Production and Growth of Size-quantized Cadmium Sulphide in the Hydrophilic Interlayer of Langmuir–Blodgett Films

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Exposure of Langmuir–Blodgett (LB) films of cadmium stearate to H_2S gas yielded size-quantized CdS in the hydrophilic interlayers of the stearic acid LB film, and the CdS formed therein could be grown by repetition of the immersion in aqueous $CdCl_2$ and exposure to H_2S gas without destroying the layered structure.

Currently quantum size effects observed in semiconductors having reduced dimensions have attracted much attention.[1] The preparation of size-quantized semiconductor particles in a variety of media, such as solutions,[2] polymers[3] and reverse micelle microemulsions has been reported.[4] Recently, Zylberajch *et al.*[5] and Smotkin *et al.*[6] independently reported that size-quantized CdS, which probably has two-dimensional features, could be formed in LB films of fatty acids by exposure of LB films of the Cd salt of the corresponding fatty acids to H_2S gas. We report here the growth of CdS produced in the hydrophilic interlayers of LB films by repeating the immersion in an aqueous solution of $CdCl_2$ followed by exposure to H_2S gas, as schematically illustrated in Fig. 1.

A benzene solution (1 mg ml^{-1}) of stearic acid was spread at 20 °C on the surface of 3×10^{-4} mol dm^{-3} aqueous $CdCl_2$ which was adjusted to pH 5.8 by adding $NaHCO_3$, and a monolayer of cadmium stearate was formed after the reaction between Cd^{2+} and stearic acid. Monolayers of cadmium stearate were deposited on well cleaned CaF_2 or borosilicate glass substrates at a surface pressure of 30 mN m^{-1} by using a film balance (Sanesu Keisoku Co., Ltd., FSD-20). CaF_2 substrates carrying 20 monolayers on each side were used for IR and UV–VIS measurements, while glass substrates carrying 15 monolayers on each side were used for X-ray diffraction (XRD) measurement. The sulphidation of films (step *A* in Fig. 1) was carried out by exposure to a flow of H_2S gas (25 ml min^{-1}) for 15 min and the intercalation of Cd ions (step *B* in Fig. 1) was performed by immersing the films in aqueous $CdCl_2$ (3×10^{-3} mol dm^{-3}, pH 5.8) for 3 h.

Changes in the carboxylate groups and the growth of CdS during the sulphidation and the intercalation processes were followed by IR spectroscopy (Fig. 2) on a Nihon Bunko

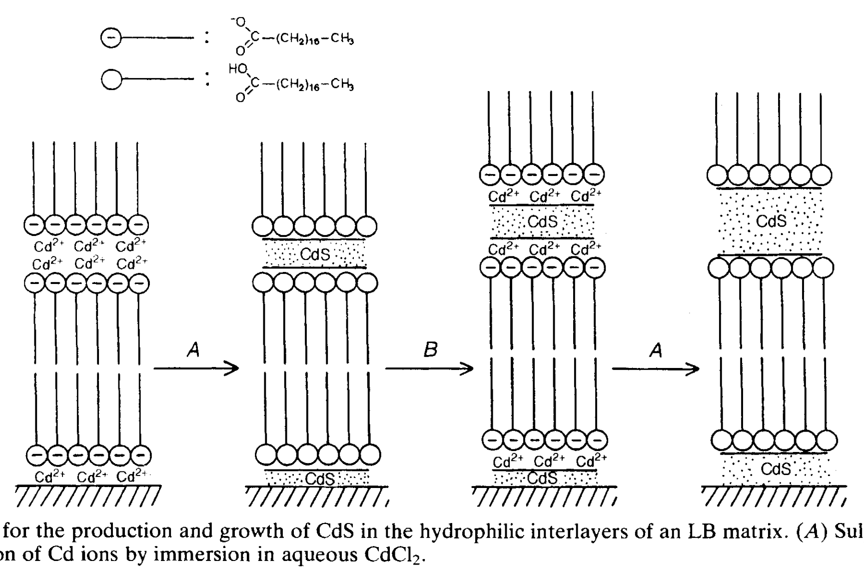

Fig. 1 Proposed scheme for the production and growth of CdS in the hydrophilic interlayers of an LB matrix. (*A*) Sulphidation by exposure to H_2S gas; (*B*) intercalation of Cd ions by immersion in aqueous $CdCl_2$.

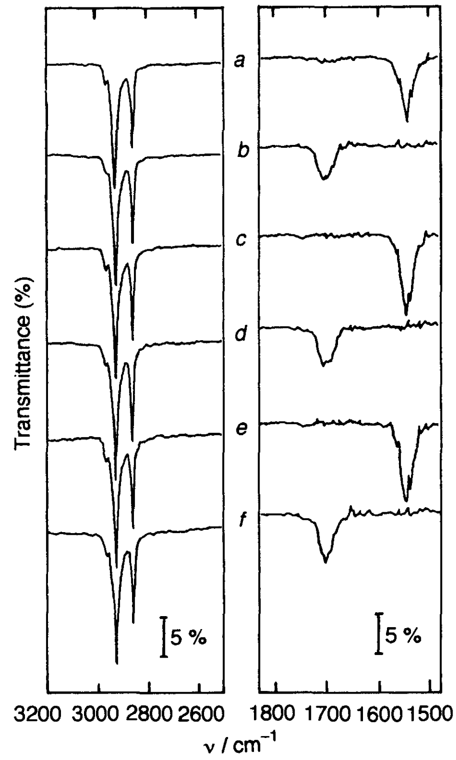

Fig. 2 IR spectra of cadmium stearate LB film and composite films of CdS and LB matrix: (*a*) cadmium stearate LB film → (*b*) sulphidation → (*c*) intercalation → (*d*) sulphidation → (*e*) intercalation → (*f*) sulphidation

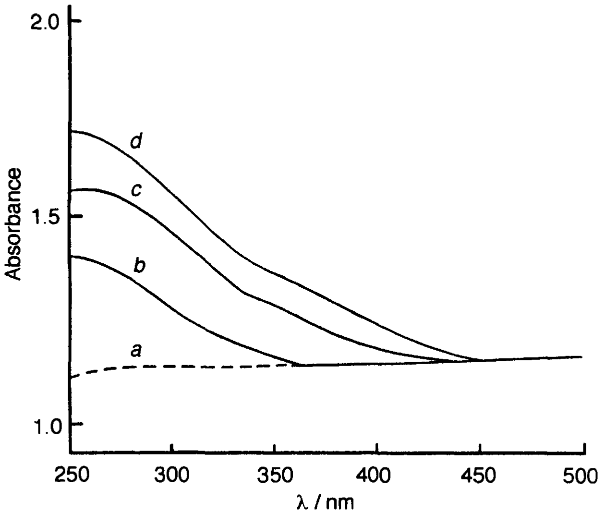

Fig. 3 UV–VIS spectra of cadmium stearate LB film and composite films of CdS and stearic acid multilayers: *a*–*d* correspond to *a, b, d,* and *f* in Fig. 2, respectively

IR-810 instrument in transmission mode and UV–VIS spectroscopy (Fig. 3) using a Shimadzu UV-3100 spectrometer in the specular reflectance mode (5° incident angle). The original LB film of cadmium stearate showed an IR absorption band at 1548 cm^{-1} assigned to the C=O stretching vibration of carboxylate ions (Fig. 2*a*) and no significant absorption in the UV–VIS spectrum (Fig. 3*a*). The sulphidation of the cadmium stearate LB film caused the band at 1548 cm^{-1} to disappear and a band at 1702 cm^{-1} characteristic of protonated carboxylic acids to appear (Fig. 2*b*). Concomitantly, the formation of size-quantized CdS was apparent from the appearance of an optical absorption due to CdS, the onset of which (370 nm) was blue-shifted from that of bulk CdS (520 nm) (Fig. 3*b*). These results show that by exposure to H_2S gas the cadmium stearate multilayer is successfully transformed into a composite film of size-quantized CdS and the stearic acid multilayer (referred to as the acid-form composite film). Although the above-mentioned results are essentially consistent with previous reports,[5,6] our new finding is the growth of CdS in the composite films without destroying the layered structure, as shown below.

When the acid-form composite film was immersed in aqueous $CdCl_2$ (step *B* in Fig. 1), the IR band at 1702 cm^{-1} was totally replaced by the band at 1548 cm^{-1} (Fig. 2*c*) while the optical absorption remained unchanged, indicating that Cd ions are intercalated into the hydrophilic interlayers of the acid-form composite film to form the salt-form composite film of CdS and cadmium stearate multilayer. Further repetition of the sulphidation–intercalation cycle caused a stoichiometric transformation of the carboxylate groups from the ionized to the protonated forms (Fig. 2*d*–*f*) as well as an increase of the optical absorbance due to CdS which was accompanied by a red shift of the onset (Fig. 3*c* and *d*). The increasing optical absorbance coupled with the decreasing onset energy provides direct evidence for the growth of CdS in the LB matrix. It is noted that CdS formed after the third sulphidation process, the absorption onset of which (450 nm) is blue-shifted from the bulk value (Fig. 3*d*), is still size-quantized.

The intensity of C–H stretching IR bands at 2925 and 2852 cm^{-1} is seen to remain unchanged through spectra *a*–*f* in Fig. 2, which indicates that no stearic acid or cadmium stearate molecules escape from the film during the repetition of the sulphidation–intercalation cycle. In addition, XRD analysis using a Rigaku 2034 diffractometer showed that the layered structure was maintained through the repetition of the sulphidation–intercalation cycle.† The basal-plane spacing (*d*) of the original LB film of cadmium stearate was 5.00 nm, which is in good agreement with a previous report,[7] and *d* increased steadily with the growth of CdS; the values of *d* for the salt-form composite films after one and two sets of the sulphidation–intercalation cycle were 5.09 and 5.23 nm, respectively.

Thus, size-quantized CdS formed at hydrophilic interlayers of LB films may be grown by the simple technique developed in this study without destroying the layered structure. Similar results were obtained with a composite film of ZnS and an LB matrix. The determination of the form of CdS (two-dimensional planes or microaggregates) is a problem to be solved.

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† The weaker XRD peaks of the acid-form composite films as compared with those of the original cadmium stearate LB films and the salt-form composite films may indicate the disarray in stacking. The full width at half maximum of (002), (003) or (004) peak of salt-form composite films was 0.19°, being comparable to that of the original cadmium stearate LB film (0.20°).