

# Langmuir–Blodgett Film Formation of a Fullerene Dicarboxylic Acid Derivative $C_{60}(\text{HOOCCHNHCHCOOH})$ and its Photocurrent Generation

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The Langmuir films of a fullerene dicarboxylic acid derivative **I**,  $C_{60}(\text{HOOCCHNH}_2\text{CHCOOH})\text{CF}_3\text{SO}_3\text{H}$  (FDA), at the air/water interface have been investigated. FDA formed a stable monolayer on pure water when dilute solution ( $1.04 \times 10^{-5}$  mol/L) was used as the spreading solution. The monolayer formation on various subphases was investigated, including solutions containing different monovalent ( $\text{Na}^+$ ,  $\text{Ag}^+$ ) and divalent ( $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ) cations. The introduction of these cations makes the monolayer more stable. The limiting molecular area is also dependent on the pH of the subphase. The surface pressure versus area isotherms at different temperature clearly indicate that FDA molecules easily aggregate at high temperature. The monolayer and multilayer LB films of FDA were deposited on quartz and glass substrates from  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , or  $\text{Cu}^{2+}$ /Phen solution subphase, and their UV–vis and XPS spectra were obtained. The data showed that for  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$ /Phen subphase the cation can be transferred onto the substrates together with FDA but not the other two. The photoelectrochemical behavior of FDA on an ITO electrode was investigated, which showed that the photocurrent is cathodic. Oxygen and negative bias are beneficial factors for the photocurrent generation. The external quantum yield is ca. 4%. © 1998 Academic

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**Key Words:** LB film; fullerene; photocurrent.

## INTRODUCTION

The discovery of Buckminsterfullerene (1) and the success in synthesizing macroscopic quantities of it (2) have opened up the way to a new exciting field of materials science. The thin films of fullerenes and fullerene derivatives (3–6) are of great interest because of their unique interesting properties. Fullerene-based films can be prepared by thermal evaporation (6), solution casting (6, 7), spin casting (6, 8), LB technique (6, 9–16), self-assembly (6, 17), etc. The Langmuir–Blodgett (LB) technique is one of the best meth-

ods in forming high-quality uniform and ordered thin films (18). This method has been widely used for investigation of pure fullerene, fullerene/calix[8]arene and fullerene/CdS complexes, and fullerene derivatives (9–16). In most cases, only multilayers were obtained at the air/water interface. The fullerenes and their derivatives were found to aggregate easily. It was also found that if hydrophilic oxygen or nitrogen containing groups were introduced onto the sphere of fullerenes, the stability and transferability of the monolayers could be enhanced remarkably (11–16).

In the present work we report the Langmuir film formation of a dicarboxylic  $C_{60}$  derivative (19) and the effects of spreading solutions, temperature, pH value, and various cations in the subphase. The photocurrent generation of its monolayer modified ITO electrode and the factors influencing the photocurrent are also reported such as the bias, gas atmosphere, wavelength, and electron acceptor.

## MATERIALS AND METHODS

### Materials

The fullerene dicarboxylic acid derivative **I**,  $C_{60}(\text{HOOCCHNH}_2\text{CHCOOH})\text{CF}_3\text{SO}_3\text{H}$  (FDA) (Fig. 1), was synthesized as we reported earlier (19). XPS spectra show that once **Ib** is spread onto water phase, it changes into form **Ia**. Methyl viologen diiodide ( $\text{MV}^{2+}$ ) was synthesized by refluxing 4,4'-bipyridyl with excess methyl iodine in ethanol for 6 h. The product was filtered and washed with ethanol several times, recrystallized with ethanol twice, and then dried under vacuum. The final product was checked by NMR, and the spectrum indicated it was highly pure.

### Langmuir and Langmuir–Blodgett Film Formation

All Langmuir and LB films were prepared on a computer-controlled Nima LB trough (Model 2001, Nima Technology

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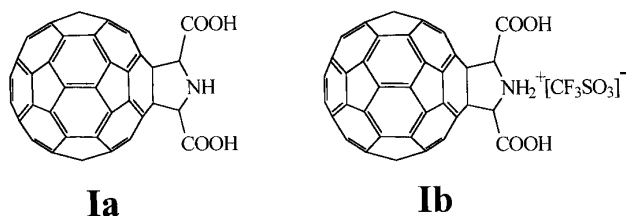


FIG. 1. Structure of FDA.

Ltd., England). The spreading solutions were prepared by dissolving Ib in THF to produce solutions with concentrations of 0.0104 mg/mL ( $1.04 \times 10^{-5}$  mol/L, solution A) and 0.104 mg/mL ( $1.04 \times 10^{-4}$  mol/L, solution B) or in about 5 mL THF and then diluted by chloroform to produce a concentration of 0.107 mg/mL ( $1.07 \times 10^{-4}$  mol/L, solution C). Deionized water (pH  $5.5 \pm 0.1$ ,  $18.2 \pm 0.1$  M $\Omega$  cm) prepared by EASYpure RF compact ultrapure water system (Barnstead Co., USA) was used as subphase or solvent of subphase in all experiments. To control the temperature of subphase, a Haake circulator (Mess-Technik GmbH u. Co., Germany) with a DC1 temperature control module and a K15 bath vessel was used. The temperature and pH value of the subphase were measured by a GP353 ATC pH meter (EDT Instruments LTD., UK) and a IX501A pH meter (Peking University, China). In each experiment, 6.00 mL (A or C) or 1.50 mL (B) of solution was spread at the air/water interface very carefully, and the solvent was allowed to evaporate for at least 30 min before compression. The compression speed is 40 cm<sup>2</sup>/min. Quartz slides (10  $\times$  30 mm, for UV-vis spectra use), normal glass slides (20  $\times$  20 mm, for XPS spectra use), and ITO coated glass slides (20  $\times$  50 mm, for photoelectrochemical measurement) were

employed as substrates, and all slides were carefully hydrophilically pretreated. All the LB films were deposited onto the slides at a rate of 4.0 mm/min (vertical dipping) at a constant surface pressure of  $25.0 \pm 0.1$  mN/m.

### Spectroscopic Measurement

The absorption spectra of the films and the solutions were measured by a Shimadzu UV-3100 spectrophotometer. The X-ray photoelectron spectra of the LB films were measured by a VG ESCA LAB-5 Multitechniques photoelectron spectrometer (VG Co., UK), and Al was used as the target of X-ray source.

### Photoelectrochemical Measurement

The photoelectrochemical studies and the measurement of cyclic voltammetry were performed by using a model 600 voltammetric analyzer (CH Instruments Inc., U.S.) and a 500 W xenon lamp (Ushio Electric, Japan). A variety of interferential filters (Toshiba, Japan) was used to obtain the different wavelengths. To avoid the thermoeffect, an IRA-25S filter (Toshiba, Japan) was used to cut the IR light. The intensities of incident beams were standardized by a power and energy meter (Scientech 372, Boulder CO., U.S.) and the K<sub>3</sub>Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> chemical actinometer. A three-electrode configuration was used throughout. A platinum electrode was used as the counter electrode; a saturated calomel electrode was used as the reference; and the FDA LB monolayer film modified ITO electrode was used as the working electrode. KCl solution (1.0 mol/L) was used as the electrolyte solution in all photocurrent measurement experiments.

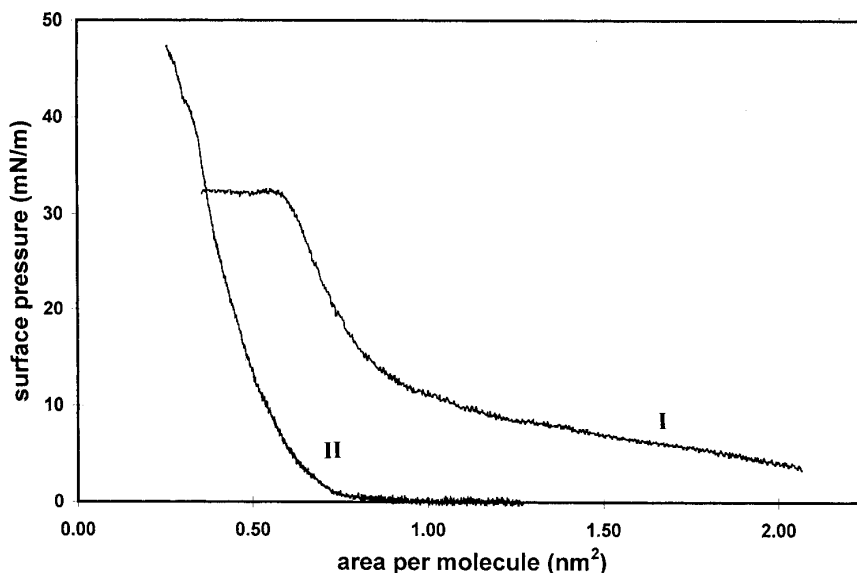
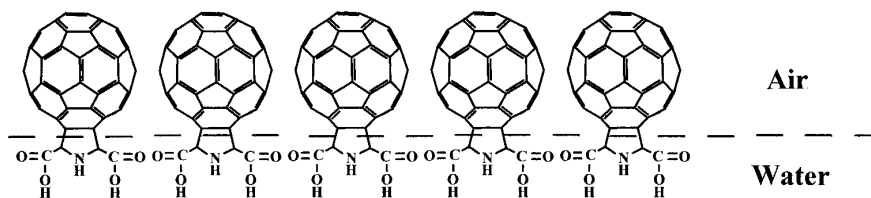


FIG. 2. Surface pressure-area isotherms. (I) Solution A ( $1.04 \times 10^{-5}$  mol/L); (II) solution B ( $1.04 \times 10^{-4}$  mol/L).



**SCHEME 1.** Possible orientation of FDA molecules on water surface.

## RESULTS AND DISCUSSION

### Concentration of Spreading Solutions

Surface pressure versus molecular area ( $\pi$ -A) isotherms are frequently used to indicate the quality, stability and the phase change of the monolayer in air/water interface. Two spreading solutions were used to measure the  $\pi$ -A isotherms, one of which is dilute (solution A) and the other of which is relatively concentrated (solution B) (Fig. 2). When dilute spreading solution (A) was used (spreading speed ca. 10 drops/min, each drop is 10  $\mu$ L), a stable FDA monolayer on the pure water subphase can be obtained. The limiting molecular area is ca. 0.95 nm<sup>2</sup>, which is close to the limiting molecular area of pure C<sub>60</sub> and its other derivatives (9–16). The orientation of FDA molecules on the water surface is proposed as in Scheme 1. The hydrophilic groups of the FDA dip into the water subphase, and the hydrophobic spheres of C<sub>60</sub> float on the water surface. For the concentrated spreading solution (B), the  $\pi$ -A isotherm showed the limiting molecular area to be about 0.51 nm<sup>2</sup>, which indicates that the film on the air/water interface is multilayer.

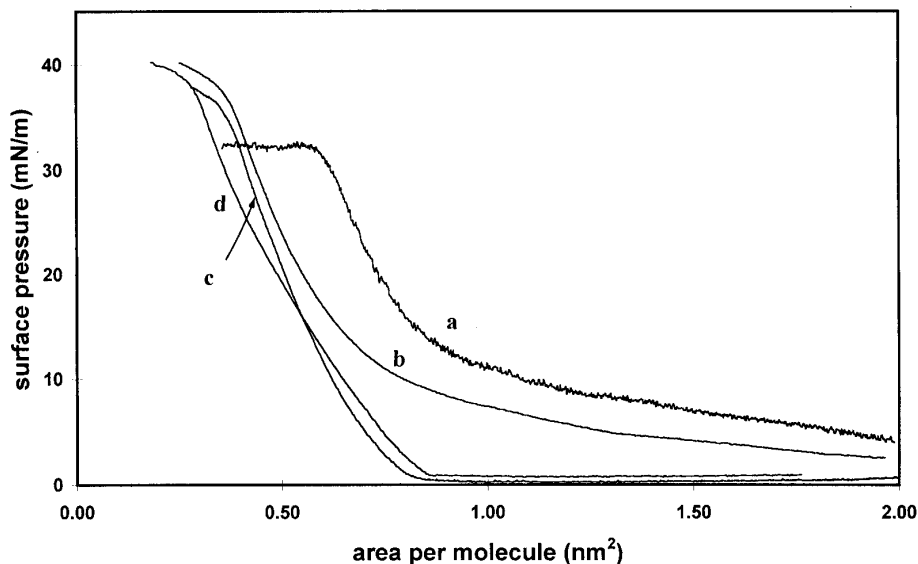
### Temperature of the Subphase

The  $\pi$ -A isotherms of FDA with concentration of 1.04  $\times 10^{-5}$  mol/L at the ultrapure water subphase were recorded at temperatures of 287  $\pm$  1, 298  $\pm$  1, 309.5  $\pm$  1, and 321  $\pm$  1 K (Fig. 3). The limiting molecular area decreased from 0.95 to 0.63 nm<sup>2</sup> when the subphase temperature increased from 287 to 321 K. This indicates that higher temperature can cause the formation of multilayer. It is well known that fullerene and its derivatives are easy to aggregate (20), and it is very difficult to prepare the monolayer. For this reason, all of the other experiments in this paper were carried out at 287  $\pm$  1 K.

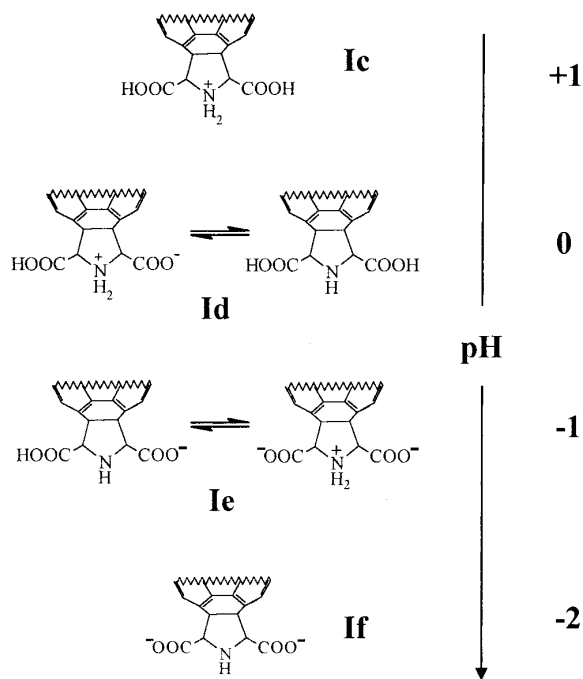
### pH Value of the Subphase

The FDA can be considered as a derivative of iminodiacetic acid. Similar to other amino acids, the change of the pH value of the subphase can influence the equilibrium between the different species of FDA significantly (Scheme 2).

The  $\pi$ -A isotherms of FDA with solution A on different pH value subphase are shown in Fig. 4a, and the influence



**FIG. 3.** Surface pressure–area isotherms of FDA at different temperatures: a, 287  $\pm$  1 K; b, 298  $\pm$  1 K; c, 309.5  $\pm$  1 K; d, 321  $\pm$  1 K.



**SCHEME 2.** Different species of FDA molecule versus the change of pH value.

of the pH value on limiting molecular area is shown in Fig. 4b. The changes of limiting area with pH value may be explained as follows: at lower pH, FDA would be positively charged and exists as form Ic, so the strong static repulsion between different FDA molecules at the interface results in a larger limiting molecular area. When the pH increases, FDA gradually changes from the neutral zwitterion form Id to the uninegatively charged form Ie, then eventually to the divalent anion If at strongly basic condition. When FDA exists as Ie or If form, the repulsion between the molecules

**TABLE 1**  
Influence of Cations in the Subphase on Film Formation

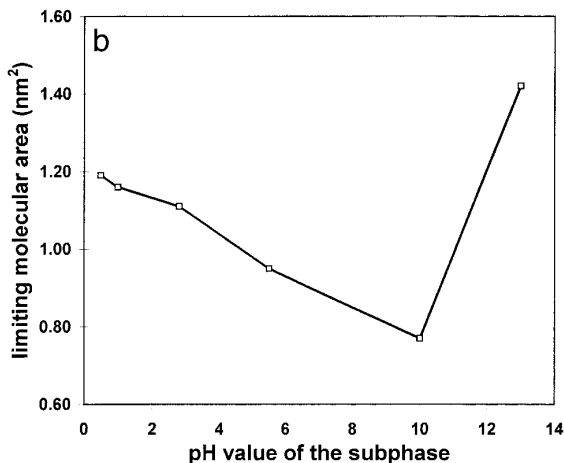
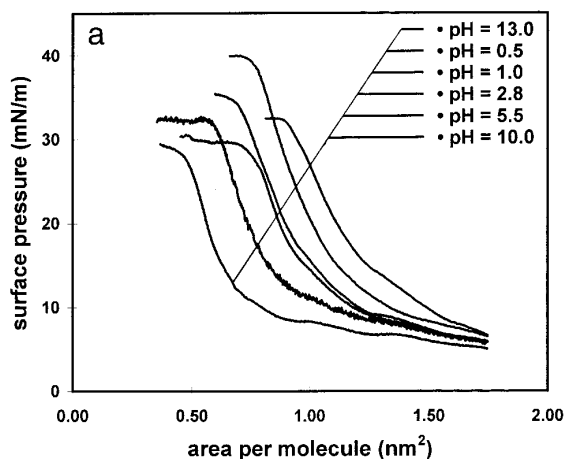
Subphase	Ionic radii (pm)	Concentration ( $10^{-3}$ mol/L)	pH	Limiting molecular area ( $\text{nm}^2$ )	Collapse pressure (mN/m)
NaCl	97	1.0	5.5	1.12	35.5
AgNO <sub>3</sub>	126	1.0	5.4	1.07	44.0
CaCl <sub>2</sub>	99	1.0	5.5	1.02	36.9
CdBr <sub>2</sub>	97	1.0	5.4	1.03	42.0
CuCl <sub>2</sub>	72	1.0	5.3	1.23	34.2
CuCl <sub>2</sub> /Phen	—	1.0/5.0	7.0	1.30	39.4

are also intense and consequently results in a larger limiting molecular area.

The neutral form of FDA apparently should have the smallest limiting molecular area, based on static repulsion. But the smallest limiting molecular area appears at slightly basic condition, not in the expected lower pH range. This may be due to the fact that the equilibrium between FDA species in solid state film at the air/water interface is slightly different from that in the bulk water solution. The pH value measured is that in the bulk solution.

#### Influence of Cations in the Subphase

To investigate the influence of cations in the subphase, the  $\pi$ -A isotherms were measured under various conditions. Typical data are shown in Table 1. Two monovalent metal cations, Na<sup>+</sup> (NaCl) and Ag<sup>+</sup> (AgNO<sub>3</sub>), were tested. When AgNO<sub>3</sub> was used, the experiment was carried out in a dark room. The results for these two monoanions are quite different. When AgNO<sub>3</sub> solution was employed as the subphase, a smaller limiting molecular area ( $1.07 \text{ nm}^2$ ) but a higher



**FIG. 4.** (a) Surface pressure–area isotherms of FDA at different pH; (b) effluence of pH value of the subphase on limiting molecular area.

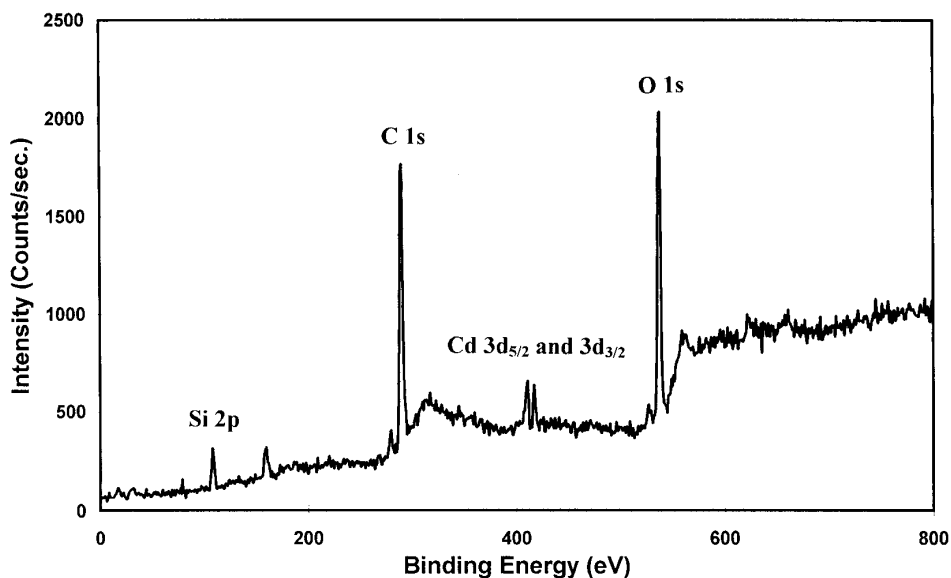


FIG. 5. XPS spectra of the FDA Langmuir-Blodgett films deposited on  $\text{CdBr}_2$  solution ( $1.0 \times 10^{-3}$  mol/L) subphase.

collapse pressure (44.0 mN/m) were observed than those for the NaCl.

$\text{Cu}^{2+}$  ( $\text{CuCl}_2$ ),  $\text{Ca}^{2+}$  ( $\text{CaCl}_2$ ), and  $\text{Cd}^{2+}$  ( $\text{CdBr}_2$ ) were tested as the divalent cations.  $\text{CuCl}_2$  solution was used in two ways: one is 0.0010 mol/L  $\text{CuCl}_2$  solution (pH 5.3) and the other is  $\text{CuCl}_2/1,10$ -phenanthroline (Phen) (0.0010/0.0050 mol/L) aqueous solution (pH 7.0). Table 1 shows that the monolayer on two  $\text{Cu}^{2+}$  solution subphases has larger limiting molecular area and smaller collapse pressure than those with  $\text{Ca}^{2+}$  or  $\text{Cd}^{2+}$  solution as subphase. These results show that the introduction of the metal cations in the subphase can make the FDA monolayer more stable (larger limiting molecular area and higher collapse pressure).

#### Langmuir-Blodgett Film

In this section, solution C was employed as the spreading solution. Four different subphases ( $\text{CaCl}_2$ ,  $\text{CdBr}_2$ ,  $\text{CuCl}_2$ ,  $\text{CuCl}_2/\text{Phen}$ ) were selected to prepare the FDA monolayer and multilayer (5-layer, Y-type) films. When  $\text{CaCl}_2$  solution was used as the subphase, the XPS spectra of the monolayer revealed clearly the C 1s peak but no calcium or chlorine in the film. The 5-layer LB film showed basically the same results except the C 1s peak is stronger than the 1-layer film using the silicon (from glass substrate) peaks as the reference. However, the  $\text{CdBr}_2$  solution subphase gave different results, both XPS spectra of 1-layer and 5-layer LB films (Fig. 5) showed clearly Cd  $3d_{5/2}$  and  $3d_{3/2}$  peaks. Similar to the  $\text{CaCl}_2$  solution subphase, no halogen (bromine) peak is observed.

The UV-vis spectra of the LB films of FDA with pure water and  $\text{CuCl}_2$  solution as the subphase showed that the

films prepared under these two conditions are similar. The XPS spectra showed no Cu signal after repeated searching. The LB films prepared from  $\text{CuCl}_2/\text{Phen}$  solution subphase gave quite different results. The UV-vis spectra and XPS spectra of these films showed evident signal of the Cu/Phen. In the UV-vis spectra of the multilayer the intensity of all the absorption bands decreased after the film was washed with pure water. The XPS spectra showed that after water washing, the intensity of C 1s and N 1s peaks decreased much more than that of Cu. This indicates that the Phen ligand was washed preferentially over Cu.

#### Photocurrent Generation from the FDA LB Film Modified ITO Electrode

*Effects of  $\text{O}_2$  and  $\text{N}_2$ .* The working band of the incident light is ca. 320–800 nm when the IRA-25S filter was used. The absorbency of the ITO coated glass slide increases very sharply at wavelengths below 320 nm. When the experiment was carried out under nitrogen atmosphere and only IRA-25S filter was used, the photocurrent from the FDA-ITO electrode was 180–200 nA; on the other hand, when oxygen was introduced into the electrolyte solution, the photocurrent increased rapidly and was stable several minutes later at ca. 3700–4000 nA. If nitrogen was introduced into the solution again, the photocurrent decreased. So oxygen can promote the photocurrent generation.

*Action spectrum and the external quantum yields.* To study the effect of different wavelength on the photocurrent generation, we used a series of TOSHIBA interferential filters and a monoprism monochromator to obtain monochrome band. The normalized action spectrum and the UV-

vis absorbency spectrum of the FDA-ITO electrode are shown in Fig. 6. The action spectrum matched very well with the absorbency spectrum. The external quantum yields are calculated using the following equation:

$$\text{quantum yield} = \frac{\text{number of electrons generated}}{\text{number of photons absorbed by the FDA-ITO}} \times 100\%.$$

According to the absorbency of the film, the intensity and wavelength of the incident light, and the photocurrent generated, the external quantum yield is calculated to be ca. 4%. The values of the external quantum yield are basically the same at different wavelengths of the incident light.

**Open circuit photovoltage and effect of bias.** The effect of bias was investigated. It was found that positive bias make the photocurrent decrease whereas negative bias make it increase, indicating that the photocurrent is cathodic. There is an approximate linear relationship between the photocurrent and the bias in the range from  $-0.10$  to  $0.40$  V versus SCE (Fig. 7). The open circuit photocurrent is ca.  $0.22$  V (the value of the bias when the photocurrent is zero). Cyclic voltammetry is also used to determine the open circuit photovoltage. The intersection of the CV curve measured under irradiation and the CV curve measured in dark (scan rate  $50$  mV/s) is the open circuit photovoltage, which is also shown to be  $0.22$  V.

**Effects of electron acceptor and the cations in film.** When  $MV^{2+}$  was used as an electron acceptor in the electrolyte solution, the photocurrent does not show any evident change and the open circuit photovoltage remains at  $0.22$  V. A  $Cd^{2+}$ -intercalated FDA-ITO (FDA/Cd-ITO) electrode

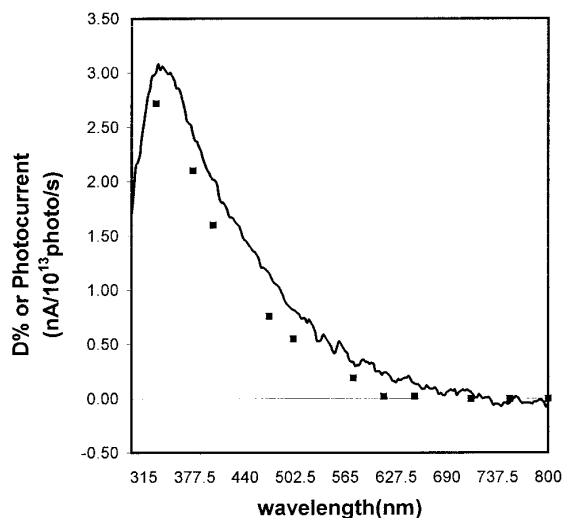


FIG. 6. The normalized action spectrum and absorbency spectrum of the FDA-ITO electrode.

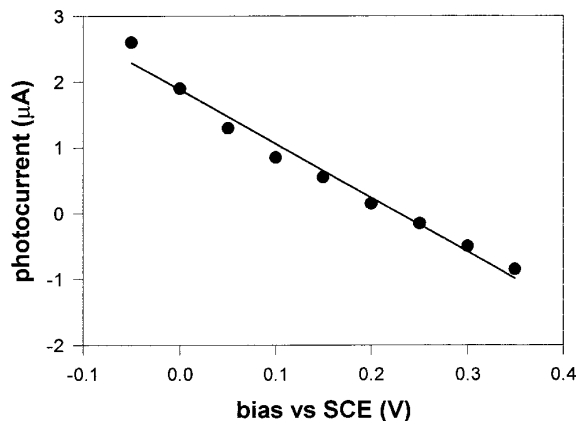


FIG. 7. The relationship between the photocurrent and the bias.

was prepared by using  $CdBr_2$  solution ( $0.001$  mol/L) as the subphase, and it showed no noticeable change of photocurrent generation compared with the FDA-ITO electrode.

## SUMMARY

FDA can form stable monolayer at the air/water interface, and this monolayer can be easily transferred onto quartz and normal glass substrates. Dilute solution and low temperature facilitate the monolayer formation. The monolayer is also strongly dependent on the conditions of the subphase. Both strongly acidic and basic solutions transform FDA into charged species and result in large limiting molecular area. The presence of metal cations including mono- and divalent ions in the subphase all improves the stability of the monolayer. XPS data indicate that  $Cd^{2+}$  can be deposited together with FDA and becomes intercalated into the FDA monolayer. But  $Cu^{2+}$  as its  $CuCl_2$  solution cannot be deposited. Only when the chelating agent Phen was introduced into the subphase could some  $Cu^{2+}$  then be intercalated into the FDA monolayer. The FDA-ITO electrode generates large cathodic photocurrent. The photovoltage is ca.  $0.22$  V and the external quantum yield is ca. 4%.

## ACKNOWLEDGMENTS

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