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Fabrication of a Polymer Trilayer Structure Acting as a Photoelectric Cell at Interdigitated Array Microelectrodes

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A convenient fabrication method of a polymer trilayer photoelectric cell has been developed. The device is constructed by electropolymerization of $[Co(C_5H_4CCl{=}CHCHO)_2]PF_6$ and $Fe_2(C_{10}H_8)(C_{10}H_7CCl{=}CHCHO)$ at indium-tin oxide (ITO) interdigitated microarray (IDA) electrodes followed by a coverage with a film of soluble poly(3-n-hexylthiophene). Relationship of redox potentials for the three layers and the photocurrent spectrum indicate the acceptor-sensitizer-donor (A-S-D)-type photoelectron-transfer mechanism.

The acceptor-sensitizer-donor combination is an important electron-transfer system relating to the biological photosynthesis.[1)] Its artificial models in both homogeneous[2)] and heterogeneous systems[3)] have been extensively developed in the present decade. On the other hand, thin polymer films with redox functions have been utilized to realize molecularly functional electrochemical or electronic devices in recent years.[4)] The purpose of this study is to realize an A-S-D-like structure with such functional polymer films. We report here a construction of a polymer trilayer device comprising two redox polymers, poly(cobaltocenium salt) (poly-Cc^+)[5)] and poly[bis(fulvalene)diiron] (poly-BFD),[6)] and one π-conjugated polymer, poly(3-n-hexylthiophene) (PHT).[7)] Facile trilayer fabrication becomes possible by a usage of electropolymerized films, poly-Cc^+ and poly-BFD, PHT that is soluble in non-polar organic solvents and thus easily processable, and ITO-IDA electrodes with 100 fingers.[8)] The action of the device as a photoelectric cell and evidential supports to the A-S-D-type photoelectron transfer mechanism are described.

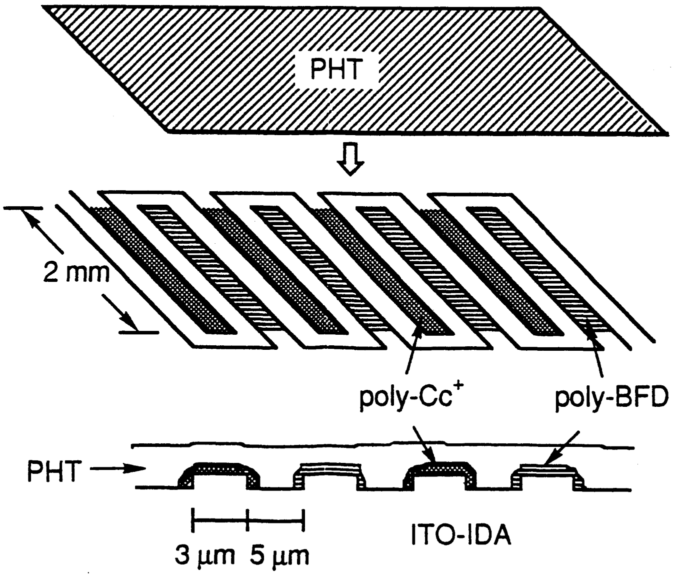

Fig. 1. Schematic illustration of a trilayer device, ITO/poly-Cc^+/PHT/poly-BFD/ITO.

A typical procedure of the trilayer device fabrication is as follows (see Fig. 1). Electrochemical reduction of 0.5 mmol dm^{-3} $[Co(C_5H_4CCl{=}CHCHO)_2]PF_6$ was carried out at half of fingers in ITO-IDA in 0.1 mol dm^{-3} n-Bu_4NBF_4-CH_3CN by consecutive potential scans between -0.4 and -1.9 V *vs*. Ag/Ag$^+$ (10 mmol dm^{-3} $AgClO_4$ in 0.1 mol dm^{-3} n-Bu_4NClO_4-CH_3CN) for 60 cycles at 0.1 V s^{-1}. This electrolysis formed thin coatings (0.1 µm-thickness) of poly-Cc$^+$ exhibiting reversible redox reactions at $E^{0'}$ = -1.37 V *vs*. Ag/Ag$^+$. The other half of the IDA fingers were coated with thin films (0.08 µm-thickness) of poly-BFD by electrochemical reduction of 0.3 mmol dm^{-3} $Fe_2(C_{10}H_8)$-$(C_{10}H_7CCl{=}CHCHO)$ in n-Bu_4NBF_4-CH_3CN by consecutive potential scans between +0.8 and -2.5 V *vs*. Ag/Ag$^+$ (starting from -0.4 V) for 30 cycles at 0.1 V s^{-1}. The poly-BFD/ITO-IDA underwent reversible two-step 1e$^-$ oxidation reactions at $E^{0'}$ = -0.05 and +0.50 V *vs*. Ag/Ag$^+$. The middle layer of the trilayer structure was made by drop-coating a solution of PHT in CH_2Cl_2 on the ITO-IDA doubly precoated with the metallocene polymers as described above. Cyclic voltammetry of PHT/ITO in 0.1 mol dm^{-1} n-Bu_4NBF_4-MeCN showed that the oxidation and reduction of PHT occur at *ca*. +0.5 and *ca*. -2.0 V *vs*. Ag/Ag$^+$, respectively. The energetic diagram of redox potentials for the three layers is shown in Fig. 2. Redox potentials of poly-Cc$^+$ and poly-BFD locate between the conduction and valence bands of PHT; this situation is necessary for the A-S-D combination.

Figure 3 shows current *vs*. voltage characteristics of the device, ITO/poly-Cc$^+$/PHT/poly-BFD/ITO in dark and under a white light irradiation to the PHT side of the device through IR-cut filter with a xenon lamp at 0.35 W cm^{-2} . The device was immersed in CH_3CN during the measurements in order to minimize the effects of temperature variation due to the light irradiation. Considerable negative photocurrents are generated under illumination and much smaller photocurrents flow in positive bias. It should be noticed that

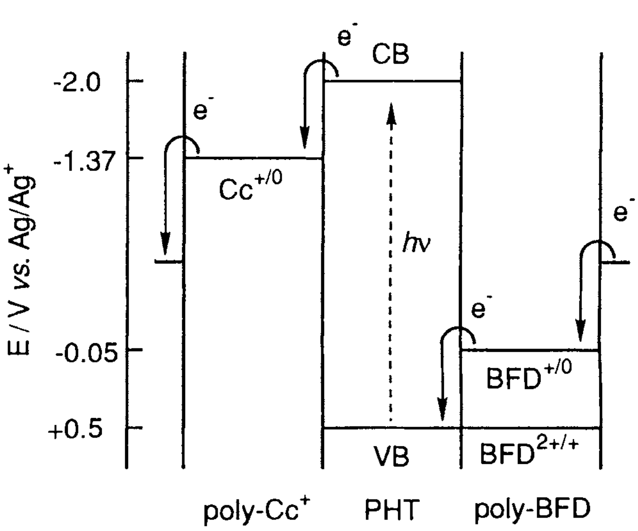

Fig. 2. Energetic diagram and a possible photo-electron transfer mechanism of a trilayer device.

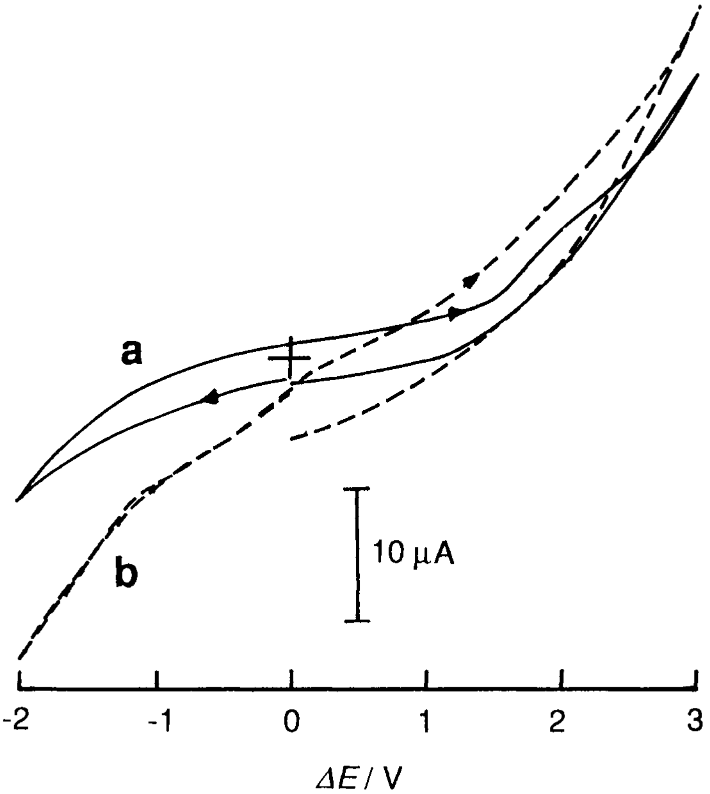

Fig. 3. Current *vs*. voltage characteristics of poly-Cc$^+$/PHT/poly-BFD immersed in CH_3CN at the scan rate of 10 mV s^{-1}: (a) in dark, (b) under white light irradiation at 0.35 W cm^{-2}.

the PHT monolayer structure, ITO/PHT/ITO did not give such negative photocurrents at $\Delta E = 0$ V in the i-ΔE curve under illumination. This indicates that two redox polymer layers with different $E^{0'}$ at both sides of PHT play a crucial role to regulate the direction of photocurrents in the trilayer structure. The direction of photoelectron flow shown in Fig. 3 is consistent with the one given in Fig. 2.

The photo-response of the current at $\Delta E = 0$ V is presented in Fig. 4, where *ca.* 70 nA of the steady-state photocurrents flow. The action spectrum of the steady-state photocurrent at $\Delta E = 0$ V for the trilayer device is shown in Fig. 5a. The incident beam was monochromatized with interference and color filters. The action spectrum shows that high photocurrent values are obtained in the short wavelength region below 460 nm. This is fairly analogous to the absorption spectra of PHT (Figs. 5b,c). This result supports the photocurrent generation mechanism involving photo-activation of the PHT layer as illustrated in Fig. 2. This is understandable since π-conjugated organic polymers have photo-conduction properties.[9] An advantage of the

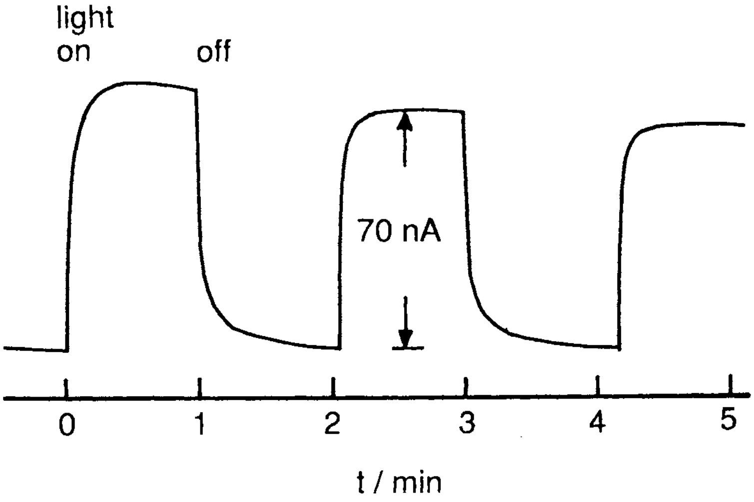

Fig. 4. Photocurrent *vs.* time characteristics of poly-Cc^+/PHT/poly-BFD.

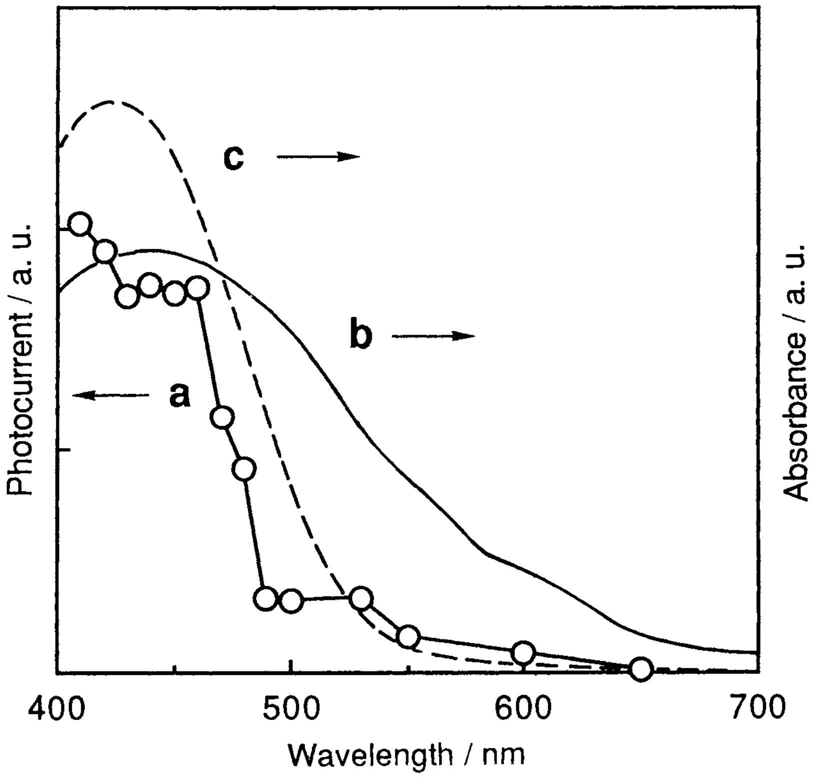

Fig. 5. Photocurrent *vs.* wavelength for the trilayer device (a), and absorption spectra of PHT ((b) film, (c) in CH_2Cl_2). The photocurrent spectrum was normalized for variations in photon flux.

present combination is that the photo-energy is absorbed mostly in the PHT layer since the molar absorption coefficients of d-d transition for poly-Cc^+ and poly-BFD in the visible region are significantly smaller than that of PHT.[4,5] Our preliminary experiments using a trilayer structure, poly-Cc^+/poly(1-ethynylnaphthalene)[10]/poly-[$Fe(C_5H_4CH_2Cl)_2$][5] have not resulted in generation of effective photocurrents. This should be because the potential of valence band for poly(1-ethynylnaphthalene) (*ca.* 0.2 V *vs.* Ag/AgCl)[10] is more negative than the oxidation potential of poly-[$Fe(C_5H_4CH_2Cl)_2$] ($E^{0'}$ = 0.5 V *vs.* Ag/AgCl)[4], and thus the A-S-D type electron-transfer system can not be constructed.

The steady-state photocurrent *vs.* ΔE characteristics of the poly-Cc^+/PHT/poly-BFD device were to examine the photoelectric ability. Photoelectric cell parameters obtained are as follows; j_{oc} = 2.2 µA cm^{-2}, V_{oc} = 2.2 V, F.F. = 0.22, photo-efficiency φ = 0.001%. Although the photo-efficiency is very small probably because of the large gap between the fingers, the V_{oc} value, 2.2 V is fairly large and comparable with the band gap energy of PHT. The photo-efficiency could be improved by designing the composition of polymers and electrodes, and the study is now in progress in this direction.

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