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Dye sensitization of low-bandgap semiconductor electrodes: cuprous oxide photocathode sensitized with methyl violet

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Abstract. When illuminated, dye-coated semiconductor electrodes inject electrons (holes) into the conduction (valence) band so that the photoresponse of high-bandgap semiconductors is extended to the visible region. It is found that when low-bandgap semiconductor electrodes are coated with dyes, the photocurrent in the bandgap region wavelengths is also enhanced. The effect is explained as originating from suppression of the recombination of carriers generated by photons captured directly by the semiconductor surface.

1. Introduction

Dye sensitization of semiconductor surfaces (i.e. injection of carriers into the bands by photoexcited dye molecules adsorbed at the surface) has attracted the attention of physicists and chemists for more than half a century. As far back as 1938, the electron transfer process involved in photographic sensitization of silver halides was studied. Franck and Teller suggested that sensitization is caused by formation of polarons with the liberation of energy [1]. The currently accepted carrier injection mechanism was first proposed by Mott and Gurney in 1938 [2]. Subsequently dye sensitization of the semiconductor/electrolyte interface was investigated by many workers and it was established that anodic (cathodic) sensitization occurs when an excited dye molecule adsorbed at the semiconductor surface injects electrons (holes) into the conduction (valence) bands [3–10]. The type of sensitization (i.e. cathodic or anodic) depends on the band positions of the semiconductor and energy levels of the dye [3]. If they are located as in figure 1(*a*) an electron excited from the lower singlet level (S_0) to upper excited singlet level (S_1) is transferred to the conduction band. When the energy levels are as in figure 1(*b*), upon excitation an electron from the valence band is transferred to the unoccupied lower level (equivalently holes are injected into the valence band). More recent studies have shown that not only the singlet but also the triplet excited states are effective in charge injection to the bands [11]. The current interest in dye sensitization is mainly as a means of extending the spectral response of photoelectrochemical cells (PECs) based on stable high-bandgap semiconductor electrodes to the visible region. The attractive features of dye-sensitized PECs are the following:

(i) High-bandgap semiconductors insensitive to the visible spectrum are generally the ones that resist photocorrosion. Dye sensitization affords a method of extending the spectral response of PECs based on such materials to the visible region.

(ii) The spectra response can be easily controlled as a wide variety of dyes are available, or dyes with appropriate spectra response could be easily synthesized.

(iii) Electron transfer in dye-sensitized PECs involves only one band (i.e., a conduction band in an anodically sensitized process and a valence band in a cathodically sensitized process). As a result electron–hole recombinations are reduced and dye-sensitized photocurrent generation becomes less sensitive to defects and traps in the semiconductor.

At the same time dye-sensitized systems also have serious disadvantages:

(i) They have very low quantum and energy conversion efficiencies. The quantum efficiency depends on the light absorption cross section, which increases with the increase in surface concentration (SC) of the dye. However, when the SC is increased, photoexcited dye molecules that are in contact quench each other (concentration quenching) dissipating excitation energy into heat.

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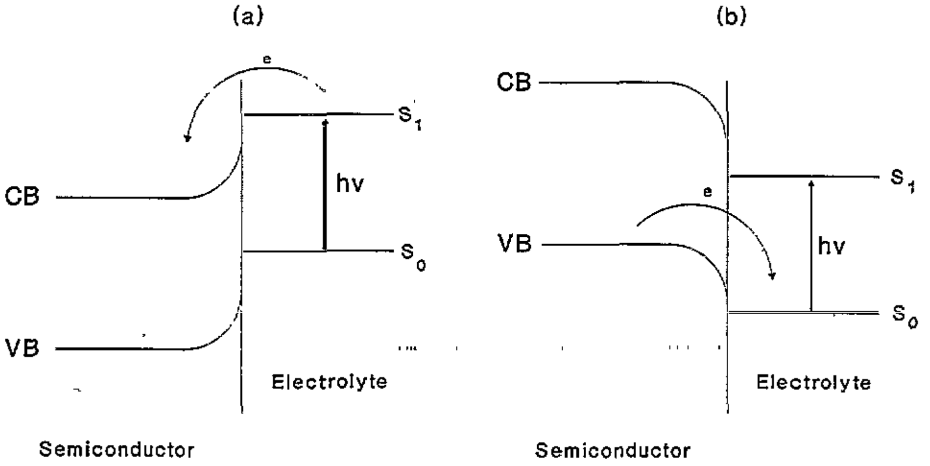

Figure 1. (*a*) Anodic and (*b*) cathodic dye sensitization: energy level diagram showing the charge injection process.

(ii) Only dye molecules adsorbed at the surface of the semiconductor electrodes are involved in the charge injection process. Most dyes are poorly adsorbed on familiar semiconducting materials. Furthermore, adsorbed dyes tend to leach into the solution.

(iii) Dyes used for sensitization undergo photodegradation.

According to a recent report most of the above problems are circumvented in a novel dye-sensitized PEC based on a colloidal TiO_2 membrane [10]. Here the claim is that increased surface roughness increases light harvesting [10]. At the same time concentration quenching is decreased, because the dye concentration at the surface of each colloidal particle remains more or less at the monomolecular level.

All works on dye-sensitized PECs are based on high-bandgap materials (e.g., TiO_2, ZnO_2, CuCNS) for the obvious reason that the photoresponse of these stable semiconductors can be extended to the visible region by this technique.

In this paper we report our observations on dye sensitization of low-bandgap semiconductor cuprous oxide (p-type, bandgap ~ 2.3 eV). The most interesting finding of this investigation is that dye sensitization not only extends the photoresponse to the absorption spectrum of the dye, but also enhances the photocurrent in the bandgap region of the spectrum.

2. Experiment

Cuprous oxide was thermally grown on copper plates (2 × 3 cm) by heating in an oven to 850 °C for ~ 3 min. Before heating, plates were mechanically polished and cleaned ultrasonically with a detergent. The dye used for sensitization was the cationic dye methyl violet. The commercial dye in the chloride form is highly water soluble and cannot be adsorbed onto the Cu_2O surface. We found that the salicylate of methyl violet is only sparingly soluble in water (solubility is further suppressed in the presence of sodium salicylate) and can be made to adsorb on Cu_2O. Methyl violet salicylate is made from the chloride by the following method. A strong solution of the chloride form of the dye is heated with an excess of sodium salicylate. When the solution is cooled, methyl violet salicylate precipitates. The precipitate is filtered, washed with water and dried. Cu_2O plates are coated with the dye by keeping them immersed in an alcoholic solution (30% ethanol) of the dye. By varying the duration of immersion or the dye concentration, different levels of adsorption can be achieved. The SC of the dye on the Cu_2O plates is determined by extraction of the coated dye into 99.9% ethanol and spectrophotometric estimation.

The electrolyte used in the PEC was 0.1 M KI containing 10^{-3} M of iodine and 0.1 M sodium salicylate. A Pt mesh was used as the counter electrode and the Cu_2O photocathode was biased (Hotkuto Denko HA-301 potentiostat) at −0.07 V versus an Ag/AgCl electrode that gave zero dark current. The photocurrent action spectrum (plot of photocurrent versus wavelength) was obtained using a Nikon monochromator auto-scanner (AS-(101)) with a light chopper and a lock-in amplifier (Stanford Research Systems SR 530). Light intensities were measured with an International Light Radiometer and also compared with a calibrated silicon solar cell. The variation of the short-circuit photocurrent with the SC of the dye was also investigated using a white light source (60 W tungsten filament lamp).

3. Results and discussion

Cathodic dye sensitization occurs via the following steps. Photoexcited dye molecules D* inject holes into the valence band of Cu_2O to yield the dye anion D^-

$$h\nu + D \longrightarrow D^* \tag{1}$$

$$D^* \longrightarrow D^- + \underset{\substack{\downarrow \\ \text{valence band.}}}{h^+} \tag{2}$$

Dye anions transfer electrons to I_3^- ions, regenerating the dye

$$2D^- + I_3^- \longrightarrow 3I^- + 2D. \qquad (3)$$

At the counterelectrode I^- ions donate electrons yielding free iodine, which combines with I^- in the electrolyte to regenerate I_3^-

$$2I^- - 2e^- \longrightarrow I_2 \qquad (4)$$

$$I^- + I_2 \longrightarrow I_3^-. \qquad (5)$$

Figure 2 shows the photocurrent action spectrum of the sensitized photocathode for several SCs of the dye. For comparison the action spectrum in the absence of the dye is also indicated (curve a). In the presence of the dye, a clear photoresponse is seen in the absorption region of the dye (the absorption spectrum of the dye is shown in figure 3). A slight red-shift in the photocurrent action spectrum peak position with respect to the absorption peak of the dye indicates that surface adsorbed dye is responsible for the charge injection. It is also seen that the sensitized photocurrent is higher at lower SCs of the dye. At higher SCs, when dye molecules are in close contact, the excited molecules quench each other (concentration quenching) dissipating excitation energy into heat, i.e.

$$D^* + D^* + D^* + \ldots \longrightarrow D + D + D + \ldots + \text{heat}. \qquad (6)$$

As the light absorption cross section increases with the increase of SC, the two opposing effects lead to a critical SC for which the photocurrent is optimum.

The interesting new observation we have made is that, in the presence of the dye, the photocurrent corresponding to direct-bandgap excitation of Cu_2O (i.e. the region around 475 nm, figure 2) is also enhanced. We give the following explanation. Light passing through the dye layer on the photocathode surface causes direct excitation of Cu_2O, generating electron-hole pairs. Adsorbed dye molecules on the surface accept electrons to yield D^- (figure 4) which participates in the reaction (3), just as in the case of the sensitized process. The rapid acceptance of electrons by the dye molecules suppresses recombination of electron-hole pairs, enhancing the photocurrent in the bandgap wavelength region. When the SC of the dye is low, the number of dye molecules available for electron acceptance is small. However, higher SCs of the dye cut off light incident on the Cu_2O surface. Thus, initially the photocurrent in the bandgap region of the action spectrum increases with the increase of the SC of the dye and then begins to decrease (figure 1). If the variation of the photocurrent with SC of the dye is plotted with a white light source (e.g. tungsten filament lamp), a curve of the shape shown in figure 5 is obtained. The double peak originates from the existence of sensitized photocurrent and enhanced photocurrent in the bandgap wavelength

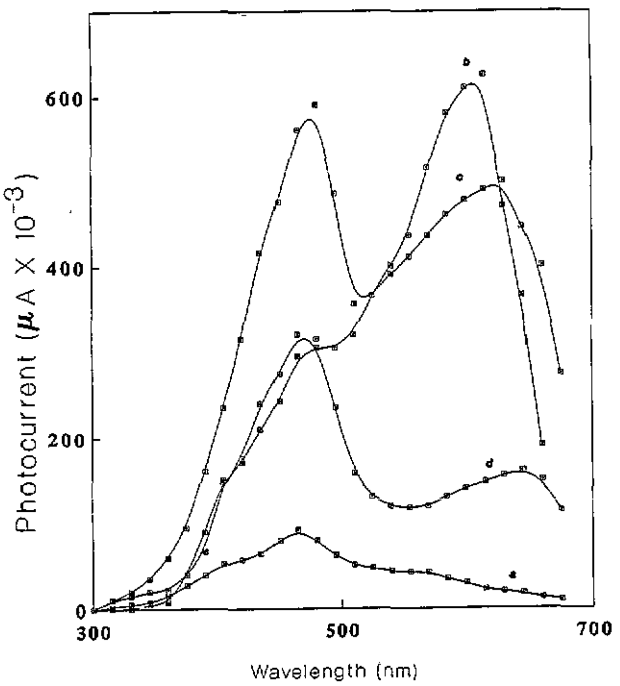

Figure 2. Photocurrent action spectrum of Cu_2O sensitized with surface concentration (molecule cm^{-2}) of methyl violet: (a) 0, (b) 4.5×10^{14}, (c) 25×10^{14}, (d) 150×10^{14}.

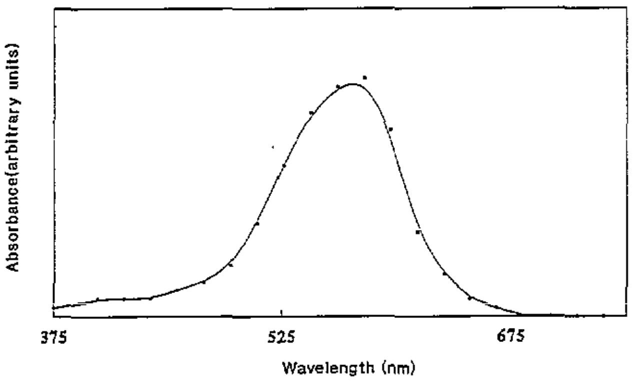

Figure 3. Absorption spectrum of an aqueous solution of methyl violet.

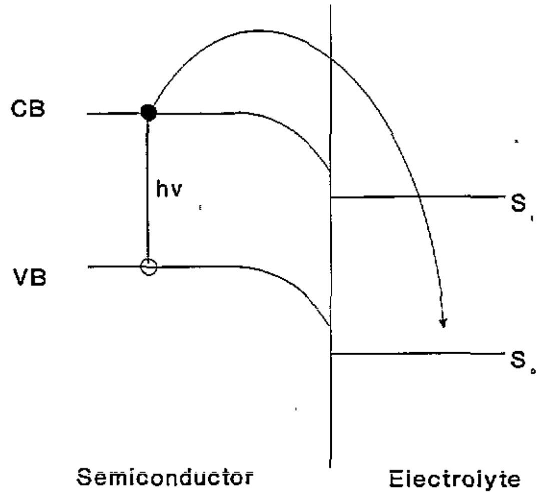

Figure 4. Energy level diagram showing absorption of a photon by a semiconductor, generating an electron-hole pair of which the electron is transferred to the lower level (S_0) of the dye molecule to yield D^-.

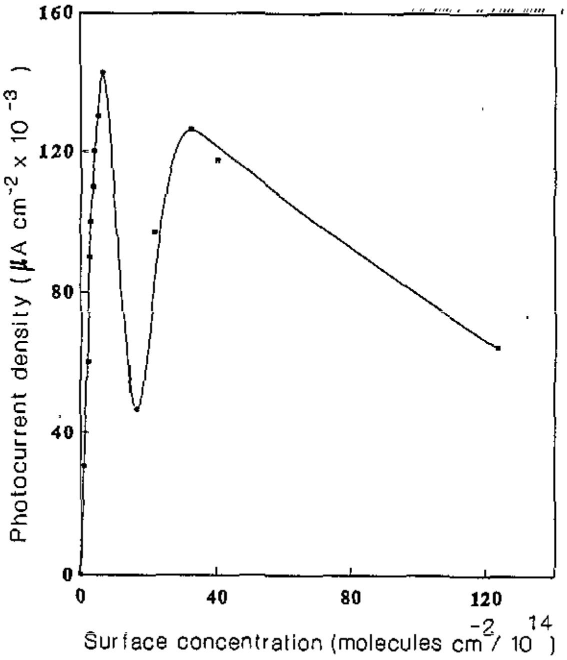

Figure 5. Variation of the photocurrent with the surface concentration of the dye. Cathode illuminated with 60 W tungsten filament lamps.

region. We have noticed that Cu_2O sensitized with other dyes (e.g. rhodamine 6B) shows the same effect. Again this effect can be observed in other low-bandgap semiconductors.

References

[1] Franck J and Teller E 1938 *J. Chem. Phys.* **6** 861
[2] Gurney R W and Mott N F 1938 *Proc. R. Soc.* A **164** 151
[3] Memming R 1972 *Photochem. Photobiol.* **16** 325
[4] Gerischer H 1972 *Photochem. Photobiol.* **16** 243
[5] Matsumura M, Nomura Y and Tsubomura H 1977 *Bull. Chem. Soc. Japan* **50** 2533
[6] Tsubomura H, Matsumura M, Nomura Y and Amamia T 1979 *Nature* **262** 402
[7] Alonso N, Bety V M, Charter P and Ern V 1981 *Rev. Phys. Appl.* **16** 5
[8] Tennakone K, Kahanda M, Kasige C, Abeysooriya R, Wijenayake R H and Kaviratna P 1984 *J. Electrochem. Soc.* **131** 1575
[9] Tennakone K, Karunamuni J and Dewasurendra M 1986 *Sol. Energy Mater.* **13** 447
[10] Regan B O and Gratzel M 1991 *Nature* **353** 737
[11] Kamat P V and Patrick B 1992 *Electrochemistry in Colloids and Dispersions* ed R A Mackey and J Texter (New York: VCH)