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Chlorophyll-sensitized microporous cuprous iodide photocathode

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Abstract

A method is given for deposition of a microporous film of cuprous iodide on indium–tin oxide glass substrate. Characteristics of the photocurrent spectra of the chlorophyll-sensitized film under back-wall and front-wall illumination are described.

Keywords: Microporous film; Cuprous iodide; Chlorophyll-sensitized film

1. Introduction

The dye sensitization of wide-band-gap semiconductors is becoming a promising method of devising practically viable photoelectrochemical cells (PECs) [1–8]. Wide-band-gap semiconductors are generally photocorrosion resistant in electrolytic media and, consequently, the problem instability owing to photodegradation of the semiconductor is negligible [1–8]. Dye sensitization affords a way of extending the spectral response of wide band gap materials to the visible region. Again in a dye-sensitized PEC, the excited dye molecules adsorbed at the semiconductor surface inject electrons (holes) into the conduction (valence) band. Thus the minority carriers, the holes (electrons), are not encountered and recombination losses from defects in the semiconductor are non-existent or minimal [6].

The major drawback of dye-sensitized PECs had been the low energy conversion efficiency. At monolayer or submonolayer coverage of the dye, the quantum efficiency of charge injection per molecule of adsorbed dye approaches unity. However, in order to increase the energy conversion efficiency, the light absorption cross-section needs to be increased by increasing the surface concentration of the dye. When this is done, several other factors which tend to decrease the quantum efficiency are encountered. Thick dye layers are insulating and also cut off light that should be incident on the dye molecules adsorbed at the semiconductor surface. Furthermore, when the surface concentration of the dye is increased, deactivation of excited molecules by mutual interaction (concentration quenching) is promoted. The above problems are elegantly overcome in the dye-sensitized microporous (colloidal) TiO_2 photoelectrodes developed by Gratzel and coworkers [5–8]. In a dye-sensitized microporous electrode, light intercepts many semiconductor particles lightly covered with the dye. Thus the light absorption cross-section is increased, maintaining a large effective surface area.

In the dye-sensitized PEC developed by Gratzel and coworkers [5–8] and other modifications of this system, colloidal TiO_2 is deposited on indium–tin oxide (ITO) glass. It is interesting to examine the possibility of using other semiconductors as dye-sensitized microporous photoelectrodes. The present work describes the preparation and properties of microporous cuprous iodide photocathode and sensitization with chlorophyll.

2. Experimental details

Cuprous iodide was prepared by mixing equimolar (0.3 M) solutions of copper sulphate and potassium iodide. The precipitate of CuI was separated by filtration washed with sulphurous acid (to remove free iodine) followed by warm distilled water and dried (110 °C). Potassium iodide (0.5 g) was dissolved in acetone (30 ml) and the solution agitated with CuI (0.2 g) until all CuI was dissolved. When I^- ions are present, CuI dissolves in acetone to form the complex ion CuI_3^{2-} (in an aqueous medium CuI_3^{2-} disproportionate to CuI and I^-; consequently, unlike in acetone, CuI is dissolved only by a saturated solution of KI). CuI (p-type semiconductor band gap, about 3.1 eV [9]) is electrochemically deposited on ITO glass plates by the following method. ITO glass plates (linear dimensions, 1 cm × 2 cm; sheet resistance, about 15 Ω) were cleaned with NaOH (0.1 M), washed and dried. CuI solution in acetone is electrolysed with ITO glass plate as the anode and a platinum mesh as the counterelectrode. Current is potentiostatically (Hotkuto Denko HA-301 potentiostat) maintained at 12 mA cm^{-2} for about 15 s.

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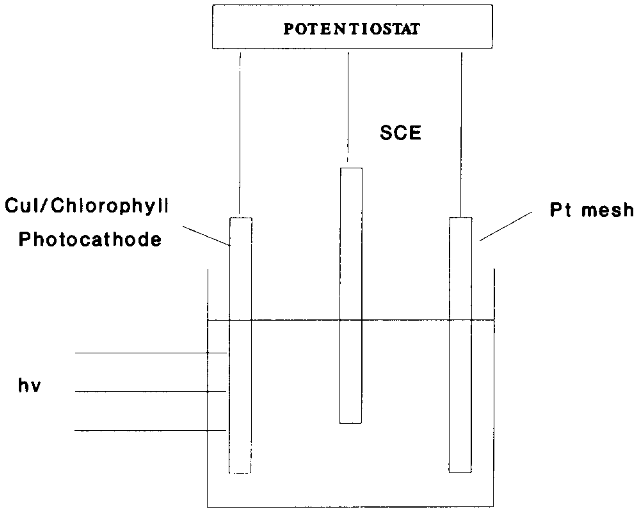

Fig. 1. Schematic diagram of the experimental set-up.

Growth at high current density in a short duration of time deposits colloidal size crystallites. The reaction occurring at the anode is

$$CuI_3^{2-} - 2e^- \longrightarrow CuI + I_2 \quad (1)$$

Addition of a few drops of glacial acetic acid and sodium dodecyl sulphate (about 50 mg) improves the transparency of the film (acidic pH and the presence of the surfactant sodium dodecyl sulphate suppress the coagulation of colloidal particles). The thickness of the film is estimated by noting the increase in mass of the ITO glass plate after deposition of CuI (density of CuI, 5.6 g cm^{-3}). The conditions described above gave films of thickness approximately 2 μm.

Chlorophyll was extracted from spinach with acetone. All accessory pigments and most chlorophyll b was removed by repeated solvent extraction with hexane and methyl alcohol. Thin layer chromatography indicated that the hexane extract was contaminated with chlorophyll b. No attempt was made to purify the product further. Solid chlorophyll was obtained by evaporation of the hexane extract. Chlorophyll was coated on the CuI film by keeping the plates immersed in a solution of chlorophyll in acetone. Chlorophyll-coated CuI films were also prepared by adding chlorophyll to solution used for electrodeposition of CuI. Plates prepared by this method had higher transparency and gave more easily reproducible results.

To carry out photoelectrochemical measurements, CuI-coated plate was placed in $KI + I_2$ ($[I^-] = 0.1$ M; $[I_2] = 7.5 \times 10^{-6}$ M) solution in a fibre glass rectangular vessel. A three-electrode configuration was adopted and a platinum mesh (2 cm × 2 cm) was used as the counterelectrode. In all measurements, the working electrode was biased (Hokutodenko HA-301) at −0.2 V with respect to a standard calomel electrode (SCE) to obtain the optimum photoresponse. Photocurrent action spectra were obtained with a monochromator (Nikon Monochromator, Auto-Scanner AS-C 101) coupled to a light chopper and a lock-in amplifier. The stability of the cell under short-circuit conditions was examined under illumination with a 100 W tungsten filament lamp. A schematic diagram representing the experimental set-up is shown in Fig. 1.

3. Results and discussion

Fig. 2 shows the action spectrum of the CuI photocathode (unsensitized) under front-wall (FW) (i.e. through the electrolyte) and back wall (BW) (i.e. through the ITO substrate into the CuI film) illuminations. In the latter spectrum, the photoresponse in the band gap region (about 408 nm) is sharp and much enhanced whereas, in the former, only a feeble photoresponse is observed. As a result of diffusion-controlled charge transfer between colloidal semiconductor particles in microporous photoelectrodes, these action spectra are generally different and have characteristics similar to what we have observed [10–12].

Fig. 3 gives the action spectra of photocathodes sensitized with chlorophyll. Here the sensitized photocurrent is conspicuously seen in both BW and FW spectra, but the sensitized response is more pronounced in the BW mode of illumination. Again in the sensitized cathodes, the band gap response of CuI is much more strongly peaked in the BW mode than in the FW mode. Peaks in the sensitized spectrum are seen near 615 and 583 nm. These correspond to absorption peaks in chlorophyll. The absorption spectrum of chlorophyll solution used for sensitization is shown in Fig. 4. A slight red shift in the action spectrum results from adsorption of chlorophyll on CuI.

Fig. 5 shows the time development of the photocurrent, when the cell is illuminated with a 100 W tungsten filament

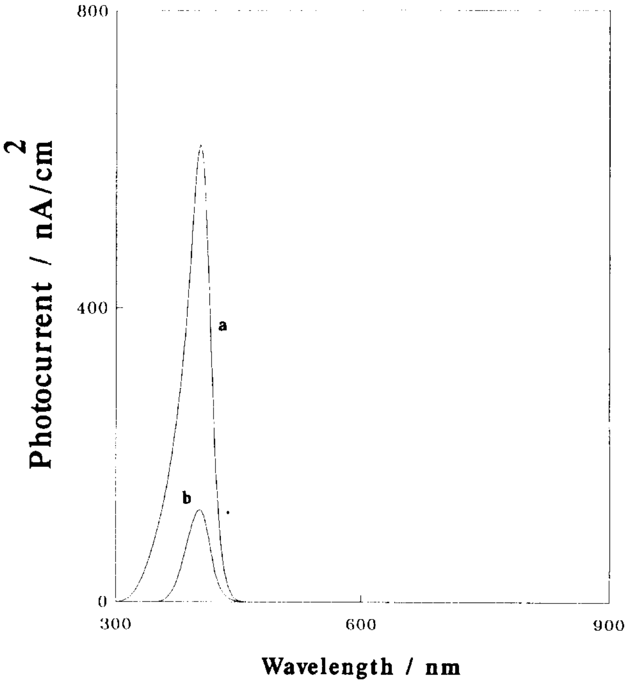

Fig. 2. Photocurrent action spectrum of the CuI photocathode (unsensitized): curve a, BW illumination; curve b, FW illumination.

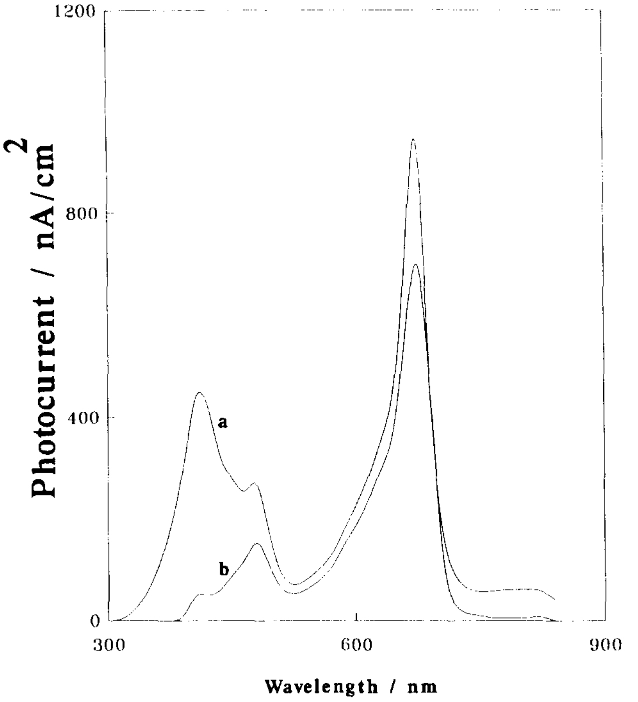

Fig. 3. Photocurrent action spectrum of CuI photocathode sensitized with chlorophyll: curve a, BW illumination; curve b, FW illumination.

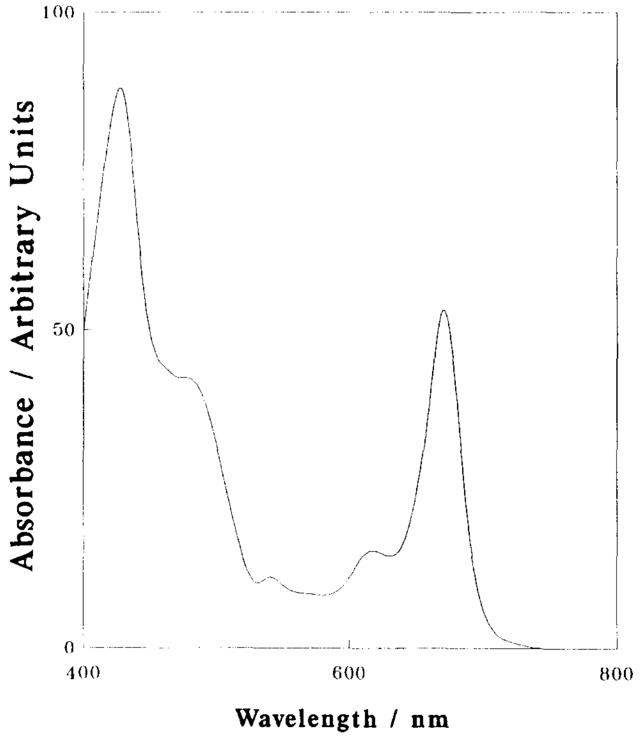

Fig. 4. Absorption spectrum of chlorophyll solution used for coating the electrodes.

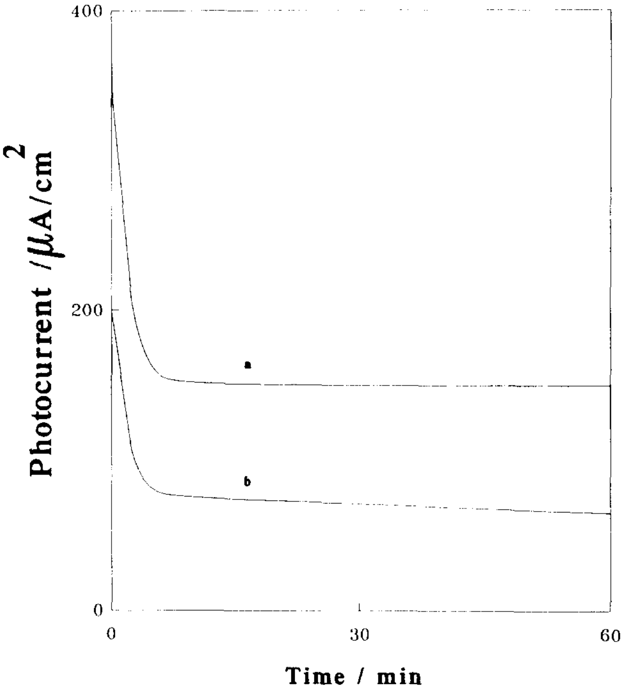

Fig. 5. Time development of the photocurrent when the cell is illuminated with a 100 W tungsten filament lamp: curve a, BW illumination; curve b, FW illumination.

lamp. Reasonably good stability is seen; the decay of the photocurrent 1 h exposure to light was about 0.5 μA h^{-1} for the BW mode and 10 μA h^{-1} for the FW mode. The higher stability of the BW mode is an indication of the difference between the charge transfer kinetics of the two modes. Rapid charge transfer in the BW mode suppresses degradation of the pigment.

CuI can be deposited on ITO glass by vacuum evaporation. Such films are not microporous and sensitization with chlorophyll gives photocurrents smaller by more than one order of magnitude. The above investigation clearly demonstrates the superiority of semiconductor electrodes of microporous surface structure in dye sensitization by giving an example from an unconventional semiconductor.

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