

STUDY OF THE GOLD NANOCRYSTALLINE THIN FILMS PRODUCED AT THE WATER/TOLUENE INTERFACE

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ABSTRACT

This study describes a quick and simple approach for producing gold nanocrystalline films at ambient temperature. By employing this straightforward and novel technique of monolayered, thin films

comprising Au nanocrystalline adhered over extremely wide portions of the interface between water and toluene, stable aqueous sols of gold containing HAuCl_4 and $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ were maintained in contact with octylamine in toluene. Advanced methods, including UV-vis spectroscopy, X-ray diffraction, and transmission electron microscopy (TEM), were used to examine the size and crystallinity of thin film deposits.

KEYWORDS: Au nanoparticles, interfacial region, water/oil, thin film.

INTRODUCTION

A thin film is a layer of a material deposited on a substrate that ranges in thickness from one atom to several microns.^[1] During the last few years, researchers have been working on a simple and very effective route to deposit various types of materials as films, which depends on the interfacial region between two immiscible liquids. This allows the deposition of high-quality films of different types of materials on substrates utilizing a very simple method, cheap equipment, and surrounding deposition conditions, for instance, temperature, pressure, and amount of precursor. There is increasing interest in thin films of noble metal nanoparticles thin films because of their unusual properties and potential applications in future electronics.^[2-10] Several technologies involving chemical and physical means have been evolved to prepare metal nanocrystals. For instance, chemical reduction using reduction

agents is one of these techniques.^[11-15] The interfacial region between two immiscible liquids has been studied for many reasons, but recently because it is easy to trap and assemble nanocrystals.^[6-10] Assemblies created by this method are less prone to defects because of the dynamic character of the medium and economy in cost. Many groups have demonstrated the assembly of nanocrystals at the liquid/liquid interface.^[2-6] Previous studies have often relied on specially designed ligands to trap nanocrystals. The fairly complex structure of designer ligands has meant that it has hitherto been impossible to carry out systematic studies of the influence of ligand structure on the assembly process. Moreover, the properties of the films obtained by interfacial deposition have not been investigated. Au nanoparticles created by the reduction of nanoparticles in the aqueous phase are able to have shapes with small surface morphology if connected to other morphologies. The suspension of spherical Au nanoparticles usually displays a ruby red color because of the spread of light by the nanoscale material, but the increase in the size of nanoparticles, as well as a variation in the surrounding the environment of the nanoparticles, may adjust the optical properties of the colloid.^[16,17] It is possible to synthesize gold nanoparticles in different shapes, such as nanospheres, nanorods, nanoshells, and nanoprisms, for many applications. Fig. 1 shows the morphologies of gold nanoparticles.

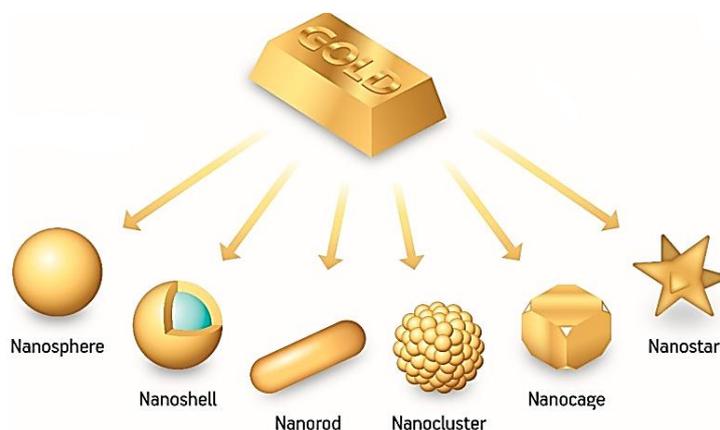


Figure 1: Scheme of gold nanoparticle assemblies and morphologies this figure taken from reference.^[18]

In this paper, we report a new simple strategy for the assembly of Au nanocrystals into thin films at the water-oil interface using octylamine. As a stabilizer, gold nanoparticles were created by reduction of their salts with sodium citrate as the reducing agent. Synthesizing gold nanocrystals using reduction of HAuCl_4 with sodium citrate produces spherical gold

nanocrystals that are enclosed by a layer of citrate ions that give a negative charge to the nanocrystals, stopping aggregation via electrostatic repulsion.^[18,19]

Experimental Section: Synthesis of gold sol: Citrate capped Au nanoparticles were prepared utilizing a method already reported.^[20] 0.5ml of HAuCl₄ solution was diluted with 20 ml of water and brought to a boil. To the previous solution, 1.5 ml of 0.5% sodium tri-citrate was added while stirring. The heating was switched off as soon as the solution turned wine-red and the stirring continued till the solution cooled to room temperature.

Gold thin films: The thin film was obtained at a volume of 0.6 ml of the Au solution prepared above, diluted to 10 ml with distilled water, and stood in contact with 10 ml of toluene solution containing 0.2 ml of octylamine. 4 mL of ethanol was injected into the water layer to start the reaction. After 24 hours, a shiny film of Au had formed at the interface of liquids and was transferred to the glass substrate (fig.2).

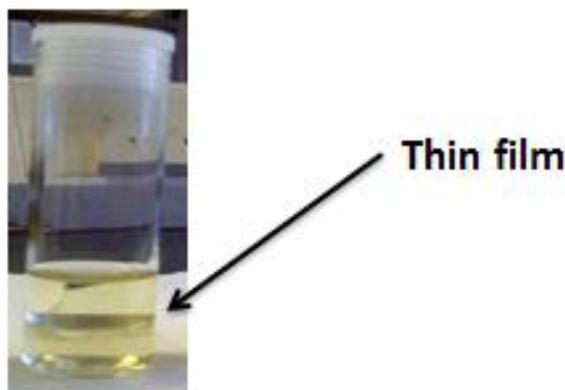


Figure 2: Shows Au thin film at the interfacial region between water/toluene.

RESULTS AND DISCUSSION

The TEM image in figure (3) reveals a number of multiply twinned particles are present across the entire microscopic grid with a mean diameter of 19 nm. We exhibit the image of the film sampled after contact times of 24 hours. This image is to be compared with that of the standard film prepared previously,^[21] corresponding to a contact time of 18 h. Clearly, an increase in contact time increases the coverage of the film on the substrate, with an observable change in the average diameter of the nanocrystals. Our observations suggest that particle growth reaches saturation with time.

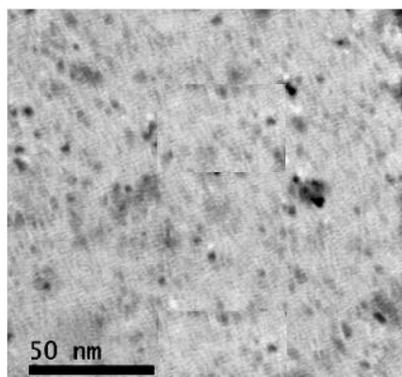


Figure 3: Transmission electron microscopic image of Au nanocrystals assembled at the water/toluene interface with octylamine in the organic layer at room temperature. The film interface formed using 10 ml of toluene containing 0.5 ml of octylamine on top of an aqueous solution.

The X-ray diffraction pattern obtained from films of Au nanocrystals exhibited four strong peaks at $2\theta = 38.11^\circ$, 44.27° , 64.42° , and 77.47° , which corresponded to (111), (200), (220), and (311) crystalline planes of the face center cubic lattice of metallic gold. The intense diffraction at 38.11° shows that the preferred growth orientation of Au is a long (111) plane. The growth of the (111) reflection reflects the increase in particle size. The crystallite sizes were calculated by the Scherrer equation.^[22] The grain sizes were obtained from the widths corresponding to the (111) reflections of Au. A mean of grain size of 15 nm was obtained, somewhat lower than the TEM estimates. These findings are supported by similar results reported in other studies.^[23,24] $d = 0.9\lambda / \beta \cos\theta$. (see fig.4).

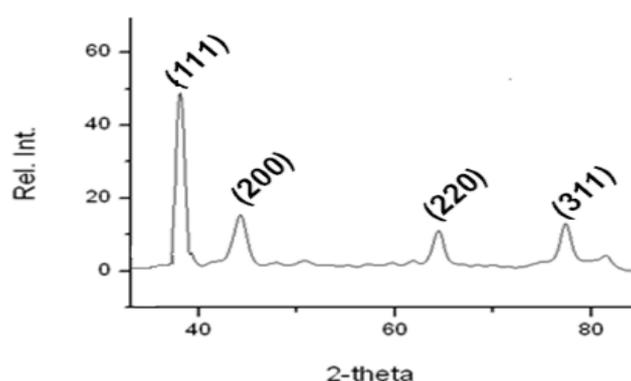


Figure 4: X-ray diffraction patterns of Au thin film obtained by reacting 1ml Au sols diluted to 10ml of water stood in contact with 10ml toluene containing 0.5ml octylamine.

The UV absorption spectra of a citrate-capped dispersion of nanocrystals and of the interfacial films assembled with octylamine in figure 4 exhibited a broad band due to the

surface plasmon which depends on the size and shape of particles. The wavelength of upper absorption is significantly red-shifted from that of the colloid (410 nm), occurring at 439 nm in the film of nanocrystals. Shifts in peak positions are governed by the dielectric constant surrounding individual nanocrystals.^[25,26,27]

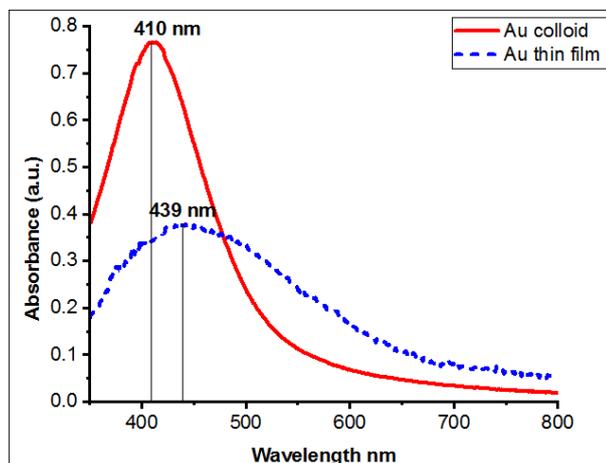


Figure 5: The UV-visible spectra of the citrate-capped Au nanoparticles (dashed curve) and for the assemblies of Au nanocrystals at the water toluene interface using octylamine (solid curve).

CONCLUSIONS

We have shown a simple way to assemble Au nanocrystals into monolayer films at the water/toluene interface and at room temperature for 24 hours by using octylamine, which is held in contact with toluene. The particle size of Au which was produced by the citrate reduction was, on average, 19 nm. X-ray diffraction showed that the Au films were composed of cubic grains. The absorption maximum of the assembly is shifted from the value of 410 nm for the colloid to 439 nm in the Au nanocrystalline film.

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