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Chelation Effect of Alizarin Dyes on the Semiconductor-Aqueous Solution Systems

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Synopsis. The dye-sensitized photocurrents produced by some semiconductor (titanium dioxide single crystal or zinc oxide sinter) in electrolyte solutions containing alizarin dyes were studied. The photocurrent was concluded to be caused by the sensitization of the alizarin dyes chelated to the semiconductor electrodes.

When an *n*-type semiconductor is anodically polarized, a current is induced by light whose photon energy is greater than the band gap of the semiconductor.[1] In cases where the electrolyte solutions contain cyanine dyes or xanthene dyes, photocurrents arise by light absorbed by the dyes.[2] In many cases, such a dye-sensitized anodic photocurrent is believed to be caused by the electron transfer from the excited dye adsorbed on the electrode surface into the electrode.[3–7] However, the effect of light on the dye in the bulk of the solution to produce an electrochemically active species might also be present.[7] These two mechanisms cannot be distinguished experimentally, if one uses a dye-electrolyte solution, as has been done by most previous authors.

This paper presents some results on the sensitized photocurrent by alizarin dyes chelated to the semiconductor electrodes. Very recently, similar work was reported by Danzmann and Hauffe, mainly on azo dyes and zinc oxide single crystal.[8]

Experimental

Titanium dioxide single crystal disks with the (001) face and zinc oxide sintered disks, both *n*-type semiconductors, were used. The structure of the electrodes was mostly the same as described previously.[6,9] The surface of the TiO_2 disk was scratched by rough silicon carbide abrasive to make the surface area large. The potential of the semiconductor electrodes *vs.* the reference electrode (SCE) was controlled by a Hokutodenko HA-101 potentiostat and the current was measured with the aid of a Yokogawa Hewlett Packard LS-2D electrometer. A 500 W xenon lamp (Ushio electric Inc.) was used as a light source, the light being monochromatized by using a Japan Jarrell-Ash, 0.25 m, Ebert type monochromator. The solutions contained 0.2 mol/l Na_2SO_4 as the supporting electrolyte. Oxygen was removed by bubbling with high purity nitrogen gas before measurements. Alizarin, Alizarin S, and quinalizarin were used as the photosensitizer. They belong to the mordant dyes and are known to make lakes with metal oxides. A Simadzu SL-50L spectrometer was used for the measurements of absorption spectra.

Results and Discussion

When TiO_2 powder was added into an aqueous solution of alizarin at the pH of 4.3, the powder colored reddish purple. Figures 1 a) and b) show the absorption spectrum of an aqueous solution of alizarin and that of a potassium bromide disk containing the colored powder, respectively. The absorption spectrum of an ethanol solution of titanium tetrachloride and alizarin nearly coincided with that of the colored TiO_2 powder. It is therefore concluded that the coloration is caused by a chelate compound formed between alizarin and titanium ion at the surface of the TiO_2 powder. The absorption spectrum of the chelate compound on a TiO_2 single crystal was measured through the single crystal, which was similar to that formed on the powder.

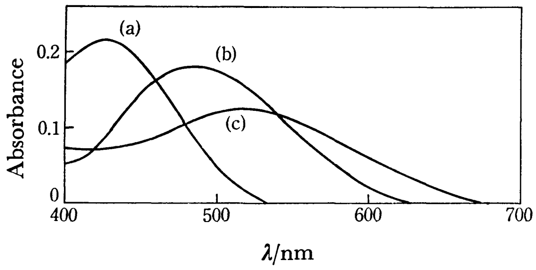

Fig. 1. Absorption spectra of alizarin and the colored powder; (a) a 5.2×10^{-6} mol/l aqueous solution of alizarin, pH=4.3, measured with a 10 cm cell, (b) colored TiO_2 powder in a KBr disk, the absorbance of TiO_2 powder being subtracted, (c) colored ZnO powder in a KBr disk, the absorbance of ZnO powder being subtracted.

When ZnO powder was added into an aqueous alizarin solution, the powder colored purple whose absorption spectrum is shown by Fig. 1 c). This coloration is also considered to be due to the chelate formation at the ZnO surface.

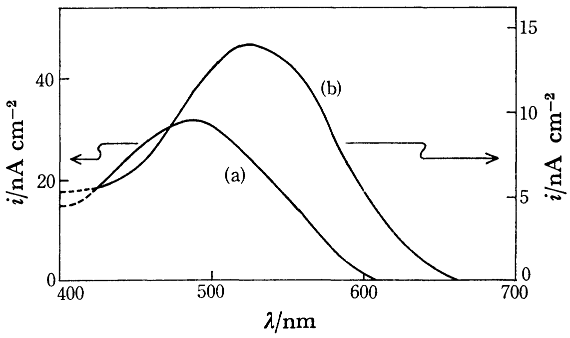

Fig. 2. Photocurrent action spectra in the solution of 5.2×10^{-6} mol/l alizarin at the anodic bias of 0.5 V. The photocurrents are corrected so that they correspond to the values for a uniform light intensity at all wavelengths. (a) For the TiO_2 electrode, with the illumination intensity $I=1.4\times10^{14}$ photons/cm² s. In these conditions the dark current i_d was 10 nA/cm². (b) For the ZnO electrode, $I=4.6\times10^{13}$ photons/cm² s. $i_d=4$ nA/cm².

Figure 2 shows the action spectra of the photocurrents for the TiO_2 and ZnO electrodes in the alizarin–electrolyte solution. They were obtained with a weak illumination intensity, so that the photocurrents did not change during the measurements and the wavelengths were scanned at the high speed of 250 nm/min. The intensity of the photocurrent was also confirmed to be proportional to the illumination intensity at several wavelengths. The action spectra nearly agree with the absorption spectra of the solutions. Consequently, the photocurrents are concluded to be caused by the sensitization due to the chelate compounds formed on the surface of the electrodes and not by the photochemical reactions of the dye in the solution. When each of the electrodes was dipped in a 5.2×10^{-6} mol/l alizarin solution for a while, washed with water, dipped into an electrolyte solution free from dye, and the photocurrents were measured, their action spectra agreed with those shown in Fig. 2. In this case, the intensities of the photocurrents were nearly the same as those observed in the alizarin–electrolyte solution systems. This indicates that the chelate compounds formed on the electrode surfaces are insoluble. The intensities of the photocurrent decayed gradually with illumination, the decay being the faster, the higher the illumination intensity. In the case of the TiO_2 electrode the decayed photocurrents recovered to the initial values, when the electrode was kept in the dark solution for a day. This seems to show that electrons are supplied by some means from the solution to the chelate compound.

Photocurrent measurements were also made for Alizarin S and quinalizarin which form chelate similar to that of alizarin. The action spectra for Alizarin S were confirmed to agree with the absorption spectra of the chelate compounds on the TiO_2 and ZnO powders. For the case of quinalizarin, the photocurrents also seem to be due to the chelate compounds, for their action spectra do not agree with the absorption spectrum of the dye in solution.

Concerning the photo-active species, two structures are considered; one is the alizarin dye directly coordinated to the metal ion which is still in the lattice of the oxide, and the other is the complete chelate compound physically adsorbed on the oxide surface. At present, we cannot decide which of the two models is the correct one. Trial to obtain a stoichiometric chelate compound in a pure state failed.

The present results show that the photo-electrochemical measurements provide a highly sensitive means to obtain the electronic spectra of very small quantities of materials on the solid–liquid interface.

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