Efficient photosensitization of nanocrystalline TiO₂ films by tannins and related phenolic substances

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Abstract

Treatment of nanocrystalline TiO₂ films with tannins and related phenolic substances produces Ti^{4+}–tannin or Ti^{4+}–phenol charge transfer complexes firmly bonded to the surface of TiO₂ crystallites. Efficient photosensitization originating from the complexes generates high photocurrents in a photoelectrochemical cell.

1. Introduction

The dye-sensitized nanocrystalline (microporous) TiO₂ photoelectrochemical cell (PEC) developed by Grätzel and coworkers [1–6] is receiving much attention as a cheap solar energy conversion molecular electronic device. The performance of this cell largely depends on the dye used to sensitize the TiO₂ nanocrystallites. The matching of the absorption spectrum of the dye to the solar spectrum, the photoredox properties of the dye and the anchorage of the dye to the surface of the nanocrystallites are crucial parameters determining the efficiency and stability of the cell. The sensitizers developed by Grätzel and coworkers [1,2] are ruthenium polypyridyl complexes with carboxylate ligands which enhance the adsorption of the dye. More recently, it has been shown that ruthenium polypyridyl complexes with phosphonated ligands anchor even better to the TiO₂ surface, preventing desorption of the dye and improving the efficiency [7]. An alternative to coating of the charge transfer complex on TiO₂, based on a foreign transition metal (Ru in the above cases), is to look for substances that complex with Ti^{4+} ions on the surface of TiO₂ crystallites (i.e. surface derivatization) to form an insoluble charge transfer species. Phenolic compounds and tannins are known to complex strongly with Ti^{4+} to yield coloured insoluble compounds. As expected, we found that high photocurrents can be obtained with TiO₂ microporous electrodes, sensitized by merely warming the electrode in an aqueous solution of tannin or related phenolic substances such as gallic acid.

2. Experimental details

Microporous layers of TiO₂ were coated onto conducting fluorine-doped tin oxide glass (sheet resistance, approximately 50 $\Omega/\square$) by the following two methods [3,8].

(1) Titanium isopropoxide (1 ml) and glacial acetic acid (5 ml) were added to propan-2-ol (10 ml) and the mixture, which was frequently stirred, was exposed to a moist atmosphere with a relative humidity of approximately 85%. Hydrolysis of titanium isopropoxide produced fine crystallites of TiO₂ and the above procedure prevented their agglomeration. The conducting tin oxide coated glass sheet was placed on the surface of a hot plate (surface temperature, approximately 150 °C) and the solution was evenly spread on the surface using a glass rod and allowed to dry. The plate was then sintered at 450 °C for 10 min, allowed to cool and the loosely bound outer crust of TiO₂ was wiped off (a layer of fine TiO₂ crystallites firmly affixed to the glass was formed beneath the outer crust). The process was repeated several times until a fully covered semitransparent film was deposited on the glass.

(2) TiO₂ powder (Degussa) was ground in a mortar with acetic acid and a few drops of the non-ionic surfactant Triton X-100. The paste was spread onto the conducting glass plate and sintered in air for 25 min.

Nanocrystalline TiO₂ films prepared by the first method were found to be superior and generated somewhat higher photocurrents. The phenolic substances, gallic acid and catechol, were used as purchased from Aldrich. Commercial tannin (BDH) was purified by extraction into ethyl acetate
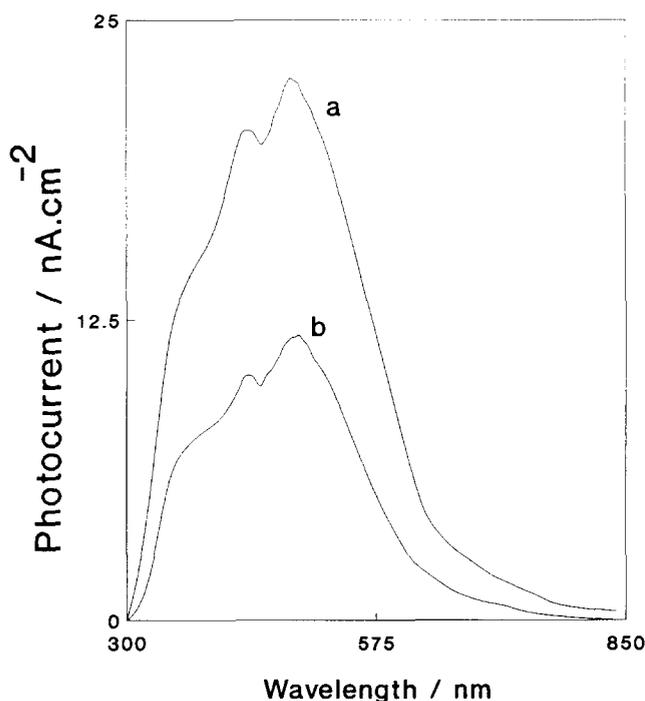
Fig. 1. Photocurrent action spectra of a TiO₂ nanocrystalline film treated with: (a) gallic acid; (b) catechol.

from saturated aqueous solution and by partitioning with water after dilution with hexane (50% by volume) [9,10]. Tannin was extracted from black tea by the following method. Ceylon black tea was boiled with water for approximately 15 min, the residue was removed and the solution was shaken and washed with hexane followed by toluene to extract lipophilic substances. The solution was then shaken with an equal volume of ethyl acetate which extracts most tannins and related polyphenols. When the ethyl acetate extract was diluted with hexane (50% by volume) and partitioned by adding water, tannins and polyphenols were transferred to water [9,10]. By a further partitioning of the aqueous extract (from ethyl acetate) with butan-1-ol, two components with different TiO₂ sensitizing spectral characteristics were separated. Hydrolysable gallotannin [1–13] and ellagitannin [1–13] were also extracted from gall nuts and pomegranate bark by the methods described in the literature [9,10].

TiO₂ electrodes were coated with surface complexed Ti⁴⁺ derivatives of gallic acid, catechol and different types of tannins by warming the plates in an aqueous solution of each substance for approximately 45 s. During this treatment, the TiO₂ surface acquired a characteristic yellowish brown tint owing to the formation of the complex. The surface complexed layer on TiO₂ crystallites is highly resistant to chemical (unaffected by dilute acids, alkalis and mild oxidizing agents) and the following procedure was adopted to clean the coated plates. Plates were boiled in a strong solution of KMnO₄ and digested in a solution of sulphurous acid ($Na_2SO_3 + H_2SO_4$) to remove the oxides of manganese. Electrodes cleaned by this method can be used repeatedly without any loss of efficiency.

Photoelectrochemical measurements were carried out in the three-electrode configuration under potentiostatic conditions (Hokutodenko potentiostat HA-301) in $KI + I_2$ ($KI = 0.5$ M, $I_2 = 2 \times 10^{-3}$ M, pH adjusted to 3.5 with HCl). In all experiments, holding the working electrode at approximately 0.53 V vs. a saturated calomel electrode (SCE) was found to give the maximum short-circuit photocurrent. The time development of the photocurrent under short-circuit conditions was examined on illumination with a 100 W tungsten filament lamp and a solar simulator (intensity, approximately 950 W m⁻²). Photocurrent action spectra were recorded using a monochromator–light chopper–lock in amplifier arrangement.

Colloidal solutions of TiO₂ particles surface complexed with gallic acid, tannin, etc., required for obtaining the absorption spectra (Shimadzu UV-3000 spectrophotometer), were prepared according to the following procedure. Titanium isopropoxide was hydrolysed by hydrochlorid acid and the TiO₂ sol was separated by dialysis. When an aqueous solution of gallic acid, catechol or tannin was added, the semitransparent sol turned deep reddish brown as a result of complexation.

3. Results and discussion

The compounds used for the sensitization of TiO₂ (gallic acid, catechol and tannin) do not have chromophores of their own. However, complexation with Ti⁴⁺ ions on the surface of TiO₂ nanocrystallites produces a charge transfer complex firmly bonded to the surface. The photocurrent action spectra of the electrodes sensitized by gallic acid and catechol are shown in Fig. 1. The two spectra are similar: the gallic acid sensitized electrode shows peaks at 435 and 480 nm and catechol sensitization gives a spectrum of the same shape with peaks at 435 and 489 nm. However, the photocurrent is much more intense in the case of gallic acid. When the electrodes are illuminated with a 100 W tungsten filament lamp, the short-circuit photocurrents observed are 2.0 and 0.9 mA cm⁻² for gallic acid and catechol respectively. The optical absorption spectrum of the TiO₂ sol mixed with gallic acid, shown in Fig. 2, peaks at 480 nm, corresponding to absorption by the surface complex; the rising portion of the curve on the left-hand side of the figure originates from band gap absorption by TiO₂ particles. The photocurrent action spectrum of the electrode treated with commercial tannin is similar to that of gallic acid (Fig. 3, curve a) and shows peaks at 435 and 480 nm. Tannin obtained from black tea by ethyl acetate extraction as described in Section 2 gives an action spectrum with peaks at 435, 510 and 585 nm (Fig. 3, curve b). When an aqueous solution of this extract is shaken with butan-1-ol, two different components can be separated. Electrodes sensitized by the aqueous portion yield a spectrum identical to that of commercial tannin (peaks at 435 and 480 nm). The tannin component in butan-1-ol can be transferred to water after dilution with hexane (50% by volume). An electrode

sensitized by this solution possesses an action spectrum with a single peak at 585 nm.

Electrodes treated with tannins (commercial tannin or tannins from tea) yield high photocurrents in comparison with gallic acid treated electrodes. Commercial tannin and tea tannin (component with peaks at 435 and 480 nm) generate short-circuit photocurrents of 6–8 mA cm^{-2} when illuminated by the solar simulator (intensity, approximately 950 W m^{-2}). Tea tannin, whose action spectrum peaks at 585 nm, records even higher photocurrents (7–9 mA cm^{-2}), perhaps due to better matching of the absorption spectrum of the tannin–Ti^{4+} complex and the emission spectrum of the light source. There is also a marked difference in the stabilities of the electrodes sensitized using gallic acid and tannin. In the case of tannins, the rate of decay of the photocurrent (solar simulator at 950 W m^{-2}) is less than approximately 5% h^{-1}, whereas in the case of gallic acid the rate is 16% h^{-1}. Presumably the complexes of condensed tannins are more resistant to oxidative photodegradation at the TiO$_2$ surface. Even in the case of condensed tannins (i.e. commercial tannin and tea tannin), purification improves the stability, suggesting that the oxidative degradation of impurities, cutting out light, is at least partly responsible for the decay of the photocurrent.

In a two-electrode PEC adopting a Pt counter-electrode, the natural biasing of the TiO$_2$ electrode is insufficient to generate photocurrents as high as in the three-electrode system. On replacement of Pt by a porous carbon counter-electrode, the performance of the cell is improved, giving short-circuit photocurrents of 3–4 mA cm^{-2} and open-circuit voltages exceeding 0.5 V (solar simulator at approximately 950 W m^{-2}).

Condensed tannins [11–13] (e.g. commercial tannins obtained from barks of Quebracho and Wattle) are polymeric materials of uncertain structure, incorporating gallic acid, catechol, etc. as structural precursors. The interesting observation made here is that gallic acid, catechol and most tannins (including hydrolysable gallotannins and ellagitannins [12]) give similar photocurrent action spectra. A common property of these substances is the presence of many hydroxyl groups attached to benzene rings. Possibly, chelation of these groups and Ti^{4+} ions on the surface of TiO$_2$ is responsible for the creation of charge transfer sites. We have not succeeded in identifying the substance in black tea responsible for the different spectrum. This substance is absent in fresh tea leaves, suggesting that it is an oxidized polyphenol. None of the above substances has the capability of sensitizing other wide band gap semiconductors (e.g. ZnO, CuI, CuCNS), showing that surface complexation with Ti^{4+} is essential for sensitization. Tannins form strongly coloured complexes with Fe^{3+}, but these complexes are not adsorbed by TiO$_2$ and are ineffective in sensitizing TiO$_2$. The ability of carboxylate groups to surface derivatize with TiO$_2$ and facilitate photoinduced charge transfer is well established. Most tannins also possess carboxylate groups; it is possible that they may play an important role in generating an enhanced sensitized photocurrent.
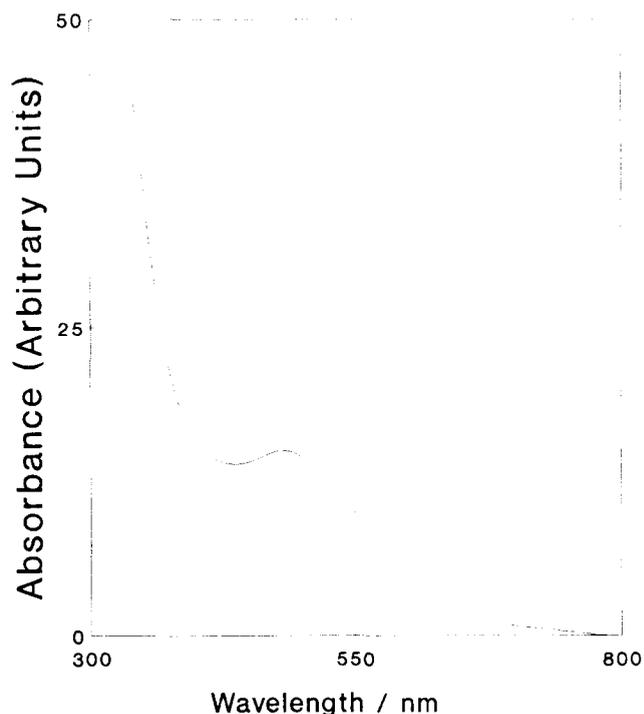
Fig. 2. Absorption spectrum of TiO$_2$ sol complexed with gallic acid.
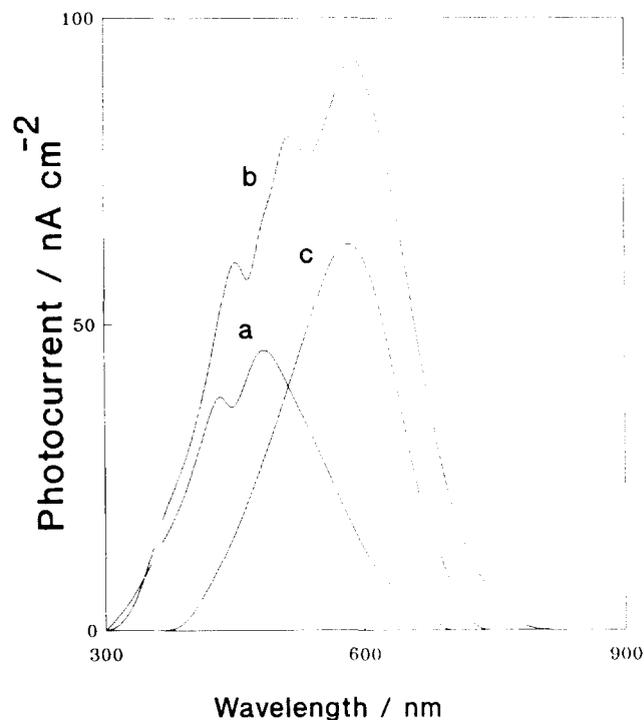
Fig. 3. Photocurrent action spectra of a nanocrystalline TiO$_2$ film treated with: (a) purified commercial tannin; (b) tannin extracted from tea; (c) tea tannin component separated by butan-1-ol extraction.

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