

Rectifying Photocurrent Flow across the Junction of a Polymer Bilayer Film

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Polymer bilayer photoelectrodes consisting of an electron-mediator film as the inner layer and a sensitizer film as the outer layer coated on tin dioxide or gold film electrodes showed rectified photocurrent.

In an attempt to limit the direction of the current flow in a photoelectrode process, bilayer polymer films having an electron-mediator film as an inner layer were studied. We have previously reported that transparent tin dioxide electrodes (SnO_2 OTE) coated with a polymer dye, *i.e.*, linear polyethylenimine containing merocyanine (Mc) as grafted pendants, showed remarkable photocurrent upon illumination of visible light under potentiostatic conditions in the presence of hydroquinone.^{1,2} In this photoelectrochemical system the direction of the photocurrent hinges on the electrode potential as well as the type of the redox species added to the electrolyte solution. Anodic photocurrent observed at a positive electrode potential in the presence of an electron donor is thought to be offset to some extent by the back flow of electrons to any possible acceptor sites in the polymer dye film, *e.g.*, by the electron transfer from the electrode to the oxidized form of the dye (Mc^{++}) that may be formed by electron transfer from the photoexcited dye (Mc^*) to water molecules.³ One of the reasons for the back flow of electrons may be related to a rather weak rectifying effect of the Schottky-type barrier of the SnO_2 OTE.⁴

As an electron-mediating polymer we synthesized linear polyethylenimine covalently linked with anthraquinone- β -carboxylic acid *via* an amide bond. This polymer [PEI-AQ (30 mol%)] was first coated on a SnO_2 OTE from methanol

solution by a spin coating technique. After drying the film thoroughly a polymer dye, linear polyethylenimine covalently linked with Mc [PEI-Mc (35 mol%)]¹ was then spin-coated

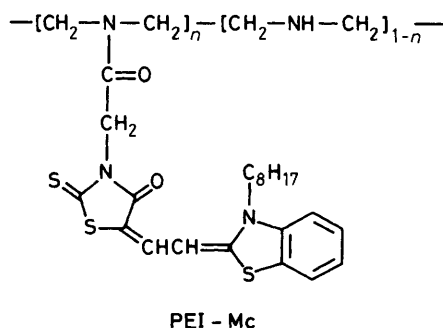
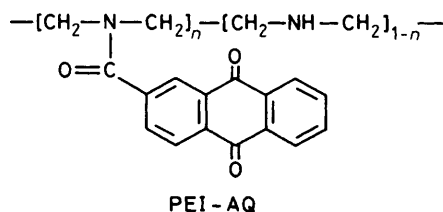
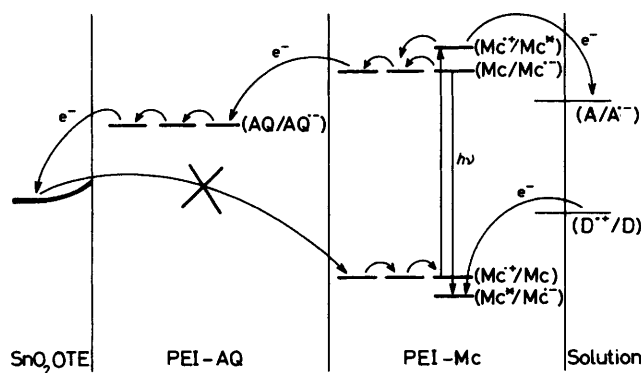


Table 1. Photocurrents observed on polymer dye films (PEI-Mc) with or without the rectifying inner layer (PEI-AQ).^a

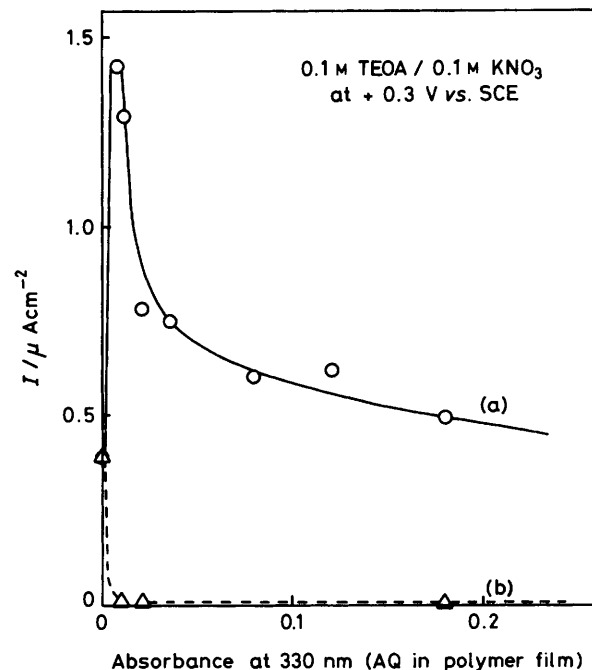
Electrode	With or without rectifying inner layer	Photocurrent ($\mu\text{A cm}^{-2}$) ^c at various potential vs. SCE		
		-0.2 V	0 V	+0.3 V
SnO ₂ OTE	Without	-0.60	-0.25	+0.38
	With	+0.95	+1.10	+1.43
Au film ^b	Without	-1.38	-1.05	-0.55
	With	+0.50	+0.68	+1.05

^a Absorbance at 545 nm for the PEI-Mc layer is 0.17 ± 0.01 ; at 330 nm for the PEI-AQ layer it is 0.01. ^b Prepared by vacuum evaporation of gold on a Pyrex glass plate. ^c Steady-state photocurrents at 545 nm were measured under potentiostatic conditions in the aqueous system containing 0.1 M KNO₃ and 0.1 M TEOA.

**Figure 1.** Schematic illustration of the pathways of electron transfer in the polymer bilayer/SnO₂ electrode.

from chloroform solution onto the PEI-AQ film. The choice of the solvent for the coating is critical to keep the two layers from mixing as well as to prevent pin holes. The thickness of each layer is described in this article in terms of the absorbance at 330 and 545 nm associated with the AQ and Mc groups in the respective polymer layers. Photocurrents were measured under potentiostatic conditions by using a standard electrochemical cell with a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference. The cell was filled with an aqueous solution of 0.1 M KNO₃ containing 0.1 M triethanolamine (TEOA). The solution was purged with argon to expel air. The SnO₂ OTE coated with the polymer bilayer film, used as a working electrode in the electrochemical cell, was illuminated with 545 nm light using a 500-W xenon lamp combined with a monochromator (JASCO CT-10). Comparison of the photocurrent action spectra of the respective single-layer electrodes of PEI-Mc and PEI-AQ confirmed that the photocurrents observed with the bilayer electrode at 545 nm were solely due to the excitation of Mc dye residues, *i.e.*, with PEI-AQ film there was no light absorption and hence no photocurrent was generated at 545 nm.

Figure 1 depicts the relative energy levels and the possible pathways of the electron transfer for the bilayer photoelectrode process. The AQ/AQ^{•-} (or maybe more likely AQ/HAQ) level may act as a mediating level for only the photoanodic electron flow, whereas the back electron flow from the electrode to the polymer dye layer may be impossible. The electron transport through the polymer dye film is considered to be due to the electron self-exchange mechanism as discussed previously.^{1,2} In order to eliminate the additional complexity of back electron transfer, TEOA, a sacrificial donor, was used in the present work in place of

**Figure 2.** Photocurrent vs. thickness of inner layer (a) SnO₂/PEI-AQ/PEI-Mc, (b) SnO₂/AQ in polystyrene/PEI-Mc. The thickness of the inner layer is represented by its absorbance at 330 nm; the absorbance of the outer layer (PEI-Mc) is constant (0.18 at 545 nm).

hydroquinone in the previous studies,^{1,2} although the photocurrent observed was lower in the case of TEOA presumably owing to the higher oxidation potential.

Figure 2 shows the photoanodic current as a function of the thickness of the inner layer. Note that the intercept is the value obtained using the conventional single layer of polymer dye film. The maximum anodic photocurrent was observed at an absorbance of the inner layer of about 0.02. The thickness of the inner layer, calculated roughly from the absorbance, was about 150 Å. The sharp drop of the photocurrent with increasing thickness of the inner layer suggests that the mediating electron transport process is competing with some electron scavenging processes which may involve the back electron transfer from the AQ/AQ^{•-} level to the Mc^{•+}/Mc level. For comparison, a polystyrene film blended with anthraquinone was used as an inner layer. As is evident from Figure 2, the photocurrent was drastically suppressed, and a trace of photocurrent was observed only when the inner layer was extremely thin. A trace of cathodic photocurrent was also observed at negative electrode potentials, suggesting that the

polystyrene blend film merely acts as potential barrier between the SnO₂ OTE and the PEI-Mc film and no rectifying mechanism is operative. The implication of these results is that the films should be swollen with an electrolyte solution as in the case of the PEI-AQ film so that the anthraquinone groups can act as electron mediating acceptor sites in the polymer layer. This is apparently because the movements of the compensating counterions, the solvent, and polymer chains are necessary in the polymer matrices for the electrochemical process to take place.

It should be stressed that, as presented in Table 1, the PEI-AQ/PEI-Mc bilayer photoelectrodes showed no cathodic photocurrent even at negative electrode potentials, which is strong evidence of the rectifying effect of the inner layer. The same effect of the PEI-AQ inner layer applies to gold film electrodes. A gold film electrode coated with a single PEI-Mc layer showed only a cathodic photoprocess pre-

sumably because of the lack of the potential barrier on the metal film surface. On the other hand the bilayer coat on the gold film generated only photoanodic current. These results indicate that a rectifying interface was created on the gold surface which otherwise produces no such rectifying junction with a redox solution under ordinary conditions.

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References

- 1 Y. Morishima, M. Isono, and S. Nozakura, *Chem. Lett.*, 1981, 1149.
 - 2 Y. Morishima, M. Isono, and S. Nozakura, *Chem. Lett.*, 1982, 1427.
 - 3 F. Mizutani, M. Yoshiura, and K. Iriyama, *J. Chem. Soc., Chem. Commun.*, 1980, 393.
 - 4 F. Mollers and R. Memming, *Ber. Bunsenges. Phys. Chem.*, 1972, 76, 469.
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