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ENHANCED QUANTUM EFFICIENCY OF THE SENSITIZED PHOTOCURRENT OF ZnO ELECTRODE BY THE J-AGGREGATE OF CYANINE DYES

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Sensitized photocurrent spectra of ZnO electrode show distinct peaks at the J-band of the two cyanine dyes, 1,1'-diethyl-2,2'-quinocyanine chloride(dye I) and 3,3'-dimethyl-9-phenyl-4,5,4',5'-naphthothiacarbocyanine chloride(dye II). Quantum efficiencies of the anodic photocurrent by dye I and the cathodic photocurrent by dye II have high values of about 1.0 under suitable conditions.

The mechanism of electron transfer and resonance transfer processes between the solids and dye molecules adsorbed on them is an interesting problem for physical chemists.1) Recently, several reports have been published on the accurate determination of the quantum efficiency and action spectrum of the dye-sensitized photocurrent of ZnO electrode by electrochemical techniques.2) The aggregation of cyanine dyes is well known in the field of photographic science, and the so-called J-aggregate has various photochemically interesting properties. Most part of the previous works on the spectral sensitization by the J-aggregate has been limited to the silver halide emulsion.1) Outside of it, no systematic study has been carried out yet. We think that the investigation of the sensitization mechanism of the solids by the molecular aggregates will offer some significant information to the design of the model system of photosynthesis. In this letter, we report on the spectral sensitization of ZnO thin film electrode by the J-aggregates of two cyanine dyes.

A c-axis oriented film of ZnO was deposited on a commercial Nesa glass (Matsuzaki Shinku Ltd.) by using a magnetron sputtering technique of Kawabata.3) Film thickness of ZnO was about 3 μm and an average donor density after a vacuum treatment was estimated to be ca. 10^{17} to 10^{18} cm^{-3}. The ZnO film electrode(working electrode) was mounted as a window of an electrochemical cell, with the ZnO side facing the electrolyte solution to avoid the absorption of incident photons by the dye molecules in the bulk solution. A platinum plate and a saturated KCl Ag/AgCl electrode served as the counter electrode and the reference electrode, respectively. The potential of the ZnO electrode is expressed vs. the Ag/AgCl electrode. As the light source, a 500 W xenon arc lamp(Ushio Denki Ltd.) was used in combination with a Shimadzu grating monochrometer having a transmittance half width of ca. 5 nm and a cut-off filter VY-45(Toshiba Ltd.). Photocurrents were measured with an electronic picoammeter Type TR-8641(Takeda Riken Ltd.) under potential-controlled condition by means of a Hokuto Denko potentiostat Model HA-104. The solution, which was flushed with high purity nitrogen before the measurement, contained 0.05-0.2M KCl as a supporting electrolyte and 5×10^{-4}-10^{-3}M dyes. The action spectrum of sensitized photocurrent was corrected so that it corresponds to the values for a uniform number of photons incident to the electrode at all wavelengths. The number of photons was determined by the ferrioxalate actinometry at 365 nm[4)] together with a photometer Type IL-600(International Light Ltd.). It was about $6\times10^{14}\mathrm{cm}^{-2}\mathrm{s}^{-1}$ at 500 nm. The absorption spectrum of the dye adsorbed on ZnO was recorded on a Shimadzu spectrophotometer Model MPS-5000. A dyed sample was prepared by immersing a ZnO film in the electrolyte solution for one hour and then wiping off the excess solution on the surface. A dye-free ZnO film was used as reference. Thus, the quantum efficiency of photocurrent is obtained by the quotient (photocurrent/rate of photon absorption).

Figure 1 gives absorption spectra of the bulk solution and the adsorbed layer of dye I. The longest wavelength maxima of them at 574 and 575 nm correspond to the J-bands of dye I in the solution and on ZnO, respectively. There exist two peaks at the shorter wavelength region in both spectra(shorter-wavelength bands). Figure 2 shows typical action spectra of both anodic and cathodic photocurrents. There are three peaks around 575, 530 and 495 nm, which are responsible for the J-band and the shorter-wavelength bands, respectively. The J-band has larger quantum efficiency of the anodic photocurrent than the other bands. The absolute value of them is rather sensitive to the pretreatment conditions of the ZnO electrode. In the repeated experiments, they were in the range of 0.3-1.0(575 nm),0.1-0.5(530 nm) and 0.2-1.0(495 nm) at the electrode potential of 0.6 V. It is found that an addition of a small amount of 2-(p-dimethyl-aminostyryl)-benzothiazolinium iodide, a well-known supersensitizer, substantially enhances the anodic photocurrents at all three peaks when the quantum efficiencies for the host dyes are rather small. The quantum efficiency of the cathodic photocurrent at the J-band in Fig. 2 is 0.01.

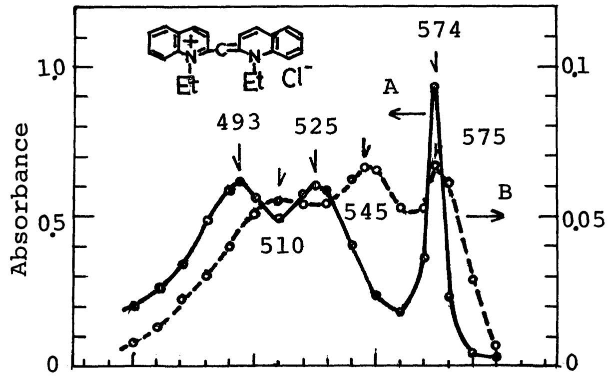

Fig. 1. The absorption spectra of dye I.
A; Bulk solution (0.2M KCl,1×10^{-3}M dye, pH 4.6). Light pass is 100μm.
B; Dye layer adsorbed on ZnO.

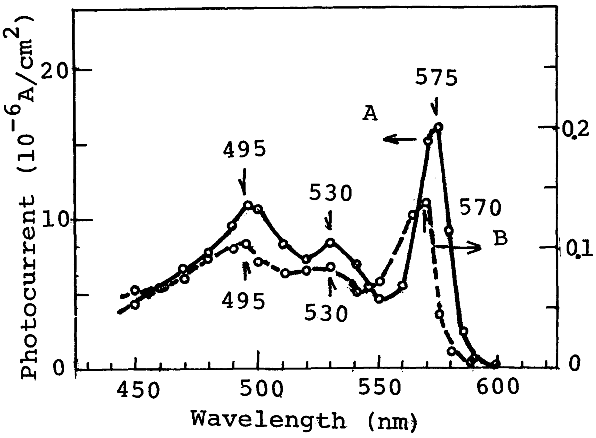

Fig. 2. Action spectra of dye I layer at the ZnO electrode.
A; Anodic photocurrent at the electrode potential 0.6 V.
B; Cathodic photocurrent at the electrode potential -0.5 V.
Incident photon number is $6.6\times10^{14}/\mathrm{cm}^2\mathrm{s}$.

The J-aggregate of dye II has scarecely been studied until now. Figure 3 gives absorption spectra of the bulk solution and the adsorbed layer of dye II. The absorption maxima of them are at 690 and 693 nm, respectively(J-band), which are both red-shifted from a monomer band at 603 nm observed in the methanolic solution. Figure 4 shows typical action spectra of both anodic and cathodic photocurrents. They show a suitable match with the absorption spectra. The quantum efficiencies at the J-band(705 nm) are 0.004 for anodic photocurrent and 0.5-1.0 for cathodic one.

Dependences of the photocurrent due to the J-band excitation on the electrode potential are illustrated in Fig. 5. In dye I, the anodic photocurrent rises at -0.2 V and increases with the anodic polarization until saturation is reached at ca. 0.5 V. On the contrary, the cathodic photocurrent is far larger than the anodic one in dye II. Cathodic photocurrents by both dyes increase by twice or so on bubbling of air. The open-circuit photovoltage detected by an electrometer Type TR-84M(Takeda Riken Ltd.) was negative for dye I and positive for dye II, in accordance with the enhanced anodic and cathodic photocurrents of these two dyes.

The origin of the shorter-wavelength bands in Figs. 1 and 2 is not so obvious. It seems plausible at sight that these bands are responsible for the monomer and dimer, respectively. However, we have found that another two peaks due to the J-aggregate are frequently observed at almost the same spectral region in the absorption spectrum of the concentrated solution of this dye.[5] Former studies of Tributsch and Gerischer on the spectral sensitization of ZnO electrode did not notice the contribution of these peaks.[6,7] There may be a possibility that when the shorter-wavelength bands are excited, carrier injection will take place after the radiationless energy transfer to the J-band.

Now, to interprete the enhanced quantum efficiency of anodic photocurrent in dye I, we shall take the excitation transfer between component molecules by the molecular exciton mechanism into consideration. The sharp absorption band and

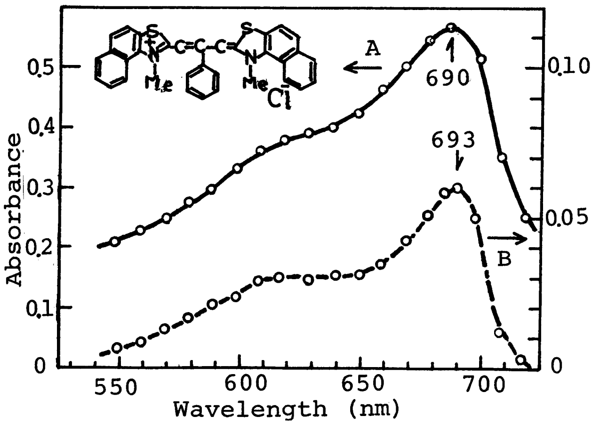

Fig. 3. The absorption spectra of dye II.

A; Bulk solution (0.05M KCl, 5×10^{-4}M dye, 10vol% methanol, pH 6.0). Light pass is 100μm.

B; Dye layer adsorbed on ZnO.

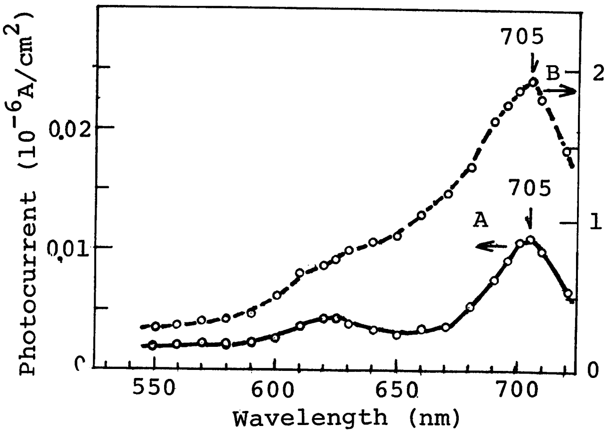

Fig. 4. Action spectra of dye II layer at the ZnO electrode.

A; Anodic photocurrent at the electrode potential 0.6 V.

B; Cathodic photocurrent at the electrode potential -0.6 V.

Incident photon number is 5.5×10^{14}/cm^{2}s.

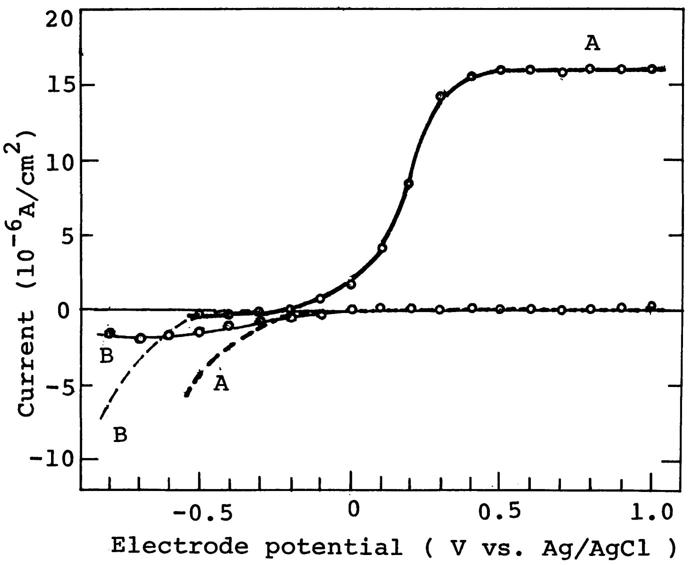

Fig. 5. Photocurrent-potential curves at the excitation of J-band.

A; Dye I at 575 nm.

B; Dye II at 705 nm.

— — — — — The background dark current.

resonance fluorescence of the J-band correspond to a large spreading velocity of molecular exciton. So that, the J-band seems to have originally an ability to harvest the excitation energy to the sensitization center where carrier injection is preferable, in contrast to the monomeric state whose excitation energy localizes within an individual molecule. Molecular exciton will ionize on collision with some crystal defects or impurity molecules and inject an electron into the conduction band of ZnO. The supersensitizer molecule will capture a positive hole and facilitate the ionization of exciton.

The large cathodic photocurrent and reduced anodic photocurrent by dye II will correspond to the rather lower exciton level than dye I. Therefore, we may expect a possibility of hole injection into the valence band of ZnO as an additional mechanism of cathodic photocurrent. The increase of dissolved oxygen concentration will be effective for cathodic photocurrent as it will oxidize the exciton.

On the practical aspect, enhanced quantum efficiency seems to be significant for us. Applications to the electrochemical solar cell and to the design of the photosynthesis system are now in progress.

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