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Influence of colloidal subphase pH on the deposition of multilayer Langmuir–Blodgett films of gold clusters

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Negatively charged carboxylic acid derivatized gold colloidal particles have been immobilized at the air/water interface using positively charged fatty amine Langmuir monolayers. The degree of cluster incorporation into the Langmuir monolayer has been systematically controlled by varying the charge on the surface amine through the colloidal subphase pH. This affects the quality of multilayer gold cluster films transferred to different substrates by the Langmuir–Blodgett method. Pressure–area isotherms were measured to follow cluster adsorption at the air/water interface while characterization of the multilayer films was undertaken using quartz crystal microgravimetry, UV–VIS spectroscopy, contact angle measurements, transmission electron microscopy, ellipsometry and X-ray photoelectron spectroscopy. Incorporation of clusters into organic matrices in the manner outlined is promising for the synthesis of superlattice structures, mixed cluster systems, *etc*., which cannot be realized by current experimental methods.

Introduction

Nanoparticle research has witnessed tremendous growth due to the unusual chemical and physical properties demonstrated by this intermediate state of matter.[1] More correctly, the research activities could be termed 'nanoscale architecture' since the generation and organization of nanoscale structures are of equal importance in the realization of viable device applications. More sophisticated studies have used scanning tunnelling microscopy (STM)[2,3] and atomic force microscopy (AFM)[4] to investigates the organization of nanoscale structures. Simpler and perhaps experimentally more exciting routes are also being actively pursued, one of which is based on a marriage of colloid chemistry and the principles of self-assembly for the growth of monolayer colloidal films.[5–7] The synthesis of nanoparticles under the ordering influence of organic templates such as Langmuir monolayers has also received considerable attention,[8–11] motivated partly by attempts to mimic the process of biomineralization. In a slightly different approach, nanoparticles have also been grown in organic matrices such as Langmuir–Blodgett (LB) films by a chemical insertion procedure.[12–17]

Fendler and co-workers 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 LB technique.[18–21] The growth of multilayer nanoparticle films by the LB technique was also shown to be possible through the interaction of suitably derivatized colloidal particles from the subphase with the polar group of Langmuir monolayers.[22–24] This latter approach for the deposition of lamellar particulate films has not received much attention and in this paper we demonstrate that reasonably compact multilayer gold cluster films can be transferred to solid supports by the LB method. We would like to mention here that gold clusters have been incorporated in LB films through chemical and/or photochemical reduction of aqueous chloroauric acid in the presence of a Langmuir monolayer of different surfactants by Fendler *et al.*[25] This differs significantly from the approach adopted in this investigation. We have used an aromatic bifunctional molecule, 4-carboxythiophenol (4-CTP), as the stabilizing surfactant molecule for colloidal gold particles. The thiol group of 4-CTP is known to form a strong covalent linkage with gold[26] leading to carboxylic acid derivatized metal clusters. Monolayers of octadecylamine (C_{18} amine) molecules are then used to immobilize the gold colloidal particles at the air/hydrosol interface after which facile transfer of the monolayer to solid substrates is possible. Regulation of the charge on the amine Langmuir monolayer by changing the pH of the gold colloid subphase can be used to control the degree of electrostatic interaction between the Langmuir monolayer and the gold clusters. Thus, the cluster density at the monolayer/hydrosol interface can be varied and as a consequence, in the LB film as well. We present below the results of our investigation.

Experimental

The gold hydrosol was prepared by citrate reduction of chloroauric acid ($HAuCl_4$) salt solution as described by Lee and Meisel.[27] The colloidal particles were then capped with 4-CTP by mixing a solution of the bifunctional molecule in absolute ethanol with the gold hydrosol to obtain a capping molecule concentration of 10^{-5} M. The capping of the gold clusters, which can be viewed as a three-dimensional self-assembly of 4-CTP molecules on the gold cluster surface,[26] was followed using UV–VIS spectroscopy which yielded a shift in the surface plasmon resonance from 525 to 530 nm. The surfactant-stabilized hydrosol had a pH of 3, was violet in color and clear, indicating that no flocculation of the clusters had occurred. The surfactant-stabilized gold clusters were observed under transmission electron microscopy (TEM) and a cluster diameter of 100 ± 30 Å was measured.

In order to follow the kinetics of immobilization of the clusters at the air/water interface, measurements of the surface pressure as a function of the monolayer area (π–A isotherms, subphase temperature = 25 °C) were performed on a Nima model 611 trough by dispersing a known quantity of octadecylamine in chloroform on the surface of the gold hydrosol used as the subphase. Care was taken to spread the monolayer only after the bifunctional molecule dispersing agent, absolute ethanol, had fully evaporated, which required typically 15 min. After a further 15–20 min of equilibration of the Langmuir monolayer, π–A measurements were carried out as a function of time for different values of the subphase pH ranging from 8 to 12. The pH of the subphase was adjusted using NaOH solution. This range was motivated by the fact that the pK_a values of the amine and the bifunctional molecules are 10.6 and 4.5, respectively. Thus, in the pH range mentioned above, one can systematically vary the charge on the amine molecules (protonated to yield -NH_3^+) while the carboxylic acid groups on the gold cluster remain fully ionized (-COO^-) throughout this range, thereby altering the strength of electrostatic interaction between the amine molecules and gold clusters.

After stabilization of the π–A isotherms was achieved, the monolayer was compressed to 25×10^{-5} N cm^{-1} surface pressure and the change in area with time at this pressure was monitored. After equilibration of the monolayer at this pressure, the monolayers were transferred to quartz and Si(111) wafer substrates at constant pressure by sequential dipping of the substrate in the monolayer-covered subphase in the classical LB deposition scheme.[28] It was observed that reproducible transfer of the gold cluster–C_{18} amine monolayer was possible only if a monolayer of lead arachidate was predeposited on the substrates rendering them hydrophobic. The transfer ratio during the upward and downward strokes of the substrate, determined from movement of the Langmuir trough barrier, was close to 0.5 and 1, respectively. Multilayer films corresponding to 2, 4, 6, 8, 10, 12 and 20 monolayers (ML) were deposited onto quartz and Si substrates for UV–VIS and ellipsometry measurements, respectively, and onto a gold-coated AT-cut quartz crystal for quartz crystal microgravimetry (QCM) measurements. QCM measurements were undertaken using an Edwards FTM5 microbalance with a frequency resolution of ± 1 Hz (mass resolution 12 ng cm^{-2}, 6 MHz quartz crystal). The quartz-crystal frequency change was converted to mass loading using the standard Sauerbrey[29] formula. Ellipsometry measurements were carried out on the multilayer films using a Gaertner L 118 manually operated null ellipsometer operated in the polarizer–compensator–sample analyzer (PCSA) mode at an angle of incidence of 70°. The light source was a 5 mW He–Ne laser (6328 Å wavelength) and the null condition was determined using a photomultiplier tube. Optical absorption spectra of the above films as well as the gold hydrosol were obtained on a UV–VIS Hewlett-Packard 8452 diode array spectrometer (2 nm spectral resolution). A 4 ML gold cluster–octadecylamine complex film was also transferred onto a formvar-coated electron microscope grid for TEM measurements at a colloidal subphase pH = 8. TEM measurements on the LB film were made on a Phillips TEM 301 T instrument operated at 80 kV and a magnification of 57000. The TEM measurement conditions were chosen so as to minimize heating of the LB film.

Formation of LB films was monitored using X-ray photoemission spectroscopy (XPS). Au 4f, C 1s, O 1s, S 2p and N 1s core level spectra of a 4 ML gold cluster film on hydrophobized quartz were recorded at a pressure of better than 1×10^{-9} Torr in a VG Scientific ESCA 3 MK II machine using unmonochromatized Mg-Kα radiation (energy = 1253.6 eV). Contact angle measurements were made on all the films using a Rame Hart 100 goniometer.

Results and Discussion

As mentioned earlier, capping of the gold sol resulted in a red-shift in the surface plasmon resonance from 525 to 530 nm as well as a damping of the plasmon resonance indicative of surface capping.[30] The stability of the carboxylic acid derivatized gold clusters at pH 8 and above was determined from UV–VIS measurements and was found to be excellent, hence any influence of this aspect on the nature of the π–A isotherms with time can be ruled out.

π–A isotherms

The π–A isotherms of the C_{18} amine monolayer on the surfactant-stabilized gold hydrosol at pH 8 and 11.5 are shown in Fig. 1(a) and (b), respectively. In Fig. 1(a), the π–A isotherm of octadecylamine on pure water at pH 8 is shown for comparison (curve 1). The family of curves indicated as 2 are the isotherms of octadecylamine on the gold hydrosol as a function of time. The solid line refers to the isotherm measured after 30 min of spreading of the amine monolayer, while the dashed and dotted lines correspond to the isotherms recorded after 60 and 90 min of spreading of the octadecylamine. It is clear that there is a fairly rapid expansion of the monolayer (*cf.* curve 1), which indicates complexation of the gold clusters to the protonated amine groups of the Langmuir monolayer. The π–A isotherms stabilize within 60 min of spreading the monolayer and an equilibrium lift-off area of 37 $Å^2$ $molecule^{-1}$ obtained, which is considerably larger than that for the amine on water (*ca.* 20 $Å^2$ $molecule^{-1}$, curve 1). We repeat here that at pH 8, both the amine (-NH_3^+) and carboxylic acid (COO^-) groups are expected to be fully charged. Since the as-prepared gold colloidal particles are known to be negatively charged, a control π–A isotherm was recorded with time of the octadecylamine monolayer on the uncapped colloid subphase at pH 8. No expansion of the monolayer was observed, thus underscoring the importance of capping with 4-CTP for adsorption at the Langmuir monolayer. The π–A isotherms of the amine monolayer at pH 9 showed slower expansion with a smaller lift-off area of 32 $Å^2$ $molecule^{-1}$ indicating weaker electrostatic interaction. This may be due to reduced protonation of the amine group, which would indicate a pK_a value for the surface amine group slightly less than that reported. Such shifts in the pK_a values as well as a broader pH range over which the groups are ionized are known for surface groups.[31] At pH 11.5, there is no significant expansion of the monolayer with time [Fig. 1(b)], solid curve (60 min) and dotted curve (180 min). The take-off area is close to 18 $Å^2$ $molecule^{-1}$, which agrees well with the close packing area expected for unprotonated amine groups.[32] The above results clearly show that controlling the charge on the amine monolayer through the hydrosol pH leads to a variation in the electrostatic interaction between the fully charged clusters and the Langmuir monolayer and, consequently, the differing levels of complexation of the clusters with the surface monolayer. Thus, through judicious choice of the ionizable cluster capping molecule and the amphiphilic molecule in the Lang-

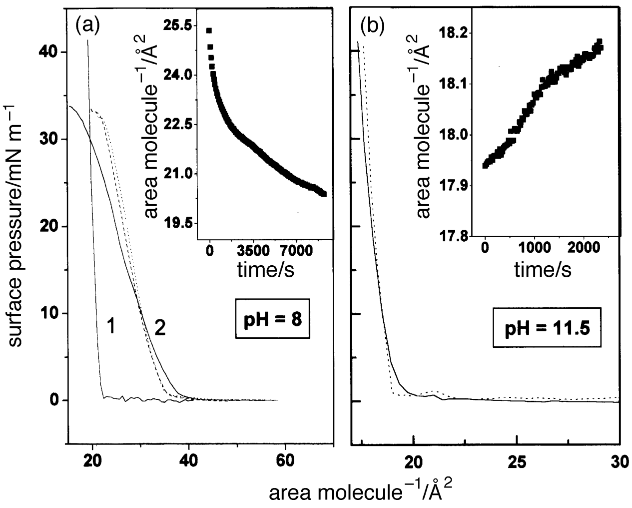

Fig. 1 (a) π–A isotherms at pH 8. Curve 1 (solid line) octadecylamine on water; family of curves 2, amine on gold hydrosol (solid line), t_F 30 min; dashed line, t = 60 min; dotted line, t = 90 min after spreading the amine monolayer. Inset shows variation in molecular area with time after compression to surface pressure = 25 nM m^{-1}. (b) π–A isotherms of octadecylamine on the gold hydrosol at pH 11.5. Solid line, after t = 60 min; dashed line, after t = 90 min of spreading the amine monolayer. Inset shows variation in molecular area with time after compression to a surface pressure of 25 mN m^{-1}.

muir 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 (DODAB = dioctadecyl dimethylammonium bromide; HMP = hexametaphosphate).[22] However, modification of cluster density at the monolayer colloidal subphase interface as described above has not been recognized till now and may have important applications.

Some other observations pertinent to transfer of the monolayers to form LB films can be made from Fig. 1. The gold 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^{-1} was chosen for the transfer. The monolayers were compressed to this pressure and the variation in monolayer area with time recorded. This is plotted in the inset of Fig. 1(a) (pH 8) and (b) (pH 11.5). Little change in the area molecule^{-1} is seen for the monolayer at pH 11.5 while a large reduction from 25.5 to 19.5 Å^2 molecule^{-1} over a period of 150 min was recorded for the monolayer at pH 8. This indicates that the kinetics associated with cluster immobilization is extremely slow and sensitive to the surface charge density. The monolayer area stabilized at 19.5 Å^2 molecule^{-1} after nearly 270 min of compression. The nature of the monolayer area–time dependence at pH 9 was similar to the lower pH data. From the above, optimum conditions for transfer of the gold cluster–amine monolayer were determined to be a surface pressure of 25 mN m^{-1} and an equilibration period of *ca.* 300 min.

TEM studies

Fig. 2(a) shows a typical TEM of the 4 ML gold cluster–octadecylamine film. It is observed that there are regions within the film where the gold clusters are close packed with large gaps between such 'domains'. The particle size histogram [Fig. 2(b)] was determined from the micrograph shown in Fig. 2(a) and other micrographs taken at different points on the surface. A Gaussian fit to the data is shown as a solid line and yields a mean cluster size of 125 Å and a standard deviation of 30 Å. This data is used in the interpretation of the QCM and ellipsometry results presented below. While it appears that there is an increase in the average size of clusters in the LB film compared with the clusters in the hydrosol, further work is required in order to determine whether this is significant and is currently being pursued.

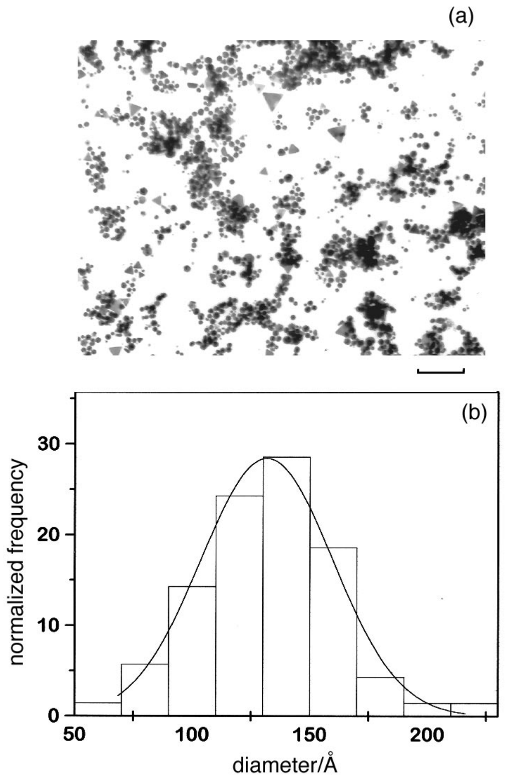

Fig. 2 (a) Typical TEM micrograph of a 4 ML gold cluster–octadecylamine LB film. The scale bar corresponds to 1200 Å. (b) Particle size histogram obtained from TEM measurements of the 4 ML gold cluster–octadecylamine film. The solid line is a Gaussian fit to the data; the parameters of the fit are listed in the text.

QCM and UV–VIS studies

Growth of the gold cluster–amine LB films by sequential transfer was followed using QCM and UV–VIS measurements. Fig. 3 shows a plot of the mass uptake with the number of immersion cycles of a gold-coated quartz crystal into hydrosol subphase at pH 8, 9 and 11.5. It is to be noted that one immersion cycle of a substrate (one dip) corresponds to transfer of two monolayers (one bilayer) in the Y-type LB film deposition scheme. The gold film was hydrophobic and hence a lead arachidate monolayer was not deposited for these measurements. Good transfers were obtained for a film immersion rate of 25 mm min^{-1} and 15 min drying between immersions. It is seen from the figure that there is a systematic increase in mass uptake per dip as the pH is reduced from 11.5 to 8. The mass transfer per dip was determined from a least-squares fit to the data which is clearly linear (solid lines are the regression curves). At pH 11.5, 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 11.5. The cluster density in the film at pH 8 (maximum mass transfer per dip observed) was determined from the QCM mass uptake assuming an average cluster size of 125 Å, determined from TEM measurements (Fig. 2), and a surface coverage of 30% calculated. This value is larger than the surface coverage of 15% obtained by Natan *et al.* for self-assembled gold clusters.[7] The larger surface coverage observed for clusters immobilized in an LB matrix may be due to screening of the charge on the clusters by the amine molecules and/or additional stabilization arising due to the van der Waals interactions between the alkyl chains of the amine molecules coordinated to the clusters. An intermediate mass uptake dip^{-1} for pH 9 indicates a smaller gold cluster density in the bilayer and, as will be shown below, is consistent with UV–VIS measurements of the LB films. The important point to note from Fig. 3 is the linearity in the plot at all pH values which indicates fairly uniform monolayer-by-monolayer transfer of 125 Å diameter gold clusters complexed to amine monolayers.

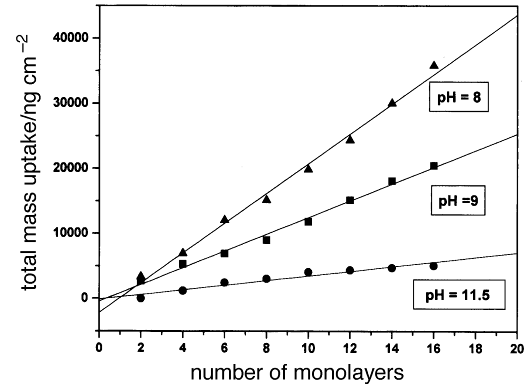

Fig. 3 Mass uptake with number of monolayers transferred from QCM measurements, at various hydrosol pH values. Solid lines are linear fits to the data.

UV–VIS spectroscopy is an ideal tool for following the film growth process of gold cluster films due to the strong surface plasmon resonance exhibited by this metal. Fig. 4(a) 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 8. The plasmon resonance occurs at 650 nm for all the films and a monotonic growth in resonance intensity is observed as the film thickness increases. As mentioned above, no transfer of the gold clusters was observed by QCM at pH 11.5 and this is corroborated by UV–VIS measurements of an 8 ML film on quartz (dashed line), which shows no indication of the expected surface plasmon resonance. For comparison, the absorption spectrum recorded for a 6 ML LB film transferred at subphase pH 9 is shown (dotted line). The plasmon resonance of this film (and for other thickness films at this pH) occurs at 580 nm. This large shift in the surface plasmon resonance with subphase pH may be attributed to flocculation of the colloidal particles.[33] Fig. 4(b) shows the variation in the intensity at the surface plasmon resonance with film thickness. Here again we see a systematic increase in the absorbance with film thickness for pH 8 and 9 with a linear regression curve fitting the data very well. The linearity in the absorbance data again clearly indicates transfer of the monolayers with nearly the same cluster density per monolayer.[22] The slope of the curve at pH 9 is less than that obtained for pH 8 indicating less gold cluster density per monolayer at pH 9, in total agreement with QCM data. The QCM and UV–VIS data clearly show that multilayer films of colloidal particles can be deposited by the LB technique. Furthermore, the gold cluster density in the hydrophilic regions of the film can be controlled by variation of the colloidal subphase pH.

Ellipsometry measurements

The thickness of the multilayer gold cluster–octadecylamine LB films transferred onto Si(111) substrates at a colloidal subphase pH of 8 was determined ellipsometrically as outlined below. The complex refractive index of the gold cluster–octadecylamine multilayer films was determined using the Maxwell–Garnett effective medium formalism.[34] In this formalism, the effective relative permittivity of the gold cluster–amine film is given by:[34]

$$\varepsilon_{\text{eff}} = \varepsilon_{\text{m}}(1 + \tfrac{2}{3}f\alpha)/(1 - \tfrac{1}{3}f\alpha) \qquad (1)$$

where ε_{m} is the relative permittivity of the ambient medium (octadecylamine bilayers in this study), f is the filling fraction of gold clusters in the film and α is proportional to the polarizability of the clusters. The polarizability factor is given by:

$$\alpha = 3(\varepsilon_{\text{f}} - \varepsilon_{\text{m}})/(\varepsilon_{\text{f}} + 2\varepsilon_{\text{m}}) \qquad (2)$$

where ε_{f} is the cluster relative permittivity. For simplicity, we have assumed a uniform distribution of gold particles of size 125 Å. The filling factor was determined from QCM measurements to be 27% and the real and imaginary parts of the refractive index for gold at a wavelength of 6328 Å were taken from the data of Johnson and Christy[35] to be 1.315 and 1.524, respectively [$\varepsilon_{\text{f}} = (1.315 + \text{i}\ 1.524)^2$], while ε_{m} was taken to be $(1.5)^2$. The film thickness for different LB films was then determined by solving the exact equation of ellipsometry[36] with the film refractive index calculated using eqn. (1) and (2). Fig. 5 shows a plot of the thickness determined ellipsometrically for the multilayer films transferred onto Si(111) substrates. It is seen that there is a linear increase in the thickness indicating uniform transfer to the gold clusters in the monolayers during each immersion cycle. This result is in agreement with the QCM and UV–VIS results presented earlier. A least-squares fit to the data shown in Fig. 5 yielded a thickness per bilayer of 55 Å. Assuming a thickness per bilayer of 50 Å for the amine molecules[37] and a cluster size of 125 Å, the expected thickness per bilayer is well in excess of that measured ellipsometrically. This result clearly indicates considerable disorder within the gold cluster–octadecylamine monolayers in terms of packing of the clusters. Clusters transferred during successive immersions can then fill gaps in the base multilayer films leading to a much smaller thickness per bilayer as observed. This highlights an important aspect of the study, *i.e.*, while QCM and UV–VIS measurements show that the number of clusters transferred per immersion cycle is the same, they do not provide information on the disorder in the films, which has been shown indirectly through ellipsometry measurements. The disorder in the films is not surprising given the dimensions of the gold clusters (125 Å) comprised with the dimensions of the octadecylamine bilayer (50 Å). It may be pointed out here that the ellipsometry results are in agreement with those of the TEM studies of a 4 ML gold cluster LB film (Fig. 2), which show aggregates of clusters separated by large gaps.

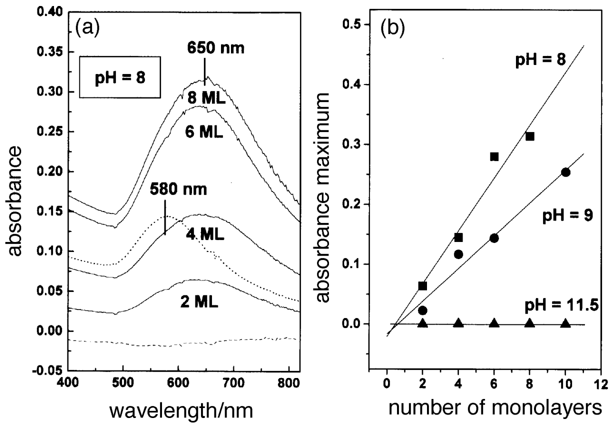

Fig. 4 (a) UV–VIS spectra of the gold cluster LB films transferred to hydrophobized quartz substrates of varying thicknesses at colloidal subphase pH 8. Dashed line, 8 ML film deposited at pH 11.5; dotted line, 6 ML film deposited at pH 9. (b) Variation of the absorption maximum with film thickness for LB films transferred onto hydrophobized quartz at various colloidal pH values (▲), (●), (■). The solid lines are linear fits to the data.

XPS and contact angle studies

While good sequential transfer of the monolayers by the LB technique could be attained, the consequences of a disordered film structure, as observed in the ellipsometry and TEM studies, of the gold cluster LB films needs further investigation. Angle-dependent XPS was used to understand the organization of the gold clusters in the amine organic matrix as previously shown for lamellar systems such as LB films.[38]

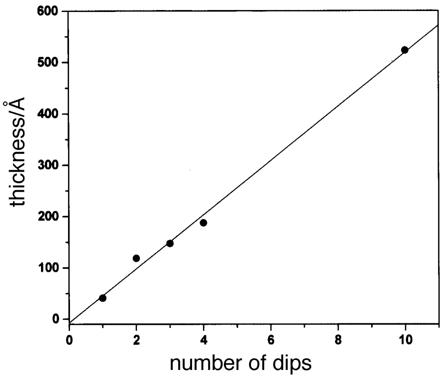

Fig. 5 Ellipsometric thickness as a function of film thickness for LB films of the gold cluster–octadecylamine complex transferred onto Si(111) substrates. The solid line is a linear fit to the data.

It was found that the ratio of the C 1s to Au $4f_{7/2}$ signals at 60 and 30° electron take-off angles was 24 and 20, respectively. This indicates that at least a fraction of the gold clusters are on the film surface, which is contrary to the expected structure of the clusters embedded below a 25 Å thick amine hydrocarbon chain. Contact angle measurements of the films yielded a mean value of 55°, which is considerably less than that recorded for the lead arachidate covered surface of 105° indicating a more hydrophilic surface. This is only possible if some of the carboxylic acid derivatized clusters are present on the surface as indicated by the XPS measurements. This result also strongly suggests the presence of gaps between clusters in the films. Clusters transferred during successive immersions may then turn over in the gaps to maximize the van der Waals interactions between the alkyl chains of the amine molecules coordinated to the cluster surface and the molecules in the base film, thus exposing the more hydrophilic carboxylic acid groups to the surface. We emphasize that this is a tentative explanation for the results obtained. There was no evidence for an additional component in the Au 4f signal arising from the Au—S thiolate bond (expected $E_b = 84.6$ eV) in full agreement with the findings of Schiffrin and co-workers.[38] While the quantitative aspects of the XPS studies relevant to this work are presented here, a more detailed chemical analysis will be published elsewhere.[40]

To summarize, it has been demonstrated that multilayer films of gold clusters of varying cluster density can be grown by the LB technique through changes in the colloidal subphase pH. The strategy has been to derivatize colloidal gold clusters and to immobilize them electrostatically at the Langmuir monolayers of fatty amines and then to transfer the gold cluster amine monolayers onto solid substrates. We believe this approach for the incorporation of clusters and/or nanoparticles in organic matrices has many advantages over the chemical insertion route receiving attention at present.[12–27] Some of these are as follows.

(1) Since ordering of the clusters is accomplished at the air/water interface, a disruption of ordering of the lamellar phase is not expected, unlike in the formation of, *e.g.*, CdSe by treatment of Cd–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.[13]

(2) Well defined superlattice structures are possible in this scheme through alternate transfers in different hydrosol subphases 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) owing 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 be directed towards realizing mixed metal and semiconductor cluster films and superlattice structures mentioned above.

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