# THE CHARACTERISTICS OF A p-CuCNS PHOTOCATHODE SENSITIZED WITH ACRIDINE ORANGE

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A copper plate coated with p-CuCNS and sensitized with Acridine Orange thiocyanate is found to be an excellent system for studying dye-sensitization. The variation of the photocurrent quantum efficiency of this photocathode with surface concentration of the dye is studied. Sub-monolayer quantities of platinum on the surface of the sensitized photocathode are found to have a marked influence on the photocurrent quantum efficiency and stability of the cell.

#### 1. Introduction

Dye-sensitized (DS) photoelectrochemical cells (PECs) and semiconductor catalysts have attracted much attention as promising devices for conversion and storage of solar energy [1-8]. The advantages of DS systems are: (1) Easy control of the spectral response. (2) The possibility of using high band gap materials that are resistant to photocorrosion. However, DS devices suffer from the following defects: (1) Although the semiconductor remains stable the dyes undergo rapid photodegradation. (2) Sensitization is effective only if the dyes are firmly affixed to the surface of the semiconductor. (3) Concentration quenching severely limits quantum efficiencies [9,10].

We have found that cuprous thiocyanate (p-type semiconductor of band gap 3.2 eV [8,11]) is an ideal material for studying dye-sensitization, because it readily adsorbs cationic dyes having  $CNS^-$  as the anion [8]. In an earlier paper [8] we have described a DS PEC based on CuCNS. Here we report our observations on how the photocurrent quantum efficiency of a p-CuCNS photocathode sensitized with Acridine Orange (A) changes with the surface concentration of the dye and also how the quantum efficiencies are influenced by deposition of trace quantities of platinum on the dye adsorbed surface.

#### 2. Experimental

CuCNS was deposited on  $3 \times 3$  cm copper plates electrochemically by the method described in ref. [8]. The quality of the deposit is greatly improved and

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reproducible results are obtained if the copper plates are cleaned ultrasonically (Branson B-92 ultrasonic cleaner was used) after anodic polishing in dilute  $H_2SO_4$ . CuCNS deposited plates were coated with thiocyanate of Acridine Orange (ACNS) by keeping them immersed in a well agitated solution of the dye (0.05 g in  $dm^3$  of water containing 10% ethanol). The amount of dye deposited was determined by measuring the concentration of the dye spectrophotometrically. Dye concentration was also determined by extraction of the deposited dye with alcohol and spectrophotometric estimation. Both methods gave similar results. ACNS was prepared from ACl (Aldrich) by heating the solid dye with a concentrated solution of KCNS, when double decomposition converts ACl into ACNS. The product is purified by recrystallization. Of the several cationic dyes tested, Acridine Orange was found to be most suitable for this investigation. The solubility of ACNS in water at 26°C is ~ $1.3 \times 10^{-5}$  mol dm<sup>-3</sup> compared to ~ $2.0 \times 10^{-2}$  mol dm<sup>-3</sup> for ACl. In 0.1 mol dm<sup>-3</sup> KCNS, which is the electrolyte used in the PEC, the solubility of ACNS is further suppressed ( $\leq 10^{-8}$  mol dm<sup>-3</sup>). This is a tremendous advantage. Even if very thin layers of dye are deposited, measurements can be performed without depletion of the dye into the solution.

Dye coated plates were platinized by the following method [12–14]. Plates were immersed in a citrate buffer ( $pH \approx 4.7$ ) containing  $8 \times 10^{-8}$  mol dm<sup>-3</sup> chloroplatinic acid and irradiated with an tungsten filament lamp. (Intensity at the surface of the plate 250 W m<sup>-2</sup>.) The amount of Pt deposited was estimated spectrophotometrically by noting the decrease in concentration of chloroplatinic acid.

A platinum foil was used as the counter-electrode and the photocathode was biased (-0.40 V vs SEC) to give zero dark voltage (Hokuto Denko, HA-301 potentiostat was used). Light intensities were measured using an Eppley Bolometer (Model PSP). Photocurrent spectra were ascertained with an Applied Photophysics Monochromator and a 100 W tungsten filament lamp. Absorption spectra of dye coated CuCNS plates were measured with a Unicamp SP 500 Series II spectrophotometer.

## 3. Results and discussion

In the absence of a sensitizer a CuCNS coated plate shows no photoresponse in the visible region (even in the UV region the photoresponse in the absence of a dye is insignificantly small [8]). Fig. 1 shows the plot of photocurrent quantum efficiency (short circuit photocurrent/number of photons incident per second  $\times$  electronic charge) vs wavelength of incident light when the plate is coated with ACNS. The peak position in the photocurrent spectrum ( $\lambda = 470$  nm) is quite close to the peak point in the absorption spectrum of the dye in solution or the diffuse reflectance spectrum of the dye coated surface. Fig. 2 shows the variation of the quantum efficiency with surface concentration of dye molecules at the peak wavelength and 589 nm. The highest quantum yield occurs when the surface concentration of the dye is  $\sim 6.3 \times 10^{14}$  molecules/cm<sup>2</sup> (i.e.,  $\sim 3$  monolayers as estimated from the area of a dye molecule  $\approx 1.5 \times 10^{-14}$  cm<sup>2</sup>, fig. 3 gives the dimensions of a



Fig. 1. Plot of quantum efficiency of photocurrent vs wavelength when the surface concentration of the dye is (a)  $\sim 10^{15}$  molecules cm<sup>-2</sup>, (b)  $\sim 10^{14}$  molecules cm<sup>-2</sup>. 1 – Unplatinized plate; 2 – platinized plate; 3 – absorption spectrum of aqueous Acridine Orange; 4 – diffuse reflectance spectrum of Acridine Orange coated CuCNS plate (absorbance in arbitrary units).

dye molecule) and this is not dependent upon the wavelength. The I–V curve for the cell at the optimum surface concentration of the dye for white light (100 W tungsten filament lamp at intensity 250 W  $m^{-2}$ ) is shown in fig. 4. The power conversion efficiency is found to be quite small.

The deposition of trace quantities of Pt modifies the photocurrent quantum efficiencies in an interesting way. At higher dye concentrations ( $\geq 6 \times 10^{14}$  molecules/cm<sup>2</sup>) the deposition of trace quantities of Pt increases the quantum efficiency (fig. 1a). When the dye concentrations are lower the opposite effect is seen (fig. 1b), i.e. Pt deposition lowers the photocurrent quantum efficiency. In the former case the highest quantum efficiency is obtained when the surface concentration of Pt is ~ 10<sup>11</sup> molecules/cm<sup>2</sup>. At higher dye concentration ( $\geq 6 \times 10^{11}$  molecules/cm<sup>2</sup>) Pt deposition has a marked influence on the stability of the cell (fig. 5). The decay of photocurrent due to degradation of the dye (CuCNS remains completely stable) is suppressed by Pt deposition.

The above observations can be understood on the basis of the presently available knowledge on the electron transfer process in dye-sensitization [1-5]. The cathodic sensitization of a p-type material is supposed to occur via the following mechanism. When an electron in the dye molecule is excited from lower level into the upper level, and electron from the valence band is transferred into the half-occupied lower



Fig. 2. The plot of photocurrent quantum efficiency vs surface concentration of the dye (molecules  $cm^{-2}$ ).  $1 - \lambda = 470$  nm;  $2 - \lambda = 589$  nm.



Fig. 3. Acriding Orange dye molecule.



Fig. 4. The I-V curve for the cell (illumination: 100 W tungsten filament lamp at 250 W m<sup>-2</sup>, counter electrode biased to give zero dark voltage).



Fig. 5. Time development of the photocurrent. 1 – Unplatinized plate; 2 – platinized plate (dye concentration  $\approx 6 \times 10^{14}$  molecules/cm<sup>2</sup>).

level. An electron acceptor present in the solution could accept this electron regenerating the neutral dye molecule. KCNS solution acts as a redox owing to the existence of  $CNS^-$  as well as  $(CNS)_2^-$  ions (atmospheric O<sub>2</sub> generates  $(CNS)_2^-$  ions in KCSN solution [8]). The reactions occurring at the electrodes can be summarized as in the following subsections.

## 3.1. Photocathode

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

where D denotes a dye molecule,  $D^*$  an excited dye molecule and  $D^-$  a dye molecule that has gained one electron. The hole generated is transferred into the valence band.

## 3.2. Anode

 $CNS^-$  ions are discharged near the anode yielding CNS free radicals, which combine with  $CNS^-$  ions to regenerate  $(CNS)_2^-$  ions, i.e.,

$$CNS^{-} + e \rightarrow CNS$$

$$CNS^{-} + CNS \rightarrow (CNS)_{2}^{-}.$$
(2)

In addition to the reactions (1), the following dissipative processes could also take place:

- (a) Electron-hole recombination, i.e., electrons from  $D^-$  could be transferred to the conduction band and they could recombine with the holes.
- (b) Concentration quenching, i.e., the excited dye molecules D\* interact among themselves and deexcite converting excitation energy into heat.

The light absorbtion cross section increases with the increase in surface concentration of the dye. However, this also increases the rate of concentration quenching. A maximum in the plot of quantum efficiency of photocurrent vs surface concentration of the dye (fig. 2) results from the competition of these opposite effects.

Platinum deposition increases the photocurrent quantum efficiency by increasing the rate of the last step of the reactions (1). It is well known that Pt acts as a good electron transfer catalyst [15,16]. The electrons in  $D^-$  are transferred to Pt and reduction of  $(CNS)_2^-$  occurs at Pt islets on the dye surface, i.e.,

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

The fact that trace quantities of Pt are effective in enhancing the quantum efficiency suggests that a Pt islet can collect electrons from a large number of dye molecules in

its vicinity, perhaps by electron transfer from molecule to molecule. When the surface concentration of the dye is small Pt deposition decreases the quantum efficiency of photocurrent possibly because of the suppression of electron transfers to Pt islets by discontinuities in the dye layer.

## 3.3. Photocorrosion

In addition to the last step of the reaction [1],  $D^-$  could also transfer electrons to the hydrogen ions in the solution to produce nascent hydrogen which degrades the dye by reduction. However, in a platinized photocathode, the nascent hydrogen generated at the Pt islets forms molecular hydrogen. This is proved by the following observation: When the electrolyte in the PEC is deaerated, small quantities of hydrogen are liberated and can be detected with a polarographic detector. An increase in concentration of the electron acceptor increases quantum efficiency, however corrosion is not suppressed. This indicates that in a platinized cathode, the electron transfers occur at the Pt islets.

# 4. Conclusion

Energy and quantum conversion efficiencies of dye sensitized PECs are generally low and at present they would not be practical devices. The above investigation suggests that the efficiency and stability of these cells may be improved. The Pt islets on a dye coated p-type semiconductor surface act like reaction centers in natural photosynthesis, which have the capacity to concentrate electrons. Further studies on dye-sensitized PECs and catalysts of this type might give clues to development of solar energy conversion systems that closely mimic natural photosynthesis. A knowledge about dimensions and distribution of Pt islets may be obtained with a SEM picture. Unfortunately we did not have these facilities.

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