

## PHOTOREDUCTION OF WATER AND NITROGEN WITH HYDROUS CUPROUS OXIDE

K. TENNAKONE <sup>a,b</sup>, A.H. JAYATISSA <sup>b</sup>, K.R.S.S. KEKULAWALA <sup>b</sup> and S. PUNCHIHEWA <sup>a</sup>

<sup>a</sup> *Institute of Fundamental Studies, Hantana, Kandy, Sri Lanka*

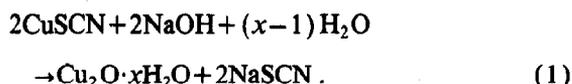
<sup>b</sup> *Department of Physics, University of Ruhuna, Matara, Sri Lanka*

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Hydrous cuprous oxide is found to photoreduce water and dinitrogen. This unusual behaviour of the hydrous in contrast to the dehydrated oxide is attributed to its highly negative flat band potential.

In the past decade semiconductor photocatalysis has attracted a great deal of attention [1-5]. The aim of such studies is to initiate chemical reactions of economic value utilising sunlight. Of these the most important are: (1) photocleavage of water; (2) photofixation of nitrogen; (3) photoreduction of carbon dioxide. At present none of these reactions can be carried out to a practically viable extent, but significant progress has been made in devising new catalysts and understanding the reaction mechanisms [1-5]. The hope is that the continuation of this effort will eventually lead to efficient practical systems. So far most investigations on semiconductor photocatalysis have been carried out with familiar materials such as TiO<sub>2</sub>, CdS and Fe<sub>2</sub>O<sub>3</sub>. It is possible that more promising catalysts may be found among unconventional materials. In this note we describe somewhat unusual photocatalytic properties of hydrous cuprous oxide. An aqueous suspension of hydrous cuprous oxide is found to photogenerate hydrogen from water or photoreduce dinitrogen to ammonia with self-destruction. Loading with electron and/or hole transfer catalysts is found to be unnecessary and the yield of ammonia is much higher when compared to other photocatalytic systems reported in the literature [6-13].

The catalyst was prepared by the hydrolysis of a stable cuprous salt (CuSCN; CuI can also be used) by the following procedure. 2.5 g of CuSCN mixed with 250 ml of 3 N NaOH was magnetically stirred for 1 h to complete the reaction



The brownish yellow precipitate of Cu<sub>2</sub>O · xH<sub>2</sub>O was separated by filtration and washed until the filtrate was free from SCN<sup>-</sup>. The precipitate when dried in a desiccator approximates to the formula Cu<sub>2</sub>O · xH<sub>2</sub>O with x ≈ 3.5-2.5. However, as drying is found partially to inactivate the catalyst, the moist compound was used in all experiments and the equivalent weight of Cu<sub>2</sub>O estimated from the quantity of CuSCN used in reaction (1). The diffuse reflectance spectrum (Hitachi 7J-3200 spectrophotometer) shown in fig. 1 suggests that the band gap of the material is 2.6 eV (compared to 2.3 eV for Cu<sub>2</sub>O). Hall tests performed with the desiccator-dried compound show that it is p-type.

Water photolysis experiments were carried out in a 35 ml thermostatted (26°C) quartz reaction vessel (Applied Photophysics) provided with a polarographic detector for monitoring the hydrogen concentration ([H<sub>2</sub>]). All solutions were purged with argon. The light source used was a 200 W medium pressure Hg lamp.

The nitrogen photoreduction experiments were conducted in a double-walled photochemical reactor of capacity 350 ml (Applied Photophysics) filled with a water-cooled 450 W medium pressure Hg lamp at the central axis. The suspension in the reactor was bubbled with purified N<sub>2</sub> (passed successively through wash bottles containing chromic acid, NaOH

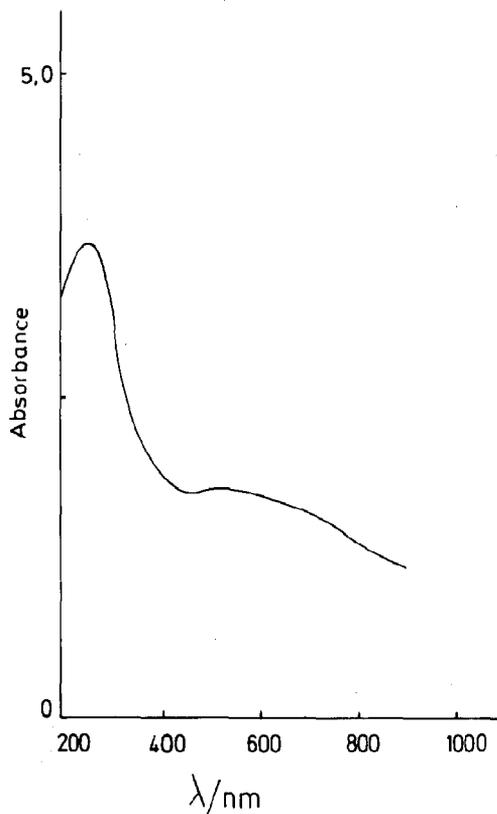


Fig. 1. Diffuse reflectance spectrum of cuprous oxide.

and water to remove organic matter, ammonia, oxides of nitrogen and the spray). The outgoing gas was passed through a trap containing 0.1 M HCl to capture any escaping ammonia. After irradiation for a measured time the contents of the reactor were distilled and ammonia was estimated colorimetrically by the indophenol blue method [6]. All reagents used were tested for ammonia contamination. A blank experiment without irradiation gave  $7 \mu\text{mol l}^{-1}$  of  $\text{NH}_3$  and this quantity remained independent of the duration of bubbling. In all other measurements the above value was taken as the zero level.

The results of the water photolysis experiment are shown in fig. 2a. It can be seen that in the absence of a sacrificial agent in the solution,  $[\text{H}_2]$  reaches a peak value and thereafter decreases progressively. A darkening of the catalyst is also observed. In the presence of sodium acetate (0.2 M) the discoloration of the catalyst is suppressed and the reduction in  $[\text{H}_2]$  is not observed. The photochemical reactions occurring can be expressed as follows:

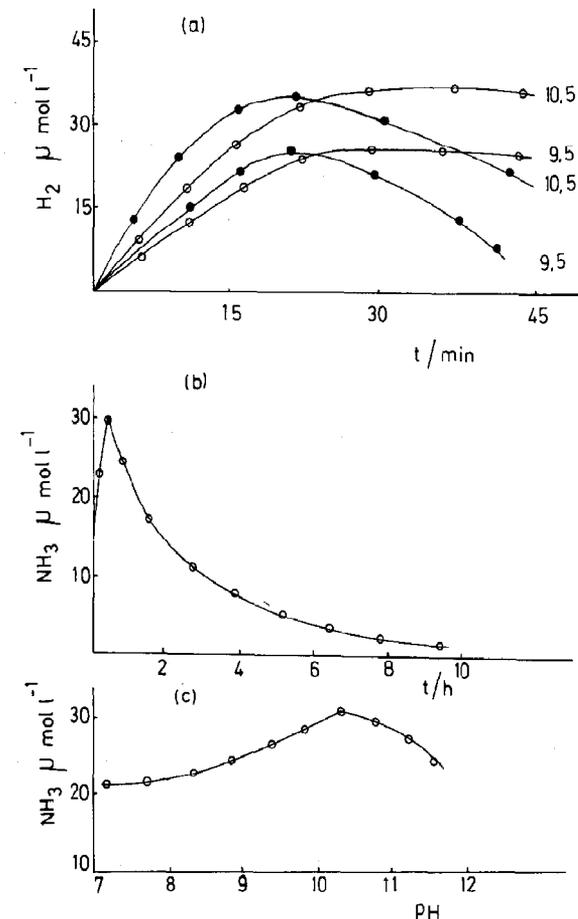
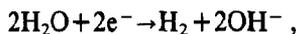
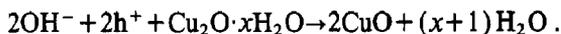


Fig. 2. (a) Plot of  $[\text{H}_2]$  versus time: ●, absence of any sacrificial agent; ○, presence of sodium acetate (0.2 M). (Numbers indicated near each curve are the pH values.) (b) Plot of  $[\text{NH}_3]$  versus time at pH 10.5. (c) pH variation of the optimum  $\text{NH}_3$  yield.



↑

conduction band



↑

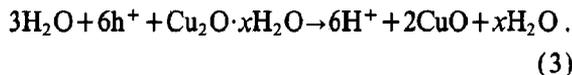
valence band

(2)

When sodium acetate is present, the holes are consumed by oxidising acetate to  $\text{CO}_2 + \text{H}_2\text{O}$  and oxidation of the catalyst is suppressed. The decrease of  $[\text{H}_2]$  upon prolonged irradiation is undoubtedly a result of the oxidation of  $\text{H}_2$  by  $\text{CuO}$  in a back-reaction. In a separate experiment we have noted that irradiated suspensions of  $\text{CuO}$  absorb hydrogen. (The

reduction product seems to contain  $\text{Cu}_2\text{O}$  and  $\text{Cu}$ .)

The ammonia production in the second experiment is shown in fig. 2b. It can be seen that  $[\text{NH}_3]$  reaches a peak and then continues to decrease. The optimum yield ( $30 \mu\text{mol l}^{-1}$ ) is much higher compared to other systems reported in the literature [6-13]. The electron and hole transfer reactions can be written as



Since we have not detected any hydrazine, nitrates or nitrites, the loss of ammonia on prolonged irradiation could occur only as the result of its oxidation (to water and nitrogen) with concomitant reduction of  $\text{CuO}$  to  $\text{Cu}_2\text{O}$  (unhydrated). The ammonia produced will consume some  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  with the formation of cuprous and cupric ammonium complexes. This becomes noticeable as a blue tint in the photolysis solution, especially on exposure to air. When boiled these complexes decompose into ammonia and do not interfere with the method of detection. The concentration of ammonia is insufficient to dissolve the catalyst completely.

In order to reduce nitrogen and water, hydrous cuprous oxide must have a highly negative flat band potential (compared to the dehydrated oxide which is inactive). Although we have not succeeded in determining the exact value of the band potential, this becomes apparent when the photocurrent onset potentials of  $\text{Cu}_2\text{O} \cdot x\text{H}_2\text{O}$  and  $\text{Cu}_2\text{O}$  are compared (fig. 3). The hydrous oxide shows a large shift of the onset potential in the negative direction compared to the unhydrated oxide. Furthermore the shift becomes more pronounced when the  $pH$  is increased (a surface of hydrous copper oxide needed for this measurement was prepared by keeping a  $\text{CuSCN}$  coated copper plate [14] immersed in  $\text{NaOH}$ ). The  $pH$  variation of the optimum  $\text{NH}_3$  yield shown in fig. 2c can also be explained qualitatively. Thermodynamically a lower  $pH$  is favourable for nitrogen reduction. However, more negative flat band potentials needed for charge transfer are achieved at higher  $pH$ s. The existence of an optimum  $pH$  is a consequence of these two opposing factors. Apart from the highly negative flat band potential, the efficient chemisorp-

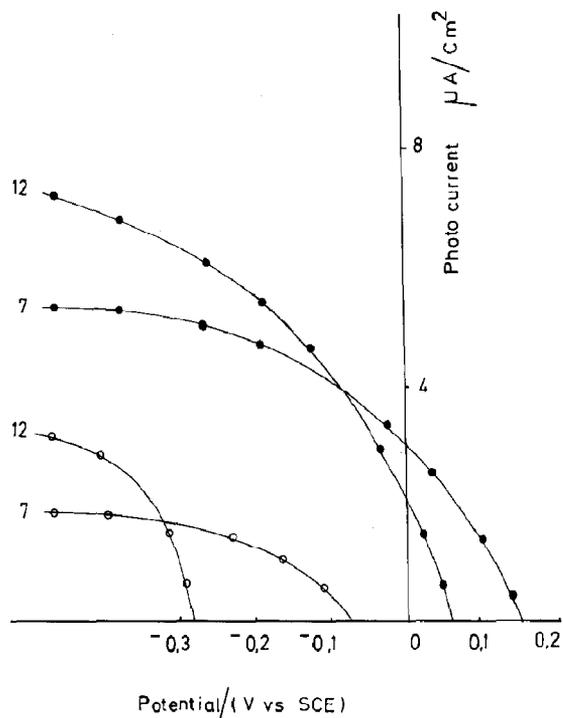


Fig. 3. Plot of photocurrent versus potential: ●,  $\text{Cu}_2\text{O}$ ; ○,  $\text{Cu}_2\text{O} \cdot x\text{H}_2\text{O}$ . (Numbers indicated near each curve are the  $pH$  values.)

tion of  $\text{N}_2$  could play an important role. We have not succeeded in elucidating the structure of  $\text{Cu}_2\text{O} \cdot x\text{H}_2\text{O}$  or the reason why it has a band gap and flat band potential different from that of  $\text{Cu}_2\text{O}$ . The possibility that the hydrous  $\text{Cu(I)}$  oxide we have prepared is mixed with a small quantity of  $\text{Cu(II)}$  oxide cannot be ruled out.

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