Photovoltaic and electrical properties of Langmuir–Blodgett films incorporating hypocrellins derivatives ☆

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Abstract

The photoelectrochemical behavior of mercapto-substituted hypocrellin B (MSHB), deposited on SnO_2 optically transparent electrodes by means of the Langmuir–Blodgett technique, have been investigated. Addition of electron donors leads to a remarkable enhancement of the photocurrents and photovoltages. Effects of the electron donor concentration, LB film layers, and illumination time on the magnitude of the photocurrent were studied in detail. The usefulness of hypocrellin derivatives as efficient organic photoelectrical conversion materials is suggested. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: LB films; Hypocrellin derivatives; Photoelectric effect; Supersensitization

1. Introduction

The primary photochemical event in photosynthesis is the light-induced charge separation. At present, the solar energy transfer and utilities become one of the most active fields of the new energy source investigation. Developing novel solar energy cells by simulating photosynthesis becomes the pursuing object of scientists in the world. Inorganic semiconductor solar energy cells have been applied in the military and aerospace fields, but the high cost and complicated fabrication process have hampered their extensive development. However, the solar energy cells made from organic materials have intrigued many people due to mainly low cost and ease of fabrication, a great deal of investigation has been made [1] and progress in this area has been obtained. To date, however, organic solar cells stand still far from practical stage because of their much lower efficiencies than those of traditional inorganic ones.

In the past years there has been much interest in energy transfer, electron transfer and photodynamic therapy of hypocrellins (hypocrellin A or hypocrellin B) and their derivatives [2–7]. But little attention has been paid to the photoelectrochemical phenomena resulting from electron transfer. We note here, hypocrellins have good thermal,

chemical stability and excellent photoelectric conversion property. Especially, according to our experiments, the semiquinone radical resulted from hypocrellins and their derivatives accepting an electron kept fairly stable at room temperature. So the successful fabrication of ordered LB films of hypocrellins with special functional structure will set up a new way to their extensive application in optics, microelectronics, photoelectrochemistry, biosensors and mimic biology process.

These considerations have led us to use an optically transparent electrode (OTE) made of SnO_2, on which a single mercapto-substituted hypocrellin B (MSHB) monomolecular layer was deposited by the use of a Langmuir film balance with a rather simple procedure. SnO_2 is an electrode material well characterized [8,9] and has heretofore been employed in a number of photoelectrochemical investigations [10–13]. Electron injection from excited dyes to the conduction band of SnO_2 can take place with high efficiency [11–13], and the backward electron flow is effectively prevented because of the rectifying property of the semiconductor–solution interface.

2. Experimental

2.1. Materials

The preparation of 5,8-didodecylmercapto substituted hypocrellin B (5,8-DDMS-HB) and 5-dodecylmercapto

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substituted hypocrellin B (5-DMS-HB) was reported in our previous work [14]. All solvents, editic acid (EDTA), triethanolamine and ascorbic acid were of analytical grade and purchased from Beijing Chemical Plant, China.

As the substrate for monolayer deposition, SnO_2 optically transparent electrode was 3×3 cm in size with one side being coated with SnO_2 layer 200 nm thick. The SnO_2 layer had a specific resistance of 4×10^{-3} ohm cm^{-1} and an optical transmittance of 80–90% in the visible region above 400 nm. The donor density of the electrode was estimated to be ca. 10^{20} cm^{-3} from the slope of the Mott–Schottky plots [15]. Prior to the deposition of MSHB monolayer, the electrode was washed repeatedly with hot organic solvents such as petroleum ether, acetone, and methanol, and was then treated with hot concentrated sulfuric acid and rinsed with water. The electrode was preserved in doubly distilled water before use.

2.2. Monolayer formation and deposition

For the formation of MSHB monolayer, a Joyce–Loebl Langmuir Trough 4 was employed. The monolayer film was formed by injecting a 100–200 µl of 1×10^{-4} M MSHB chloroform solution onto the aqueous surface. The surface pressure was measured by the Wilhelmy method and the surface pressure–area isotherm (P–A curve) was measured at 25°C for 5,8-DDMS-HB and 5-DMS-HB by compressing the film at the rate of 20 cm^2 min^{-1}.

The procedure of deposition of a monolayer onto the electrode surface was as follows. SnO_2 OTE was immersed vertically in the aqueous subphase (pH 5.8) prior to spreading the MSHB chloroform solution, and when the monolayer was formed to give a stable surface pressure after the chloroform was volatilized for 15 min, the OTE plate was lifted up under the constant surface pressure, 25 mN m^{-1}, in most cases. In order to prevent the glass side of the SnO_2 OTE from forming LB films, two pieces of electrodes were put together before use. All experiments were carried out at room temperature Fig. 1.
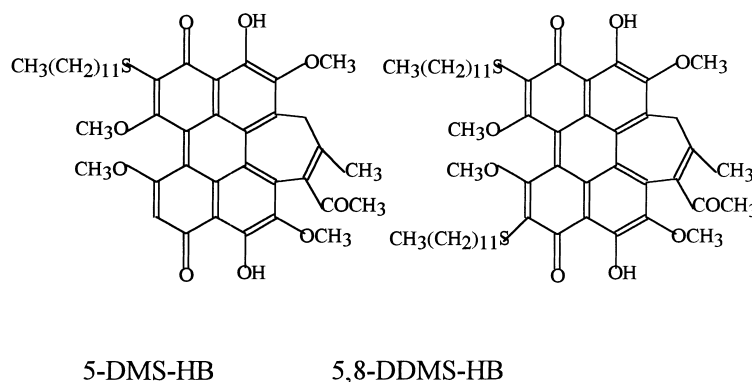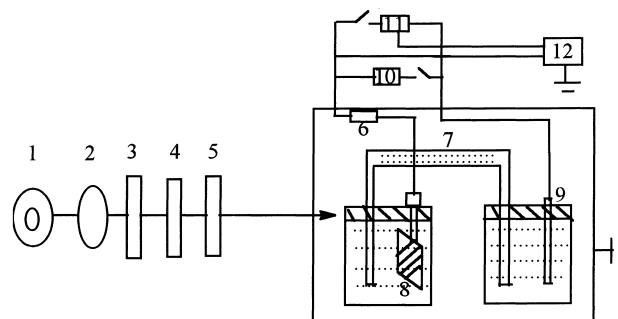
Fig. 2. Schematic diagram of the photocurrent measurement: 1, light source; 2, focusing lens; 3, slit; 4, cut-off filter; 5, monochromator; 6, adjustable resistance; 7, agar salt bridge; 8, MSHB deposited SnO_2 OTE; 9, saturated calomel electrode (SCE); 10, picoammeter; 11, potentiostat; 12, recorder.

2.3. Photoelectrochemical measurements

Fig. 2 shows a schematic diagram of photoelectrochemical measurements. In order to increase the signal-to-noise ratio (S/N) of photoelectric signals, a bicell was used as the photocell that was linked by an agar salt bridge. Experiments have proved that this kind of photocell had a lower signal than a single photocell had. The supporting electrolyte was 0.1 M KCl and during all experiments the solution was flushed with high purity nitrogen. The electrolyte solution contained, where necessary, electron donor (D) of different concentrations. The potential of SnO_2 electrode was controlled by means of a potentiostat, Model GDM-8045, where a saturated calomel electrode (SCE) served as the reference electrode. The experimental photovoltaic cell could be shown as: SnO_2/5,8-DDMS-HB (5-DMS-HB) LB film/ 0.1 M KCl/saturated KCl/SCE. The electrochemical cell thus prepared as well as all the electrical cables were shielded with an iron box against electromagnetic perturbations.

As the light source, a 500 W xenon arc lamp was used in combination with a monochromator having a transmittance half-band width of ca. 10 nm and the spectral range 350–

5-DMS-HB   5,8-DDMS-HB

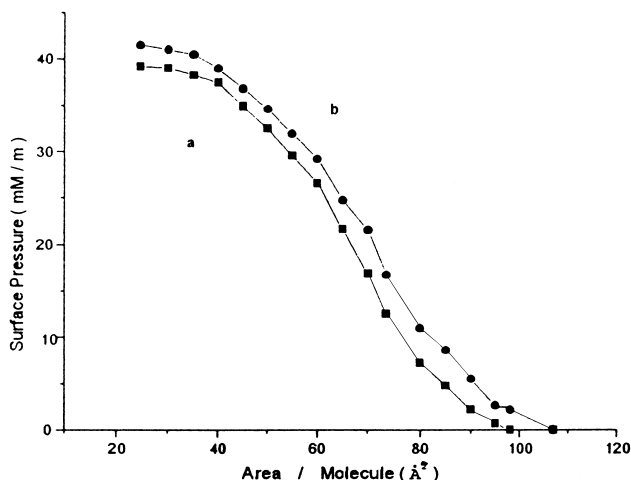Fig. 1. The chemical structure of 5-DMS-HB and 5,8-DDMS-HB.

Fig. 3. Surface pressure–area isotherm of 5,8-DDMS-HB (a) and 5-DMS-HB (b) monolayer. Aqueous subphase, pH-5.8, air atmosphere at 25°C.

800 nm. In illumination experiments with wavelengths above 390 nm, a cut-off filter was used. Photocurrents and photovoltages were measured with a home-made picammeter and potentiostat and recorded by a computer with a software for data treatment.

3. Results and discussion

3.1. Monolayer properties

Fig. 3 shows a typical surface pressure–area isotherm for 5,8-DDMS-HB and 5-DMS-HB on an aqueous subphase (pH 5.8) at 25°C. It indicates that MSHB has good film-forming properties at the air/water interface. At surface pressures around 25 mN/m, where the areas occupied by 5,8-DDMS-HB molecule and 5-DMS-HB molecule are 90.0 and 88.5 Å^2, respectively, the film is expected to exist in the most packed state. Based on the PCMODEL software, we can calculate the area of the hypocrellin B is ca. 105 Å^2, the value occupied by a MSHB molecule at 25 mN/m implies that under this condition the hypocrellin ring plane lies nearly flat on the aqueous surface.

3.2. Absorption spectra

It is important to understand the intermolecular energy and electron transfer to study the effects of molecular state on the spectral properties, therefore we compared absorption spectra of the MSHB LB films with that of the MSHB chloroform solution.

The absorption spectrum of 5,8-DDMS-HB LB films on SnO_2 OTE (dash line) and in the solution (solid line) is illustrated in Fig. 4 (the absorption spectrum of 5-DMS-HB is not shown). As shown in the figure, the absorption bands of the MSHB LB film are red-shifted relative to that in solution with concomitant broadening of $\nu_{1/2}$ (the width of half-band). These changes are attributed to molecular orderly orientation and close arrangement, which results in the overlap of the large π bands of hypocrellin, then, the intermolecular transition energy decreases and the absorption bands are red shifted. Similar phenomenon was reported in the porphyrin LB films [16].

3.3. Typical photoelectric response of MSHB LB films

Owing to a large forbidden gap (3.7 eV [9]), a small thickness (200 nm) and a cut-off filter, the background anodic photocurrent due to SnO_2 excitation was negligibly small in the visible region. A typical photocurrent response
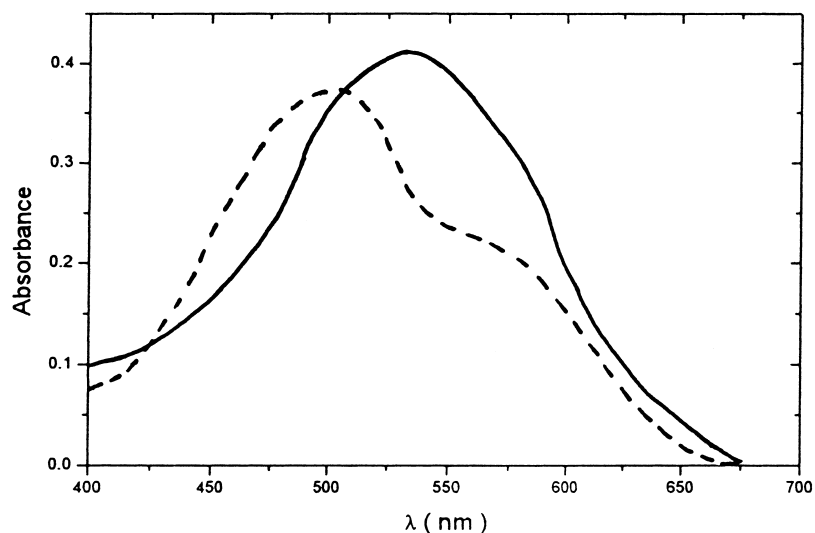

Fig. 4. UV–vis absorption spectra of 5,8-DDMS-HB in CHCl$_3$ and LB monolayer film. (CHCl$_3$ solution (- - -), LB film (———)).
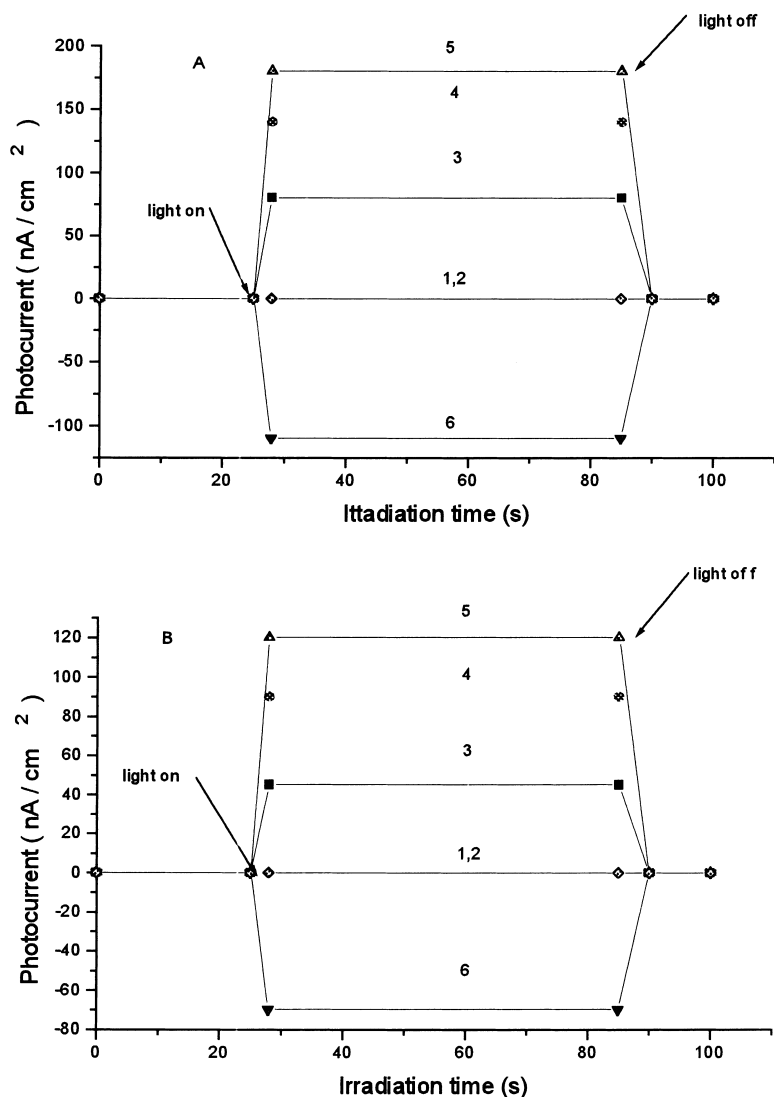
Fig. 5. Typical photocurrent responses of 5,8-DDMS-HB and 5-DMS-HB. (A) 5,8-DDMS-HB; (B) 5-DMS-HB. Clean SnO_2 OTE (curve 1), 5,8-DDMS-HB or 5-DMS-HB LB film (1 layer) with electrolyte composition of 0.1 M KCl aqueous solution containing no electron donors (curve 2), 0.1 M triethanolamine (curve 3), 0.08 M ascorbic acid (curve 4), 0.08 M EDTA (curve 5) and 0.08 mM tetrachlorobenzoquinone (curve 6), respectively. Light source: 500 W xenon arc light (>390 nm).

signal of MSHB LB films is illustrated in Fig. 5. Because of the excellent reproducibility and stability of photocurrents, the present potentiostatic conditions. In the absence of electron donors, no photocurrent was observed upon the onset of illumination. Adding electron donors to electrolyte, the photocurrent showed a rapid rise once the light was turned on, it reached a maximum and kept constant after the illumination time was extended. Turning off the light, the current rapidly decreased down to the zero level. The maxima of photo-current of 5,8-DDMS-HB monolayer in the presence of different electron donors are 180 nA cm^{-2} (triethanolamine), 140 nA cm^{-2} (ascorbic acid), 80 nA cm^{-2} (EDTA), respectively. The photocurrent flowed to SCE electrode, which indicated that electrons were injected from hypocrellin molecules to the conduction band of SnO_2. But when the electrolyte solution contains electron acceptor

tetrachlorobenzoquinone (80 mM), the direction of photocurrent is reversed.

The photovoltage was also measured for 5,8-DDMS-HB and 5-DMS-HB monolayers in the presence of electron donors, and the result is shown in Fig. 6. Curve 1,2 are the photovoltage–time response curves of 5,8-DDMS-HB LB film and 5-DMS-HB LB film (1 layer), the electrode solution was 0.1 M KCl aqueous solution containing 0.1 M triethanolamine. The photovoltage rapidly reached a maximal of 240 mV once the sample was irradiated. During the illumination, the photovoltage kept constant. Turning off the light, the photovoltage showed a slow exponential decay. When electrolyte solution was changed to 0.1 M KCl aqueous solution containing 80 mM tetrachlorobenzoquinone, the photovoltage–time response curve of 5,8-DDMS-HB LB film was shown in curve 3. The photovoltage appeared to be
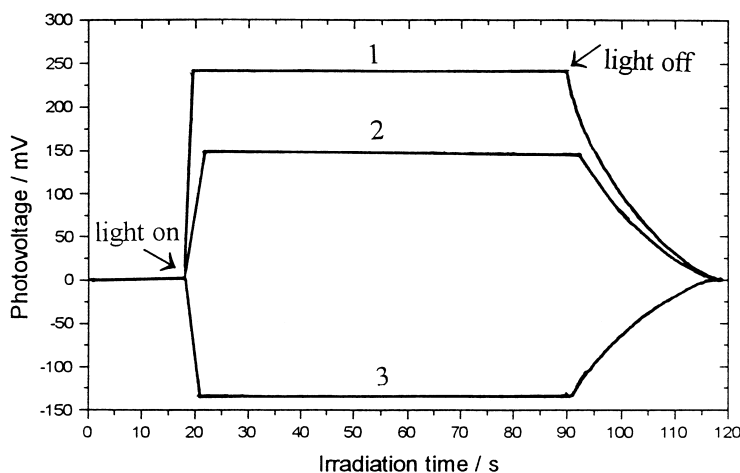
Fig. 6. Typical photovoltaic responses of 5,8-DDMS-HB and 5-DMS-HB. Electrolyte composition: aqueous solution of 0.1 mol/l KCl. The light source was the same as in Fig. 5.

−140 mV at the moment of irradiation and kept constant during the illumination. Turning off the light, the photovoltage also showed slow exponential decay. But, the direction of photocurrent is reversed. The large and stable photovoltage response of MSHB LB films photocell is an excellent property, indicating that MSHB LB film has a potential application value as photovoltage device.

3.4. Mechanism of photoelectric effect

We considered that the photoelectric response of MSHB LB films was due to photoinduced charge transfer mechanism. For our inference, the photocurrent difference of MSHB LB films was compared in either the presence or absence of electron donors/acceptors in the electrolyte solution. The results are shown in Fig. 5. When an electron donor triethanolamine (0.1 M) and an electron acceptor tetrachlorobenzoquinone (1 mM) was added to the 0.1 M KCl electrolyte solution, the photocurrent was greatly increased than that without electron donors and acceptors. The observed photocurrent increase is considered to be essentially the same as the supersensitization [17–19] reported heretofore on other dye–semiconductor combinations. Two possible schemes have been proposed to account for the mechanism of supersensitization. One is the reduction of oxidized dye (MSHB) resulting in the regeneration of photoactive state, and the other is the direct reduction of excited dye (MSHB) leading to the prevention of intramolecular recombination and/or of energy transfer to the conduction electrons. Owing to the presence of electron donors, the excited MSHB[*] abstracts electron from electron donors, giving anion radical MSHB[−], which has stronger ability in donating electron than MSHB[*] has, then the efficiency of electron injection to the conduction of SnO_2 electrode was increased. To 5,8-DDMS-HB, the supersensitization of electron donor triethanolamine is the strongest of the three electron donors that we use. It is noticeable that, different from chlorophyll a LB films electrochemical cell [19], the direction of photocurrent is reversed when the electrolyte solution contains electron acceptor tetrachlorobenzoquinone (1 mM). The reason is that tetrachlorobenzoquinone captures directly the electron of the excited MSHB[*], producing cation radical MSHB[+], leading to the electron injection from the out-circuit to the oxidized MSHB[+], resulting in the reverse photocurrent in comparison with the former condition. Similar phenomenon was observed in the R-phycoerythrin/semiconductor photocell [20].

A schematic diagram for electron transfer processes at a MSHB deposited SnO_2 electrode is illustrated in Fig. 7. When electrolyte solution contains electron donor (D), the electron is flowed from the ground state of D to the excited state of MSHB, then the anion radical MSHB[−] injects electrons to the conduction band of SnO_2. The darked curve is also illustrated in the figure. It shows the direction of electron transfer when the electrolyte solution contains electron acceptor (A), the electron flows from the oxidized
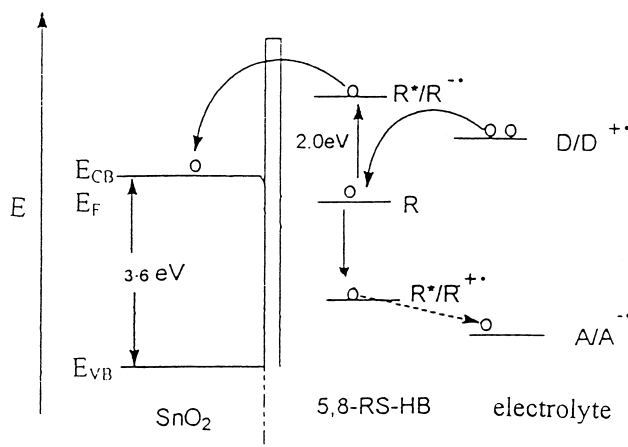

Fig. 7. Schematic diagram for the electron transfer at 5,8-DDMS-HB monolayer on SnO_2 OTE. E_{CB}, E_{VB} and E_F denote the potentials (V vs. SCE) of the conduction band, valence band, and Fermi level of SnO_2, respectively.
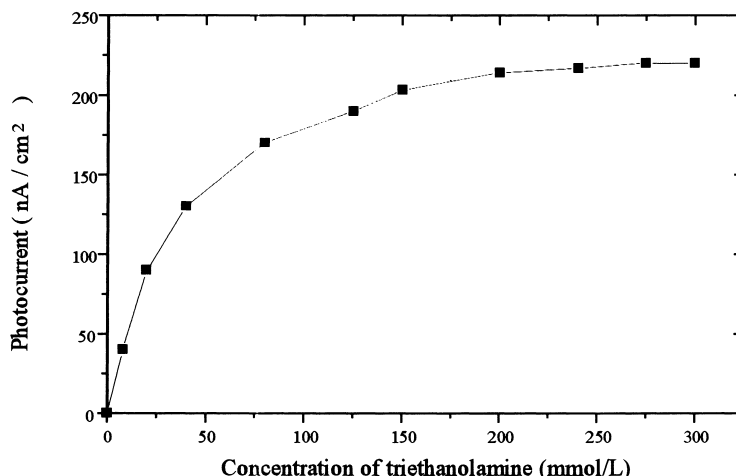
Fig. 8. Dependence of 5,8-DDMS-HB photocurrent on triethanolamine concentration. Electrolyte, KCl 0.1 M (pH 8.8); electrode potential, +0.1 V vs. SCE. The sample was 5,8-DDMS-HB LB film (1 layer) and the light source is the same as in Fig. 5.

state of MSHB to the electron acceptor, then MSHB$^{+\bullet}$ accepts an electron from out-circuit, resulting in the reverse photocurrent. In the absence of an electron donor, the photocurrent remains negligibly small owing to the back transfer of an injected electron and/or an energy transfer followed by quenching, via the thin space charge layer. The coexistence of an electron donor could facilitate the undirectional electron injection by the mechanism mentioned above.

3.5. Effect of electron donor concentration

As described above, addition of triethanolamine leads to an enhancement of the photocurrent due to the excitation of MSHB. Fig. 8 shows the dependence of the photocurrent on triethanolamine concentration, at +0.1 V vs. SCE and pH 5.8. The photocurrent increases with increasing triethano-

lamin concentration and reaches a limiting value at [triethanolamine]~0.3 M. At this moment, the quantum efficiency of photoelectron conversion is the highest.

3.6. Effect of the number of LB film layers and illumination time

With an increase in the number of layers of 5,8-DDMS-HB LB films, on the one hand, the photocurrent should go up due to the increase in the surface density of 5,8-DDMS-HB; on the other hand, the photocurrent would drop because of the increase of film resistance and the probability of charge recombination due to the decrease of the degree of orderly arrangement in the films. Thus, the dependence of the photocurrent on the number of layers would not be directly proportional. The tendency presented in Fig. 9 is in accordance with the above analyses, which indicates that not only
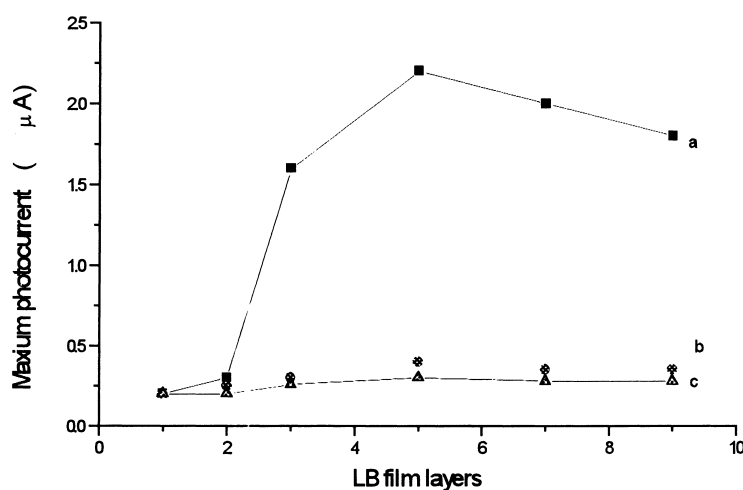

Fig. 9. Dependence of 5,8-DDMS-HB photocurrent on film layers. (a) triethanolamine (0.1 M), (b) ascorbic acid (0.1 M), (c) EDTA (0.1 M). The electrolyte and light source are the same as in Fig. 5.
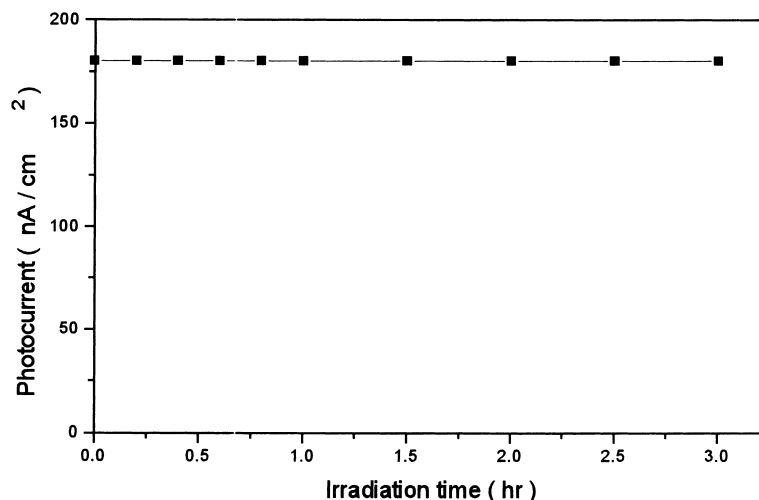
Fig. 10. Time course of 5,8-DDMS-HB photocurrent in the presence of triethanolamine; common electrolyte, KCl 0.1 M (pH 5.8).

the number of layers but also the film resistance and its degree of orderly arrangement would determine the photocurrent of 5,8-DDMS-HB.

To investigate the stability of 5,8-DDMS-HB to illumination, we measured the photocurrent at a 5,8-DDMS-HB monolayer electrode as a function of illumination time, in the presence of triethanolamine in a neutral electrolyte solution. The result is shown in Fig. 10. When the electrolyte contained triethanolamine, the photocurrent did not exhibit any decay characteristics along with the illumination time. This implies an excellent stability of the 5,8-DDMS-HB monolayer in spite of the continuous electron injection to SnO_2 from the excited state of 5,8-DDMS-HB. In this case, apparently triethanolamine is being oxidized quantitatively against the electric charge passing through the interface, as has been reported for other dye–semiconductor system [21]. Also we measured the photocurrent of 5,8-DDMS-HB multilayers electrode as a function of illumination time (data not shown). The result indicated that the photocurrent decreased a little with the illumination time.

As a result, to 5,8-DDMS-HB and 5-DMS-HB, the photoelectric effect of monolayer is better than that of multilayers.

4. Conclusion

5,8-DDMS-HB and 5-DMS-HB have good film-forming properties on the air/water interface. Photocells made from these MSHB LB films have apparent photoelectrochemical effects. The photoelectric response of MSHB LB film photocell can be attributed to photoinduced charge transfer between MSHB molecules and SnO_2 semiconductor. This kind of photocell may generate large and stable photocurrent and photovoltage, and has stable optics property. We could say that 5,8-DDMS-HB and 5-DMS-HB may become one of the most useful organic photoelectric conversion materials.

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