

SPECTRAL SENSITIZATION OF PHOTO-ELECTROCHEMICAL REACTIONS
OF CADMIUM SULFIDE SINGLE CRYSTAL ELECTRODE

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The spectral sensitization of photo-electrochemical reactions of cadmium sulfide single crystal electrode with rhodamine B and quinoxaline has been investigated. The photosensitive region of the electrode could be extended to longer wavelength by addition of each dye into the electrolyte solution.

Investigations of semiconductor electrodes have recently been carried out extensively.¹⁾ Until the mid-1960's, the cadmium sulfide single crystal as an electrode material was studied only by Williams²⁾ and Tyagai,^{3),4)} with regard to the photovoltaic effect and the potential distribution at the electrode-electrolyte interface, respectively. In the past few years, the cadmium sulfide electrode has drawn attentions of a number of investigators.⁵⁾⁻⁹⁾

The spectral sensitization of semiconductors by organic dyes, one of the most important problems in the fields of photography and electrophotography, has been studied by means of electrochemical arrangements where semiconductor single crystals serve as electrodes. The advantages of the electrochemical method are i) single crystals of semiconductors, whose energy band structure, surface orientation and the surface area exposed to the electrolyte solution are known clearer, are employed; ii) quantitative discussion is possible through the direct measurement of current flowing across the semiconductor-electrolyte interface in the course of the sensitization process; and iii) the effect of coexisting substances can easily be investigated simply by adding them to the electrolyte solution.

Cadmium sulfide (CdS) is a material widely utilized in the photo-electric conversion system such as the photometer and the solar cell. Because of the rather large forbidden band width (2.4 eV), its photosensitivity is restricted in the wavelength region below 520 nm, and the spectral sensitization has been studied through measurements of photoconductivity¹⁰⁾ in the aim of extending the photosensitivity towards longer wavelengths.

Spectral sensitization of CdS single crystal by means of electrochemical method was once attempted by Tributsch et al. using chlorophyll as the sensitizing dye,¹¹⁾ where no sensitized current was observed. Otherwise, spectral sensitization of CdS has not been reported within the framework of the electrochemical measurement system.

In the present study we could observe the spectral sensitization of CdS single crystal by two sorts of organic dyes in the electrochemical system, and obtained some informations concerning the mechanism of the spectral sensitization on the basis of experimental results.

CdS single crystal (n-type) employed in the present study was supplied by Teikoku Tsushin Kogyo Co., Ltd. The crystal was undoped, with the carrier density of $7.4 \times 10^{16} \text{ cm}^{-3}$ (determined by measurements of the Hall effect). The form of the electrode was a wafer having the dimension of $10 \times 10 \times 1.0 \text{ mm}$. In order to establish an ohmic contact with the conducting wire, indium was vacuum-evaporated or electroplated onto a small part of the electrode surface. The crystal face exposed to the electrolyte solution was polished with alumina powder, etched in HCl, and then washed with water.

Platinized platinum electrode, with the apparent surface area of 10 cm^2 , was used as the counter electrode. The electrode potential of CdS electrode was controlled by means of an external dry cell, and the electrolytic current was detected by measuring the potential drop at a constant-value resistor connected in series in the circuit, by means of a Keithley Electrometer 610 C.

The light source was a 500 W xenon lamp (Ushio Electric), and the wavelength of the illuminating light was selected with the use of a monochromator (Shimadzu) or color filter glasses (Toshiba Kasei).

The illumination of the electrode-electrolyte interface was given either through the bulk of the CdS electrode attached as a window of the cell or via a quartz window and the dye-containing electrolyte solution. In the latter case, the thickness of the solution layer between the quartz window and the electrode surface had to be sufficiently small and be kept constant.

As the sensitizing dyes, rhodamine B and 1,1'-diethyl-2,2'-quinocyanine iodide were employed. The electrolyte was either 0.2 M Na_2SO_4 or 1 M KCl aqueous solution. All chemicals used were reagent grade.

Sensitization with Rhodamine B

Under anodic polarization, the photocurrent of CdS electrode is produced in the wavelength region below 520 nm, which coincides with the forbidden band width of CdS (2.4 eV). The electrode reaction corresponding to the intrinsic photocurrent has been assigned to the dissolution of cadmium in the form of Cd^{2+} into the solution, as a result of trapping of holes in the valence band produced by the band-to-band transition to sulfur.^{2),5)}

By the addition of rhodamine B into the electrolyte solution, a further photocurrent was observed in the spectral region of dye absorption. The solid curve in Fig. 1 indicates the anodic photocurrent in the presence of rhodamine B in the electrolyte solution as a function of the wavelength of the incident light. The broken curve represents the photocurrent after the correction for the light absorption by the dye within the solution layer between the quartz window and the electrode surface. Since the peak of the latter curve nearly coincide with that of the absorption spectrum of rhodamine B, we can conclude that the photocurrent was produced as the consequence of light absorption by dye.

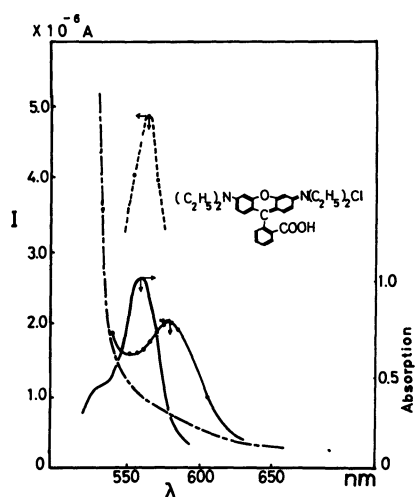


Fig. 1. Spectral distribution of photocurrent with the addition of rhodamine B into the electrolyte solution. Illumination: through quartz window. Rhodamine B : 5×10^{-5} mol/l, Na_2SO_4 : 0.2 mol/l.

---: blank photocurrent without dye
 —○—: photocurrent with dye
 -·-·-: photocurrent after the correction for light absorption by dye
 —: absorption curve of dye (10^{-5}M)

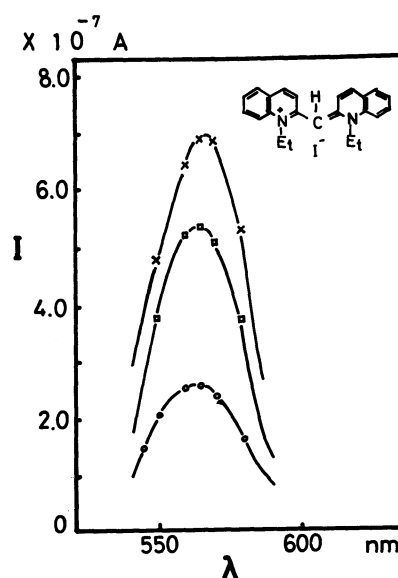


Fig. 2. Spectral distribution of photocurrents after subtraction of the blank photocurrent with the addition of 1,1'-diethyl-2,2'-quinocyanine into the electrolyte solution.

(dye concentration)

—○— : 3.0×10^{-5} mol/l
 —□— : 7.5×10^{-5} mol/l
 —×— : 1.0×10^{-4} mol/l

The magnitude of the sensitized photocurrent (the anodic photocurrent produced in the spectral range of dye absorption) was not perfectly reproducible from one measurement to another, even where we supposed that their experimental conditions were kept the same. This may suggest that the adsorption of rhodamine B is greatly affected by a minor change, introduced in the etching process, in the surface state of the CdS electrode, owing presumably to the weak adsorbability of the dye. A similar situation has been reported by other investigators on GaP electrode.^{1), 12)}

The dependence of the sensitized photocurrent on the dye concentration was measured. The sensitized photocurrent increased with the increase in dye concentration and gradually approached a saturation value. Such a behavior is supposed to have a correlation with the adsorption characteristics of rhodamine B. A rough measurement of the adsorption isotherm of rhodamine B - CdS powder system confirmed this assumption. A detailed investigation in this respect will be reported elsewhere.

Sensitization with 1,1'-diethyl-2,2'-quinocyanine

As the solubility of this dye in water is rather small, the dye was first dissolved in a small quantity of ethanol and then diluted with water. In its absorp-

tion spectrum, together with the two main absorption bands, i.e., the monomer band at 530 nm and the dimer band at 490 nm, the third band appears at about 575nm, either by increasing the dye concentration or by adding a strong electrolyte such as KCl into the solution. The latter band is assigned to the J-aggregate absorption band, and its formation is associated with the decrease in the absorption intensity of the monomer and the dimer bands.

Considering the photosensitivity region of CdS single crystal, it is expected that the spectral sensitization, if any, with this dye can more easily be detected in the J-aggregate region.

Curves in Fig. 2 show the anodic photocurrents after subtraction of the blank photocurrent as a function of the wavelength of the incident light, with addition of 1,1'-diethyl-2,2'-quinocyanine into the electrolyte (1 M KCl) solution. Each of them has a maximum at around 568 nm, which nearly coincides with the J-aggregate absorption peak.

Contrary to the case of rhodamine B, the detection of spectral sensitization by quinocyanine was almost always possible regardless of the condition of surface pretreatment of the electrode, suggesting presumably the strong adsorbability of this dye onto CdS.

The effect of KCl addition is illustrated in Fig. 3. With a constant dye concentration, the sensitized photocurrent increases with the increase in the quantity of KCl added to the electrolyte solution. The sensitized photocurrent in the J-band showed a rapid decay with time within a few minutes after the set-in of illumination, and reached a stationary value, while for the blank photocurrent such a behavior was not detectable. Figure 4 illustrated this situation. Such a phenomenon could be elucidated by taking into account the oxidation of aggregated dye molecules through the sensitization process (electron injection to the electrode), and the small desorbability of the oxidized species or the slow regeneration of the dye molecules from the oxidized species.

We continued illumination until the stationary sensitized photocurrent was reached, and, turning off the light, kept the system in darkness for a constant period of time and then re-illuminated the interface. The value of the sensitized photocurrent appearing at the set-in of re-illumination depended upon the darkness period, as shown in Fig. 4. This behavior would be a further support for the oxidation-regeneration hypothesis for the spectral sensitization process in this system. The identification of the oxidized species of dyes in terms of the spectral sensitization, however, has never been reported so far. We are at present carrying out investigations in this point of view.

Effect of Reducing Agents

Both for rhodamine B and the cyanine dye, the addition of hydroquinone, which does not show any absorption in the visible region, into the dye-containing electrolyte solution remarkably enhanced the sensitized photocurrent (supersensitization), while the dark current undergoes no detectable change. This fact could be accounted for by assuming that hydroquinone regenerates the dye molecules converted to the oxidized species in the course of the sensitization process, and brings about an increase in the effective dye concentration at the cadmium sulfide electrode surface.

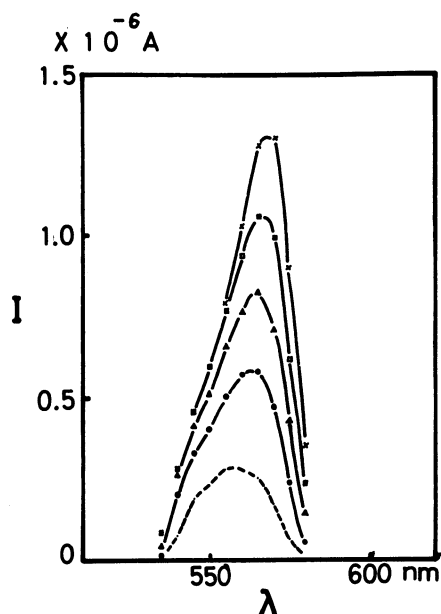


Fig. 3. Effect of KCl addition on the sensitized photocurrents by 1,1'-diethyl-2,2'-quinocyanine. The blank photocurrent was subtracted from observed photocurrents. The concentration of the dye: 10^{-3} mol/l.

--- : KCl 0.01 mol/l
 —○— : KCl 0.10 mol/l
 —△— : KCl 0.20 mol/l
 —□— : KCl 0.50 mol/l
 —x— : KCl 1.00 mol/l

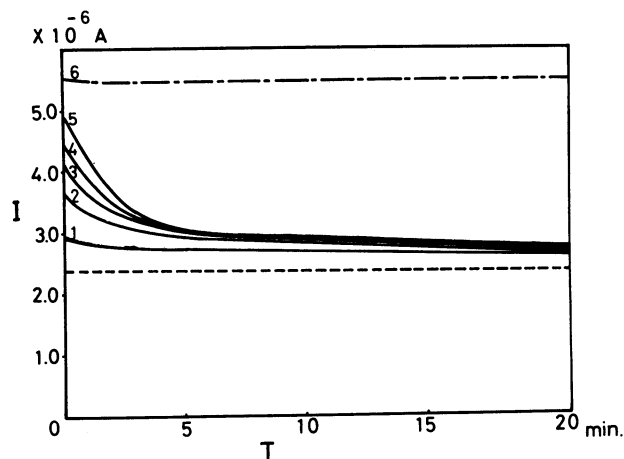


Fig. 4. Decay characteristics of the sensitized photocurrent by 1,1'-diethyl-2,2'-quinocyanine. The concentration of the dye is 1.0×10^{-4} mol/l for all measurements except the blank photocurrent. KCl : 1 mol/l. The wavelength of illumination is 560 nm.

1 : dark period 1 min.
 2 : dark period 5 min.
 3 : dark period 10 min.
 4 : dark period 20 min.
 5 : dark period 60 min.
 6 : addition of hydroquinone (10^{-3} mol/l).
 ---: the blank photocurrent.

In the case of 1,1'-diethyl-2,2'-quinocyanine, the decay characteristics of the sensitized photocurrent decreased or even disappeared by addition of hydroquinone, as shown by curve 6 in Fig. 4. This fact suggests that hydroquinone, being incorporated into the aggregated layer of dye molecules, rapidly reduces the oxidized species produced through the sensitization process and regenerates the original dye molecules.

Gerischer and Tributsch¹³⁾ reported on the ZnO electrode that supersensitization is brought about as a result of an adduct formation between the excited dye molecule and the reducing agent and subsequent increase in the tunneling probability of the excited electrons towards the semiconductor. As for whether the cause of supersensitization is the generation of the dye or the adduct formation, we cannot yet distinguish the possible one from another at the present stage.

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