

Langmuir–Blodgett Films of Carboxylic Acid Derivatized Silver Colloidal Particles: Role of Subphase pH on Degree of Cluster Incorporation

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In this paper, we demonstrate that reasonably ordered multilayer films of silver clusters can be deposited by the Langmuir–Blodgett (LB) technique. The approach consists of electrostatically immobilizing negatively charged carboxylic acid derivatized silver colloidal particles at the air–water interface using positively charged fatty amine Langmuir monolayers. The degree of cluster incorporation into the Langmuir monolayer has been controlled by varying the charge on the amine molecules through the colloidal subphase pH. Pressure–area isotherms were used to follow adsorption of the silver colloidal particles at the amine surface, while quartz crystal microgravimetry (QCM), optical absorption spectroscopy, infrared spectroscopy, contact angle measurements, and optical interferometry were used to characterize the multilayer LB films. The films were found to grow in the classical Y-type mode. Optical interferometry indicated a bilayer thickness of 106 Å, which yields a cluster size of ~55 Å, in reasonable agreement with a mean cluster size of 73 Å determined from transmission electron microscopy. Incorporation of clusters into inorganic matrices as outlined in the paper shows promise for the growth of superlattice structures, mixed cluster systems, etc., which are not realizable by currently used experimental methods.

Introduction

The area of nanoparticle research has witnessed tremendous growth due to the unusual chemical and physical properties demonstrated by this intermediate state of matter.¹ Many approaches are currently being pursued for the synthesis and organization of nanoparticles with potential applications in mind. While the more sophisticated methods have relied on the use of the scanning tunneling microscope,^{2,3} there has been considerable interest in the simpler and perhaps more versatile chemical methods which are based on either a two step process involving synthesis of colloidal nanoparticles and immobilization via self-assembly^{4,5} or in a single step by chemical synthesis under or within the ordering influence of an organic template.^{6–9}

Fendler and others have recognized that the air–water interface can be used for the organization of surfactant stabilized nanoparticles and have shown that multilayer films of the nanoparticles can be deposited using the versatile Langmuir–Blodgett (LB) technique.^{10,11} The growth of multilayer nanoparticle films by the LB technique was also shown to be possible through interaction of suitably derivatized colloidal particles from the subphase with the polar group of the Langmuir monolayer.^{12,13} This latter approach for the deposition of lamellar particulate films has not received much attention, and in this paper we demonstrate that lamellar multilayer silver cluster films can be transferred onto solid supports by the LB method. To the best of our knowledge, formation of metal cluster films by this method has not been demonstrated until now. We have used an aromatic bifunctional molecule, 4-carboxythiophenol (4-CTP), as the stabilizing capping molecule for colloidal silver particles. The thiol group is known to form a strong covalent linkage with silver,¹⁴ thus leading to carboxylic acid derivatized silver colloidal clusters. Monolayers of octadecylamine (C₁₈-amine) molecules are then used to immobilize the silver colloidal particles on the surface of the

hydrosol after which facile transfer of the monolayer to solid substrates is possible. The charge on the amine monolayer can be controlled by varying the colloidal subphase pH. This leads to variation in the degree of cluster incorporation into the Langmuir monolayer and consequently, in the built-up LB films as well. We present below the results of our investigation.

Experimental Details

The silver hydrosol was prepared by borohydride reduction of AgSO₄ salt solution as detailed by Vukovic and Nedeljkovic.¹⁵ The colloidal solution had a pH of ~10 and was clear and light yellow in color. Optical absorption studies were performed on the as-prepared sol using a UV/vis Hewlett-Packard 8452 diode array spectrometer (2 nm spectral resolution) and yielded a surface plasmon resonance at 386 nm. The colloidal particles were then capped with 4-carboxythiophenol by dispersing the surfactant molecule (10^{–5} M concentration) in the hydrosol using absolute ethanol. The surface plasmon resonance shifted to 405 nm on capping with the bifunctional molecule. At a pH close to 10, the carboxylic acid groups on the silver clusters are expected to be completely ionized, leading to good stability of the silver sol over many weeks as indicated by optical absorption spectroscopy measurements. Transmission electron microscopy measurements on the 4-CTP capped silver sol was performed using a Philips TEM 301 T instrument operated at 80 KV. Figure 1A shows a representative micrograph of the silver clusters, while the particle size distribution histogram is plotted in Figure 1B. A mean cluster size of 73 Å and a standard deviation of 12.3 Å is obtained from a Gaussian fit to the histogram.

In order to follow the kinetics of immobilization of the clusters at the air–water interface, surface pressure–area isotherm measurements (π –A isotherms, subphase temperature = 25 °C) were performed on a Nima Model 611 Langmuir trough by dispersing a known quantity of octadecylamine in chloroform on the surface of the silver hydrosol used as the subphase. Care was taken to spread the amine monolayer only after the bifunctional molecule dispersing agent, absolute

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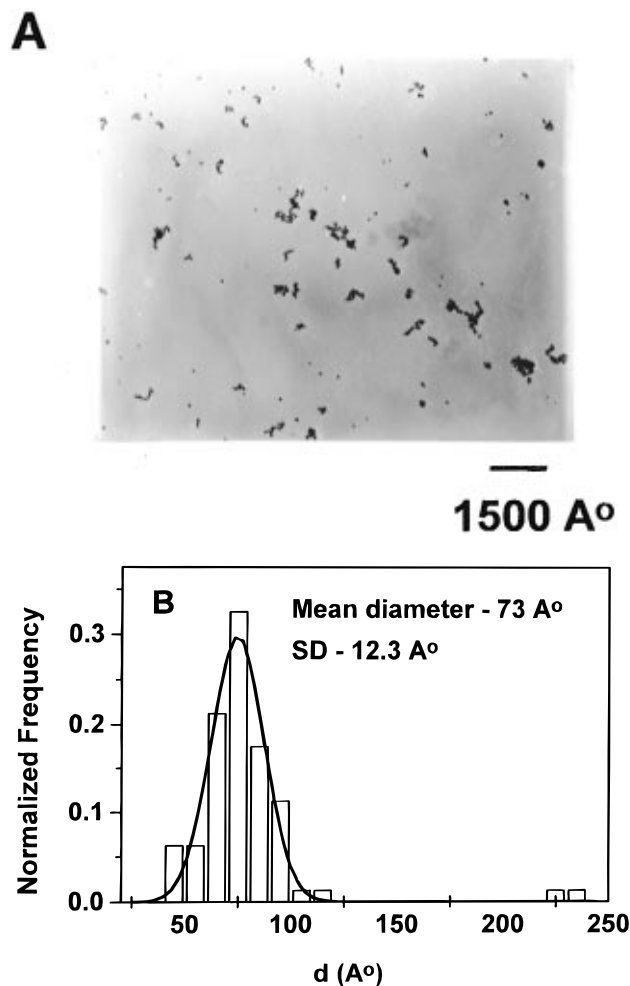


Figure 1. (A) Representative transmission electron micrograph of the 4-CTP capped Ag hydrosol. The scale bar corresponds to 1500 Å. (B) Histogram of the particle size distribution in the 4-CTP capped Ag hydrosol. The solid curve is a Gaussian fit to the histogram. Parameters obtained from the fit are given in the figure.

ethanol, had fully evaporated, which required typically 15 min. After a further 15–20 min equilibration of the Langmuir monolayer, π -A measurements were carried out as a function of time for two different values of the colloidal subphase pH of 9 and 12. The pH of the subphase was adjusted using dilute H_2SO_4 and NaOH. This range was motivated by the fact that the pK_A values of the amine and bifunctional molecules are 10.6 and 4.5, respectively. Thus, for the pH values mentioned above, one can systematically vary the charge on the amine molecules (protonated to yield $-\text{NH}_3^+$), while the carboxylic acid groups on the silver cluster remain fully ionized ($-\text{COO}^-$), thereby altering the strength of electrostatic interaction between the amine molecules and silver clusters. At pH = 9, the surface charge density on the Langmuir monolayer is expected to be maximum, while, at pH = 12, the Langmuir monolayer is completely unprotonated and the charge would be negligible.

After stabilization of the π -A isotherms was achieved, the monolayer was compressed to 25 mN/m surface pressure and the monolayer allowed to equilibrate for 1 h. A small isobaric reduction in the area per molecule was observed. After 1 h, the monolayers were transferred onto quartz and Si (111) wafer substrates by sequential dipping of the substrate in the monolayer covered subphase in the classical Langmuir–Blodgett deposition scheme¹⁶ at a deposition rate of 25 mm/min. A drying period of 15 min between immersions was found to be important for obtaining uniform films. It was observed that good transfer

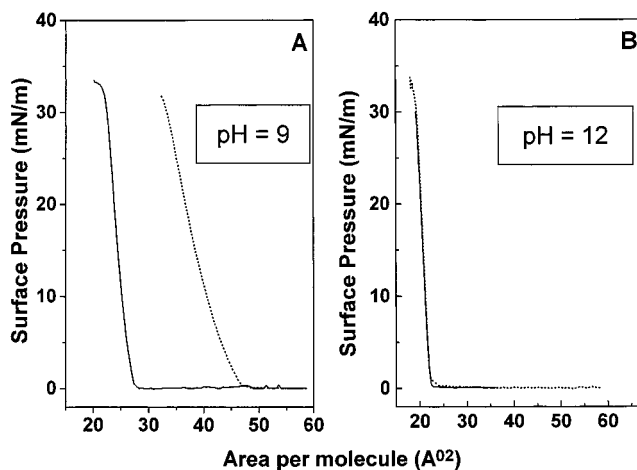


Figure 2. (A) π -A isotherms of octadecylamine on surfactant stabilized silver hydrosol (pH = 9) after 30 min of equilibration (solid curve) and 90 min of equilibration (dotted curve). (B) π -A isotherms of octadecylamine on surfactant stabilized silver hydrosol (pH = 12) after 30 min of equilibration (solid curve) and 90 min of equilibration (dotted curve).

ratios (close to 100% on both the upward and downward movements) were obtained only if a monolayer of lead arachidate was predeposited on the substrates, rendering them hydrophobic as previously observed by Fendler *et al.*^{12b} Multilayer films of different thicknesses were deposited onto quartz substrates for optical measurements and onto a gold coated AT-cut quartz crystal for quartz crystal microgravimetry (QCM) measurements. QCM measurements were done using an Edwards FTM5 microbalance with a frequency resolution of ± 1 Hz, which, for the 6 MHz crystal used, yields a mass resolution of ± 12 ng/cm². The quartz crystal frequency change was converted to mass loading using the standard Sauerbrey¹⁷ formula. The thickness of the multilayer LB films was determined using optical interferometry. A thick LB film (40 monolayers) of the silver colloidal particles complexed with octadecylamine was deposited at a colloidal subphase pH of 9 onto a Si(111) wafer for Fourier transform infrared spectroscopy (FTIR) measurements. The infrared characterization of the film was carried out on a Nicolet 60 SXB FTIR spectrometer operated in the transmission mode at a resolution of 2 cm⁻¹. A total of 500 scans yielded a good signal to noise ratio for the infrared spectra.

Results and Discussion

As mentioned earlier, capping of the silver sol with 4-CTP resulted in a red shift in the surface plasmon resonance from 386 to 405 nm as well as a damping of the plasmon resonance indicative of surface capping.¹⁸ The stability of the carboxylic acid derivatized silver clusters at pH values of 8 and above was determined from optical absorption measurements to be excellent, and hence any influence of this aspect on the nature of the π -A isotherms with time may be ruled out.

The π -A isotherms of the C₁₈-amine monolayer on the surfactant stabilized silver hydrosol at pH = 9 and pH = 12 are shown in Figure 2A,B, respectively. The solid line in Figure 2A refers to the isotherm recorded 30 min after spreading of octadecylamine, while the dotted line is the isotherm recorded after 90 min. A large expansion in the monolayer is observed which indicates complexation of the silver clusters to the protonated amine groups of the Langmuir monolayer. The liftoff area after equilibration was determined to be 45 Å²/molecule, which is considerably larger than the liftoff area for the uncomplexed amine of ~ 20 Å²/molecule. We repeat here

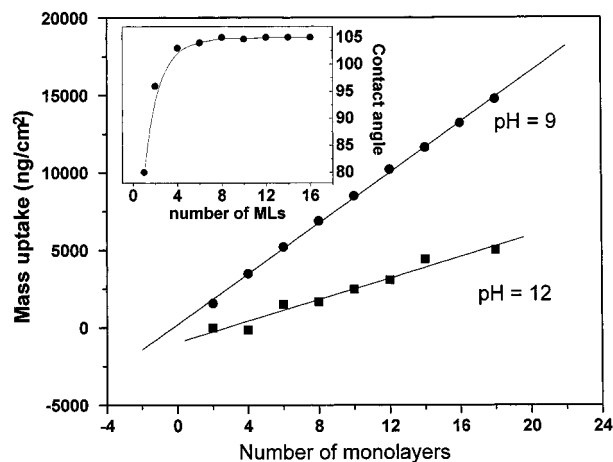


Figure 3. QCM mass uptake with time as a function of the number of monolayers transferred with the hydrosol at pH = 9 (filled circles) and pH = 12 (filled squares). The solid lines are linear least squares fits to the data. The inset shows the contact angle variation with the number of monolayers transferred onto lead arachidate coated quartz substrates.

that, at pH = 9, both the amine ($-\text{NH}_3^+$) and carboxylic acid ($-\text{COO}^-$) groups are expected to be fully charged. At pH = 12, there is a negligible expansion of the monolayer with time (Figure 2B: solid curve, 30 min after equilibration; dotted curve, 90 min after equilibration), indicating little adsorption of the silver clusters. The takeoff area is close to $20 \text{ \AA}^2/\text{molecule}$, which is close to that obtained for uncomplexed amine molecules. We believe it is important to establish the contribution of electrostatic interactions in the immobilization of the clusters since it is conceivable that hydrogen bonding between the carboxylic acid groups and the protonated amine groups could also lead to immobilization. Thus, lack of complexation as observed from the π -A isotherms at pH = 12 underscores the importance of electrostatic interactions vis-a-vis hydrogen bonding interactions which are known to be operative in the bonding of glutamine to phospholipids at the air-water interface.¹⁹ Thus, through judicious choice of the ionizable cluster capping molecule and the amphiphilic molecule in the Langmuir monolayer, regulation of the colloidal particle density in the Langmuir monolayer can be achieved through simple subphase pH variation. In earlier studies, attractive electrostatic interaction between the polar groups of the Langmuir monolayer and charged surfactant molecules on the nanoparticles was used for immobilization of the clusters as demonstrated in the deposition of DODAB-HMP-stabilized CdS clusters-DODAB sandwich multilayers.^{12b} However, modification of cluster density at the monolayer-colloidal subphase interface as described above has not been recognized until now and may have important applications.

Some other observations pertinent to transfer of the monolayers to form LB films can be made from Figure 2. The silver cluster complexed amine monolayer shows a region of fairly large incompressibility which is important for the transfer process. From the isotherms, a surface pressure of 25 mN/m was chosen for the transfer.

The growth of the silver cluster-amine LB films by sequential transfer was followed using QCM, optical absorption, and optical interferometry measurements. Figure 3 shows a plot of the mass uptake with number of monolayers transferred onto a gold coated quartz crystal with the hydrosol subphase at pH = 9 and 12. The gold film was hydrophobic, and hence a lead arachidate monolayer was not deposited for these measurements. It is seen from the figure that there is an increase in mass uptake per dip as the pH is reduced from 12 to 9. The mass transfer

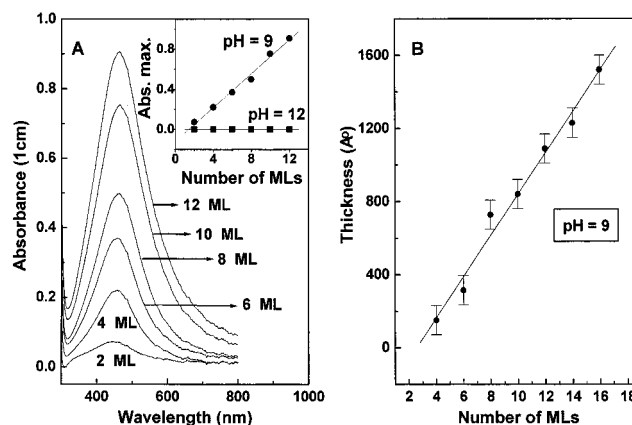


Figure 4. (A) Optical absorption spectra of several multilayer amine-silver cluster LB films deposited on hydrophobized quartz substrates at a pH = 9. The inset shows the variation of the surface plasmon resonance intensity at 460 nm with silver cluster film thickness at pH = 9 (filled circles) and at pH = 12 (filled squares). (B) Silver cluster film thickness as a function of number of monolayers transferred as determined from optical interferometry. The solid line is a linear least squares fit to the data.

per dip was determined from a least squares fit to the data which is clearly linear (solid lines are the regression curves). At pH = 12, the mass uptake is consistent with transfer of *only the amine monolayer*. This agrees with π -A isotherms which show no complexation of the clusters at pH = 12. Calculations based on the mass uptake per dip at pH = 9 yield $\sim 30\%$ coverage by 73 \AA diameter clusters at unity transfer ratios during the downward and upward strokes. This value of surface coverage is larger than the 15% obtained for self-assembled gold colloidal films by Natan *et al.*^{5b} While the low surface coverage for self-assembled colloidal films has been explained in terms of repulsive electrostatic interactions between the clusters, the larger value obtained for the films of this study may be due to shielding of the negative charges on the silver clusters by the positively charged amine molecules. Another factor that needs to be considered is the attractive van der Waals interactions between the hydrocarbon tails of the amine molecules which can lead to stability of the silver cluster assembly at higher surface coverages. The important point to note from Figure 3 is the linearity in the plot at pH = 9 which indicates monolayer by monolayer transfer of the 73 \AA diameter silver cluster- C_{18} -amine complex.

The inset of Figure 3 shows the variation in contact angle²⁰ with the number of monolayers of the silver clusters transferred onto hydrophobized quartz substrates. The lead arachidate monolayer had a contact angle of $\sim 80^\circ$. The constancy of the contact angle at 105° beyond 4 monolayers of the silver cluster film clearly indicates transfer of the clusters with the amine monolayer on top, as expected for Y-type growth of the film. Therefore, any reorganization due to size constraints can be ruled out, and lamellar film growth is indicated.

Optical absorption spectroscopy is an ideal tool for following the film growth process of silver cluster films due to the strong surface plasmon resonance exhibited by this metal.¹⁸ Figure 4A shows the absorption spectra recorded as a function of the number of monolayers in the built-up LB films on hydrophobized quartz substrates at subphase pH = 9. The plasmon resonance occurs at 460 nm for all of the films, and a monotonic growth in resonance intensity is observed as the film thickness increases. As mentioned above, no transfer of the silver clusters was observed by QCM at pH = 12, and this was corroborated by optical absorption measurements of different thickness films on quartz which showed no indication of the expected surface

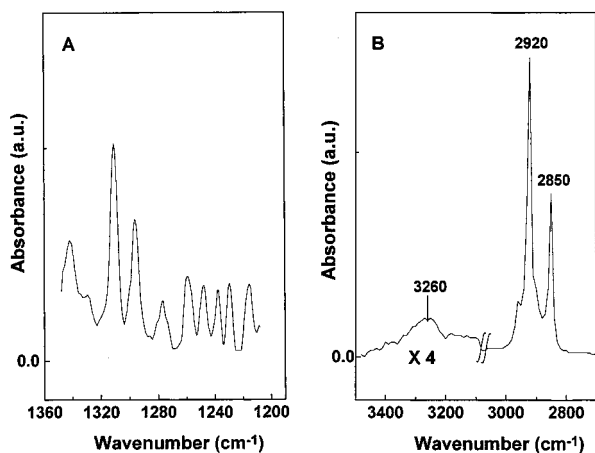


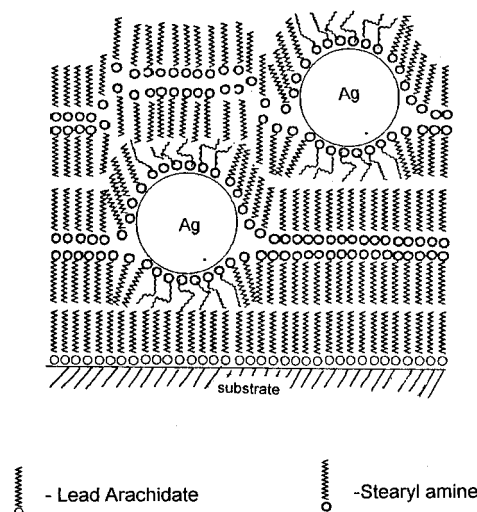
Figure 5. (A) Transmission FTIR spectrum of a 40 monolayers of silver cluster- C_{18} -amine complex film in the region of the methylene twisting and wagging progression frequencies. (B) Transmission FTIR spectrum of a 40 monolayers of silver cluster- C_{18} -amine complex film in the region of the C-H and NH_2 stretching frequencies.

plasmon resonance. The inset of Figure 4A shows the variation in the intensity maximum at the surface plasmon resonance with film thickness. As indicated in Figure 4A, a systematic increase in the absorbance with film thickness is seen at $pH = 9$ with a linear regression curve fitting the data very well. The linearity in the absorbance data clearly indicates a good monolayer by monolayer transfer.^{12b} At $pH = 12$, there was no transfer of the clusters (inset of Figure 4A, filled squares). This is in agreement with QCM results which indicated transfer of only the amine film which does not contribute to absorption in this spectral region. It was also observed that there were no changes in the optical absorption spectra for the built-up silver cluster films at room temperature over time intervals of up to months, indicating good stability of the silver cluster films. The QCM and optical absorption data indicate that lamellar multilayer films of colloidal particles can be deposited by the LB technique.

The thickness of multilayer silver cluster films grown on quartz substrates at $pH = 9$ was measured using optical interferometry. Figure 4B shows a plot of the measured thickness versus the number of monolayers in the silver cluster film. The film thickness clearly grows linearly with the number of monolayers in the film, and the solid line is a linear least squares fit to the data. The slope of the curve yields a thickness increment of $\sim 106 \text{ \AA}/\text{monolayer}$. The amine bilayer thickness is $\sim 50 \text{ \AA}$ ^{21a,b} from which we calculate a cluster diameter of 56 \AA . This is in reasonable agreement with the cluster size of $73 \pm 12 \text{ \AA}$ determined from TEM studies of the hydrosol.

While the QCM, optical absorption, and interferometry characterization of the silver cluster-amine complex LB films indicate layer-by-layer growth in the classical Y-type transfer sequence, the presence of clusters of the dimensions used in this study is expected to introduce some distortions in the packing and orientation of the C_{18} -amine molecules in the layers. This aspect can be studied using infrared spectroscopy as demonstrated by Yang *et al.*^{13b} for $\alpha\text{-Fe}_2\text{O}_3$ -stearate LB films. Figure 5A shows the FTIR spectrum of a 40 monolayers silver cluster- C_{18} amine film in the region $1200\text{--}1350 \text{ cm}^{-1}$. The band progressions from the methylene wagging and twisting vibrational modes can clearly be seen. The presence of the progression bands as well-resolved peaks is a clear indicator of close packing of the alkyl chains of the amine molecules in the monolayers.^{8a,13b,22} It is known that the methylene wagging and twisting vibrational modes have their transition dipole moments parallel to the alkyl chain axis.²³ The presence of the progression bands shown in Figure 5A for spectra measured in the

CHART 1: Probable Structure of the Silver Cluster-Octadecylamine LB Film



transmission mode as adopted in this study indicates a tilt of the amine hydrocarbon chains in addition to close packing. Additional evidence for close packing is obtained from the spectrum of the C-H stretching region (Figure 5B). The peak positions of the antisymmetric and symmetric methylene stretching vibrations are determined to be 2920 and 2850 cm^{-1} , respectively, which is characteristic of alkyl chains in a close-packed, crystalline microenvironment.²² The C-H stretching frequencies are known to shift to higher values (2928 and 2856 cm^{-1} for the antisymmetric and symmetric vibrations, respectively) if disorder exists in the chains.²² Another interesting observation from Figure 5B is the position of the NH_2 antisymmetric stretching vibration at 3260 cm^{-1} . This frequency for pure amine films has been found to be 3331 cm^{-1} , while the band shifts to 3200 cm^{-1} for primary amine salts.²⁴ The intermediate value of 3260 cm^{-1} obtained by us for carboxylic acid terminated silver cluster-alkylamine complexes is novel and, to the best of our knowledge, has not been reported so far.

The attachment of the negatively charged silver clusters to amine molecules at the air-water interface is similar to anion incorporation in fatty amine Langmuir monolayers previously demonstrated,^{21,24} the silver clusters in this case acting as "giant" counterions. From the QCM, optical absorption, optical interferometry, and FTIR measurements, we conclude that lamellar growth of the silver cluster-amine films has been achieved with some distortion of the amine hydrocarbon chains around the silver colloidal particles. Taking a cue from Yang *et al.*^{13b} and in analogy with the structure obtained for other fatty amine LB films,^{21b} a tentative structure for the silver cluster films could be as shown in Chart 1.

To summarize, it has been demonstrated that multilayer films of silver clusters can be grown by the LB technique. The strategy has been to suitably derivatize colloidal silver clusters, and electrostatically immobilize them in Langmuir monolayers of fatty amines and to transfer the silver cluster amine monolayers onto solid substrates. We believe this approach for the incorporation of clusters/nanoparticles in organic matrices has many advantages over the chemical insertion route receiving attention at present.^{8,9} Some of them are listed below:

(1) Since ordering of the clusters is accomplished at the air-water interface, significant disruption of ordering of the lamellar phase is not expected, unlike in the formation of, e.g., CdSe by treatment of cadmium arachidate LB films with H_2Se vapor where growth of the clusters occurs in the interlamellar spaces

of the LB film *in the solid phase* and would lead to considerable strain in the film and ultimate loss of lamellar structure, as has been observed.^{8b}

(2) Well-defined superlattice structures are possible in this scheme through alternate transfers in different hydrosol sub-phases with different Langmuir monolayers.

(3) A wide range of nanoparticle films can be deposited (after identification of suitable surfactant–monolayer interaction capable of cluster immobilization) due to the advances in colloid chemistry, while the chemical reaction route is currently limited to a small number of nanoparticle systems.

(4) Simultaneous incorporation of different clusters within the *same interlamellar spaces* is possible by choosing appropriate hydrosol mixtures. This is also inaccessible currently to the chemical insertion route.

Future work will focus on studying the temperature stability of the metal cluster superlattice structures, understanding the nature of ordering of the hydrocarbon chains around the metal colloidal particles, and realizing mixed cluster films.

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