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A nanoporous solid-state photovoltaic cell sensitized with copper chlorophyllin

K. Tennakone *, G.R.R.A. Kumara, K.G.U. Wijayantha, I.R.M. Kottegoda, V.P.S. Perera, G.M.L.P. Aponsu

Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka

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Abstract

A fully solid-state dye-sensitized photovoltaic nanoporous $n-TiO_2/copper chlorophyllin/p-CuI cell was constructed by depositing p-CuI onto a nanoporous film of <math>n-TiO_2$ coated with copper chlorophyllin. The photo-excited pigment is found to inject electrons into $n-TiO_2$ and holes into p-CuI, generating a photocurrent and photovoltage that are significant for a solid-state dye-sensitized cell. © 1997 Elsevier Science S.A.

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1. Introduction

Dye-sensitized photoelectrochemical cells based on nanoporous TiO₂ are receiving considerable attention as practical solar energy conversion devices [1-8]. The cells developed by Gratzel and coworkers [6,9,10] are reported to have efficiencies exceeding 10% and reasonably good stability. Unfortunately the liquid electrolyte presents several technological problems such as dye desorption, solvent evaporation and seal imperfections. Again, as charge transport involves chemistry, undesirable chemical reactions that lead to irreversibility (i.e. those other than reactions of the redox cycle) are not completely ruled out. The ideal solid-state dye-sensitized cell should be a fully solid-state device, where the liquid is replaced by a solid conductor [10]. For an n-type nanoporous semiconductor film coated with a dye, the natural choice is a p-type semiconductor that accept holes from dye cations. In the n-type semiconductor/dye/p-type semiconductor (NDP) device (Fig. 1), the photoexcited dye molecules sandwiched between two semiconductors inject electrons into the n-type material and holes into the p-type material, i.e.

D+h
$$\nu$$
→D*
D*→D++e⁻
↓
conduction band n-type semiconductor
D+→D+h+

valence band p - type semiconductor

As the other parallel reactions, i.e.

$$D + h\nu \rightarrow D^{*}$$

$$D^{*} \rightarrow D^{-} + h^{+}$$

$$\downarrow$$
valence band p - type semiconductor
$$D^{-} \rightarrow D + e^{-}$$

$$\downarrow$$
(2)

conduction band n – type semiconductor

are also realizable. The actual physical process is injection by the excited dye molecule of electrons into the conduction band of the n-type material and holes into the valence band of the p-type material, i.e.

^{*} Corresponding author.

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Fig. 1. (a) The construction of the nanoporous n-TiO₂/chlorophyllin/p-CuI photovoltaic cell. (b) A schematic energy level diagram illustrating the relative band positions of TiO₂ and CuI and the energy levels of the dye.

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

$$D^* \rightarrow D + e^-$$

valence band n-type material

+
$$h^+$$

 \downarrow (3)
conduction band p-type material

The advantage of a device based on the above concept is complete suppression of recombination within the two semiconductors, as only one type of carrier is confined to each semiconductor.

NDP devices of nanoporous structure are highly restrictive with respect to the choice of semiconductor and dye. TiO₂ is undoubtedly one of the best n-type materials, because of its stability and the availability of methods of preparation of nanoporous films. The dye selected must affix firmly to the surface of the TiO_2 and be compatible with the deposition technique used for the p-type semiconductor, which has to be transparent to visible light and therefore of high band gap. Furthermore, the relative positions of the bands of the semiconductors, ground and excited levels of the dye, must be located as in Fig. 1(b). We have found that the p-type semiconductor CuI (band gap approximately 3.1 eV) can be readily deposited onto porous TiO₂ from a solution in acetonitrile to fill the intercrystallite pores. A photovoltaic n-TiO₂/dye/p-CuI cell with cyanidin as the dye gave a short-circuit photocurrent and open-circuit voltage as high as 2.5 mA cm⁻² and 375 mV respectively [11]. Porphyrin pigments are known to be good sensitizers for TiO₂ in photoelectrochemical cells [12,13]. We have found that an NDP cell with nanoporous TiO₂ as the n-type material and CuI as p-type material can also be constructed using copper chlorophyllin as the dye. This report describes the method of construction and the performance of the nanoporous n-TiO₂/ chlorophyllin/p-CuI cell.

2. Experimental details

The following method was used for deposition of nanoporous films of TiO_2 onto conducting transparent oxide (CTO) glass (1.5 cm \times 2.0 cm, sheet resistance approximately 10 Ω/\Box). Titanium isopropoxide (1 ml), glacial acetic acid (5 ml) and isopropanol (15 ml) are mixed and 5 ml of water is added drop by drop to the mixture which is stirred continually [11]. Fine crystallites of TiO₂ are produced by hydrolysis of titanium isopropoxide and the above procedure prevents their agglomeration. The CTO glass plate is placed on the surface of a hot plate (surface temperature approximately 125 °C) and colloidal TiO₂ is spread evenly on the surface and allowed to dry. The plate is then sintered at 450 °C for 20 min and the process is repeated until a fully covered semi-transparent film has been deposited.

The porous TiO₂ film deposited onto CTO glass by the above method is coated with copper chlorophyllin by the following method. Chlorophyllin (sodium-copper salt, Sigma, 5 mg) is dissolved in 1 ml acetone containing 1% water by volume (chlorophyllin copper-sodium salt is insoluble in anhydrous acetone). The TiO₂ coated CTO glass plate is kept immersed in this solution (contained in a test-tube), boiled for 1 min and allowed to cool. The dye coated film is rinsed with water and dried in a current of dry nitrogen in the dark. CuI was deposited onto the chlorophyllin coated porous TiO₂ films as described below. A solution of CuI was prepared by dissolving 0.6 g CuI in moisture-free acetonitrile. The dyed TiO₂ coated CTO glass plate is dipped in the CuI solution and then dried several times until pores of the TiO₂ film are filled with CuI. For functioning of the cell, it is essential that the CuI layer extends above the TiO₂ film. This is best achieved by spraying the CuI solution onto the surface of the plate, heated to 150 °C. Spraying is repeated until the surface resistance is reduced 50–60 Ω/\Box . Electrical contact to the CuI surface was made by evaporation of gold. In some experiments, the electrical contact was made by pressing gold or graphite coated CTO glass onto the CuI surface and sealing the cell with epoxy resin.

The photocurrent action spectrum of the cell was recorded using a Nikon monochromator auto-scanner AS-C-101 coupled to a light chopper and a lock-in amplifier. Time development of the photocurrent was monitored under different conditions to determine the effect of oxygen, moisture and UV light. Light intensities were measured using the Ekopyronometer (model Ms 801).

3. Results and discussion

The cell generates a short-circuit photocurrent of 2 mA cm⁻² and an open-circuit voltage of 435 mV (solar simulator 800 W m⁻²). The energy conversion efficiency is approximately 0.7%. If moisture and oxygen are not excluded during sealing, the photocurrent undergoes rapid decay (at a rate of approximately 10 μ A min⁻¹) with photodegradation of chlorophyllin. When UV light is filtered ($\lambda \le 348$ nm, using NaNO₃ solution), the rate of decay is significantly reduced (i.e. 1 μ A min⁻¹). Dye degradation is almost completely suppressed in the absence of oxygen, moisture and



Fig. 2. (a) Photocurrent action spectrum of the nanoporous $n-TiO_2/chlorophyllin/p-CuI$ cell. (b) Absorption spectrum of an aqueous solution of chlorophyllin.

UV light ($\lambda \le 348$ nm), but the photocurrent continues to decay at a much slower rate (approximately 0.3 μ A min⁻¹). The pigment undergoes rapid degradation in the presence of moisture, oxygen and UV light owing to the photocatalytic activity of TiO₂. We are not certain of the mechanism that causes decay of the photocurrent even in the absence of moisture, oxygen and UV light. Perhaps warming of the cell during operation affects the contact of the dye and the two semiconductor (CuI and TiO₂) surfaces.

The photocurrent action spectrum of the cell is shown in Fig. 2(a). Peaks in the action spectrum are slightly red shifted with respect to those in the absorption spectrum shown in Fig. 2(b). (Pigments absorbed on surfaces generally give red-shifted spectra compared with those in dilute solution.) The peak at 360 nm in the action spectrum originates from band gap excitation in nanoporous TiO_2 . In the absorption spectrum of chlorophyllin in water (Fig. 2(b)) the more prominent peak is that at 406 nm, but in the action spectrum

of the cell (Fig. 2(a)) this peak is suppressed, because CuI absorbs strongly in the vicinity of this peak (the band edge of CuI is located at approximately 408 nm).

The above results indicate that, just as in the case of wet cells, porphyrin type pigments can be used to construct fully solid-state cells based on nanoporous TiO_2 . In a fully solid-state dye-sensitized cell, the preservation of the contact between the dye and the two semiconductors is important for stability of the cell. Chlorophyllin does not seem to satisfy this requirement.

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