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## Letters

### Utilization of Surfactant-Stabilized Colloidal Silver Nanocrystallites in the Construction of Mono- and Multiparticulate Langmuir–Blodgett Films

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Oleic acid-stabilized 100-Å-diameter silver particles have been spread at air–water interfaces in a Langmuir film balance. Surface pressure *vs* surface area isotherms, reflectivity measurements, and Brewster-angle and transmission electron microscopies demonstrated that increasing surface pressure resulted in the transition from gaseous and liquid phases of mixed oleic acid/silver particle domains to closely packed, well-separated monoparticulate silver domains which ultimately collapsed to multiparticulate layers. Sequential transfer to solid substrates by the Langmuir–Blodgett technique led to the formation of multiparticulate layers of silver clusters.

#### Introduction

The unique optical and electrooptical properties of ultrathin silver films and nanosized silver particles have prompted the increasing interest of chemists, physicists, and materials scientists in this area.<sup>1–3</sup> Silver particulate films, generated under monolayers by electrocrystallization<sup>4,5</sup> and chemical reduction,<sup>6</sup> represent an intermediate between solid films and colloidal particles. Importantly, the silver particulate films are nanocrystalline in nature and can be investigated *in situ* under surfactant monolayers, as well as *ex situ* subsequent to their transfer to solid substrates. Thus, silver particulate films, like the analogous semiconductor particulate films developed in our laboratories,<sup>7</sup> provide a membrane-mimetic approach to advanced materials.<sup>8</sup>

Preparation of monoparticulate layers of dodecylbenzenesulfonic acid-stabilized CdS nanoclusters and their subsequent sequential transfer to solid substrates by the Langmuir–Blodgett (LB) technique have furnished an alternative means for superlattice construction.<sup>9</sup> This methodology has been extended to other nanoparticulate layers. The preparation and characterization of oleic acid-stabilized silver particulate layers are the subjects of the present paper.

Although traditionally prepared in aqueous solution, metal particles may also be dispersed in nonaqueous solution. This can be achieved by a solvent extraction/reduction technique in nonpolar solvent,<sup>10,11</sup> by physical methods such as the gas evaporation technique,<sup>12</sup> in polar solvents such as methanol and ethanol in the presence of polymeric stabilizers,<sup>13,14</sup> by reduction of an organometallic

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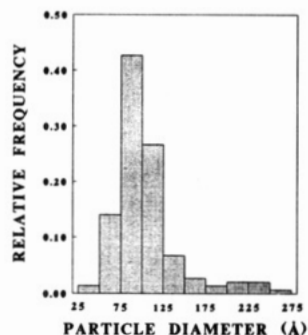
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**Figure 1.** A histogram showing particle size distribution of silver colloids in the silver/oleic acid stock solution.

precursor dissolved in ethylene glycol,<sup>15</sup> and by a phase transfer method.<sup>16,17</sup> The phase transfer technique was selected since it yields a solution with a high concentration of silver particles with respect to the stabilizing surfactant concentration.

Spreading of the hexane solution of colloidal silver on an aqueous solution produced a mixed thin film comprising domains of 2-D lattices of silver particles and domains of oleic acid. The particulate film was further used to produce solid-state layers of silver particles by using the LB film technique. The domains of close-packed silver particles were comparable to those formed of gold crystallites on a carbon-coated, polymer-covered Cu grid support by an electrophoretic technique.<sup>18</sup> The optical properties of colloidal metal particles are known to vary with the density of packing due to depolarization effects.<sup>18–21</sup> The technique described here enables the lattice of silver particles to be transferred to an optically transparent substrate and, thus, permits investigation of the optical properties of the particulate films.

### Experimental Section

Phase transfer of colloidal silver from aqueous solution to hexane was achieved using the method of Hirai et al.<sup>16</sup> An aqueous colloidal dispersion of silver was prepared using the Carey Lea method,<sup>22</sup> by dissolution of 4.67 g of sodium citrate dihydrate and 2.5 g of ferrous sulfate in 20.0 mL of water, followed by the addition of a solution of 0.83 g of silver nitrate in 8.0 mL of water with vigorous stirring. The resulting dispersion of silver particles was then centrifuged and the separated solid pellet redispersed in 300 mL of water. Phase transfer was carried out by the combination of 25 mL of the silver sol, 25 mL of hexane, 30  $\mu$ L of oleic acid, and 0.8 mL of 0.1 M NaOH. The mixture was emulsified by vigorous stirring for 4 h, and phase transfer was subsequently induced by the addition of 2.5 g of NaCl with stirring. On standing for 3 h, the silver particles transferred from the lower aqueous solution to the upper hexane solution. A 10-fold dilution of this solution with hexane yielded the stock solution of surfactant-coated silver nanocrystallites which was used for spreading at the air–water interface. Particle size analysis of transmission electron micrographs taken of this solution demonstrated a mean diameter of 103 Å and standard deviation of 38 Å (Figure 1). The stock solution remained unchanged for 3–4 days, after which time a small quantity of dark precipitate was observed. Consequently, only freshly-prepared dispersions were used for each series of experiments.

The concentration of silver in the stock solution was determined by atomic absorption spectroscopy using an Instrumentation

Laboratory IL-S11 atomic absorption spectrometer. The hexane/silver dispersion was prepared for analysis by permitting the hexane to evaporate from 0.5-mL aliquots of the stock silver solution, dissolving the solid residue in 1.0 mL of concentrated HNO<sub>3</sub>, and diluting to a total volume of 25.0 mL in a volumetric flask. A series of standard solutions were prepared by dilution of a standard silver solution. Comparison of the absorption of the sample solution with those of the standard solutions yielded the concentration of silver in the stock solution.

Surface pressure vs surface area isotherms were determined by using a Lauda Langmuir film balance. A 400–750- $\mu$ L sample of the silver stock solution was spread on a water subphase (purified by a Millipore Milli-Q system with a resistivity of 18 M $\Omega$  cm) by using a Hamilton syringe in 50–100- $\mu$ L portions so as to avoid initial multilayer formation.<sup>23</sup> Evaporation of the spreading solvent was permitted for 30 min prior to compression of the film. Compression and expansion were then carried out by using a moving barrier rate of 0.30 cm/s. LB films were prepared by compression of the particulate film to a surface pressure of 15–30 mN/m and maintenance of the film at constant pressure. Either glass or silanized glass substrates were dipped into and out of the film at a rate of 1.0 cm/min with residence times of 30 s and 4.5 min in the solution and air, respectively.

Absorption spectra of all samples were determined by using an HP 8452A diode-array spectrometer.

Examination of the particulate films by Brewster-angle microscopy (BAM) was carried out in a homemade trough by using a 10- $\mu$ W He/Ne laser as the illumination source.<sup>24</sup> Transmission electron microscopy (TEM) was employed to examine the structure of the films at high magnification. Samples were prepared either by dipping 400-mesh, C-coated, formvar-covered Cu grids vertically through the air–solution interface and picking up the film from underneath or by placing a grid on the top surface and then picking it up horizontally. They were viewed using a JEOL 2000EX electron microscope operating at 120 kV. *In situ* reflectivity measurements were also carried out in order to determine the thickness of the film, using an experimental setup described previously.<sup>25</sup>

### Results and Discussion

Surface pressure ( $\pi$ ) vs surface area ( $A$ ) isotherms, measured on compression of films obtained from spreading 0.6 mL of the silver colloid solution, are shown in Figure 2a. A  $\pi$ – $A$  curve for oleic acid only is illustrated in Figure 2b. Isotherms of very similar shape and position, with respect to the surface area axis, were obtained on spreading of 0.4- and 0.75-mL silver colloid solutions. The isotherms were reproducible within the precision of the trough (10% of surface pressure and surface area), and the films were fairly uniform, as viewed by the eye. The Ag/oleic acid isotherms show five distinct regions, as marked in Figure 2a, and can be interpreted in terms of a film composed of two distinct, immiscible components. In conjunction with the TEM visualization of the film structure (see below), these can be regarded as surfactant-stabilized Ag colloids and oleic acid not associated with Ag (that is, oleic acid present in a purely organic environment). In the case of simple immiscible surfactants, the immiscible compounds comprising the monolayer can exist as domains and, provided that these are of sufficient magnitude to be representative of the bulk materials, the resultant monolayers will begin to collapse at the lower characteristic collapse pressure. Continuation of compression until all domains of the first material have collapsed then leads to a second pressure increase until the higher collapse pressure is achieved.<sup>26</sup> Discussion of the present system cannot be simplified to such a

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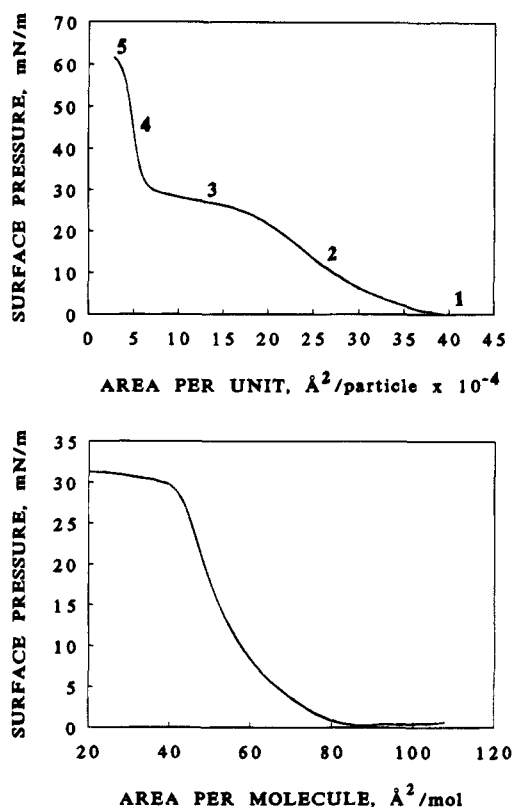
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**Figure 2.** Surface pressure *vs* molecular area isotherms of thin films on distilled water subphases of (a, top) 0.6 mL of Ag/oleic acid solution where labels 1–5 refer to the different phases of the monolayer structure, as discussed in the text and (b, bottom) oleic acid.

**Table 1. Silver Particulates on Monolayers**

diameter, Å	area occupied per silver particle, determined from the isotherm, Å <sup>2</sup> /particle	diameter of silver particle occupying that area, assuming perfect close-packing, Å
103 <sup>a</sup>	$7.8 \times 10^4$ ( $3.5 \times 10^4$ ) <sup>b</sup>	300
87.5 <sup>c</sup>	$4.8 \times 10^4$ ( $2.5 \times 10^4$ ) <sup>b</sup>	236

<sup>a</sup> Mean diameter is  $(n_1d_1 + n_2d_2 + n_3d_3 + \dots)/(n_1 + n_2 + n_3 + \dots)$  where  $n_i$  is the number of particles of diameter  $d_i$ . <sup>b</sup> Calculated area occupied per silver particle, assuming ideal close-packing (Å<sup>2</sup>/particle). <sup>c</sup> Median diameter is the diameter of the particles corresponding to the highest  $n_i$ .

degree since the “silver colloid” and “oleic acid” domains are unlikely to remain completely immiscible at high compression. Thus, a general discussion of Figure 2a suggests that regions 1 and 2 correspond to the gaseous and liquid phases of the mixed film. Plateau 3 occurs at  $\pi = 30$  mN/m, a value comparable to the collapse pressure of the oleic acid monolayers (see Figure 2b), and can thus be interpreted in terms of the beginning of the collapse of the oleic acid domains. The silver domains change size and shape throughout these pressure regimes. Further compression of the silver domains occurs during stage 4 and continues until collapse at stage 5. Full compression of the Ag film (region 5 in Figure 2a) resulted in the development of a distinct yellow color and shiny surface. The film was very rigid at high compressions and was observed to crease at the collapse pressure and then crumple along the moving barrier with further compression. These results are consistent with observations made on the collapse of monolayers formed from spherical latex particles<sup>27</sup> and organoclay platelets.<sup>28</sup>

The mechanism of interaction between the silver colloids and the oleic acid, both in the hexane solution and on the water surface, is uncertain. Indeed, the mechanism of phase transfer of the particles from aqueous to organic solution has not yet been resolved.<sup>16,29</sup> This phase transfer can in many ways be compared to the formation of MELLFs (metal liquid-like films) of surfactant-stabilized silver particles at an aqueous/organic interface.<sup>30–33</sup> Extensive work has been performed on these systems, and it has been demonstrated that the surfactant, organic solvent, and organic acid present are all important in defining the stability of the interfacial film. For the system discussed in this paper, it seems only possible to say that the silver particles are stabilized by adsorbed citrate ions and a coating of the surfactant. The interaction between the surfactant and metal is important, although its exact nature has not been determined.<sup>31</sup> The surfactant enshrouds the particle, thus preventing direct contact and precipitation, possibly in a micellar-type structure.

The area occupied per silver particle was calculated from a knowledge of the mean particle size, the concentration of silver in the spreading solution, and the critical area per particle (corresponding to the concept of head-group areas in surfactant monolayers). The critical area per particle quantity was determined from the surface pressure *vs* surface area isotherm as the point at which a tangent drawn to the solid phase of the film (stage 4, Figure 2a) intersects the surface area axis.<sup>26</sup> The results are given in Table 1. Thus, the experimentally-determined occupied area per particle is approximately 2 times larger than the theoretical value, which was calculated assuming ideal hexagonal close-packing of the silver particles and neglecting the presence of the surfactant.

Electron microscopic examination of the particulate film demonstrates that the magnitude of the limiting area per particle is consistent with the structure of the compressed film (Figure 3c,d);<sup>10,11</sup> the oleic acid makes a significant contribution to the critical area per particle, forming separate domains and occupying interparticle gaps. Electron micrographs clearly show that the particulate film is indeed composed of two phases: the surfactant-stabilized silver particles and the domains of oleic acid only. Thus, the previous analysis of the isotherms in terms of a mixed film is reasonable. The image of the silver particles in the original hexane spreading solution, presented in Figure 3a, demonstrates that some small aggregates are present. However, when this solution is spread on the aqueous subphase, the aggregation is reversed and a thin film, which appears from the micrographs to be one particle thick, is formed. At large areas per silver particle, small domains of silver particles can be observed (Figure 3b, uncompressed). Compression results in an increase in the size of these domains and in the formation of 2-D close-packed areas of silver particles, which are shown in Figure 3c and at higher magnification in Figure 3f ( $A = 1.1 \times 10^5$  Å<sup>2</sup>/particle,  $\pi = 30$  mN/m). The silver domains occupy approximately half of the total area of the entire film and are uniformly distributed over the entire monolayer. Figure 3f clearly shows that the particles within the domains are unaggregated and appear to be in the form of a true monoparticulate layer. The particles are isolated from one another by approximately 100 Å, which presumably corresponds to a surfactant

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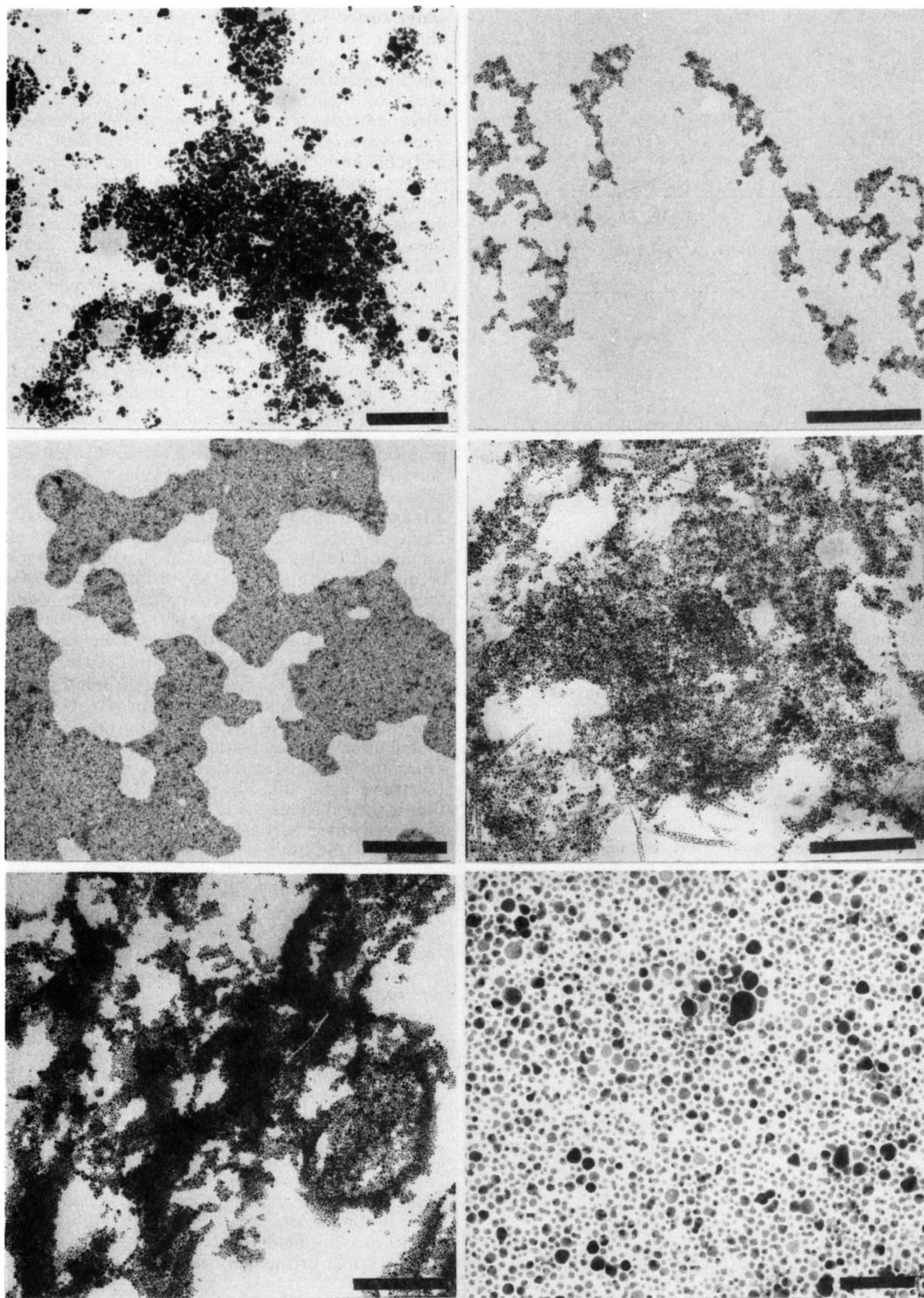
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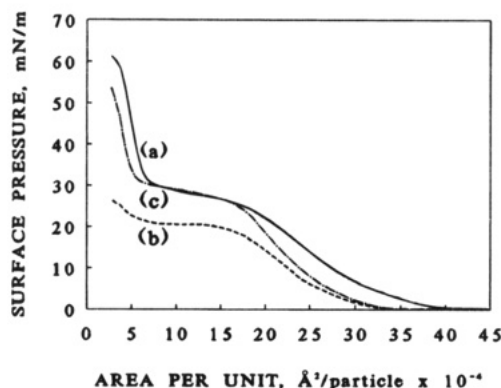
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**Figure 3.** Transmission electron microscopic images of the silver/oleic acid stock solution (a, top left), of the uncompressed particulate film at (b, top right)  $A = 5.0 \times 10^5 \text{ \AA}^2/\text{particle}$  and  $\pi = 0 \text{ mN/m}$ , (c, middle left)  $A = 1.1 \times 10^4 \text{ \AA}^2/\text{particle}$  and  $\pi = 30 \text{ mN/m}$ , (d, middle right)  $A = 4.8 \times 10^4 \text{ \AA}^2/\text{particle}$  and  $\pi = 50 \text{ mN/m}$ , and (e, bottom left)  $A = 2.8 \times 10^4 \text{ \AA}^2/\text{particle}$  and  $\pi = 70 \text{ mN/m}$ , and of an enlargement of a silver particle domain in Figure 5c, showing the close-packing of the silver colloids (f, bottom right). Scale bars in (a), (b), (d), and (e) correspond to 500 nm. The scale bars in (c) and (f) represent 1  $\mu\text{m}$  and 100 nm, respectively.



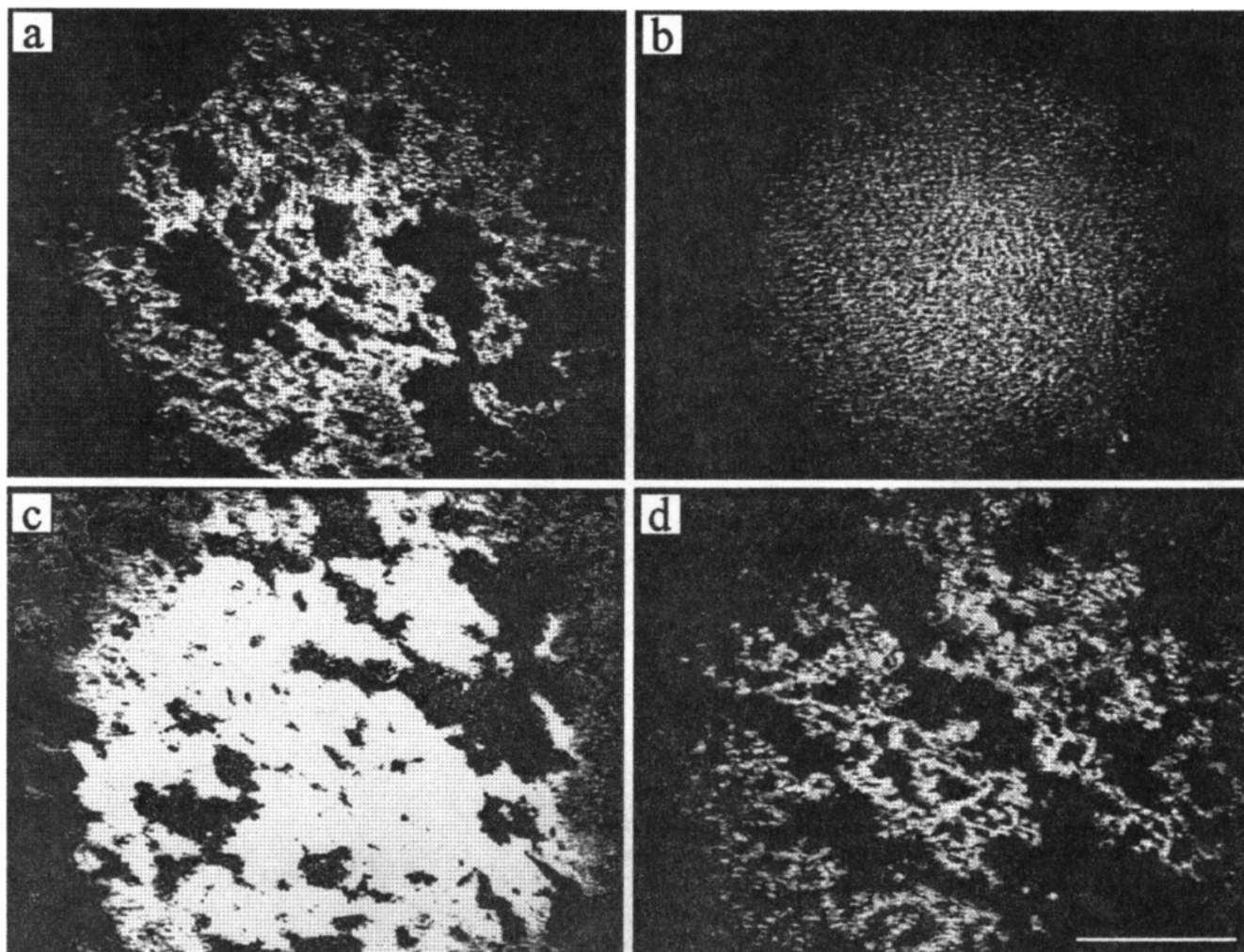


**Figure 4.** Surface pressure vs molecular area isotherms for the (a) compression, (b) expansion, and (c) recompression of a film formed from spreading 0.6 mL of the Ag/oleic acid stock solution on distilled water.

coating. Had these silver domains exceeded a single particle thickness, then the halo surrounding each of the particles would not have been visible. Further compression to  $A = 4.8 \times 10^4 \text{ Å}^2/\text{particle}$  and  $\pi = 50 \text{ mN/m}$  (Figure 3d) results in some aggregation of the particles within the silver domains and in a further reduction in the percentage of the area occupied by oleic acid. Complete collapse at  $A = 2.8 \times 10^4 \text{ Å}^2/\text{particle}$  and  $\pi = 70 \text{ mN/m}$  (Figure 3e) is accompanied by considerable aggregation of the silver

colloids and by the formation of thick multiparticulate layers. Even in the solid state, approximately half of the total area of the film is occupied by oleic acid (Figure 3c,d). The experimentally determined values for the area occupied per silver particle are, therefore, consistent with the proposed structure of the film. *In situ* reflectivity measurements further supported the proposed structure of the film.<sup>9</sup> The reflectivity curve of the silver particulate film at  $\pi = 30 \text{ mN/m}$  showed considerable deviation from that obtained from pure water only. Analysis of the reflectivity curves gave values of the refractive index of  $n = 1.66$  and of the film thickness of  $d = 134 \pm 13 \text{ Å}$ . This approximates very closely the mean diameter of a single particle, suggesting that the film does not have any extensive 3-D structure. The relative low value of the refractive index can be attributed to the presence of oleic acid in the film.

Compression/expansion/recompression curves of the silver particulate films (formed by the spreading of 0.6 mL of the stock solution) are shown in Figure 4. The plateau region corresponding to the collapse of the oleic acid domains occurs at the same pressure and is of identical length; the two regions of the isotherms displaying increases in surface pressure are somewhat steeper, reflecting a film of greater initial order and lower surfactant content. However, films compressed to complete collapse did not reexpand to their original state; the film fractured parallel to the moving barrier to give thin

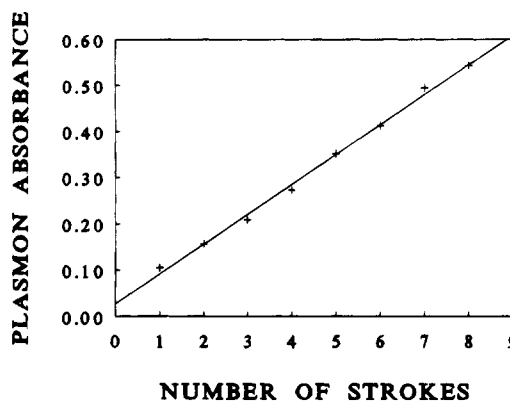


**Figure 5.** Brewster-angle microscopic images of a 0.2-mL silver stock solution (equivalent to 0.8 mL on the isotherm trough) at surface area per molecule values of (a) uncompressed film,  $A = 5.0 \times 10^5 \text{ Å}^2/\text{particle}$ , (b) during compression,  $A = 3.2 \times 10^5 \text{ Å}^2/\text{particle}$ , (c) during compression,  $A = 1.5 \times 10^5 \text{ Å}^2/\text{particle}$ , and (d) reexpanded,  $A = 5.0 \times 10^5 \text{ Å}^2/\text{particle}$ . The scale bar represents 1 mm for all images.

strips of material. Compression to pressures  $<30$  mN/m gave fully expandable films whose macroscopic structures were identical both prior and subsequent to compression.

The structure of the film was investigated *in situ* by BAM. Images corresponding to a film spread at surface concentrations of (a) uncompressed,  $A = 5.0 \times 10^5 \text{ \AA}^2/\text{particle}$ , (b)  $A = 3.2 \times 10^5 \text{ \AA}^2/\text{particle}$ , (c)  $A = 1.5 \times 10^5 \text{ \AA}^2/\text{particle}$ , and (d) reexpanded,  $A = 5.0 \times 10^5 \text{ \AA}^2/\text{particle}$  are shown in Figure 5. Compression of the film from  $A = 5.0 \times 10^5 \text{ \AA}^2/\text{particle}$  to  $A = 3.2 \times 10^5 \text{ \AA}^2/\text{particle}$  produced a very uniform film. Further compression to  $A = 1.5 \times 10^5 \text{ \AA}^2/\text{particle}$  produced a highly refractive, densely packed film. Full reexpansion to  $A = 5.0 \times 10^5 \text{ \AA}^2/\text{particle}$  yielded a film with structure very similar to that prior to compression. Figure 5b, thus, corresponds to a more tightly packed film (stage 2, Figure 2a) and Figure 5c to the pressure regime in which collapse of the oleic acid domains is occurring (stage 3, Figure 2a). The black and white areas on the images are likely to derive from domains principally composed of oleic acid and silver particles, respectively.

A graph of the maximum silver surface plasmon absorption at 470 nm, with respect to the number of immersions of a silanized glass slide through the particulate monolayer ( $n$ ), is shown in Figure 6 and displays good linearity. The LB film was formed while maintaining a constant surface pressure of 27 mN/m (as demonstrated by TEM, the silver crystallites were nonaggregated under these conditions). The measurement of transfer ratios during the deposition process was complicated by changes in the surface area of the film which occurred even in the absence of dipping while maintaining constant pressure. At a higher number of depositions ( $>10$ ), the efficiency of deposition was observed to decrease. This is consistent with the extrusion of oleic acid from the monolayer and the accompanying increase in the rigidity of the film; highly viscous films traditionally display low transfer ratios.<sup>26</sup> The quality of the LB films formed will necessarily suffer from the limitation that the structure of the particulate film varies as a function of time. However, that the absorption of the LB film varies linearly with the number of layers deposited suggests that the structure of the



**Figure 6.** A graph showing the intensity of the plasmon absorption of silver particles in an LB film with respect to the number of strokes ( $n$ ) of a silanized glass plate through the silver particulate film.

component layers does not vary considerably over the time space of the experiment.

### Conclusion

The formation of mixed films comprised of silver nanocrystallites and oleic acid is described. Separate domains of surfactant-coated silver particles and of oleic acid are formed on compression. Within the silver domains, the particles appear to form a true monoparticulate layer. The films could be transferred to solid substrates by the LB technique. Changes in the sizes of silver particles in a given monoparticulate layer and in the number of monoparticulate layers deposited on optically transparent substrates will provide a means for the systematic variation between nanometer-thick films which mostly transmit and those which mostly reflect light. This, in turn, will open the door to the construction of a variety of novel optical and electrooptical devices.

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