# CUPROUS THIOCYANATE: A SUPERIOR PHOTOCATALYST FOR OXIDATION OF WATER

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Cuprous thiocyanate (a p-type semiconductor) was found to photo-oxidize water in the presence of sacrificial electron acceptors more readily than most materials generally used for this purpose Photocatalytic properties of p-CuCNS are compared with those of  $n-TiO_2$ .

## 1. Introduction

Semiconductor dispersions capable of photogenerating oxygen from water have attracted much attention [1]. Most systems of this kind reported in the literature employ n-type semiconducting materials [1-5]. However, n-type materials more readily photoadsorb  $O_2$ , producing  $O_2^-$  and removing any oxygen resulting from reactions with the valence band holes [6-7]Photoadsorbed O2 is consumed in secondary photocorrosion, e.g., in CdS [2] or forms bound peroxocomplexes, e.g, in TiO<sub>2</sub> [5]. p-type semiconductors on the other hand photoadsorb  $O_2$  less readily [6, 7] and the minority carriers (electrons) tunneling into the solution become easily available to the electron acceptor. Unfortunately, the familiar p-type materials are unsuitable as oxygen-generating photocatalysts because of rapid photocorrosion (e g. Cu<sub>2</sub>O, CuO, p-SiC) and/or unfavourable band positions (e.g. p-GaP). We have found that cuprous thiocyanate is a photostable p-type semiconductor of band gap 3 2 eV [8,9], with a conduction band at -0.78 V versus SCE(pH 7). As expected, p-CuCNS was found to be an efficient photocatalyst for  $O_2$  generation from aqueous persulphate at a rate faster than TiO<sub>2</sub> (bare or CuO<sub>2</sub> coated); it is superior to all familiar n-type materials with comparable band positions

#### 2. Experimental

CuCNS was prepared by adding 0.1 M solution of KCNS dropwise to 0 1 M copper sulphate kept saturated with SO<sub>2</sub> (Analar grade reagents were used) The white precipitate of CuCNS washed and dried at 70°C was found to consist of microcrystals with a surface area of approximately  $10 \text{ m}^2 \text{ g}^{-1}$ . The diffuse reflectance spectrum of the powder taken with a Unicamp SP 500 spectrophotometer indicated an optical absorption edge at 375 nm, corresponding to a band gap of 3.2 eV [8]. Hall measurements, thermoelectric tests and cathodic photoeffects [8] showed that the material is p-type Capacitance measurements were carried out with CuCNS deposited on copper plates and the flat-band potential of CuCNS was estimated to be -0.78 V versus SCE(pH7) A quartz cell (35 ml in volume) thermostatted at 26°C and equipped with a calibrated membrane polarographic detector (Applied Photophysics) was used to detect  $O_2/H_2$  and their photo-uptake rates The light source used was a 200 W medium-pressure Hg lamp and light intensities were measured with an International Light IL 700 radiometer. The cell containing the dispersion (25 mg CuCNS in 35 ml) was degassed with N<sub>2</sub> and the O<sub>2</sub> evolution rate was noted For comparison, the  $O_2$  photogeneration rate from  $T_1O_2$ (anatase BDH) bare and loaded with RuO<sub>2</sub> was also recorded As TiO<sub>2</sub> dispersions had higher light absor-

0 009-2614/85/5 03 30 © Elsevier Science Publishers B V (North-Holland Physics Publishing Division) bance per unit weight than CuCNS dispersions, the quantity of  $T_1O_2$  giving the same absorbance (350 nm) was determined spectrophotometrically

### 3. Results and discussion

Fig 1 compares the photo-oxidation rates of water for the catalysts p-CuCNS and n-TiO<sub>2</sub> with persulphate as the electron acceptor. It is seen that the rate is faster for p-CuCNS. Fig. 2 illustrates photo-uptake of O<sub>2</sub> by illuminated dispersions of these two materials having the same light absorbance. The oxygen photouptake is slow and the saturation is reached quickly in the case of CuCNS



Fig 1.  $O_2$  evolution from 10 mg of potassium persulphate in 35 ml of water for catalysts CuCNS, TiO<sub>2</sub> and TiO<sub>2</sub>/RuO<sub>2</sub> (0 3 wt%) Weights of the catalysts used were 25, 15, 15 mg respectively (a dispersion of 25 mg of CuCNS gives the same absorbance at 350 nm as 15 mg of TiO<sub>2</sub>).



Fig 2  $O_2$  photo-uptake by CuCNS (25 mg) and TiO<sub>2</sub> (15 mg) suspended in 35 ml of water Illumination as described in section 2

The conduction band position of CuCNS is more favourably placed for photoreduction of water than that of  $TiO_2$ . However, it was noted that  $TiO_2$  (even in the absence of Pt and RuO<sub>2</sub>) photoreduces water at a rate much faster than CuCNS Hydrogen photogeneration rates of the two catalysts with propan-2-ol as the electron donor are indicated in fig 3. Hydrogen photo-uptake rates of  $TiO_2$  and CuCNS are found to be similar (fig 4) The superiority of  $TiO_2$  as a catalyst for photoreduction of water probably arises from the second factor mentioned in the introduction In an n-type semiconductor, holes tunnel into the solution and their reaction with the electron donor is the rate-determining step for photogeneration of hydrogen.

The above investigations demonstrate that stable p-type materials with correct band positions are better photocatalysts for oxidation of water. p-CuCNS is



Fig 3. H<sub>2</sub> evolution from 35 ml of 25% propan-2-ol Catalysts CuCNS (25 mg) and TiO<sub>2</sub> (15 mg)

not the ideal material for this purpose, it is sensitive only to UV light and chemically unstable in alkaline solution. The search for new p-tyre materials suitable for photooxidation of water may be a fruitful area of investigation

#### References

- [1] M. Grätzel, ed, Energy resources through photochemistry and catalysis (Academic Press, New York, 1983)
- [2] N.M. Dmitrijevic, S. Li and M. Grātzel, J Am. Chem Soc 106 (1984) 6565.
- [3] J.R. Darwent and A Mills, J. Chem. Soc. Chem. Commun (1982) 107.



Fig 4 Photo-uptake of  $H_2$  by CuCNS (25 mg) and TiO<sub>2</sub> (15 mg) suspended in 35 ml of water

- [4] J. Haupt, J Peretti and R van Steenwinkel, Nouv J. Chum 8 (1984) 633.
- [5] D Duonghong and M Gratzel, J Chem. Soc. Chem Commun (1984) 1597
- [6] J.M. Herrmann, J. Disdier and P. Pichat, J. Chem. Soc. Farady Trans. I 77 (1981) 2815.
- [7] S.R Morrison, Electrochemistry of metal and semiconductor electrodes (Plenum Press, New York, 1980).
- [8] K Tennakone, M. Kahanda, C. Kasige, P. Abeysooriya, R.H Wijenayake and P. Kaviratne, J Electrochem. Soc 131 (1984) 1574.
- [9] K Tennakone, J. Phys. D 16 (1983) L5.