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Dye-sensitised solid-state photovoltaic cells

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Abstract. A thin layer of dye sandwiched between p–CuCNS deposited on copper substrate and $n-SnO_2$ coated transparent glass was found to yield photocurrents resulting from light absorption in the dye. The mechanism of photocurrent generation is discussed.

1. Introduction

The photo-effects at the dye-coated semiconductor surface are well known in connection with silver halide photography. As far back as 1938 the electron transfer process involved in sensitisation of silver halides was studied and the correct explanation given by Gurney and Mott [1]. Subsequently the dye sensitisation of the semiconductor electrolyte interface was investigated by many workers [2-9] and it was established that anodic (cathodic) sensitisation occurs when an excited dye molecule adsorbed at the semiconductor surface injects electrons (holes) into the conduction (valence) bands. The type of sensitisation occurring depends on the relative locations of the band positions of the semiconductor and the energy levels of the dye. If they are located as in figure 1(a) an electron excited from the lower (S_0) to the upper energy 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

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valence band is transferred to the unoccupied lower level (i.e. holes are injected into the vB).

Recently there has been a renewed interest in dye sensitisation as a means of extending the spectral response of photo-electrochemical cells (PECS) based on high-band-gap materials [7–12]. The dye sensitised (DS) PECS have the following advantages.

(i) The semiconductors that resist photocorrosion are the high-band-gap materials. Dye sensitisation affords a method of extending their spectral response to the visible region.

(ii) The spectral response can be easily controlled as a wide variety of dyes are available.

(iii) The interfacial electron transfer in DS PECS involves only one band (a conduction band in an anodically sensitised process and a valence band in a cathodically sensitised process). As a result electronhole recombinations are minimal and DS photocurrents become less sensitive to defects and traps in the semiconductor [13].

Unfortunately, the DS PECS have two serious defects.



Figure 1. An energy level diagram illustrating dye sensitisation. (*a*) Anodic sensitisation. (*b*) Cathodic sensitisation.

(i) The dyes used for sensitisation undergo photodegradation.

(ii) To increase the light absorption cross section, the surface concentration (sc) of the dye has to be increased. However, when the sc is increased, the photo-excited dye molecules which are in contact quench each other (concentration quenching) dissipating excitation energy into heat.

The latter process can be minimised if a means is found to disperse the dye molecules avoiding intimate contact, e.g. by depositing a thin layer of a solid having large interstitial cavities [14]. In DS PECS, the dyes degrade because the electron transfer and the excitation of dye molecules takes place in an environment containing reactive ions and molecules. The problem of dye degradiation does not arise in DS cells where electrolytes are not employed. Although forming an effective contact as in a PEC could be an almost insurmountable problem that limits the use of such devices as practical solar cells, the DS semiconductor solid-state cell could find applications in micro and molecular electronic devices. In this work we describe a DS solidstate photovoltaic cell made from p-CuCNS and n-SnO₃. The variation of the quantum efficiencies with the sc of the dye are determined and compared with an equivalent DS PEC system. β -CuCNS (p-type semiconductor of band gap $\approx 3.6 \text{ eV} [11]$) was chosen at it is an ideal semiconductor substrate for the study of dye sensitisation. In series of reports we have discussed the properties of β -CuCNS and DS PECS based on this material [11, 15–18]. The crystals of β -CuCNS grow as pyramids consisting of 3R and 2H polytypes in syntactic coalescence. In fact the structure is a three-dimensional polymer composed of layers of close packed interbonded CuCNS units, where the adjacent layers are bonded to each other by strong Cu–S bonds [19–20]. As a result of the polymeric nature, thin films of β -CuCNS free from cracks and pin-holes can be easily deposited on copper surfaces [11, 15]. These films are firmly affixed to the substrate and quite readily adsorb other substances notably the thiocyanates of cationic dyes [15, 17].

2. Experimental details

Copper plates $(5 \times 5 \text{ cm})$ were mechanically polished to obtain a flat surface and then ultrasonically cleaned. CuCNS was deposited by immersing the plates in an aqueous solution of KCNS (0.05 M) containing acetic acid (0.01 M) and propan-2-ol (1% by volume). The small quantity of thiocyanic acid generated reacts with copper to form a film of β -CuCNS

$$KCNS + CH_3COOH \rightarrow CH_3COOK + HCNS$$
 (1)

$$4Cu + 4HCNS + O_2 \rightarrow 4CuCNS + 2H_2O.$$
 (2)

Propan-2-ol assists the removal of grease from the surface. The thickness of the film can be controlled by changing the duration of immersion. To determine the thickness of the CuCNS film the plate was digested with dilute NaOH to extract NaCNS, which is estimated spectrophotometrically with FeCl₃. The films of CuCNS prepared by this method are largely free from cracks and pin holes if precautions are taken to clean the surface and avoid contamination with grease.

The dyes in this investigation were Rhodamine B (R) and Methyl Violet (M). The commercial dyes that are chlorides (Rhodamine B and Methyl Violet supplied by BDH were used) are converted into the thiocyanates DCNS (D = M or R) by double decomposition with a boiling saturated solution of KCNS, i.e.

$$DCl + KCNS \rightarrow DCNS + KCl.$$
 (3)

As DCNS is less soluble than DCl (3) proceeds in the forward direction. DCNS was purified by recrystallisation. The structural formulae shown in figure 2 were used to determine the monolayer thickness of the dye films.

CuCNS surfaces were coated with dyes by the following method. Plates were immersed in a solution of DCNS (containing 5–10% ethyl alcohol to increase the solubility of the dye). Depending on the duration of immersion and the strength of the dye solution, varying sc of the dye gets adsorbed into the surface. The scs were determined by extracting the dye with ethyl alcohol and spectrophotometric estimation. The absorption spectra of dyes in solution and the diffuse reflectance



Figure 2. Thiocyanates of Rhodamine B (*a*) and Methyl Violet (*b*).



Figure 3. The construction of the CuCNS/dye/SnO₂ cell.

spectra of the dye-coated surfaces were obtained using the Hitachi U-3200 spectrophotometer.

The photovoltaic cell was assembled (figure 3) simply by keeping the conducting surface of NESA glass (SnO₂ transparent film on glass, surface resistance $\approx 1.2 \times 10^2 \,\Omega \,\mathrm{cm^{-1}}$) in contact with the dye-coated surface. Photocurrents were measured with an electrometer (Advantest TR 8652). A 250 W halogen lamp and a monochromator (Applied Photophysics) were used to determine photocurrent spectra. The light intensities were measured using an International Light IL 700 Radiometer.

3. Results and discussion

Figure 4 shows the variation of the photocurrent quantum efficiency (where φ is the short-circuit photocurrent/electronic charge × number of photons incident per second) with the sc of the dye. The photocurrent spectra at the peak sc of the dye are compared with the absorption spectra of the dyes in solution and the diffuse reflectance spectra of the dyecoated surfaces in figure 5. It is seen that the peak position in the photocurrent spectra are nearly in agreement with the peaks in the optical spectra. The deviation of the profile of the diffuse reflectance spectra from the photocurrent spectra at shorter wavelengths arise from absorption in the CuCNS substrate. It follows that only the light absorption by the dye is contributing to the photocurrent.

The photophysical processes associated with current generation can be summarised as follows.

(i) Excitation of dye molecules from the $S_{\scriptscriptstyle 0}$ to the $S_{\scriptscriptstyle 1}$ state

$$h\nu + D \rightarrow D^*.$$
 (4)

(ii) Hole and electron transfer by the excited dye molecules to the valence band of p-CuCNS and the conduction band of $n-SnO_2$

$$D^* \rightarrow D + h^+ + e^- \qquad (5)$$

$$\downarrow \qquad \downarrow \qquad \downarrow$$

$$VB CuCNS \quad CB SnO_2.$$

The above charge transfer could occur via different steps, i.e.

or

$$D^* \rightarrow D^+ + e^- \qquad \qquad \downarrow \qquad (7)$$

$$CB SnO_2$$

$$D^+ \rightarrow D + h^+ \qquad \qquad \downarrow$$

$$VB CuCNS$$



Figure 4. The variation of the photocurrent quantum efficiency at the peak wavelength with the sc and monolayer thickness of the dye. (A) Rhodamine B (B) Methyl Violet.



Figure 5. The photocurrent spectra (full curve) compared with the diffuse reflectance spectra of the dye-coated surfaces (broken curves) and the absorption spectra of the dye solution (dotted curves). (a) Rhodamine B and (b) Methyl Violet.

where D^* , D^- , D^+ denote excited dye molecules, dye anions and dye cations, respectively, The individual sensitisation of CuCNS and SnO₂ with the dyes R or M results in cathodic and anodic photocurrents, in agreement with the above scheme. However, when the dye layer approaches monolayer dimensions, these two models become indistinguishable, i.e. the charge separation is essentially the process (5). In addition to the above, the following dissipative processes can also take place.

(iii) Recombination of the electron-hole pairs

$$D + e^- + h^+ \rightarrow D + heat.$$
 (8)

(iv) De-excitation of excited molecules by the emission of radiation

$$D^* \to D + h\nu'. \tag{9}$$

(v) Concentration quenching, i.e. quenching of the excited molecules by each other

$$D^* + D^* \rightarrow D + D + heat.$$
(10)

The photocurrent quantum efficiency of the cell depends on the rate constraints of the processes (4), (5), (8), (9) and (10), the barrier fields at CuCNS/D/SnO₂ and the internal resistance of the system. The rates of the processes (4), (5), (8) and (9) depends linearly on [D] the sc of the dye, whereas that of (10) varies as $[D]^2$. Thus one would expect that at least to a first approximation, the photocurrent quantum efficiency of the cell would vary with sc of the dye according to the expression

$$\varphi = A[D] - B[D]^2 \tag{11}$$

where A and B are constants. Although deviation from the parabolic expression (11) is noticeable at both low and high sc of the dye, the results are in reasonable agreement with (11) as shown in figure 6 where $d\varphi/d[D]$ is plotted against [D]. The table 1 gives the values of the parameters A, B and the quantum efficiency at the optimum sc of the dye ([D]_{op}). A DS CuCNS photocathode in aqueous KI + I₂ (figure 7) also shows a variation of φ with [D] of the same form as (11) [21]. The values of the relevant parameters of the wet and dry cells are compared in the table 1. Although the values of the parameters A, B and φ_{max} differ widely, it



Figure 6. The plot of $d\varphi/d[D]$ against [D]. (A) Rhodamine B (B) Methyl Violet. ([D] in molecules cm^{-2}).

System	$\lambda_{peak}(nm)$	10 ¹⁴ [D] _{op}	A (cm ²)	B (cm⁴)	$arphi_{Max}$
Rhodamine dry cell	540	3.1	7.6×10 ⁻²¹	3.3×10 ⁻³⁶	1.8×10 ⁻⁶
Methyl Violet dry cell	570	10.9	14.0×10 ⁻²¹	$22.5 imes 10^{-36}$	1.7 × 10 ⁻⁶
Rhodamine wet cell	550	11.2	7.8×10 ⁻¹⁵	$3.5 imes 10^{-30}$	4.4
Methyl Violet wet cell	580	14.2	1.71 × 10 ⁻¹⁵	$0.61 imes 10^{-30}$	1.2

Table 1. The maximum quantum efficiencies and the values of parameters A, B and $[D]_{op}$ for the dry and wet cells. $([D]_{op}$ in molecules cm⁻²).

is interesting to note that $[D]_{op}$ is of the same order of magnitude for both types of cell. We are not in a position to give a quantitative explanation of this observation. The quantum efficiency of the dry cells are minute compared with the wet cells. The severe difficulty in the dry cells is the establishment of a good contact with the electrode avoiding short-circuiting while maintaining the thickness of the dye layer at monolayer dimensions (the $[D]_{op}$ corresponds to few monolayers (figure 4)). The open-circuit voltages are largely independent of the sc of the dye (R sensitised cell $\approx 90 \text{ mV}$, M sensitised cell $\approx 96 \text{ mV}$, dark voltages are negligible). The power conversion efficiencies are of the order 10^{-7} - 10^{-8} .

If methods are found for sandwiching a monolayer thickness of the dye between two semiconductor electrodes, where at least one is transparent, the power and quantum efficiencies can be increased. The enhancement of the barrier fields at the ends (i.e. the semiconductor dye junctions) might be capable of suppressing concentration quenching which is in competition with the charge separation process. Recently photovoltaic cells [22–24] and molecular electronic devices based on organic materials have attracted attention. It is likely that studies on the organised assemblies [25–26] of dyes



Figure 7. The variation of the photocurrent quantum efficiency at the peak wavelength with the sc and monolayer thickness of the dye in a wet PEC sensitised with (A) Rhodamine B (B) Methyl Violet.

sandwiched between transparent semiconductor electrodes will lead to new developments having practical implications.

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