n_D - 1}{n_F - n_C}$$

Equation 2.3. Defines the Abbe number. The value of ν is used to evaluate the dispersion of light in materials: high values correspond to small chromatic aberrations. n_D, n_F and n_C are respectively the measured refractive indices of the material at the wavelength of the Fraunhofer D, F and C spectral lines (589.3 nm, 486.1 nm and 656.3 nm, respectively).³³

Abbe number was above 40; this value corresponds to materials with low light dispersion characteristic (Equation 2.3), making the samples suitable for optical applications.

As the degree of interaction between the PEEL and the NPs is low, this technique can theoretically be applied to any low vapour pressure monomer in order to obtain similar results. The amount of titanium oxide inserted into the matrix was calculated to be approximately 1.4 vol% of the nanocomposite. Considering the low loading amount of titanium oxide NPs, the photodegradation of organic moieties is seemingly negligible.²²

The low sputtering rate of our device affected the amount of titanium that could be sputtered, therefore, this limited the refractive index increase. By using higher sputtering rate devices this deficiency can be overcome, allowing the production of transparent resins featuring higher concentrations of TiO₂ NPs.

2.4 Conclusion

Our new molten matrix sputtering (MMS) was applied to a Ti target for the first time, synthesizing titanium oxide NPs of less than 5 nm embedded in PEEL. TiO₂ or TiO particles could be formed by controlling the atmosphere in the sputtering chamber. The optical properties of the obtained PEEL containing titanium oxide NPs was varied systematically by changing the atmosphere of the sputtering chamber. Urethane resins incorporating titanium

oxide NPs were obtained and the formation of TiO₂ positively contributed to increasing the refractive index of NP-embedded resin. The limiting factor in increasing the refractive index of the nanocomposite material was the sputtering rate, which was limited by an overheating of the titanium sputtering target. In the samples prepared in this study, NP agglomeration was not observed and the samples were stable over time. This preparation method is advantageous in allowing for the control of NP oxidation, optical properties, and achieving enhanced refractive indices in these kinds of NP-monomer systems.

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3 SYNTHESIS OF PHOTOLUMINESCENT COPPER NANOPARTICLES COMPLEXES VIA SPUTTERING ONTO THIOL

3.1 Introduction

3.1.1 Applied photoluminescent nanomaterials for biology

Over the past few years, there have been a lot of research about photoluminescent nanomaterials, and researchers' focus have been moving from organic dyes and quantum dots, to inorganic metallic nanoparticles. Cytotoxicity of quantum dots, as well the poor stability of the organic dyes have been important reasons, among others to start looking for new kind of materials. The improvement in the quality of the photoluminescence media with the introduction of inorganic metal NCs has allowed the development of many in vivo bio-imaging techniques.^[34-39] The most common materials used so far for the synthesis of photoluminescent NCs have been gold and silver, as they combine stability, to oxidation resistance and a high quantum yield.^[40,41] The numerous studies and the applications are promising, therefore it is important to develop new methods for the synthesis of fluorescent media.

3.1.2 Aim of this chapter

Experiments with gold and silver showed that it is possible to achieve high photoluminescence intensity,^[35-42] with sharp peaks, from metallic nanoclusters. The results obtained so far are impressive, as much as the price of the two noble metals' raw materials. For large scale applications, it is important to keep the prices down as much as possible, therefore we propose the use of thiol stabilized copper nanoclusters. Even though copper is more prone to oxidation compared to gold or silver,^[43] much research have been done in this direction, and copper nanoclusters have found possible application in many fields, such as catalysis, energy harvesting, bioimaging, sensors, medical field.^[44-55] The great interest in copper has led to the development of numerous approaches towards controlled syntheses of copper nanoparticles. Reduction of precursors triggered in various ways^[55-59] not only facilitated great progress in the field, but also opened up new challenges. However, for most chemical methods, copper salts, reducing agents, and protecting agents are required, causing problems related to impurity of the generated copper nanoclusters. As a quite new technique, sputtering into liquid permitted clean synthesis of fine and well dispersed nanoparticles.^[60-67] In fact, we used magnetron sputtering to disperse, at standard conditions, copper nanoclusters into pentaerythritol tetrakis (3-mercaptopropionate), which is a low vapour pressure liquid rich in sulphur. We describe the synthetic method, and characterize the products. We show that by sputtering into liquids allows to synthesize luminescent copper nanoclusters (emission at 445 nm), that with storage time turn into Cu₂S nanoparticle, which have luminescence at 630 nm. This is a definitely interesting feature, as it allows, if controlled, extra possibilities of tailoring chemically the products of this PVD technique. In fact copper sulphides have a broad range properties that can be tuned by varying the sulphur content, are stable, and therefore have broad potential applications.^[68-71]

The combination of a top-down technique under vacuum conditions and the use of a suitable liquid medium provides the possibility of controlling the physicochemical properties of the nanoparticles, and that is the results we pursue in this research.

3.2 Experimental section

3.2.1 Materials

Pentaerythritol tetrakis (3-mercaptopropionate), called PEMP from now on, was purchased from Sigma Aldrich, and used as received. Circular copper sputtering target 99.99% purity, 6cm in diameter, 3mm thick, was purchased by Nilaco (Japan). Solvents used

for sample purification, such as acetone, acetonitrile, toluene and chloroform were purchased from Kanto Chemicals.

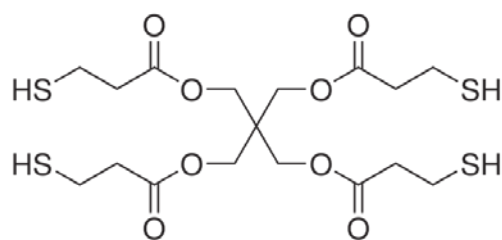


Figure 3.1. Molecular structure of pentaerythritol tetrakis (3-mercaptopropionate).

3.2.2 Synthesis by sputtering

The synthesis of copper nanoparticles was carried out following a standard procedure for sputtering into liquid. Before starting the synthesis it is important to eliminate impurities from the liquid medium, in particular volatile ones, like water. In order to do that, PEMP was heated to 100°C while being stirred in the vacuum (down to about 0.1 Pa) for two hours. Right after this treatment, 7 g of it were put in a Petri dish, and placed into the sputtering chamber. Vacuum up to $5 \cdot 10^{-3}$ Pa was done, after which Ar gas was injected. Multiple argon gas injections and evacuations were done in order to make the atmosphere in the chamber as uniform as possible. After this, once the pressure reached 2 Pa, sputtering could be initiated. The target-to-sample distance was set at 6cm, the temperature at 25°C and the sputtering current at 20mA, which can provide a satisfactory sputtering rate in case of Cu. Using such experimental parameters, the cathode voltage was 215 V. Sputtering was carried out for two hours for each sample, which was then taken and used for characterization for optical characterization.

Some experiments of sputtering into PEMP in air (without using any Ar gas) were carried out, in order to better understand the degree of oxidation of copper nanoparticles, and the role of the oxide in the chemical development of the compound.

3.2.3 Characterization

3.2.3.1 UV-Visible absorption spectra measurement

UV-Visible spectra were taken using a Shimadzu UV-1800 spectrophotometer on liquid using a fused quartz cuvette with 1 cm optical path. The samples were used as produced, without any dilution or treatment, and measured in the range between 200 to 1100 nm. In some cases a 1mm optical path fused quartz cuvette has been used instead.

3.2.3.2 Photoluminescence (PL) measurement

Photoluminescence measurements were performed on the same samples using a Jasco FP-6600 spectrofluorometer. 3-dimensional mapping, with excitation ranging from 200 to 800 nm wavelength and emission ranging from 300 to 900 nm wavelength, was performed first in order to identify all the photoluminescence peaks position. No cutoff filter was required for the measurement. Excitation and emission bandwidth were set to have, respectively, 5nm and 6 nm spectral bandwidth, whereas the measurement was carried out at a scan rate of 10,000 nm/min, with 10 nm steps. After PL mapping, more refined 2-dimensional spectra were taken, using 1 nm steps and a lower scan rate (2,000 nm/min).

3.2.3.3 Transmission Electron Microscopy (TEM) measurement

TEM and STEM measurements were performed using respectively a JEOL 2000 FX (200kV) and a FEI Titan G2 60-300 (300kV). TEM samples were prepared by depositing a droplet of dispersion onto a carbon-coated copper grid (or Mo grid in case EDS measurement was also performed) that was then dipped into acetonitrile for 40 minutes.

3.2.3.4 X-ray Photoelectron Spectroscopy (XPS) measurement

XPS measurements were performed using a JEOL JPS-9200. For XPS measurements, nanoclusters dispersed in PEMP were mixed with chloroform (sample: CHCl_3 = 1:4, weight ratio) then nanoclusters were separated from the matrix by an ultracentrifuge device (Himac CS 150GX Micro Ultracentrifuge) at 100,000 rpm for 30 min. The obtained nanoclusters were washed once more time with chloroform, centrifuged and then deposited on a pre-treated Si wafer. The surface treatment for Si wafers was performed by dipping Si wafers in aqueous solution of hydrofluoric acid (5%) to remove the oxide layers and smoothen the surface. After that the wafers were rinsed with water and ethanol, then dried and underwent ultraviolet-ozone cleaning to remove residual organic contamination on Si surface.^[72] The binding energy of Si (2p) was used as the reference for correcting the charging effect. The stored Cu-nanocomposite samples were stored in the liquid form in a glass container in the dark, and the XPS samples were prepared just before the measurement.

The binding energy of Cu, whatever its oxidation state, lies, with the sole exception of CuO, in a very narrow range of binding energies. Therefore, in order to understand the oxidation state of Cu it's common practice to recur to the Modified Auger parameter, defined by the following equation:

$$\alpha' = K(C_1 C_2 C_3) + E_b(C) = E_s - E_A + E_b(C)$$

in which $K(C_1C_2C_3)$ is the kinetic energy of a core level transition among the energy levels C_1 , C_2 and C_3 , whereas E_b is the binding energy of a core level C . The kinetic energy can be obtained by subtracting to the x-ray source energy E_s (in case of Mg filament is 1253.4 eV) the binding energy of the main Auger peak E_A (in the case of copper it's the LMM transition).

As the Modified Auger parameter comprises the subtraction of two measurable components, it is unaffected by eventual surface charge shifts. Wagner plot obtained from NIST XPS web database for Cu is shown in Figure 3.2, and it shows how the understanding of the Cu oxidation state has to go through the Modified Auger Parameter.

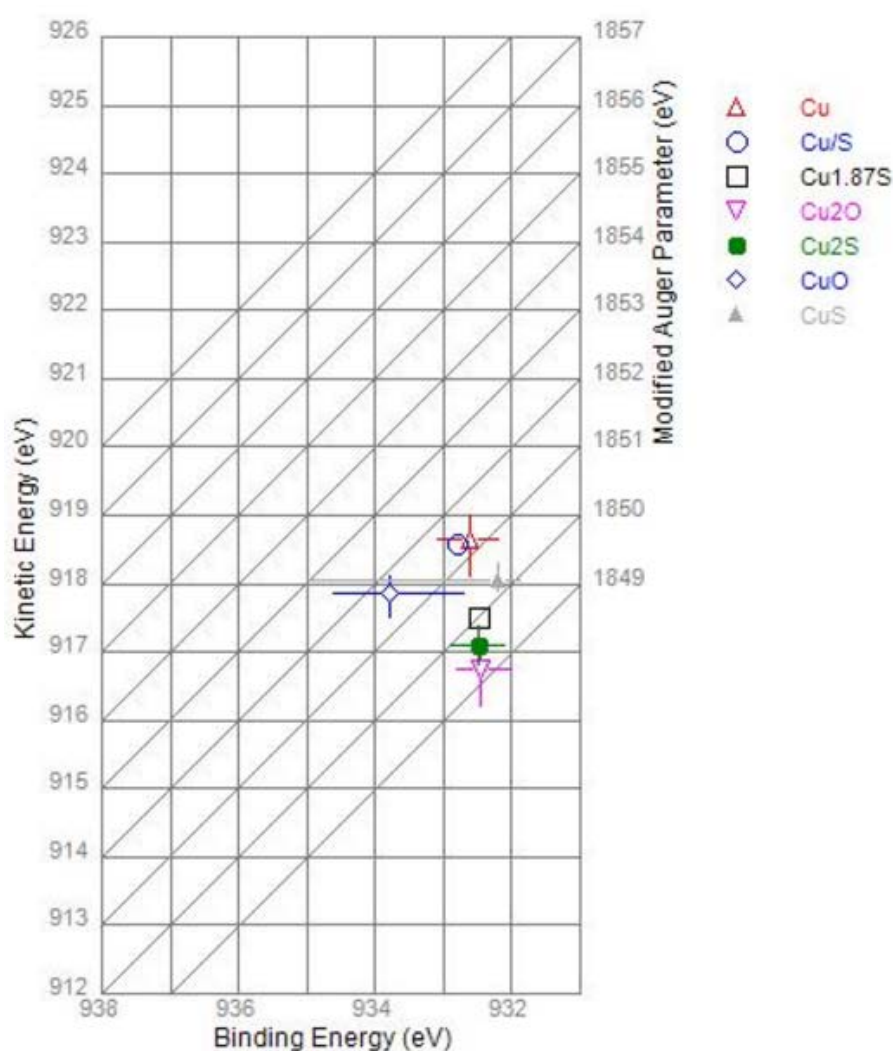


Figure 3.2. Wagner plot for copper compounds to show how the Auger parameters vary with different oxidation state.

3.3 Results and discussion

3.3.1 Characterization of as-synthesized samples

In figure 3.3 are shown UV-Visible spectra, photoluminescence and TEM image of some of an as-synthesized sample. As we can see, there isn't any absorption due to plasmon peak resonance of the copper nanoparticles, revealing that the copper dispersed in the sample occurs only in the form of very small nanoclusters. Furthermore, the synthesized nanoclusters showed sharp photoluminescence with excitation and emission maxima at 400 and 445 nm respectively, which is typical for copper nanoclusters (Figure 3.3b). Using the Jellium model,^[38] whose equation 3.1 for copper is shown below, it was possible to calculate the size of the nanoclusters based on the emitted photoluminescence.

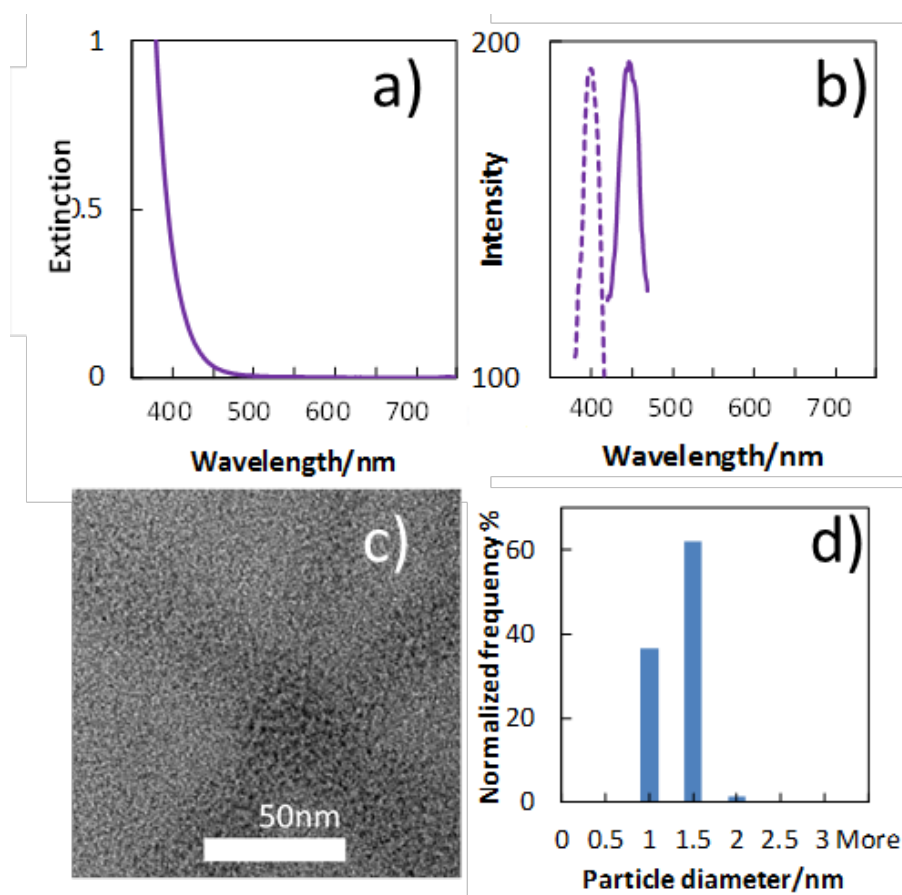


Figure 3.3. UV-Vis spectrum (a), photoluminescence spectra (b), TEM image (c), and size distribution (d) of the as-synthesized copper nanoclusters dispersed in PEMP. Dashed and solid curves in b correspond to excitation and emission spectra, respectively.

It indicated that the fluorescent nanoclusters with an emission at 445 nm are composed of 16 metal atoms. This size is close to the particle size of 1.1 ± 0.2 nm (diameter) observed by TEM (Figures 3.3c and 3.3d).

$$N = \left(\frac{E_{Fermi}}{E_{emission}} \right)^3$$

Equation 3.1. Estimation of the number of copper atoms in a cluster according to the Jellium model approximation. For emission at 445 nm, the number of copper metal atoms in a cluster is $N = 16$.

3.3.2 Optical properties of the nanocluster dispersion

As shown before, the as-synthesized samples do not show significant light absorption at visible frequencies. Different story happens when samples are stored at room temperature (20° C) for some time. In fact, as shown in Figure 3.3, an absorption peak started to appear at 480

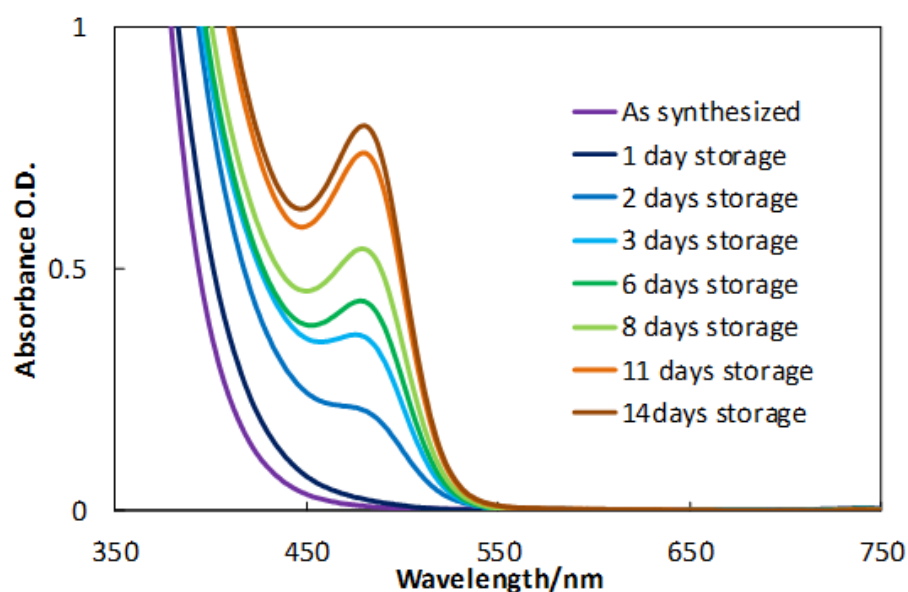


Figure 3.3. UV-Visible spectrum of as-synthesized and samples stored in the dark at 20°C for 1, 2, 3, 6, 8, 11 and 14 days. A sharp absorbance at 480 nm wavelength appears as the sample is stored for some time.

nm after two days of storage. The peak increased in intensity with time, and it continued for about ten days, after which the growth was much slower.

The change in the optical absorbance corresponded to a change in the photoluminescence (PL) properties over time (Figure 3.4). With storage time, the strong PL emission of the as-synthesized samples at 445 nm gradually decreased in intensity (band I, excitation wavelength: 400 nm); simultaneously a new PL emission band appeared at 630 nm (band II, excitation wavelength: 510 nm). Notably, neither the position of the original peak at 445 nm nor that of the new emission band at 630 nm changed during storage, meaning that the sources of the PL did not change. The increase in the intensity of band II the PL spectrum indicated formation of more PL centers. To clarify the origin of the new photoluminescence emission band, we further analyzed the particle size, structure, and composition during storage.

Samples that were, instead, stored at -20°C did not show any significant changes in terms of UV-Visible absorption or photoluminescence (Figure 3.5), meaning that at lower temperature, even though PEMP does not freeze, particle growth and chemical composition remains stable.

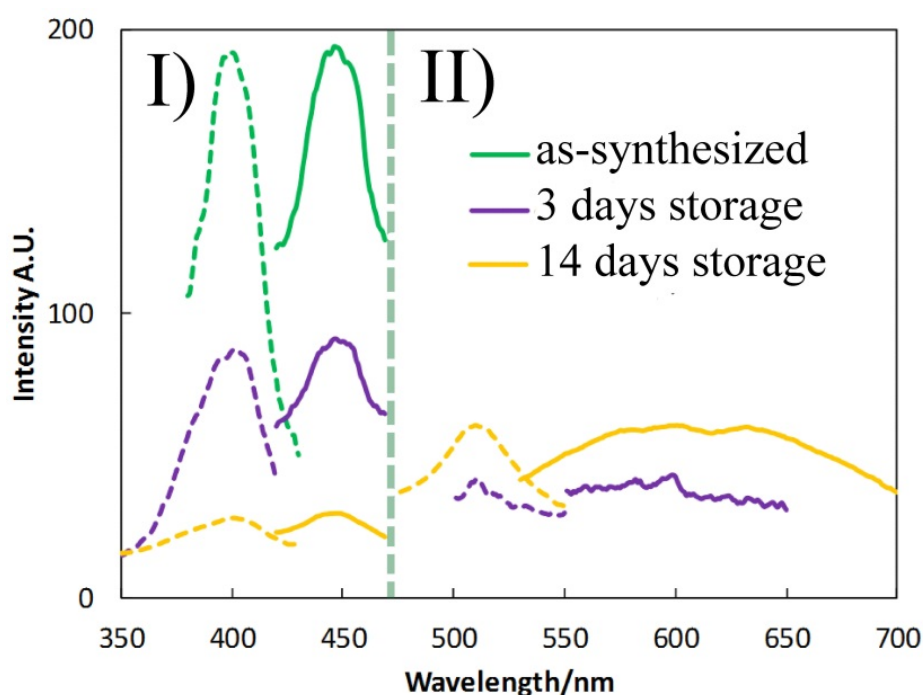


Figure 3.4. Photoluminescence spectra of the nanoclusters dispersed in PEMP for the as-synthesized and stored samples. Dashed and solid lines correspond to the excitation and emission spectra. Area I corresponds to the excitation at 400 nm and the emission at 445 nm; and area II corresponds to the excitation at 510 nm and the emission at 630 nm.

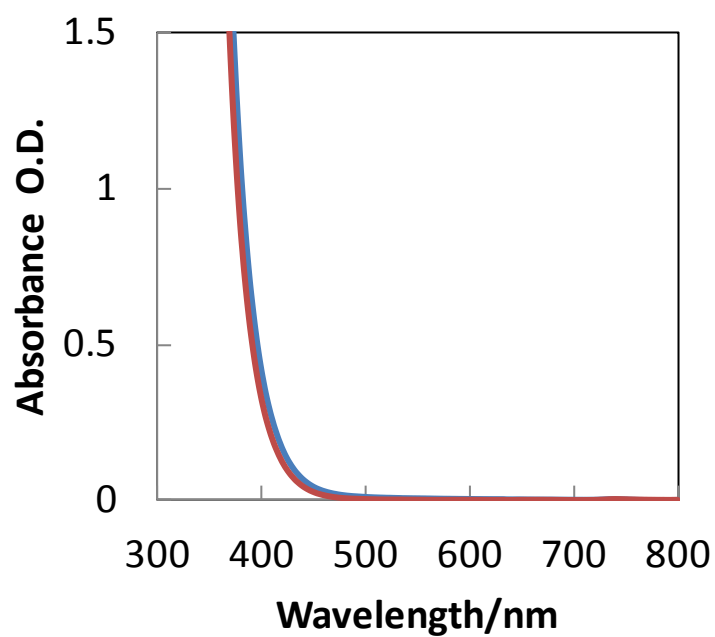


Figure 3.5. UV-Visible absorbance of an as-synthesized sample into PEMP (red line) and one stored for 10 days at -20°C (blue line). The absorbance didn't show significant changes over time, meaning that low temperatures stop the sulfidation of the nanoparticles.

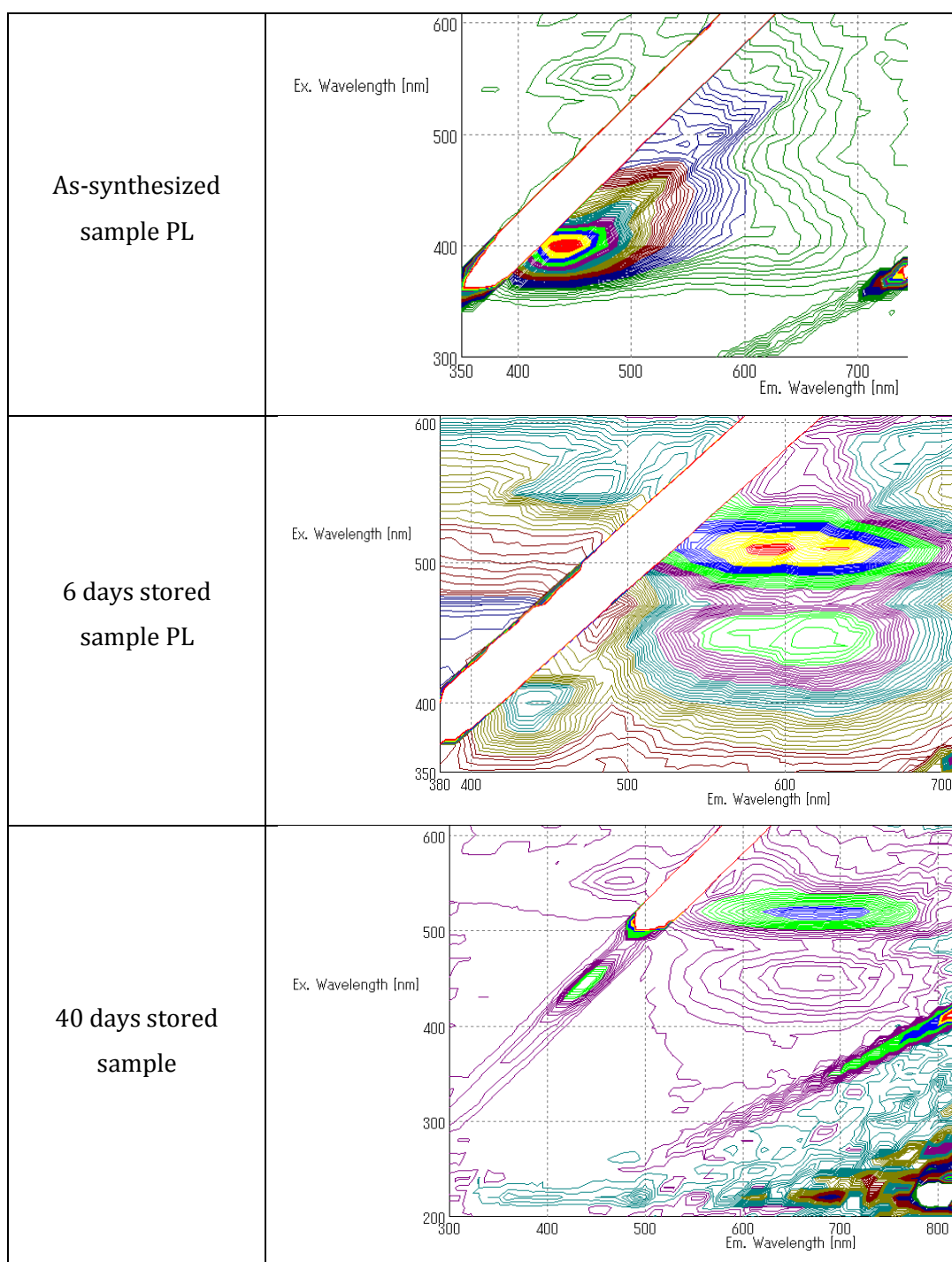


Figure 3.6. Photoluminescence qualitative 3d mapping of the nanoclusters dispersed in PEMP for the as-synthesized and stored samples.

The qualitative 3d PL showed in image 3.6 clearly explain the behavior of the optical properties. The as-synthesized sample shows photoluminescence at 445 nm that could be

linked to copper nanoclusters. With storage time, the intensity of the PL at 445 slowly decreases, whereas an emission peak at 630 nm (excitation at 435 nm) increases in intensity. A slight growth has been observed (Figure 3.8), but it does not justify the appearance of the new peak. In fact, metallic copper shows luminescent properties only for small nanoclusters; when the size

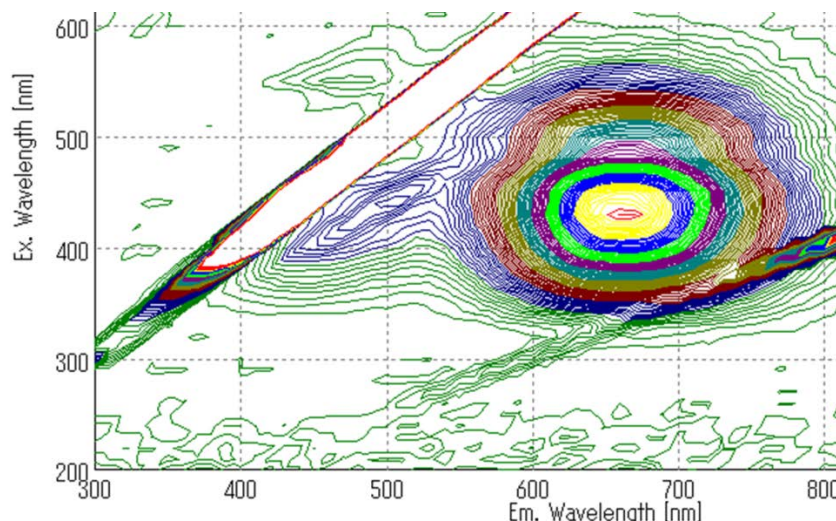


Figure 3.7. PL that appears when sputtering into PEMP in air.

increases it does not show PL anymore.^[59] Oxidation of Cu nanoclusters seems to occur, changing the optical properties of the sample: we tried an experiment sputtering using air instead of Ar gas as sputtering seed, and we obtained a sample showing different optical properties, and whose photoluminescence (excitation 430 nm and emission 630 nm) is shown in figure 3.7. In samples stored for longer time, we see a different photoluminescence, with a similar emission, 630 nm, but a different excitation (this time at 510 nm). We believe that this second PL peak forms due to the formation of Cu_2S , that can form naturally at room temperature. The thiol-rich monomer is the source for sulphur, which can detach from the molecule thanks to the presence of copper oxide, that works as catalyst.

Storage of samples sputtered in air into PEMP, as expected, show a shift in the PL peak, towards an emission at 630 nm and excitation at 510 nm. In figure 3.8 is shown how the transformation of the nanoparticle products occurs in the same way with storage time. Note that, also when sputtering into air, some PL emission is visible at around 450 nm, due to the presence of metallic copper nanoclusters. The proof of their formation will be given by the XPS measurement shown in paragraph 3.3.4. In figure 3.9 is shown a catchy image showing the photoemission colour changed with storage time.

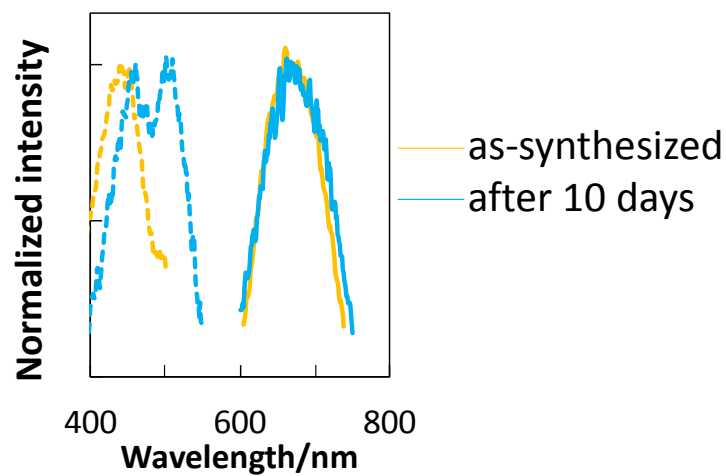


Figure 3.8. 2-dimensional PL spectra for as-synthesized sample sputtered in air, and the same sample after storage for 10 days in the dark at room temperature.

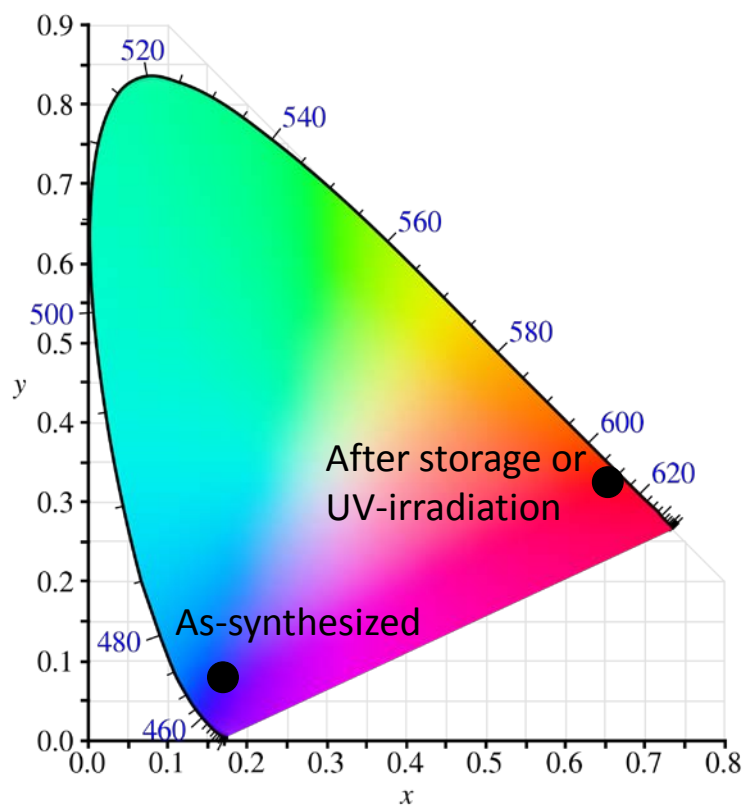


Figure 3.9. Graphical scheme showing the position of the emitted photoluminescence in a CIE 1931 color space.

3.3.3 TEM for stored samples

In order to clarify the origin of the new photoluminescence emission band, we further analysed the particle size, structure, and composition during storage. Images of the nanoclusters and size distribution diagrams were obtained for the stored samples (Figure 3.10) to evaluate if the change in the optical properties was accompanied by particle growth. The average particle diameter increased over time, moving from 1.1 ± 0.2 nm for the as-synthesized sample (Figure 3.3b and 3.3c) to 1.6 ± 0.2 for the sample stored for three days at room temperature without light, to 1.9 ± 0.3 nm for the sample stored for fourteen days (Figures 3.10a and 3.10b). The average particle size increased gradually over the first few days and reached the final value after about five days (Figure 3.12). The HAADF image of the particle acquired after seven days of storage clearly showed the formation of monoclinic Cu_2S with respective d-spacings of 2.4 Å, 2.7 Å, and 3.3 Å for the (204), (240), and $(\bar{1}04)$ planes. This measurement allowed us also to exclude the possibility of copper oxide as final product, as 3.3 Å and 2.7 Å lattice planes can't belong to any copper oxide. The increase in the particle size with time is in accordance with the conversion of copper to Cu_2S . A 93% volume increase is reportedly associated with this conversion.^[74,75]

At last, in figure 3.13 is shown the particle size distribution of the products when sputtering using air instead of argon gas. Keeping all the other sputtering parameters unchanged, the particle size is small, 1.7 ± 0.3 nm, and therefore comparable to the samples sputtered using Ar.

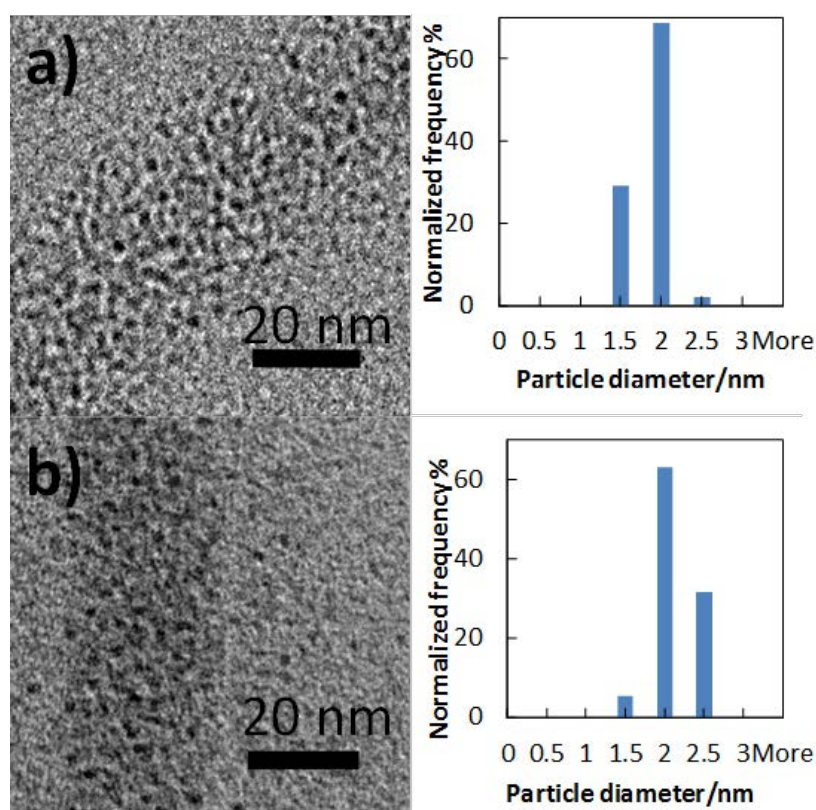


Figure 3.10. Particle TEM images and relative particle size distributions of the obtained nanoclusters dispersed in PEMP for samples stored for (a) 3 days and for (b) 14 days at room temperature in the dark.

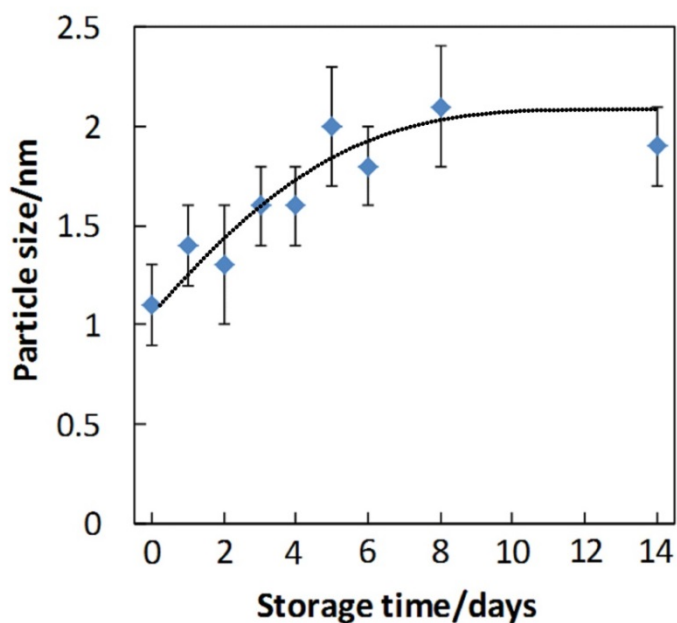


Figure 3.11. Particle growth with time as observed by TEM. Particles grow for the first few days after synthesis, to reach their final stable size just below 2.0 nm diameter.

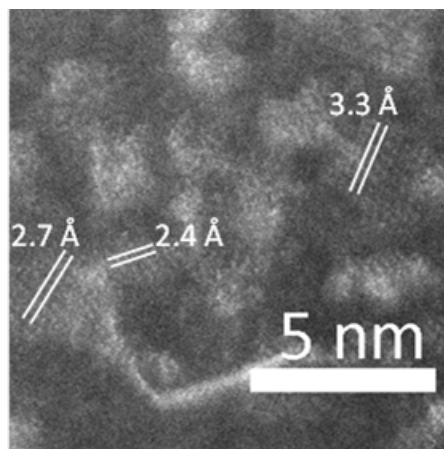


Figure 3.12. HAADF image of nanoclusters after 7 days of storage at room temperature in the dark. The lattice spacings indicate the formation of Cu_2S .

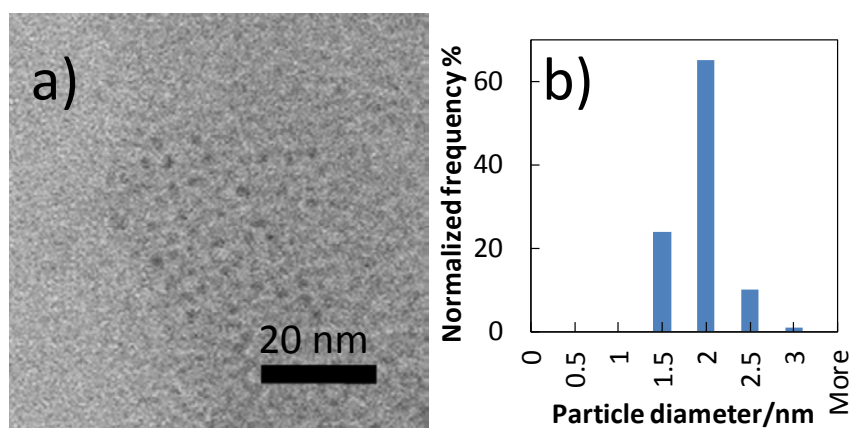


Figure 3.13. TEM image (a) and particle size distribution (b) for a sample sputtered into PEMP under air instead of Ar. The average particle size is 1.7 ± 0.3 nm.

3.3.4 Chemical analysis via XPS

3.3.5 X-ray Photoelectron Spectroscopy measurement

XPS measurement is an extremely powerful tool when it comes to characterize the surface of materials, as it can provide direct information about the oxidation state of surface elements, with a scanning depth of just a few nanometres. Two kinds XPS measurements were performed: XPS of the samples sputtered into liquid, and XPS of Cu sputtering in air.

The purpose of the two experiments was to analyse, respectively, the sputtered nanoclusters once dispersed into PEMP, and the products of sputtering into different atmospheres.

The samples sputtered into PEMP were filtered and analysed after different storage time: as-synthesized, and after 3 and 8 days of storage at room temperature. XPS data regarding the measurements, have been resumed in table 3.1, together with the reference data for the Cu 2p 3/2 peak, Cu Modified Auger parameter, and the S 2p 3/2 peak, and shown in figure 3.14.

The measurement from the sample sputtered into PEMP under Ar atmosphere showed, for all the cases, Cu(I) to be the main components. Cu(II) clearly was not present, as it is always generates secondary peaks at around 942 eV binding energy. No significant changes have been observed in the Auger parameter value for stored samples, meaning that the composition of the nanoparticles reached its final stable state quickly, or during the sample preparation process.

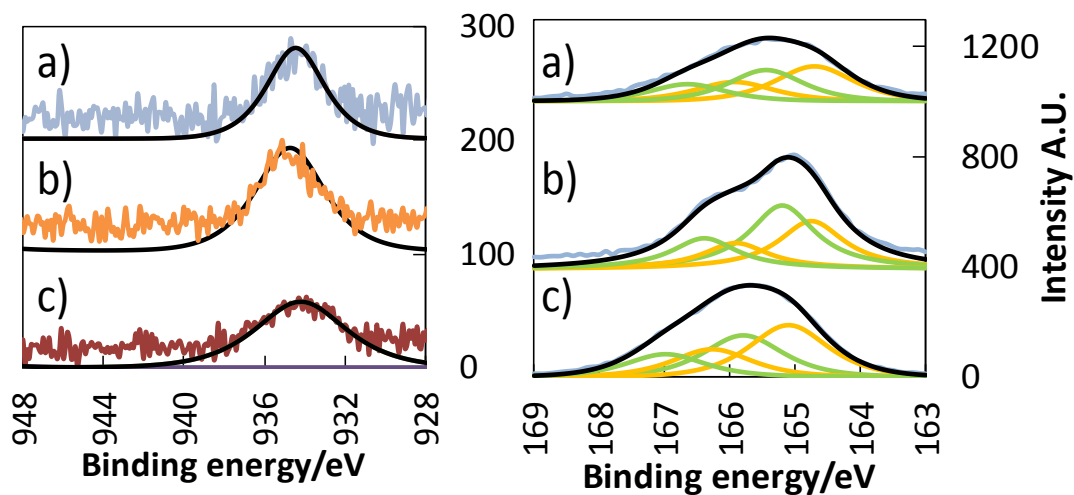


Figure 3.14. Narrow scan XPS spectra of Cu 2p and S 2p for as-synthesized nanoclusters in PEMP. The samples were stored for a) 8 days and b) 3 days, whereas c) is the XPS for an as-synthesized sample.

Table 3.1. XPS results for Cu samples sputtered into PEMP and stored for various amount of time. The discrepancy in the binding energy of Cu is due to the big charge effect caused by the great amount of thiol moieties in excess. The Modified Auger parameter is not affected by such energy shifts.

Sample	Modified Auger parameter for Cu (eV)	XPS binding energy of Cu ₂ p 3/2 (eV)	XPS binding energy of S ₂ p 3/2 (eV)
As-synthesized	1848.4	934.2	165.1
3 days storage	1848.3	934.7	165.0
8 days storage	1848.5	934.4	164.7
Ref. Cu (0)	1851.2 ± 0.2	932.6 ± 0.2	
Ref. Cu (I)	1849.4 ± 0.4	932.4 ± 0.2	
Ref. C-S-H			163.8 ± 0.4
Ref. Cu ₂ S	1849.8 ± 0.2	932.5 ± 0.2	161.9 ± 0.4
Ref. CuS	1850.2 ± 0.3	932.2 ± 0.2	162.1 ± 0.6

A second XPS experiment was done in order to understand if copper oxidizes quickly and easily during the synthesis of nanoparticles. In order to do so, we decided to sputter, in air, on a pre-treated silicon wafer. The aim of this experiment was to verify what kind of copper oxide species form, and whether metallic copper is also present in such sputtering conditions. A depth profile study was performed, to make sure that the film exposed to the x-rays was same as the as-sputtered material.

Figure 3.15 shows the results of the experiment. The surface of the sample showed clear formation of CuO, as signaled by the presence of the copper secondary peaks at binding energies between 940 and 945 eV. Also, the broad Cu 2p 3/2 peak indicates the high oxidation state of surface copper. We sputtered away just few atomic layers using Ar⁺, in order to see the spectra on the second row. Cu 2p_{3/2} peak became much sharper, and we deconvoluted it to be Cu(0) and Cu(I). The two peaks have similar binding energy (only 0.4 eV difference), but they differ in terms of full width half maximum values (higher in the case of Cu(I)), as well as in the modified Auger parameter values. The above mentioned deconvolution seems to fit very well with the data, indicating the fact that even when sputtering using air as atmosphere, some metallic copper products form.

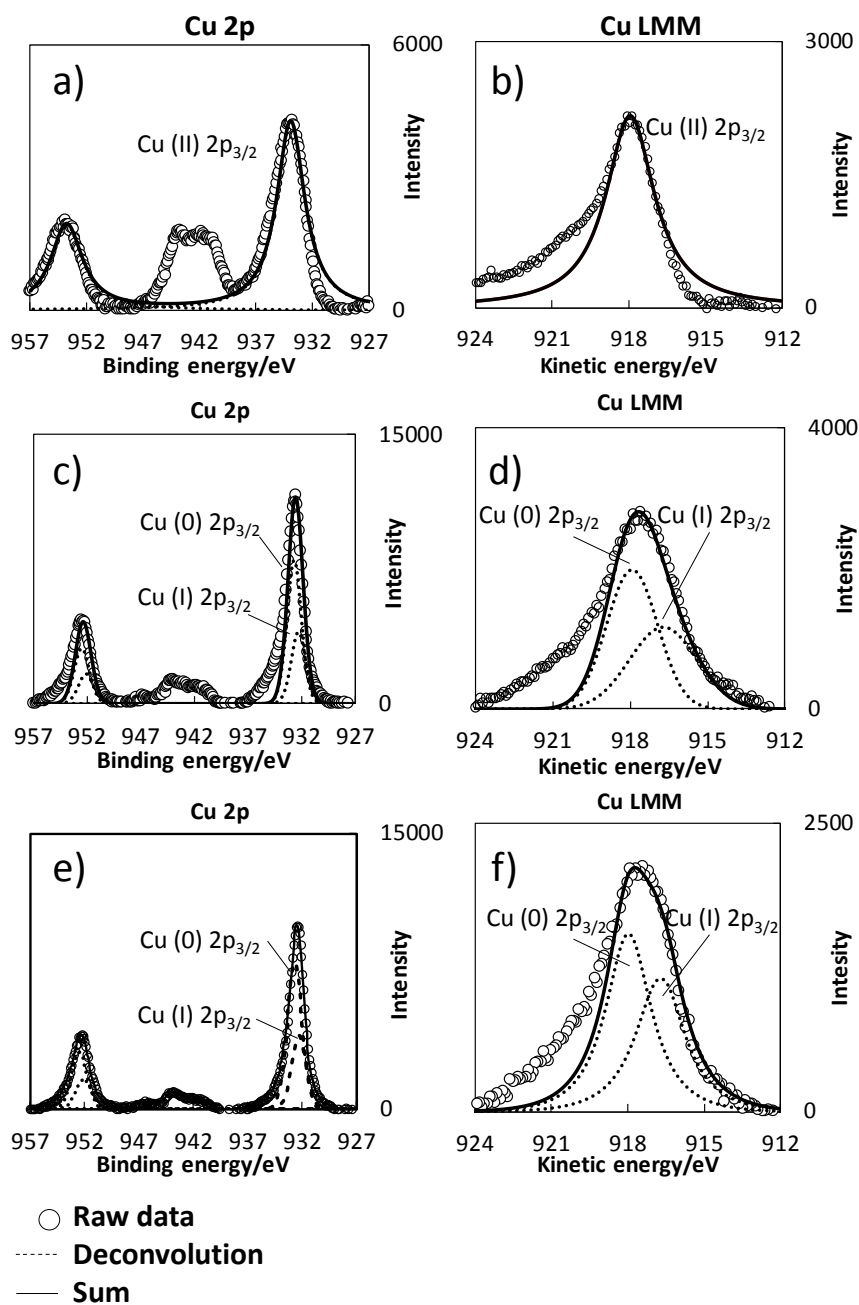


Figure 3.15. XPS depth profile of a sample sputtered onto a silicon grid in air. From the top, as-synthesized film (a,b), after a few nanometers etching (c,d), and after few tens of nanometers etching (e,f). The presence of Cu(I) and Cu(0) can be deduced by deconvoluting the Auger peak and calculating the modified Auger parameter. For as-sputtered material, CuO was detected, in fact there are clear secondary peaks between 940 and 950, that are caused by Cu^{2+} . After etching, the Cu(II) component decreases in intensity, while Cu and Cu(I) components appear. Tables 3.2 and 3.3 explain the results.

Table 3.2. XPS peak positions and modified Auger parameter for the depth profile measurement on a sample sputtered in air on a silicon substrate. The presence of Cu(0) and Cu(I) throughout the sample shows that the formation of Cu(II) was due to post-sputtering oxidation of the sample, with exposure to air.

Sample	XPS binding energy of Cu2p 3/2 (eV)	FWHM (eV)	Cu LMM Auger Kinetic energy (eV)	Modified Auger parameter for Cu (eV)
As-sputtered	933.9	1.5	917.9	1851.8
Few nm etch	932.3	0.8	918.7	1851.0
	932.7	0.9	917.2	1849.9
Strong etch	932.3	0.8	918.7	1851.0
	932.7	0.9	917.2	1849.9

Table 3.3. Typical copper binding energy values depending on its oxidation state, and compound. Source: xpsfitting.com, an XPS web database.

Compound	Cu 2p _{3/2} (eV)	Std. Dev. (+/- eV)	FWHM, 10 eV Pass Energy	FWHM, 20 eV Pass Energy	Modified Auger Parameter	Std. Dev. (+/- eV)
Cu(0)	932.63 a)	0.025 b)	0.79	0.83	1851.24	0.025 b)
Cu(I) Oxide	932.18	0.12	0.88	0.98	1849.17	0.03
Cu(II) Oxide d)	933.76	0.11	3.00	3.00	1851.33	0.05
Cu(II) Hydroxide d)	934.67	0.02	2.74	2.85	1850.92	0.09

b) As defined by Kratos calibration procedure

c) GL(90) peak-shape

d) Shake-up peaks are present (see Figure 1 for shape)

The collected data show important features. First of all, the presence of metallic copper observed in samples sputtered into air can justify the presence of PL emission at 445 nm for all the samples, whether they were synthesized in Ar or air. The Cu(I), referable to Cu₂O, forms with sputtering in both conditions, with a different degree. In case of sputtering into Ar, only a thin layer of oxide forms around the nanoparticles, and that will be

responsible for the transformation into copper sulfide. Copper sulfide formation is also confirmed by the appearance of the absorption peak in the UV-Vis spectra at 480nm.^[57]

3.4 Conclusion

In this chapter we introduced a simple method, by sputtering into thiol, to synthesize luminescent copper nanoclusters. The capping monomer PEMP resulted to be suitable for the formation of copper clusters, that showed photoluminescence with emission at 445 nm wavelength. The average size of the obtained nanoparticles was measured to be 1.1 ± 0.2 nm with a narrow size distribution for as-synthesized samples, while it increased with storage time to 1.9 ± 0.3 nm after 14 days. The increase in size was attributed to the sulfidation of the nanoparticles. Sulfidation, possible due to the high amount of thiol present in the monomer (Figure 3.1), was mediated by the presence of copper oxide, which forms naturally with exposure of the samples to air. This process, that occurs slowly, over a couple of weeks time, shows anyway an interesting feature for the technique, as it could be used to synthesize two different types of photoluminescent nanoparticles. Copper sulfide showed photoluminescence at 630 nm, with a Stokes shift of 0.6 eV. Concluding, this chapter shows one application of magnetron sputtering into liquid for the synthesis of copper nanoclusters and copper sulfide nanoparticles.

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4 UV-MEDIATED SYNTHESIS OF COPPER SULFIDE NANOPARTICLES VIA MAGNETRON SPUTTERING ONTO LIQUID

4.1 Introduction

Among the many strategies developed for the synthesis of photoluminescent copper composite nanoparticles, in this chapter we explore a simple method to synthesize copper sulfide nanoparticles, with emission at 630 nm wavelength. Referring to the results obtained when sputtering copper into the thiol rich pentaerythritol tetrakis (3-mercaptopropionate), and considering the absorbance in the UV-region of copper oxides, we developed a way to accelerate the sulfidation process of copper oxide, to form Cu_2S .

In chapter 3 we showed how, with sputtering time, an absorption peak appeared at 480 nm wavelength, due to the formation of copper sulphide over time. We also observed that by lowering the temperature it is possible to stop the mechanism, and avoid any sulfidation of the nanoparticles.

With the experiment shown in this chapter we aim at achieving a better control over the chemical changes within the nanoparticles, and therefore we've developed a method to make the transformation go faster. To our understanding, the way copper sulfide forms is mediated by the presence of copper oxide and the conversion of oxide to sulfide. As previous studies^[107] showed the possibility to transform Cu-thiolate into Cu_2S via thermal activation,

we proposed the use of UV-light instead as initiator for the process. In fact, by irradiating UV-light on as-synthesized copper nanocluster dispersions, it is possible to provide enough energy to accelerate the reaction. In this way we obtained photoluminescent copper sulfide nanoclusters in only few hours under UV-light irradiation at room temperature. The reaction took less than a 1/50th of the time it took in the previously investigated storage method. The results are impressive and contribute a feasible way to produce highly emitting copper sulfide nanoclusters well dispersed in monomers. Furthermore, the finding helps understanding the transformation of copper nanoclusters in rich thiol capping moiety environment obtained via sputtering methods.

4.2 Experimental section

4.2.1 Materials

Pentaerythritol tetrakis(3-mercaptopropionate) (PEMP) with an average molecular weight of 488.66 g/mol was purchased from Sigma Aldrich, and used as received. Circular copper sputtering target 99.99% purity, 6cm in diameter, 3mm thick, was purchased by Nilaco (Japan).

4.2.2 Synthesis by sputtering

We refer to chapter 3 for the synthetic method of copper nanoclusters and copper oxide nanoparticles into PEMP, as we followed the exact same procedure. Other than that, we ran some sputtering experiments purging air instead of Ar gas into the sputtering chamber, in order to see the effects of copper oxides on the reaction dynamics.

4.2.3 UV-light irradiation

Once observed that sulfidation of copper nanoclusters was taking place in normal conditions, we ran an experiment during which samples were exposed to UV-light. We used a 9.0 W 365 nm wavelength UV-light source to irradiate sideways samples placed into a quartz glass cuvette placed 5 cm away from the lamp, in order to avoid the heating of the samples. We then characterized the UV-irradiated samples after regular time intervals.

4.2.4 Characterization

4.2.4.1 UV-Visible absorption spectra measurement

UV-Visible spectra were taken using a Shimadzu UV-1800 spectrophotometer on liquid using a fused quartz cuvette with 1 cm optical path. The samples were used as produced, without any dilution or treatment, and measured in the range between 200 to 1100 nm. In some cases a 1mm optical path fused quartz cuvette has been used instead.

4.2.4.2 Photoluminescence (PL) measurement

Photoluminescence measurements were performed on the same samples using a Jasco FP-6600 spectrofluorometer. 3-dimensional mapping, with excitation ranging from 200 to 800 nm wavelength and emission ranging from 300 to 900 nm wavelength, was performed first in order to identify all the photoluminescence peaks position. No cutoff filter was required for the measurement. Excitation and emission bandwidth were set to have, respectively, 5nm and 6 nm spectral bandwidth, whereas the measurement was carried out at a scan rate of 10,000 nm/min, with 10 nm steps. After PL mapping, more refined 2-dimensional spectra were taken, using 1 nm steps and a lower scan rate (2,000 nm/min).

4.2.4.3 Transmission Electron Microscopy (TEM) measurement

TEM and STEM measurements were performed using respectively a JEOL 2000 FX (200kV) and a FEI Titan G2 60-300 (300kV). TEM samples were prepared by depositing a droplet of dispersion onto a carbon-coated copper grid (or Mo grid in case EDS measurement was also performed) that was then dipped into acetonitrile for 40 minutes.

4.3 Results and discussion

4.3.1 UV-Visible spectra

UV-visible spectra analysis was the quickest and firstly used tool for the evaluation of the chemical changes in our samples. In fact, the appearance of the absorbance peak at 480 nm related to Cu_2S is clearly visible by naked eye, and it is the most direct way to control the state of the reaction. In order to obtain some quantitative data, we performed an experiment in which the UV-Visible absorbance was measured every 2 hours of UV-light irradiation, after 2 hours of sputtering copper into PEMP. (Figure 5.1). With time the absorption peak at 480 nm, previously observed by simply storing the samples at room temperature, appears.

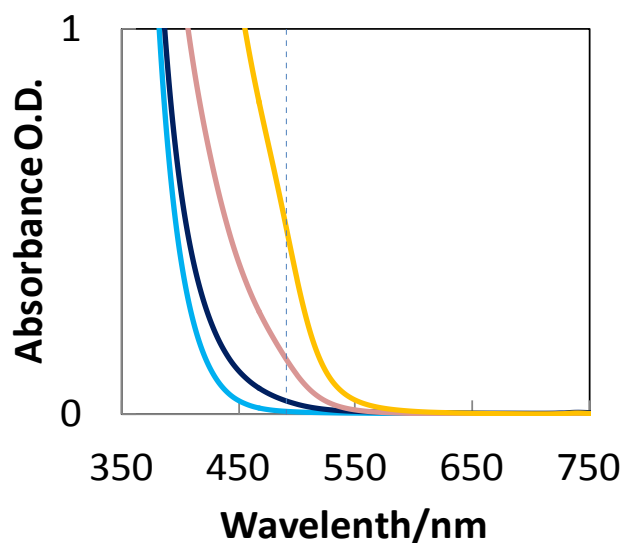


Figure 5.1. . UV-visible absorbance of an as-synthesized sample, and the one of the same sample after being irradiated by UV-light for 2 h (blue line), 4 h (pink line) and 6 h (orange line). The formation of an absorption peak at 480 nm, whose position is indicated by a dotted line, becomes gradually evident.

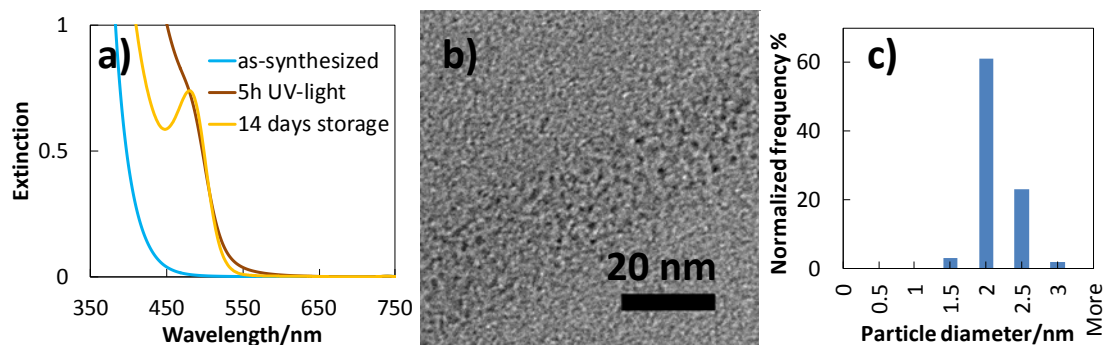


Figure 5.2. (a) Comparison of UV-Visible absorbance for an as-synthesized sample, a 14 days stored one, and another one irradiated for 5 hours under 365 nm UV-light. (b) TEM image of the UV-irradiated sample, and its relative size distribution (c). The average particle diameter is of 1.9 ± 0.3 nm.

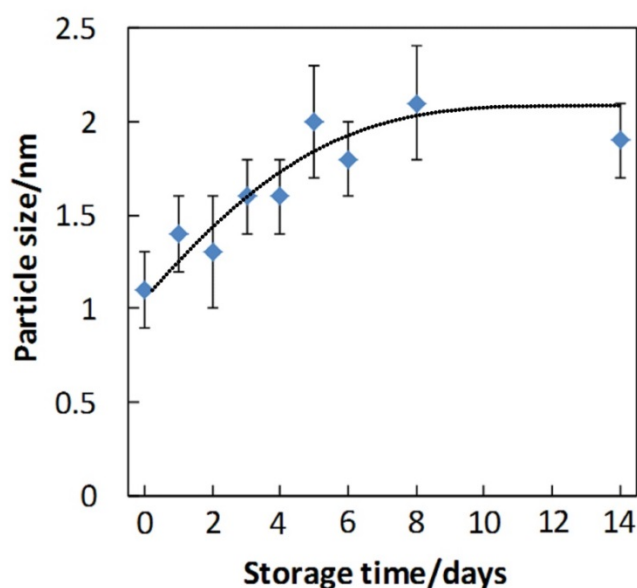


Figure 5.3. Particle growth with time as observed by TEM. Particles grow for the first few days after synthesis, to reach their final stable size just below 2.0 nm diameter.

In figure 5.2a we compared the speed of the reaction under UV-light irradiation and at normal storing conditions. It appears that UV-light can speed up the reaction to a rate of more than 50 times faster when compared to normal storage. To the observed change in the UV-Visible absorption spectra corresponded a change in the particle size, according to what observed when storing the samples at room temperature (Figure 5.2b, 5.2c, Figure 5.3). The particle size increased in both cases from 1.1 ± 0.2 nm to 1.9 ± 0.3 nm, and justified by a change in the particle composition and structure, from the cubic copper nanoclusters, to the monoclinic Cu_2S structure. The increase in the particle volume is due to the difference packing density among the two compounds, and it amounts to about 93%. Copper oxides structures can't justify any significant changes in the volume, as they all have a packing density similar to the one of copper.

4.3.2 Photoluminescence

The PL spectra was also observed regularly with UV-light irradiation time, to see whether to the similar behaviour of storage and irradiation time corresponded a similar behaviour of the photoluminescence properties. The analysis gave positive results, and we could observe a very similar behaviour, as shown in figure 5.4 and 5.5 below. The evolution of the PL source with storage time in the dark at room temperature was similar to the one

occurred under UV-irradiation. PL measurement could be used to, step by step, understand the changes lying beneath the other observations.

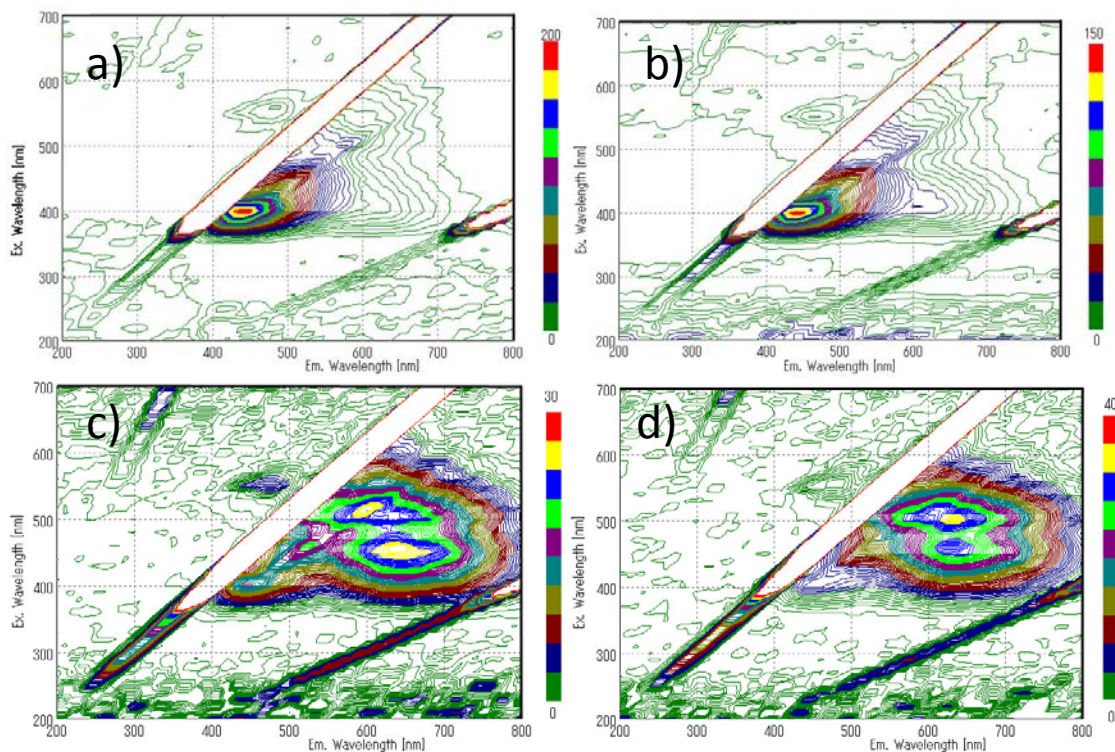


Figure 5.4. From (a) to (d) it's shown the evolution of the photoluminescence of copper nanoclusters under UV-light irradiation: PL mapping images were taken at intervals of 2 hours of UV-light irradiation. Gradually the initial PL at 445 nm disappears, to leave a final product that emits light at 630 nm wavelength.

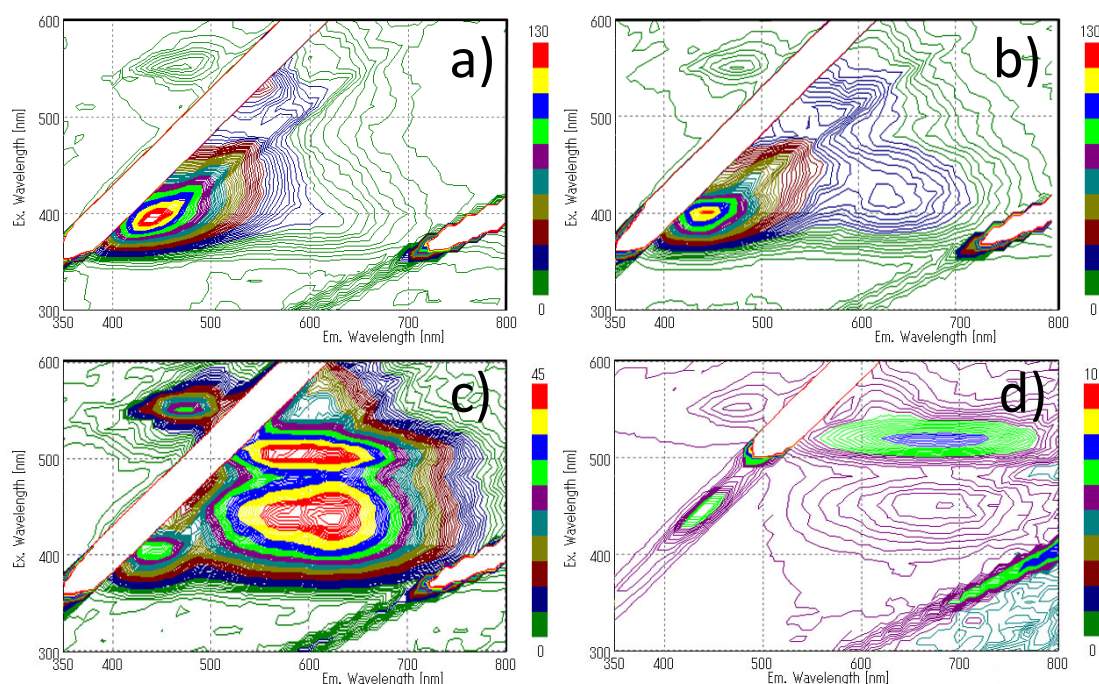


Figure 5.5. As a comparison, from (a) to (d) it's shown the evolution of the photoluminescence of copper nanoclusters with storage time at room temperature in the dark. a) as-synthesized sample, b) after 3 days of storage, c) after 14 days of storage, and after 40 days of storage d).

4.3.3 Particle sulfidation mechanism

The results shown above suggested that the oxidation of the as-synthesized copper nanoclusters during storage served as an intermediate step for the formation of copper sulfide nanoclusters. The formation mechanism for copper sulfide NCs is depicted in Figure 5.6. The first step involves the oxidation of copper to copper oxides. The second step corresponds to the conversion of copper oxides to copper sulfide nanoclusters. The formation of copper sulfide nanoclusters results in the increase of particle size in comparison with that of the as-synthesized copper nanoclusters. This transformation is accompanied by an absorption maxima at 480 nm in UV-Vis spectra and the new arising red emission in photoluminescence spectra. Storage at room temperature induces the oxidation of copper that mediates the formation of copper sulfide. Furthermore, UV-light irradiation on the samples could enhance the reaction speed, to form photoluminescent copper sulfide NCs in a much shorter time.

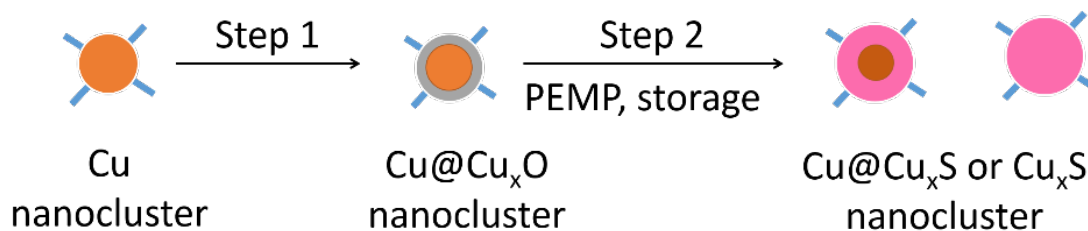


Figure 5.6. Formation mechanism of copper sulfide nanoclusters from copper nanoclusters in PEMP

4.4 Conclusion

In this chapter we used a simple method to synthesize luminescent copper sulfide nanoclusters via UV-light irradiation of copper sputtered copper nanoclusters in a thiol-rich environment. The capping monomer PEMP resulted to be suitable for the stabilization of the copper NCs, and could provide, with its 4 thiol moieties, sufficient sulfur for the NCs composition change. Particle size and PL properties were analyzed and compared with other experiments in which UV-light was not used to enhance the reaction kinetics. This results are important as they show that UV-light-initiated transformation of copper NCs to form Cu_2S nanoclusters is possible at room temperature.

4.5 References

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5 SYNTHESIS OF PHOTOLUMINESCENT COPPER NANOCCLUSERS VIA SPUTTERING ONTO THIOL

5.1 Introduction

High emission quantum yield and good stability are crucial in many applications such as bioimaging.^[75-83] The organic dyes are widely used in applications for single molecular imaging. However, they suffer rapid photofading,^[78,79] thus limiting a long time imaging. Semiconductors quantum dot have been developed with higher photostability and larger molar extinction coefficient compared to organic fluorophores. The semiconductor quantum dots often have bigger size (several nm to some tens of nm), high tendency of aggregation, and have toxicity issues related to their heavy metal content.^[78,79] Recently, metallic nanoclusters show interesting photoemission properties.^[75-84] They have much smaller size (from few to hundreds of atoms), typically less than 2 nm, compared with semiconductor quantum dot. At the same time, metal nanoclusters such as gold, silver, copper offer high extinction coefficient, stability, with high potential for surface functionalization and biocompatibility. These advantages make metal nanoclusters a promising candidate, satisfying extreme requirements for in vivo single molecular imaging.

Copper and copper composite nanomaterials are gaining increasing attention from fundamental and application basis. Copper is much cheaper than noble metals but provide high photoluminescence and its great ability to mix with other elements opens up an almost

infinite range of uses for this metal. However, compared with gold or silver, making and stabilization of copper nanoclusters are more challenging to oxidation stability. Therefore, more efforts are needed from scientists in order to make the usage of copper nanoclusters a reality for applications. So far, many strategies have been developed to synthesize copper nanoclusters. Some of the most common methods include chemical reduction in solution^[85-88] and ultrasonic radiation^[89] to reduce copper ions and using organic capping molecules, biomolecules (e.g. DNA^[90]), to control the growth of the nanoclusters.

On the other hand, top-down techniques^[91-100] (cluster beam deposition,^[91] sputtering^[92-100]) that do not need reducing agents, have been used to produce metal nanoclusters from the bulk metal source. The great advantage of these techniques over chemical reduction methods is the high purity of the nanoclusters that can be achieved, as the synthesis is done under vacuum conditions using a controlled atmosphere. However, in these techniques, a solid substrate were often needed to support the bare metal nanoclusters.^[101,102] This limits the use of the metal nanoclusters for various in vivo bio-applications where well dispersed nanoclusters in a suitable solvents are in demand. Recent progress in sputtering has shown that introducing a liquid substrate to replace the solid substrates allowed for direct preparation of liquid dispersion of metal and metal oxide nanoclusters.^[94-99] The liquid substrates are based on molten salts and low vapor pressure liquids such as polymer,^[96-99] vegetable oil,^[103] and ionic liquids^[94,95,100]. Moreover, when stabilizing molecules are added into the liquid substrate or sputtering atmosphere, it is possible to control particle size and properties (oxidation, surface functionalization, plasmonic/fluorescent properties). Previous works reported successful preparation of gold^[94,96,97,100], silver^[99] and plasmonic copper^[98] nanoparticles with controllable size.

5.1.1 Aim of this chapter

In the previous part of the thesis we worked on the synthesis of copper nanoclusters sputtering onto pentaerythritol tetrakis (3-mercaptopropionate), and could obtain well disperses photoluminescent nanoparticles. Due to the high amount of thiol present in the capping monomer, the clusters turned slowly into copper sulphide nanoparticles. In this chapter we describe the preparation of stable-blue emitting copper nanoclusters by sputtering copper into a solution of polyethylene glycol 600 (PEG) and 11-mercaptoundecanoic acid (MUA). PEG and MUA were chosen, respectively, for the low vapour pressure and good capping ability with Cu. With this experiment we aim at understanding the formation mechanism of the nanoparticles, and observe the stability of the products. The

photoluminescence properties and possible formation pathways of copper nanoclusters with respect to the concentration of MUA were studied and discussed.

5.2 Experimental section

5.2.1 Materials

Polyethylene glycol (PEG, an average molecular weight of 600 g/mol), was purchased from Wako (Japan). 11-mercaptoundecanoic acid (MUA, 95 %, an average molecular weight of 218.36 g/mol and a melting point of 50 °C) was purchased from Sigma Aldrich. PEG and MUA (Figure 4.1) were vacuum dried at 100 °C for 2 h to remove eventual volatile substances right before the synthesis. Copper 99.5% pure sputtering target (ϕ 50 mm, 3 mm thickness) was purchased from Nilaco, Japan and used as received. Acetone, methanol, and chloroform were used as received.



Figure 4.1. Molecular structure of polyethylene glycol (left) and of 11-mercaptoundecanoic acid (right).

5.2.2 Synthesis by sputtering

A modified magnetron sputtering device (Figure 4.2) was used for preparation of nanoclusters in low vapor pressure liquids. A mechanical stirrer was installed for breaking the surface tension of the liquid, therefore avoiding the formation of a thin metal film, and for mixing the liquid to form a uniform sample. An oil rotary pump and a turbo molecular pump were used to evacuate the sputtering chamber. A temperature control system was also installed, to keep both the sputtering copper target and the liquid substrate at controlled temperatures. The atmosphere in the chamber was controlled by evacuating multiple times (8 times) the chamber up to 10⁻³ Pa, then injecting Ar gas up to 101 Pa. During the sputtering experiment the Ar gas flux was controlled in order to have a constant pressure of 2.0 Pa in the sputtering chamber. Using such experimental parameters, the cathode voltage was 215 V. The target-to-sample distance was set at 6cm, the temperature at 40 °C and the sputtering

current at 20mA, which can provide a satisfactory sputtering rate in case of Cu. The higher temperature was set to provide a low enough viscosity of the medium, as well to make sure MUA didn't crystalize during the experiment (MUA melting point is at 50 °C). MUA of various amount (0, 0.07, 0.10, 0.21, and 1.00 g) was pre-heated to melt at 50 °C then mixed with 7.0 g of PEG to form the liquid substrate that was contained into a petri dish of 26 cm² surface area. Sputtering was carried out for 60 minutes for each sample, which was then taken and used for characterization for optical characterization. Some experiments of sputtering into PEG in air (without using any Ar gas) were also carried out.

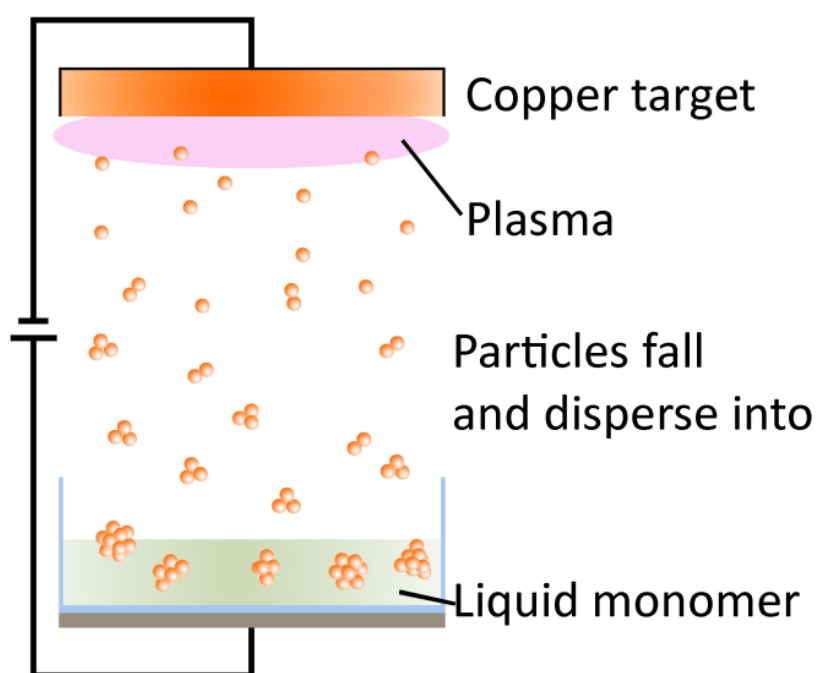


Figure 4.2. Schematic representation of the sputtering mechanism into liquid.

5.2.3 Characterization

5.2.3.1 UV-Visible absorption spectra measurement

UV-Visible spectra were taken using a Shimadzu UV-1800 spectrophotometer on liquid using fused quartz cuvettes with 1 cm and 1mm optical path. The samples were used as produced, without any dilution or treatment, and measured in the range between 200 to 1100 nm.

5.2.3.2 Photoluminescence (PL) measurement

Photoluminescence measurements were performed on the same samples using a Jasco FP-6600 spectrofluorometer. 3-dimensional mapping, with excitation ranging from 200 to 800 nm wavelength and emission ranging from 300 to 900 nm wavelength, was performed first in order to identify all the photoluminescence peaks position. No cutoff filter was required for the measurement. Excitation and emission bandwidth were set to have, respectively, 5nm and 6 nm spectral bandwidth, whereas the measurement was carried out at a scan rate of 10,000 nm/min, with 10 nm steps. After PL mapping, more refined 2-dimensional spectra were taken, using 1 nm steps and a lower scan rate (2,000 nm/min).

5.2.3.3 Transmission Electron Microscopy (TEM) measurement

TEM and STEM measurements were performed using respectively a JEOL 2000 FX (200kV) and a FEI Titan G2 60-300 (300kV). TEM samples were prepared by dipping the carbon-coated copper grid (or Mo grid in case EDS measurement was also performed) into the PEG sample for 20 seconds, then dipping the grid into methanol for 20 minutes, and let it dry.

5.2.3.4 X-ray Photoelectron Spectroscopy (XPS) measurement

XPS measurements were performed using a JEOL JPS-9200. For XPS measurements, nanoclusters were separated from the liquid matrix by microfiltration using acetone as solvent (sample : solvent = 1 : 15, vol/vol) and PTFE membrane (pore size of 0.2 μm , Advantec, Japan). The obtained yellowish powder that remained on the filter membrane was placed on a pre-treated Si wafer for XPS measurement. The surface treatment for Si wafers was performed by dipping Si wafers in aqueous solution of hydrofluoric acid (5%) to remove the oxide layers and smoothen the surface. After that the wafers were rinsed with water and ethanol, then dried and underwent ultraviolet-ozone cleaning to remove residual organic contamination on Si surface.^[104] The binding energy of Si (2p) was used as the reference for correcting the charging effect. The stored Cu-nanocomposite samples were stored in the liquid form in a glass container in the dark, and the XPS samples were prepared just before the measurement.

The binding energy of Cu, whatever its oxidation state, lies, with the sole exception of CuO, in a very narrow range of binding energies. Therefore, in order to understand the oxidation state of Cu it's common practice to recur to the Modified Auger parameter, defined by the following equation:

$$\alpha' = K(C_1 C_2 C_3) + E_b(C) = E_s - E_A + E_b(C)$$

in which $K(C_1 C_2 C_3)$ is the kinetic energy of a core level transition among the energy levels C_1 , C_2 and C_3 , whereas E_b is the binding energy of a core level C. The kinetic energy can be obtained by subtracting to the x-ray source energy E_s (in case of Mg filament is 1253.4 eV) the binding energy of the main Auger peak E_A (in the case of copper it's the LMM transition).

As the Modified Auger parameter comprises the subtraction of two measurable components, it is unaffected by eventual surface charge shifts. Wagner plot obtained from NIST XPS web database for Cu is shown in figure 4.3, and it shows how the understanding of the Cu oxidation state has to go through the Modified Auger Parameter.

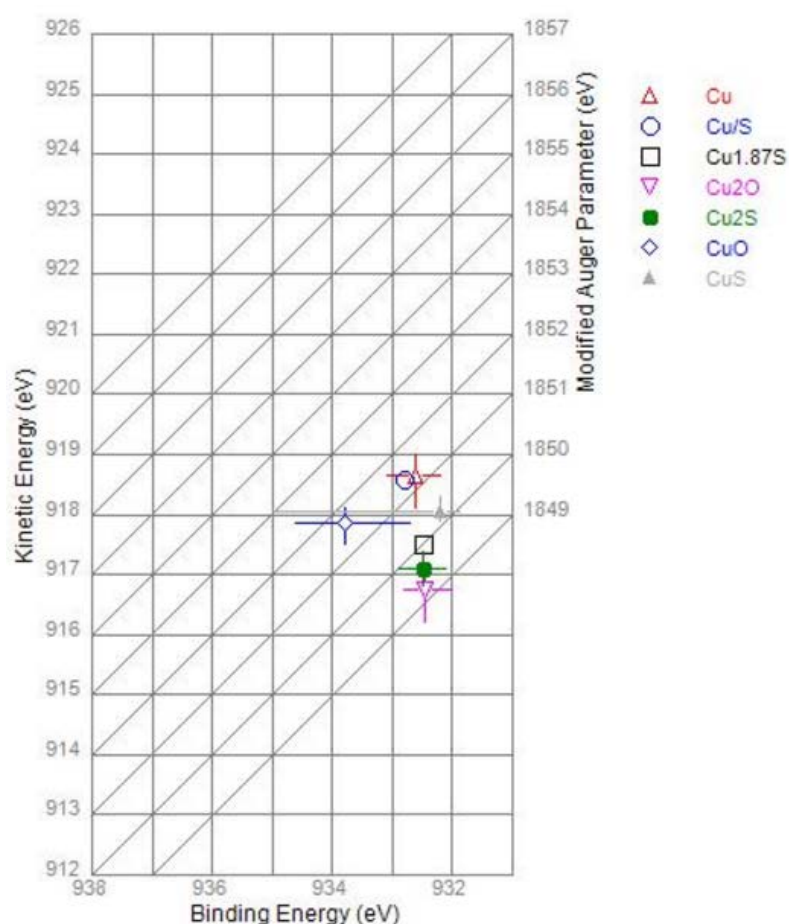


Figure 4.3. Wagner plot for copper compounds to show how the Auger parameters vary with different oxidation state.

5.3 Results and discussion

5.3.1 UV-Visible spectra

Copper nanoclusters dispersed in MUA and PEMP gives a transparent yellow dispersion (Figure 1). UV-Vis spectra of the resulting dispersions showed that there clearly was no surface plasmon resonance from metallic copper nanoparticles (Figure 4.4). In the absence of MUA, higher absorption was observed in the UV-Vis spectrum of the copper nanoparticles dispersed in PEG. This sample, however, did not show photoluminescence emission. When we observed the particle size (shown later in Figure XXX) we found that copper particles were formed with an average particle sizes of 2.6 ± 0.6 nm and showing a broader particle size distribution when compared with samples sputtered using MUA and PEG. It is common for metal nanoparticles

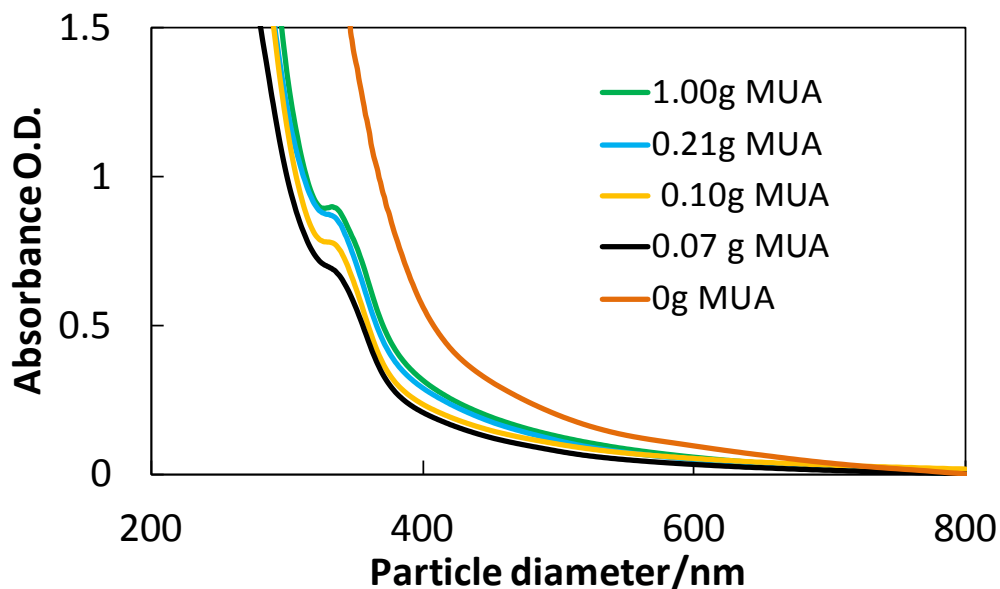
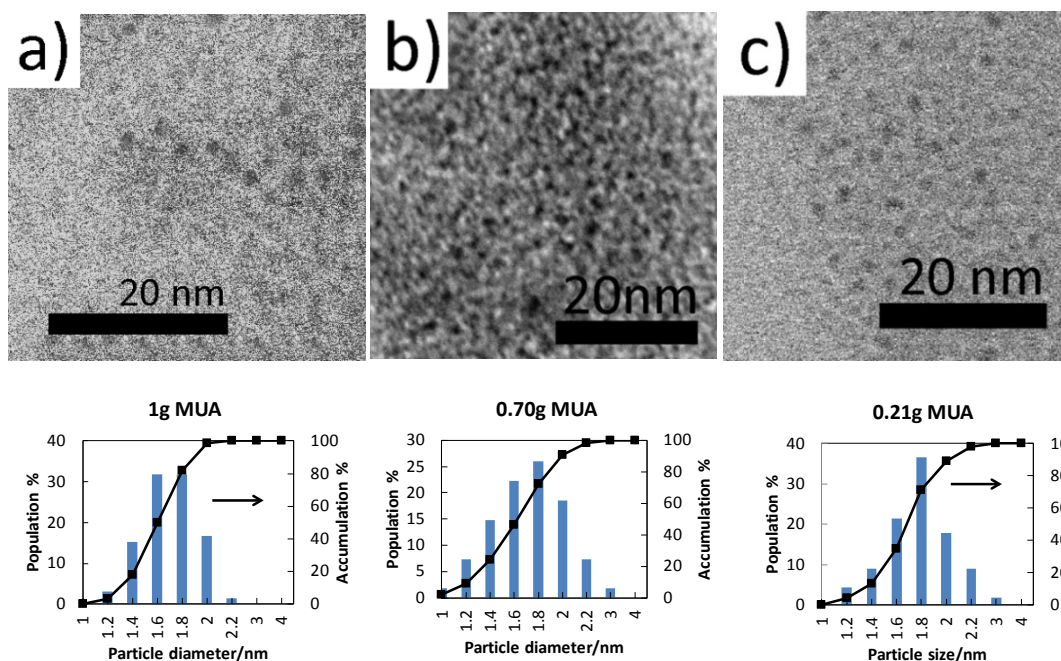


Figure 4.4. UV-Visible spectra for the sputtered copper nanoclusters dispersed in PEG and MUA. The amount of MUA was varied between 0 (only PEG) and 1.00 g.

with a size larger than 2 nm not to have photoluminescence. Using MUA (0.07 – 1.00 g), a clear peak at 350 nm in UV-Vis spectra (Figure 4.4) was observed for all samples, indicated the formation of copper nanoclusters.

5.3.2 TEM images of sputtered Cu into PEG

TEM was used to verify the size and size distribution of MUA stabilized copper nanoclusters for various MUA amounts. The results (Figure 4.5) showed that samples containing 0.10g of MUA or more, have particle sizes in the range of 1.6 ± 0.3 nm. It has to be noted that the fraction of nanoclusters with size less than 1.6 nm was increased as a function of MUA amount (Figure 4.6). This suggested that the primary sputtered copper atoms and nanoclusters could experience further aggregation to certain sizes in the liquid substrate to form the nanoclusters as observed in Figure 4.5. The higher amount of MUA, the larger amount of small active photoluminescent centers were stabilized. Similar phenomenon was observed in case of sputtered gold and silver nanoparticles in thiolate medium.^[96,97,100,106]



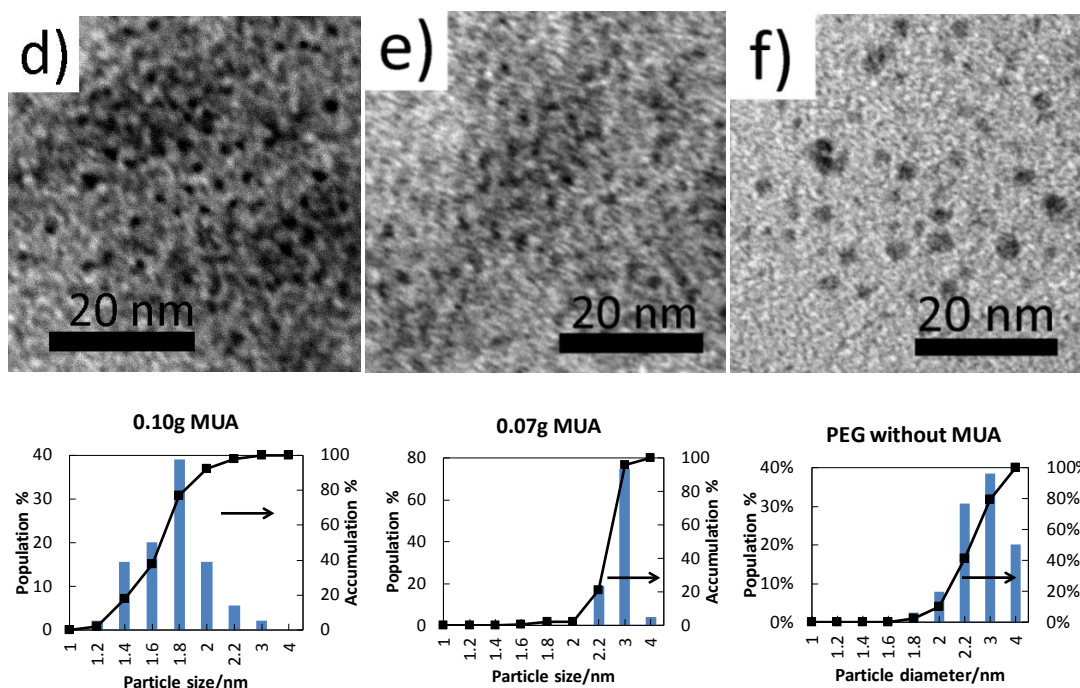


Figure 4.5. TEM images of the sputtered samples with the amount of MUA (a) 1.00 g, (b) 0.70 g, (c) 0.21 g, (d) 0.1, (e) 0.07 g, and (f) 0 g, and relative particle size distribution.

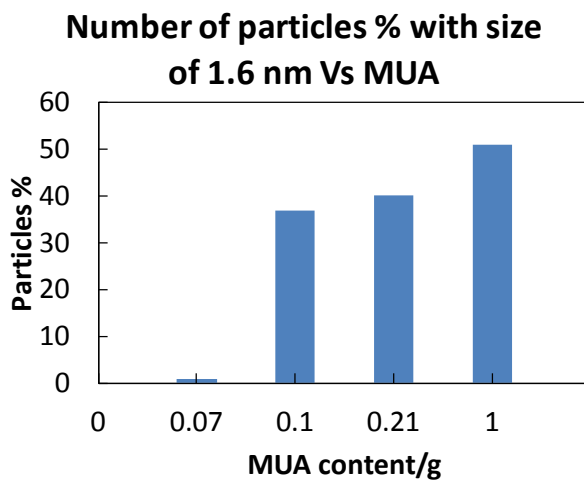


Figure 4.6. The graph shows the fraction of nanoclusters with size of and less than 1.6 nm plotted versus the amount of MUA used.

5.3.3 Photoluminescence

The PL spectra (Figure 4.7) of these dispersions in MUA and PEG exhibited an emission peak maxima at 445 nm and an excitation peak maxima at 393 nm. The peak maxima and the shape of the PL spectra are identical among these samples, suggesting an identical nature (i.e. their sizes, composition) of the photoluminescence centers in these samples. However, the intensity of the peaks increased with an increase in the MUA amount used in the liquid substrate. This result indicates that the number of photoluminescence centers increases according to the amount of the stabilizing agent, MUA. Because all samples underwent the same sputtering parameters (i.e. time, current, substrate temperature and target-liquid distance), except for the substrate composition, the total volume of sputtered copper (number of copper atoms) in liquid substrate could be considered the same for all cases. Therefore, an increase in the photoluminescence centers indicated that the aggregation state (size and size distribution as well as the intra-clusters structure) of copper nanoclusters in the liquids were affected by the MUA concentration. Considering the Jellium model for copper^[84] (Eq. 4.1), based on the emission spectra of the the dispersion, the active photoluminescent centers were estimated and they would be composed by ~16 atoms. With this number, the metal core size of the photoluminescent centers was thought to be less than 1 nm.^[105]

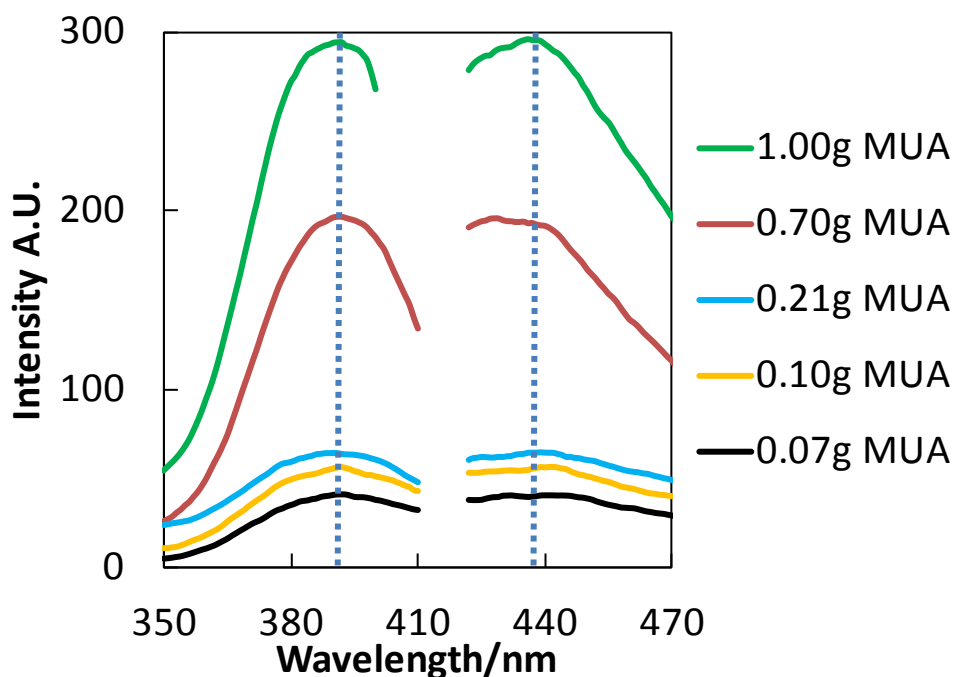


Figure 4.7. PL spectra for samples sputtered at various MUA amounts (0.07-1.00 g).

$$N = \left(\frac{E_{Fermi}}{E_{emission}} \right)^3$$

Equation 4.1. Estimation of the number of copper atoms in a cluster according to the Jellium model approximation. For emission at 445 nm, the number of metal atoms in a cluster is $N = 16$.

5.3.4 X-ray Photoelectron Spectroscopy (XPS) measurement

We confirmed the composition of the obtained nanoclusters in the solution using XPS. The results, showed in Figure 4.8, indicate the formation of Cu(0) and Cu(I) as a minor component. The absence of secondary peaks between 936 and 945 eV in binding energy indicates the absence of copper (II) oxides. The presence of Cu(I) is possible, owing to the fact that the surface of the nanoclusters was bound with thiol to form Cu-thiol complex. The XPS spectrum for S 2p showed the presence of S in different bounding states with metal element for samples prepared using MUA of 0.10 g to 0.21 g. The S in free thiol molecules (unbound state) was found for sample prepared with maximum amount of MUA (1.00 g) owing to some excess MUA molecules that couldn't be removed after filtration. Therefore our samples are composed of metallic copper nanoclusters capped with MUA on their surface.

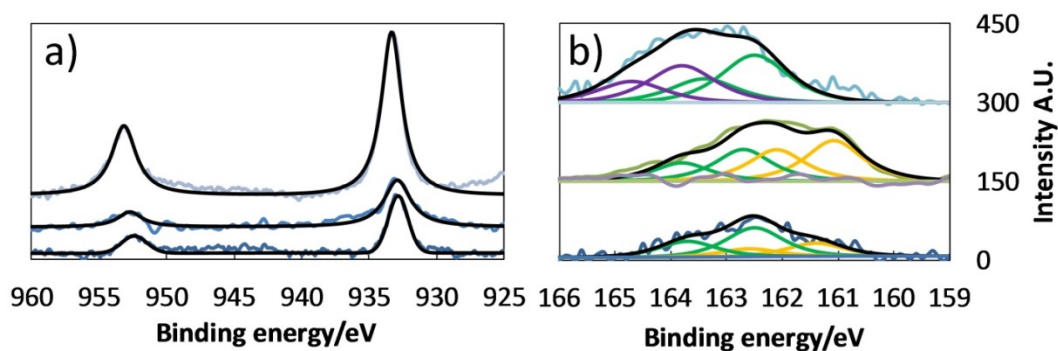


Figure 4.8. Narrow scan XPS spectra of Cu 2p (a) and S 2p (b) for nanoclusters prepared using 1.00, 0.21 and 0.10 g of MUA in PEG from top to bottom, respectively. The light blue and black curve are the raw and sum spectra, respectively. S 2p spectra were deconvoluted into two components labelled with purple, green, and orange for different states of S.

Table 4.1. XPS data results for the Cu and S 2p 3/2 binding energy for the various samples

Sample	XPS binding energy of Cu 2p 3/2 (eV)	XPS binding energy of S 2p 3/2, purple curve (eV)	XPS binding energy of S 2p 3/2, green curve (eV)	XPS binding energy of S 2p 3/2, orange curve (eV)
1.00g MUA	933.3	163.9	162.4	
0.21g MUA	932.9		162.5	160.9
0.10g MUA	932.9		162.4	161.2
Ref. Cu(0)	932.6 ± 0.2			
Ref. Cu(I) oxide	932.4 ± 0.2			
Ref. C-S-H		163.8 ± 0.4		
Ref. Cu ₂ S	932.5 ± 0.2	161.9 ± 0.4		
Ref. CuS	932.2 ± 0.2	162.1 ± 0.6		

5.3.5 Particle formation mechanism

Figure 4.9 shows the illustration for the possible formation mechanism of copper nanoclusters in solution of MUA and PEG in relation to their photoluminescent properties. Depending on the amount of MUA in the solution, the aggregation of primary sputtered metal atoms and clusters can form nanoclusters with similar sizes but composing of active PL nanoclusters (large amount of MUA) or large sized unactive PL nanoclusters (grey particles, Figure 4.9). This was responsible for the identical PL excitation/emission maxima (one type of active PL centers), but the increase in PL intensity of the resulting dispersion for high amount of MUA used.

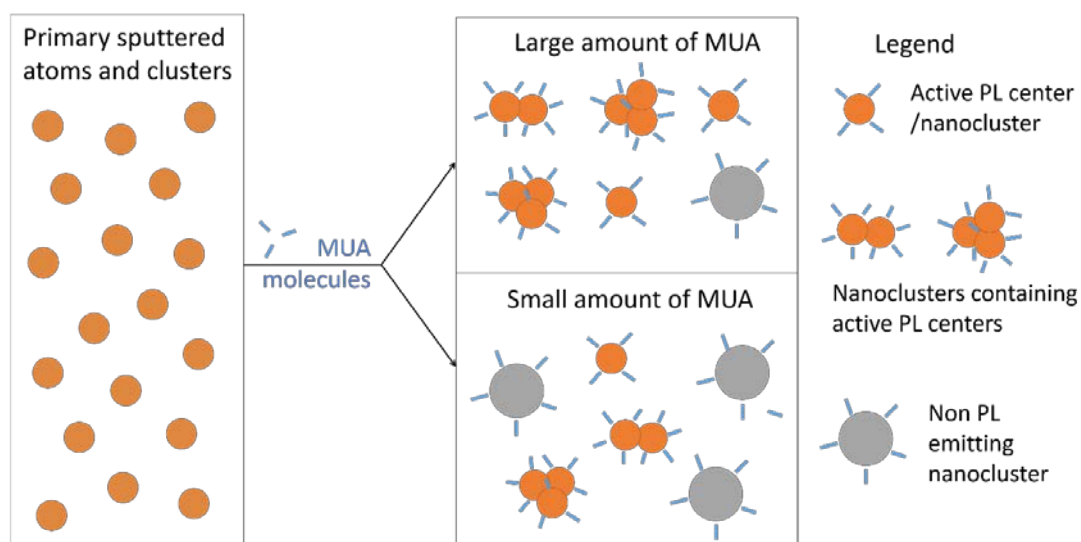


Figure 4.9. Formation mechanism of copper nanoclusters in relation to the MUA amount.

5.4 Stability with storage

In order to compare the synthesized samples with the previously synthesized ones sputtering onto PEMP, we stored the samples and heated them up, in order to see whether observable changes in the optical properties were becoming evident. In this case either oxidation or growth or sulfidation of the nanoclusters would have generated changes in both PL and UV-Visible absorbance. In Figure 4.10 it is shown a sample stored at room temperature in the dark for 30 days: the only slight change in the PL means that the nanoclusters are stable over time, and that either oxidation and sulfidation do not occur.

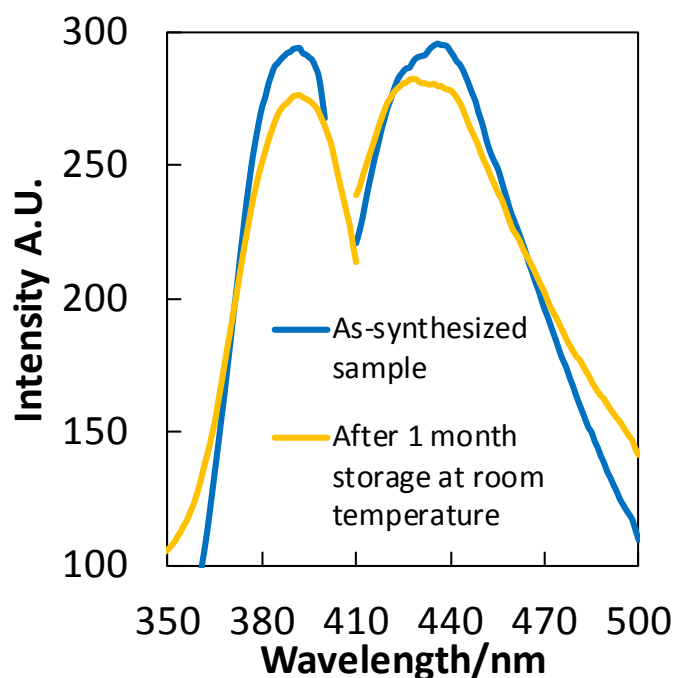


Figure 4.10. Evolution of the photoluminescence intensity over time. A sample containing 1 g of MUA was stored at room temperature for 30 days, and PL was measured again. The intensity decreased only slightly.

5.5 Conclusion

In conclusion, in this chapter we demonstrated that our modified green and facile sputtering technique allowed for achieving highly stable blue emitted copper nanoclusters dispersed in liquid. The increase of photoluminescence intensity was obtained by simply increasing the amount of MUA. The changes in MUA concentrations did not vary the position of the photoluminescence peak maxima and particle size for MUA content above 0.1g. This indicates the formation of photoluminescent centers and their secondary aggregation to form larger sized active photoluminescent nanoclusters.

5.6 References

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6 CONCLUDING REMARKS

The studies presented in this thesis contribute with different approaches to nanoparticles synthesis, for uniform, well dispersed, and highly pure nanoclusters with controlled composition in liquid via sputtering. The understanding of the formation mechanism of nanocluster in relation to the liquid medium and the sputtering atmosphere opens new doors for synthesis of inorganic compounds nanoparticles via sputtering onto liquids.

Publications on the thesis

1. **M. Porta**, M. T. Nguyen, T. Yonezawa, T. Tokunaga, Y. Ishida, H. Tsukamoto, Y. Shishino, and Y. Hatakeyama, Titanium Oxide Nanoparticle Dispersions in a Liquid Monomer and Solid Polymer Resin Prepared by Sputtering, *New Journal of Chemistry*, 2016, **40(11)**, 9337-9343 DOI: 10.1039/C6NJ01624C
2. **M. Porta**, M. T. Nguyen, T. Yonezawa, and Y. Ishida, Highly Stable and Blue-emitting Copper Nanocluster Dispersion via Magnetron Sputtering onto Liquid, *RSC Advances*, 2016, **6(107)**, 105030-105034 DOI: 10.1039/C6RA17291A.
3. **M. Porta**, M. T. Nguyen, T. Yonezawa, and Y. Ishida, Matrix Sputtering into Liquid Mercaptan: From Blue-Emitting Copper Nanoclusters to Red-Emitting Copper Sulfide Nanoclusters, 2016, *Langmuir*, DOI: 10.1021/acs.langmuir.6b03017.

Related publications

4. F. C. P. Masim, M. Porta, W.-H. Hsu, M. T. Nguyen, T. Yonezawa, A. Balčytis, S. Juodkazis, and K. Hatanaka. Au Nanoplasma as Efficient Hard X-ray Emission Source, *ACS Photonics*, 2016. DOI: 10.1021/acsp Photonics.6b00692.
5. W.-H. Hsu, F. C. P. Masim, **M. Porta**, M. T. Nguyen, T. Yonezawa, A. Balčytis, X. Wang, L. Rosa, S. Juodkazis, and K. Hatanaka, Automatic Positioning System for Femtosecond Laser-induced X-ray Emission from Au Nano-sphere Suspension, *Optic Express*, 2016, **24**, 19994-20001. DOI:10.1364/OE.24.019994.
6. F. C. P. Masim, W.-H. Hsu, C.-H. Tsai, H.-L. Liu, **M. Porta**, M. T. Nguyen, T. Yonezawa, A. Balcytis, X. Wang, S. Juodkazis, and K. Hatanaka, MHz-ultrasound Generation by Chirped Femtosecond Laser Pulses from Gold Nano-colloidal Suspensions, *Optics Express*, 2016, **24**, 17050-17059. DOI: 10.1364/OE.24.017050.

7. K. Hatanaka, **M. Porta**, F. C. P. Masim, W.-H. Hsu, M. T. Nguyen, T. Yonezawa, A. Balcytis, and S. Juodkakis, Efficient X-ray Generation from Gold Colloidal Solutions, *Cond-mat.mes-hall*, 2016. arXiv:1604.07541.
8. F. C. P. Masim, H.-L. Liu, **M. Porta**, T. Yonezawa, A. Balcytis, S. Juodkakis, W.-H. Hsu and K. Hatanaka, Enhanced Photoacoustics from Gold Nano-colloidal Suspensions Under Femtosecond Laser Excitation, *Optics Express*, 2016, **24**, 14781-14792. DOI: 10.1364/OE.24.014781.