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Electron Microscopic Evidence for the Preparation of Langmuir-Blodgett Film Systems without Any Micro-Pores

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Electron microscopic examinations of Langmuir-Blodgett film structure were able to help the preparation of the film systems without any micro-pores on the electron microscopic scale.

The presence of uncontrollable imperfectness in Langmuir-Blodgett (LB) film structure should influence the physico-chemical properties of the film systems.[1] An LB-film of merocyanine dye (5-[2-(3-octadecyl-2-benzothiazolylidene)-ethylidene]-3-carboxylmethyl-2-thioxo-4-thiazolidinone, referred to as NK 2684) was able to be prepared on an SnO_2 optically transparent electrode (OTE) and the pigmented electrode was found to act as a photo-cathode under the photoelectorchemical conditions employed in our previous study.[2] When a single monolayer of cadmium arachidate (CdA) was deposited between the SnO_2 layer and the dye LB-film, the cathodic photo-current generation was found to be almost negligible.[2] This finding seemed to suggest that a single CdA monolayer might have an appropriate film structure enough to act as an insulator. At that time, however, we were unable to obtain any information on the micro-structure of a CdA monolayer, due to the lack of a suitable method for the analysis of LB-film micro-structure. Recently, we added a new replica method for transmission electron microscopic observation of LB-film surface structure with plasma-initiated polymerized film by glow discharge.[3] The replica method seems to be a powerful tool for the micro-structural analysis of the extremely small and ultra-thin samples such as LB-film systems and biomaterials with high resolution (empirically up to 0.6 nm[4]) and without introduction of any

significant artifact such as shadowing and stanining.[3-5] We demonstrate here the feasibility of the replica method for the preparation of LB-film systems without any-micro-pores on the electron microscopic scale showing some replica images of LB-films. The practical resolution of the replica method was found to be approx. 2 nm, when each relica image demonstrated in this paper was further expanded.

A monolayer of CdA on an aqueous subphase and an LB-film of CdA on an SnO_2 OTE were prepared under the same conditions used in our previous study.[2] Briefly, an aliquot of 1×10^{-4} mol·l^{-1} arachidic acid (AA) in chloroform was delivered onto an aqueous subphase containing 1×10^{-4} mol·l^{-1} $CdCl_2$, whose pH was adjusted to 6.0 by the addition of Na_2HCO_3 and a monolayer of CdA was formed on the aqueous subphase after the reaction between cadmium ions and AA molecules. The monolayer thus prepared reached a collapsing point around 65.3 mN/m and the monolayer deposition was conducted at a surface pressure of 30.0 mN/m at 20 °C. Deposition of the CdA monolayer onto the SnO_2-coated and SnO_2-free sides of an OTE (Matsuzaki Shinku Ltd.) was performed totally with a deposition ratio of unity.[2] A plasma-initiated polymerized film was prepared onto the CdA monolayer-coated side under the same conditions used in our previous report.[3] When the thus polymer-covered sample was soaked into a mixed solution (hydrogen fluoride : nitric acid : acetic acid = 1 : 1 : 4, volume ratio), a single replica stage film was obtained. Each replica film thus prepared was examined in a JEM 100 S or 1200 EX electron microscope (JEOL).

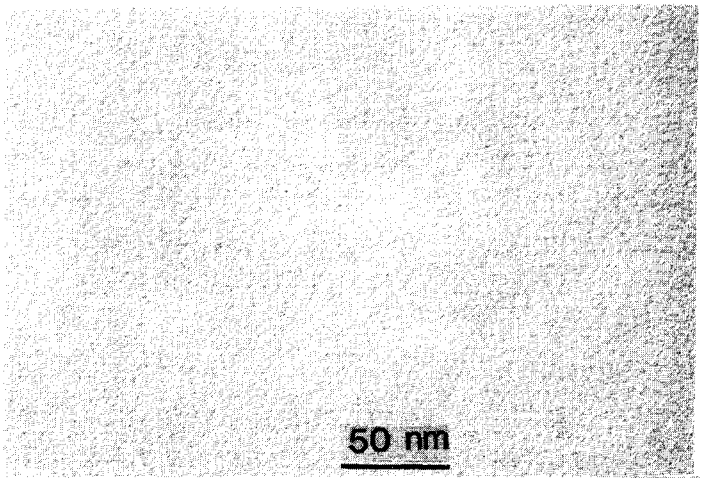

Fig. 1. A typical replica image of a single CdA monolayer-coated SnO_2 electrode.

Figure 1 shows a typical electron micrograph of the replica film prepared from an SnO_2 OTE, on which a single monolayer of CdA was deposited. As seen herein, any micro-pores in the replica image were unable to be visualized on the electron microscopic scale. In Fig. 1, the length of a scale bar is 50 nm. The practical resolution of the replica method is too low to visualize the plausible lattice defects in the monolayer. However, the replica image shown in Fig. 1 seems to support our previous finding[2] that the photoelectrochemical interaction between the SnO_2 layer and the NK 2684 LB-film was inhibited by the insulation of a single CdA monolayer between them.

The surface chemical conditions employed in our previous report[2] and this studies were semi-empirically optimized in a laboratory of one of the authors (K.I.) on the basis of the surface chemical properties of CdA molecules in preparing their mono- and multilayers on various subphases under various environments. However, the conditions thus semi-empirically optimized in a laboratory of K.I. were not always able to permit the preparation of a CdA LB-film of high quality in any other laboratories. Fig. 2 shows a typical replica image of a CdA LB-film prepared in another laboratory of one of the authors (T.I.) according to the same manner used in Fig. 1. The LB-film, whose replica image is shown in Fig. 2, was prepared by the deposition of three CdA monolayers on an SnO_2 OTE. There exist numerous film-structural defects in each monolayer on an SnO_2, although the deposition ratio in preparing the LB-film was found to be unity. This finding seems to suggest that estimation of the so-called deposition ratios in preparing LB-films is unable to reveal the plausible presence of micro-pores in a monolayer as a component of an LB-film (a multilayer). Fortunately, when the spreading solution was delivered onto the buffer solution (pH 6.08) at 18.0 ± 0.4 °C and its deposition onto an SnO_2 OTE was conducted at a surface pressure of 25 mN/m with a deposition ratio of unity, an LB-film of CdA without any micro-pores in its replica image was also to be prepared in a laboratory of T.I.

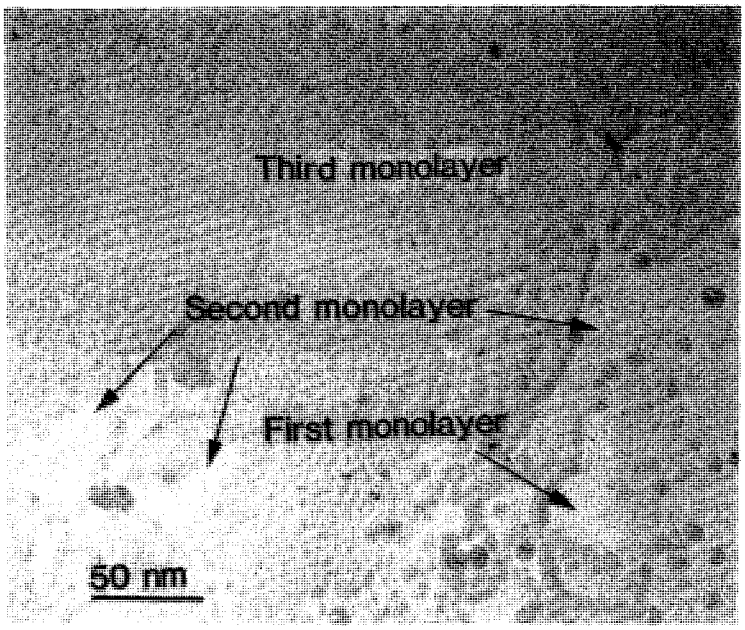

Fig. 2. The replica image of an SnO_2, on which three monolayers of CdA were deposited. For explanations, see the text.

As demonstrated above, at the present stage, the quality of LB-films seems to be laboratory-dependent even if their preparation was conducted under the same manner described in the literature. Standardization of the conditions for preparation of LB-film systems of high quality is thus essentially required for future applications, for an example, in electronics (e.g., ultra-thin insulators in micro-electronic devices such as Josephson junction). In this standardization study, the replica method employed in this study is undoubtedly useful by its nature.

We demonstrate here another example to show the feasibility of the

replica method for the preparation of LB-films having their smooth surfaces. Fig. 3 shows a replica image of two NK 2684 monolayers deposited on a single CdA monolayer-coated SnO_2 OTE. The pigmented electrode was prepared under the same conditions employed in our previous study.[2] As shown in Fig. 3, the surface of the dye LB-film was found to be smooth showing no significant structural defects on the electron microscopic scale.

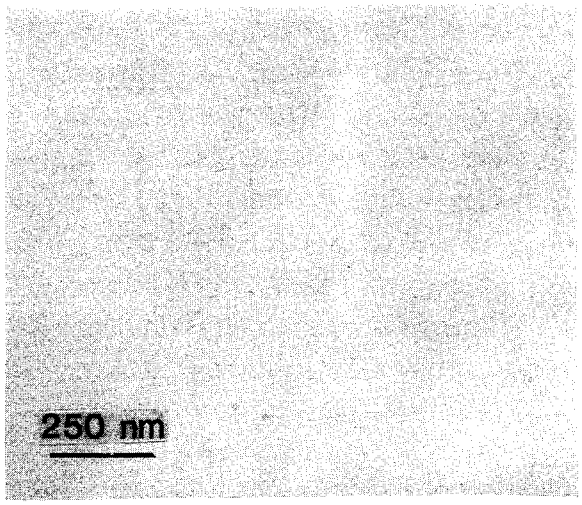

Fig. 3. The typical replica image of the pigmented electrode. For explanation, see the text.

After the completion of this study, we have been impressed that the so-called LB-film technique is useful for the future construction of micro-electronic devices. As demonstrated in Figs. 1 and 3, we have been able to prepare the LB-films without any micro-pores on the electron microscopic scale. It has generally been recognized that the electric property of an organic film system should be strongly dependent on the molecular arrangement and orientation in it, its macro- and micro-structural defects, and the species, concentration and distribution of impurities in it. In order to assist the evolution of an LB-film system applied for the micro-electronic devices, the developement of a method for the determination of LB-film structure at the molecular scale should be required. A method for the purification of LB-film components is also essentially required.[1] We recommend here the use of the replica method for the standardization study of an LB-film system.

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