

KINETICS OF PHOTOCURRENT GENERATION AND QUANTUM EFFICIENCY OF SENSITIZED PHOTOCATHODES

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Summary

The photocurrent quantum efficiencies of CuCNS photocathodes sensitized with various dyes are measured as a function of the surface concentration of the dye and the concentration of the electron acceptor in the solution. An attempt is made to relate the observed variation in the quantum efficiencies with the surface concentration of the dye to the kinetics of charge transfer and photophysical processes occurring at the sensitized interface.

1. Introduction

Dye sensitization of semiconductor-electrolyte interfaces has become an object of attention for many workers as it is a technique that might be adapted for use in solar energy conversion devices [1 - 11]. The values for the photocurrent quantum efficiency ϕ of dye-sensitized (DS) photoelectrochemical cells (PECs) are very low [5, 6]. Nevertheless these cells have a number of interesting features: (1) there is the possibility of using high band-gap materials that resist corrosion; (2) the spectral response can be easily controlled; (3) the interfacial charge transfer in DS PECs, in contrast with that in unsensitized PECs, involves only one band (a conduction band in an anodically sensitized process and a valence band in a cathodically sensitized process). Consequently the electron-hole recombinations are minimal and the DS photocurrents become less sensitive to defects and traps in the semiconductor [12].

The energetics of charge transfer in DS electrodes have been thoroughly explored [1 - 3, 13]. However, the kinetics of the photocurrent genera-

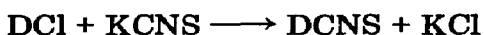
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tion process have received much less attention. It is rather difficult to make accurate measurements of ϕ of DS PECs as a function of the experimental variables, *e.g.* the surface concentration of the dye and the concentration of the redox couple in the electrolyte. Generally, sensitized surfaces cannot be prepared under controlled conditions to give reproducible results. In earlier reports [14 - 16] we have shown that CuCNS (a p-type semiconductor of bandgap equal to about 3.2 eV [17]) is an ideal material for studying dye sensitization for the following reasons. (1) As a result of the polymeric nature of CuCNS, thin films of this material free from cracks and pinholes can be deposited on copper substrates quite easily [14 - 16]. (2) CuCNS surfaces readily adsorb thiocyanates of cationic dyes. (3) The adsorbed dye does not leach into the solution. (4) CuCNS is completely photostable and does not react with electrolytes such as KI-I₂ or KCNS [14 - 16].

In this work we have measured the photocurrent quantum efficiencies of p-CuCNS photocathodes in KI-I₂ sensitized with different dyes, as a function of the surface concentration of the dye and the concentration of the electron acceptor (I₃⁻) in the electrolyte. We obtained a relationship that describes the variation in ϕ with the surface concentration of the dye.

2. Experimental details

CuCNS was deposited on copper plates (3 cm × 3 cm) by the method described in ref. 14. A deposit free from cracks and pinholes is obtained if the copper plates are cleaned ultrasonically (a Branson B-92 ultrasonic cleaner was used) after anodic polishing in dilute HCl. The thiocyanates of cationic dyes DCNS were prepared from their chlorides DCl (D ≡ methyl violet, rosaniline, rhodamine B, rhodamine 6G, acridine orange, acridine yellow and safranin (Aldrich and BDH brands were used)) by heating the solid dye with a saturated solution of KCNS. The chloride is then converted into the thiocyanate by double decomposition.



In each case the solubility of DCNS was found to be less than that of DCl. The products were purified by recrystallization. CuCNS-deposited plates were coated with DCNS by keeping them immersed in a well-agitated solution of the dye (0.05 g in water (1 dm³) containing 10% alcohol). The amount of dye deposited depends on the length of the immersion time. The surface concentration of the dye was determined by extraction of the dye with alcohol and spectrophotometric estimation (Hitachi U-3200 spectrophotometer). The electrolyte was aqueous KI (0.1 mol dm⁻³) containing varying amounts of iodine (I₃⁻ ions act as the electron acceptor, [I₃⁻] ≈ [I₂]). Argon was flushed through the solution to remove dissolved oxygen. A platinum foil was used as the counterelectrode and the photocathode was biased (about -0.4 V *vs.* the standard calomel electrode; a Hokuto Denko HA-301 potentiostat was used) to give zero dark photo-

currents. Light intensities were measured using an Epply bolometer (model PSP). Photocurrent spectra were determined with an Applied Photophysics monochromator and a 100 W tungsten filament lamp.

3. Results

The time development of the short-circuit photocurrent of a DS CuCNS photocathode is indicated in Fig. 1. Measurements of the quantum efficiency

$$\phi = \frac{\text{short-circuit photocurrent}}{\text{electronic charge} \times \text{number of photons incident per second}}$$

were carried out in the steady region. The very slow decay of the photocurrent noticeable after 1 - 2 h is due to photodegradation of the dye. The plots of ϕ vs. λ for photocathodes sensitized with rhodamine B and methyl violet are shown in Fig. 2. The variation in ϕ (at the peak wavelength λ_{peak}) with the surface concentration D_0 of the dye is shown in Fig. 3. The plots of $d\phi/dD_0$ vs. D_0 are straight lines with negative slopes (Fig. 4) indicating that

$$\phi = AD_0 - BD_0^2 \quad (1)$$

where A and B are constants. There is an optimum surface concentration $[D_0]_{\text{op}} = A/2B$ that gives the maximum quantum efficiency $\phi_{\text{max}} = A^2/4B$. The parameter A increases with the increase in $[I_3^-]$ and approaches a nearly constant value, while B slowly decreases with the increase in $[I_3^-]$ and

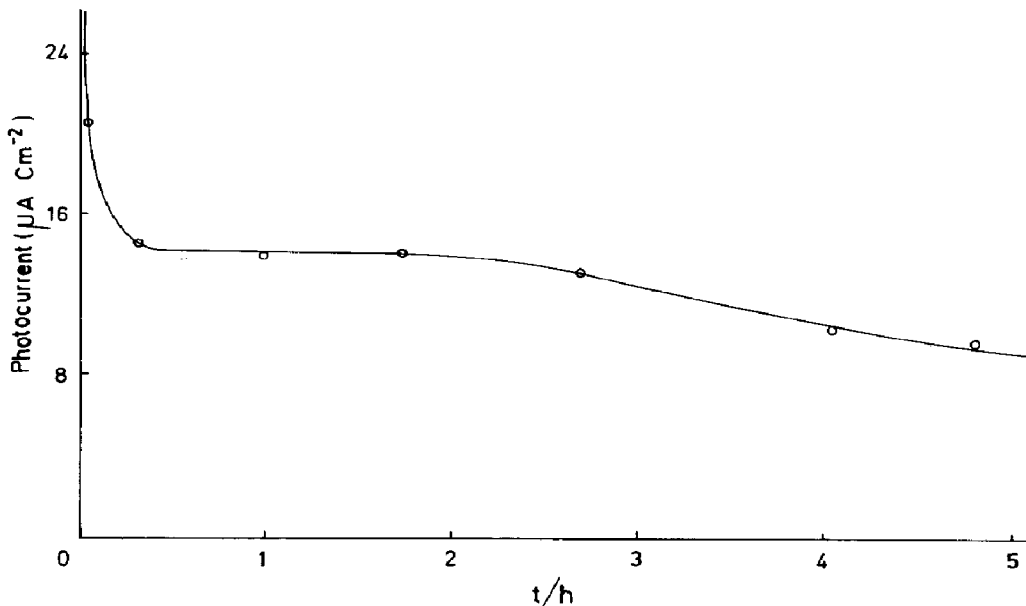


Fig. 1. Time development of the photocurrent of a CuCNS photocathode sensitized with rhodamine B.

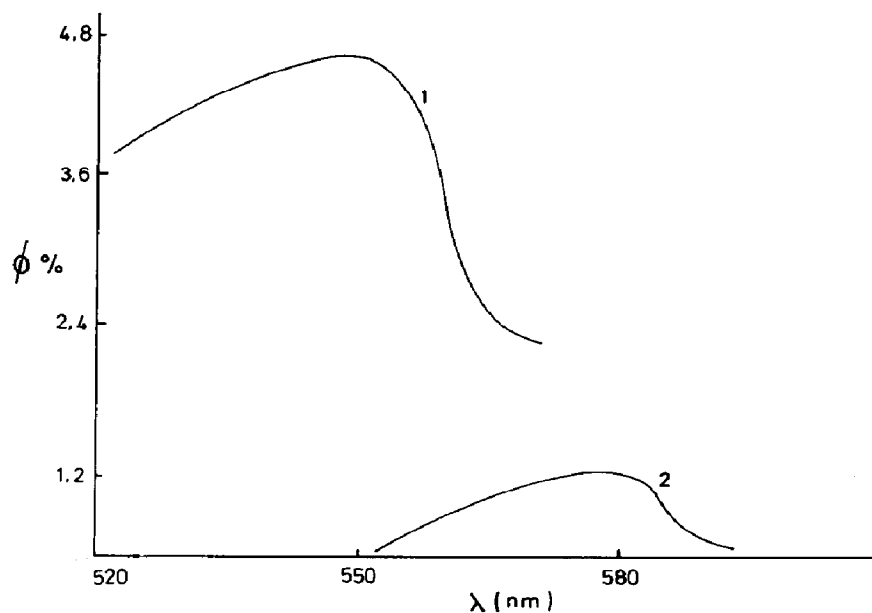


Fig. 2. Variation in quantum efficiency with wavelength ($D_0 = [D_0]_{\text{OP}}$; $[I_3^-] \approx 3 \times 10^{-4} \text{ mol dm}^{-3}$): curve 1, rhodamine B; curve 2, methyl violet.

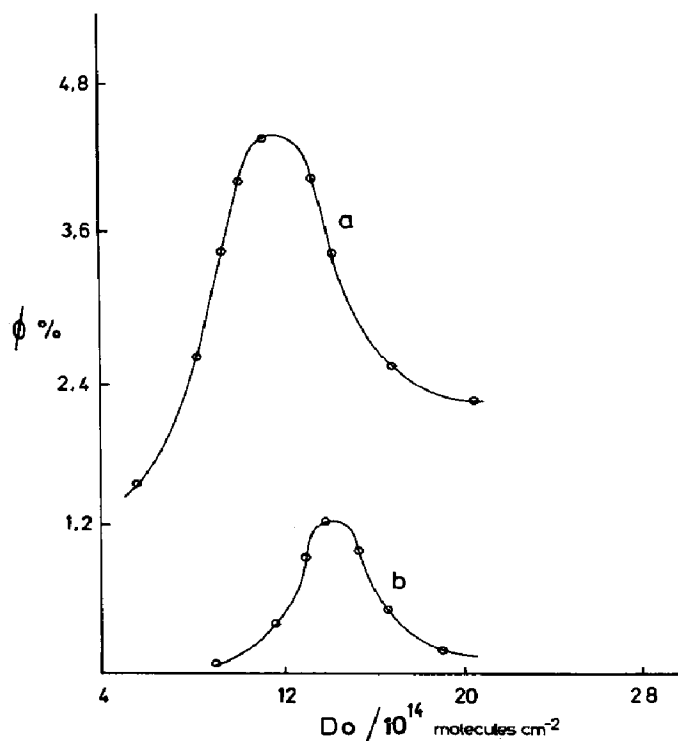


Fig. 3. Plot of ϕ (at λ_{peak}) vs. surface concentration D_0 of the dyes rhodamine B (curve a) and methyl violet (curve b). $[I_3^-] \approx 3 \times 10^{-4} \text{ mol dm}^{-3}$.

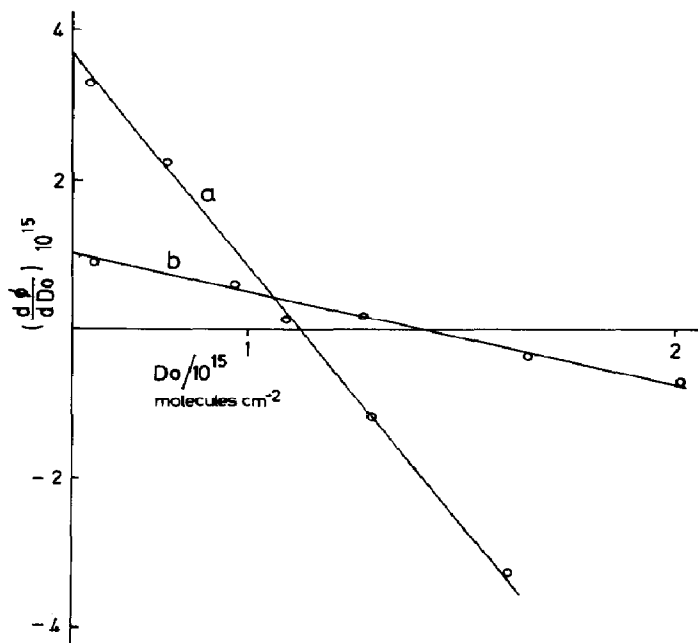


Fig. 4. Plot of $d\phi/dD_0$ vs. D_0 : line a, rhodamine B; line b, methyl violet.

rapidly reaches a steady value. At very high values of $[I_3^-]$, A and B are again found to decrease with the increase in $[I_3^-]$. The variation in A , B and ϕ_{\max} with $[I_3^-]$ for a cathode sensitized with rhodamine B is shown in Fig. 5. All the other dyes tested show the same behaviour. Table 1 gives the values of A , B and ϕ_{\max} for various dyes in the region where they are largely independent of $[I_3^-]$. In each case the quantum efficiencies are measured at the peak wavelength.

TABLE 1

The values of $[D_0]_{\text{op}}$, A , B and ϕ_{\max} for CuCNS photocathodes in KI- I_2 ($[I_3^-] \approx 3 \times 10^{-4}$ mol dm $^{-3}$) sensitized with different dyes

Dye	λ_{peak}	$[D_0]_{\text{op}}$ ($\times 10^{14}$ molecules cm $^{-2}$)	A ($\times 10^{-15}$ cm 2)	B ($\times 10^{-30}$ cm 4)	ϕ_{\max} (%)
Rhodamine B	550	11.2	7.8	3.5	4.4
Rhodamine 6G	550	14.5	3.8	1.3	2.8
Rosaniline	544	76.2	0.31	0.02	1.2
Methyl violet	580	14.0	1.71	0.61	1.2
Acridine orange	490	24.0	1.95	0.41	2.3
Safranine	545	33.9	0.63	0.09	1.1
Acridine yellow	450	39.7	0.42	0.05	0.84

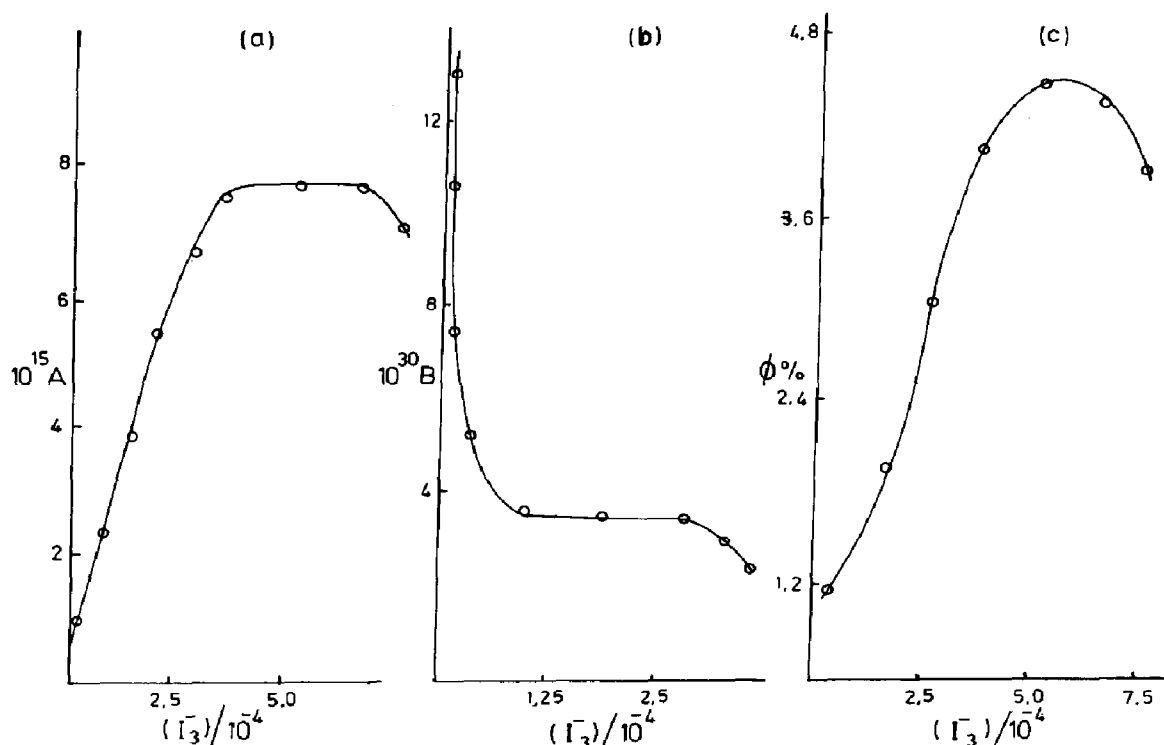
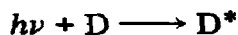


Fig. 5. Plot of (a) A vs. $[I_3^-]$, (b) B vs. $[I_3^-]$, (c) ϕ vs. $[I_3^-]$ for a cathode sensitized with rhodamine B (surface concentration $D_0 \approx [D_0]_{op}$; $[I_3^-]$ in mol dm⁻³).

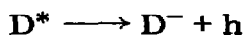
4. Theory and discussion

The cathodic sensitization of the semiconductor-dye-electrolyte interface is known to occur via the following processes.

(i) Excitation of dye molecules from the S_0 to the S_1 state



(ii) Hole transfer by excited dye molecules to the valence band

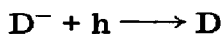


(iii) Charge transfer from the dye anion to an electron acceptor



In addition to the above, the following dissipative processes can also take place.

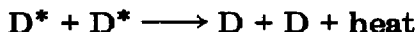
(iv) Recombination of the dye anions with the holes



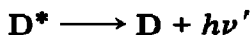
(v) Quenching of the excited dye by a species Y in the electrolyte



(vi) Concentration quenching, *i.e.* quenching of excited molecules by each other



(vii) De-excitation of excited molecules by emission of radiation



In addition to the above, the constraints at the interface must also be taken into account. Holes are rapidly removed by the applied bias, and therefore the total surface charge consisting of the acceptor states in the semiconductor, dye anions and other adsorbed ionic species on the surface of the dye layer and ions in the electrical double layer of the electrolyte must remain neutral. Again if D^* , D^- and D are the surface concentrations of the excited dye molecules, dye anions and non-excited dye molecules respectively, we have

$$D^* + D^- + D = \text{constant}$$

Solutions for (i) - (vii), subject to the above constraints, yield expressions that approximate to the form of eqn. (1). However, precise measurements of the individual rate constants are necessary to interpret the results quantitatively.

Experimental data indicate that deviations from eqn. (1) occur at higher surface concentrations of the dye. (According to eqn. (1) the second derivative of ϕ should always be negative. However, Fig. 3 shows that there is a tendency for this quantity to become positive at higher concentrations of the dye.) It is not possible to determine at this stage (*i.e.* without a knowledge of the relative magnitudes of the rate constants) whether this effect is included in the reactions (i) - (vii) or whether it arises as a consequence of another process.

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