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Photolysis of p-type β-CuCNS dispersions in aqueous medium

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Abstract

Aqueous dispersions of the p-type semiconductor β-CuCNS generate hydrogen with self-sacrifice. The reaction mechanism is determined and related to the photoelectrochemical properties of β-CuCNS.

1. Introduction

The photoelectrochemical properties of semiconductor particulate dispersions have attracted much attention both practically and fundamentally [1–7]. The photocatalytic ability of semiconductor particles in the photodecomposition of water [8–10], reduction of nitrogen and carbon dioxide [11–14], extraction of metals [15] and mineralization of organic contaminants in water [16, 17] is widely known continues to be an active area of research. Studies on electron transfer kinetics [18] and particle size effects [19–21] of semiconductors are of fundamental significance and have given much impetus to the theoretical development of the subject. Semiconductor materials whose particulate properties have been extensively investigated include the oxides and chalcogenides (*e.g.* TiO_2, ZnO, CdS, CdSe). Cuprous thiocyanate (CuCNS), which is a p-type semiconductor with a band gap of approximately 3.6 eV [22], is an unconventional material with interesting properties. The method of preparation of polycrystalline powder or thin films on copper substrate, its semiconductor properties and its suitability for dye sensitization have been described previously [22–28].

In this work, the UV photolysis of aqueous suspensions of CuCNS is reported. UV photolysis causes the liberation of hydrogen with self-sacrifice of the material. The mechanism of corrosion is determined and related to the photoelectrochemical properties of CuCNS.

2. Experimental details

Cuprous thiocyanate was prepared by mixing aqueous solutions of $CuSO_4$ (0.1 M) and KCNS (0.1 M) in the presence of sulphur dioxide, which acts as a reducing

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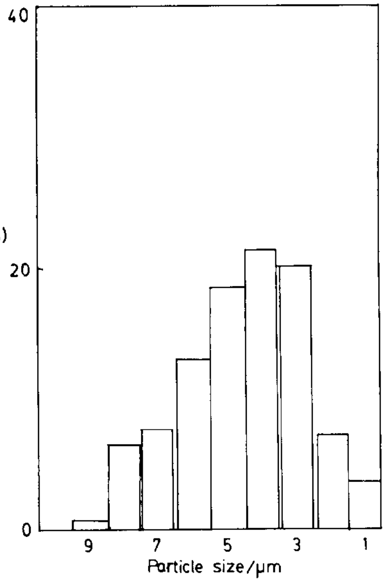
agent. The precipitate was washed and dried over silica gel in a vacuum desiccator. The IR spectrum showed an absorption peak at 2173 cm^{-1} which is characteristic of β-CuCNS [22]. It is known that β-CuCNS is composed of layers of a close-packed network of CuCNS units, where the adjacent layers are bonded to each other by strong Cu–S bonds [23]. The particle size distribution in an aqueous suspension, as measured by a HORIBA particle size distribution analyser (CAPA-700), is shown in Fig. 1 and the specific surface area was found to be 0.75 m^2 g^{-1}. The absorption spectrum of the aqueous suspension (Fig. 2) shows a band edge at 345 nm (Shimadzu UV 3000 double beam spectrophotometer was used). A peak in the fluorescence spectrum (Shimadzu RF-5000 spectrofluorophotometer) at 362 nm (Fig. 3) is also characteristic of the material and indicates that fluorescence results from recombination of photoregenerated carriers. CuCNS compacted into pellets (diameter, 13.0 m; thickness, approximately 1 mm; at a pressure of 40 MPa) was used to obtain the Mott–Schottky plots. A Hewlett-Packard LCR meter 4192A and a Kenwood DL-707 digital multimeter were used to measure the capacitance and voltage respectively.

The photolysis experiments were carried out in a thermostatically-controlled (26 °C) double-walled photochemical reactor (Applied Photophysics; volume, 500 cm^3) mounted with a 400 W medium pressure mercury lamp (no filter was used) which was housed in the inner quartz jacket. In each experiment 0.50 g of CuCNS powder suspended in 300 cm^3 of distilled water was photolysed and the suspension was purged with nitrogen (99.99%) prior to irradiation. During photolysis the contents of the reactor were continuously purged with nitrogen at a rate of 11.0 cm^3 min^{-1}. pH adjustments were made with dilute sulphuric acid and significant changes in pH were not observed with the progress of photolysis. Evolved gases were estimated volumetrically at atmospheric pressure by gas chromatography (Shimadzu gas chromatograph GC-9AM; column, molecular sieve 5A; carrier gas, argon).



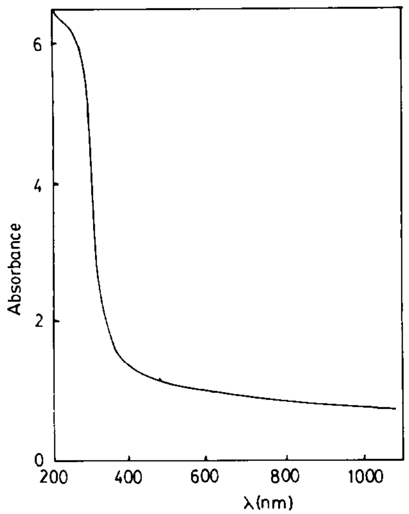


Fig. 1. Particle size distribution in an aqueous suspension of CuCNS.

Fig. 2. Absorption spectrum of an aqueous suspension of CuCNS.

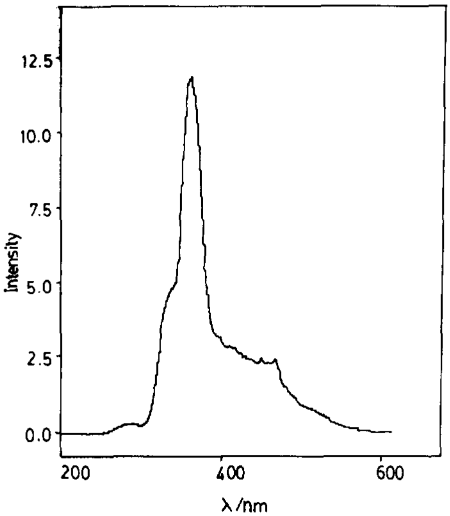


Fig. 3. Fluorescence spectrum of an aqueous suspension of CuCNS (excitation wavelength, 240 nm).

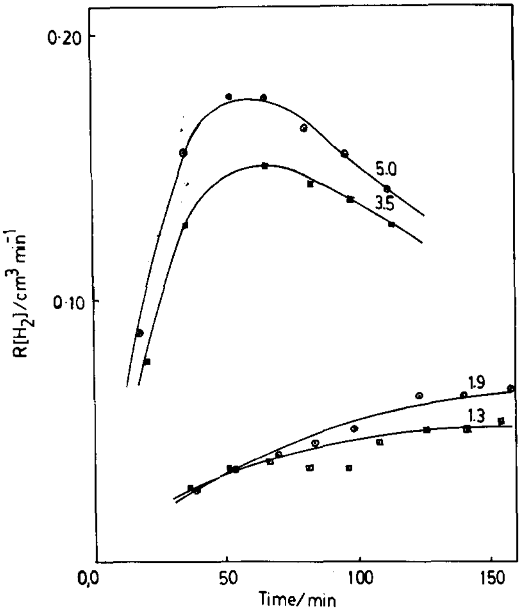


Fig. 4. Hydrogen liberation in the photolysis of aqueous CuCNS. The numbers on the curves are the pH values.

3. Results

Figure 4 shows the production of hydrogen during the photolysis. At higher pH values, the rates of hydrogen evolution are higher. The progressive decrease in the reaction results from the degradation of CuCNS. Finally, the solution contains a black

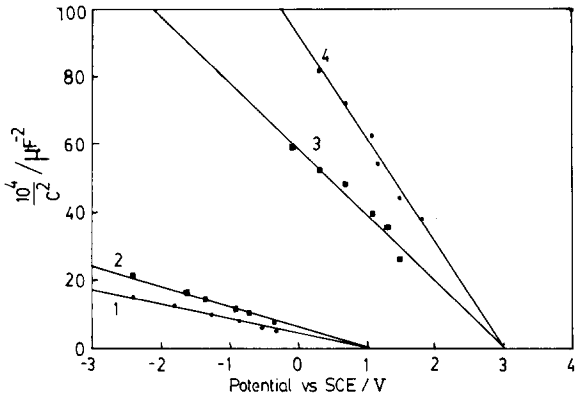


Fig. 5. Mott–Schottky plot ($1/C^2$ vs. V) for compacted pellets of CuCNS: 1, pH 3.5, $\nu=500$ Hz; 2, pH 3.5; $\nu=1$ kHz; 3, pH 5.0, $\nu=500$ Hz; 4, pH 5.0, $\nu=1$ kHz (ν is the frequency).

residue which is determined to be copper sulphide (close to the stoichiometric composition of CuS) by chemical analysis. The irradiated solution contains CNO^-, CN^-, Cu^{2+} and SO_4^- ions. CO_2, a product of the further photolysis of OCN^-, is not observed by gas chromatography.

The reactions which lead to self-sacrifice of CuCNS with concomitant hydrogen generation are as follows. Photons absorbed by CuCNS generate electron–hole pairs. The transfer of conduction band electrons to water liberates hydrogen via the reaction

$$H_2O + e^- \longrightarrow \tfrac{1}{2}H_2 + OH^- \tag{1}$$

Electrons can also participate in the reaction

$$CuCNS + e^- \longrightarrow CuS + CN^- \tag{2}$$

leading to the degradation of CuCNS. Possible hole-consuming reactions are

$$2h^+ + CN^- + H_2O \longrightarrow CNO^- + 2H^+ \tag{3}$$

and

$$8h^+ + CuS + 4H_2O \longrightarrow Cu^{2+} + SO_4^{2-} + 8H^+ \tag{4}$$

where CN^- and CuS are the degradation products of CuCNS originating from the conduction band reaction. CuCNS is resistant to direct attack by the photogenerated holes. This is supported by the observation that it remains largely stable during photolysis in aqueous medium in the presence of strong oxidizing agents. In fact, CuCNS acts as an efficient catalyst for the photogeneration of oxygen from persulphate [24]. Furthermore, in oxygenated solutions CuCNS remains largely stable during irradiation. Again there is no evidence for direct hole-consuming reactions leading to the formation of Cu^{2+}. The values of the flat band potential at pH 3.5 and 5.0, derived from the Mott–Schottky plot (Fig. 5), are -2.6 V and -0.6 V (*vs.* saturated calomel electrode (SCE)) respectively. The flat band potential increases in the positive direction with an increase in pH. We were unable to identify any surface species associated with this effect.

4. Conclusions

The observed variation in hydrogen yield with pH during photolysis can be explained as follows. According to the observed shift of the flat band potential with pH, the conduction band reactions are favoured at low pH, whereas the valence band reactions are favoured at high pH. If hole consumption becomes the rate-determining step, higher rates of hydrogen evolution can occur at higher pH. Thus the flat band potential data explain the observed hydrogen evolution rates.

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