

Polymer-Mediated Assembly of Gold Nanoclusters

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Received June 22, 2000. In Final Form: September 13, 2000

Low molecular weight, ≤ 4000 , polymers containing amine functionalities such as polyethyleneimine or poly-L-lysine serve as a scaffold for assembly of carboxylic acid functionalized gold clusters. The assembly produces at the liquid–air interface of the reaction medium, free-standing, space-filling films that are one monolayer thick. Assembly was promoted through the formation of peptide bonds by the addition of a carbodiimide but also proceeds in the absence of the carbodiimide by ion pairing. The morphology of the films is sensitive to the nature of the acid coating on the gold clusters with mercaptododecanoic acid and mercaptosuccinic acid forming more regular films than those coated with thioctic acid.

Introduction

The area of nanotechnology has undergone a remarkable growth in the past few years. This development has been fueled by the expectation that unusual properties of matter that become evident as the dimensions of the structural components of a device shrink under 100–10 nm may be exploited. A few examples of inroads made to uncover some of the potential benefits that might be accrued in the future are given as follows: the use of semiconductor nanocrystals as fluorescent biological labels,¹ quantum dot bioconjugates for ultrasensitive detection,² a single-electron transistor,³ a single-electron memory device operating at room temperature,⁴ a quantum cascade laser.⁵

As attractive and promising as these developments sound, the obstacles required to fabricate nanostructured devices are daunting. The difficulties stem from their very nature, which require specialized tools and techniques to (a) generate particles or features ≤ 10 nm, (b) assemble these features or promote assembly into a working arrangement, and (c) establish electrical or optical access from the macroscopic world down to the dimensions of the device. Progress in all these areas is being made, particularly in the first two. Colloidal particles are prepared at ever decreasing sizes and narrower distributions exploiting the confinement provided by inverse micelles⁶ or dendrimers.⁷ Alternatively, new direct synthetic methods have enabled the preparation of small

clusters of gold.⁸ Assembly of metallic clusters into two-dimensional arrays has been achieved by exposing treated surfaces to derivatized colloids so that acid–base or chemical affinity interactions would drive assembly.⁹ Three-dimensional assembly is also feasible producing superlattices, which crystallize directly¹⁰ or through the intervention of an appropriate polymeric material to create a “brick and mortar” structure.¹¹ Finally, devices that incorporate macroscopic access to nanostructured assemblies have been fabricated.¹²

We have prepared free-standing films of gold clusters, about 4 nm in size, assembled through the interaction between low molecular weight polymers containing amine functionalities and the carboxylic acid moieties coating the gold clusters. Differences were observed, as revealed by transmission electron microscopy, in the structure of these films depending on the nature of the coating of the gold particles. Attempts were made to elucidate the physicochemical factors affecting the morphology of the films. This is a preliminary result of a broader effort to

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fabricate single electron devices using biomolecules as scaffolding for assembly.

Experimental Section

Chemicals. Poly-L-lysine as the hydrobromide with average molecular weights of 1–4k and 30–70k were purchased from Sigma. 12-Mercaptododecanoic acid was prepared according to a published procedure.¹³ A methanolic solution of fourth generation hydroxy-terminated polyamido dendrimer and polyethyleneimine with average molecular weights of 2k and 25k as well as all other chemicals were purchased from Aldrich and used without further purification. High resistivity water (18 M Ω cm) was obtained from a Barnstead deionizer fed with distilled water.

Colloid Preparation. Two procedures were followed. Gold, 0.5 mmol as HAuCl₄, was coated directly in methanolic solutions according to the procedure described by Chen and Kimura¹⁴ using 1.25 mmol of acid of either mercapto succinic acid or thioctic acid. In a second procedure, clusters coated with mercaptododecanoic acid were obtained by a modification of the preparation given by Zhao and Crooks¹⁵ which involves the use of polyamido dendrimers and electroless displacement of a copper metal colloid by Au(III) ions. In the present study, the dendrimer-enclosed gold clusters, about 5 μ mol, were treated with 12-mercaptododecanoic acid using $1/3$ equiv of thiol to the original gold ions used for the copper displacement. The reaction was conducted in 30 mL of a 2:1 mixture of water and tetrahydrofuran. The insoluble product became apparent as turbidity after 15 min of stirring. The mixture was extracted with 4.0 mL of toluene and then centrifuged. A film containing the reddish gold colloid coagulated at the interface. The clear aqueous solution was replaced with an equal volume of 0.1 N hydrochloric acid and the mixture stirred vigorously and centrifuged. The gold colloid that coagulated at the interface again was isolated and dissolved in 4.0 mL of dimethylformamide (DMF). The DMF solution, free of dendrimer, was stable for many weeks and could be diluted with water without any precipitate being formed. The same procedure is applicable to gold clusters coated with alkyl-terminated thiols. However in that case, the coated gold clusters free of the initial dendrimer were transferred to the organic phase.

The gold clusters coated with mercaptosuccinic acid had an average diameter of 1.5 nm as measured by peak broadening in the X-ray diffraction pattern. This preparation was highly susceptible to electron beam damage producing visible agglomeration after a few seconds of exposure. Interestingly, the clusters were much more stable when incorporated into films obtained after reaction with polyethyleneimine. In contrast to this preparation, the clusters coated with thioctic acid were 3.0 nm in diameter. Both products were obtained as the sodium salt and converted to the acid prior to reaction with the polymer. The succinic acid-coated clusters were water soluble, but the thioctic acid-coated clusters were not soluble in water. These were separated by centrifugation and washed prior to dissolution in DMF.

Film Formation. Films formed at the liquid–vapor interface of reaction mixtures obtained after a few minutes of stirring of a solution containing the carboxylic acid-coated gold colloids and equivalent amounts of polyethyleneimine or poly-L-lysine. The films were apparent as a reflective coating on the surface and could be isolated as platelets as large as 1–2 mm on each side. In some instances peptide linkages between the acid and the polymer were made through the intervention of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, EDC, by itself or through an intermediate step involving the use of *N*-hydroxysuccinimide, NHS, to modify the carboxylic acid into an amine-reactive NHS ester. The reaction mixtures between colloids and polymers also produced powdery black precipitates in addition to the floating films. The films may be isolated and further purified by transferring the supernatant liquid containing the film to a clean dish and then washing repeatedly with water and methanol and carefully replacing the underlying liquid with a pipet or a syringe. Finally an appropriate support is set at the bottom and all the

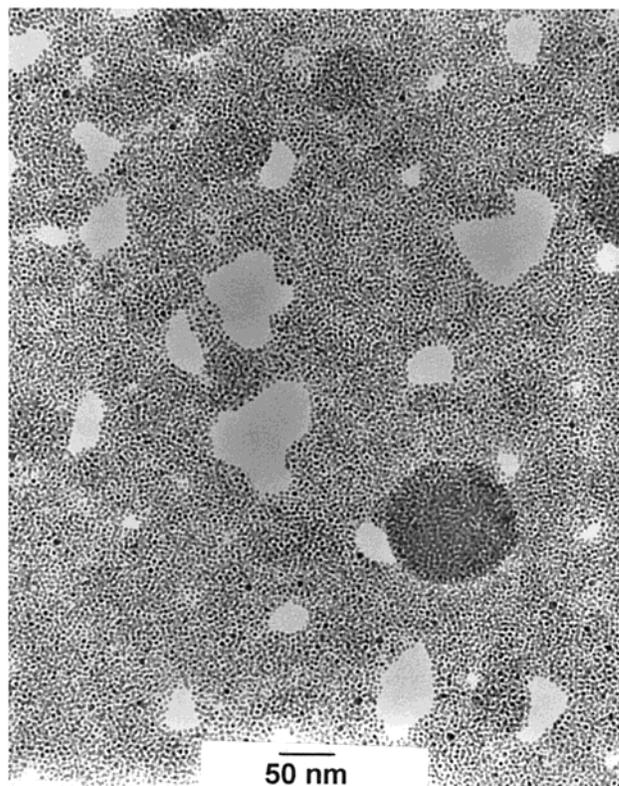


Figure 1. Micrograph of film collected at the surface of the reaction mixture of low molecular weight polyethyleneimine and gold clusters coated with mercaptododecanoic acid.

liquid is withdrawn causing the film to deposit on the support. We have initiated electrical characterization of the films isolated in this manner and will report the results soon.

Characterization. The coated colloids were characterized by X-ray diffraction, XRD, to confirm purity and to derive an average crystallite size according to the Scherrer equation. In addition to this, infrared spectra of the coated colloids were also obtained. The free-standing films were placed directly on Formvar-coated copper grids for transmission electron microscopy, TEM, to examine particle size and spatial organization. Infrared spectra of the films and the solids were obtained after thorough washing to remove the reaction medium in order to assess the local molecular environment giving rise to the association.

Results and Discussion

The morphology and microstructure of a film obtained through the reaction between mercaptododecanoic acid and the low molecular weight polyethyleneimine without the addition of carbodiimide is illustrated with the micrograph in Figure 1. The film appears to be a monolayer. In some cases superposition of small circular assemblies on top of an underlying layer was observed. The gold clusters appear as a space-filling continuous film with no evidence of a regular geometric orientation as those found in two-dimensional superlattices. However, there is a periodicity in the arrangement of what appear to be aggregates of clusters strung along, a few units at a time. The periodicity was confirmed by observation of a diffraction ring in the TEM corresponding to a center-to-center distance of 5.9 nm, a value that encompasses the 4 nm average crystallite size derived from the XRD pattern and also the direct observation in the TEM. These dimensions indicate a very compact structure with considerable interpenetration of the organic moieties.

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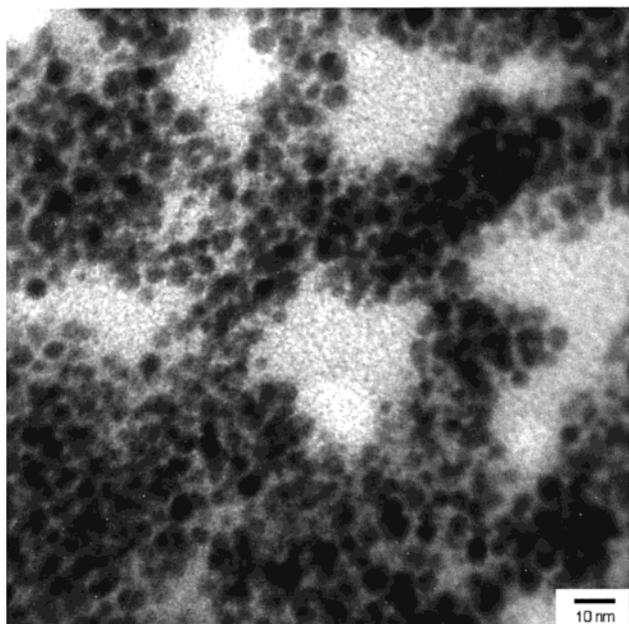


Figure 2. Micrograph of film collected as above but containing gold clusters coated with thioctic acid.

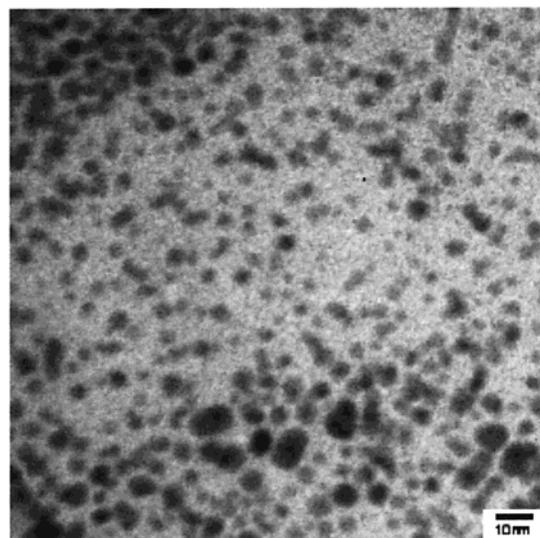
Similar bundling and interdigitation were observed¹⁶ on superlattices of silver nanocrystals coated with thiolates. The microstructure of the platelets isolated from the surface of the reaction medium obtained under similar conditions but containing gold coated with mercaptosuccinic acid is very similar. However, the reaction product obtained with gold clusters coated with thioctic acid is different, showing a more open structure as can be seen in Figure 2. That micrograph reveals irregular openings in the film and relatively long bridging sections suggesting some directionality at certain points.

A series of experiments was conducted to elucidate the local molecular environment leading to the assembly as well as other physicochemical factors affecting this process. The findings of that study are the following:

Interesting chemical facts were uncovered, namely, the presence or absence of peptide bonds, controlled by the addition (or withholding) of carbodiimide even when supplemented by the addition of *N*-hydroxysuccinimide is not required for film formation and does not alter the morphologies observed. Film formation occurs with poly-L-lysine as well as with polyethyleneimine; however, in both cases there is no film formation or solids with the high molecular weight preparations of either polymer. Examination of the evaporation residue obtained from the liquid containing the high molecular weight polymer by TEM showed wide separation between clusters as well as the presence of some assembly. However the assembly revealed a much more open structure than that obtained with the low molecular weight polymer; see Figure 3a. Further, samples of the liquid obtained from the low molecular weight polymer reaction media showed interesting small range assembly of what appear to be precursor structures of the films as illustrated in Figure 3b.

Spectroscopic analysis by Fourier transform infrared, FTIR, spectroscopy revealed that the procedure described for the preparation of colloids via the dendrimer route produced colloids coated with the carboxylic acid functionality that are free of the dendrimer. The latter is concluded after examining a film of the colloid left as an

a



b

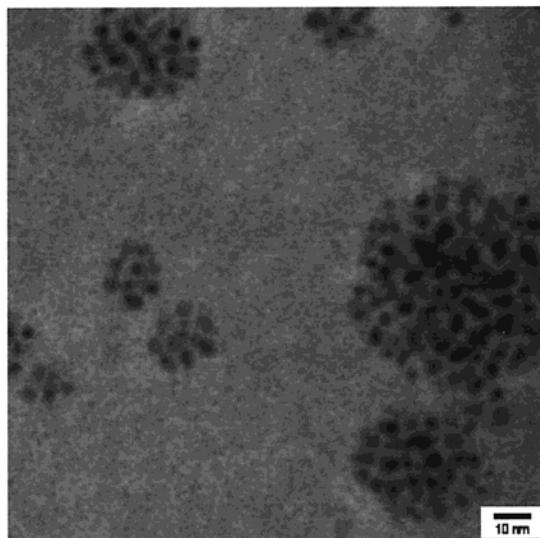


Figure 3. (a) Evaporation residue from liquid containing the reaction mixture between high molecular weight polyethyleneimine and gold clusters coated with thioctic acid. (b) Evaporation residue from liquid of a reaction mixture similar as in Figure 1 but promoted with carbodiimide.

evaporation residue on single crystal silicon as explained below. Hence the dendrimer served as a useful and, more importantly, a disposable nanoreactor. The spectrum, see Figure 4, corresponds almost exactly to that of free dodecanoic acid; absent are the dendrimer with typical bands of at 1658 and 1561 cm^{-1} and DMF with a typical carbonyl stretch at 1676 cm^{-1} . A small band seen at 1600 cm^{-1} is apparently due to residual toluene. Other relevant observations were that in every case, the films or insoluble residues from the polymer-acid reaction, see Figure 5, showed a pair of bands at about 1560 and 1400 cm^{-1} , which are characteristic of the carboxylate moiety, COO^- , and thus are indicative of acid-base chemistry and underlie the ionic association driving the assembly of the gold clusters. There are precedents for this type of association.^{9a,17} However in the previous experiments, the polymeric base was first adsorbed onto a surface and thus trapped appropriately coated colloids. All spectra shown in Figure 5 reveal the presence of the carboxylate bands

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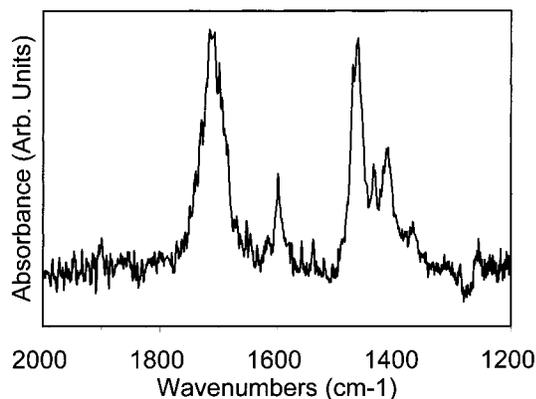


Figure 4. Infrared spectrum of gold coated with mercaptododecanoic acid.

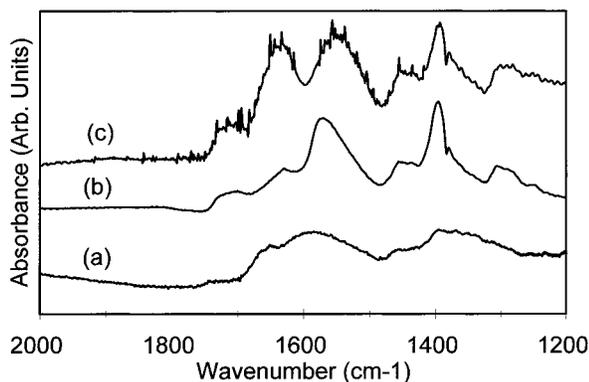


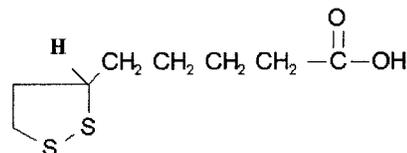
Figure 5. Infrared spectra of (a) film isolated from same reaction mixture as in Figure 1. (b) Solids isolated from same reaction mixture as in Figure 2. (c) Solids isolated from the reaction mixture, promoted by EDC and *N*-hydroxysuccinimide, between low molecular weight polyethyleneimine and gold clusters coated with thioctic acid.

where (a) was obtained from a film while (b) and (c) were obtained from solids. The presence of peptide bonds in (c) is clearly evident by the presence of a band at 1636 cm^{-1} .

Unanticipated findings of this study which cannot be readily explained are the failure of the high molecular weight polymers to form either films or solids and the reason underlying the morphology of the films of thioctic acid coated clusters. It seems possible that the high molecular weight polymers fail to form compact structures

that can self-assemble but instead act as a solubilizing agent to maintain the gold particles strung along irregular and disorderly chains.

Thioctic acid, in its oxidized form, is a disulfide whose structure is given below. It is possible that unlike the single thiol of the two other acids examined, the presence of both a disulfide and the ring structure in thioctic acid could lead to a more rigid conformation for the coating on the gold particles and thus be preserved after association with the amine polymers.



Conclusions

Free-standing films that appear to be one monolayer thick have been produced with carboxylic acid-functionalized gold clusters using low molecular weight polymers containing amine functionalities such as polyethyleneimine or poly-L-lysine as a scaffold for assembly. It was observed that peptide bond formation was not necessary for the formation of this assembly, proceeding as well by ion pairing in the absence of agents such as a carbodiimide or *N*-hydroxysuccinimide. The morphology of the films was found to be sensitive to the nature of the acid coating the gold clusters, with the clusters coated with the mercaptododecanoic acid and mercaptosuccinic acid forming more regular films than those coated with the thioctic acid. The formation of these two-dimensional array films may be exploited to fabricate devices for single electron charging.

Acknowledgment. Research was sponsored partially by the Engineering Research Program of the Office of Basic Energy Sciences, U.S. DOE, and partially by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC, for the U.S. DOE under Contract No. DE-AC05-00OR22725. The authors wish to express gratitude to Professor R. M. Crooks for access to a preprint of his work.

LA0008737