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A Dye-sensitized Photocatalyst (p-Type CuCNS) for the Generation of Oxygen from Aqueous Persulphate

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p-CuCNS coated with Rhodamine B and then photoplatinized is found to photogenerate oxygen from aqueous persulphate with the dye remaining photostable. The photochemical mechanisms involved are discussed.

Dye-sensitization has attracted much attention as a means of extending the spectral response of semiconductor electrodes and catalysts based on high-band-gap materials.[1-9] However, dye-sensitized systems suffer from three major defects. (1) Although the semiconductor remain stable, the dyes undergo photodegeneration. (2) The dye has to be kept firmly affixed to the surface, as only the dye molecules adsorbed at the semiconductor are effective in photoinduced charge transfer. (3) Concentration quenching limits the quantum efficiency. These problems become more critical in a sensitized-particle system,[6-9] and few hydrogen-photogenerating systems based on this approach have been demonstrated.[7-9] Oxygen photogeneration from dye-sensitized systems is more difficult, as the dyes are very susceptible to oxidative degradation. We have found that p-CuCNS coated with Rhodamine B (RH) and then platinized (CuCNS/RH/Pt) acts as a stable catalyst for visible-light photodecomposition of aqueous persulphate.

Experimental

CuCNS was prepared by adding 0.1 mol dm^{-3} solution of KCNS dropwise to 0.1 mol dm^{-3} copper sulphate kept saturated with SO_2. (AnalaR grade reagents were used.) The white precipitate of CuCNS washed and dried at 70 °C was found to consist of microcrystals with surface area of *ca.* 10 m^2 g^{-1}. The diffuse reflectance spectrum shows a band edge at 375 nm[10-12] corresponding to a band gap of 3.8 eV. Hall and photoelectric tests indicate that the material is p-type.[10-12] CuCNS readily adsorbs cationic dyes where the anion is CNS^-.[10-12] The thiocyanate of RH was made from the commercial chloride by the following method. RH chloride and a saturated solution of KCNS were kept boiling for several hours, during which double decomposition converted the chloride into the less soluble thiocyanate (the solubility of RH thiocyanate at 30 °C is 1.0×10^{-4} mol dm^{-3} compared to 2×10^{-3} mol dm^{-3} for the chloride). The thiocyanated dye was separated, rinsed with water and recrystallized from an alcoholic solution. CuCNS was coated with the dye by magnetically stirring 10 mg with 25 cm^3 of the dye solution of varying concentrations (10^{-4}–10^{-6} mol dm^{-3}) and the dye-coated powder was separated by centrifuging. To estimate the concentration of the adsorbed dye, the optical density of the solution before and after agitation with CuCNS was estimated spectrophotometrically.

The dye-coated powders were platinized as follows: 10 mg of the material was suspended in a solution containing 0.1 mol dm^{-3} potassium citrate and 10^{-5} mol dm^{-3} of chloroplatinic acid.[13, 14] The solution was stirred magnetically and irradiated for 1 h with a tungsten filament lamp (intensity *ca.* 1 W m^{-2}). The Pt content of the resulting catalyst was *ca.* 1 wt%. Experiments were also performed with platinized CuCNS which was subsequently dyed (CuCNS/Pt/RH). In this case the light source used for the platinization was a 90 W medium-pressure Hg lamp. The other catalysts used for comparative experiments were platinized by similar methods. In the case of ZnO, rose bengal (RB) was also used as the sensitizer because anionic dyes are better adsorbed on oxide semiconductors.[3]

Oxygen evolution rates from the aqueous persulphate were monitored with a calibrated membrane polarographic detector fixed to a thermostatted (26 °C) 35 cm^3 quartz reaction cell (Applied Photophysics). The light source used was a 100 W tungsten filament lamp. The catalyst in aqueous suspension without any sacrificial agents was also tested for O_2 and/or H_2 evolution by the same method. Light intensities were measured with an International Light IL 700 radiometer.

Results and Discussion

Fig. 1 shows the photogeneration of O_2 from a persulphate solution (pH *ca.* 7) in the presence of the catalyst CuCNS/RH/Pt. The variation of initial reaction rates with the concentration of adsorbed dye (the surface concentration of the dye is in mmol g^{-1} estimated as described in the experimental section) are presented in fig. 2. Higher dye concentrations increase the light absorption cross-section; however, they also increase the concentration quenching. Thus the curve of fig. 2 shows a maximum corresponding to a surface concentration of the dye of *ca.* 1.8×10^{15} molecule cm^{-2}. Fig. 3 shows the variation of the initial reaction rates with pH when the dye concentration corresponds to the maximum in the curve of fig. 2. The variation of the initial reaction rate with pH is more gradual than in more familiar photoelectrochemical water-splitting systems. This may be attributed to the influence of pH on degradation of the dye in an oxygen environment. (After 10–20 h there is a noticeable decrease in the reaction rate, possibly resulting from O_2 accumulation.) The unplatinized catalyst CuCNS/RH evolves O_2 from persulphate at a much slower rate (fig. 1), with a clear indication of fading of the dye owing to photodegradation, and the reaction stops completely within 2–3 h. The catalyst CuCNS/Pt/RH, where the dying was carried out after platinization shows similar behaviour. However, with the CuCNS/RH/Pt no fading of the dye is observed, and the reaction continues for > 10–20 h. When the dye is absent O_2 evolution in visible light is not seen from the platinized or unplatinized catalyst. CuCNS is sensitive to light of wavelength $\lambda < 340$ nm, and u.v. light readily evolves O_2 from persulphate.[12] As the percentage of light of wavelength $\lambda < 340$ nm is small in a tungsten-filament lamp, the use of u.v. filters was unnecessary in experiments with dyed catalysts, *i.e.* undyed catalysts did not produce detectable quantities of O_2 with a tungsten-filament lamp.

Experiments with macroscopic electrodes show that CuCNS sensitized with RH is photocathodic.[10] We have also noted that in the case of semiconductors which become photoanodic upon sensitization, platinization did not stabilize them during the photooxidation of water. Fig. 1 illustrates photoregeneration of O_2 from persulphate in the presence of sensitized and platinized ZnO. Here dyes undergo rapid photodegradation. Again the catalysts behave similarly irrespective of the order in which the dye coating and platinization are carried out.

The anodic and cathodic sensitizations of the semiconductor–electrolyte interface can be understood as follows.[1,2] If the relative locations of the band positions and the energy levels of the dye are as in fig. 4(*a*), an electron excited from the lower to the upper level can be transferred to the conduction band, and dye molecules accept electrons from ions in the solution. When the locations of the energy levels are as in fig. 4(*b*) an electron from the valence band is transferred to the lower level of the dye (the conduction band of CuCNS is located at -0.78 *vs.* SEC, pH 7). The dye molecules that have accepted these

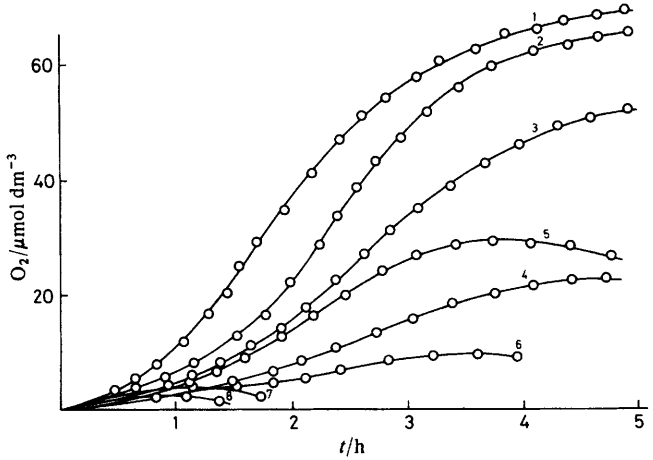


Fig. 1. O_2 photogeneration from different sensitized catalysts: (1) CuCNS/RH (0.35)/Pt, (2) CuCNS/RH (0.25)/Pt, (3) CuCNS/RH (0.50)/Pt, (4) CuCNS/RH (0.10)/Pt, (5) ZnO/RB (0.30)/Pt, (6) CuCNS/RH (0.35), (7) CuCNS/RH (0.35), (8) ZnO/RB (0.30). (1)–(6) are from 0.01 mol dm^{-3} solution of $K_2S_2O_8$ (pH 7), whereas (7) and (8) are in the absence of any sacrificial agent. The dye concentrations in mmol $g_{catalyst}^{-1}$ are indicated in brackets (catalyst weight = 10 mg).

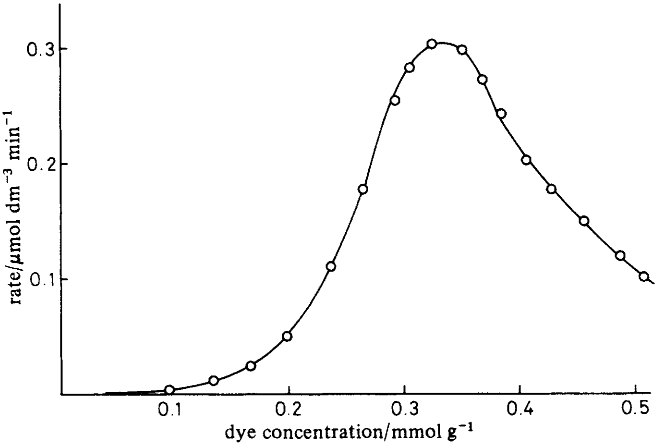


Fig. 2. Variation of the initial O_2 generation rate with the dye concentration (mmol g^{-1}) in the catalyst.

electrons transfer them to ions in the solution. Thus at a semiconductor–electrolyte interface of the first type, the coated regions act as oxidation sites, whereas in those of the second type such regions are reduction sites. The junction characteristics could be different for microparticles. However, if we assume that they also behave as macroscopic electrodes, when the dyed powder is photoplatinized Pt is deposited on top of the dye layer if the interface is of the second type, and on undyed regions if the interface is of the first type. Fig. 5 illustrates the structure of the two types of catalysts. The layer of Pt formed above the dye layer in the catalyst of the second type prevents the photodegradation of the dye, and in addition Pt acts as a good electron-transfer agent.[15] Experiments with macroscopic electrodes shows that CuCNS coated with RH[10] and ZnO coated with RH or RB[3, 4] behave as interfaces of second and first types, respectively.

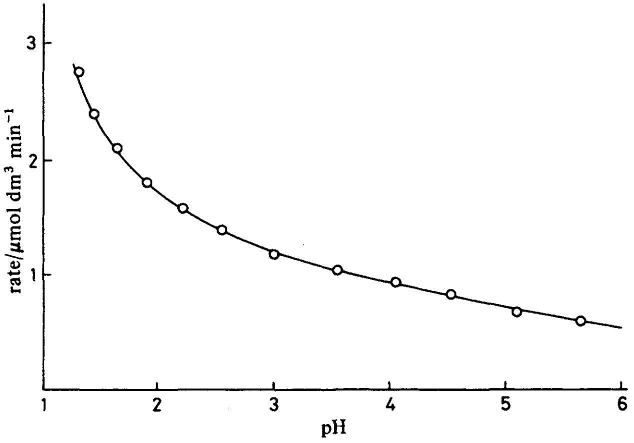
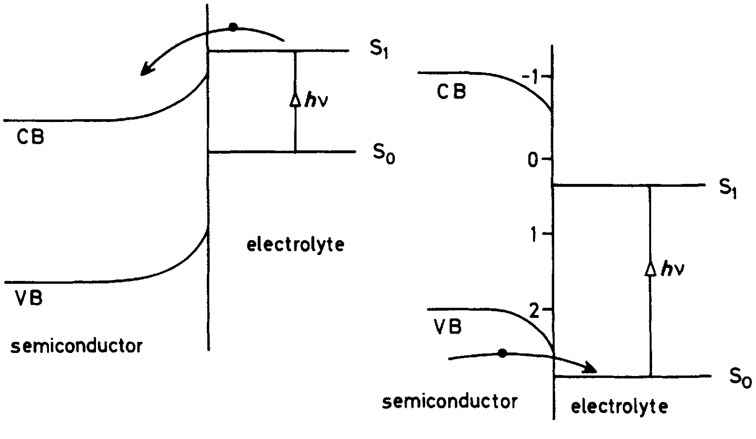


Fig. 3. Variation of the initial reaction rate with pH.



(*a*) (*b*)

Fig. 4. Energy-level diagram showing sensitization at the semiconductor/dye/electrolyte interface. S_0 and S denote the ground and excited electronic levels of the dye. (*a*) Type 1, anodic sensitization; (*b*) type 2, cathodic sensitization at a CuCNS surface, pH 7 (drawn to scale).

We did not have facilities to determine whether the oxygen originates from H_2O or persulphate. However, as in other examples of the photogeneration of O_2 from persulphate with semiconductor catalysts,[16] it is very likely that O_2 comes from H_2O. In such a situation reactions steps leading to the photogeneration of carriers at the surface of the catalyst CuCNS/RH/Pt can be represented as follows:

$$D + h\nu \rightarrow D^* \tag{1}$$

$$\begin{array}{cccc} D^* \rightarrow & D^- & + & h^+ \\ & \downarrow & & \downarrow \\ & D + Pt(-) & & \text{VBCuCNS.} \end{array} \tag{2}$$

Electrons and holes participate in the following oxidation and reduction processes:

$$2H_2O + 4h^+(\text{VB CuCNS}) \rightarrow O_2 + 4H^+ \tag{3}$$

$$S_2O_8^{2-} + 2e(Pt) \rightarrow 2SO_4^{2-}. \tag{4}$$

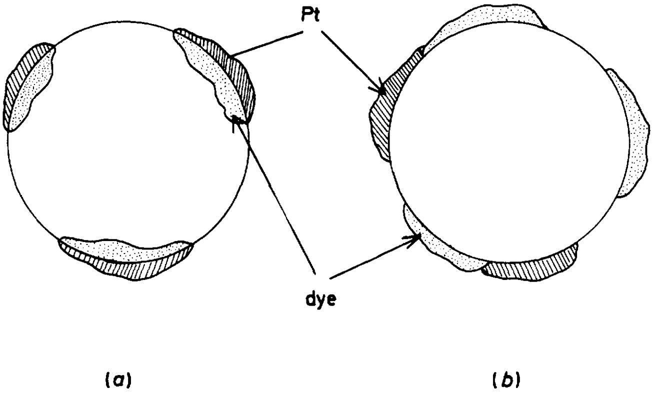


Fig. 5. Structure of catalysts formed in photoplatinization of dyed semiconductor particles when the sensitization is (*a*) type 2 and (*b*) type 1.

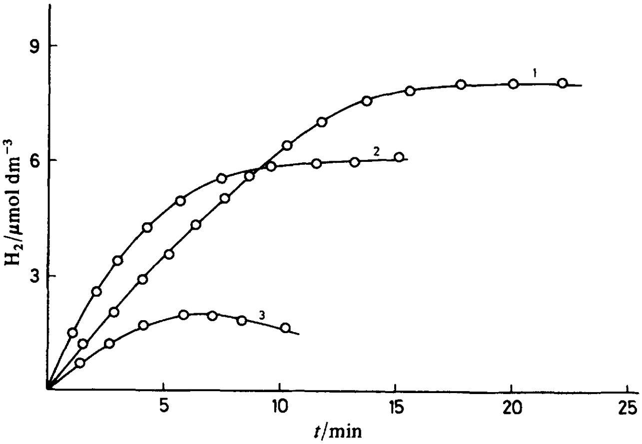


Fig. 6. H_2 photogeneration with the catalyst CuCNS/Rh (0.35)/Pt from (1) 0.5 mol dm^{-3} pyrogalol, (2) 0.05 mol dm^{-3} acetic acid and (3) in the absence of a sacrificial electron donor in the electrolyte.

The excited dye molecule D* injects holes into the valence band of CuCNS to form D^-. The holes and the electrons in the dye anions accumulate in CuCNS and Pt, respectively; the holes oxidize water and the electrons reduce persulphate into the sulphate ions. It is possible that the reaction (3) takes place at regions on the surface of the catalyst that are not coated with dye. This is supported by the following observation. O_2 evolution from the catalyst CuCNS/RH/Pt dyed with RH for a second time occurs after an induction period of 3–4 h. It was also noted that the higher the dye concentration, the longer is the induction period. During the induction period dye deposited on the unplatinized regions is oxidized, leaving bare CuCNS. Because of the low reaction rate we could not obtain action spectra with a monochromator. However, by using filters it was verified that the reaction rate is fastest near the peak of the absorption spectrum of the dye (*ca.* 540 nm).

Aqueous suspensions of the catalyst CuCNS/RH in the absence of electron acceptors evolve a small quantity of O_2 upon irradiation (white light), with sacrificial reduction of the dye (fig. 1). However, the platinized catalyst CuCNS/RH/Pt produces trace quantities of H_2 without O_2 evolution (fig. 6). What is happening here is probably oxidation of the dye in unplatinized regions with concomitant reduction of H_2O. The initial increase of the O_2 evolution rate followed by a rapid decrease (curves 7 and 8 of fig. 1) results from oxidative degradation of the dye. The initial H_2 evolution rate is 18 μmol h^{-1} compared to 2 μmol h^{-1} for O_2. The slow O_2 evolution rate (*ca.* half the H_2 evolution rate) could arise from the loss of O_2 *via* degradation of the dye. More enhanced H_2 evolution is seen in the presence of sacrificial reducing agents such as acetic acid and pyrogalol (fig. 6).

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