Solar Energy Materials 13 (1986) 447–452
North-Holland, Amsterdam

THE PHOTOSTABILITY OF A DYE ADSORBED SEMICONDUCTOR ELECTRODE IN A SOLUTION OF ANOTHER FLUORESCENT DYE

K. TENNAKONE

Photochemistry Group, Institute of Fundamental Studies, 380/72, Bauddhaloka Mawatha, Colomob 7, Sri Lanka, and
Department of Physics, University of Ruhuna, Matara, Sri Lanka

J. KARUNAMUNI and M. DEWASURENDRA

Department of Physics, University of Ruhuna, Matara, Sri Lanka

Received 11 January 1986; in revised form 6 March 1986

It is found that the photodegradation of methyl violet adsorbed onto a p-CuCNS photocathode can be suppressed if the electrolyte contains another fluorescent dye, e.g. rhodamine B or fluorescein. It is suggested that stabilization results from energy transfer between excited dye molecules in the solution and the adsorbed dye.

1. Introduction

The photosensitization of electron transfer across the semiconductor electrolyte interface is a well known phenomenon that would possibly play an important role in future solar energy conversion devices [1–7]. By sensitization a photoelectrochemical cell based on a high band gap semiconductor can be made sensitive to visible light. This is attractive because photostable semiconductors are wide band gap materials. Unfortunately the sensitized photoelectrochemical devices suffer from two serious defects: (1) As a result of concentration quenching, the quantum efficiencies of sensitized systems are rather low [8,9]; (2) Dyes photodegrade rapidly, and most efficient redox couples are ineffective in suppressing their photodegradation significantly [1–7]. We have found that photodegradation of methyl violet adsorbed onto a p-CuCNS (cuprous thiocyanate is a p-type semiconductor of band gap 3.2 eV [7–10] surface can be suppressed if the redox couple used is itself a fluorescent dye such as rhodamine B or fluorescein. This conclusion is based on a study of the stability of p-CuCNS photocathodes sensitized with the cationic dyes methyl violet (M) and rhodamine B (R), which rendered water insoluble by replacing the anion (Cl^- in commercial dyes) with the complex ion $Zn(CNS)_4^{2-}$.

2. Experimental

CuCNS was deposited on 3 × 3 cm copper plates electrochemically by the method described in ref. [7]. A peculiar property of CuCNS is that it readily adsorbs dyes containing an ionic or a covalently linked CNS ligand [7]. The plates were coated with thiocyanates of methyl violet (MCNS) and rhodamine (RCNS) by keeping them immersed in the dye solution for 30 min (0.1 g/dm^{-3} of water containing 10% of ethanol). The thiocyanates were prepared from respective chlorides by heating them with a strong solution of KCNS and recrystallization [7]. Thiocyanates of R and M are water soluble: when a dye adsorbed plate is immersed in water, the dye is gradually solved in the solution.

To study the photoeffects at a semiconductor/adsorbed dye D_1/dye D_2 solution interface, it is essential that the solubility of D_1 is suppressed as far as possible. This could be done because methyl violet and rhodamine cationic dyes become water insoluble [11] when the anion is the complex ion $Zn(CNS)_4^{2-}$ (the solubility of $M_2Zn(CNS)^4$ is approximately 10^{-6} mol dm^{-3} at 30°C compared to 10^{-3} mol dm^{-3} for MCl). To convert the adsorbed dye into the insoluble form, the plates coated with thiocyanated dyes were kept immersed in a solution containing 1 mol dm^{-3} of KCNS and 1.5 mol dm^{-3} $ZnSO_4$, when anion exchange transform XCNS into $X_2Zn(CNS)_4$. The thickness of the adsorbed dye layer was determined by extracting the dye with ethanol and spectrophotometric estimation.

As the cell works better in the backwall mode, the anode used was a brass frame coated with copper sulphide [7]. The supporting electrolyte was 0.1 mol dm^{-3} Na_2SO_4. Familiar redox agents (e.g. I^-/I_3^-) as well as different water soluble dyes were added to the electrolyte and a change of the photocurrent was observed under short-circuit conditions. Photocurrent spectra were determined with an applied photophysics monochromator and a 250 W halogen lamp.

3. Results and discussion

The time development of photocurrents in cells with p-CuCNS/$M_2Zn(CNS)$ photocathodes in the presence of different redox agents are shown in fig. 1. In the absence of a redox couple the photocurrent undergoes rapid decay. Familiar redox couples (e.g. I/I_3^-) reduce the decay to some extent. A dramatic increase in the stability is noted when a fluorescent dye (rhodamine chloride or fluorescein) which could also act as a redox couple is added to the solution. Again it was noted that this effect is not present when methyl violet chloride is added to a cell with a photocathode of p-CuCNS/$R_2Zn(CNS)_4$. The photocurrent spectrum of p-CuCNS/$M_2Zn(CNS)_4$/R in the solution system is compared with emission and absorption spectra of the dyes in fig. 2. It is seen that the photoresponse is the strongest near the overlap region of the absorption spectrum of the $M_2Zn(CNS)_4$ coated surface and the emission spectrum of rhodamine in aqueous solution.

The cathodic sensitization of a p-type semiconductor is supposed to occur via the following mechanism [1–3]. When an electron in the dye molecule is excited from a lower level into an upper level, an electron from the valence band is transferred into the half-occupied lower level (fig. 3). A reducing agent present in the solution could accept this electron regenerating the dye. The photocorrosion of the dye, which is generally a reduction in a cathodic process, can also be understood. The electron

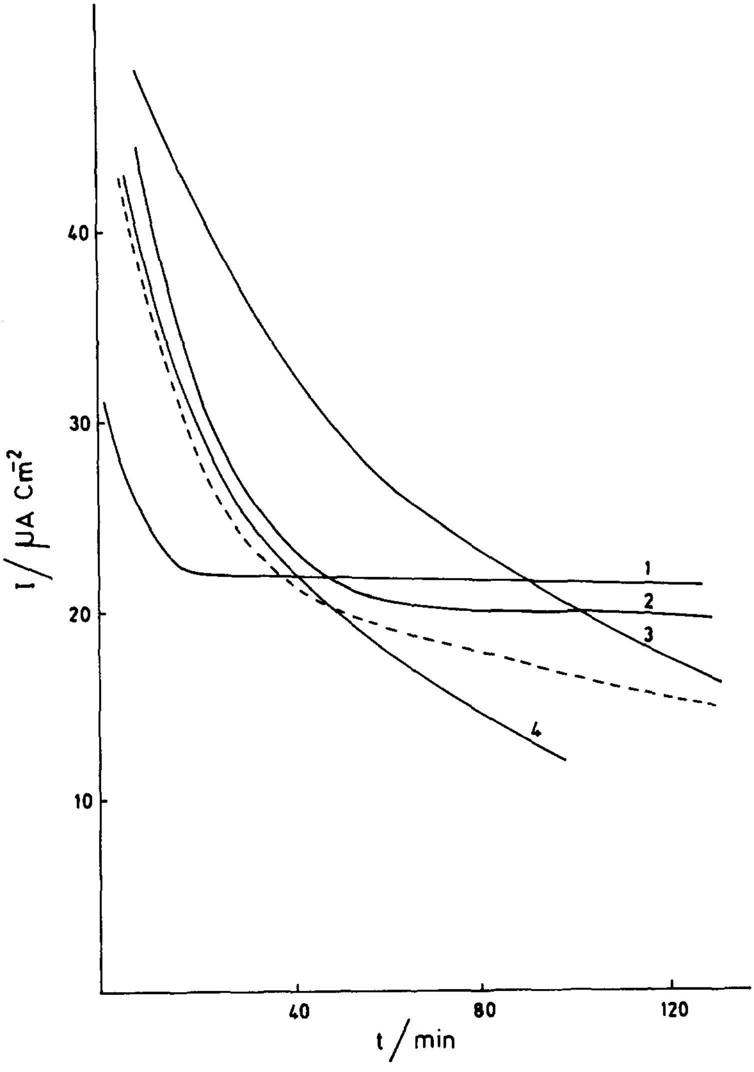

Fig. 1. Time development of the photocurrent in a p-CuCNS photocathode sensitized with $M_2Zn(CNS)_4$. (1) Rhodamine B ($x \times 10^{-4}$ mol dm^{-3}); (2) Fluorescein (3×10^{-4} mol dm^{-3}); (3) I^-/I_3^- ($I^- = 8 \times 10^{-3}$ mol dm^{-3}, $I = 8 \times 10^{-4}$ mol dm^{-3}) in solutions; (4) In absence of a redox couple. The dashed curve gives the time development of the photocurrent when p-CuCNS is sensitized with $R_2Zn(CNS)_4$ and the solution contains $\sim 10^{-4}$ mol dm^{-3} of M (supporting electrolyte: 0.1 mol dm^{-3} Na_2SO_4, light intensity = 480 W m^{-2} from a halogen lamp).

transferred to the dye molecule sometimes accepts other positive ions in the solution, e.g, H^+ generating highly reactive free radicals that degrade the dye by reduction. When a second dye D_2 is present in the solution, a different process becomes predominant. Molecules of D_2 excited by absorption of light transfer

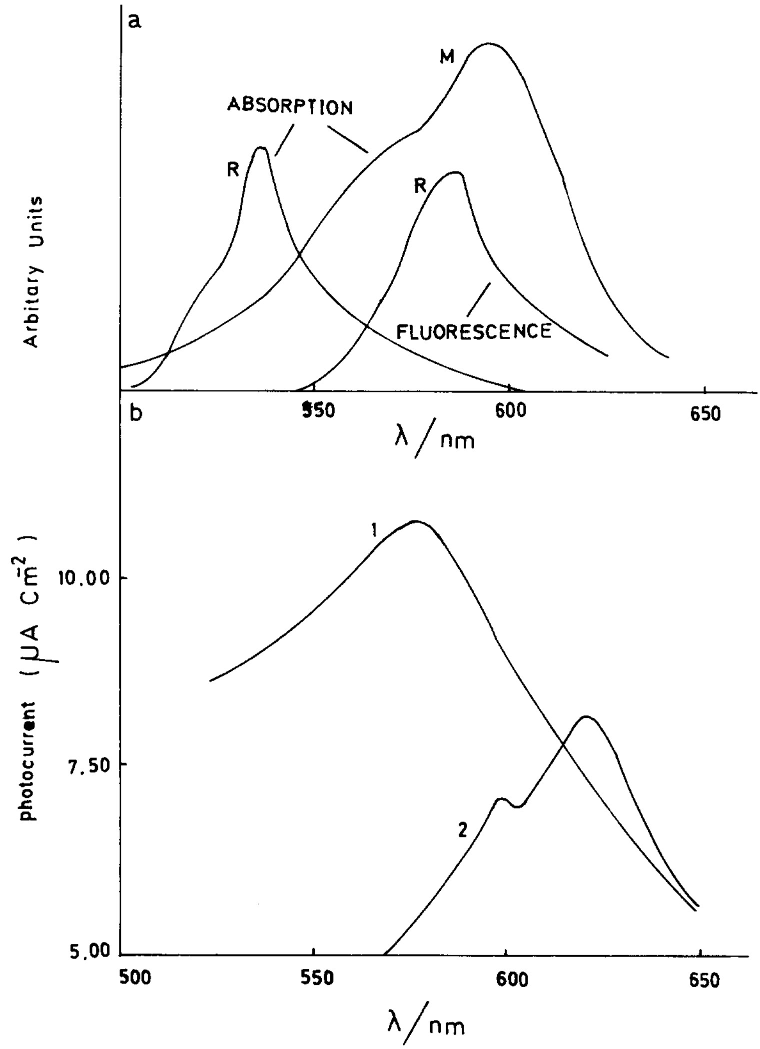

Fig. 2. (a) Absorption spectra of rhodamine B (R) and methyl violet(M), and the fluorescene spectrum of rhodamine B. (b) Photocurrent spectrum of a p-CuCNS photocathode sensitized with $M_2Zn(CNS)_4$. (1) Rhodamine B in solution; (2) In absence of a dye in the solution.

energy to molecules of the first dye D_1 on the surface of the photocathode with charge exchange, i.e., D_2 accepts an electron donated by D_1 and an electron from the valence band of the semiconductor is transferred to D_1^+, D_2^- in the solution combines with H^+ ions to form the reduced leuo compound L_2. The leuo compound is oxidized back to the dye at the anode. Reactions occuring near the electrodes can be represented as follows:

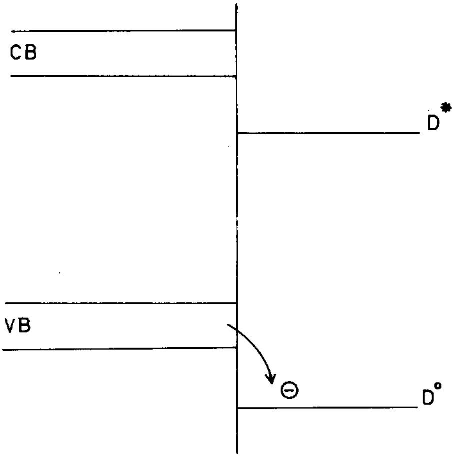

Fig. 3. Energy diagram for cathodic sensitization at a p-type semiconductor/dye interface. The half-occupied lower level and the excited level are denoted D_0 and D^*.

Photocathode:

$$h\nu + D_2 \rightarrow D_2^*,$$
$$D_2^* + D_1 \rightarrow D_1^+ + D_2^-,$$
$$D_2^- + H^+ \rightarrow L_2,$$
$$D_2^+ + e\ (\text{valence band}) \rightarrow D_2;$$

Anode:

$$OH^- + L_2 \rightarrow D_2 + H_2O + e.$$

In principle the cell is completely regenerative: D_1 adsorbed onto the surface of the photocathode cannot degrade because D_1^+ almost instantaneously accepts an electron from the valence band (electron transfer to D^+ from the valence band is a faster process compared to electron transfer from a species in the solution [5]. Resonance energy transfer occurs most effectively when the emission spectrum of the fluorescent dye D_2 overlaps the absorption spectrum of the dye D_1 that accepts excitations. A blue shift of the first spectrum with respect to the second favours energy transfer [10,11]. This is clearly evident in the photocurrent spectrum where the photoresponse is seen to be the strongest in the overlap region of two spectra (fig. 2). If the roles of the two dyes M and R are interchanged, i.e., $D_1 = R$, $D_2 = M$, the energy transfer is inefficient and stabilization is not seen (fig. 1).

The quantum conversion efficiency at the peak position (570 nm) depends on concentration of R, because of light cutoff from the solution and concentration quenching among molecules of R. A maximum quantum efficiency of $\sim 8\%$ is seen when the concentration of R $\sim 3 \times 10^{-4}$ mol dm^{-3} and the adsorbed dye layer is $\sim$ 5–8 monolayers thick.

4. Conclusion

The above method of suppressing photodegradation of dyes in a sensitized photoelectrochemical cell could apply to systems based on other semiconductors (p- or n-type). However, with more familiar semiconducting materials, e.g., TiO_2 and $SrTiO_3$, we have not succeeded in finding a method that will firmly affix the dyes making them insoluble. This method may also be extended to stabilize sensitized photcatalysts. Again further studies on sensitized photoelectrochemical systems based on several dyes could help to understand the mechanisms of light induced energy and charge transfer at the semiconductor/dye/electrolyte interface.

References

[1] H. Gerischer and H. Tributsch, Ber. Bunsenges. Phys. Chem. 72 (1968) 437.
[2] E. Michel-Beyerle, H. Gerisher, F. Rebentrust and H. Tributsch, Electrochim. Acta 13 (1968) 1509.
[3] R. Memming, Photochem. Photobiol. 16 (1972) 325.
[4] H. Tsubomura, M. Matsumura, Y. Nomura and T. Amamia, Nature 261 (1979) 402.
[5] J. Moser and M. Gratzel, J. Am. Chem. Soc. 106 (1984) 6557.
[6] T. Shimidzu, T. Iyoda and Y. Koide, J. Am. Chem. Soc. 107 (1985) 35.
[7] K. Tennakone, M. Kahanda, C. Kasige, P. Ageysooriya, R.H. Wijenayake and P. Kaviratne, J. Electrochem. Soc. 131 (1984) 1575.
[8] H. Tsubomura, Photochemistry and Light Energy Conversion (Tokyo Kagku Dojin, Tolyo, 1980).
[9] K. Itoh, V. Chiyokawa, M. Nakao and K. Honda, J. Am. Chem. Soc. 106 (1984) 1630.
[10] K. Tennakone, J. Phys. D16 (1984) L5.
[11] V.N. Alexeyv, Qualitative Chemical Semimicroanalysis, translated by P.K. Agasyan (Mir Publishers, Moscow, 1975).
[12] J.M. Coxon and B. Halton, Organic Photochemistry (Cambridge University Press, 1974) p. 13.
[13] A. Rest, in: Light, Chemical Change and Life, eds. J.D. Coyle, R.R. Hill and D.R. Roberts (The Open University Press, Milton Keynes, 1982).