A TECHNIQUE FOR REDUCING THE RATE OF CONCENTRATION QUENCHING IN A DYE-SENSITIZED PHOTOELECTRODE

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Summary

It is shown that if a thin layer of a solid substrate having large interstitial cavities is deposited on a semiconductor surface it can be made to adsorb dyes without formation of aggregates. Consequently, a photoelectrode made by this technique gives higher photocurrent quantum efficiencies owing to a reduction in the rate of concentration quenching. Observations on CuCNS photocathodes sensitized after deposition of a thin layer of cuprous cobalticyanide are presented to illustrate the phenomenon.

1. Introduction

Dye sensitization has received considerable attention as a means of extending the spectral response of photoelectrochemical cells (PECs) based on high bandgap materials [1 - 6]. Unfortunately, the dye-sensitized PECs have low photocurrent quantum efficiencies ϕ. It is known that in a sensitized photoelectrode ϕ can be enhanced by using efficient redox couples [1 - 4], optimization of dye adsorption [4, 6] or increasing the donor density of the semiconductor [5]. However, the principal factor that limits the ϕ of these systems is concentration quenching (CQ) [7, 8]. The excited dye molecules, instead of participating in the electron (or hole) transfer reaction with the semiconductor, dissipate energy via CQ. The only way to suppress CQ is to devise a method of dispersing dye molecules on the surface, minimizing the formation of aggregates. In an earlier work we reported that CuCNS (a p-type semiconductor with a bandgap of about 3.2 eV [6, 9]) is an excellent material for studying dye sensitization, because of the extreme ease with which it adsorbs thiocyanates of cationic dyes [6]. As a method

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of making photoelectrodes that adsorb dyes without aggregation, we have attempted to deposit on the top of a CuCNS surface a thin film of inert substrate of solid insulating material having large interstitial cavities. The idea is that if the dimensions of these cavities are sufficiently large for "fitting" the dye molecules a layer of the dye where the molecules are separated from each other will be adsorbed on the composite interface. Heavy-metal hexacyanides (Prussian-blue-type compounds) have a large free internal volume per unit cell. After investigating several water-insoluble hexacyanides, we found that a layer of cuprous cobalticyanide can be deposited on a CuCNS surface and that photoelectrodes made by this method give higher quantum efficiencies.

2. Experimental details

CuCNS was electrochemically deposited on 3 cm × 3 cm copper plates by the method described in ref. 6. The quality of the deposit is greatly improved and reproducible results are obtained if the copper plates are cleaned ultrasonically (a Branson B-92 ultrasonic cleaner was used) after anodic polishing in dilute H_2SO_4. A layer of cuprous cobalticyanide was deposited on top of the CuCNS by keeping the electrode immersed in a solution of potassium cobalticyanide (0.05 M) for 10 min. Cuprous cobalticyanide is formed by double decomposition:

$$K_3[Co(CN)_6] + 3CuCNS \longrightarrow Cu_3[Co(CN)_6] + 3KCNS \qquad (1)$$
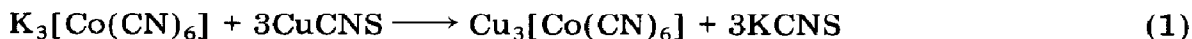
The quality of $Cu_3[Co(CN)_6]$ deposited was determined by spectrophotometric estimation for KCNS with $FeCl_3$. Samples of $Cu_3[Co(CN)_6]$ was also prepared by boiling CuCNS powder with $K_3[Co(CN)_6]$. The electrical conductivity and density of $Cu_3[Co(CN)_6]$ were found to be about 10^{-8} Ω^{-1} cm^{-1} and 1.3 g cm^{-3} respectively. CuCNS and CuCNS/$Cu_3[Co(CN)_6]$ plates were coated with thiocyanates of methyl violet (MCNS) or rhodamine B (RCNS) by being immersed in a well-agitated solution of MCNS or RCNS (0.5 g per litre of water containing 10 vol.% alcohol). Plates were washed with distilled water to remove the excess dye. The amount of dye deposited was determined by extracting the dye with alcohol and spectrophotometric estimation. MCNS and RCNS were prepared from MCl and RCl (Aldrich) by heating the solid dye with a saturated solution of KCNS, when double decomposition converted the chloride into the thiocyanate. The products were purified by recrystallization. The electrolyte was a 0.1 M aqueous solution of KCNS. This electrolyte has the following advantages: (1) MCNS and RCNS are practically insoluble in 0.1 M KCNS, and consequently the adsorbed dye does not pass into the solution; (2) CuCNS and $Cu_3[Co(CN)_6]$ remain photostable in aqueous KCNS; (3) KCNS acts as a redox couple owing to the existence of CNS^- and $(CNS)_2^-$ ions [6]. A platinum foil was used as the counterelectrode and the CuCNS electrode was potentiostatted at −0.4 V *vs.* the standard calomel electrode (SCE) (Hokuto Denko A-301

potentiostat). The diffuse reflectance spectra were measured with a Unicam SP 500 Series II spectrophotometer, the light intensities were measured using an Eppley bolometer and the photocurrent quantum efficiencies were determined with an Applied Photophysics monochromator.

3. Results and discussion

Figure 1 gives the plot of ϕ at the peak wavelength (580 nm and 550 nm respectively for MCNS and RCNS) vs. the surface concentration s of the dye for CuCNS/Cu$_3$[Co(CN)$_6$] plates, sensitized with MCNS and RCNS. ϕ is given by

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

An increase in s increases the light absorption cross-section; however, this also increases CQ. The existence of an optimum dye surface concentration s_{oc} results from competition between these two opposing effects. Figure 2 shows the variation in ϕ in CuCNS/dye and CuCNS/Cu$_3$[Co(CN)$_6$]/dye photocathodes with the wavelength when $s = s_{oc}$. It is clear that the latter system has higher values for ϕ compared with the former. The effect is more pronounced when $s \geqslant s_{oc}$ of the CuCNS/Cu$_3$[Co(CN)$_6$]/dye system.
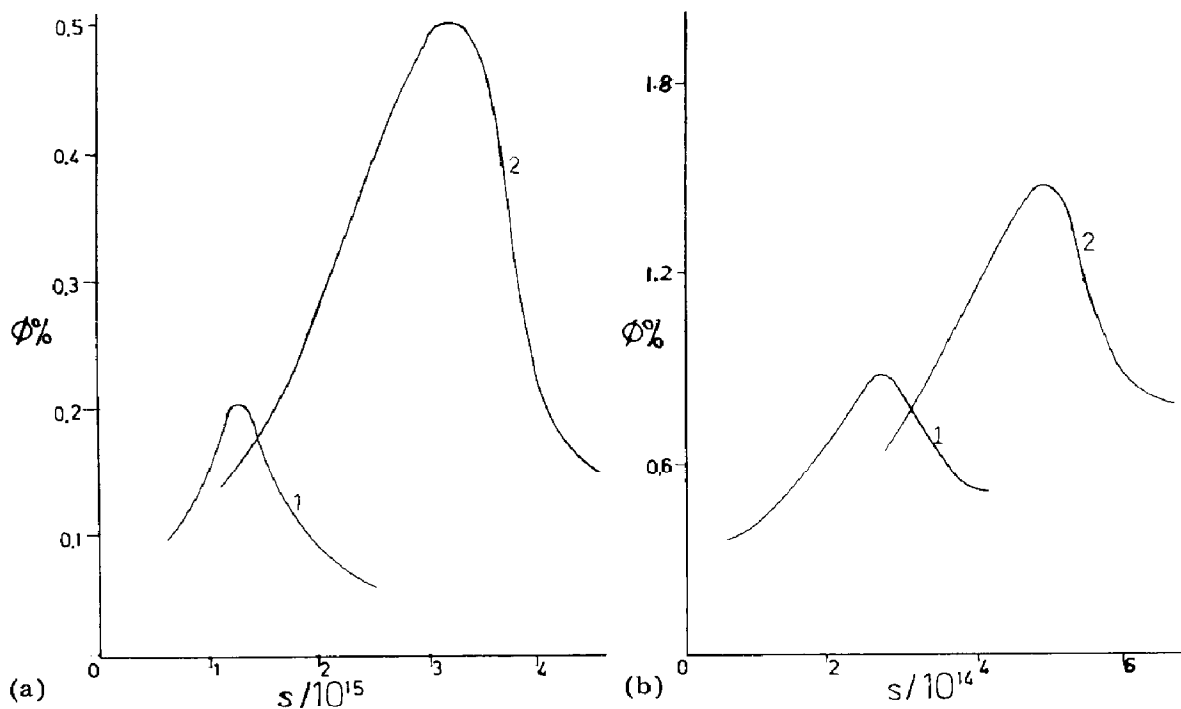

Fig. 1. Plot of photocurrent quantum efficiency at peak wavelength vs. surface concentration s (molecule cm^{-2}) of the dye for (1) CuCNS and (2) CuCNS/Cu$_3$[Co(CN)$_6$] sensitized with (a) MCNS and (b) RCNS.
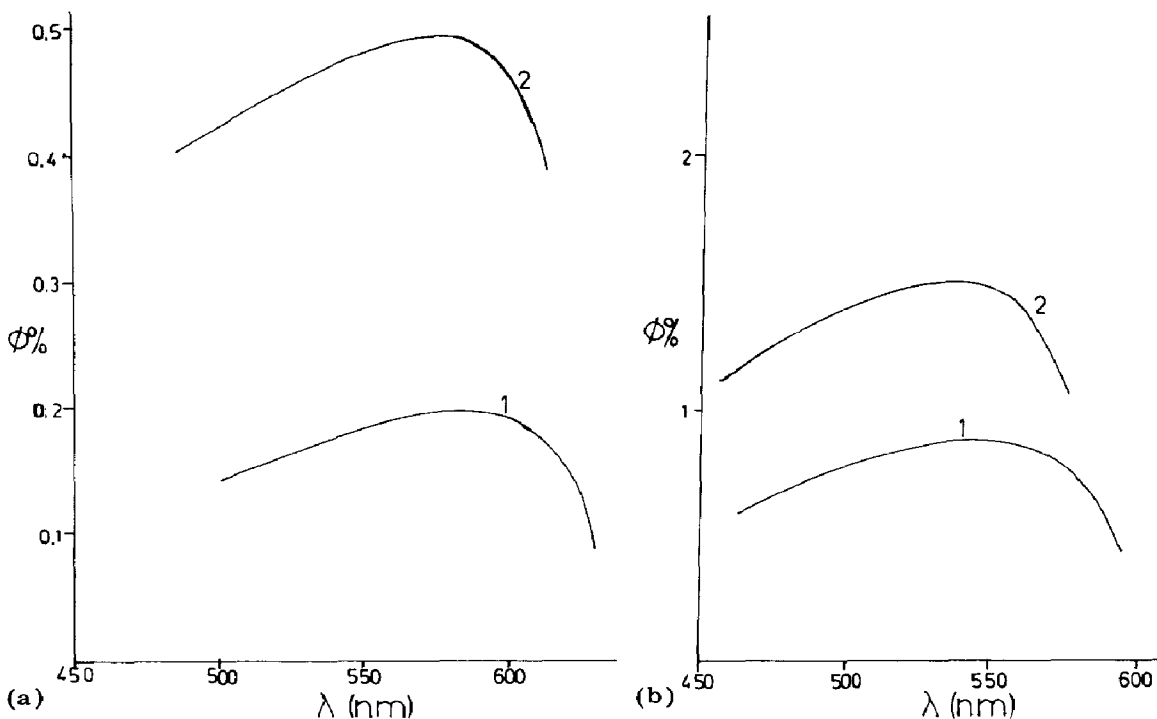
260

Fig. 2. Variation in quantum efficiency with wavelength at the respective optimum surface concentration: CuCNS (curves 1) and CuCNS/Cu$_3$[Co(CN)$_6$] (curves 2) sensitized with (a) MCNS and (b) RCNS.

The above observations can be understood when we consider the crystal structure of Cu$_3$[Co(CN)$_6$]. Heavy-metal hexacyanides form face-centered cubic lattices with metal ions at the corners of cubes (1/8 unit cell) joined along the edges by C≡N$^-$ ions, the lattice constant being 10 - 11 Å [10, 11] (Fig. 3(a)). When allowance is made for the dimensions of the ions, the edge of a square cavity will have a length of about 3 - 4 Å. The linear dimensions of the rigid units of the dye molecules are about 3 Å (Fig. 3(b)). Thus, parts of dye molecules could "fit" into the cavities, enhancing dye adsorption. This is supported by the following observation. When a CuCNS/Cu$_3$[Co(CN)$_6$] electrode with $s > s_{oc}$ is kept submerged in circulating water, the dye leaches into the solution initially at a rapid rate, but when s approaches s_{oc} the rate is drastically reduced. The same behaviour is not seen in CuCNS/dye electrodes: in this case the dye leaches into the solution continuously.

In a CuCNS/dye photocathode there is no way to control the formation of aggregates of the dye molecules. All one can expect is that the probability of aggregation is smaller at lower dye concentrations. However, in the CuCNS/Cu$_3$[Co(CN)$_6$]/dye system, aggregation of dye molecules is less likely to occur, provided that loosely adsorbed dye is washed away. Here s_{oc} corresponds to occupation of each cavity by one dye molecule (Fig. 3(c)). It is interesting to note that the number of cavities per unit area (about 4 ×
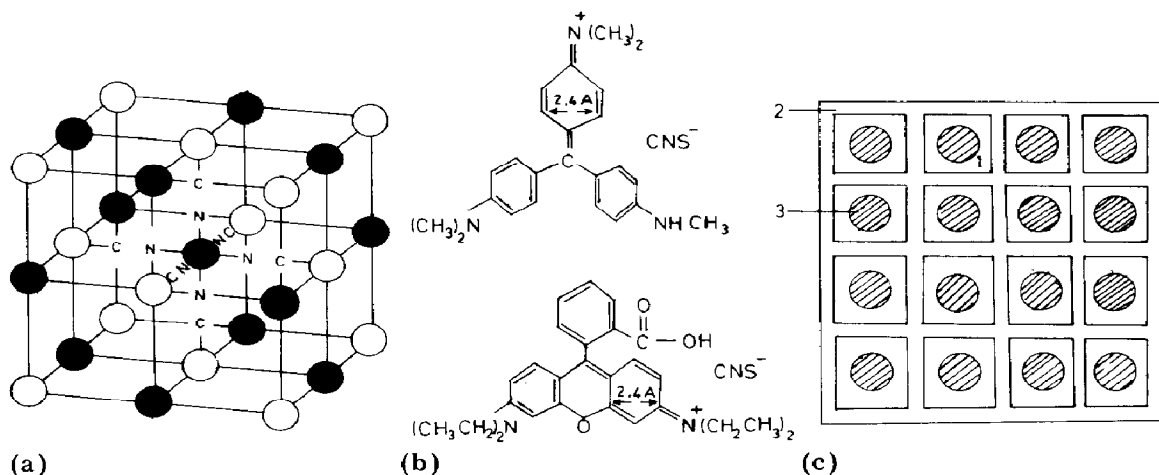
Fig. 3. (a) Crystal structure of $Cu_3[Co(CN)_6]$ (●, Co^{3+}; ○, Cu^+). (b) Dye molecules MCNS and RCNS. (c) Schematic diagram illustrating the structure of $CuCNS/Cu_3[Co(CN)_6]/dye$, when $s = s_{oc}$. Regions marked 1, 2 and 3 correspond to areas covered by CuCNS, $Cu_3[Co(CN)_6]$ and dye respectively.
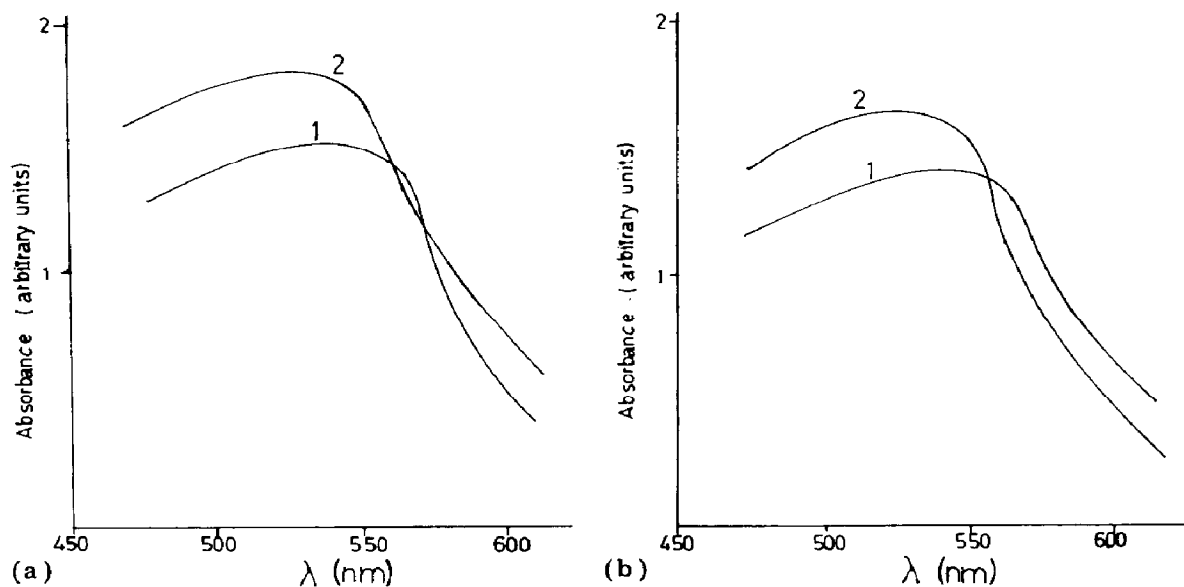

Fig. 4. Diffuse reflectance spectra of (a) MCNS and (b) RCNS, coated on CuCNS (curves 1) and $CuCNS/Cu_3[Co(CN)_6]$ (curves 2).

10^{14} cm^{-2}) is close to the observed value of s_{oc} for $CuCNS/Cu_3[Co(CN)_6]/$ dye systems.

There is another observation which supports the above explanation. It is known that the absorption spectra of the aggregates of dye molecules are red shifted with respect to those of individual molecules [12, 13]. Figure 4 shows the diffuse reflectance spectra of MCNS and RCNS on CuCNS and $CuCNS/Cu_3[Co(CN)_6]$, and it is seen that the former spectra are slightly red shifted with respect to the latter (diffuse reflectance spectra of CuCNS and

CuCNS coated with $Cu_3[Co(CN)_6]$ are almost indistinguishable in the visible region and the above effect could not arise from the difference between the substrates). The same red shift is noticeable in the photocurrent spectra (Fig. 2).

4. Concluding remarks

In the absence of a dye, the photoresponse shown by $CuCNS/Cu_3$-$[Co(CN)_6]$ is even more feeble than that of CuCNS. Thus the effect we have noticed could not arise from a difference between the photoelectrochemical properties of CuCNS and CuCNS coated with $Cu_3[Co(CN)_6]$. Thin layers of $Cu_3[Co(CN)_6]$ give better results as this material has a high electrical resistivity. The method of preparation described in Section 2 gave layers 20 - 30 Å thick (as estimated by measurement of the weight deposited).

Acknowledgment

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