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Preparation of Ordered Colloid Monolayers by Electrophoretic Deposition

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Citrate- and alkanethiol-stabilized gold colloids have been electrophoretically deposited onto carbon-coated copper grids. The colloid particles form ordered monolayers, and the core-to-core interparticle spacing is determined by the size of the alkane chains on the stabilizers used in the preparation of the sols. In the case of longer alkane chains, some interpenetration of the chains occurs when the gold particles form monolayers. When the gold sols are stabilized by sodium 3-thiopropionate, they can be reversibly coagulated and peptized by cycling the pH between 3 and 7. The method has also been used to form ordered monolayers and bilayers of latex particles.

Introduction

The ordering of colloidal particles in two dimensions has been examined by several groups over the last decade or so.¹⁻⁵ Large protein molecules or micrometer-sized polystyrene latices have generally been employed because of their monodispersity. In the case of latex particles, the two-dimensional structures have usually been produced by confining the concentrated dispersion between two glass plates. The samples were then examined with an optical microscope. We were interested to see whether nanosized metal particles can form ordered structures. Such structures may be useful models for electron transport across grain boundaries in metals.⁶⁻⁸

In order to examine ordering in metal colloid systems, a well-defined electrostatic or steric barrier must be created at the metal particle surface to offset the large van der Waals attractive force between metal particles. (The Hamaker constants of gold and silver in water are 3×10^{-19} and 5×10^{-19} J, respectively,⁹⁻¹¹ up to an order of magnitude higher than the values for polymeric latices.) One approach is to cap the surface with strongly adsorbed molecules which form chemical bonds directly with surface metal atoms. This approach has been very successful with semiconductor colloids.¹² Schmid and co-workers have also pioneered this approach in the preparation of both

metal colloids and nonmetallic clusters.^{13,14} They have prepared gold colloids using triphenylphosphine derivatives as adsorbates, which can be concentrated to form powders which are fully redispersible in water.¹⁵ These colloids readily form densely packed monolayers on microscope grids;⁶ however no significant ordering was reported to occur. We have chosen to look at the effects of alkanethiols as stabilizers for gold sols because the recent work by Whitesides and co-workers has demonstrated that a wide variety of these molecules form well-defined monolayers on gold metal surfaces.¹⁶⁻¹⁹ In this paper we demonstrate that both conventional, citrate ion-stabilized gold sols and thiol-capped gold particles can produce ordered two-dimensional arrays. Since optical microscopy has insufficient resolution for the study of colloid structures synthesized from nanosized gold particles, we have employed electrophoretic deposition (EPD) for the preparation of ordered 2D gold colloid monolayers on carbon-coated copper mesh grids. The two-dimensional ordering of the nanosized particles has then been verified by electron microscopy and electron diffraction.

Experimental Section

Octadecanethiol, dodecanethiol, octanethiol, mercaptopropionic acid, sodium 4-mercaptobenzoate, and sodium mercaptoethanoate were procured from Sigma and were at least 99% purity. Monodisperse latex particles with carboxylate surface functional groups were obtained from Sigma as a 10% solids suspension with a nominal particle size of 0.44 μm (type CLB-4, lot 100H0863). KAuCl_4 was a product from Matthey. The tannic acid used was the Mallinckrodt Product No. 8835 explicitly recommended by Slot and Geuze.²⁰ Water was Milli-Q grade with a conductivity of less than 0.1 $\mu\text{S cm}^{-1}$. Colloidal gold was prepared using the citrate method described by Turkevich et al.²¹ The standard deviation of the size distribution in the sols was consistently about 10%. Smaller particles were prepared using the protocol employed by Slot and Geuze²⁰ in which tannic acid is added together with citric acid to the auric salt solution. When the

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(1) (a) Pieranski, P.; Strzelecki, L.; Pansu, B. *Phys. Rev. Lett.* 1983, 50, 900. (b) Pansu, B.; Pieranski, P. *J. Phys. (Paris)* 1984, 45, 331. (c) Pieranski, P. *Phys. Rev. Lett.* 1980, 45, 569.

(2) Van Winkle, D. H.; Murray, C. A. *Phys. Rev. A* 1986, 34, 562.

(3) Onoda, G. Y. *Phys. Rev. Lett.* 1985, 55, 226.

(4) Giersig, M.; Kunath, W. *Eur. J. Biol. Suppl.* 1989, 27, 28.

(5) Denkov, N. D.; Velez, O. D.; Kralchevsky, P. A.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K. *Langmuir* 1992, 8, 3183.

(6) Dusemund, B.; Hoffmann, A.; Salzmann, T.; Kreibig, U.; Schmid, G. *Z. Phys. D* 1991, 20, 305.

(7) Brom, H. B.; van Staveren, M. P. J.; de Jongh, L. J. *Z. Phys. D* 1991, 20, 281.

(8) Kreibig, U.; Fauth, K.; Granqvist, C.-G.; Schmid, G. *Z. Phys. Chem. (Munich)* 1990, 169, 11.

(9) Derjaguin, B. V.; Muller, V. M.; Rabinovich, Ya. I. *Kolloid Zh.* 1969, 31, 304.

(10) Parsegian, V. A.; Weiss, G. H.; Schrader, M. E. *J. Colloid Interface Sci.* 1977, 61, 356.

(11) Parsegian, V. A.; Weiss, G. H. *J. Colloid Interface Sci.* 1981, 81, 285.

(12) (a) Nosaka, Y.; Yamaguchi, K.; Miyama, H.; Hayashi, A. *Chem. Lett.* 1988, 605. (b) Fischer, Ch.-H.; Henglein, A. *J. Phys. Chem.* 1989, 93, 5578. (c) Hayes, D.; Micic, O.; Nenadovic, M. T.; Swayambunathan, V.; Meisel, D.; *J. Phys. Chem.* 1989, 93, 4603.

(13) Schmid, G.; Lehnert, A.; Kreibig, U.; Adamczyk, Z.; Belouschek, P. *Z. Naturforsch.* 1990, 45b, 989.

(14) Schmid, G.; Klein, N.; Korste, L.; Kreibig, U.; Schöner, D. *Polyhedron* 1988, 8, 605.

(15) Schmid, G.; Lehnert, A. *Angew. Chem.* 1989, 101, 773.

(16) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1989, 111, 321.

(17) Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* 1989, 111, 7155.

(18) Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir* 1988, 4, 365.

(19) Whitesides, G. M.; Laibinis, P. E. *Langmuir* 1990, 6, 87.

(20) Slot, J. W.; Geuze, H. J. *Eur. J. Cell Biol.* 1985, 38, 87.

(21) Eustätt, B. V.; Turkevich, J. *J. Am. Chem. Soc.* 1963, 85, 3317.

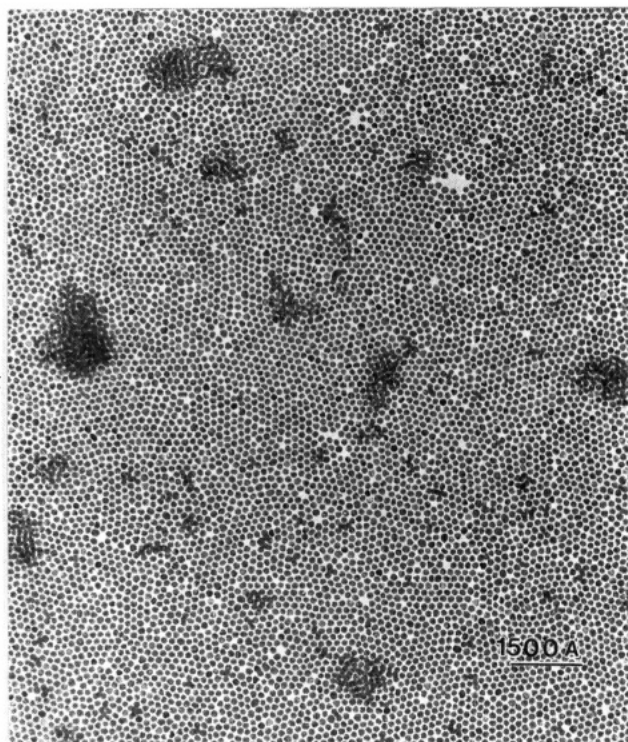


Figure 1. Electron micrograph of a 2D gold colloid monolayer prepared on carbon-coated copper grids (coating thickness 100 Å) by electrophoresis of a 0.5 mM citrate stabilized Au sol at an applied positive voltage of 50 mV.

stabilizing citrate and chloride ions were to be replaced by water-soluble thiolates, the gold sol was first added to Amberlite MB-1 ion exchange resin and excess citrate or tannate ions were removed. The conductivity of the sol decreased over 0.5 h to $<2 \mu\text{S cm}^{-1}$. The exchange resin was then removed by decantation. Then 0.1 mL of 10 mM aqueous thiol was added to 10 mL of the stirred gold sol. The thiol was added as the sodium salt. The amount added was equivalent to at least three monolayers. The gold sols were then equilibrated for several hours with the thiol to ensure that complete adsorption had taken place. Bain et al. have previously shown that although the gold surface becomes autophobic after only 2 s in contact with millimolar thiol solution, the adsorbate film thickness reaches its equilibrium value only after several hours.¹⁶

The other three thiols used ($\text{C}_8\text{H}_{17}\text{SH}$, $\text{C}_{12}\text{H}_{25}\text{SH}$, $\text{C}_{18}\text{H}_{37}\text{SH}$) are insoluble in water. In order to exchange the stabilizers, 4 mL of gold was added to 6 mL of THF while stirring slowly. The gold sol was stable in THF–water mixtures. The alkanethiol in THF was then added by micropipette (0.50 mL, 1 mM) with gentle stirring. The sols so prepared were stable for several hours. That the stabilizers were exchanged could be demonstrated by careful extraction of the gold sol into 2 mL of cyclohexane.

The electrophoretic deposition was carried out with 5-mL solutions in a Perspex cell. A copper sheath and screw used to pin the microscope grids were immersed into the solution through a Perspex cover. This also served as an electrical contact. The copper microscope grids were coated with 100 Å amorphous carbon film. This was polarized prior to immersion. Aluminum foil (3 cm²) served as the counter electrode. The spacing between the electrodes was 0.2 cm. A conventional dc power supply was used to generate the applied voltage. After deposition was complete the grid was removed while the electrodes were still polarized, to prevent any desorption of colloid particles occurring. The polarization was then switched off, the remaining thin film of adsorbed solvent was allowed to evaporate. The coated grids were then examined in a Philips CM 12 electron microscope.

Results and Discussion

In Figure 1, a typical electron micrograph of an ordered, gold colloid monolayer is shown. Only a few percent of

the coated area contains multilayers. The micrograph shows that the monolayer is built up of a large number of smaller crystalline domains, each containing 50–200 particles in the form of hexagonally close packed colloid particles. The monolayer is built up from these individual domains to form a large polycrystalline monolayer. Close examination clearly shows that “grain boundaries” tend to form at particles which are either aspherical or too large to fit into the lattice. The size of the monolayers is limited by the tendency of the monolayers to tear as they are removed from the solution after deposition. However we have previously shown that monolayers several micrometers long and containing several hundred thousand particles may be prepared.²² The field necessary for the formation of the monolayers is surprisingly small, less than 1 V cm^{-1} . However, in no case did we find any significant ordering if the grid was placed in the gold sol without an applied anodic bias. Indeed if, after electron microscopy, a grid was placed back in the sol and a cathodic bias of -50 mV applied, the gold colloids desorbed. Thus the films are formed by electrophoretic deposition and not by chemical adsorption.

In Figure 2a, a high-resolution micrograph of part of a single domain is shown. With the microscope in diffraction mode, weak diffraction of the electron beam from such two-dimensional colloid lattices was readily observed. However accurate lattice parameters could not be obtained because of the unusually large lattice constant. In order to examine the ordering of the particles more statistically, the best of a series of micrographs, as selected by light-optical diffraction, were digitized using a DATACOPY densitometer. A sampling distance of 6.5 Å was employed. The data were then processed on a microVAX computer using the SEMPER software package.²³ In Figure 2b, the results obtained after Fourier transformation of the micrograph in Figure 2a are shown. The 141 Å sized gold colloid particles crystallize into a hexagonal close packed lattice with an average core-to-core separation of 151 Å. Thus the thickness of the stabilizing layer between the particles is 10 Å. Furthermore second- and third-order reflexes are evident which confirms the strong degree of ordering in the film. The absence of higher ordering at lattice constants of about 5 Å, shows that the individual gold particles are randomly oriented within the hexagonal lattice. High-resolution micrographs in which the lattice planes of neighboring particles could be discerned also showed little evidence of alignment. The ordering of the particles is determined by the surface adsorbates, and the crystallographic orientation of the colloids plays no significant role.

As far as we are aware, such extensive two-dimensional ordering of nanosized metal colloid particles has not been observed before. However the preparation of densely packed monolayers has already been reported by Dusemund et al.⁶ These monolayers did not show significant crystallinity. Monte Carlo simulations showed that in the case where the adsorption of particles from solution was statistical, well-dispersed monolayers should form because of the electrostatic repulsion between the particles.¹³ However the structures observed by Dusemund et al. were clearly different to the fractal type aggregates previously observed by Enüstün and Turkevich²¹ or Weitz et al.²⁴ and demonstrated the important role of the adsorbates in determining the structure of condensed metal particle systems.

(22) Giersig, M.; Mulvaney, P. *J. Phys. Chem.* **1993**, *97*, 6334.

(23) Saxton, W. O.; Pitt, T. J.; Horner, M. *Ultramicroscopy* **1979**, *4*, 343.

(24) Weitz, D. A.; Lin, M. Y.; Sandroff, C. J. *Surf. Sci.* **1985**, *158*, 147.

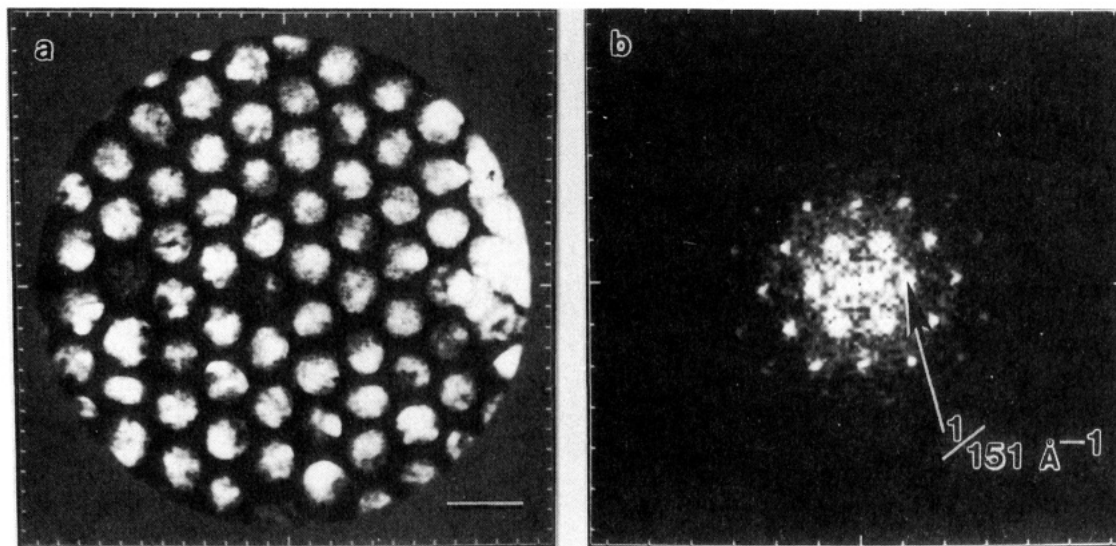


Figure 2. (a) Electron micrograph of part of a single 2D domain. Scale bar is 200 Å. (b) Power spectrum of (a) showing hexagonal close packing with the first-, second-, and third-order reflexes. The first reflex-, which also indicates the size of the lattice unit cell, amounts to $1/151 \text{ Å}^{-1}$.

The mechanism of growth of the lattices was investigated by varying the time of polarization in the solution. After a grid was examined in the microscope, it was repolarized and then reimmersed in the sol. Although the coating of the grids obviously varied from mesh to mesh, the trends were clearly reproducible. Typical results are shown in Figure 3, for a grid polarized for various periods of time in a sol of citrate-stabilized gold particles. After 5 s, the grids were sparsely covered, and the gold particles existed predominantly as randomly distributed isolated particles. After 10 s of polarization (i.e., 5 s further polarization of the same grid), 10–25% of the grid surface was coated, but there were clear signs of clustering. Gold particle triplets were very common and could not be explained statistically. After 15 s, there was clear evidence for island formation. The triplets were no longer seen, and had apparently “grown”. The islands showed clear ordering, but the crystallographic axes of neighboring islands were not correlated. After 35 s the grid was largely covered, and the individual domains had converged or coalesced.

It is clear from these results that attractive surface forces must exist between adsorbed gold particles. The presence of ordered structures at low coverages implies that the particles are mobile on the surface and tend to aggregate. Deposition is therefore not entirely statistical. At the present time, we can only suggest that the diffuse layer repulsion between the negatively charged gold colloid particles is reduced upon adsorption due to shielding of the surface charge by the positive charge on the carbon electrode, thereby facilitating coalescence. This is consistent with the fact that Dusemund et al. find the particles to be well dispersed when adsorption from solution is driven solely by chemical forces.¹³ The islands formed at low coverage are well-ordered. As the deposition continues these islands fuse to form the final monolayer coating but are unable to rotate or realign in order to form a single monocrystalline film. Consequently, EPD leads to the formation of a large number of ordered domains, and under such conditions the preparation of a single, monocrystalline lattice is not likely. One might expect that, if the adsorbed particles experienced stronger attractive forces, the rate of “surface nucleation” would decrease and the individual ordered domains would be larger.

The electron micrographs in Figures 1–3 were obtained with conventional citrate-stabilized gold sols. The ori-

entation of the adsorbed citrate ions on the surface of the gold particles is unknown. If the interparticle spacing of 10 Å is due to steric repulsion between overlapping adsorbate molecules, the thickness of the citrate groups is about 5 Å. Such a thickness corresponds reasonably with the size of a sodium citrate molecule, only if all three carboxyl groups are surface coordinated.

In the case of electrostatically stabilized latex monolayers, the interparticle spacing can be varied by either adjusting the surface charge on the particles or varying the ionic strength of the solution. The gold colloid monolayers described here are sterically stabilized, and the interparticle spacing and the monolayer geometry can be most easily varied by changing the size of the colloid stabilizer.

In Figure 4, the observed stabilizer thickness is shown as a function of the estimated fully-extended chain length for a series of thiol stabilizers. In each case, ordered monolayers were prepared by EPD, and micrographs taken. The interparticle spacing was then calculated from the core-to-core distance found by Fourier analysis of the ordered domains in electron micrographs. This value, which corresponds to the “bilayer thickness”, was then divided by two to yield the apparent stabilizer thickness in the adsorbed state. To estimate the chain length we have used the empirical form derived by Bain et al. based on crystallographic data and their own ellipsometric data on both thioalkanes and ω -mercaptocarboxylic acids.¹⁷ In the first case it was found that the hydrocarbon length obeyed $l = 2.5 \text{ Å} + 1.27n \text{ Å}$, where n is the number of CH_2 groups, and 2.5 Å takes into account the thiol and methyl terminating functional groups. For the carboxylic acids, the terminating moiety contribution was estimated at 3.0 Å. We compared these values with those from a computer graphics model and found reasonable agreement. For the citrate and thiobenzoic acid stabilizers we used the computer-generated values of 5.5 and 7.2 Å, respectively. In the case of citrate, the molecule was assumed to be coordinated via all three carboxyl groups. It is worth noting that Tanford has assumed 1.5 Å per CH_2 group when estimating the extended hydrocarbon chain lengths in micelles.²⁵ As can be seen from Figure 4, the agreement

(25) Tanford, C. *The Hydrophobic Effect. Formation of Micelles and Biological Membranes*, 2nd ed.; Wiley: New York, 1980.

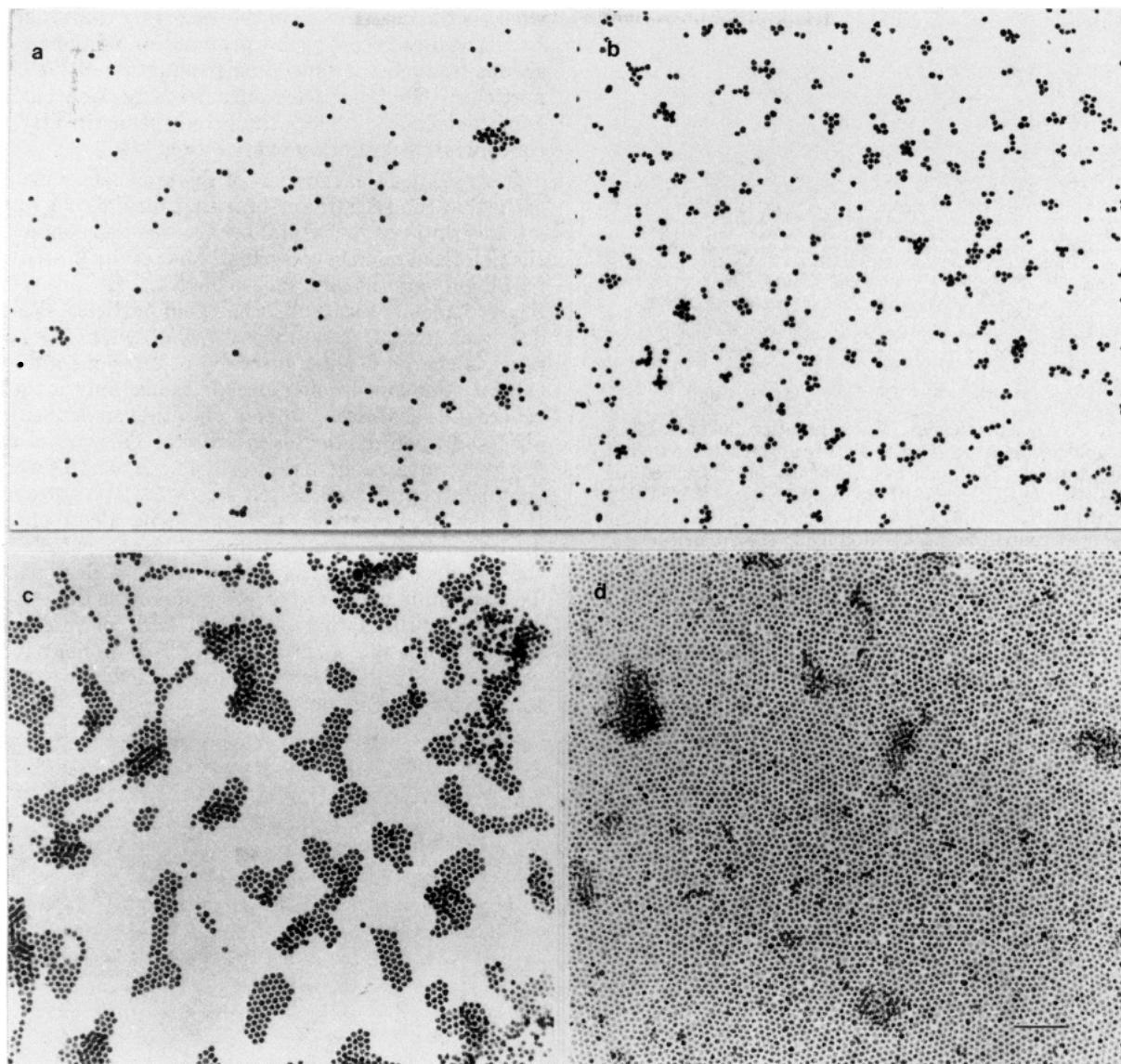


Figure 3. Electron micrographs of 2D gold colloid lattices after different periods of electrophoretic deposition from a 0.5 mM Au sol. The polarization times are (a) 5 s, (b) 10 s, (c) 15 s, and (d) 35 s. Trisodium citrate ion was used as a stabilizer.

at smaller chain lengths between observed and calculated chain lengths is good and suggests that the stabilizers are oriented almost vertically at the colloid surface. At longer chain lengths, the observed particle-particle separation is clearly too small to be consistent with nonoverlapping hydrocarbon chains. Whitesides and co-workers found that thioalkanes were oriented at 30° to vertical, but this is still insufficient to bring agreement with experiment (dotted line in Figure 4). It thus seems that the packing of the colloid particles results in considerable interdigitation of the alkane chains.

A second means to alter the monolayer geometry is to vary the gold particle size. Slot and Geuze have shown that the tannic acid catalyzed reduction of AuCl_4^- by citrate ion produces gold sols with particle sizes ranging from 20 to 100 Å depending on the tannic acid: citric acid ratio.²⁰ In Figure 5, three electron micrographs are shown of ordered gold colloid monolayers. The monolayer geometry has been varied by altering *both* the mean particle size and the stabilizer thickness. In Figure 5a, 35 Å sized gold particles were stabilized with octanethiol, in Figure 5b the gold particles had an average diameter of 141 Å, and thiobenzoic acid was the stabilizer, and in the last micrograph, the mean size was 185 Å, and the smallest stabilizer, 3-mercaptopropionic acid, was used. The mean

interparticle spacing decreases from 22 Å in Figure 5a, to 16 Å in Figure 5b, and finally down to 9.5 Å in the last micrograph. The interparticle spacing for a given stabilizer molecule does not vary significantly for different gold particle sizes. That is the particle curvature does not seem to affect the packing of the adsorbate molecules at the surface. In all cases the particles form well-ordered hexagonal-close-packed domains. EDAX analysis of the gold monolayers revealed only small S signals ($\text{Au:S} > 50$), which due to normal aerial contamination could not be used to estimate the surface coverage. (We found small sulfur signals even in the absence of thiols). The metal volume fraction varies considerably in the three monolayers. The volume fraction, f , may be approximated by

$$f = (d/d_{\text{inter}})^3 \quad (1)$$

where d is the mean particle size and d_{inter} the average core-to-core spacing determined by diffraction. For the three gold monolayers shown in Figure 5, this yields 0.22, 0.72, and 0.86, respectively. The use of thiols as adsorbates allows considerable flexibility in the design of the monolayers. The sol particles stabilized with mercaptopropionic acid have similar properties to those prepared by Schmid and Lehnert using triphenylphosphine ligands.¹⁵ A gold-colored precipitate is formed after concentration of the

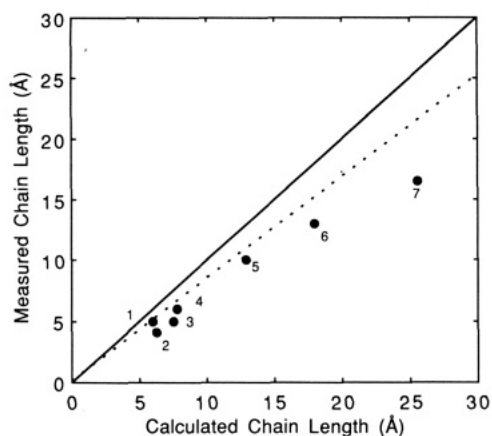


Figure 4. Average particle-particle separation between 141 Å diameter gold particles in a 2D lattice as a function of the stabilizer chain length used. The stabilizer molecules are (1) trisodium citrate, (2) $\text{HSCH}_2\text{COONa}$, (3) $\text{HS}(\text{CH}_2)_2\text{COONa}$, (4) $\text{HSC}_6\text{H}_4\text{COONa}$, (5) $\text{C}_8\text{H}_{17}\text{SH}$, (6) $\text{C}_{12}\text{H}_{25}\text{SH}$, and (7) $\text{C}_{18}\text{H}_{37}\text{SH}$. The stabilizer chain length was calculated using the empirical data of Bain et al.¹⁷ The continuous line assumes the stabilizer molecules are aligned perpendicular to the surface. The dotted line is the value for orientation at 30° to vertical.

sols by rotary evaporation, and removal of excess electrolyte. The sols redisperse completely in water at pH > 5. Schmid's colloids were stabilized by sulfonate groups

whereas the headgroups in this case are carboxyl groups. At pH values below 5, the protonation of the carboxyl groups leads to the *reversible* coagulation of the colloidal particles. Gold particles stabilized by long chain alkanethiols could also be partially redispersed in THF, after concentration by rotary evaporation.

It is still not clear in view of the tenacious adsorption of the thiols and citrate ions onto the colloidal gold, whether any desorption of the stabilizer occurs upon contact with the polarized microscope grids. The results presented so far all indicate that the sheath of adsorbate ions remains firmly attached to the adsorbed gold particles. We have also been unable to establish to what extent the colloidal particle charge is neutralized by counterions after deposition. For low applied electric fields, only monolayer coverage takes place, whereas multilayer deposition is observed when the field is increased. This suggests that the gold particles are able to shield the electrode charge completely at low applied field strengths. It is also possible that the gold particles undergo some electrochemical oxidation upon adsorption, which allows them to decrease their surface charge, thereby facilitating close packing. To determine whether the electrophoretic deposition is affected by the nature of the particles, or whether the presence of ionic surface charges is sufficient for the generation of ordered monolayers, we have also used EPD to prepare latex monolayers.

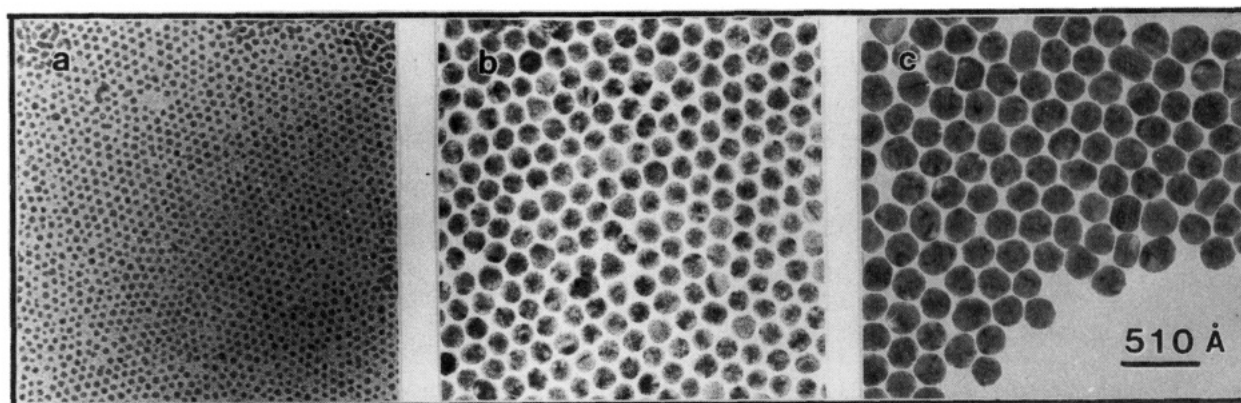


Figure 5. Electron micrographs of thiol-stabilized gold colloid lattices prepared with different ratios of particle size to stabilizer thickness: (a) octanethiol stabilized 35 Å gold particles; (b) thiobenzoic acid stabilized 141 Å gold particles; (c) sodium 3-mercaptopropionate stabilized 185 Å gold particles.

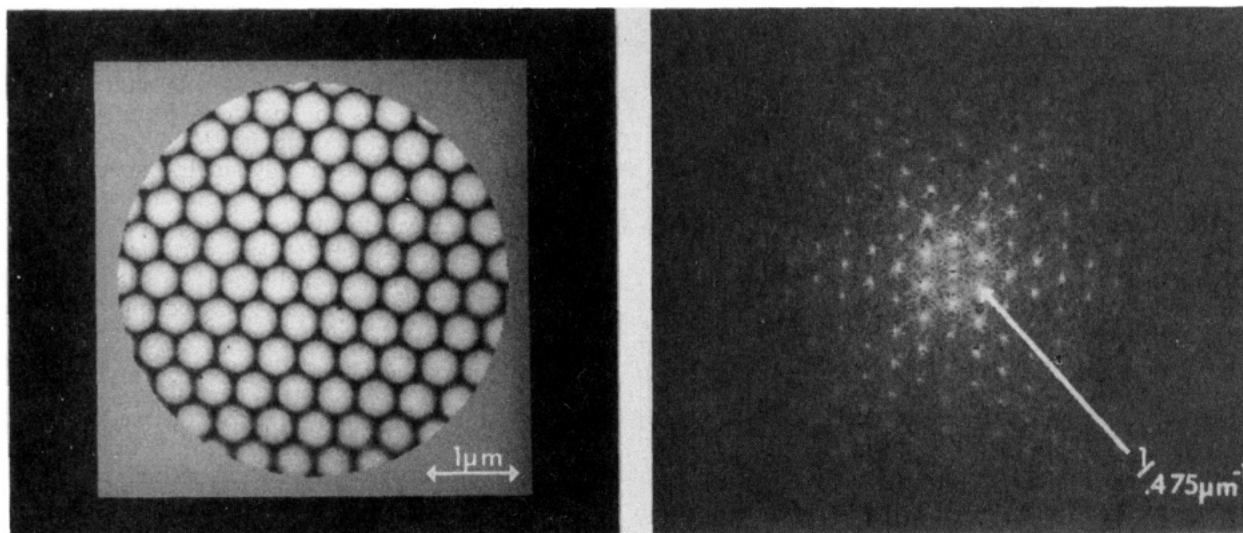


Figure 6. (a, left) 2D ordered latex monolayer prepared by electrophoresis of a 1% (w/v) latex sol at +2.0 V cm^{-1} , no added electrolyte. The latex was negatively charged. Mean particle size 0.44 μm . (b, right) Fourier transform of (a) showing numerous higher order reflexes. The interparticle core-to-core spacing is 0.475 μm .

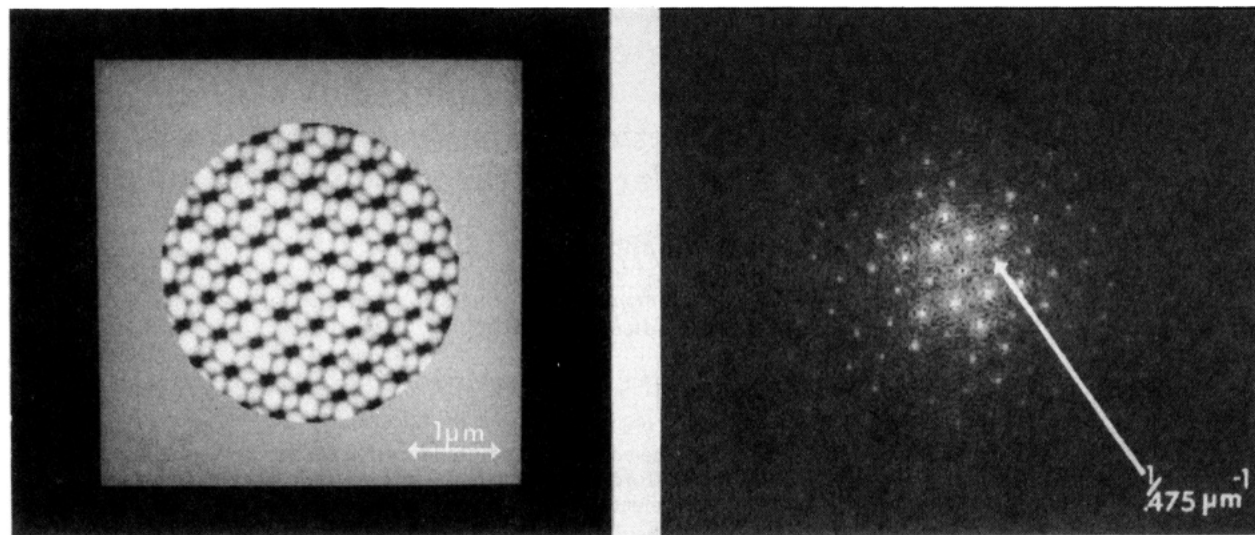


Figure 7. (a, left) Micrograph of a latex bilayer prepared by EPD of a 1% (w/v) latex sol in an electric field of $+5 \text{ V cm}^{-1}$. (b, right) Fourier transform of (a) showing ordering and an identical lattice size of $0.475 \mu\text{m}^{-1}$.

In Figure 6, an electron micrograph of an electrophoretically deposited latex monolayer is shown. The particle size was $0.44 \mu\text{m}$. The sol solution contained 1% (w/v) latex, and was prepared by dilution of the stock sol with distilled water. The exact ionic strength is unknown. There was no evidence for ordering within the sol prior to deposition. Much higher potentials had to be applied in order to generate latex monolayers, due to the larger particle size and higher electrolyte concentrations. Clearly, strong adsorption can only occur if the particle size is smaller than the diffuse layer thickness over which the electrode potential decays. For the $185\text{-}\text{\AA}$ gold sols, the particle size was approximately equal to the diffuse layer thickness, since the ionic strength was about 0.001. In the case of the latex particles ($0.44 \mu\text{m}$ diameter, diffuse layer thickness $<100 \text{\AA}$), the electric field at the carbon electrode decays rapidly over the diameter of the adsorbed particles. The exterior surface of the latex particle therefore experiences a much smaller electrostatic potential, and a correspondingly larger electric field must be used to generate the colloid monolayers.

Even higher fields ($>5 \text{ V cm}^{-1}$) produced ordered bilayers of latex particles (Figure 7). In the case of the bilayers, the same lattice parameters are obtained, showing that the second layer packs identically to the first. Thus the substrate has minimal effect on the equilibrium monolayer structure. The diffraction analysis also reveals that the particles are not quite touching. The particle size of $0.44 \mu\text{m}$ is 35 nm smaller than the core-to-core spacing of $0.475 \mu\text{m}$. Thus ordered monolayers of insulating particles can also be prepared by EPD. The technique can also be used

to prepare monolayers of quantized semiconductor particles²⁶ and may be a useful alternative to the use of air-water monolayers and Langmuir-Blodgett films for preparing optical devices based on nanosized semiconductor materials.²⁷

Conclusions

In this and a preceding communication,²² we have demonstrated that EPD is a useful technique for examining the surface chemistry of colloidal metals. Two-dimensional gold colloid monolayers have been prepared, and it has been shown that they crystallize in a hexagonal close packed lattice. The equilibrium particle-particle spacing has been shown to depend on the thickness of the stabilizer chain length. Electrophoretic deposition at low field strengths ($<1 \text{ V cm}^{-1}$) does not appear to result in the loss of stabilizer molecules from the particle surface. We are currently using atomic force microscopy to directly measure the forces of interaction between metal surfaces in the presence of alkanethiols.²⁸

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(26) Giersig, M. Unpublished results.

(27) (a) Scoberg, D.; Grieser, F.; Furlong, D. N. *J. Chem. Soc., Chem. Commun.* 1992, 515. (b) Zhao, X. K.; Yuan, Y.; Fendler, J. H. *J. Chem. Soc., Chem. Commun.* 1990, 1248. (c) Zylberajch, C.; Ruaudel-Teixier, A.; Barraud, A. *Thin Solid Films* 1989, 179, 9.

(28) Biggs, S.; Mulvaney, P. Manuscript in preparation.