Nature and Properties of Ultrathin Nanocrystalline Gold Films Formed at the Organic–Aqueous Interface

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Ultrathin nanocrystalline films of gold formed at different temperatures at the organic-aqueous interface have been investigated by X-ray diffraction, electron microscopy, atomic force microscopy, and electronic spectroscopy. The films are smooth and continuous over relatively large length scales and are generally ~ 100 nm thick. The size of the nanocrystals is sensitive to the reaction temperature, which also determines whether the film is metallic or an activated conductor. The surface plasmon band of gold is highly red-shifted in the films. Alkanethiols perturb the structure of the films, with the magnitude of the effect depending on the chain length. Accordingly, the position of the plasmon band and the electrical resistance of the films are affected by interaction with alkanethiols; the plasmon band approaches that of isolated nanocrystals in the presence of long-chain thiols.

Introduction

Ultrathin films of metal nanocrystals constitute a novel class of materials with a unique combination of nominally zero and two dimensionalities. There has been much interest in the synthesis of monodisperse nanocrystals and their self-organization in two-dimensional arrays.^{1,2} Whetten et al.³ subjected a thiol-protected Au organosol to centrifugation to separate out fractions containing nanocrystals of different mean sizes, and thereby obtained well-ordered two-dimensional arrays of sizeselected nanocrystals. Harfenist et al.4 found that Ag nanocrystals from a cluster beam were stable in air once coated with alkanethiols, and formed extended two-dimensional arrays. Fitzmaurice and co-workers⁵ obtained continuous films of thiolized Ag nanocrystals covering micron-sized areas. Nanocrystals of Ag capped with fatty acids are found to yield cubic or hexagonal close-packed structures.^{6,7} Colloidal dispersions of Co nanocrystals capped with fatty acids self-assemble to yield hexagonally ordered arrays.^{8,9} Well-ordered arrays of magic nuclearity nanocrystals, Pd₅₆₁ and Pd₁₄₁₅, have been obtained after replacing the polymer coating by alkanethiols by a phasetransfer process.¹⁰ Schmid et al.¹¹ have reported an ordered twodimensional array of small Au₅₅ nanocrystals on a polymer film. Ordered two-dimensional lattices containing thiolized Au particles of two different sizes have been reported by Kiely et al.,¹² who find that nanocrystals of different radii follow the radius ratio rules of metal alloys. Arrays consisting of Au and Ag nanocrystals of different sizes,¹³ of Au-Ag^{14,15} and Fe-Pt¹⁶ alloy nanoparticles, and of core-shell nanopartices^{17,18} are also known.

There have been a number of reports on metal nanocrystal assemblies at the air-water interface using the Langmuir-Blodgett (LB) method. For example, Chi et al.¹⁹ have reported the preparation of monolayers of Au₅₅ nanocrystals by spreading its chloroform sol over the aqueous layer in an LB trough and then transferring it onto a substrate. Large-scale ordered arrays of such nanocrystals have been obtained by Brown et al.²⁰ Sastry

properties of the nanoclusters and the spacers, nanocrystalline devices capable of lasing and rectification have been obtained.³¹ Unlike most of the literature procedures for the synthesis of nanocrystalline films involving two steps, we have developed a simple one-step synthesis of nanocrystal arrays at the liquid—liquid interface wherein an organometallic compound dissolved in an organic layer reacts with the reducing agent present in the aqueous layer at the interface.³² A careful examination has shown that the material formed at the interface is an ultrathin nanocrystalline film consisting of closely packed metal nanocrystals coated with the organic species present at the interface. The film at the interface is essentially freestanding and can be deposited onto a substrate for further investigation or could be converted to either an organosol or a hydrosol by using

and co-workers synthesized hydrophobically modified Au nanoparticles and organized them into lamellar films by the LB

method.²¹ The LB method has been exploited to study collective

properties of nanocrystals. Capped metal nanocrystals possess

size-dependent charging energies,22 and therefore, a layer of such

nanocrystals in the form of a film can be visualized as a network

of discrete charging units connected by tunnel junctions, with

characteristics depending on both the particle size and the

interparticle separation.²³ Bourgoin et al.²⁴ have carried out

electrical measurements on strongly interconnected Au nano-

crystals at the air-water interface and found Coulomb blockade

behavior. Diode-like characteristics have been observed using

CAFM measurements on a Au nanoparticle film supported on

a self-assembled gadolinium stearate monolayer.²⁵ Furthermore,

transport measurements have been carried out on layer-by-layer

assemblies, wherein nanocrystalline films interspersed with

bifunctional molecules built sequentially²⁶ have revealed that

transport through such films can be influenced by altering either

the nanocrystal diameter or the spacer length.²⁷ Similar results

have been obtained from a study of the conductivity of a two-

dimensional array of nanocrystals with patterned electrodes.^{28,29}

A Mott-Hubbard type metal-insulator transition has been

observed at room temperature by compressing a LB film of Ag

nanoparticles capped with dodecanethiol.³⁰ By tuning the

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appropriate capping agents.³² This novel method of obtaining ultrathin metal nanocrystalline films offers a fair degree of control of the properties of the films. We have now explored how the various reaction parameters can influence properties of the films. The parameters that we have studied are the concentration of the precursors, temperature, and contact time at the interface. The structures of the films have been examined by employing transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray diffraction (XRD). We have investigated the electrical properties of the Au films formed at the interface using the four-probe method. We have subjected the films to chemical modification by adsorbing alkanethiols and monitored the changes in the optical and electrical properties. The study has revealed that variation in the organometallic precursor concentration affects the size of the nanocrystals only slightly, while a change in the interface temperature or the contact time has a marked effect on the properties of the films. Adsorption of alkanethiols and conjugated thiols alters the properties of the films significantly, with the effect depending on the alkane chain length or the effective conjugation in the molecule.

Experimental Section

Ultrathin gold films were prepared at the toluene-water interface as follows. First, Au(PPh₃)Cl (Ph, phenyl) was prepared based on a known procedure.³³ Tetrakishydroxymethylphosphonium chloride (THPC) was obtained from Fluka and used without further purification. Water used in the experiments was double distilled using a quartz apparatus. In a typical preparation, 10 mL of a 1.5 mM solution of Au(PPh₃)Cl in toluene was allowed to stand in contact with 16 mL of 6.25 mM aqueous NaOH in a 100-mL beaker at 300 K. Once the two layers stabilized, 330 μ L of 50 mM THPC was injected into the aqueous layer using a syringe with minimal disturbance to the toluene layer. The onset of reduction was marked by a faint pink coloration of the liquid-liquid interface. The reduction thus initiated was allowed to proceed without disturbance for several hours. With the passage of time, the color became more vivid, finally resulting in a robust golden yellow film at the liquid-liquid interface. The aqueous and organic layers below and above the film were, however, transparent.

We have employed four different temperatures for the film growth, namely 30, 45, 60, and 75 °C. The films thus formed were transferred to mica or glass substrates after about 12 h depending on the temperature, when no further growth of the film was seen. To study the effect of contact time at the interface, the growth of the film was arrested after a specific period by simply transferring the film onto the substrate. Thus, films were collected after 30, 45, 60, 120, and 240 min of growth at 45 °C. Films were also prepared with different initial concentrations of the metal precursor (2, 8, and 16 mM). For adsorption studies, alkanethiols procured from Aldrich were used. In addition, a conjugated molecule, dimercaptodiphenylacetylene, was prepared following a literature procedure.³⁴ In all our investigations, film from the central region of the interface was used.

Transmission electron microscopy (TEM) was carried out using a JEOL 3010 operating at 300 kV. A tiny portion of the film was placed on a copper grid coated with thin carbon film and left to dry overnight. The films deposited on a mica or glass substrate were used directly for scanning electron microscopy (SEM) measurements on a Leica S-440 i microscope. Contact and tapping mode atomic force microscopy (AFM) images were obtained on films deposited on mica substrates employing a



Figure 1. Transmission electron micrographs of ultrathin nanocrystalline Au films prepared at the liquid—liquid interface at (a) 30, (b) 45, (c) 60, and (d) 75 °C. The histograms of particle size distribution are also shown. The scale bars correspond to 50 nm. A high-resolution image of an individual particle is shown in the center.

multimode scanner from Digital Instruments operated with a Nanoscope IV controller. X-ray diffraction measurements on the films deposited on glass were made with a Seiferts 3000 TT diffractometer (Cu Ka radiation). X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ESCALAB MK-IV spectrometer equipped with an Al Ka (1486.6 eV) source. The binding energies reported here are referenced to the C(1s) level at 284 eV. Samples for XPS were prepared by transferring the films onto graphite substrates. UV-visible spectra were recorded using a Perkin-Elmer Lambda 900 spectrometer by placing the film deposited on glass perpendicular to the beam in a regular quartz cuvette. Thiol adsorption experiments were carried out by filling the quartz cuvettes with 2.5 mL of the thiol solution (10 mM) in toluene. Four-probe electrical resistance measurements were measured in the 40-300 K range on the nanocrystalline films deposited on mica using a homemade setup connected to a Keithley multimeter. Rectangular electrical contacts separated from each other by 1 mm were made by gold sputtering using an Al mask. No noticeable damage was seen following deposition of the electrodes.

Results and Discussion

In Figure 1 we show TEM images of the nanocrystalline gold films obtained at the liquid—liquid interface held at different temperatures. The films comprise close-packed arrays of nanocrystals separated from one another by ~ 1 nm. In the film prepared at 30 °C (Figure 1a), the particles appear uniformly spherical with a narrow size distribution. High-resolution images show that the nanocrystals were by and large single crystalline as shown in the inset in the center of Figure 1. The image shows distinct (111) planes with a separation of ~ 2.3 Å. With increase in the interface temperature, however, particles of uneven shapes and sizes tend to form; some of them exhibit multiply twinned structures (see Figure 1d). The histograms shown alongside reveal how the size range of the nanocrystals increases progressively with the increase in temperature. The mean diameters of



Figure 2. X-ray diffraction patterns of nanocrystalline Au films obtained at different temperatures after transferring to glass substrates (radiation Cu K α).

the nanocrystals formed at 30, 45, 60, and 75 °C are 7, 10, 12, and 15 nm, respectively. While hexagonal close packing, typical of self-assembled nanocrystals,² is found in films prepared at 30 °C, those prepared at higher temperatures exhibit increased disorder. Thus, the high-temperature films somewhat resemble sputtered nanogranular gold films. Irrespective of the order in the film, the interparticle separation is, however, nearly constant at ~1 nm, perhaps due to the organic coating present on the particles. Note that what is shown in TEM micrographs in Figure 1 is only a monolayer structure of the film.

The crystallinity of the Au nanoparticles in the films is also revealed by the X-ray diffraction patterns shown in Figure 2. While the films obtained at 45 and 60 °C exhibit prominent (111) peaks (d = 2.33 Å), the film obtained at 30 °C shows weak and broad reflections due to the small particle size. The growth of the (111) peak with the increase in the interface temperature reflects the increase in the particle size. The particle sizes estimated from the width of the X-ray reflections are 5 and 6 nm for 45 and 60 °C, respectively, somewhat lower than the TEM estimates.

The morphology of the nanocrystalline films was monitored using SEM. As can be seen in the images in Figure 3, the films are fairly smooth and continuous over several tens of micrometers, although a few micropits and cracks are present. The film prepared at 30 °C shows a relatively greater number of pits and cracks, and that formed at 60 °C exhibits longer cracks with very few pits. The widths of the pits and cracks do not generally exceed 300 nm. The AFM images covering a few micrometers yield a root-mean-square roughness in the range 30-35 nm with a maximum peak-to-valley distance of \sim 80-100 nm. For thickness measurements, images acquired at the broken edges of the films were used. The image in Figure 4a shows one such boundary of the 30 °C film on mica substrate, and the height profile in Figure 4b gives an estimate of the thickness to be ~ 60 nm, which corresponds to around eight monolayers of nanoparticles. The jagged line profile on the right corresponds to the variation in the film thickness with trenches of \sim 7 nm indicating missing particles in the top layer. Several such measurements have shown the thickness of the films to be in the 40-140 nm range. The above observations suggest that the growth of the Au film is essentially limited to the liquid-liquid interface. We did not, however, observe any discernible trend in the film thickness with the interface temperature.

Electron transport properties of the films are interesting as demonstrated in Figure 5. As seen from the figure, the resistance of the 30 °C film is in the range of megaohms (M Ω) while that of the 45 °C film is in the kiloohm (k Ω) range for the given configuration of the electrodes. The resistance of the films



Figure 3. Scanning electron micrographs of nanocrystalline Au films obtained at (a) 30 and (b) 60 °C after transferring to mica substrates. The scale bars correspond to 1 μ m.



Figure 4. (a) Contact mode AFM image showing the boundary of Au film on a mica substrate; (b) *z*-profile of the film boundary.

formed at higher temperatures (60 and 75 °C) is on the order of few ohms. Interestingly, we observe a "metallic type behavior" in the films prepared at higher temperatures (Figure 5c,d), where the size of the nanocrystals is also higher (see Figure 1c,d). Assuming the average thickness of the films to be 100 nm, we estimate the values of the temperature coefficient of resistance to be $\sim 1.7 \times 10^{-11}$ and $4.7 \times 10^{-11} \Omega$ m/K,



Figure 5. Temperature variation of electrical resistance of nanocrystalline Au films prepared at (a) 30, (b) 45, (c) 60, and (d) 75 $^{\circ}$ C (current used 10 mA).

respectively, for the 60 and 75 °C films. These values are to be compared with the value of $8.22 \times 10^{-11} \Omega$ m/K of bulk gold. However, the estimated resistivity values ($\sim 10^{-4} \Omega$ cm) are higher than that of bulk gold ($1.3 \times 10^{-6} \Omega$ cm). These values are comparable to the reported resistivity of Au monolayer films anchored to polystyrene substrate.³⁵ The films obtained at 30 and 45 °C are essentially activated conductors with small activation energies of 11 and 1 meV, respectively, as estimated from the Arrhenius plots. The presence of pits in these films may contribute to the high resistance (see Figure 3a). The electrical behavior of the films found by us resembles that of the protected Au-monolayer cluster films reported by Murray et al.³⁶ and of the dithiol-linked nanoparticle network by Brust et al.³⁷

The Au films formed at all four temperatures exhibit a strong absorption band around 700 nm. This wavelength is rather long compared to the plasmon absorption observed at \sim 540 nm in colloidal Au nanocrystals in solution.³⁸ The position and the intensity of the plasmon band in such nanocrystal assemblies are truly indicative of the state of aggregation of the nanocrystals.38-43 The red-shifted band observed here may arise from the proximity of the nanocrystals in the film. This can be seen from Figure 6, where we demonstrate how the intensity of the plasmon absorption band grows as a function of the preparation time allotted for the film at the liquid-liquid interface held at 45 °C. In the initial stages, the film is very fragile, looks dull red like colloidal gold, and exhibits the plasmon band centered around 600 nm. After 1 h of growth at the interface, the film becomes robust with a typical golden yellow color and gives rise to a band at 670 nm. After 120 min of growth at the interface, we find that the band is shifted to even longer wavelength at ~690 nm with an accompanying increase in the intensity. Beyond 120 min, the absorption band shows negligible changes. At this stage, the film is presumably well packed with fully grown nanocrystals, increasing the electronic coupling. This system is somewhat comparable to the one described by Rechberger et al.³⁹ and by Haynes et al.,⁴⁰ who monitored optical properties of interacting nanoparticles by varying the interparticle distance. The red shift of the plasmon band with decreasing distance was interpreted by these workers



Figure 6. Evolution of electronic absorption spectra with growth of nanocrystalline Au film at the interface. Interface temperature was 45 °C. The spectra were measured ex situ. Each time the growth was arrested by transferring the film to a glass substrate.



Figure 7. Temperature variation of electrical resistance of nanocrystalline Au films after 45 and 180 min of growth at the liquid–liquid interface at 75 $^{\circ}$ C (current used 10 mA). The corresponding TEM micrographs of the films are shown along with the histograms.

as due to the increasing dipole–dipole interaction between the particles. Similar observations have been made in the case of evaporated metal films.⁴⁴

We have carried out resistance measurements on the films collected at the different stages of growth at the liquid-liquid interface held at 75 °C. In Figure 7, we show how the film collected after 45 min of growth behaves like an activated conductor while that collected after 180 min is metallic. The latter is similar to the data shown in Figure 5 corresponding to the film that was collected after 12 h of growth at the interface at 75 °C. TEM images shown alongside in Figure 7 provide an estimate of the mean particle sizes of 11 and 14 nm, respectively. These values may be compared with those obtained from Figure 1. Clearly, the contact time and the temperature have a similar influence on the film properties. The films prepared with different initial concentrations of the AuPPh₃Cl precursor reveal that, with low concentrations of 2 mM or less, the films are extremely thin and unstable despite standing for several hours at the interface at room temperature. Furthermore, the aqueous layer developed coloration due to formation of the Au sol. At higher concentrations of the precursor (8 and 16 mM), good quality films were obtained within 24 h. The TEM images, however, revealed no noticeable differences in the size of the nanocrystals (mean 15 nm).

In the Au nanocrystalline films investigated in the present study, the nanocrystals are likely to be stabilized by the triphenylphosphine ligands from the precursor, giving rise to



Figure 8. (a) Electronic absorption spectra of an Au film before and after treatment with hexadecanethiol solution for 6 h. Tapping mode AFM images are shown alongside (scan area 500×500 nm). (b) Variation in absorption maximum with alkane chain length of thiol adsorbed. The films were obtained at 75 °C after 180 min.

narrow separations (~ 1 nm). The Au(4f) spectrum of the 30 °C film indeed showed a broad doublet, which could be fitted to two Au species with $4f_{7/2}$ binding energies of 84 and 85.2 eV. This is consistent with the picture of a metallic core surrounded by a layer of Au atoms bound to the capping agents.⁴⁵ The latter may consist of triphenylphosphine ligands and ionic species from THPC. The X-ray photoelectron spectrum also revealed the presence of phosphorus and chlorine in the film. Properties such as the electrical conductivity and the shifts in the surface plasmon band seem to originate from the interactions between the particles across the organic spacer. Small particles can have charging energies of a few hundred millielectronvolts,²² and in such cases, charge hopping across the film may not be a thermally activated process in the temperature range studied (40-300 K), making the film an activated conductor. With an increase in the particle size, the charging energy decreases to a few millielectronvolts and the film essentially becomes metallic, as do the films prepared at 60 and 75 $^{\circ}\text{C}.$ Their resistivity is higher than that of bulk gold perhaps due to irregular grain boundaries and defects.

We have investigated the properties of the nanocrystalline Au films subjected to chemical perturbation brought about by interaction with *n*-alkanethiols of varying chain lengths (Figure 8). For this purpose, a portion of the film (75 °C, 180 min) on glass was dipped in a 10 mM toluene solution of an alkanethiol for 6 h. The electronic absorption spectrum recorded following the interaction with hexadecanethiol (see Figure 8a) exhibits a plasmon band that is blue shifted from 697 to 569 nm. This



Figure 9. (a) Temperature variation of electrical resistance of Au films (75 $^{\circ}$ C, 180 min) before and after treatment with hexadecanethiol and hexanethiol. (b) Temperature variation of electrical resistance of an Au film (45 $^{\circ}$ C, 60 min) before and after treatment with dimercapto-diphenylacetylene.

observation suggests that the electronic coupling between the particles is considerably reduced following the attachment of the thiol. Interaction with thiol also brings about a change in the morphology of the film as shown in the adjoining AFM images. Interestingly, the effectiveness of the alkanethiols in perturbing the Au films seems to depend on the hydrocarbon chain length. The plot in Figure 8b shows that the plasmon band position varies linearly with the chain length with a slope of 5.6 nm per methylene unit. In Figure 9, we show how the electrical property of a film can change depending on the thiol employed to perturb it. Thus, upon interacting with hexadecanethiol, a metallic film (75 °C, 180 min) behaves like an activated conductor (Figure 9a) with a reversal of slope around 150 K. Such a temperature-dependent change in conduction through nanocrystal superlattices has been interpreted as due to a "metal-insulator" transition.³⁰ On the other hand, hexanethiol with a shorter chain length essentially retains the metallic nature of the pristine film (see Figure 9a). This is in accordance with the observation of Shiigi et al.,35 who found that Au nanocrystal films coated with shorter chain length thiol are more conducting. Interestingly, on interaction with dimercaptodiphenylacetylene, a conjugated molecule,⁴⁶ the resistance of a film (45 °C, 60 min) decreases, becoming metallic (see Figure 9b). A more detailed study is underway to address these issues.

Conclusions

The present study of the properties of ultrathin nanocrystalline Au films prepared at the liquid—liquid interface under different conditions has revealed many interesting features. The size of the nanocrystals constituting the film markedly increases with the temperature employed for preparation, but the concentration

of the organometallic precursor has little effect. The nanocrystals are generally separated by ~ 1 nm under the conditions of preparation employed by us. The films are generally smooth and continuous over a length scale of several micrometers, the overall thickness being in the range of 40–140 nm. Electrical resistance measurements using the four-probe method show that the film prepared at room temperature behaves as an activated conductor with a high resistance ($\sim few M\Omega$). The resistance gradually decreases with increase in preparation temperature, vielding metallic films. UV-vis absorption spectra reveal that the surface plasmon band of gold is red-shifted markedly in the films, likely due to electronic coupling between particles. Interaction with alkanethiols perturbs the films considerably, the magnitude of the perturbation depending on the chain length of the thiol. Such perturbation also affects the electrical properties of the films, with the long chain thiols increasing the resistance. Interaction with dimercaptodiphenylacetylene, on the other hand, decreases the resistance of the film.

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