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SYNTHESES OF SOME POLYMERIC DYES AND SENSITIZED PHOTOELECTRODE PROCESSES BY THE POLYMER-COATED ELECTRODES

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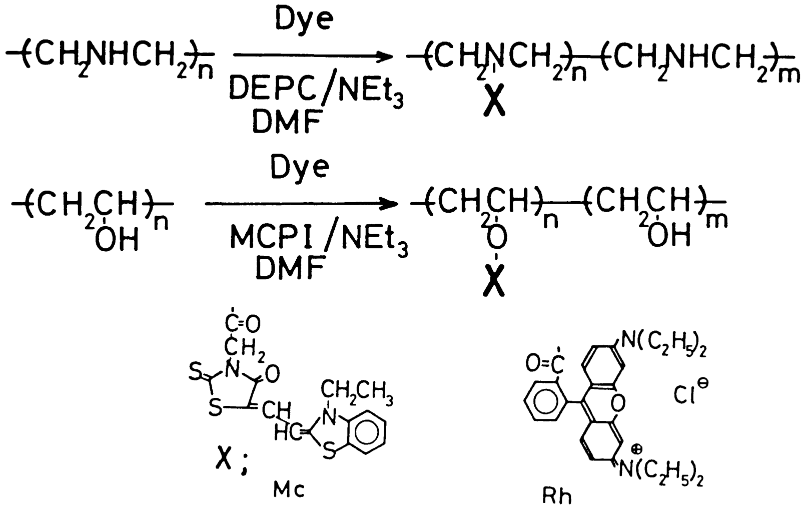
Merocyanine (Mc) and rhodamine B (Rh) were incorporated into polyethylenimine (PEI) and poly(vinyl alcohol) (PVA) by using diethylphosphoryl cyanide or 1-methyl-2-chloropyridinium iodide as the coupling reagents. Under the illumination of visible light, SnO_2 OTE (Optically Transparent Electrode) coated with PEI-Rh film exhibited remarkable spectrally sensitized photocurrent, and Pt electrodes coated with PVA-Mc and PEI-Mc films showed photocathodic currents.

As an extension of a series of our works on the photosensitized electron transfer of the polymers consisting of polycyclic aromatic groups$^{1,2)}$, we have turned our attention to the polymers containing pendant dyes. In particular, our interest has been directed toward the photoelectrochemical properties of these polymeric dyes in the form of thin film. We wish to report in this article on the syntheses of such polymeric dyes and on the preliminary results of the photosensitizing effect of these films in some photoelectrochemical processes.

We have used polyethylenimine (PEI) and poly(vinyl alcohol) (PVA) as backbone polymers and chosen merocyanine (Mc) and rhodamine B (Rh) as pendant dyes. Rh is one of the best investigated sensitizers for the photovoltaic effect of semiconductor electrodes$^{3)}$ and Mc has been receiving an increasing attention$^{4)}$ since a thin-film solar cell with high sunlight engineering efficiency has been reported$^{5)}$.



The carboxylic acid groups of these dyes were used to combine with PEI and PVA through amide and ester bonds, respectively, using diethylphosphoryl cyanide (DEPC)[6] and 1-methyl-2-chloropyridinium iodide (MCPI)[7] as coupling reagents, respectively. A representative example for the synthesis of PEI-Mc is as follows: To a stirred solution of DMF containing 0.2 g of PEI and 0.44 g of Mc were added 1 ml of DEPC and 1 ml of triethylamine. The mixture was stirred at 70°C for 48 h. After DMF was evaporated under reduced pressure, the product was precipitated from a methanol solution into an aqueous 5-% Na_2CO_3, washed with pure water, ether, and tetrahydrofuran, successively, and then dried. The content of Mc in the polymer was determined to be 13 mol% by N/S ratio in elemental analysis and confirmed by 100-MHz NMR spectra. In all other cases the reactions were carried out in the similar manner. The purifications of PEI-Rh and PVA-Rh were mainly resorted to dialysis against water for 10 days. The details of the syntheses, purifications, and characterizations of these polymers will be reported in the subsequent article[8].

The cast films of the polymeric dyes were prepared on the SnO_2 OTE or Pt plate electrode from DMF solutions of known concentration. Evaporation of the solvent left well adhered polymer films on the substrates. SnO_2 OTE used in the present study were prepared according to a literature[9]. The ohmic contact was made with indium solder.

For the photoelectrochemical measurements with the Pt electrodes coated with the polymer film, a conventional three-electrode, two-compartment cell was used: One compartment was equipped with Pt wire as a counter electrode and filled with phosphate buffer (pH 6.68) containing 0.1 M triethanolamine, and the other compartment with a quartz window was equipped with a Pt plate working electrode and a SCE reference electrode and filled with 0.1 N HCl. These two compartments were connected with a KCl salt bridge. After both compartments were deoxygenated by flushing Ar, the polymer-coated Pt working electrode was irradiated with a 500-W xenon lamp with a cut-off filter (UV-35, Toshiba Glass Co.). Photocurrents were measured with a Yokogawa-Hewlet-Packard Model 4304B Electrometer. The working electrode was potentiostatted at 0.05V vs SCE by a Hokuto Denko Potentiostat Model HA104. Fig.1 shows the photoresponse of the Pt electrode coated with PVA-Mc (Pt/PVA-Mc). On illumination, the rest potential of the photoelectrode was shifted in the anodic direction. Cathodic photocurrent was observed under the potentiostatic condition. Table I contains the results for the various samples. For the preparation of Pt/M-Mc, a solution of the monomer model of PEI-Mc applied on the electrode had to be evaporated as quickly as possible by blowing the hot air to prevent the crystals from growing too large in size, but still neither uniform nor well adhered

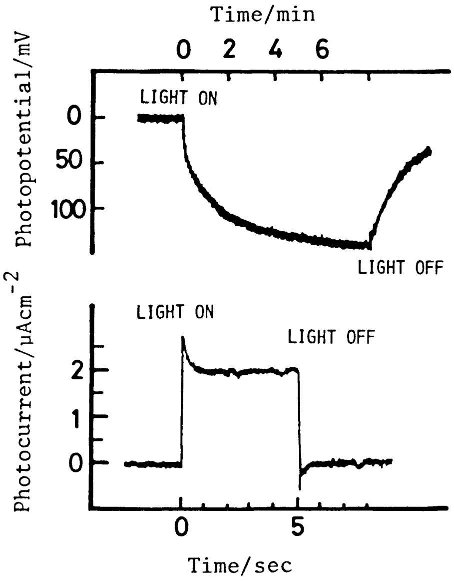


Fig.1. Photoresponse of Pt plate electrode coated with PVA-Mc film : filter, UV-35(λ>350nm); Photocurrent was measured under the potentiostatic condition(0.05V vs SCE).

Table I Cathodic Photocurrent at Pt Electrode Coated with Various Merocyanines[a)]

Merocyanine	Photocurrent/μAcm^{-2}
M-Mc[b)]	0.52
PEI-Mc(13 mol%)	1.43
PVA-Mc(25 mol%)	2.00

a) Filter, UV-35(λ>350nm); Electrode potential, 0.05 V vs SCE.

b) Monomer model for PEI-Mc (diethylamine was used as a monomer model for PEI).

film could be obtained. The photocurrent at the Pt/M-Mc had a tendency to decrease during the measurement because the fine crystals of the dye easily scaled off the electrode surface. Therefore, the initial maximum value was recorded in Table I.

Fig.2 shows the spectral-sensitized photocurrent at the SnO_2 OTE coated with PEI-Rh film. PEI-Rh film, insoluble in water, adhered so firmly on the SnO_2 OTE surface that it never scaled off during the experiment. The photocurrent was measured with a single compartment cell containing 0.1 M KNO_3 and 1 × 10^{-3}M hydroquinone. The results are presented in Table II. The remarkable sensitized photocurrents were observed with the SnO_2 electrodes coated with polymeric dyes as compared with those sensitized by the solutions, although the quantitative estimation of the quantum efficiency has yet to be done. In general it seems to be commonly believed that only the dye molecules directly adsorbed on the surface of the electrode are responsible for the photocurrent[10-12)]. The application of insoluble dye multilayers on the electrode has generally been unsuccessful mostly because of the high ohmic resistance, and an increased self-quenching[3)]. In order to overcome the former problem, some kind of electron relay mechanism should be operative through the film, while to minimize the latter problem, each dye molecule may have to be separated in a rigid medium in such a distance that the excited state can not be dissipated through mutual interactions whereas the high efficiency of the energy migration between the dyes remains intact.

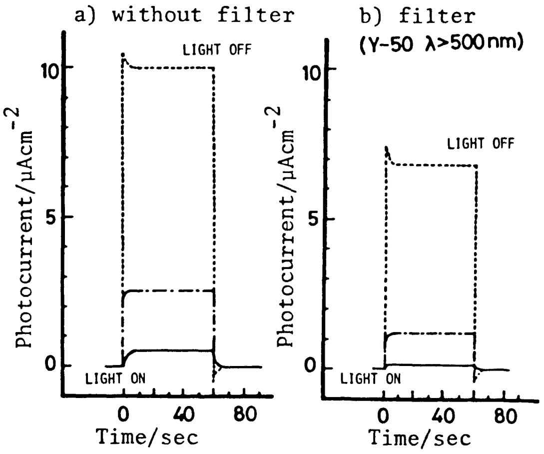


Fig.2. Photocurrent vs time at SnO_2 OTE; $1x10^{-3}$M hydroquinone/0.1M KNO_3: 0.5V vs SCE; 500W xenon lamp;———, without dye;—·—, Rh in solution ($5x10^{-5}$M); -----, PEI-Rh film on the electrode($3.4x10^{-5}$mmol/cm^2).

Table II Dye-Sensitized Photocurrent at SnO_2 OTE[a)]

Sensitization	Photocurrent/μAcm^{-2}	
	without filter	with Y-50(λ>500nm)
without	0.45	0.07
Rh in solution(5×10^{-5}M)	2.5	1.2
PVA-Rh(71 mol%) in solution(1×10^{-5}M)	0.77	0.30
PEI-Rh(52 mol%) film(3.4×10^{-5} mmol/cm^2)	10.0	6.8
PEI-Mc(13 mol%) film(5.6×10^{-5} mmol/cm^2)	5.5	2.3

a) 0.1 M KNO_3, 1×10^{-3} M hydroquinone, 0.5 V vs SCE.

A search for these possibilities with the polymeric dye films may be a feasible approach. It should be emphasized that the most striking features of the polymeric dye-coated electrodes are simplicity of fabrication and stability in the handling.

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