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STABILITY OF CUPROUS THIOCYANATE COATED CUPROUS OXIDE PHOTOCATHODE IN AQUEOUS THIOCYANATE

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Abstract—It is found that a thin coating of cuprous thiocyanate suppresses photocorrosion of cuprous oxide in aqueous KCNS. The method of deposition of cuprous thiocyanate on cuprous oxide surface and the performance of a photoelectrochemical cell based on this electrode are described.

INTRODUCTION

Studies on stabilization of photoelectrochemical cells (PECs) have attracted a great deal of attention[1–5]. It is well known that low band gap semiconductors sensitive to the visible spectrum degrade very rapidly, whereas high band gap semiconductors insensitive to the visible spectrum remain photostable. One simple technique of stabilization of PECs attempted earliest is to coat the surface of a low band gap material that is matched to the visible spectrum with a thin protective layer of a wide band gap electrochemically inert semiconductor[6–9]. In this scheme incident light passes through the protective film of the large band gap material where it is absorbed generating charge carriers. The minority carriers then tunnel through the protective layer into the electrolyte transferring the charges to the ions. This scheme operates effectively only if the following conditions are satisfied[8]. (1) The work function of the two semiconducting materials are nearly equal so that the two Fermi-levels line up and the potential barrier at the interface become negligible. (2) The band edge of the small band gap material overlap the surface states of the large band gap material. (3) For effective tunnelling to take place the protective film must not be thicker than 50–100°A. The last condition presents severe problems, with familiar stable semiconducting materials such as TiO_2. All available deposition techniques yield films with cracks and pinholes causing photocorrosion.

In this work we report our observations on a system where a very high degree of photostability can be achieved by the above method. We have found that highly photo-unstable cuprous oxide (p-type semiconductor of band gap $\simeq$ 2.3 eV[10–11]) surface can be coated with a defect- (cracks or pinholes) free very thin layer of cuprous thiocyanate (p-type semiconductor of band gap $\simeq$ 3.6 eV) and this protected photocathode remains almost completely stable in KCNS solution.

EXPERIMENTAL

Cu_2O deposited plates were made by heating 7 × 11 cm copper sheets in an oven to 850°C. The outer film of CuO was removed by etching in dilute acetic acid. A thin layer of CuCNS was coated on Cu_2O by keeping the plate immersed in 0.1 mol dm^{-3} solution of KCNS containing 10 % (by vol.) of glacial acetic acid and 5% (by vol.) of propan-2-ol for approx. 30 min. The small amount of thiocyanic acid generated *via* the reaction,

$$KCNS + CH_3.COOH \rightarrow HCNS + CH_3.COONa,$$

reacts with Cu_2O to form a thin layer of CuCNS, *ie*

$$Cu_2O + 2HCNS \rightarrow 2CuCNS + H_2O.$$

Propan-2-ol acts as a surfactent that removes grease from the Cu_2O surface. The plate was washed with deionized water and dried. A back wall type PEC was constructed from this plate with a cupric sulphide coated copper window (same dimensions as the photocathode) as the counter electrode and 0.5 mol dm^{-3} KCNS solution as the electrolyte. In order to obtain reproducible open circuit dark voltages (10–20 mV) cupric sulphide counter-electrode was made by the following method. The copper window was immersed in 5% solution Na_2S and then left overnight in a saturated solution of H_2S (CuS electrode made by this method is only feebly photosensitive and does not interfere with the performance of the cell). Action spectra of the cells were determined using Applied Photophysics Monochromator. Light intensities were measured with International Light IL 700 Research Radiometer. Tungsten filament lamp (60 W) at 7×10^{-4} W cm^{-2} was used to study the stability of the cell. For comparison unprotected Cu_2O photocathodes in 0.5 mol dm^{-3} solution of KCNS and 0.5 mol dm^{-3} solution of KI (containing 10^{-3} mol dm^{-3} of I_2) were also studied. The counter-electrodes used in these cells were also CuS windows prepared in the manner described earlier. The average thickness of CuCNS films on Cu_2O were estimated by the following method. After each experiment the photocathode was washed and kept immersed in a warm solution of NaOH of known volume for several hours. Thiocyanate ions enter into solution *via* the double decomposition

$$2\,NaOH + 2\,CuCNS \rightarrow Cu_2O + 2NaCNS + H_2O.$$

Solution is acidified with HNO_3 and CNS^- concentration is estimated colorimetrically with $FeCl_3$. From a knowledge of the total amount of CNS^- depleted into the solution, the monolayer thickness of the CuCNS film can be estimated. In most cases the method we have adopted for deposition of CuCNS on Cu_2O gave films of average thickness 5–10 monolayers.

RESULTS AND DISCUSSION

KCNS solution acts as a redox couple due to existence of CNS^- as well as $(CNS)_2^-$ ions[11–12]. A small amount of thiocyanogen may be introduced into the solution but this is not essential, atmospheric oxygen generates sufficient $(CNS)_2^-$ ions[11]. At the photocathode $(CNS)_2^-$ ions accept electrons to yield CNS^- ions, *ie*

$$(CNS)_2^- + e \rightarrow 2\,CNS^-. \tag{1}$$

Near the anode CNS^- ions discharge electrons producing CNS free radicals that combine with CNS^- ions to regenerate $(CNS)_2^-$ ions, *ie*

$$\begin{aligned} CNS^- - e &\rightarrow CNS \\ CNS + CNS^- &\rightarrow (CNS)_2^-. \end{aligned} \tag{2}$$

In absence of a protective layer of CuCNS, a Cu_2O photocathode degrades very rapidly. Possible mechanisms of photocorrosion are (a) in addition to reaction (1), H^+ ions can also accept electrons to yield nascent hydrogen that reduces Cu_2O to Cu, (b) uneven illumination, difference in surface light absorption coefficients and other non-uniformities create regions of different potential in the photocathode, short-circuiting across these cathodic and anodic regions deteriorates the anodic regions by the following mechanism. In the anodic region CNS free radicals generated *via* (1) react with Cu_2O to yield a mixture of CuO and CuCNS:

$$Cu_2O + CNS \rightarrow CuO + CuCNS.$$

Chemical analysis of degradation products indicate that (a) is the predominant mode of photocorrosion when pH is acidic or neutral and (b) is favoured when the pH is alkaline. A protective layer of CuCNS inhibits both these modes of corrosion.

Figure 1 compares the rate of decay of the photocurrent near the maximum power point (intensity of illumination 7×10^{-4} W cm^{-2} from a tungsten filament lamp) of Cu_2O protected by CuCNS in KCNS, unprotected Cu_2O in KCNS and unprotected Cu_2O in KI (containing a trace of I_2). When a protective film of CuCNS is present no detectable decay is seen until a lapse of 5–8 h. Even this slow decay (approx. 0.1 μA cm^{-2} h^{-1}) is found to result from a deterioration of the CuS anode. When the anode is replenished photocurrent returns to the original value. If this is repeated a noticeable decrease in photocurrent (1–5 μA) is seen after 48–72 h. This could be attributed to a gradual build up of the CuCNS layer that decreases the rate of tunnelling. When the thickness of the film is estimated, 20% increase was detectable after 90 h. Perhaps another redox electrolytic medium not containing CNS^- ions could eliminate the remaining photocorrosion. Unfortunately we were not able to find another efficient redox couple that is chemically inert to CuCNS. Figure 2 gives the plot of *IV* vs *I* for a Cu_2O photocathode with a protective CuCNS film approx. 8 monolayers thick. As with other PECs based on polycrystalline Cu_2O[5], the conversion efficiency is very low, approx. 0.45%.

When the action spectra of Cu_2O and CuCNS-coated Cu_2O are compared (Fig. 3) no significant

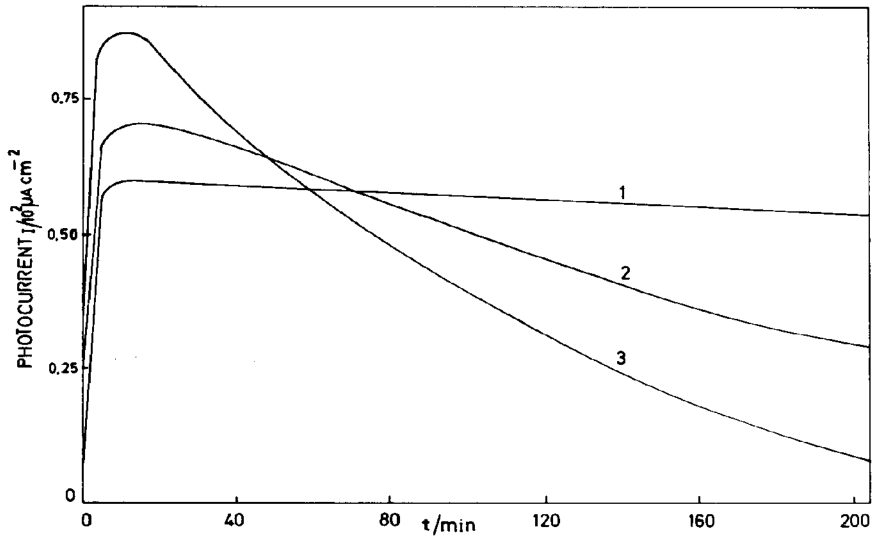

Fig. 1. Time variation of the photocurrent, 1—Cu_2O protected with CuCNS in 0.5 mol dm^{-3} KCNS, 2—Cu_2O unprotected in 0.5 mol dm^{-3} KCNS, 3—Cu_2O unprotected in 0.5 mol dm^{-3} KI containing 10^{-3} mol dm^{-3} of I_2 (intensity of illumination 7×10^{-4} W cm^{-2} from a tungsten filament lamp).

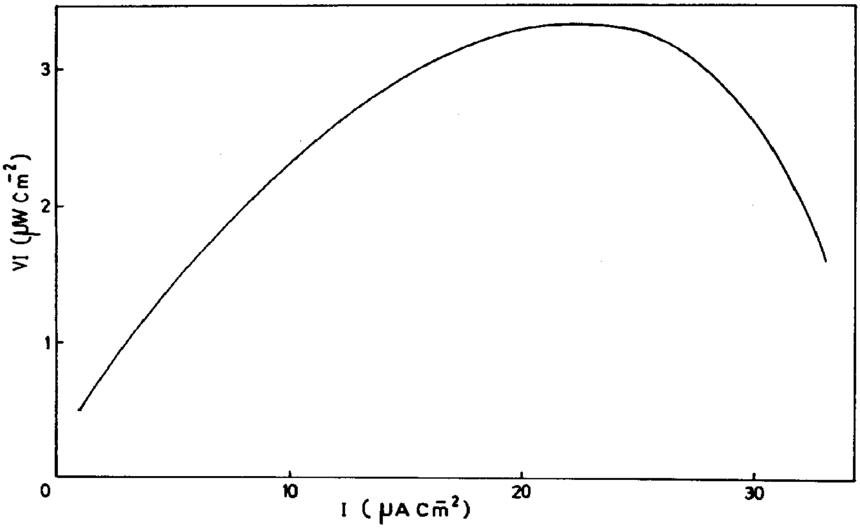

Fig. 2. Plot of *IV vs I* for a cell with a protective film of CuCNS.

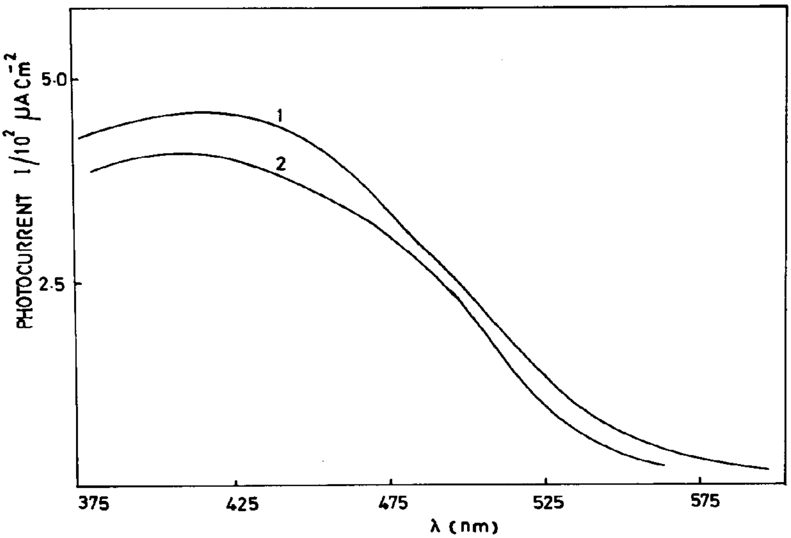

Fig. 3. Action Spectra, 1—Cu_2O protected with CuCNS in KCNS, 2—unprotected Cu_2O in KI.

differences are seen indicating that light is absorbed mainly by the Cu_2O substrate.

The authors are not aware of any reports on detailed solid state structure of CuCNS. Most heavy metal thiocyanates have polymeric structures[13]. It is possible that this property helps formation of thin films free from pinholes and cracks.

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