Control of Size of CdS Formed in Organized Molecular Assembly Films by Molecular Structure and Film Orderliness

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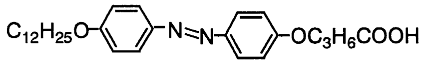
The size of quantized CdS formed in Langmuir-Blodgett (LB) films was precisely controlled by the occupied molecular area of amphiphile and the repetition number of the sulfidation-intercalation cycle, because the concentration of Cd^{2+} ions introduced in the hydrophilic interlayers was determined by these two factors. The size of CdS formed in the bilayer film was fairly larger than that in corresponding LB film, showing the influence of the orderliness of the matrix film on the formation of CdS in the hydrophilic interlayers.

Synthesis of nanosized semiconductors has been extensively studied for their unusual physical and chemical properties and potential applications.[1,2] In particular, a growing attention has been recently devoted to the synthesis of nanosized semiconductors in a well ordered manner using organized molecular assemblies (OMA) such as Langmuir-Blodgett (LB) and bilayer films.[3-8] Since the precursor metal ions are concentrated and arranged in the hydrophilic interlayers of metal ion-containing OMA films, the layers can be used as a unique reaction field for the synthesis of nanosized semiconductor in a two-dimensionally controlled manner. If the amount and the spacial arrangement of the metal ions in the interlayers are well regulated, the OMA-aided synthesis will have wide application for controlled synthesis of nanosized semiconductors. We have already reported that the amount and the size of quantized metal sulfides could be increased stepwisely in the hydrophilic interlayers of a stearic acid LB film by repeating processes of intercalation of metal ions and sulfidation.[5,6] In this paper, we report that the size and the energy gap of CdS in LB films can be controlled not only by the repetition of intercalation-sulfidation process but also by the occupied molecular area of LB-constructing amphiphiles. Also reported is the effect of orderliness of OMA films by comparing the energy gap of CdS formed in LB and bilayer films of a phosphate amphiphile.

Amphiphiles **1** ~**4**, which vary in the occupied molecular area (A_{mol}) from 0.21 to 0.41 nm^2 as shown in Figure 1,[9] were used as LB-constructing molecules. Cd-salt monolayers were prepared by spreading benzene solutions (1 $g \cdot dm^{-3}$) of these amphiphiles on the surface of aqueous $CdCl_2$ (3×10^{-4} $mol \cdot dm^{-3}$, pH 5.8) at 20 °C. Vertical-mode LB deposition at 10 $mm \cdot min^{-1}$ was performed at a surface pressure of 25 $mN \cdot m^{-1}$ using a film balance and a lifter (USI system FSD 110A). Y-type LB films were built up successfully with a transfer ratio of unity on well-cleaned borosilicate glass, quartz and CaF_2 substrates. Bilayer films of Cd-salt of **4**[10] were also prepared on these substrates by casting its chloroform solution. Synthesis of CdS in these films was carried out by the same manner as that previously reported.[6] The Cd-salt films were exposed to a flow of H_2S gas (105 $cm^3 \cdot min^{-1}$) for 1 h at room temperature, which is referred to as the sulfidation (**S**) process. The sulfidized films were then immersed in an aqueous solution of $CdCl_2$ (1×10^{-2} $mol \cdot dm^{-3}$, pH 5.8) for 5 h followed by rinsing with pure water for 5 min. The immersion treatment is referred to as intercalation (**I**) process. Thereafter, the films were subjected alternately to the **S** and **I** processes. In this paper, the samples after the **I** and **S** processes are denoted as **I**(n) and **S**(n) films, respectively, where n is the number of specified processes undergone by the films.

Chemistry of production and growth of CdS in the OMA films was followed by IR (Perkin-Elmer 1650 FT-IR) and UV-Vis (Shimadzu UV-3100) spectroscopies. We already reported for LB film of **1** that the CO stretching IR band of the ionic carboxylate group (COO^-) at 1548 cm^{-1} was totally replaced with that of the acidic one (COOH) at 1702 cm^{-1} during the **S** process. The same behavior was observed for the LB films of **2** and **3** having a carboxylate head group. In the case of Cd-salt films of **4**, observed during the **S** process was a replacement of PO stretching IR band[11] of the ionic phosphate group (POO^-) around 1185 cm^{-1} with that of acidic one (POOH) around 1220 cm^{-1}. Concomitantly, the production of quantized CdS in these films was confirmed by the appearance of an optical absorption due to CdS, the onset (λ_{os})[12] of which was blue-shifted from that of bulk CdS (520 nm).[13] The subsequent **I** process on the sulfidized films caused the transformation of IR bands of carboxylic and phosphoric acids back to those of respective ionic forms with the UV-Vis absorption and the CH stretching IR bands remaining unchanged. During further repetition of the **S**-**I** cycle, the stoichiometric and reversible transformation between the acidic and ionic forms was observed in IR measurement accompanied with an increase in UV-Vis absorbance and a red-shift of λ_{os}. The increasing absorbance and the red-shifting λ_{os} provide direct evidence for increases in the concentration and the size of quantized CdS,

$C_{17}H_{35}COOH$ **1** $C_8F_{17}C_{10}H_{20}COOH$ **2**



3

$(C_{16}H_{33}O)_2POOH$ **4**

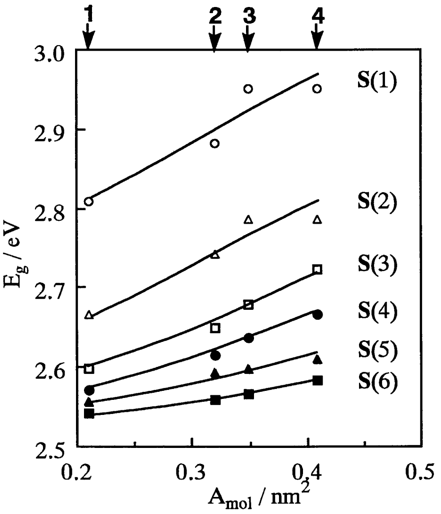


Figure 1. Dependence of the energy gap (E_g) of CdS formed in LB films of **1**~**4** on the occupied molecular area (A_{mol}).

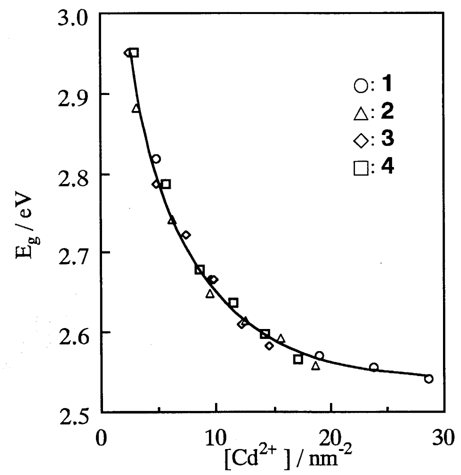


Figure 2. Dependence of E_g of CdS formed in LB films of **1**~**4** on the number of Cd^{2+} ions per unit area ([Cd^{2+}]).

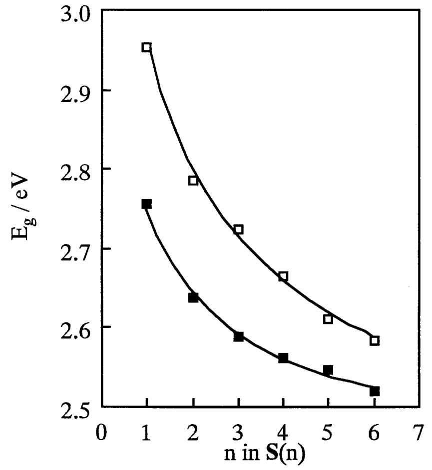


Figure 3. E_g of CdS formed in **S**(n) films of **4**; □: **4**-LB, ■: **4**-bilayer.

respectively. It has been revealed that amphiphiles having not only the COOH head group but POOH one can be used for the OMA-aided synthesis of CdS if they form stable multilayer films.

Optical energy gap (E_g) of CdS formed in LB films was calculated from λ_{os} value, and its dependence on the A_{mol} of amphiphiles and the number of **S**-**I** cycle, n in **S**(n), are depicted in Figure 1. In each LB matrix of **1**, **2**, **3** or **4**, E_g value decreased with an increase in the repetition number of **S**-**I** cycle, and those after the six cycle were still larger than that of bulk CdS. These results are consistent with our previous finding that the size of quantized CdS increases with repeating **S**-**I** cycle. Figure 1 also shows that at a given n the E_g value increases thus the size of CdS decreases with an increase in A_{mol}. Since the concentration (per unit area) of Cd^{2+} ions in the hydrophilic interlayers naturally decreases with an increase in A_{mol}, it is suggested that the size of CdS decreases as the concentration of Cd^{2+} ions decreases. Define the total number of Cd^{2+} ions per area introduced in the hydrophilic layers, [Cd^{2+}], as n/A_{mol}; the definition is based on the stoichiometric intercalation of Cd^{2+} ions at each **I** step, and as stated above this is true under the present experimental conditions. As shown in Figure 2, the relation between E_g and [Cd^{2+}] is expressed by one correlation curve irrespective to the kind of amphiphiles and the repetition number of the **S**-**I** cycle, clearly showing that the size of CdS is almost exclusively controlled by the concentration of Cd^{2+} ions introduced in the hydrophilic interlayers of LB films. Grieser et al[7] reported that there was no relationship between [Cd^{2+}] and the size of CdS formed in LB films. Their conclusion, however, seemed to be premature because they compared λ_{os} values of only two **S**(1) films of different amphiphiles and different LB deposition types.

Figure 3 compares the dependence of the E_g value of CdS in LB and bilayer films of **4** on the repetition number of the **S**-**I** cycle. At each stage, the E_g value of the bilayer system is fairly smaller than that of the LB system, in other words, CdS formed in the bilayer system is larger in size than that formed in the LB film. X-Ray diffraction analysis (Rigaku 2034) showed that both original films gave distinct 00ℓ Bragg peaks typical for the layered structure but the peaks intensity of the bilayer film was weaker than that of the LB film. In addition, 00ℓ Bragg peaks could be observed even at n=4 in both **S**(n) and **I**(n) films in the LB system, while they disappeared at n=3 in the bilayer system. These XRD results imply that the LB film has more ordered stacking than the bilayer film. Therefore it is concluded that the orderliness of the film also affects the size of the formed CdS. It might be expected that the mobility of Cd^{2+} ions and/or the formed CdS in the less ordered bilayer film is higher than that in the well orderd LB film and the higher mobility makes easier the growth of CdS.

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