Preparation of thin polycrystalline films of cuprous iodide and photoelectrochemical dye-sensitization

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Abstract

A simple method is given for the preparation of thin polycrystalline films of copper iodide on a copper substrate. Dye-sensitization of the surface with Rhodamine 6G and the construction of a photoelectrochemical cell are described.

1. Introduction

It is well known that thin polycrystalline films of semiconductor materials can function as the light-harvesting surface in photoelectrochemical cells (PECs) [1–6]. In this connection thin films of familiar semiconductor materials (e.g. oxides and chalcogenides) have received most attention [1–6]. An additional advantage of PECs is that high bandgap materials can be sensitized to the visible spectrum by affixing dyes to the surface of the semiconducting photoelectrode [7–12]. For this purpose, the semiconducting surface must readily adsorb suitable dyes. We have noted that cuprous iodide, a semiconductor with a bandgap of approximately 3.1 eV, has the ability to adsorb cationic dyes [12], where the anionic ligand is I^-. In this note we describe a simple technique for the preparation of thin films of CuI on a copper substrate and the construction of a dye-sensitized PEC.

2. Experimental details

Copper plates (4×5 cm^2) were mechanically polished and ultrasonically cleaned with a detergent. To remove oxide and grease films on the surface, the cleaned plates were kept immersed in an alkaline solution of potassium cyanide (0.1 M in KCN and 0.2 M in NaOH) for 15 min. The plates were rinsed with water to remove KCN and NaOH, washed with propan-2-ol and kept suspended in chamber C of the set-up shown in Fig. 1. Pure argon or nitrogen was passed through the system in the direction shown in Fig. 1. The wash-bottle A contained propan-2-ol, and a few crystals of iodine were placed at the bottom of chamber B. The iodine vapour was carried over to chamber C by the argon

stream (50 ml min^{-1}), where it reacted with copper to form a thin film of CuI. The thickness of the film could be adjusted by varying the duration of exposure or controlling the rate of flow. The propan-2-ol vapour assisted the formation of a uniform layer and lowered the vapour pressure of the iodine (the iodine partial pressure was estimated to be about 0.2 of the atmospheric pressure). To estimate the thickness of the film, the CuI-coated plate was digested with NaOH, when CuI released I^- to the solution via the reaction

$$CuI + NaOH \longrightarrow CuOH + NaI \qquad (1)$$
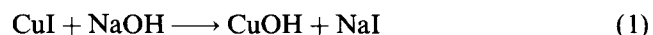
The extract was neutralized with HCl and chlorine was passed through to liberate the iodine, which was estimated colorimetrically. The variation of the thickness of the film with time was also monitored. The thickness of the film was calculated from the amount of CuI formed, assuming that the density of the film material was same as the bulk density of CuI. The diffuse reflectance spectrum of the surface was obtained using a Shimadzu GC–9AM spectrophotometer. The flat-band potential of the CuI film was determined from a Mott–Schottky plot (*i.e.* a plot of C^{-2} vs. V, where C was the capacitance and V the potential across the space charge layer). For this purpose, the capacitance of the CuI-coated plate when immersed in Na_2SO_4 and KI/I_2 solutions was measured as a function of the potential across the space charge layer at frequencies of 500 Hz and 1 kHz.

The dye used in sensitizing the surface was Rhodamine 6G iodide. As the commercial dye (BDH) is the chloride, the iodide form was obtained as follows. The chloride form of the dye was boiled with a saturated solution of KI, when double decomposition converted the chloride into the iodide. Rhodamine 6G iodide, which is less soluble than the chloride, was separated by
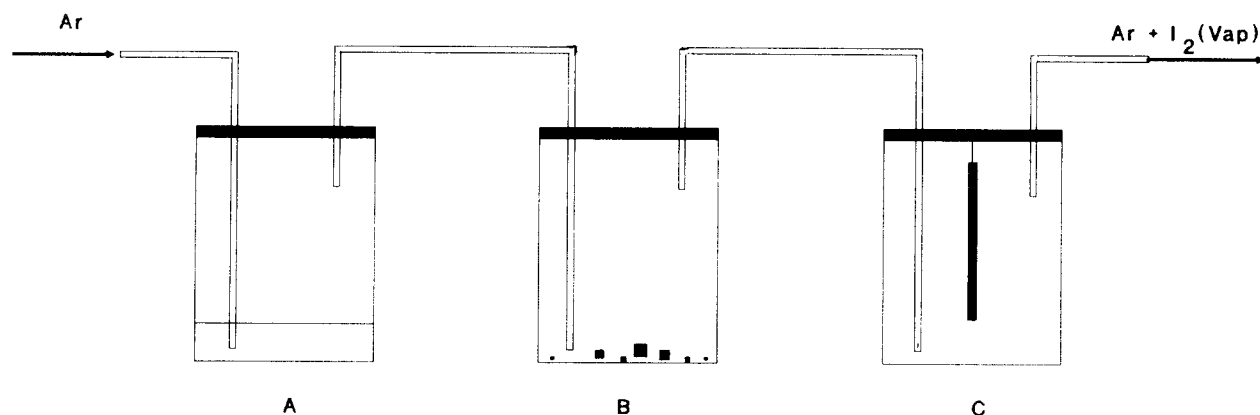
Fig. 1. The experimental set-up used in the preparation of CuI thin films on a copper substrate: A, wash-bottle containing propan-2-ol; B, vessel containing iodine crystals; C, chamber where the copper plate is suspended.

filtration and purified by recrystallization. The CuI-coated plates, when kept immersed in an aqueous solution of the Rhodamine 6G iodide, readily adsorbed it and the amount adsorbed could be controlled by varying the concentration of the solution or the duration of immersion. The amount of dye adsorbed was determined by extraction with ethanol followed by spectrophotometric estimation.

The electrolyte used in the PEC was an aqueous solution of KI (0.01 M) containing iodine (0.001 M). A Pt mesh was used as the counterelectrode and the photocathode was biased (Hokuto Denko HA-301 potentiostat) to give zero dark potential. The cell was illuminated with a 60 W tungsten filament lamp and the IR light was removed with a water shield. Light intensities were measured using an International Light Radiometer and also compared with a calibrated silicon solar cell. The time development of the short-circuit photocurrent under potentiostatic conditions was monitored with a XY/t recorder. A Nikon Monochromator Auto-scanner As-C 101 was used to record the photocurrent action spectrum. A PEC was also constructed with a copper-sulphide-coated copper window (Fig. 6) as the counterelectrode. The $I-V$ characteristics of the cell were obtained and the efficiency estimated.

3. Results and discussion

The film was found to grow at a nearly constant rate of about 2 μm per min, suggesting that the growth was limited by the interfacial reaction

$$2Cu + I_2 \longrightarrow 2CuI \qquad (2)$$

The diffuse reflectance spectrum of the CuI-coated plate (the thickness of the coating being about 8 μm) is shown in Fig. 2. There is a band edge near 400 nm corresponding to a bandgap of about 3.1 eV. The
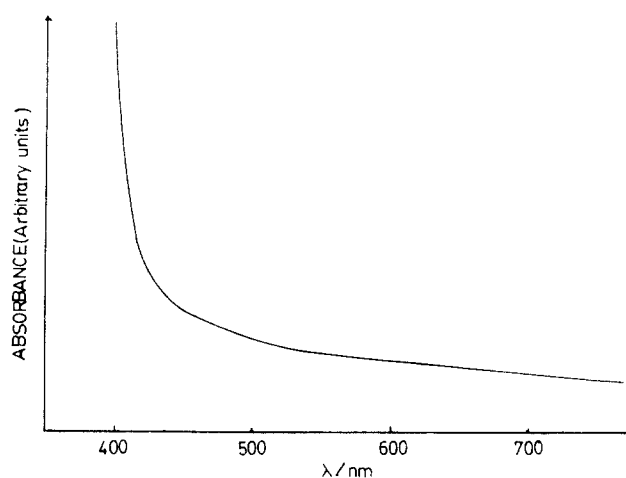

Fig. 2. Diffuse reflectance spectrum of the CuI-coated plate.

Mott–Schottky plot is shown in Fig. 3; the plots for the two frequencies (500 Hz, 1 kHz) intersect at a common point on the V axis and the positive slope indicates photoanodic behaviour. Neither the presence of the dye nor the composition of the electrolyte changed the plots significantly. The conduction band position derived from the plot is $-0.16\ V$ vs. a standard calomel electrode (SCE). Thus I^-/I_3^- which has a redox potential located between the bands can be adopted as a reversible electrolyte. In the absence of a dye, a CuI-coated plate in the I^-/I_3^- solution showed only a feeble photoresponse (cathodic current around 1 μA; dark curren near zero) when illuminated with visible light. Figure 4 curve (a) shows the time development of the (cathodic) photocurrent when the dye was added to the solution. As a result of dye adsorption on the surface, the photocurrent rapidly increased, reached a peak, and then decreased on prolonged illumination. The optimum surface concentration of the dye corresponding
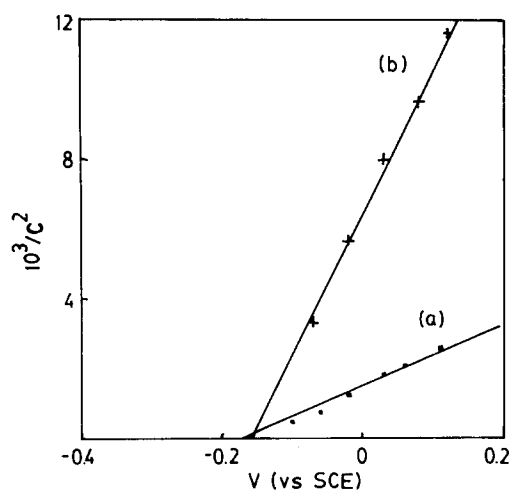
Fig. 3. Mott–Schottky plot (plot of C^{-2} vs. V; C, capacitance measured in μF; V, potential across the space charge layer) at frequencies of (a) 500 Hz; (b) 1 kHz.
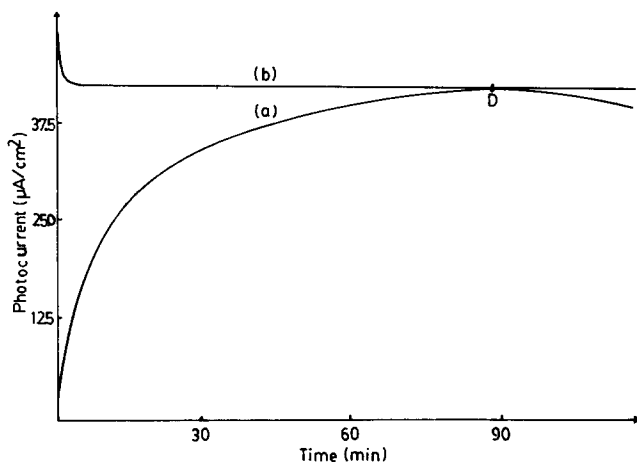

Fig. 4. (a) The time development of the short-circuit photocurrent, when the CuI-coated plate was kept in a 1×10^{-5} M solution of Rhodamine 6G iodide containing KI (0.01 M) and iodine (0.001 M); (b) time development of the photocurrent when a plate coated with dye to the optimum concentration was placed in a fresh solution of that electrolyte.

to the peak position (i.e. the point D in Fig. 4) was found to be 1.5×10^{15} molecules cm^{-2}. The equivalent thickness estimated from the structural formula of the dye is about 8.

When a plate coated with the dye to the optimum surface concentration was kept in a fresh I^-/I_3^- electrolyte (containing no dye), there was a nearly stable photocurrent (Fig. 4 curve (b)). The cathodic sensitization of a semiconductor surface occurs when the excited dye molecules adsorbed on the surface of the semiconductor inject holes into the conduction band [8]. Here, upon excitation of the dye molecule, an electron from the valence band is transferred to the lower unoccupied

level. The reactions occurring at the electrodes are as follows.

3.1. Photocathode

$$D + h\nu \longrightarrow D^*$$

$$D^* \quad \longrightarrow D^- + h^+$$
$$\uparrow$$
$$\text{Valence band}$$

$$(3)$$
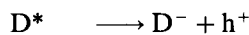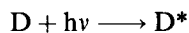
$$2D^- + I_3^- \longrightarrow 3I^- + 2D$$
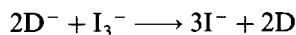
The hole generated is transferred to the valence band. Excited dye molecules instead of participating in the above hole transfer reaction could also de-excite by concentration quenching, when several excited molecules de-excite collectively generating heat, i.e.

$$D^* + D^* + D^* \text{---} \longrightarrow D + D + D \text{---} \quad (4)$$
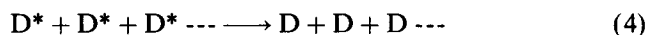
An increase in the surface concentration of the dye increases the photo-absorption cross-section. However, since concentration quenching also increases with increasing surface concentration, there exists an optimum dye surface concentration.

3.2. Anode

I^- ions donate electrons to the anode yielding iodine, which combines with I^- in the electrolyte to regenerate I_3^-, i.e.
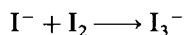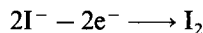
$$2I^- - 2e^- \longrightarrow I_2$$
$$I^- + I_2 \longrightarrow I_3^- \quad (5)$$

The photocurrent action spectrum is compared with the absorption spectrum of the dye in Fig. 5. The peak of the action spectrum is slightly red-shifted with respect to the photocurrent spectrum. The construction of the PEC with the copper-sulphide-coated counterelectrode
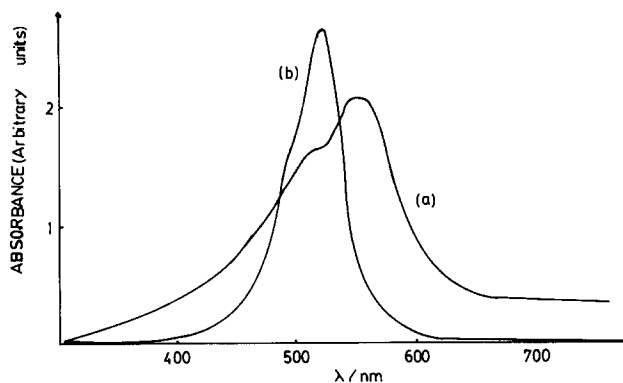

Fig. 5. (a) Photocurrent action spectrum of the sensitized CuI surface; (b) absorption spectrum of Rhodamine 6G iodide in an aqueous medium.
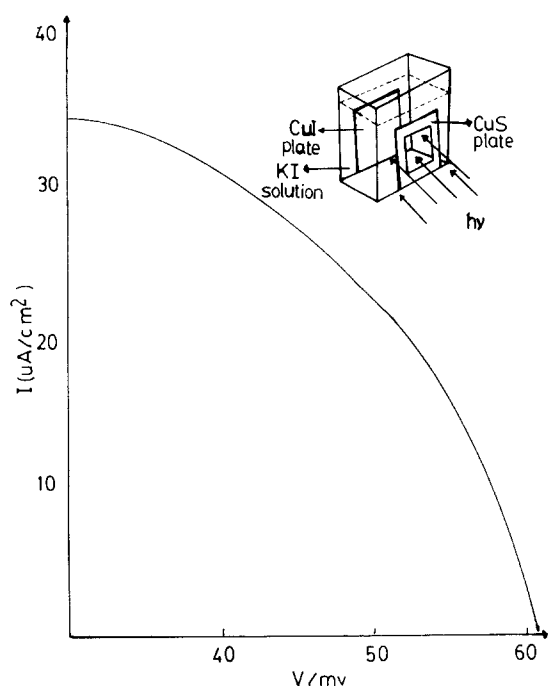
Fig. 6. *I-V* characteristics of the PEC with a CuI electrode sensitized with Rhodamine 6G iodide and a copper-sulphide-coated window as the counterelectrode. Inset: construction of the PEC with copper-sulphide-coated counterelectrode.

and its I–V characteristics are shown in Fig. 6. The efficiency at the maximum power point was found to be approximately 0.6%. The cell is not completely stable owing to photodegradation of the dye. It was observed

that the photocurrent decayed with time at a rate of about $4 \, \mu A \, cm^{-2} \, h^{-1}$. When the dye was removed by dissolution in alcohol, the CuI surface was found to remain intact.

The simplicity of this method of preparing CuI polycrystalline films makes CuI a good material for the study of dye-sensitization. Iodides of cationic dyes adsorbed on to CuI remain firmly affixed and leaching to the solution is minimal in the presence of I⁻ in the solution.

References

1 H. Gerischer, *Electrochem. Acta, 35* (1990) 1677.
2 M. Matsumura, Y. Nomura and H. Tsubomura, *Bull. Chem. Soc. Jpn., 50* (1979) 2533.
3 A. Heller, *Acc. Chem. Res., 14* (1981) 154.
4 M. S. Wrighton, *Acc. Chem. Res., 12* (1979) 303.
5 A. Nozik, *Philos. Trans. R. Soc. London, Ser. A, 295* (1980) 453.
6 H. Tsubomura, M. Matsumura, K. Nakatani, K. Yamamoto and K. Maeda, *Sol. Energy, 21* (1978) 93.
7 H. Gerischer and H. Tributsch, *Ber. Bunsenges. Phys. Chem., 72* (1968) 437.
8 R. Memming, *Photochem. Photobiol., 16* (1972) 325.
9 J. Moser and M. Gratzel, *J. Am. Chem. Soc., 106* (1984) 6557.
10 K. Tennakone, M. Kahanda, C. Kasige, R. Abeysooriya, R. H. Wijenayake and P. Kaviratne, *J. Electrochem. Soc., 131* (1984) 1575.
11 B. O. Regan and M. Gratzel, *Nature, 353* (1991) 737.
12 K. Tennakone, C. A. N. Fernando, M. Dewasurendra and M. S. Kariapper, *Jpn. J. Appl. Phys., 26* (1987) 561.