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A dye-sensitized nano-porous solid-state photovoltaic cell

K Tennakone, G R R A Kumara, A R Kumarasinghe,
K G U Wijayantha and P M Sirimanne

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

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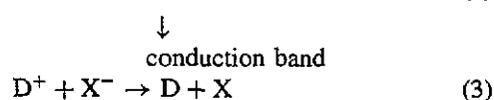
Abstract. A photovoltaic cell was fabricated by sandwiching a monolayer of the pigment cyanidin adsorbed on nano-porous n-TiO₂ film (deposited on conducting tin oxide glass) within a transparent polycrystalline film of p-CuI, filling the intercrystallite pores of the porous n-TiO₂ film. Photoexcited dye is found to inject electrons into n-TiO₂ and holes into p-CuI, generating photocurrents and photovoltages that are impressively high for a dye-sensitized solid-state photovoltaic cell.

1. Introduction

The fascinating phenomenon of dye-sensitization (DSN) of the semiconductor surface (injection of carriers into the bands by photoexcited dye molecules adsorbed at the surface) was first observed more than a century ago and continues to arouse the interest of physicists and chemists. In 1873 Vogel [1] made the important discovery that dye-coated silver halide grains sensitize the photographic film to the absorption spectrum of the dye. The mechanism of DSN was explained by Mott and Gurney [2] as originating from transfer of an electron by the excited dye molecule to the conduction band of the silver halide. Subsequent studies [3–6] confirmed that anodic (cathodic) sensitization occurs when excited dye molecules adsorbed at the surface of the semiconductor inject electrons (holes) into the conduction (valence) band and the type of sensitization (anodic or cathodic) depends on the band positions of the semiconductor and the energy levels of the dye. More recently, much attention was diverted to DSN as a means of extending the spectral response of photoelectrochemical cells (PECs) based on high-bandgap materials that are photostable in electrolytic media [7–11]. Apart from the ability to use high-bandgap stable materials, dye-sensitized (DS) PECs possess another advantageous property, namely that the semiconductor could be a low-purity polycrystalline material. The reason for this is that DSN involves only one band (the conduction band in an anodically sensitized process and the valence band in a cathodically sensitized process) and electrons and holes are not both produced in the same material. Consequently recombinations arising from impurities and defects are nonexistent.

The principle behind DS PECs is simply the following. Dye molecule D adsorbed at the semiconductor surface is photoexcited from the ground level S₀ to the excited level S* (singlet or triplet) and injects electrons into the conduction band (in an anodic process) creating the dye

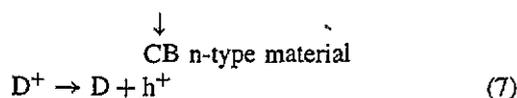
cation D⁺. Immediately thereafter the dye cation accepts an electron from the species X⁻ of the redox couple X⁻/X in the electrolyte, regenerating the dye, and diffusion-controlled migration of X to the cathode maintains the equilibrium of the redox electrolyte; that is



↑
cathode

Despite the above-mentioned attractive features, the major drawback of DS PECs had been their low conversion efficiency. At monolayer or submonolayer coverage of the dye, the quantum efficiency of charge injection per molecule of the 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 efficiency, are encountered. Thick dye layers are electrically insulating and also cut off light that should be incident upon the dye molecules that are adsorbed at the semiconductor surface. Furthermore, when the surface concentration of the dye is increased, de-activation of the excited molecules by mutual interaction (concentration quenching) is promoted. The above problems are elegantly overcome in the DS nano-porous (nano-porous means a porous film containing crystallites of nanometre size) TiO₂ photoelectrodes developed by Gratzel and co-workers [12–15]. In a DS nano-porous electrode each TiO₂ crystallite is covered with the dye at monolayer concentrations. However, light intercepts many particles, increasing the

effective light absorption cross section. PECs made from DS nano-porous TiO₂ electrodes are known to have efficiencies approaching 10%. Unfortunately, the liquid electrolyte presents several technological problems such as dye desorption, solvent evaporation and degradation and seal imperfections. The ideal DS solar cell is a fully solid-state device, in which the liquid is replaced by a solid conductor. A solid electrolyte is unsuitable because of the low mobility of ions. Naturally, the choice should be a p-type semiconductor that accepts holes from the dye cation [16]. In this n-type semiconductor/dye/p-type semiconductor (NDP) device, the photoexcited dye molecules sandwiched between the two semiconductors inject electrons into the n-type material and holes into the p-type material; that is



↓
VB p-type material.

The occurrence of carrier injection from the excited dye molecules into the bands of the two semiconductors in an NDP device was demonstrated by one of the authors of the present paper (KT) and his collaborators by construction of the n-SnO₂/methyl violet/n-SnO₂ solid-state photovoltaic cell [17]. This cell possessed a photocurrent action spectrum concurrent with the absorption spectrum of the dye. As expected, the quantum efficiency was minute, owing to the non-porous nature of the CuCNS film on which the dye was coated and partly due to imperfect dye/n-SnO₂ contact. Conversion efficiencies are greatly increased when the dye is coated onto a nano-porous n-TiO₂ electrode and a transparent p-type semiconductor deposited on top of it, to fill the pores of the porous electrode. In order to do this, the prospective p-type semiconductor and the dye are required to have special properties. (i) The p-type material must be transparent to the visible spectrum, where the dye absorbs light (the semiconductor must have a high bandgap). (ii) A method must be available for depositing the p-type material without dissolving or degrading the monolayer of dye on TiO₂ nanocrystallites. (iii) The dye must be such that the S* level is located above the bottom of the conduction band of TiO₂ and the S₀ level below the upper edge of the valence band of the p-type material. This is essential for electron transfer from the excited dye molecule to the conduction band of TiO₂ and hole transfer to the valence band of the p-type material.

The familiar high-bandgap p-type semiconductors such as SiC and GaN might satisfy the transparency and band position requirements [16]. However, the high-temperature deposition techniques of these materials will certainly degrade the dye. Again, a low-temperature deposition method (electrodeposition) is unthinkable in the case of the above semiconductors. After extensive experimentation, we found that CuI (a p-type semiconductor of bandgap about 3.1 eV) is a suitable material [18–20] and a simple relatively low-temperature process was developed

for deposition of conducting transparent films of CuI onto nano-porous TiO₂ films (or glass). The method depends on the solubility of CuI in acetonitrile. A spray and dip coating method developed by us produces transparent conducting films of CuI. Dyes known to sensitize nano-porous TiO₂ in the PECs (ruthenium complexes, chlorophyllin and porphyrins) are not amenable to the above deposition techniques, owing to their solubilities in acetonitrile. In looking for alternatives, we found that cyanidin derived from flower pigments [21–24] forms a surface complex with TiO₂ to yield a remarkably stable, chemically as well as thermally resistant and insoluble (in water, acetonitrile and all the common solvents) coating. Cyanidin was found to sensitize nano-porous TiO₂ efficiently (comparably to ruthenium complexes in wet cells).

The NDP solar cell fabricated by depositing CuI onto a nano-porous TiO₂ surface was found to deliver a short-circuit photocurrent of 1.5–2.0 mA cm⁻² in sunlight (about 800 W m⁻²), which is probably the highest recorded for a solid state cell based on a dye. The details of construction of the cell and problems that need to be resolved in improving its performance are described.

2. Experiment

Nano-porous layers of TiO₂ were coated on fluorine-doped conducting tin oxide (CTO) glass (1.5 cm × 2 cm, sheet resistance about 40 Ω □⁻¹) by the following method. Titanium isopropoxide (1 ml) and glacial acetic acid (5 ml) are added to isopropanol (15 ml) and 5 ml water is added drop by drop to the mixture which is kept stirred. Hydrolysis of titanium isopropoxide produces fine crystallites of TiO₂ and the above procedure prevents their agglomeration. The CTO glass plate was placed on the surface of a hot plate (surface temperature about 125 °C) and the solution is evenly spread using a glass rod and allowed to dry. The plate is then sintered at 450 °C for 20 min and the process is repeated until a fully covered semitransparent film has been deposited. TiO₂ film (kept in an electrolytic medium) showed a characteristic blue-shifted band edge at about 368 nm corresponding to a crystallite dimension of about 15 nm.

The flower pigment cyanidin was obtained from blood red flowers of Anthurium by the following method [21–24]. Petals of the flowers were crushed and boiled with 25% acetic acid. This process hydrolyses the glycoside (anthocyanin) yielding cyanidin acetate [21]. The residue is separated and the solution evaporated in a rotary evaporator, the product is washed with hexane, ethyl acetate and isopropanol to remove any lipids, carotene, tannins and flavonols [24]. The resulting solid mass is mainly cyanidin acetate which is further purified by chromatography [24] (on a cellulose powder packed column using acetic acid solution). Chromatographic comparison with an authentic sample confirmed that the product is cyanidin.

Absorption spectra of the pigment solution (obtained using a Shimadzu UV-3000 spectrophotometer) also confirmed that the pigment is cyanidin. A colloidal solution of TiO₂ nanocrystallites (prepared by hydrolysis of titanium isopropoxide with HCl and separated by dialysis) turns deep

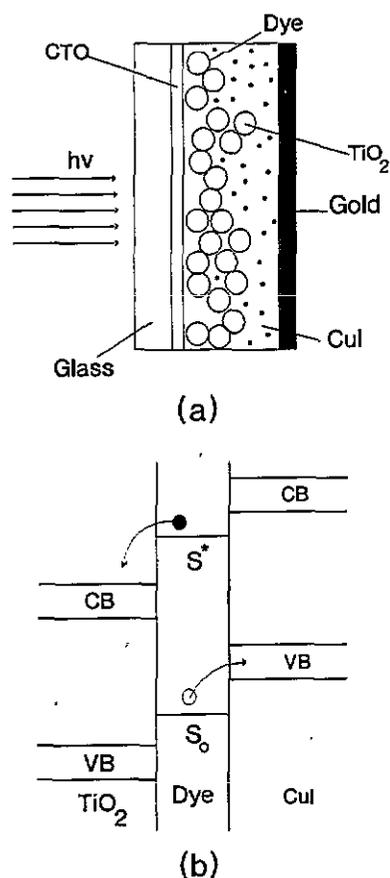


Figure 1. (a) The construction of the nano-porous n-TiO₂/cyanidin/p-CuI photovoltaic cell. (b) A schematic energy level diagram illustrating the relative band positions of TiO₂ and CuI and the energy levels of the dye.

violet on addition of cyanidin due to formation of a Ti⁴⁺-cyanidin complex on the surfaces of the TiO₂ crystallites. The absorption spectrum of this solution was also recorded.

Nano-porous TiO₂ electrodes were coated with pigment by warming them in a 15% acetic acid solution of the pigment. After this treatment the electrode surface acquired a bluish-red tint due to complexation of cyanidin with Ti⁴⁺ ions on the TiO₂ surface. (In some experiments, pigment purified by solvent extraction was used, because it gave nearly the same results as those of the chromatographically purified samples.) Pigment-adsorbed electrodes were washed with water, ethanol, hexane and dried in an argon atmosphere for 30 min.

CuI was deposited on the pigment-coated electrodes as described below. The solution of CuI was prepared by dissolving 0.6 g of CuI in 50 ml of moisture-free acetonitrile. The electrode, kept immersed in 50 ml of this solution, is boiled for 2 min to expel gases occluded in the pores of the porous TiO₂ film (the experiment was conducted in a glove box flushed with dry nitrogen). It is then withdrawn from the solution and hot nitrogen is blown through it to evaporate acetonitrile. When this process is repeated several times, pores of the TiO₂ electrode are filled with solid CuI.

The electrode is now sintered in an argon atmosphere at 150°C for 30 min. The above procedure fills the pores of the TiO₂ film, minimizing the formation of voids. However, for functioning of the cell it is essential that

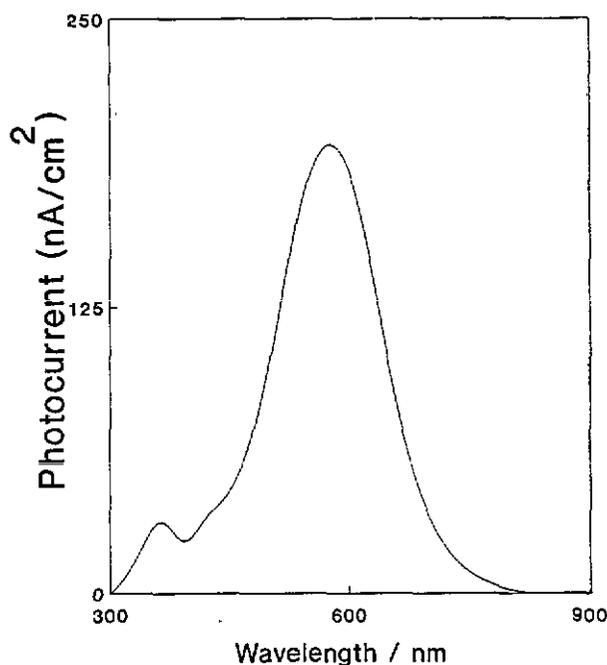


Figure 2. The photocurrent action spectrum of the nano-porous n-TiO₂/cyanidin/p-CuI photovoltaic cell.

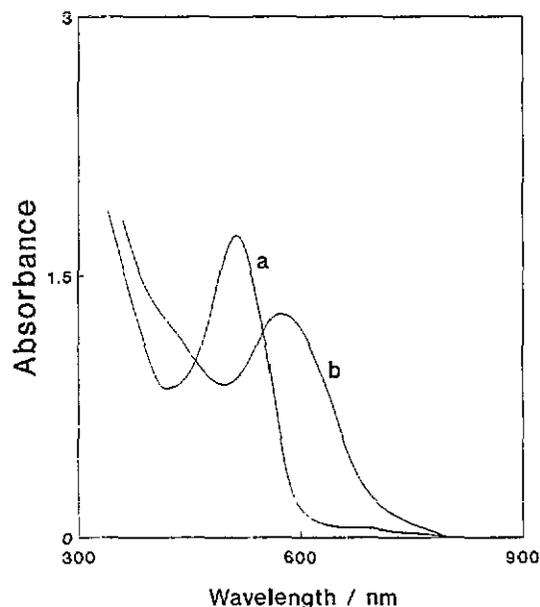


Figure 3. The absorption spectrum of (a) cyanidin acetate aqueous solution and (b) TiO₂ sol in aqueous medium treated with cyanidin.

the CuI layer extends above the TiO₂ film. This is best achieved by spraying the CuI solution onto the surface of the electrode heated to 150°C. Spraying is continued until surface resistance is reduced to 50–60 Ω □⁻¹. At this point the estimated thickness of CuI layer above the nano-porous TiO₂ film (thickness about 3.0 μm) is about 6.0 μm. The electrical contact to the CuI surface was made by evaporation of gold. In some experiments, the electrical contact was made by pressing a gold or graphite coated CTO glass onto the CuI surface.

The photocurrent action spectrum of the cell was recorded using a monochromator (Nikon monochromator,

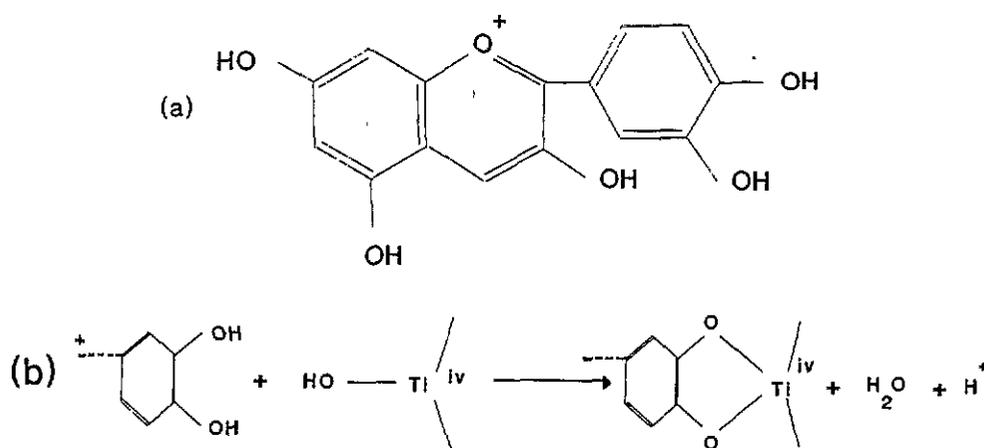


Figure 4. (a) The structural formula of the cyanidin cation. (b) The mechanism of surface complexation of cyanidin with TiO_2 .

Auto-Scanner AS-C 101) coupled to a light chopper and a lock-in amplifier. The performance of the cell was assessed in direct and simulated sunlight. To assess the effect of moisture and oxygen, the cell was placed in a chamber containing P_2O_5 or flushed with dry argon and the time development of the photocurrent was monitored. Potassium iodide solution (0.2 M) contained in a rectangular vessel (thickness about 2 cm) was used as a shield to exclude UV light ($\lambda \leq 350$ nm). Light intensities were measured using an Eko Pyranometer (Model MS 801). A Shimadzu EPMA 8705 device was used to scan the CuI film.

3. Results and discussion

The construction of the nano-porous n- TiO_2 /cyanidin/CuI photovoltaic cell is shown in figure 1(a). The schematic diagram of figure 1(b) illustrates the mechanism of photogeneration of the carriers. A dye molecule excited from the ground level S_0 to S^* injects an electron into the conduction band of TiO_2 . The unoccupied ground level is filled by transfer of an electron from the valence band of CuI. (Alternatively, a hole is injected into the valence band.) Figure 2 shows the photocurrent action spectrum of the cell which is peaked at about 571 nm. (The peak at about 360 nm in figure 2 originates from absorption in TiO_2 .) The absorption spectrum of an aqueous solution of cyanidin is peaked at about 530 nm (figure 3 curve (a)), whereas in a cyanidin solution mixed with TiO_2 sol, the absorption peak is at about 572 nm (figure 3, curve (b)) which is almost the same as the peak spectral response of the cell. When a PEC is constructed with a cyanidin coated nano-porous TiO_2 electrode (Pt foil as the counter electrode and KI plus I_2 solution as the electrolyte), the action spectrum is again seen to be peaked at about 572 nm.

Cyanidin (the structural formula is given in figure 4(a)) is strongly adsorbed on TiO_2 as a result of complexation with Ti^{4+} ions on the surface. Ti^{4+} ions on the surface of TiO_2 are bonded to hydroxyl groups, thus the cyanidin cation can readily complex with the surface Ti^{4+} ions by eliminating a proton (figure 4(b)). Complexation of Ti^{4+} with benzene derivatives containing several hydroxyl

group is well established [25–27]. Cyanidin is only weakly adsorbed on a CuI surface. If a CuI-coated CTO glass plate is kept immersed in cyanidin chloride solution for several hours, weak adsorption becomes noticeable and a PEC constructed with this electrode gives a cyanidin-sensitized spectrum peaked at about 535 nm. The above observation shows that cyanidin has the ability to inject holes into the valence band of CuI, confirming that the location of the S_0 level is favourable for hole injection into the valence band of CuI (figure 1(b)).

In direct sunlight (about 800 W m^{-2}) the cell generated a short-circuit photocurrent of about 2.5 mA cm^{-2} and an open-circuit voltage of about 375 mV. The maximum energy conversion efficiency was estimated to be about 0.8%. A solar simulator at the same intensity gave a short-circuit photocurrent of about 1.8 mA cm^{-2} and an open-circuit voltage of about 300 mV. The difference is due to better matching of the absorption spectrum of the pigment and the solar spectrum. The time development of the short-circuit photocurrent when the cell is illuminated with a solar simulator is given in figure 5. The photocurrent remained nearly stable for about 1.5–2 h and then began to decay and entered a slower decaying phase at a low value of the current density. If the cell is examined after 2.5 h then an increase in the surface resistivity of the CuI film is observed (initial resistance about $50 \Omega \square^{-1}$ changed to about $150 \Omega \square^{-1}$), suggesting that the sudden decay of the photocurrent results from deterioration of the CuI film. Electron microscopic examination showed clear evidence for pitting of the CuI film. It seems that the pitting of the film is caused by pressure building up and the release of gases, disrupting the film. Dye degradation was also observed and continued even after rapid decay of the photocurrent. Moisture is detrimental to the functioning of the cell. When the CuI surface is wetted with water, the photocurrent decays immediately and fading of the dye becomes noticeable at once. In a highly humid atmosphere, rapid decay of the photocurrent (figure 5) occurred earlier and the dye degraded at a faster rate. When the cell was placed in a chamber containing a dehydratant (P_2O_5), the stability was improved. A further enhancement in the

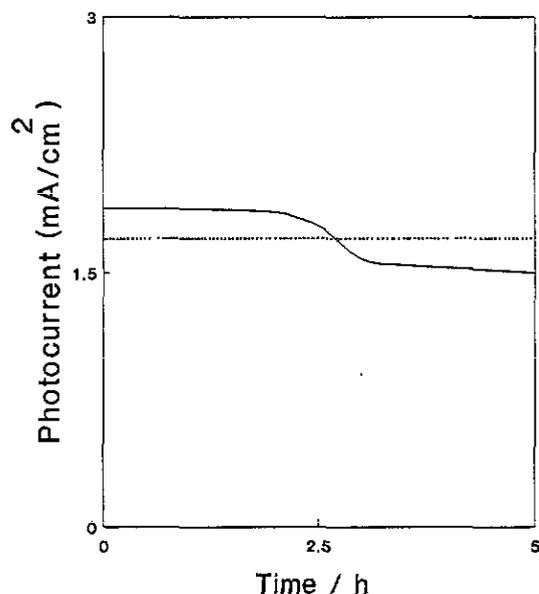


Figure 5. The time development of the photocurrent when the cell was illuminated with a solar simulator at intensity 800 W m^{-2} , in the absence (full curve) and in the presence (broken line) of the UV shield.

stability occurred when the chamber was flushed with dry argon. Excluding UV light ($\lambda \leq 350 \text{ nm}$) falling on the cell has the most dramatic effect on the stability of the photocurrent. When the UV shield was interposed between the simulator and the cell, the photocurrent remained almost completely stable (figure 5, broken line). The estimated decrease in the photocurrent after 12 h illumination was less than 0.3%. It is clear that spoiling of the cell was caused by light of wavelength λ less than the bandgap radiation of TiO_2 . This radiation generates highly oxidative free radical species (such as OH^\cdot) at the surface of TiO_2 [28] that oxidize the dye, producing carbon dioxide and water [29]. The release of accumulated gases disrupt the CuI film.

4. Conclusion

We believe that the efficiency of the cell can be increased by improving the CuI coating technique and finding other sensitizers. The present coating method undoubtedly leaves some intercrystallite pores of the TiO_2 film unfilled. Prevention of the formation of voids and parallel short-circuiting will enhance the short-circuit photocurrent, open circuit voltage and long-term stability. A suitable coating on the outer glass surface would readily filter out UV radiation that would degrade the dye and the cell can be protected from moisture by an effective sealing. Although cyanidin-type pigments are relatively unstable compounds, the Ti^{4+} -cyanidin complex on the surface of TiO_2 is highly stable, although the stability may not be sufficient for a practical device. Cyanidin could serve as a model for identification and synthesis of superior sensitizers. Another problem that we envisage is the ionic conductivity of CuI. Even though the effect is small at room temperature,

polarization arising from mobile Cu^+ ions tends to decrease the open-circuit voltage of the cell. Consequently, other high-bandgap p-type materials that yield transparent films in low-temperature depositing techniques (such as CuCNS [16, 30]) may be more suitable. Several challenging scientific and technological problems remain to be resolved. Nevertheless, the device that we have made is impressive and could motivate further research into solid-state DS photovoltaic cells.

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