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Nanoporous TiO_2 photoanode sensitized with the flower pigment cyanidin

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Abstract

The flower pigment cyanidin anchors into nanoporous films of TiO_2 by surface complexation. A photoelectrochemical cell made from cyanidin-sensitized nanoporous TiO_2, as a film deposited on conducting glass and with the $I^- + I_3^-$ redox couple in acetonitrile, generates high photocurrents of good stability. © 1997 Elsevier Science S.A.

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1. Introduction

Dye-sensitized photoelectrochemical cells based on porous nanocrystalline films of TiO_2 (nanocells) are gaining much attention as promising solar energy conversion systems [1–6]. The performance of these devices depends largely on the dye used as the sensitizer [4]. The spectral response of the cell, photocurrent quantum efficiency and stability depend on the nature of the dye. The important physical characteristics of the dye, which determine the above properties of the cell, are the absorption spectrum of the dye, the redox properties of the ground state and the excited state of the dye molecule in relation to the band positions of TiO_2 and the anchoring ability of the dye molecules to the surface of the TiO_2 nanocrystallites. Ruthenium complexes are good sensitizers for the nanocell. Carboxylate ligands anchor the dye molecules to the TiO_2 surface and promote electron injection from the photoexcited level to the conduction band of TiO_2 [1–3]. The search for alternative sensitizers is essential for the further development of the nanocell and other dye-sensitized molecular electronic devices. We have found [7,8] that anthocyanidin flower pigments complex strongly with the surface of TiO_2, and act as efficient sensitizers. These pigments are generally photounstable in vivo, but remain highly stable in a nanocell with an I^-/I_3^- redox couple in acetonitrile and generate photocurrents comparable with those from similar photoanodes sensitized with ruthenium.

2. Experimental details

Nanoporous layers of TiO_2 were coated on fluorine-doped conducting tin oxide (CTO) glass (1.5 cm×2 cm; sheet resistance, approximately 40 Ω/□) by the method described in the literature [3] using Degussa P-25 titanium dioxide. The flower pigment cyanidin [7] was obtained from the blood-red flowers of anthurium (this flower was selected because of its high cyanidin content and absence of significant quantities of tannins) by the following method. The flower spathe was crushed and boiled with 10% hydrochloric acid for 10 min. This process hydrolyses the glycoside (anthocyanin) yielding cyanidin chloride [7,8]. The solution containing cyanidin chloride was shaken with toluene to remove lipophilic substances, separated from toluene and partitioned with butan-1-ol to extract the hydrolysed anthocyanin (cyanidin chloride). When the butan-1-ol extract was diluted with hexane (25% by volume) and shaken with water, cyanidin chloride was transferred to water. Chromatographic comparison with an authentic sample showed that the solution contained cyanidin with small quantities of pelargonidin [7,8] (anthurium spathe contains pelargonidin in addition to cyanidin which is the major pigment). Pelargonidin was removed by the following procedure. The pigment extract was evaporated in a rotary evaporator and the solid residue was washed with acetonitrile. Pelargonidin chloride (which is more soluble in acetonitrile than cyanidin) was removed during washing.

The absorption spectra of the pigment solution (obtained using a Shimadzu GC 9 AM spectrophotometer) in aqueous

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and methanolic solutions, and the bathochromic shift of the peak position of the spectrum in the presence of Al^{3+}, confirmed that the pigment was cyanidin [7,8]. A colloidal solution of TiO_2 nanocrystallites (prepared by hydrolysis of titanium isopropoxide with dilute HCl and separated by dialysis) turns deep violet on addition of cyanidin solution due to the formation of the Ti^{IV} cyanidin complex on the surface of the TiO_2 crystallites. The absorption spectrum of this solution was also recorded. Nanoporous TiO_2 electrodes were coated with the pigment by warming them in a 10% aqueous solution of cyanidin chloride. After this treatment, the electrode surface acquired a deep bluish violet colour owing to the complexation of cyanidin with Ti^{IV} sites on the surface of TiO_2.

Photoelectrochemical measurements were performed in the three-electrode configuration with a Pt counter-electrode and a standard calomel electrode as the reference. The electrolyte used was an aqueous solution of $KI + I_2$ ($KI = 0.4$ M, $I_2 = 2 \times 10^{-3}$ M) or acetonitrile containing $LiI + I_2$ ($LiI = 0.2$ M, $I_2 = 2 \times 10^{-3}$ M). A cell was constructed by sandwiching a thin film of the latter electrolyte between the photoanode and a CTO glass plate as the counter-electrode. Photocurrent action spectra were recorded using a monochromator (Nikon Monochromator, Auto-Scanner AS-C-101) coupled to a light chopper and a lock-in amplifier. The time development of the photocurrent was monitored by illuminating the cell with a solar simulator (intensity, approximately 800 W m^{-2}).

3. Results and discussion

Cyanidin (structural formula given in Fig. 1(a)) is strongly adsorbed on TiO_2 as a result of complexation with Ti^{IV} ions on the surface. Surface complexation can readily occur via elimination of a proton (Fig. 1(b)). The surface complex is completely insoluble in any solvent and unaffected by strong acids and weak alkalis. Strong alkalis in the presence of oxygen denature the complex. The complete removal of the film is possible only by treatment with a strong oxidizing agent, such as potassium permanganate.

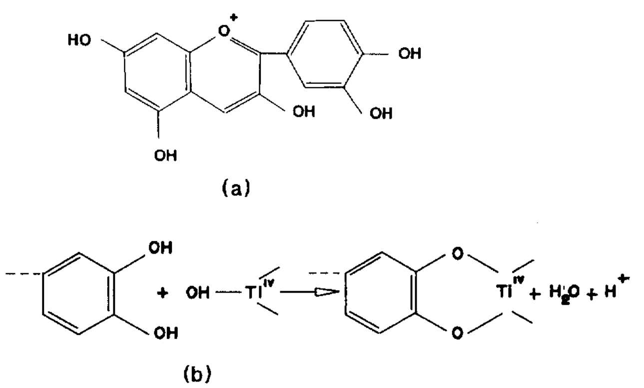

Fig. 1. (a) Structural formula of the cyanidin anion. (b) Mechanism of surface complexation of cyanidin and TiO_2.

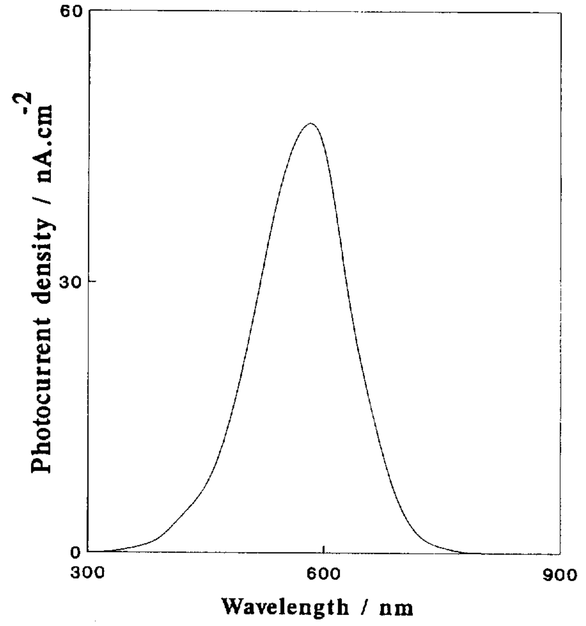

Fig. 2. Photocurrent action spectrum of the nanocell sensitized with cyanidin.

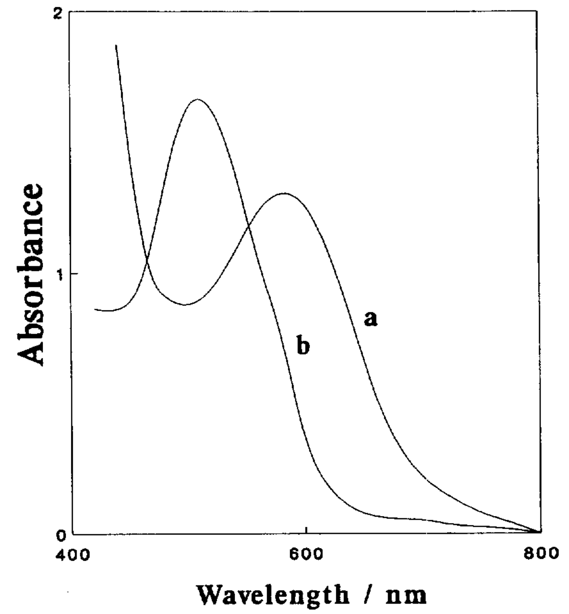

Fig. 3. Absorption spectra of a colloidal suspension of TiO_2 treated with cyanidin (a) and an aqueous solution of cyanidin (b) (pH of the solutions in both cases is 5.5).

The photocurrent action spectrum of the cell shown in Fig. 2 peaks at approximately 590 nm, which is nearly the same as the peak of the absorption spectrum of a colloidal suspension of TiO_2 treated with cyanidin (Fig. 3, curve a). The blue shift of the peak of the latter spectrum compared with that of an aqueous solution of cyanidin (peak at approximately 538 nm; Fig. 3, curve b) indicates the strong surface complexation of cyanidin to TiO_2 (it is well known that the optical absorption spectra of anthocyanidins are markedly influenced by chelation with metallic ions [7]). When the electrolyte is $KI + I_2$ in water, the cell generates an initial

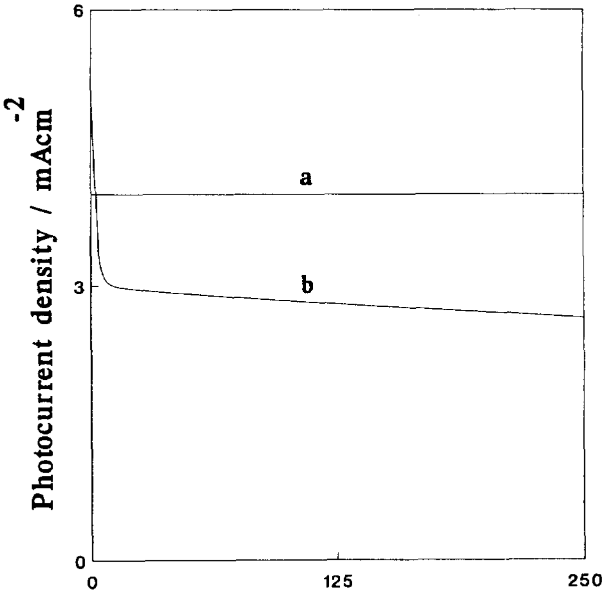

Fig. 4. Time development of the photocurrent of the nanocell sensitized with cyanidin: (a) LiI + I_2 in acetonitrile, sandwich cell with a thin film of electrolyte and a CTO glass counter-electrode; (b) aqueous KI + I_2 in three-electrode configuration.

short-circuit photocurrent of about 2.9 mA cm^{-2} and an open-circuit voltage of approximately 435 mV, and the photocurrent is observed to decay owing to degradation of the dye (Fig. 4, curve b). In aqueous medium, the minority carriers (holes) tunnelling into the solution can also be accepted by OH^- (instead of I_3^-) to generate $OH^·$ radicals which degrade the dye oxidatively. If acetonitrile is used as the electrolyte, the decay of the photocurrent is not noticeable after 6 h of illumination (sandwich cell with a thin film of the electrolyte and CTO glass counter-electrode). The short-circuit photocurrent in this case is about 3.2 mA cm^{-2} and the open-circuit voltage is 480 mV. An identical cell sensitized with ruthenium trinuclear dye generated a short-circuit photocurrent of about 2.8 mA cm^{-2} and an open-circuit voltage of approximately 600 mV. It is not clear at this stage why the cyanidin-sensitized cell generates a lower open-circuit voltage. The natural pigment cyanidin is not expected to be a suitable sensitizer for practical nanocells. However, it could serve as a model for the synthesis of more suitable pigments that chelate with the surface of TiO_2.

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