

Occurrence of single-electron phenomenon in CdS nanoclusters in Langmuir–Blodgett films of *n*-octadecyl succinic acid

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Abstract. Cadmium complex of *n*-octadecyl succinic acid (ODSA) in Langmuir films at air/water interface has been studied using surface pressure–molecular area (π – A) and surface potential–molecular area (ΔV – A) isotherms. The metal complex formed, transferred as LB film onto solid substrates, was analysed using FT-IR and was subjected to sulphidation reaction. Antisymmetric and symmetric carboxylate stretching vibrations have been used to determine the nature of the ODSA/cation complexes. CdS formed after sulphidation of the cadmium complex (ODSACd) showed possible single-electron phenomenon indicating the nanosized nature of clusters formed. Atomic Force Microscopy (AFM) measurements carried out confirmed the size of these CdS clusters.

Keywords. Single-electron phenomenon; CdS nanoclusters; Langmuir–Blodgett films; *n*-octadecyl succinic acid.

1. Introduction

Design and construction of nanoscopic structures from transition metal containing building blocks have become topics of increasing interest in recent years^{1,2}. Much effort is being devoted to gaining more insight into the molecular order of such systems using properties of Langmuir films and Langmuir–Blodgett (LB) films. It has been demonstrated that long-chain amphiphiles can be utilized as substrates for nucleation and growth of inorganic and organic crystals and that geometrical and stereochemical matching of the monolayers and crystal lattices can result in epitaxial growth^{3–5}. Investigation into epitaxial crystal growth under monolayers can be expected to produce technologically important devices. Ordered organic LB films have been used as templates for the fabrication of ordered semiconductor nanoparticles^{6–13}. Increasing interest in quantum size II–VI semiconductor systems has been stimulated by their possible applications in electronics. For instance, single-electron tunneling through CdS nanoparticles in fatty acid LB film at room temperature has been recently demonstrated¹⁴.

In this work, the interactions of Cd²⁺ ions in the subphase with monolayers of *n*-octadecyl succinic acid (ODSA) formed at the air/solution interface has been studied for various concentrations of Cd²⁺ ions in the subphase and the complex formed is characterized using surface pressure–molecular area (π – A) and surface potential–

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molecular area ($\Delta V-A$) isotherms. LB film of Cd complexes of ODSA is characterized using FT-IR spectroscopy. CdS particles in the LB film have been formed by reacting the film with Na_2S . Tunneling current has been measured and the sizes of the CdS particles confirmed by Atomic Force Microscopy (AFM).

2. Experimental

n-Octadecyl succinic acid (*n*-ODSA) was obtained from Sigma Chemicals, USA and was 99% pure. Monolayers of ODSA was formed by spreading millimolar solutions of compounds in chloroform (HPLC grade) on the surface of water (Millipore milli-Q system). The nominal *pH* of the subphase was 5.5 (using NaHCO_3). A NIMA 611 rectangular trough with a Wilhelmy balance and thermostat attached was used for the formation of the monolayer, measurement of $\pi-A$ and $\Delta V-A$ isotherms and the LB film transfer.

The films were transferred at $\pi = 20$ mN/m on the substrates made hydrophobic by transferring one layer of ferric hydroxy stearate and the transfer was of the Y-type with a ratio of 0.95. FT-IR spectra of LB films transferred on silicon substrate recorded using Perkin-Elmer Spectrum RX1 system confirmed the formation of complex.

The formation of CdS in the LB films was achieved by placing the slides in a closed jar containing Na_2S in isopropanol for 3 h. Single-electron tunneling current was measured by a commercial STM (Nanoscope II; Digital Instruments, Santa Barbara, CA) with 0.5 μm scan head. The junctions were formed using scanning tunneling microscope (STM) which allows localisation of particle position on the graphite substrate¹². *I-V* characteristics were measured by using graphite as first electrode and STM tip as the second one. For atomic force microscopy, freshly cleaved mica were used as substrates to transfer monolayers. The samples were imaged with a Nanoscope II atomic force microscope (Digital Instruments, Santa Barbara, CA). Silicon nitride tips (Digital Instruments) were used in contact mode. Line scan frequencies were between 2 and 3 Hz. The images were unfiltered except for slope removal along each scan line to level the image. For both STM and AFM, one layer of the cadmium complex was transferred.

3. Results and discussion

Figure 1a shows the $\pi-A$ isotherms of ODSA on subphase containing water and figure 1b shows those on subphase containing varying concentrations of cadmium ions. From the isotherms, it is clearly seen that ODSA shows a fairly 'liquid expanded' state in water and shows large contraction in area on subphase containing cadmium ions. Contraction in area has been generally reported for metal complexes of fatty acid monolayers¹⁵. It can be seen that even with increasing concentration of cadmium ions in the subphase, the $\pi-A$ isotherms are quite similar to one another. Further it is known that increase in concentration of cadmium ions in the subphase leads to an earlier collapse of the film. The $\Delta V-A$ isotherms in figure 1c reflect the changes in the polar region due to interactions of the Cd^{2+} ions with the carboxylate group. The drastic change in the area at $\pi = 20$ mN/m for the pure ODSA to that on cadmium subphase is clearly indicative of the complexation reaction. Such large contractions in area have been reported for nickel complexes^{16,17}. The plateau seen here is indicative of the change in the orientation of the headgroups and subsequent complexation with Cd^{2+} . As the concentration increases, the double layer potential is compensated for faster leading to lowering of the plateau seen in

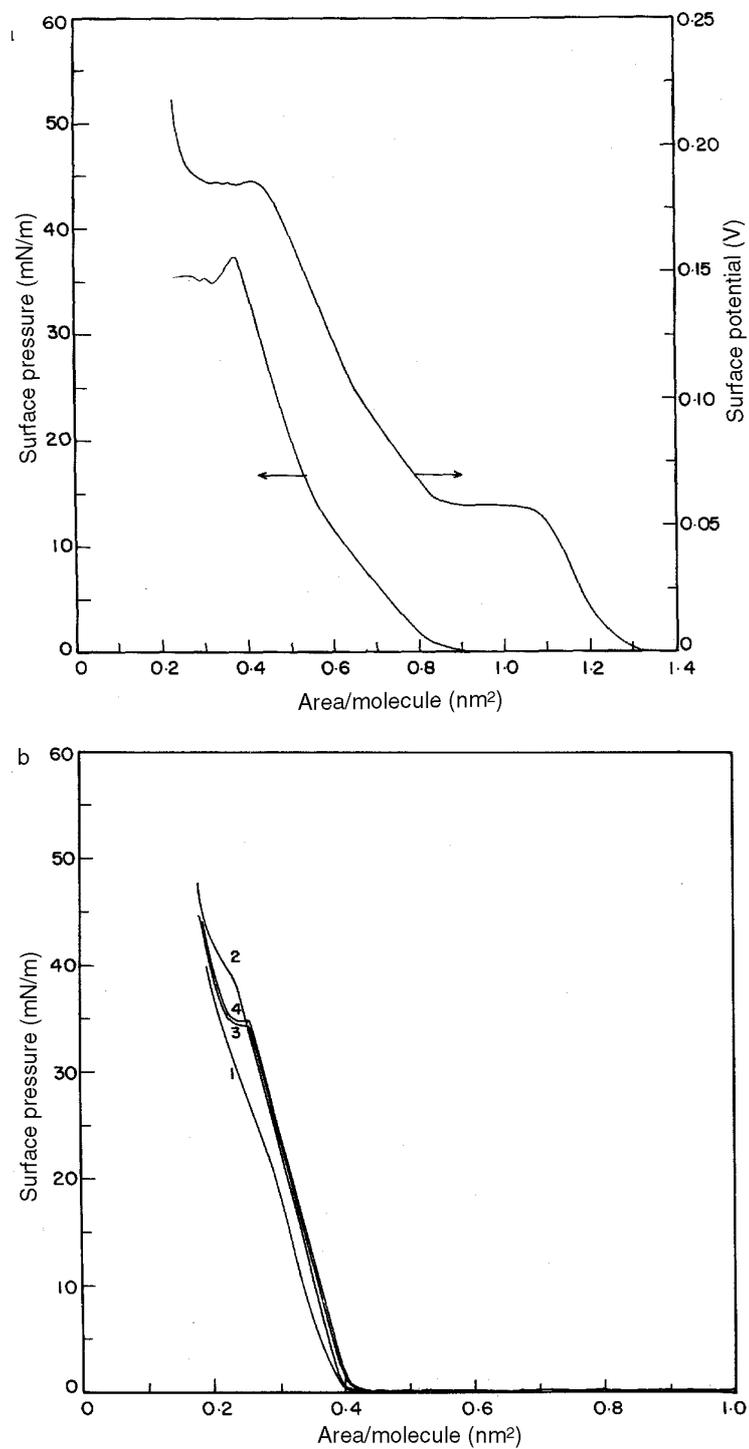


Figure 1. (a) and (b) (Caption on next page.)

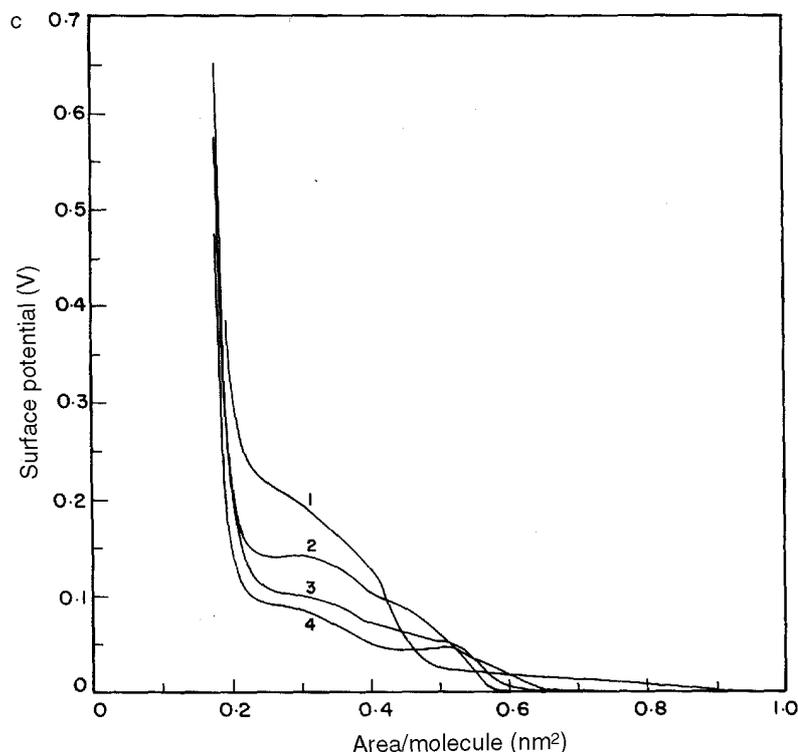


Figure 1. (a) π - A and ΔV - A isotherm of ODSA (b) π - A isotherm of ODSA on subphase containing cadmium ions of concentration ($1-10^{-6}$ M, $2-10^{-5}$ M, $3-10^{-4}$ M, $4-10^{-3}$ M). (c) ΔV - A isotherm of ODSA on subphase containing cadmium ions of concentration ($1-10^{-6}$ M, $2-10^{-5}$ M, $3-10^{-4}$ M, $4-10^{-3}$ M).

the surface potential curves. The rise in the ΔV - A curves even before a phase change in the π - A isotherms may indicate reorientation of the head groups due to complexation. Since ΔV is more sensitive than π , this is detected earlier in the ΔV - A curves.

The stability of the complex with time was checked at different pH values. The stability is expressed by the ratio $R_s = A_t/A_0$ at constant surface pressure with A_t and A_0 being the area/molecule at the time t and time = 0 respectively. Significant deviations of R_s from unity is taken as a measure of the stability parameter. In the case of the cadmium complex of ODSA, the ratio R_s lies between 0.85 and 1 for pH values from 2 to 7. An optimum concentration of 0.5 mM of $CdCl_2$ in the subphase ($pH = 5.5$) was chosen for LB transfer experiments. These films were transferred at 20 mN/m.

FT-IR spectra (figures 2a and b) confirm the complexation of cadmium ions with the carboxylate groups. The bands corresponding to the asymmetric and symmetric methylene-stretching vibrations are typical of a highly ordered state. The principal IR band assignments are listed in table 1.

The separation (Δ) between the antisymmetric and symmetric carboxylate vibrations can be used to assign the type of coordination of the complex formed¹⁸. The Δ value of ODSACd system is around 120 cm^{-1} which could be attributed to a chelating bidentate coordination. Sulphidations of the LB films were carried out by reacting with Na_2S (in

isopropanol) for 3 h. Size quantization effect exhibited by these CdS particles has already been demonstrated¹⁹ and control of such quantum-sized semiconductor particles is a recent area of interest owing to their possible interesting applications in electronics.

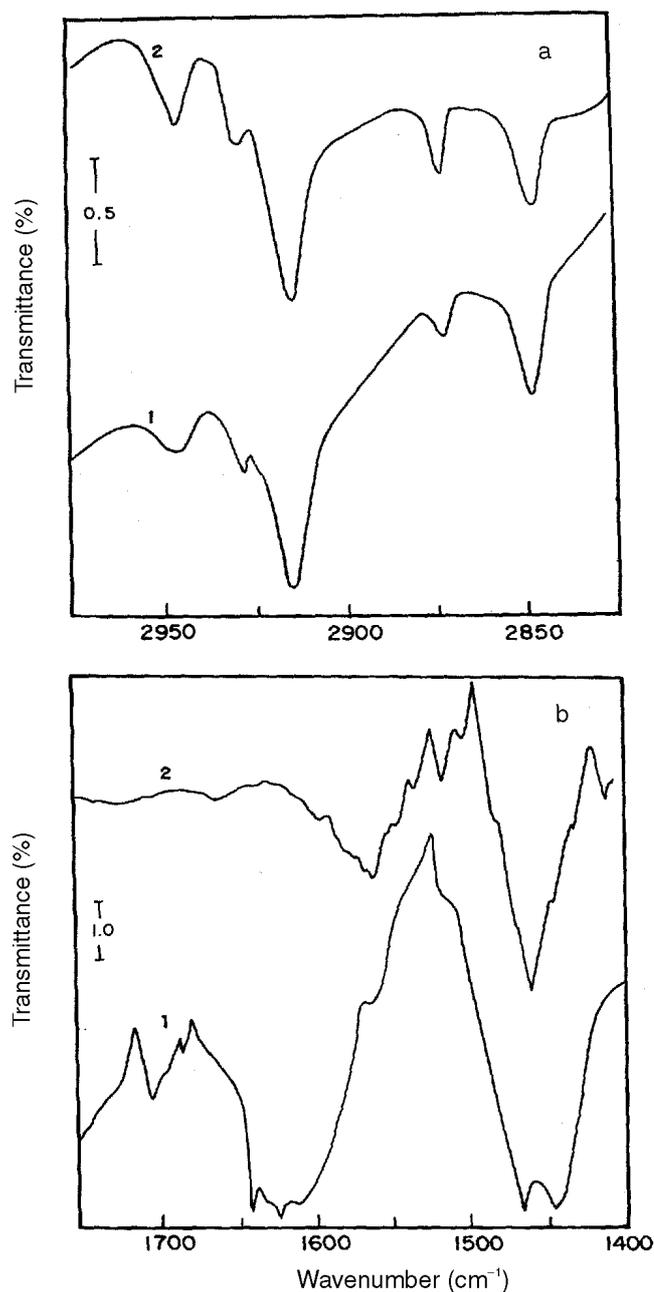
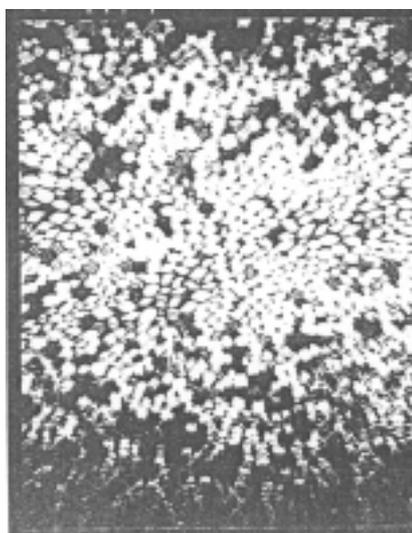


Figure 2. (a) and (b) FT-IR spectra of LB films transferred at 20 mN/m. 1 – ODSA, 2 – ODSACd.

Table 1. Principal IR band assignments.

Transition moments (cm ⁻¹)	<i>n</i> -ODSA	ODSACd
$\nu^{\text{as}}\text{CH}_3$	2947	2944
$\nu^{\text{s}}\text{CH}_2$	2917	2916
$\nu^{\text{as}}\text{CH}_2$	2848	2848
$\nu\text{C=O}$	1705	
$\nu^{\text{as}}\text{COO}$		1530
$\nu^{\text{s}}\text{COO}$		1409
δCH_2	1465, 1444	1467

**Figure 3.** AFM top view images (75 × 75 nm) for LB film OF CdS particles. The *z* scale in the images is 1.4 nm (vertical scale, black to white contrast).

In order to study their size and morphology, AFM was used to investigate LB films. Figure 3 shows uniform-sized CdS clusters formed from a single layer of ODSACd film. Such nanosized clusters are expected to show single-electron phenomenon²⁰. The *I*–*V* characteristics measured revealed possible single-electron phenomena in these clusters at room temperature. Such single-electron phenomena take place when a small conductive particle is placed between 2 electrodes and is separated from them by two tunneling gaps²¹. Also such single-electron phenomena can be observed when the electrostatic energy exceeds the thermal excitation value²². In order to observe it at room temperature, it is necessary to decrease the capacitance values and thus the size of the particles. In this regard, cadmium sulphide is a wide band semiconductor (2.42 eV). Figure 4 shows the typical *I*–*V* characteristics with step-like dependence of current upon bias voltage and a negative resistance region. The current jumps that occur in correspondence with constant bias voltage increments seem to indicate possible single-electron phenomenon. AFM

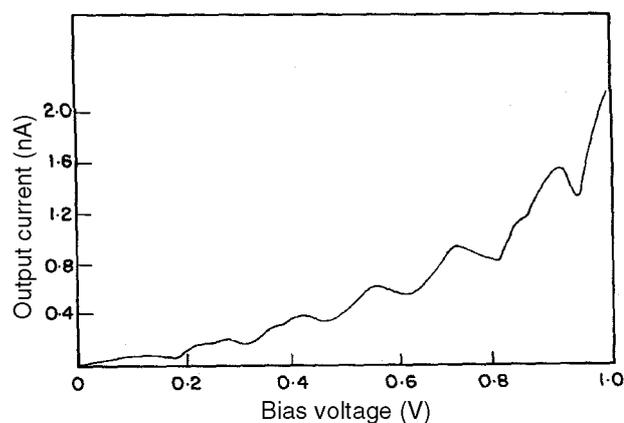


Figure 4. I - V characteristics observed in LB films of nanoclusters of CdS.

measurement carried out shows (figure 3) the uniform CdS particles of size ranging between 2 and 4 nm.

4. Conclusion

In conclusion, the results show that uniform sized particles of CdS can be fabricated using LB films as templates. Single-electron tunneling phenomena observed in these semiconductor particles may form the basis for understanding the processes involved in single-electron transistors.

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