NANO LETTERS

2001
Vol. 1, No. 2
67−70

Assembling Gold Nanoparticles as Nanostructured Films Using an Electrophoretic Approach

Nirmala Chandrasekharan and Prashant V. Kamat*

Notre Dame Radiation Laboratory, Notre Dame, Indiana 46556-0579

Received September 25, 2000

ABSTRACT

A three-dimensional array of gold nanoparticles has been assembled on a nanostructured TiO_2 template by subjecting the colloidal gold suspension to a dc electric field (50–500 V). By controlling the concentration of gold colloids in toluene and the applied voltage, it is possible to control the thickness of nanostructured gold film without inducing aggregation effects. As indicated by Atomic Force Microscopy, these gold films are highly porous and consist of nanoparticle assembly of fairly uniform size. The surface plasmon characteristics observed in these nanostructured gold films suggest that these particles retain the identity of individual nanoparticles.

Introduction. In recent years, a burst of research activities have been seen in casting nanostructured films of semiconductors and metals that display size-dependent optical, electronic, and chemical properties (see for example, references[1−8]). Few efforts have been made to cast nanostructured films of metal nanoparticles by direct electrodeposition[9,10] or by using thiol derivatized gold surfaces.[11,12] Assembling nanoclusters as thin films provides a two or three-dimensional network of nanoparticles that can suitably be functionalized with photo or electroactive groups. Of particular interest are the nanoscale metals, which have important applications in biological nanosensors and optoelectronic nanodevices.[13−15] Ultrathin polarizing films cast from gold islands are considered to be useful micro-polarizers for fiber-embedded in-line optical devices, micro-optics, and hybrid integrated optics.[16]

Previous efforts to deposit metal nanoclusters as thin films using Langmuir Blodgett film or the self-assembled monolayer approach have provided very low coverage of these particles.[17−22] Although these techniques are quite effective for assembling gold nanoparticles as two-dimensional arrays on an electrode surface, their low surface area limits their use for further chemical modification. More recently, the ordered assembly of gold nanoparticles has been achieved on copper grids[23,24] and conducting glass plates.[25] It was shown that interparticle distance could be controlled by the size of the alkane chains on the stabilizers used in the preparation of the sols. Monodisperse fractions of thiol-stabilized gold nanoparticles have also been crystallized into two- and three-dimensional superlattices.[26] The deposition of thicker films of metal nanoparticles is often difficult because close packing of nanoclusters leads to interparticle interactions. Such aggregated nanoclusters exhibit optical properties that are different from those of dispersed nanoparticles. We present here a simple method of casting three-dimensional assembly of gold nanoparticles that exhibit strong surface plasmon resonance characteristics. To the best of our knowledge, this is the first such report that highlights the feasibility of achieving relatively thick nanoporous gold films with minimal aggregation effects.

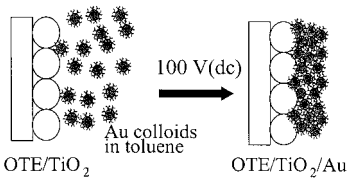
Experimental Section. Highly concentrated (12 mM) gold nanoparticles in toluene were prepared according to the previously reported procedure.[27−29] $HAuCl_4$ (Source: Aldrich) dissolved in water was extracted into the organic phase using a phase-transfer reagent, tetraoctylammonium bromide (TOAB, Source: Fluka), and reduced with $NaBH_4$. The colloids were then washed with dilute HCl and then with deionized water. Na_2SO_4 was added to remove traces of water from the colloidal solution. The gold suspension in toluene was diluted to achieve the desired concentrations (The concentration of TOAB in the resultant solution was maintained at ∼2.4 mM). Transmission electron micrographs of gold solution in THF showed nearly spherical particles with a diameter of 5−8 nm.

Nanostructured TiO_2 films were cast on Optically Transparent Electrodes (OTE, Conducting glass obtained from Pilkington, 20 ohms/□) by spreading a colloidal TiO_2 suspension over an area of 2 cm^2. The electrode was further annealed at 673 K. The colloidal TiO_2 particles had a diameter of 10−15 nm, and the film thickness was about 1 μm. The TiO_2 film deposited OTE electrode (connected to positive terminal) and another plain OTE electrode were

* To whom correspondence should be addressed. E-mail: pkamat@nd.edu; or http://www.nd.edu/∼pkamat.

10.1021/nl000184f CCC: $20.00
Published on Web 12/13/2000

Scheme 1. Electrophoretic Deposition of Gold Nanoparticles on an Optically Transparent Electrode (OTE) Modified with Nanostructured TiO_2 Film



immersed in a small glass cell containing the colloidal gold in toluene. The distance between the two electrodes was maintained at 3 mm. A dc voltage (50−500 V) was applied to initiate the electrodeposition process.

The electrophoretic deposition process was stopped at 4-min intervals, and the absorption spectrum of the electrode was recorded after being washed with toluene. We attribute this deposition process to an electrophoretic phenomenon in which the charged gold nanoparticles migrate and become deposited on the OTE/TiO_2 electrode (Scheme 1). The charging of particles during the application of the dc electric field was also apparent from the settling of gold particles when we continue the application of dc field for an extended period. (The particles can be resuspended by shaking the suspension.) The presence of porous TiO_2 film on the OTE surface was found to be essential for achieving a good deposition of gold nanoparticles. No significant deposition could be seen when we exclude TiO_2 films from the OTE surface. The gold particulate film cast on the nanostructured TiO_2 film was transparent enough to perform spectroscopic measurements.

Results and Discussion. One of the major problems encountered during the direct deposition of gold nanoparticles (e.g., by solvent evaporation technique) is the interparticle interaction leading to aggregation effects. Upon aggregation, the metal nanoparticles lose the surface plasmon absorption that are characteristic of individual gold nanoparticles. These films usually exhibit blue coloration caused by the red-shift in the absorption band.[30] Such effects have already been demonstrated by means of surface charge neutralization and pressure dependent studies in L−B films.[31,32] One way to overcome these interparticle interactions is to functionalize the gold nanoparticles with thiols. By employing the electrophoretic deposition method, Gersig and Mulveney[23,24] succeeded in assembling thiol capped gold nanoparticles as a two-dimensional array on the copper grid. In the present investigation, we focus on casting a three-dimensional network of gold nanoparticles on a nanostructured TiO_2 film using a similar electrophoretic approach.

Figure 1 shows the absorption spectra of gold films cast on nanostructured TiO_2 films. The absorption spectra were recorded at different time intervals following the deposition of gold nanoparticles using a Shimadzu spectrophotometer. At early stages of electrophoretic deposition, the absorption is dominated mainly by the TiO_2 film (spectra a and b in Figure 1). Some scattering effects also contribute to the absorption in the visible. With increasing deposition time, we observe an increase in the absorption in the visible. The

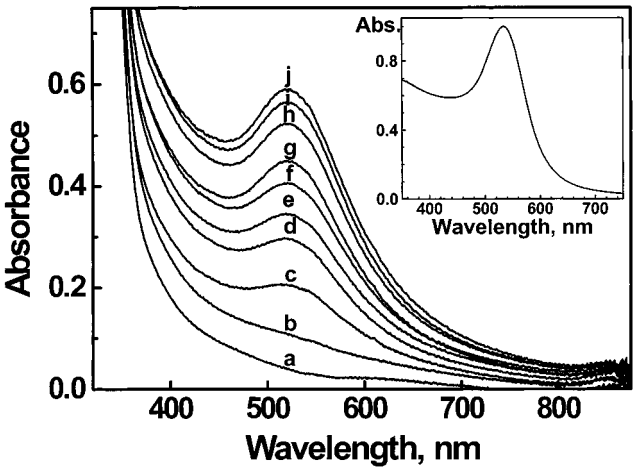


Figure 1. Absorption spectra of gold films cast on nanostructured TiO_2 films. The spectra were recorded at time intervals of (a) 0, (b) 2, (c) 10, (d) 18, (e) 26, (f) 34, (g) 46, (h) 50, (i) 58, and (j) 70 min. A dc electric field of 100 V was applied to OTE/TiO_2 electrode in contact with 2.5 mM gold colloidal suspension in toluene containing ~2.4 mM of tetraoctylammonium bromide (TOAB). The inset shows the absorption spectrum of 0.3 mM of Au colloids in toluene.

prominent absorption maximum seen at 516 nm arises from the surface plasmon band gold nanoparticles. The increase in the absorption of the surface plasmon band with time (Figure 1) represents the deposition of gold nanoparticles on TiO_2 surface as a three-dimensional array. By continuing the electrophoretic deposition for an extended period of time, we can achieve relatively thick gold films with an absorbance of the surface plasmon band as high as 2. Such a high value of absorption is an indication that a large number of gold nanoparticles (~1.13 mmol Au/cm^2) are assembled as nanostructured film.

The prominent absorption band of the gold particulate film has a spectral feature similar to the absorption spectrum (abs. max. 530 nm) of the gold colloids in toluene solution (see inset in Figure 1). However, the tail absorption in the red region (600−700 nm), as well as the broader feature of the surface plasmon band, are indicative of the fact that the interparticle interaction and/or altered medium of the immediate surroundings can influence the optical properties of the gold nanoparticles in the film. If the aggregation effects were to dominate in these films, we would have observed a broad band in the IR region (700−900 nm). As shown earlier, the surface plasmon band is very sensitive to immediate surroundings.[31,33,34] The binding of chemical species to the gold surface has a pronounced effect of dampening of the plasmon band. In the present case, the surface adsorbed TOAB in the nanostructured gold film is likely to have some influence on the dampening of the absorption band.

The electrophoretic deposition methodology described here is quite effective in assembling gold nanoparticles as a three-dimensional array without inducing interparticle interactions. These films are quite robust and do not undergo any visible changes under ambient conditions. The surface capping of TOAB is likely to act as a spacer between the adjacent particles in the film. A similar role of surfactants in

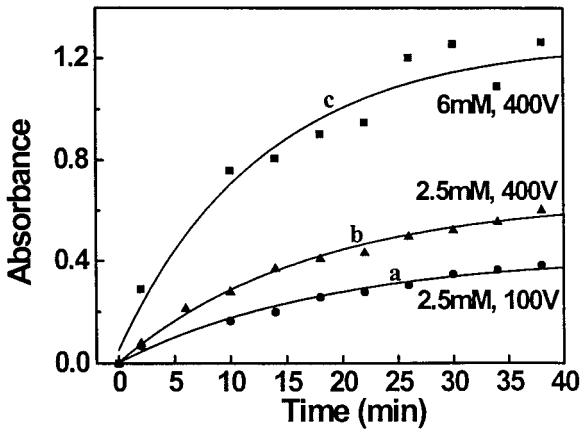


Figure 2. Growth of plasmon absorption band of the nanostructured gold film during the electrodeposition process. The experimental conditions for the deposition of gold nanoparticles on OTE/TiO_2 electrode were (a) 2.5 mM gold and 100 V; (b) 2.5 mM gold and 400 V; and (c) 6 mM gold and 400 V.

suppressing the aggregation effects of dye molecules on TiO_2 surfaces have been discussed earlier.[35] The alkane chains of the stabilizers that were used in the preparation of the gold sols have also been shown to control the interparticle distance in the ordered assembly of gold nanoparticles.[23,24]

The nanostructured TiO_2 film acts as a template for the assembly of these gold nanoparticles and, thus, influences overall deposition process. The fact that the gold nanoparticles suspended in TOAB/Toluene become deposited on positively charged TiO_2 film is an indication that the gold nanoparticles carry a net negative charge. Although the gold nanoparticles are capped with the positively charged TOAB, this organic cap is rather labile and can be readily replaced with other substituents (See for example, complexation of 1-pyrenemethylamine with gold nanoparticles in TOAB/toluene[29]). Further enhancement in the negative charge accumulation can occur during the encounter of particles with the dc electric field. The TOAB capping simply provides the necessary screening during the transit of nanoparticles to the TiO_2 film. Once the gold nanoparticles approach the positively charged TiO_2 surface, a few of the TOAB molecules are exchanged on the TiO_2 surface, and the rest protect gold nanoparticles from interparticle interactions.

The rate of gold nanoparticle deposition was dependent on both the applied voltage and initial concentration of gold solution. Figure 2 shows the rate of gold nanoparticle deposition on TiO_2 films (indicated by the increase in the plasmon absorption at 516 nm with time). At a lower dc voltage, the deposition occurs with a rate of 0.022 s^{-1}. The initial deposition rate increases with increasing concentration of gold colloids and deposition voltage. When the concentration was increased to 6 mM and the applied dc voltage was increased to 400 V, we observe an increase in the deposition rate constant of 0.067 s^{-1}. In all of these deposition conditions, the identity of the nanoparticles in the film is retained. At gold concentrations of 12 mM, the films showed aggregation effects with a broad absorption extending into the red-infrared region.

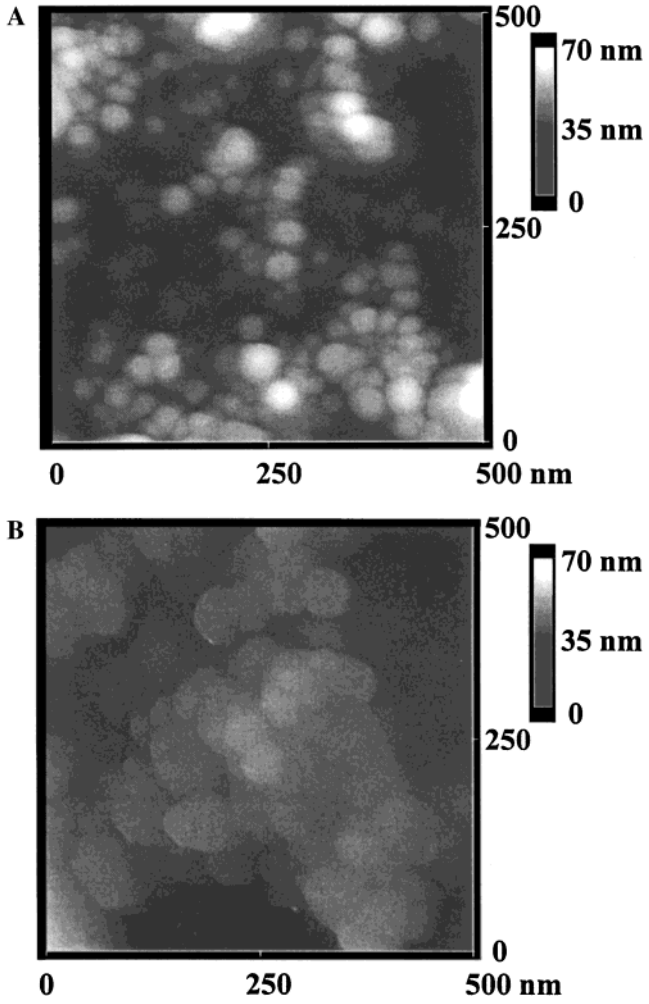


Figure 3. AFM images of gold nanoparticles assembled as thin films on OTE/TiO_2 electrode using (A) 0.25 mM and (B) 12 mM gold colloids in toluene. Imaging was done using a Nanoscope IIIa from Digital Instruments employing etched Silicon tips as probes. The image was recorded in the tapping mode after electrodepositing gold nanoparticles on an OTE/TiO_2 using a dc field of 100 V.

Figure 3 A and B show the AFM images of nanostructured gold films that were recorded following the deposition of gold nanoparticles on OTE/TiO_2 electrode. AFM images recorded in Figure 3 show that such a particle growth process is dependent on the initial gold concentration. The AFM image of the nanostructured gold film recorded in 3A exhibits an assembly of gold nanoparticles of fairly uniform size (with an average diameter of 20−25 nm). The AFM image in Figure 3B shows larger aggregated clusters of 50−60 nm diameter. We also observed significant dampening of surface plasmon band for the films containing these large size nanoclusters. Note that these films were cast using 0.25 mM and 12 mM colloidal gold solution, respectively. Obviously, a higher concentration of gold colloids leads to the rapid growth of gold nanoparticles during the electrophoretic deposition. Moreover, the particle diameters of the two examples shown in Figure 3 are significantly larger than the initial diameter (5−8 nm) of suspended gold nanoparticles. This further supports the argument that several gold nanoparticles from solution must be coalescing to form a larger particle during the electrophoretic deposition process. Choos-

ing a lower gold concentration during the electrophoresis can minimize the growth process and can yield films that exhibit strong surface plasmon absorption. Although these particles are deposited as closely packed as arrays, they retain the properties of individual particles and remain separated without undergoing aggregation or inducing bulk film effects.

The nanostructured film obtained by electrodeposition method is highly porous, thus providing a large surface area for anchoring electroactive or photoactive molecules. The ability to assemble gold nanoparticles as a 3D-array of clusters opens up new avenues for designing sensors and optoelectronic nanodevices. Nanostructured gold films of high surface area also have potential applications in catalysis and photoelectrochemistry. For example, 3-fold enhancement in the photocurrent generation efficiency can be achieved by coupling gold nanoparticles to the nanostructured semiconductor electrode surface.[36] Further work is underway to modify the nanostructured gold surfaces with electroactive and photoactive organic molecules that can bind strongly to the gold surface.

Acknowledgment. We would like to thank Dr. George Thomas for helpful discussions. The research described herein was supported by the Office of the Basic Energy Sciences of the US Department of Energy. This is Contribution No. NDRL 4228 from Notre Dame Radiation Laboratory.

References

(1) Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 183.
(2) Wang, Y.; Herron, N. *Science* **1996**, *273*, 632.
(3) Henglein, A. *J. Phys. Chem.* **1993**, *97*, 5457.
(4) Kamat, P. V. Composite Semiconductor Nanoclusters. In *Semiconductor Nanoclusters − Physical, Chemical and Catalytic Aspects*; Kamat, P. V., Meisel, D., Eds.; Elsevier Science: Amsterdam, 1997; p 237.
(5) Mulvaney, P.; Giersig, M.; Henglein, A. *J. Phys. Chem.* **1993**, *97*, 7061.
(6) Pileni, M. P. *New J. Chem.* **1998**, 693.
(7) Henglein, A. *Langmuir* **1998**, *14*, 6738.
(8) Link, S.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 4212.
(9) Trau, M.; Sankaran, S.; Saville, D. A.; Aksay, I. A. *Nature* **1995**, *374*, 437.
(10) Nakato, Y.; Murakoshi, K.; Imanishi, A.; Morisawa, K. *Electrochemistry* **2000**, *68*, 556.
(11) Gilbert, S. E.; Cavalleri, O.; Kern, K. *J. Phys. Chem. B* **1996**, *100*, 12 123.
(12) Cavalleri, O.; Kind, H.; Bittner, A. M.; Kern, K. *Langmuir* **1998**, *14*, 7292.
(13) Hickman, J. J.; Ofer, D.; Laibinis, P. E.; Whitesides, G. M.; Wrighton, M. S. *Science* **1991**, *252*, 688.
(14) Chen, S.; Ingram, R. S.; Hostetler, M. J.; Pietron, J. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Alvarez, M. M.; Whetten, R. L. *Science* **1998**, *280*, 2098.
(15) Elghanian, R.; Storhoff, J. J.; Mucic, R. C.; Letsinger, R. L.; Mirkin, C. A. *Science* **1997**, *277*, 1078.
(16) Baba, K.; Takakuwa, M.; Miyagi, M. *Optical Rev.* **1997**, *4*, 411.
(17) Amihood, D.; Katz, E.; Willner, I. *Langmuir* **1995**, *11*, 1313.
(18) Colvin, V. L.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1992**, *114*, 5221.
(19) Fan, H.; Lopez, G. P. *Langmuir* **1997**, *13*, 119.
(20) Sarathy, K. V.; Raina, G.; Yadav, R. T.; Kulkarni, G. U.; Rao, C. N. R. *J. Phys. Chem. B* **1997**, *101*, 9876.
(21) Chen, S. *J. Phys. Chem. B* **2000**, *104*, 663.
(22) Brust, M.; Bethell, D.; Schiffrin, D. J.; Kiely, C. J. *Adv. Mater.* **1995**, *7*, 795.
(23) Giersig, M.; Mulvaney, P. *Langmuir* **1993**, *9*, 3408.
(24) Giersig, M.; Mulvaney, P. *J. Phys. Chem.* **1993**, *97*, 6334.
(25) Hayward, R. C.; Saville, D. A.; Aksay, I. A. *Nature* **2000**, *404*, 56.
(26) Kiely, C. J.; Brust, M.; Bethell, D.; Schiffrin, D. J. *Nature* **1998**, *396*, 444.
(27) Brust, M.; Walker, M.; Bethell, D.; Schffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801.
(28) Fink, J.; Kiely, C.; Bethell, D.; Schiffrin, D. J. *Chem. Mater.* **1998**, *10*, 922.
(29) George Thomas, K.; Kamat, P. V. *J. Am. Chem. Soc.* **2000**, *122*, 2655.
(30) Brust, M.; Bethell, D.; Kiely, C. J.; Schiffrin, D. J. *Langmuir* **1998**, *14*, 5425.
(31) Fujiwara, H.; Yanagida, S.; Kamat, P. V. *J. Phys. Chem. B* **1999**, *103*, 2589.
(32) Kim, S.-H.; Medeiros-Ribeiro, G.; Ohlberg, D. A. A.; Stanley Williams, R.; Heath, J. R. *J. Phys. Chem. B* **1999**, *103*, 10 341.
(33) Linnert, T.; Mulvaney, P.; Henglein, A. *J. Phys. Chem.* **1993**, *97*, 679.
(34) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer: Berlin, 1995.
(35) Khazraji, A. C.; Hotchandani, S.; Das, S.; Kamat, P. V. *J. Phys. Chem. B* **1999**, *103*, 4693.
(36) Chandrasekharan, N.; Kamat, P. V. *J. Phys. Chem. B* **2000**, *104*, 10851.

NL000184F