AFM study of templated growth of cadmium sulfide nanoparticles using pure and mixed arachidate films

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Abstract

Langmuir±Blodgett (LB) multilayers of arachidic acid (AA) and octadecylamine (ODA) were used as templates in order to produce cadmium sulfide (CdS) nanoparticle arrays. Both atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) were used to characterize the film. In the absence of ODA, the cadmium arachidate trilayers were highly crystalline with a lattice constant of 0.42 nm. Upon reaction with hydrogen sulfide (H₂S), an ordered array of CdS nanoparticles with a particle separation of 4.2 nm was imaged. The existence of CdS was also confirmed by XPS. No CdS nanoparticles were formed when ODA was used as the sole component. In the presence of ODA, the crystalline structure of the AA film was disturbed, resulted in randomly distributed particles. The average particle height was reduced from 4 to 1 nm when the amount of ODA was increased. It is concluded that there is a direct correlation between the ordering of the organic template and that of the nanoparticle array. There is also a correlation between the particle size and the ratio of AA and ODA. Mixed LB films are promising in synthesizing semiconducting nanoparticle arrays of limited particle sizes. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Atomic force microscopy; Cadmium sulfide; Langmuir±Blodgett films; Nanostructures

1. Introduction

The low dimensionality of nanostructures, in which electrons are free to move in only two-, one-, or even zero-dimensions, has a profound effect on their electronic and optical properties. The practical applications of these effects are only just beginning, in such devices as lasers based on quantum wires and quantum dots (QDs). One of the major technological barriers to fabricate functional nanostructures is the ability to synthesize nanostructures of sufficiently small dimension, specific pattern, and uniform size distribution. Organic templates such as mesophases and thin films offer a more economical and versatile alternative to the ultra-high vacuum techniques. One of the organic templates being utilized is the Langmuir±Blodgett (LB) multilayer film capable of producing ordered arrays of nanoparticles similar to those produced by the molecular beam epitaxy.

A Langmuir film is an insoluble amphiphile layer of one molecule thick floating at the air/water interface. An LB film consists of multilayers of sequentially transferred Langmuir monolayers in a highly compressed state onto a solid support [1]. The state of pure Langmuir films has been extensively studied to include gaseous, liquid expanded, liquid condensed, and solid state [2,3]. Long range order in closely-packed single component Langmuir and LB films has been well established by various surface characterization techniques including the atomic force microscopy (AFM) [4], X-ray reflectivity [5], and neutron diffraction [6]. AFM is a particularly useful characterization method for LB films because it is surface sensitive. AFM has been used to image LB films with molecular resolution and to identify local defects and inhomogeneities in ordered surfaces. Schwartz et al., studied LB films of cadmium arachidate in air by AFM to determine the long range structure and the molecular ordering [7]. They show that on mica, a monolayer was unstable and images with molecular resolution were not possible. Images with molecular resolution can be obtained only on layers of odd numbers starting from 3. The overall cadmium arachidate composition in the transferred LB film has also been investigated with the Fourier Transform Infrared Spectroscopy (FTIR). It was found that the cadmium concentration and the pH of the aqueous subphase affected the chemical composition of cadmium arachidate in the film [8]. Salt formation increased with the subphase pH. The deprotonation was approximately 50% completed at pH = 5.5 and reached 100% at
pH = 6.5 [9]. Leveiller et al., found that cadmium arachidate formed a 2-3 supercell with 1:1 stoichiometric ratio of cadmium to arachidate at pH = 8.8 [10]. In this study, we maintained the subphase pH = 7 to ensure a complete deprotonation of the arachidic acid. Three layers were deposited in order to stabilize the transferred film.

Due to the limited chemical and structural variation in single component LB films, there are attempts to modify the LB film by adding other functional groups to the film surface, using organic and inorganic chemicals [11]. Various mixed hydrocarbon monolayers spread at the air/water interface have been studied [12–14]. Phase separation is the primary obstacle for the creation of mixed LB film templates. The degree of order and molecular segregation in Langmuir monolayers consisting of more than one component are much more complex and therefore less understood [15–20]. For an ideal mixture or a completely immiscible monolayer, the molar area of the mixture is the molar average of those of pure components at a given surface pressure. Non-ideal behavior is indicated by any deviation in the isotherm from that of the molar average. A poorly mixed monolayer also exhibits more than one collapse pressure, while a truly well mixed monolayer should only display one collapse pressure, probably at a different value from that of either component. Sometimes the isotherm of a mixed monolayer displays the ideal behavior with domains smaller than 100 nm in diameter as shown by the AFM technique [20]. Many groups have concentrated on mixed films with arachidic acid (AA) as one of the components because of the stability of the AA film. Other amphiphile components such as polypyrrole [21], hydroxyalkyldimethyloctadecylammonium bromide [22], C₆₀ [23] and octadecyldimethylamine oxide [24] have been incorporated into the AA LB films. Yang et al., studied the mixed monolayer of AA and octadecylamine (ODA), and found that the isotherm of AA and ODA mixture is almost identical to that of pure AA [25].

In recent years, considerable interest has been shown in preparing quantum-state semiconductor nanoparticles. Langmuir monolayers and LB multilayers have been used to nucleate and control the growth of both macro-[18,26] and micro- or nano-crystals [28,29]. One of the systems synthesized by the LB method is the sulfide of valence II metal ions such as CdS [30], PbS [31] and ZnS [32]. CdS is an important semiconducting material with a band gap energy of 2.4 eV and an exciton diameter of 60 Å [33]. The general scheme involves the slow penetration of H₂S into the two-dimensional (2D) array of deprotonated amphiphiles (such as AA), reaction with the cationic precursors (such as Cd²⁺, Pb²⁺, and Zn²⁺) electrostatically immobilized by the hydrophilic headgroup of the amphiphile, and the formation of the sulfide nanoparticles. A single layer of such nanoparticles can be formed in a Langmuir monolayer at the water surface, or nanoparticle arrays can be formed in the LB multilayer film on a solid support. Most of the characterization on the particle size and structure inside the film was inferred by the blue shift of the absorption spectra [28,34,35]. Most AFM studies have focused on the morphological change in the LB film before and after the reaction. Few images of nanoparticles were available, and in these few direct measurements, the nanoparticle size was shown to exhibit a wide range of distribution, though an epitaxy match between the crystalline lattice of the nano-crystal and that of the AA template has been postulated. In our study, we use AFM to characterize not only the morphological changes in the film during each step, but also the particle size directly after removing the LB film. Ideally mixed LB film templates can provide more control on the particle growth. Fendler et al., used AA and ODA mixed LB films as templates to grow PbS particles [25]. The morphology of the PbS micro-crystals revealed by the transmission electron microscopy (TEM) was triangular and epitaxially matched to the underlying template. To the best of our knowledge, mixed LB films have not been used as a template to control the growth of CdS nanoparticles, and no AFM images of ordered CdS nanoparticle arrays are available.

Our program has following overall objectives. (1) To characterize the miscibility and stability of mixed Langmuir layers. (2) To tailor the mixed monolayers as templates for the control of the size and distribution of the nanoparticles. In this paper, we report the AFM study on the synthesis of CdS nanoparticles using cadmium arachidate. We would like to establish that indeed it is possible to synthesize an ordered array of CdS nanoparticles. We will also report our findings on the effect of adding a cationic amphiphile on the stability of the AA film as well as the resulting nanoparticles. Lastly, a model on the nanoparticle growth mechanism under a mixed LB film will be discussed.

2. Experimental section

2.1. Materials

Arachidic acid (AA) with purity >99% and octadecylamine (ODA) with purity >98% were purchased from Sigma, cadmium chloride (CdCl₂) with purity >99% was purchased from Aldrich, potassium bicarbonate (KHCO₃) with purity >99.9% and chloroform (CHCl₃) with purity >99.9% were purchased from Fisher Scientific, and hydrogen sulfide (H₂S) gas (CP grade) was purchased from Matheson Gas Products Inc. The above chemicals were used as received. Water was deionized to 18 MΩ cm resistivity in a Nanopure system from Barnstead. Grade 3 ruby muscovite mica was purchased from Mica New York Co.

2.2. LB deposition and reaction

CHCl₃ solutions of AA (3.2 × 10⁻³ M) and ODA (3.2 × 10⁻³ M) were mixed in different proportions (AA : ODA = 1 : 0, 16:1, 4:1, 2:1, 1:1, and 0:1) and spread dropwise at the air/subphase interface to give a surface area coverage of 0.40 nm²/molecule. The aqueous subphase contains 4 × 10⁻⁴ M CdCl₂ and 4 × 10⁻⁴ M KHCO₃.
(pH = 7.1 at 21°C). A mini-trough of KSV M1200 was used to compress the Langmuir monolayer at a rate of 0.00467 nm²/molecule/min. Surface pressure versus surface area isotherms were obtained at 21°C. Three LB layers of the Y-type were deposited onto a mica substrate by the vertical dipping with a dipping speed of 1.6 mm/min at a constant surface pressure of 30 ± 0.5 mN/m. The transfer ratio of pure AA layers was monitored to be 1. However, the transfer ratios of the third layer containing ODA were reduced from 1 to around 0.8 to 0.9.

The slow H₂S infusion was carried out in the solid-bound multilayer instead of the liquid-bound monolayer film in order to limit the growth of particles [36]. Trilayer LB films were used instead of the unstable monolayer LB film. The deposited LB trilayer sample was placed in a 71.5 cm³ sealed reactor and exposed to a continuous H₂S stream for 90 min at room temperature. After the reaction, the amphiphile layers were removed gradually by rinsing gently with CHCl₃.

2.3. Characterization

Nanoscope IIIa from Digital Instruments was used. The AFM images were captured in the Contact Mode using an e-scanner with a maximum scan dimension of 16 μm in the laboratory atmosphere. Silicon nitride tips were used which have a nominal radius of curvature between 20–40 nm and an approximate spring constant of 0.06 N/m. The contact force was minimized during scanning by using a set point just above the disengagement point. Height images were captured at the highest allowable integral and proportional gains usually between 5 and 10, and a scan rate of 1 to 5 Hz. For closely-packed particles, the lateral separation as indicated by the peak-to-peak distance in the section profile is reported. The tip cannot insert between two closely packed particles, and therefore the vertical dimension, i.e. the peak-to-valley height, is meaningless. For isolated particles and clusters, only the vertical dimension was reported since the lateral dimension measured by AFM tips are highly exaggerated due to tip convolution. For the images of molecular lattices, the deflection image was used with the gains set at 0.1 and the scan rate between 20–40 Hz. All the images are raw images, flattened to remove underlying surface curvature. 2D fast Fourier transformation (fft) has been performed on images with periodic structure in order to show the unit cell dimensions. The fft-filtered image is shown together with the raw image.

X-ray photoelectron spectra were obtained on a Surface Science SSX-100 a multichannel detector. The take-off angle was 55° with respect to the surface normal, and the operating pressure was approximately 1 × 10⁻⁶ Torr. Survey spectra were recorded at a pass energy of 150 eV and a spot size of 1 × 10⁻⁵ μm. The binding energy scales for all spectra were referenced to the Au (4f7/2) peak at 84.00 eV.

3. Results

3.1. LB films of pure AA

3.1.1. Isotherm

The Langmuir isotherms of AA, ODA and mixed AA/ODA monolayers are shown in Fig. 1. Pure AA (curve a) displayed the same isotherm as expected from literature [23,37]. At large molecular separations, the floating amphiphiles lie flat on the water/subphase interface. Upon further compression to approximately 0.20 nm², the surface pressure rises steeply indicating that a close packing of vertically stretched molecules has been reached. The surface pressure levels off at 60 mN/m where the monolayer collapses into a 3D structure.

3.1.2. AFM characterization

AFM images were captured at the following stages of the experiment: (1) after LB deposition, (2) after infusion of H₂S, and (3) after removal of amphiphile layers by CHCl₃. For a cadmium arachidate monolayer on mica, AFM height images (not shown) with a mean surface roughness = 0.2 nm indicated a molecularly smooth monolayer yet without a long-range order. Fig. 2a is a height image of the cadmium arachidate trilayer on mica. The step height between the two adjacent terraces was measured in Fig. 2b to be 5.2 nm, which is the expected double layer thickness of AA. Scanning of these smooth planes revealed a molecular lattice structure shown in Fig. 2c with a pseudo-hexagonal symmetry as indicated by the 2D fast Fourier transform (fft) pattern in the inset of Fig. 2c. Fig. 2d is an fft-filtered AFM image where an average lattice constant was measured to be 0.42 nm. The above AFM data agree very well with previous studies [9]. It was concluded in those studies that the monolayer was not stable, and the multilayer segregated into odd numbered layers due to the strong headgroup–headgroup interface and the weak tailgroup–tailgroup interface in the AA LB film.

After the infusion of H₂S, morphological changes at the film surface were captured by AFM and displayed in Fig. 3a.

Fig. 1. Langmuir isotherms of AA, ODA, mixed AA and ODA monolayers: AA:ODA = (a) 1:0, (b) 16:1, (c) 4:1, (d) 2:1, (e) 1:1, and (f) 0:1.
The reaction of H$_2$S with cadmium arachidate is expected to yield AA and CdS as shown in the following reaction mechanism:

\[
\text{CH}_3\text{CH}_2\text{CO}_2\text{HCd}^{2+}\text{CH}_2\text{CH}_2\text{CO}_2\text{H} + \text{H}_2\text{S} \\
\rightarrow 2\text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{CdS}
\]

The reaction eliminates the electrostatic stabilization effect of the cadmium ions on the deprotonated AA film, thus reducing the rigidity and crystallinity of the film. The segregated film was able to relax into a mostly trilayer structure with irregular holes formed inside the film. The depth of the holes was measured in Fig. 3b to be 5.4 nm indicating little changes in the double layer thickness after the reaction.

Upon rinsing for 10 min with CHCl$_3$ to remove the amphiphile layers, a smooth surface was imaged with a highly ordered structure as shown by the raw AFM image of Fig. 3c. The crystalline structure in Fig. 3c is more clearly illustrated by its fft (inset of Fig. 3c) with a pseudo-hexagonal symmetry. A lattice constant of 4.2 nm was obtained in Fig. 3d, which is a filtered image of Fig. 3c. The large lattice constant conveniently excludes the surfaces of mica (with a lattice constant of 0.52 nm) and AA (with a lattice constant of 0.42 nm). The only likely identity of this surface is the ordered array of CdS nanoparticles where the separation between the nearest nanoparticles is 4.2 nm. This implies that the lateral diameter of the nanoparticles is less than 4.2 nm. Due to the close-packing of particles, the vertical dimension of the nanoparticles cannot be measured by the AFM tip. A mass balance would suggest the vertical dimension should be much less than 4.2 nm. Because the CdS observed was formed within the confinement of the bottom AA layer and substrate, it is most likely that the ordered array is a monolayer thick with a disk shape.

In order to substantiate the presence of CdS in the AA template, the chemical composition of the film at various stages of preparation was analyzed by XPS. We focused on the percentage of three elements C, Cd, and S as shown in Table 1. It should be noted that the absolute value of the surface composition cannot be easily obtained because of the difficulty in discriminating the C signal from the organic...
amphiphile to those from the atmosphere contaminants. However, our purpose is to observe changes in composition at different film preparation stages. Before the infusion of H$_2$S, no S signal was detected. After the reaction, S signal appears as one of the major components. Upon rinsing with CHCl$_3$, both Cd and S signals become stronger relative to the C signal, suggesting the gradual removal of the organic matrix. After 10 min of rinsing, Cd and S have an approximate 1:1 stoichiometric ratio agreeing with the formation of CdS. In summary, XPS shows that indeed CdS was formed in the organic matrix and was present after 10 min solvent rinsing. The XPS results, together with AFM images (Fig. 3c), strongly suggested an ordered array of CdS nanoparticles can be synthesized by a pure AA LB film.

3.2. Mixed LB films of AA and ODA

3.2.1. Isotherm

In Fig. 1, the isotherm of ODA (curve f) is slightly more expanded as compared to that of AA. Its slope of the condensed phase is lower than that of AA. The limiting area per molecule, by extrapolating to zero surface pressure for ODA is 0.21 nm$^2$, while for AA is 0.19 nm$^2$. The limiting area of ODA is smaller than 0.29 nm$^2$ reported by Yang et al. [25], perhaps due to the sensitive nature of the isotherm to the variation in the subphase pH and salt concentration. The isotherm of AA : ODA = 16 : 1 matches closely with that of the pure AA (curve b) because of the negligible amount of ODA dispersed in the AA matrix. But as the ODA to AA ratio was increased, the isotherm gradually shifted to the left with limiting area per molecule decreased from 0.18 nm$^2$ for AA : ODA = 4 : 1 (curves c), to 0.14 nm$^2$.

<table>
<thead>
<tr>
<th>Film type</th>
<th>C</th>
<th>Cd</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium arachidate</td>
<td>97.99</td>
<td>2.01</td>
<td>0.00</td>
</tr>
<tr>
<td>After H$_2$S infusion</td>
<td>96.16</td>
<td>2.47</td>
<td>1.37</td>
</tr>
<tr>
<td>After 30 s rinsing with CHCl$_3$</td>
<td>92.61</td>
<td>6.16</td>
<td>1.23</td>
</tr>
<tr>
<td>After 3 min rinsing with CHCl$_3$</td>
<td>88.41</td>
<td>6.73</td>
<td>4.86</td>
</tr>
<tr>
<td>After 10 min rinsing with CHCl$_3$</td>
<td>87.35</td>
<td>6.23</td>
<td>6.42</td>
</tr>
</tbody>
</table>

Table 1

Percentages of C, Cd, and S in the cadmium arachidate film at various film preparation stages by XPS analysis.
nm$^2$ for AA : ODA = 2 : 1 (curves d), and to 0.12 nm$^2$ for AA : ODA = 1 : 1 (curves e).

The isotherms of the mixed monolayers are significantly different from previous studies [25], which was obtained using a different subphase: $1 \times 10^{-3}$ M Pb(NO$_3$)$_2$ at pH = 5.8. In order to probe the effects of the subphase concentration, pH, and the type of salt on the Langmuir isotherm, a series of experiments were carried out. Table 2 summarizes the results of the subphase effects on the concentration, pH, and the type of salt on the Langmuir isotherm. The collapse pressure of all isotherms is approximately 60 mN/m

Table 2
The effect of the anion, cation, concentration, and pH of the subphase on the isothermal behavior of mixed AA and ODA Langmuir monolayers (AA : ODA = 1 : 1). The collapse pressure of all isotherms is approximately 60 mN/m

<table>
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<tr>
<th>Experiment number</th>
<th>Salt in subphase</th>
<th>Salt concentration (M)</th>
<th>Subphase pH</th>
<th>Area per molecule (nm$^2$/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pb(NO$_3$)$_2$</td>
<td>$1 \times 10^{-3}$</td>
<td>5.8</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>CdCl$_2$</td>
<td>$4 \times 10^{-4}$</td>
<td>7.0</td>
<td>0.125</td>
</tr>
<tr>
<td>3</td>
<td>CdCl$_2$</td>
<td>$4 \times 10^{-4}$</td>
<td>5.8</td>
<td>0.125</td>
</tr>
<tr>
<td>4</td>
<td>Cd(NO$_3$)$_2$</td>
<td>$1 \times 10^{-3}$</td>
<td>5.8</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>Cd(NO$_3$)$_2$</td>
<td>$4 \times 10^{-4}$</td>
<td>5.8</td>
<td>0.20</td>
</tr>
<tr>
<td>6</td>
<td>Cd(NO$_3$)$_2$</td>
<td>$4 \times 10^{-4}$</td>
<td>7</td>
<td>0.20</td>
</tr>
</tbody>
</table>

The effect of the anion, cation, concentration, and pH of the subphase on the isothermal behavior of mixed AA and ODA Langmuir monolayers (AA : ODA = 1 : 1). The collapse pressure of all isotherms is approximately 60 mN/m.

Fig. 4 displays a series of AFM images with ODA as the minor component (the initial composition is AA:ODA = 16:1). The isotherm of AA : ODA = 16 : 1 was almost identical to that of pure AA, but the AFM images of the two systems are different. Fig. 4a,b are the AFM image and a cross-section profile before the infusion of H$_2$S. The film surface is smooth with no layer reorganization exhibited by the trilayer film of pure AA. But the film is soft and displays many holes. The spherical shape of the holes implies a highly amorphous nature of the film. It should also be noted that the transfer ratio of the third layer in the presence of ODA can only reach 80–90%. The depth of the holes was measured in Fig. 4b to be a double layer thickness of AA film of around 5.2 nm. In this mixed film, the tailgroup-tailgroup interface is weaker than the headgroup-headgroup and headgroup-substrate interface. It appears that the presence of ODA, even in a small amount, has significantly reduced the degree of crystallinity in the film. ODA can disrupt the molecular packing of AA and the cross-linking of Cd$^{2+}$ to AA by forming electrostatic and hydrogen bonding with the deprotonated AA molecule. After the reaction, no significant changes occurred at the film surface as shown in Fig. 4c except that the film appeared to be softer as holes were induced and expanded by the scanning tip. After rinsing with CHCl$_3$ for 3 min, randomly distributed particles were imaged as shown in Fig. 4d. Fig. 4d displays a partially removed LB film. In the thinner part of the film as indicated by darker shades, some of the particles are separated far enough to allow AFM tip measurement of their height to be 3.5 ± 0.7 nm. It should be noted that due to exaggerated lateral dimensions by the tip, the height data are meaningful.

Increasing the ODA percentage induced larger hole formation in the trilayer film. When the AA and ODA ratio was reduced to 4:1, the holes were largely spherical as shown in Fig. 5a with a depth of 4.8 nm, measured in Fig. 5b, suggesting an amorphous and largely stable trilayer film. After the infusion of H$_2$S, the holes became larger and non-

3.2.2. AFM characterization

In order to monitor the effect of introducing ODA on the structure of AA templates, and on the size and distribution of CdS particles formed, AFM images were captured at various stages of the mixed film preparation: (1) after LB deposition on mica, (2) after infusion of H$_2$S, and (3) after removal of the amphiphile layers by CHCl$_3$. Though the exact composition of these mixed films was impossible to know due to the precipitation of the amphiphile salt, the effects of introducing ODA into the AA film on the growth mechanism can still be elucidated qualitatively and are fundamentally revealing. The data can lead to a better understanding of various factors affecting the templated growth of nanoparticle superlattices using mixed amphiphile pairs.
spherical as shown in Fig. 5c with an average depth around 5.0 nm. The straight and uniquely oriented boundaries of the holes suggest a long range crystalline order in the film after the reaction with H2S. However, the film was very soft and did not permit a molecular resolution of its crystalline lattice. The origin of the reaction induced amorphous to crystalline transition is not clear at the present time. After rinsing with CHCl3 for 3 min, randomly distributed particles with a diameter of 1.2 ± 0.3 nm were imaged in Fig. 5d. The particle size is reduced when the AA:ODA is decreased from 16:1 to 4:1 suggesting that the presence of ODA limits the growth of CdS nanoparticles.

With equal molar ratio of AA and ODA in the Langmuir monolayer, the percentage of ODA and AA bonded pairs is maximized, and the percentage of immobilized Cd²⁺ is minimized. Fig. 6a,b are AFM images of the trilayer film containing AA : ODA = 1 : 1. The trilayer film before the reaction appeared to be largely flat with a mean surface roughness = 0.2 nm. The most striking feature is that no holes were formed in this sample as opposed to the 16:1 and 4:1 ratio (Figs. 4 and 5). However, in the frictional mode with a 90° scan angle, spherical domains of uniform size diameter = 200 nm were imaged as shown in Fig. 6b. These domains were only visible in the frictional mode indicating no height difference between the dispersed domains and the continuous dispersing phase. These domains may be the condensed phase, which exhibited a higher degree of friction than the co-existing expanded phase. The same sample was imaged after the infusion of H2S, and after rinsing with CHCl3 for 3 min, and in both cases molecularly flat surfaces were exhibited. In the latter case a molecular lattice of mica was imaged. It is concluded that the film was amorphous, and no CdS particles were formed in AA : ODA = 1 : 1.

The pure ODA trilayer film was very soft and amorphous. No CdS particles were imaged after reaction or rinsing. From our observations, no CdS particles can be formed in an ODA rich film.

4. Discussion

In order to control the growth of nanoparticles in the organic template, it is essential to elucidate the various factors which affect the template structure, the particle...
Fig. 5. Structural variations in the synthesis of CdS nanoparticles in a mixed LB trilayer film with an initial composition of AA : ODA = 4 : 1 by AFM: (a) a height image after LB deposition (image size is $1 \times 1 \, \mu m$); (b) a section analysis of the height image showing an average depth of the holes of 4.8 nm; (c) a height image after reaction (image size is $1 \times 1 \, \mu m$) showing expanded holes with an anisotropic shape; and (d) a height image after rinsing with CHCl$_3$ (image size is $1 \times 1 \, \mu m$) showing particles of an average diameter $\approx 1.2 \, nm$.

Fig. 6. Structure of a mixed LB trilayer film with an initial composition of AA : ODA = 1 : 1 by AFM: (a) a height image after LB deposition (image size is $0.75 \times 0.75 \, \mu m$) showing a molecularly smooth surface with a mean surface roughness $= 0.2 \, nm$; and (b) a fictional image of the same surface at 90° scan angle (image size is $2 \times 2 \, \mu m$) showing circular domains with a uniform diameter $= 200 \, nm$. 
growth mechanism, and the structural correlation among the amphiphile template, ionic precursor layer, and nanoparticle layer. AA has been the prototype amphiphile for the study of templated nanoparticle growth because of the long range order and stability of its LB films. Extensive and careful studies have been conducted on the AA system, which either measured the size of nanoparticles indirectly, or used AFM to image randomly distributed nanoparticles of wide size distribution [25–29]. Thus, it was surprising that indeed ordered nanoparticle arrays with uniform particle size can be formed inside the trilayer film of AA. This ordered pattern of CdS nanoparticles is most likely formed by a strained growth mechanism where uniform size and distribution of nanoparticles are possible.

The most common crystalline structure of CdS is hexagonal zinc oxide (wurtzite) structure with lattice constants $a = 0.4136$ nm, and $c = 0.6713$ nm [38]. The lattice constant of (0001) plane of CdS wurtzite structure, 0.4136 nm, is slightly less than the lattice constant measured on the cadmium arachidate (01) plane, 0.42 nm. The ratio of AA to Cd is not exactly known in the LB film. Some suggests a AA-Cd-AA linkage, while others favor a AA-Cd-OH linkage [39]. In addition, it is most likely that free or weakly associated Cd$^{2+}$ is also present in the LB film together with unknown amount of water. When H$_2$S is introduced to the cadmium arachidate LB film, Cd$^{2+}$ has to diffuse into each other to form CdS nuclei. A relatively immobile layer of Cd$^{2+}$ will favor a strict epitaxy growth which gives uniform size and long range order. A small misfit is capable of forming uniform domains of a relaxed overlayer with a regular distribution of misfit dislocations. Most researchers propose a disk-shape geometry due to the layered structure of the template. In order to make a simple estimation of the number of Cd in one CdS nanoparticle, we assume a monolayer of AA-Cd-OH was converted to a monolayer of CdS nanoparticles. Then the maximum estimation of the number of Cd in one CdS nanoparticle, we assume a monolayer of AA-Cd-OH was converted to a monolayer of CdS nanoparticles. Then the maximum estimation of the number of Cd in one CdS nanoparticle, we assume a monolayer of AA-Cd-OH was converted to a monolayer of CdS nanoparticles. Then the maximum estimation of the number of Cd in one CdS nanoparticle, we assume a monolayer of AA-Cd-OH was converted to a monolayer of CdS nanoparticles. Then the maximum estimation of the number of Cd in one CdS nanoparticle, we assume a monolayer of AA-Cd-OH was converted to a monolayer of CdS nanoparticles. 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Many experiments factors that are being further investigated in details in our laboratory. The pH of the subphase plays a role in the ordering of the template and the nanoparticle layer. Most of the previous studies were done at pH < 6.5, while pH = 7 was used in our study in order to ensure a complete deprotonation of the AA layer. The surface pressure during film transfer was maintained at a higher number of 30 mN/m than what has been used by other studies. The amount of water in the transferred film can also affect the quality of the film. In our study, the transferred film was allowed to dry for more than 5 h in a desiccator before reacting with H$_2$S so that water was fully evaporated. The absence of water in the film improves the degree of order and reduce the mobility of Cd$^{2+}$. It is worth noting that the limited mobility of Cd$^{2+}$ seems to favor a controlled synthesis of nanoparticles. The mobility is highly restricted in the solid-bound LB film as compared to the liquid-bound Langmuir monolayer.

The introduction of ODA into the AA matrix, even a small amount, greatly reduces the crystallinity of the LB film, and as a result, the long range order in the 2D arrangement of CdS nanoparticles was lost. The loss of order can be also a result of the increased mobility of Cd$^{2+}$. It has been long recognized that Cd$^{2+}$ stabilizes the AA film by bridging the carboxylic headgroups of adjacent deprotonated AA molecules. The ionic association of ODA with AA releases Cd$^{2+}$ and may weaken the lateral bonding within the layer. The mobility of Cd$^{2+}$ is increased with the introduction of ODA, and a random 3D nucleation and growth mechanism is more likely as a result. The destabilization of AA film and the disruption of epitaxy growth of PbS by ODA were also observed by Yang et al., on AA rich mixed monolayers at the air/water interface [25].

Secondly, the vertical size of CdS nanoparticles is reduced with increasing ratio of ODA in the mixed film. The particle sizes measured by AFM are listed in Table 3. The particle sizes measured by AFM are listed in Table 3. The particle sizes measured by AFM are listed in Table 3. The particle sizes measured by AFM are listed in Table 3. The particle sizes measured by AFM are listed in Table 3. The particle sizes measured by AFM are listed in Table 3. The particle sizes measured by AFM are listed in Table 3. The particle sizes measured by AFM are listed in Table 3. The particle sizes measured by AFM are listed in Table 3. The particle sizes measured by AFM are listed in Table 3.

<table>
<thead>
<tr>
<th>Template (AA:ODA)</th>
<th>Average particle size (diameter, nm)</th>
<th>Size distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>&lt; 4.2</td>
<td>Uniform</td>
</tr>
<tr>
<td>16:1</td>
<td>3.5</td>
<td>± 0.7 nm</td>
</tr>
<tr>
<td>4:1</td>
<td>1.25</td>
<td>± 0.3 nm</td>
</tr>
<tr>
<td>1:1</td>
<td>No particle</td>
<td>–</td>
</tr>
<tr>
<td>0:1</td>
<td>No particle</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 3: A summary of particle size distribution synthesized in the various templates by the AFM measurement.
mixed monolayers where a large domain of the minor component formed in the continuous phase of the major component. Our study seems to suggest an intimate mixing between AA and ODA where the percentage of ODA can have an influence on the average particle size.

Fig. 7a,d is a proposed mechanism of the templated growth as a function of ODA concentration. In the absence of ODA, the immobilization and uniform distribution of Cd\(^{2+}\) induces an ordered array of CdS nanoparticles, most likely in a 2D structure, as shown in Fig. 7a. In Fig. 7b, the introduction of a small amount of ODA, i.e. AA : ODA = 16 : 1, results in the formation of 3.5 nm thick particles but without the degree of long range order due to the lessened film crystallinity and increased Cd\(^{2+}\) mobility. As more ODA is incorporated as shown in Fig. 7c, ODA reduces the density of immobilized Cd\(^{2+}\) and acts as a barrier against the clustering of Cd to form CdS. A rough estimate of the dimension of a reactive site in the well mixed 4:1 layer is about 1–2 nm which matches the value measured by AFM. It appears that the particle size is limited by the distance between ODA molecules. As the percentage of ODA reaches 50%, the 1:1 association between AA and ODA diminishes the density of immobilized Cd\(^{2+}\), and as a result CdS particles can no longer form as shown in Fig. 7d.

5. Conclusions

AFM and XPS were used to study the growth of CdS nanoparticles in trilayer LB films of arachidic acid (AA) amphiphile in the absence and presence of a second amphiphile octadecylamine (ODA). In the absence of ODA, an ordered 2D pattern of CdS nanoparticles with uniform lateral diameter of less than 4.2 nm was imaged by AFM. The nanoparticles synthesized by the LB template were shown to be between 4 to 1 nm in vertical diameter and are expected to display interesting size quantization effect. Our results suggest a high degree of mixing in AA and ODA mixed monolayers. The ODA monolayers were unstable in the presence of Cl\(^{-}\) and AA, but stable in the presence of NO\(_3\)^{−}. The presence of ODA, even a small amount (AA : ODA = 16 : 1), destroys the crystalline structure of the AA film, and reduces the number of immobilized Cd\(^{2+}\) precursors. Randomly distributed particles with a broad size variation were found in the presence of ODA (AA : ODA = 16 : 1 and 4:1). The size of the particles decreases with increasing ratio of ODA from 3.5 nm (AA : ODA = 16 : 1) to 1.2 nm (AA : ODA = 4:1). No particles were found in an ODA rich film (AA : ODA = 1 : 1 and 0:1). The degree of order and the mobility of the precursor ions are critical in the controlled
synthesis of the nanoparticles. The size and distribution of nanoparticles synthesized using the current system are further characterized by optical methods.

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