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Nanoscale growth of CdS and PbS semiconductor within calix[4]arene Langmuir- Blodgett LB film for ion sensing application.

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Keywords: Calix[4]arene, Langmuir- Blodgett (LB), Cadmium sulphide (CdS), Lead sulphide (PbS), Nanoparticles, Ellipsometry, UV-visible spectroscopy (UV-Vis), Transmission Electron Microscopy (TEM).

Abstract. The characteristics of cadmium sulphide (CdS) and lead sulphide (PbS) nanoparticles, grown inside Langmuir-Blodgett (LB) multilayer films of 5,11,17,23-tetra-tert-butyl-25,27-dicarboxymethoxy-26,28-dihydroxycalix[4]arene (I), have been studied using ellipsometry, UV-visible spectroscopy, and transmission electron microscopy (TEM). Multilayer films were formed by transferring a floating Langmuir monolayer of I onto substrates using LB deposition and water subphase containing Pb^{2+} or Cd^{2+} ions. The nanoparticles were growth by exposing cadmium- or lead-containing multilayer films of I (20-80 monolayers thick) to hydrogen sulphide (H_2S) gas for 12 hours. By Gaussian fitting of the absorbance - energy spectra, the size of the clusters and their dispersion were found to be 1.43 ± 0.18 nm and 1.21 ± 0.05 nm for CdS and PbS respectively. This is the first time that such thick LB films of an amphiphilic compound possessing such high thermal stability (m.pt. $\sim 270^\circ C$) have been used as the vehicle for the formation of CdS and PbS semiconductor particles.

Introduction

The formation of II-VI semiconductor particles with nanoscale dimensions using the Langmuir-Blodgett (LB) film deposition technique was suggested first in the 1980s by Barraud *et al.* [1,2]. CdS clusters have been studied previously as hosts inside fatty acid and calixarene LB films although the LB films contained less than 20 monolayers [3,4]. Once ionized to form the carboxylate ion, complexation with mono- or divalent cations can easily occur in order to form metal carboxylate salts. Exposure of such multilayers to gases such as H_2S allows the metal ions to form the metal sulphides. This nucleation is followed by two-dimensional segregation which leads to the growth of nanoparticles exhibiting radii of typically $\sim 1-2$ nm [5].

Calixarenes are macrocyclic compounds in which phenolic units are linked via methylene bridging groups at their ortho positions. They have a relatively rigid aromatic backbone and the parent compounds can be synthesised with differing cavity sizes. Their main advantage, in the context of ion sensing and molecular recognition, is the ease with which the upper (aryl) and lower (phenolic) rims can be modified in a stereocontrolled and regiocontrolled manner [6], coupled with the wide range of cationic [7-11] and neutral [12-14] guests they have been found to bind.

In this work, relatively thick LB films (~ 80 layers) incorporating a 1,3-substituted calix[4]arene bearing terminal carboxylic acid groups have been used as the vehicle for the growth of Cadmium sulphide (CdS) and Lead sulphide (PbS) semiconductor nanoparticles.

Material and Method

Growth of CdS and PbS nanoparticles in LB films. A solution of I in chloroform was prepared with a concentration of 0.2 mg/ml. A NIMA Langmuir trough (Model 611) with the maximum area of 580 cm² with Nima554 software was employed in this study. The surface pressure- area (Π -A) isotherms of I were recorded during compression using two types of subphase. As a control experiment, the monolayer Π -A behavior on a pure water subphase (Elga PureLab water system, resistivity > 15 M Ω cm) was recorded. In order to obtain complexes of I-Cd²⁺ and I-Pb²⁺, the water subphase was doped with either cadmium chloride (220mg CdCl₂ in 1 litre of water) or lead acetate (390 mg Pb(CH₃COO)₂ in 1 litre of water). Next, ammonium hydroxide (NH₃[aq]) was added to the subphase in order to increase the pH to ~7.5 in order to promote Cd²⁺ or Pb²⁺ uptake [3].

Using a Hamilton microsyringe, the solution of I was dispensed dropwise onto the cleaned subphase of the Langmuir trough and 5-10 minutes were allowed for evaporation of the chloroform solvent. Y- type LB deposition was employed to prepare samples ranging in thickness from 20 – 80 monolayers. The deposition surface pressure used was 20 mN/m and the substrate speed was 12 mm min⁻¹ during both the upstroke and downstroke transfer. Figure 1 shows a set of five samples including an uncoated silicon substrate for the multilayer I-Cd²⁺ LB films. The gradually darkening film can clearly be seen as the multilayer film thickness increases. This is caused fundamentally by a modification to the reflectivity of the Si/SiO₂ surface rather than the optical absorption of the calixarene which negligibly small in the visible region of the spectrum (400 – 750 nm).

In order to stimulate the growth of the semiconductor nanoparticles, the multilayer samples of I-Cd²⁺ and I-Pb²⁺ LB films were exposed to H₂S gas for 12 hours in a sealed glass chamber (standard laboratory desiccator). Under prolonged exposure, the following reaction ensues [15]:



In this experiment, Cd²⁺ or Pb²⁺ (a divalent metal) and I is the calixarene which is used in this research. It is expected that the initial nucleation of CdS or PbS molecules leads to the growth of nanoparticulate CdS and PbS primarily via diffusion at the interface between hydrophilic headgroups of adjacent monolayers, although some secondary diffusion in a direction normal to the planes of the layers is likely also to occur to a much lesser extent.

Surface studies of I-Cd / Pb LB films. An M2000V (J. A. Woollam) instrument operating in the wavelength range of 370-1000 nm was used for ellipsometry measurements.

Optical studies on both untreated (I-Cd²⁺ and I-Pb²⁺) and H₂S gas-treated (I-CdS / PbS) LB films on silica plates were recorded using a Cary 50 UV-Vis spectrophotometer. Here, cleaned blank substrates were used as references. Two sets of measurements were taken; initially I-Cd²⁺ and I-Pb²⁺ LB films on Si and the same procedure applied later for I-CdS/ PbS LB films.

Several Transmission Electron Microscopy (TEM) pictures have been taken on H₂S – gas- treated LB films on a 2000 mesh TEM grid to observe the CdS clusters within the 20 layer LB films using Philips CM200 TEM.

Result and Discussion

Space-filling models or Corey, Pauling and Koltun modelling (CPK molecular modeling) were used to determine the dimensions of the calix[4]arene molecule and consequently the orientation of the floating monolayer of I at the air-water interface. CPK modeling of such an orientation yields a projected area per molecule ranging from 2.0 - 2.4 nm² due to the conformation flexibility of the calix[4]arene ring, while from the Π -A isotherm, the area per molecule of I is measured (by extrapolation of the solid phase (8 - 20 mN/m) of the monolayer to zero surface pressure) to be ~ 2.3 nm² in excellent agreement with the modeling. Thus, the orientation of the plane of the calixarene ring I is found to be parallel to the plane of the water surface.

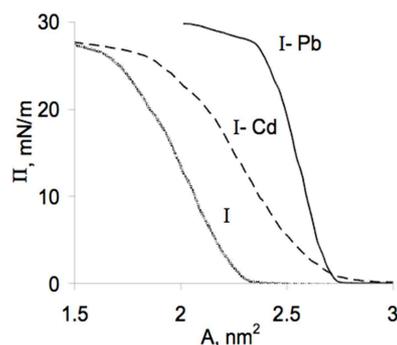


Figure 1. Π -A- isotherm of I with and without Cd salt/ Pb salt in solution of concentration 0.2 mg/ml.

Figure 1 shows that the area per molecule increases for I- Cd^{2+} and I- Pb^{2+} , confirming the presence of complexes of Cd ions and Pb ions with the calixarene. The limiting molecular area, A_{lim} , increases by $\sim 0.3 \text{ nm}^2$ for the Cd^{2+} ion and 0.4 nm^2 for the Pb^{2+} ion compared to the 2.3 nm^2 measured for a monolayer of I spread on a pure water subphase. The mechanism for this increase in size could be supplied by the terminal carboxymethoxy groups which are sufficiently flexible to flip out of the calixarene cavity in order to facilitate cation binding within the cavity. Alternatively, there is evidence in the literature for the binding of Cu^{2+} between adjacent calixarene molecules, a process that would also lead to an increase in the average area per calixarene molecule within the floating monolayer [16].

Surface assessment of the I- Cd^{2+} and I- Pb^{2+} LB films. The obtained values of thickness of I- Cd^{2+} and I- Pb^{2+} and I-CdS / PbS containing LB films are presented in Table 1 to show the dependence of the film thickness on the number of LB layers.

Table 1. Number of layers (N) and thickness (d) of I-CdS and I-PbS using ellipsometry

N	d (nm)		d (nm)	
	Before exposure (I-Cd)	After exposure (I-CdS)	Before exposure (I-PbS)	After exposure (I-PbS)
20	25.97	28.97	22.69	24.84
40	50.06	53.42	44.17	48.81
60	73.03	78.06	65.13	68.81
80	95.96	107.36	84.10	88.22

The above data are also plotted in Figure 2. All dependencies are linear with gradients of $1.16 \pm 0.01 \text{ nm/layer}$ and $1.02 \pm 0.02 \text{ nm/layer}$ for the I- Cd^{2+} and I- Pb^{2+} LB films respectively. These values are consistent with the thickness of I obtained from CPK modeling ($1.10 \pm 0.05 \text{ nm}$). After exposure to H_2S gas the film thickness increases slightly to $1.30 \pm 0.04 \text{ nm/layer}$ and $1.05 \pm 0.04 \text{ nm/layer}$ respectively, as a result of the formation of CdS and PbS nanoparticles within the multilayer film. This shows that the LB films obtained were uniform throughout the experiments with an average increase of 0.14 nm/layer and 0.03 nm/layer for I- CdS/ PbS respectively.

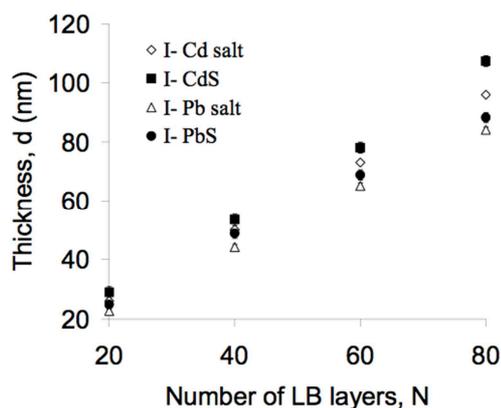


Figure 2. Graph of I-Cd / Pb and I-CdS / PbS

The increase in the average can be explained by the relatively uniform formation of nanoscale particles throughout the calixarene multilayer assembly although some slight disorder of the molecules might occur. If the formation of CdS or PbS were not uniform, then the plots of thickness versus number of deposited layers (Figure 3) would not be linear. These particles are most likely to grow in the hydrophilic region between adjacent calixarene monolayers, thus disrupting the order in that region and swelling the film. However, since very few Cd^{2+} (or Pb^{2+}) ions can be incorporated into the multilayer film (at best only two Cd^{2+} ions per calixarene molecule, but most likely less than this density), the thickness increase is local and results only in a small average increase in film thickness when measured over the areas probed by the ellipsometer (0.14 nm/layer and 0.03 nm/layer for I-CdS/ PbS respectively).

Optical absorption spectra of the I- Cd^{2+} and I- Pb^{2+} LB films.

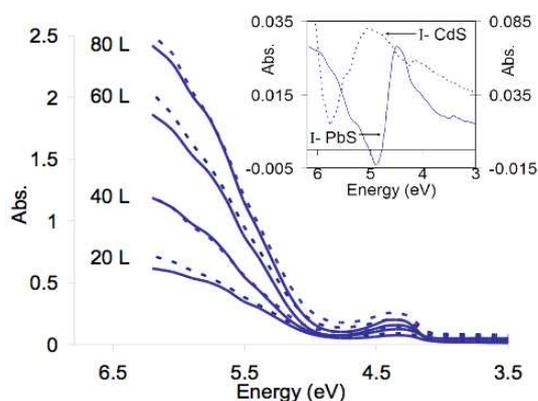


Figure 3. The absorption spectra for I-CdS multilayers where the solid lines represent before exposure and the dotted lines are after exposure to H_2S . Inset diagram shows the subtracted spectra (40L) of CdS/ PbS I-LB films.

Figure 3 shows the optical absorbance spectra for I- Cd^{2+} and I-CdS LB films on silica plates using UV-visible spectroscopy. Several features emerge due to the presence of CdS nanoparticles in the LB films. The subtracted spectra [3, 4], that is the difference in the spectra before and after exposure to H_2S gas, are shown in the inset of Figure 3, yield several clearly resolved absorption bands, which are related to electron transitions between levels of size-quantization [4]. Gaussian fitting of the spectra of I-PbS and I-CdS LB films was performed in order to derive the size distribution of CdS / PbS nanoparticles. The broadening of the spectral lines is caused by size dispersion of the nanoparticles as the value of ∂E is higher than kT (energy) at room temperature (0.025 eV) [17].

TEM imaging of the Mat 8 -CdS LB films. As an example, several TEM pictures have been taken to observe the CdS clusters within the 20 layer LB films. The nanoclusters can be seen as the dark spots in the images and due to the multilayers, some of the CdS nanoparticles tend to form different sizes of clusters as observed in figure 4. In this case, the number of cluster and cluster size increases during exposure due to the electron beam exposure stimulating the segregation process.[18]

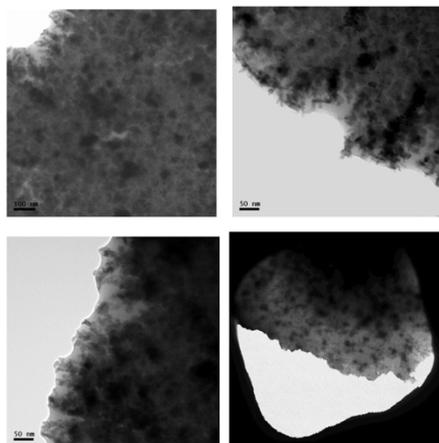


Figure 4. Several TEM images on different areas of 20 layers CdS LB film

Conclusion

CdS and PbS nanoparticles have been grown inside thick (80 layers) LB multilayer films of 5,11,17,23-tetra-tert-butyl-25,27-dicarboxymethoxy-26,28-dihydroxycalix[4]arene (I). The inclusion of Cd^{2+} and Pb^{2+} ions has been achieved by doping the water subphase with cadmium chloride and lead acetate, and subsequent exposure of deposited LB films to H_2S has led to the formation of CdS and PbS nanoparticles with average radii of 1.4 nm and 1.2 nm respectively. Calixarenes are particularly interesting candidates for thin film formation owing to their complexation properties for metal cations, making them potentially useful materials for ion sensing or ion trapping applications. In this work, the calixarene multilayer films were exploited as organic material for scaffolds to support an inorganic chemical reaction. In the future, we will capitalize upon our gained knowledge to utilize these multilayer films further as inorganic reaction media.

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