CdS/ZnS core-shell nanoparticles in arachidic acid LB films

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Abstract

Core-shell CdS/ZnS nanoparticles in arachidic acid film were prepared through a novel Langmuir–Blodgett (LB) approach. Post-deposition treatment of the precursor LB multilayers of cadmium arachidate with H_2S gas followed by intercalation of Zn^{2+} ions and further sulfidation result in the formation of CdS/ZnS nanoparticles in the LB film. The formation of these nanoparticles and resulting changes in layered structures were studied by FTIR and X-ray reflection measurements. The optical properties were studied using UV–vis absorption and photoluminescence spectroscopy. A red-shift in the absorption spectrum and enhancement of CdS excitonic emission together with reduction of surface states emission suggest that after the intercalation step, a thin layer of ZnS surrounds the CdS nanoparticles, thus forming a core–shell structure. Subsequent to the second sulfidation, a further red-shift in absorption suggests the formation of a thicker ZnS coating on CdS. Electron diffraction of CdS nanoparticles coated with thicker ZnS showed the diffraction patterns of only ZnS, as expected for core–shell structures.

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1. Introduction

II–VI semiconducting chalcogenide nanoparticles, especially sulfides and selenides have been investigated extensively, owing to their interesting opto-electronic properties [1]. The optical properties of these nanomaterials depend strongly on the size and the surface quality, which can be improved by passivating the bare surface with a suitable coating or shell material [2–5]. High luminescence efficiency and stability have been demonstrated for core–shell nanoparticles [6,7]. Core– shell nanocrystals have potential applications in light emitting devices based on quantum dots of CdSe/ZnS [8,9], nanowires of Si/CdS [10] and quantum rods of CdSe/CdS [11].

Several synthetic routes such as, chemical precipitation, solgel, microemulsion and inverse micelles have been used to grow core-shell chalcogenide nanoparticles with an emphasis on better control over size, shape and size distribution. The controlled growth of nanoparticles in supporting matrices such as, glasses, zeolites, polymers and fatty acids with tunable optical properties has been investigated. Langmuir–Blodgett (LB) technique has been used for preparing quantum size nanoparticles of sulfides, selenides and tellurides [12]. The presence of layered structure and molecular order in LB films is expected to assist in achieving better control over size, shape and size distribution of nanoparticles. Further, the possibility of depositing organic–inorganic nanocomposites with molecular level thickness control opens up the possibility of fabricating novel nanostructured devices. This approach has been explored to a limited extent for the sequential growth of chalcogenides of the same species (CdS–CdS) [13] as well as different species (PbS–CdS, ZnS–CdS, CdS–CdSe) [14–16].

In the present work, the idea of sequential growth of different species through sulfidation and intercalation of precursor cadmium arachidate (CdA) LB multilayers has been adapted to fabricate CdS/ZnS core–shell nanoparticles within arachidic acid LB matrix. The structure and optical properties of these nanoparticles have been investigated at different stages of growth, using UV–vis absorption spectroscopy, photoluminescence measurement and transmission electron microscopy.

2. Experimental details

CdA multilayers (25 monolayers, unless stated otherwise) have been deposited using KSV-3000 LB instrument. Chloroform (HPLC grade) solution of arachidic acid (Aldrich, 99%) of concentration 1 mg/ml was used to spread the monolayer on Millipore ultrafiltered water subphase (resistivity: 18.2 M Ω cm), containing CdCl₂ (5 × 10⁻⁴ M). The subphase pH was adjusted to \sim 6.4. Monolayers were transferred on CaF₂ substrates for FTIR and on quartz substrates for UV-vis, photoluminescence (PL) and X-ray reflection (XR) measurements. For transmission electron microscopy (TEM), 15 monolayers were transferred on carbon coated copper grids, which were stuck on a quartz substrate with the help of formvar solution. Multilayers were exposed to H₂S gas for the sulfidation process, which has been described earlier [17]. An aqueous solution of ZnCl₂ (5 \times 10⁻³ M) was used for the intercalation process. The precursor CdA multilayer was subjected to the following three processing steps. In step-1, the as deposited multilayer was exposed to H₂S gas for 2 h (first exposure). This was followed by step-2, in which the H₂S exposed multilayer was dipped into ZnCl₂ solution for 2 h (intercalation). After the intercalation process, the multilayers were washed in Millipore ultrafiltered water to remove excess ions. Finally, in step-3, the intercalated LB multilayer was again exposed to H_2S gas for 3 h (second exposure).

X-ray reflection measurements were carried out using Philips X'pert pro diffractometer with Cu target (K_{α} line). FTIR spectroscopy was carried out using PerkinElmer Spectrum one instrument. PerkinElmer lambda-950 spectrophotometer equipped with an integrating sphere was used for total transmittance and reflectance measurements in the UV–vis region. Jobin-Yvon HR460 monochromator and Kimmon He– Cd laser ($\lambda = 325$ nm) were used for PL measurements. Technai-G12 Cryo-TEM was used for transmission electron microscopy studies.

3. Results and discussion

The chemical changes in the LB multilayers at the completion of each of the above three steps were studied using FTIR spectroscopy and the results are shown in Fig. 1. The as deposited CdA LB multilayers exhibit the antisymmetric stretching vibrational bands of carboxylate (COO⁻) group at \sim 1545 cm⁻¹, which is usually observed for divalent fatty acid salts [18]. The doublet at 1464 and 1472 cm^{-1} is characteristic of CH₂ scissoring vibration in CdA multilayers having orthorhombic subcell packing with two molecules per unit cell [18]. Upon exposure to H_2S gas for 2 h (step-1), the peak at 1545 cm^{-1} nearly disappeared and a strong peak at $\sim 1700 \text{ cm}^{-1}$ corresponding to carbonyl stretching vibration of COOH appeared, while the CH2 scissoring doublet remained unchanged. The appearance of a strong carbonyl stretching vibration of COOH confirms the nearly complete conversion of CdA to arachidic acid (AA) and indirectly indicates the formation of CdS within AA multilayers. The IR spectra of thus formed CdS-AA multilayer after intercalation with Zn²⁺



Fig. 1. FTIR spectra at different stages of sulfidation and intercalation of precursor CdA multilayer: (a) as deposited, (b) after first H_2S exposure, (c) after intercalation and (d) after second H_2S exposure.

ions (step-2) showed the disappearance of COOH peak at $\sim 1700 \text{ cm}^{-1}$ and reappearance of the COO⁻ peak at \sim 1538 cm⁻¹. The doublet due to CH₂ scissoring vibrations was also converted into a singlet at $\sim 1464 \text{ cm}^{-1}$. The reappearance of COO⁻ peak indicates the reconversion of AA into ZnA in CdS-AA multilayers. This is further confirmed by the appearance of CH₂ scissoring band as a singlet, a characteristic feature of zinc arachidate (ZnA) LB multilayers, which are known to posses a subcell packing of one molecule per unit cell such as hexagonal [19]. Upon further H₂S exposure of 3 h (step-3), the FTIR spectra of these composite multilayers show a large reduction of the COO- peak intensity at $\sim 1538 \text{ cm}^{-1}$ and reappearance of the COOH peak at ${\sim}1700~\text{cm}^{-1},$ indicating the conversion of ZnA in the multilayers into AA and indirectly, the formation of ZnS. The formation of AA is accompanied by the appearance of the CH₂ scissoring doublet, as seen after step-1.

XR patterns (in the range of $4-20^{\circ}$) of the multilayers at the completion of each of the above three steps are shown in Fig. 2. The as deposited CdA multilayer shows well-defined Bragg peaks corresponding to (0 0 *l*) reflections indicating a highly correlated layered structure. The average bilayer period was found to be 55.2 Å, indicating that the CdA molecules are packed nearly perpendicular to the layer plane, as reported earlier [20]. After the first H₂S exposure (step-1), the multilayer showed a drastic reduction in the intensity of Bragg peaks but with no change in their positions. Though a significant reduction in layered structural order is evident, the remanent layered structures can be due to either the leftover CdA (as seen from FTIR spectrum) or AA or both. Fatty acid salts including



Fig. 2. XR patterns at different stages of sulfidation and intercalation of precursor CdA multilayer: (a) as deposited, (b) after first H_2S exposure, (c) after intercalation and (d) after second H_2S exposure.

AA are known to pack with different molecular orientations with respect to the layer planes [21]. In the present case, the remanent layered structures corresponding to the nearly perpendicular molecular packing is attributed to the influence of CdA molecules on the AA molecules, the major component of the organic matrix at this stage. Subsequent intercalation of the CdS–AA composite multilayers showed a completely different set of Bragg peaks corresponding to a bilayer period of 47.0 Å. This kind of layered structure is characteristic of ZnA multilayers, in which the molecules are packed at an angle of 32° with respect to layer normal [20], which corroborates well

with FTIR results at this stage of processing. During second sulfidation (step-3) a drastic reduction in the intensity of the Bragg peaks and a slight increase in the bilayer period were observed as reported earlier for ZnS formation from precursor ZnA multilayers [22]. The overall reduction in peak intensities during sulfidation and intercalation is attributed to reduction in layered structural order that takes place at different stages of processing.

Fig. 3(a) shows the UV-vis total transmittance (T_{total}) and total reflectance (R_{total}) spectra of CdA LB multilayers at the completion of each of the processing steps. The total mode of measurement was adopted in preference to the specular mode to account for the scattered components of transmittance and reflectance, which may be significant at shorter wavelengths. Fig. 3(b) shows the corresponding absorptance spectra $(1 - T_{total} - R_{total})$ and its derivative. After step-1, an enhanced absorption below 450 nm and a hump at around 400 nm are observed in the absorptance spectrum. The absorption onset $(\sim 450 \text{ nm})$ is clearly blue shifted with respect to the bulk absorption edge of CdS (515 nm). The hump at \sim 400 nm is attributed to the excitonic band of CdS [23]. The blue shift of the absorption onset and the presence of excitonic band are indicative of quantum confinement effects associated with the formation of CdS nanoparticles in the LB multilayers [17]. Assuming spherical shape and using effective mass approximation [23], the size of the CdS nanoparticles is estimated to be \sim 3 nm. After step-2, the absorptance spectrum taken after intercalation shows almost no change except for a slight increase in absorptance around 400 nm, together with a small red-shift (~5 nm). However, after step-3, the absorptance spectrum shows an overall increase, together with the hump, which is red-shifted to \sim 425 nm and a curvature around 300 nm. These features are more clearly seen in the corresponding derivative spectra. The overall increase in absorption and a curvature at ~300 nm after step-3 are attributed to the formation of ZnS. However, there is also a possibility of aggregation and growth of CdS (from the leftover



Fig. 3. UV-vis (a) total transmittance and reflectance spectra and (b) absorptance spectra at different stages of sulfidation and intercalation of precursor CdA multilayer: as deposited (—), after first H_2S exposure (– – –), after intercalation (· · ·) and after second H_2S exposure (– · –).

cadmium arachidate as seen from FTIR spectrum after step-1) during the second exposure (step-3), which could have a marginal contribution to the overall increase in absorptance and may also contribute partly to the observed red-shift after step-3. The observation that the positions of the CdS excitonic hump after step-2 and step-3 are red-shifted by \sim 5 and \sim 25 nm, respectively, is significant. Similar red shifts have been observed for a variety of core-shell nanoparticles including CdSe/CdS [6.24] and CdS/ZnS [25]. Peng et al. explained the red-shift of the absorption spectra of CdSe/CdS using molecular orbital model as well as particle-in-a-box model [6] and attributed the red-shift to partial leakage of carrier wave function to the shell region. In the case of CdS-AA composite multilayers, CdS nanoparticles after the first H₂S exposure are surrounded by the fatty acid matrix. Considering this matrix as a relatively high potential barrier, the electrons and holes may be confined within this potential well. After step-3, the formation of ZnS coating over the CdS nanoparticles decreases the potential barrier [26] leading to reduction in quantum confinement or extension of the electron wave function to the shell region. This results in the observed red-shift of absorption spectrum and suggests the formation of core-shell nanoparticles.

Photoluminescence spectra of CdA LB multilayers after the completion of each processing step are shown in Fig. 4. After the first H₂S exposure (step-1), LB multilayers exhibit a broad hump extending from 390 to 430 nm and a strong white luminescence centred at \sim 550 nm. The strong white luminescence is attributed to radiative recombination from the trap/ surface states arising from the imperfection of nanocrystals'



Fig. 4. PL spectra at different stages of sulfidation and intercalation of precursor CdA multilayer: after first H_2S exposure (—), after intercalation (– –) and after second H_2S exposure (· · ·). Curves (– –) and (· · ·) are shifted upwards by a factor of 2 for clarity.

surface [27,28]. The broad hump is attributed to the overlapping of quartz emission (\sim 390 nm) and the excitonic emission [29] of CdS nanocrystals. A pronounced suppression of emission from the CdS surface states and an improvement of the excitonic emission are seen after intercalation (step-2). It is reported that the surface states in chalcogenides could be due to anion and/or cation vacancies [30,31]. The pronounced suppression of surface states emission after the intercalation step indicates the presence of large amount of cation vacancies in the sulfide nanoparticles formed after the first H₂S exposure. However, it is observed that the surface states emission is not fully quenched after the intercalation step, which could be due to the presence of anion vacancies as well, in the CdS nanoparticles. It is inferred that during intercalation, in addition to the formation of ZnA within the multilayers, Zn^{2+} ions also occupy cation vacancies, thus forming ZnS on the surface of the CdS nanocrystals, leading to the reduction of surface states emission. The enhancement of the excitonic emission of CdS nanoparticles, which is now centred at \sim 410 nm and is clearly separated from quartz peak is also attributed to the formation of thin ZnS surface layer on the CdS nanoparticles. After the second H₂S exposure (step-3), the surface states emission is red-shifted to \sim 570 nm without significant reduction in intensity. Significantly, the excitonic emission of CdS nanoparticles disappears at this stage after the formation of more ZnS (after step-3), as only the peak due to quartz luminescence at \sim 390 nm is seen. The coating of the core material with higher band gap material is expected to increase the excitonic emission by reducing the surface defects [2,24]. Such an enhancement of the excitonic emission from CdS was observed only after the intercalation step but not after the second H₂S exposure. This observation suggests the formation of a thicker ZnS layer around CdS in step-3. The thickness of the shell is believed to be crucial [5-7] for the enhancement of the luminescence efficiency and beyond a certain shell thickness (typically 1-2 monolayer) [5,7], the quantum efficiency reduces due to structural defects present in the shell material.

Electron diffraction patterns of CdA LB multilayers after step-1 and step-3 are shown in Fig. 5. The pattern consists of broad diffused rings along with a few sharp rings. The diffused rings are attributed to the nanocrystalline nature of sulfide particles. The broad rings may correspond to the overlapping rings of closely spaced 'd' values. In such a case, the outer and the inner diameters of the rings were measured and the ranges of 'd' values corresponding to these extreme diameters were estimated. The electron diffraction patterns of CdS nanoparticles after step-1 are shown in Fig. 5(a). The first broad diffused ring corresponds to 'd' values extending from 3.58 Å to 3.12 Å. The next three diffraction rings are relatively sharp and correspond to 'd' values of 2.06 Å, 1.90 Å and 1.76 Å respectively. The measured 'd' values are compared with JCPDS data file 06-0314 for hexagonal (wurtzite) phase of CdS. All the diffraction rings corresponding to the above measured 'd' values are indexed and shown in Fig. 5(a). The first broad diffuse ring (d = 3.58 - 3.12 Å) corresponds to the overlap of (100), (002), (101) planes. The next three 'd' values





Fig. 5. Electron diffraction patterns at different stages of sulfidation and intercalation of precursor CdA multilayer: (a) after first H_2S exposure and (b) after second H_2S exposure.

(d = 2.06 Å, 1.90 Å and 1.76 Å) are indexed to $(1 \ 1 \ 0), (1 \ 0 \ 3)$ and (112) planes, respectively. These results clearly indicate that CdS nanocrystals formed after first H₂S exposure possess hexagonal wurtzite structure. After step-3, the electron diffraction patterns of CdS/ZnS show very different features. The first weak broad diffused ring corresponds to 'd' values extending from 3.31 Å to 2.99 Å. The next broad and intense diffraction ring corresponds to 'd' values of 2.54-2.41 Å. The next two diffraction rings on a diffused background correspond to 'd' values of 2.15 Å and 1.99 Å, respectively. These measured 'd' values are compared with the JCPDS data file 72-0162 for the wurtzite phase of ZnS (10H). The first weak diffused ring is attributed to the overlap of (100), (101), (1 0 2), (1 0 3), (0 0 10), (1 0 4) and (1 0 5) reflections, which have closely spaced 'd' values of 3.31 Å, 3.29 Å, 3.23 Å, 3.15 Å, 3.12 Å, 3.04 Å and 2.92 Å, respectively. However, as the 'd' values corresponding to the first intense broad ring of CdS also fall partly in the same range, there is a possibility of overlap of diffraction rings of CdS and ZnS, in this region of diffraction pattern. The next broad and intense ring (d = 2.54-2.41 Å) is attributed to overlap of $(1 \ 0 \ 8)$ and $(1 \ 0 \ 9)$ reflections of ZnS. Any contribution from CdS in this range is ruled out since its weak (1 0 2) reflection was not seen earlier (Fig. 5(a)). The next two rings with a diffuse background are indexed to (1011) and (1012) reflections of ZnS, respectively. It is noted that the sharp CdS rings with 'd' values corresponding to 2.06 Å, 1.90 Å and 1.76 Å, which were seen in Fig. 5(a) do not appear in this case. It is inferred from above that after the second H₂S exposure (step-3), the sample does not show any diffraction ring corresponding to hexagonal CdS. It is interesting to note that all the diffraction rings seen in this case correspond to wurtzite ZnS (10H) structure and not the usual hexagonal wurtzite ZnS (2H) structure. The presence of diffraction rings corresponding to only ZnS and complete absence of diffraction rings due to CdS, is in agreement with earlier reports on core–shell structures that as the shell thickness increases, the diffraction pattern shifts from core to that of the shell material [4,6,32]. Thus, the TEM results suggest that CdS particles may be covered with ZnS shell after the second H_2S exposure.

4. Conclusions

CdS/ZnS core-shell nanoparticles in arachidic acid LB multilayers have been fabricated using a sequential sulfidation and intercalation methodology. A small red-shift in the absorption spectrum and enhancement of CdS excitonic emission together with reduction of surface states emission suggest that after the intercalation step, a thin layer of ZnS surrounds the CdS nanoparticles, thus forming a core-shell structure. Subsequent to the second sulfidation, a further red-shift in absorption suggests the formation of a thicker ZnS coating on CdS. Electron diffraction results further support the core-shell nature of the nanoparticles.

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