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SENSITIZATION OF PHOTOELECTROCHEMICAL CELLS BY RESONANT ENERGY TRANSFER BETWEEN TWO DYES

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Abstract : It is found that when a semiconductor electrode surface in a photoelectrochemical cell is coated with a dye that can transfer a charge carrier upon excitation into an energy band and if a layer of a second dye that readily transfers the energy of photon excitation into an inner one by resonance is deposited on top of the first dye, then stability and quantum efficiency of photocurrent are both improved. Observations based on dye coated CuCNS photocathodes are presented to illustrate the phenomenon. Photochemical processes involved are discussed.

1. Introduction

It is well known that the spectral response of photoelectrochemical cells (PECs) based on high band gap semiconducting materials can be extended to the visible region by deposition of suitable dyes on the surface.[1,2,3,4,5] In addition to adjustability of the spectral response, dye sensitized PECs have the following advantages. (1) The DS photocurrent is rather insensitive to impurities and defects in the semiconductor,[6] polycrystalline .and amorphous materials when sensitized yield large photocurrents. (2) When dyes with intense absorption bands are deposited, the light absorption at a sensitized surface becomes much higher than that at a bare semiconductor surface. (3) High band gap materials are generally photocorrosion resistant. It is also known that deposition of dyes enhance the photostability of a semiconductor surface.

The chief disadvantages of DS systems are, (1) low energy and quantum conversion efficiencies, (2) photodegradation of the dye even in the presence of a redox couple. Low conversion efficiency results from poor absorption of the dye at the semiconductor surface, high electrical resistivity of the dye and concentration quenching.[1,2,3,4,5] Recently one of the authors[8] and collaborators have found that cuprous thiocyanate (CuCNS is a p—type semiconductor of band gap ≃ 3.6 eV[7]) readily absorbs thiocyanates of cationic dyes (cationic dyes whose anionic ligand CNS, the method of preparation is described.[8]) The simple method of depositing CuCNS on copper plates and the ability of these surfaces to absorb dyes readily and the fact that absorbed dyes do not pass into the electrolyte, makes CuCNS photocathodes ideal for study of dye sensitization. In this work we report our observations on the behaviour of a PEC where a thin outer layer of a dye D_2 is deposited on the first layer of a dye D_1 absorbed on CuCNS substrate. If D_2 is a fluorescent dye absorbing at a shorter wave length than D_1, the photocurrent spectrum of the system is found to be strongest in the overlap region of absorption spectrum of D_1 and fluorescence spectrum of D_2. The photocurrent quantum efficiency and stability are also found to be higher in the composite system.

2. Experimental

CuCNS was deposited on 3 x 3 cm copper plates electrochemically, by the method described by Tsubomura *et al.*[8] They were coated with thiocyanates of Methyl Violet (M) and Acridine Orange (A) by keeping immersed in the dye solution (0.01 g l^{-1}), the dyes get well absorbed within few minutes. The surface concentration of the dye was determined by noting the depletion of the dye concentration in the solution spectrophotometrically. The deposition of a layer of a second dye (e.g. A on M) over the one that is absorbed into the CuCNS substrate is a more difficult process. To achieve this the plate coated with the first dye was immersed in a solution containing the thiocyanate of the second dye (0.01 g l^{-1}) for about 6 h.

The electrolyte was a 0.1 M solution of KCNS. A platinum foil was used as the counter—electrode and the photocathode was biased (−0.40 V vs SCE) to give zero dark voltage (Hokuto Denko HA — 301 potentiostat was used). Light intensities were measured with an International Light IL 700 radiometer. The photocurrent spectra were ascertained with an Applied Photophysics Monochromator and 100 W tungsten filament lamp. Absorption spectra of dye solutions were measured with a Hitachi U — 3200 spectrophotometer.

3. Results and Discussion

CuCNS/Dye/Pt Cell : Firstly a cell sensitized with one dye (M or A) is considered. The redox action of KCNS solution depends on existence CNS^- as well $(CNS)_2^-$ ions[8] (atmospheric oxygen generate small quantities of $(CNS)_2^-$ ions in a KCNS solution[8]). The chemical reactions occuring near the electrodes are summarized below.

Photocathode

$$D + h\nu \rightarrow D^*$$

$$D^* \rightarrow D^- + \text{hole}^+$$

$$D^- + (CNS)_2^- \rightarrow 2CNS^- + D$$

Here D denotes a dye molecule, D* an excited dye molecule and D^- a dye molecule that has accepted one electron. The hole generated is transferred into the valence band of CuCNS.

Anode

At the anode CNS^- ions discharge electrons yielding CNS free radicals, that combine with CNS^- in the electrolyte regenerating $(CNS)_2^-$, ie,

$$CNS^- - e \rightarrow CNS \tag{2}$$

$$CNS^- + CNS \rightarrow (CNS)_2^-$$

Action spectra of this system for A and M are presented in Figure 1. Photocurrent quantum efficiencies are given in Table 1. The cell performs best when the dye layer is 8 — 12 monolayers thick.

Photodegradation of the dye could result from following reactions. Hydrogen ions in the solution can accept electrons from D^- to yield atomic hydrogen, which reacts with unexcited or excited dye molecules in the neighbourhood, ie,

$$D + H \rightarrow \text{reduction products of the dye} \tag{3}$$

$$D^* + H \rightarrow \text{reduction products of the dye} \tag{4}$$

Chemical analysis indicates that the photodegraded dye consists mainly of the reduced lecuobase. As the reaction (4) is faster than (3), it is probably the predominant mode of photodegradation. Since the semiconductor is photostable and the solute is regenerative, the decay of the photocurrent results almost entirely from degradation of the dye. The time development of the photocurrent in cells sensitized A and M are shown in Figure 2.

$CuCNS/D_1D_2/pt$ Cell: The above cell with a deposit of D_1 = Methyl violet (5—10 monolayers) on CuCNS and on top of D_1 a dye D_2 = Acridine Orange, (3 — 6 monolayers) has different characteristics. The photocurrent spectrum is shown in Figure 1. It is seen that the photoresponse is strongest in the overlap region of absorption spectra of A and M. For comparison Figure 1 also gives the photocurrent spectrum of a cell sensitized with a mixture two days A and M. Here in contrast to the previous case two peak positions in the spectrum corresponding to individual dyes are clearly evident. Quantum conversion efficiencies of the single and two dye systems are shown in Table 1. It is seen that quantum conversion efficiency at the peak spectral region is higher in the M/A (inner dye M outer dye A) system. Figure 2 compares the stability of different systems.

Table 1. Photocurrent quantum efficiencies of CuCNS sensitized with different dye systems. In the M/A system the wavelengths 516, 489, 580 nm indicated within the brackets corresponds to peak positions in the photocurrent spectrum of M/A, absorption spectrum of A and absorption spectrum of M respectively.

System	Quantum Efficiency %
M/A (516 nm)	1.24
M/A (489 nm)	1.20
M/A (580 nm)	0.92
M (580 nm)	1.15
A (489 nm)	0.47

A dye that shows strong fluorescence in aqueous solution (e.g. Rhodamine or Acridine Orange) when deposited as a single layer is found to degrade more rapidly than a non—fluorescent dye. However, in a two dye system much better stability and conversion efficiencies were obtained when the outer layer is a fluorescent dye. The photochemical mechanisms discussed below explain the above observations.

Light absorbed excite dye molecules D_2 in the outer layer,

$$H\nu \quad + \quad D_2 \quad \rightarrow \quad D_2^*$$

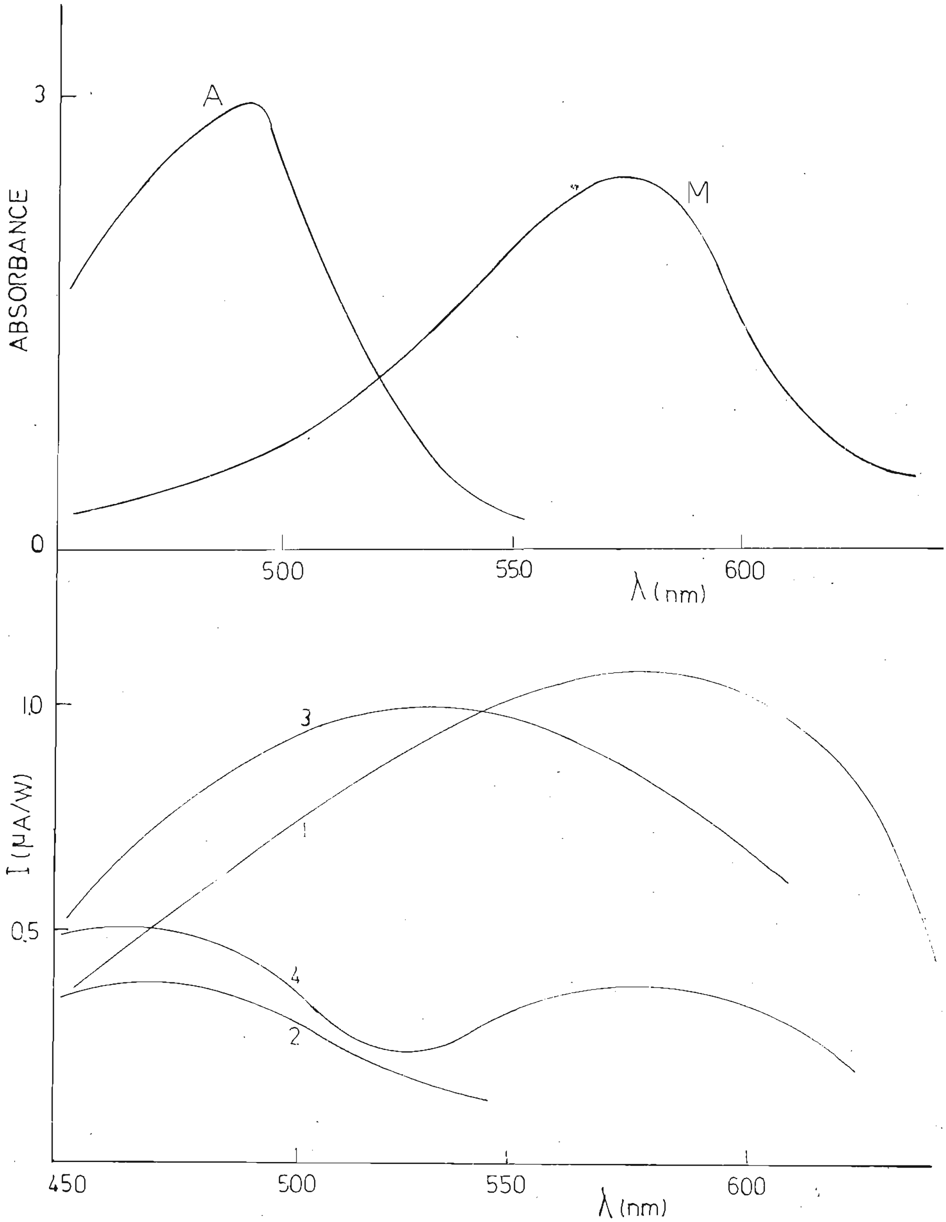

Figure 1. Photocurrent spectrum of cells sensitized with

(1) Methyl Violet
(2) Acridine Orange
(3) Acridine Orange on Methyl Violet
(4) Mixture of Acridine Orange and Methyl Violet for comparison the fluorescence spectrum of Acridine Orange and the absorption spectrum of Methyl Violet are indicated above.

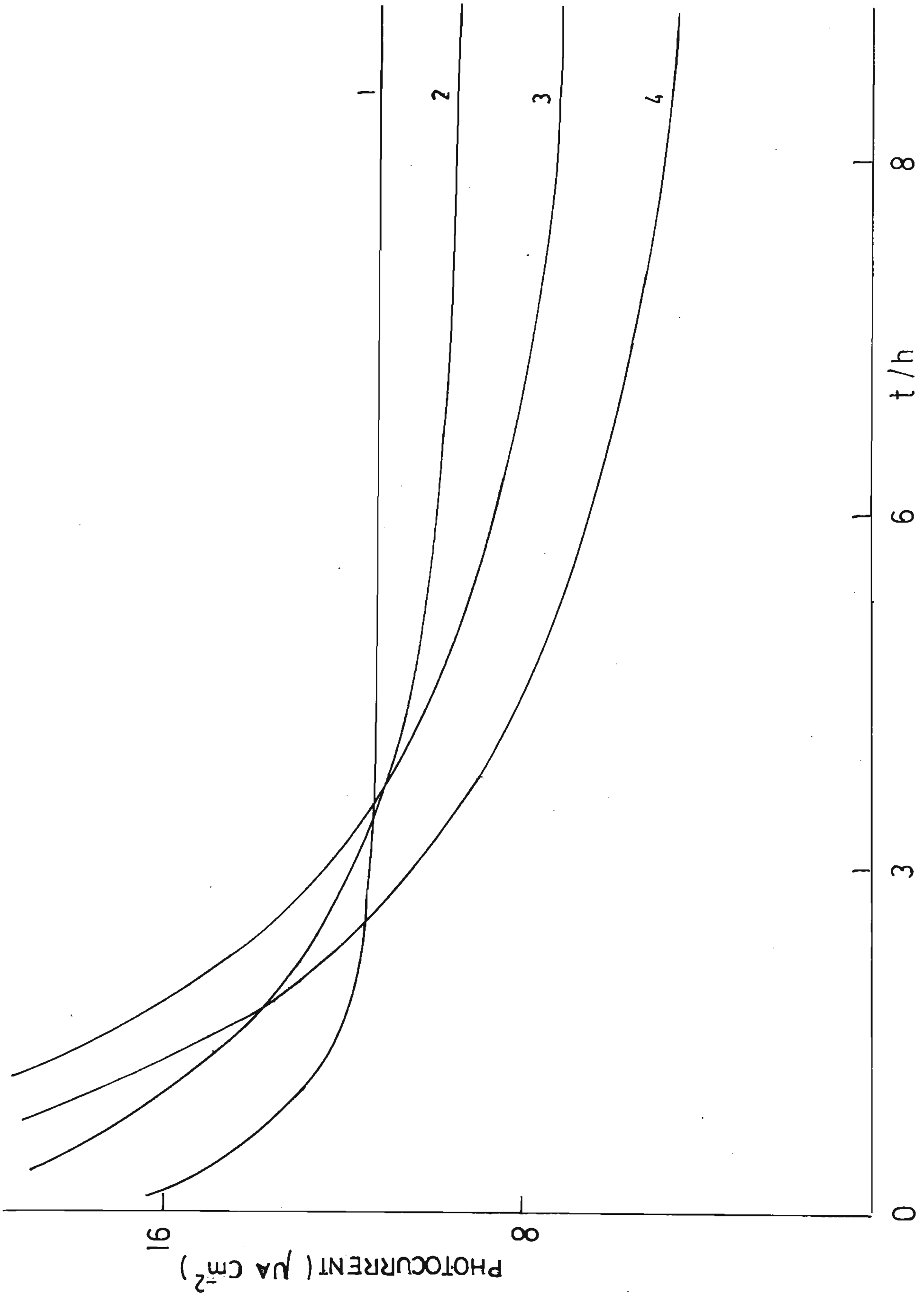

Figure 2. Time development of the photocurrent in CuCNS photocathodes sensitized with
(1) Acridine Orange on Methyl Violet
(2) Mixture of Acridine Orange and Methyl Violet
(3) Acridine Orange
(4) Methyl Violet on Acridine Orange

These transfer energy to dye molecules D_1 in the inner layer by resonance[9],

$$D_2^* \quad + \quad D_1 \quad \rightarrow \quad D_1^* \quad + \quad D_2$$

Excited D_1 molecules transfer holes to the valence band of the semiconductor as in (1),

$$D_1^* \quad \rightarrow \quad D_1^{\dot{-}} \quad + \quad \text{hole}^+$$

and electrons from D_1^- tunnels across the D_2 layer into the electrolyte, transferring electrons to reducible species in the electrolyte. The important difference here, when compared to the single dye PEC is that, if the quenching of D_2^* is rapid, the reactive excited dye molecules are not in contact with the free radicals (e.g. H) generated. Thus degradation of the dye via reaction (4) is suppressed. The energy conversion efficiency of the cell CuCNS/MA/KCNS/Pt was found to be $3 \times 10^{-3}\%$ (Figure 3).

It is well known that quenching occurs most rapidly through resonance energy transfer,[9] which takes place when two types of molecules are in contact and absorption spectrum of the acceptor overlaps the emission spectrum of the donor. The observation that fluorescent dyes (when used as the outer layer) resists photocorrosion more effectively, can be understood because, higher life time of the excited singlet state favours resonance energy transfer.

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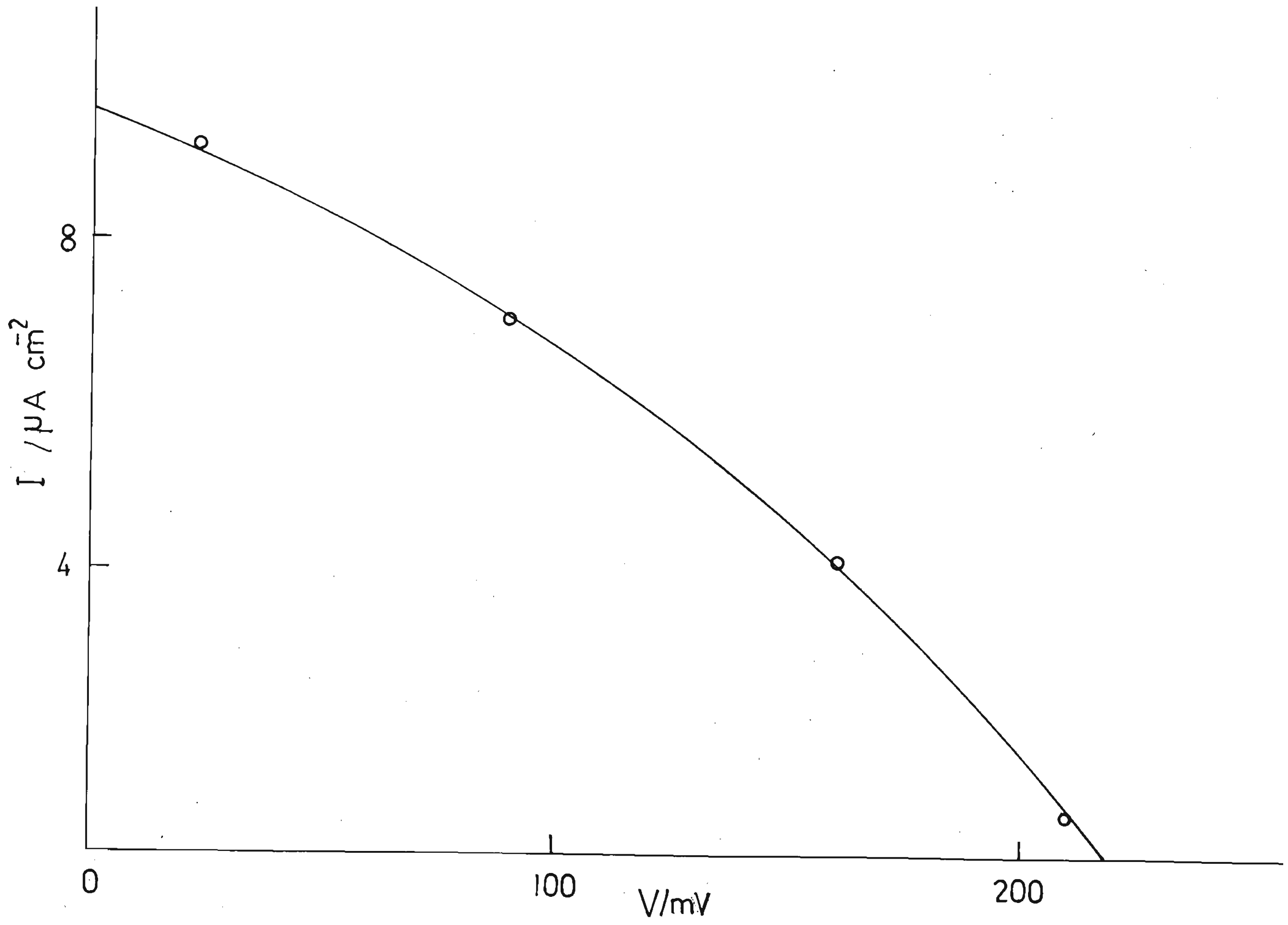

Figure 3. Plot of I vs V for the CuCNS/MA/KCNS/Pt Cell (Intensity of illumination 250 Wm^{-2} from a tungsten filament lamp).

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