

Sol-Gel TiO₂ Thin Films Sensitized with the Mulberry Pigment Cyanidin

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Received: April 19, 2007; Revised: November 28, 2007

TiO₂ films have various applications, among them solar cells and photodegradation of pollutants. In this study, we investigated TiO₂ films functionalized with the organic dye cyanidin extracted from black mulberry (*Morus nigra*). The TiO₂ was functionalized by the sol-gel method and the film was deposited on glass substrates by dip-coating. Our aim was to investigate the interaction between the semiconductor and the dye, as well as the influence of the velocity and number of deposits on the characteristics of the film. Using ultraviolet-visible spectroscopy, we observed a shift from the maximum absorption band at 545 nm for the dye's ethanol solution to 595 nm for the film, indicating interaction of the cyanidin with the TiO₂. The absorption spectra in the infrared region of the functionalized TiO₂ particles showed bands characteristic of the oxide and indicated their interaction with the dye. Using profilometry and m-line techniques, we found that the films presented thicknesses in the order of 100 nm. A SEM analysis confirmed the high density of the films.

Keywords: *TiO₂, films, cyanidin, sol-gel*

1. Introduction

Porous TiO₂ electrodes have various applications, among them solar cells and heterogeneous photoelectrocatalysis for the degradation of pollutants. In these devices, the structure of the oxide film deposited on transparent electrodes affects the energy conversion efficiency, for the size of the particles and pores interferes in the penetration of the electrolyte in solar cells and in the interaction with pollutant molecules in photocatalytic devices¹⁻³.

Solar cells based on dye-sensitized TiO₂ nanoparticles were first developed by Grätzel and coworkers⁴. Regenerative photoelectrochemical cells are composed of nanocrystalline TiO₂ films sensitized with a dye. Under a light beam, the dye absorbs photons and injects electrons into the semiconductor's conduction band. The charge carriers then scatter to the external circuit. The dye is reduced by a redox pair, which, in turn, is also regenerated in the counter electrode¹⁻⁴.

The use of natural products such as organic dyes in solar cells offers promising prospects for the advance of this technology, since photoexcitable dyes are substances that cede electrons easily, while the use of synthetic dyes involves several problems, such as their synthesis, purification and use, as well as the fact that they require rare metals⁵⁻⁸. Cyanidin is an organic dye of the flavonoid class found in leaves and fruits and responsible for the colors of various vegetal tissues, which has been studied for application as a sensitizer of this type of solar cell⁷⁻¹¹ (Figure 1).

In most of these solar energy conversion devices, the TiO₂ film is obtained by deposition of a colloidal suspension of commercial oxide particles (usually Degusa®), but the development of nanocrystalline films with large and porous surface areas has increased the efficiency of these devices. In this context, the sol-gel process has proved to be a viable alternative to produce these films, since it is a simple and versatile method for the production of oxide nanoparticles of controlled sizes. The conventional method uses the hydrolytic route, which involves the initial hydrolysis of the alkoxide precursor

followed by continual condensations between the hydrolyzed particles forming the gel. The reactions are:

Hydrolysis



Condensation



This process is carried out at room temperature, and the desired morphological properties of the particles are obtained by controlling the conditions under which the synthesis is carried out. Moreover, these materials are easily produced in film form. However, their disadvantages are the high cost of raw materials and considerable contraction in the process¹²⁻¹⁵.

The dip-coating technique, which consists of immersing a substrate in the sol at a controlled speed, has been used successfully to deposit oxide in the form of a thin film. This technique allows one not only to control the speed but also to vary the number of depositions, thereby obtaining films with controlled thicknesses¹².

In this paper, we report on the preparation of TiO₂ films functionalized with cyanidin from black mulberry (*Morus nigra*), using the hydrolytic sol-gel process to obtain the oxide and the dip-coating technique to deposit the films on glass substrates, with controlled speed and number of depositions. The interaction of the dye and the oxide was examined by UV-Vis spectroscopy and FTIR. The thermal stability of the hybrid organic-inorganic xerogel formed here was studied by thermal analysis. Surface area and pore volume were determined by nitrogen adsorption. Using profilometry and m-line techniques, we were able to ascertain that the deposited films showed thicknesses in the order of 100 nm. The micrographs obtained by scanning electron microscopy (SEM) revealed the high density

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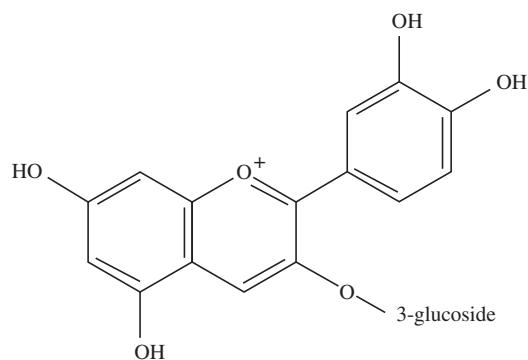


Figure 1. Molecular structure of the cyanidin.

of the films. Titanium dioxide was chosen and the semiconductor material, since it is a low-cost, abundant, and chemically inert material whose properties have already been studied. Because TiO_2 is white and therefore does not absorb visible light, it is the cyanidin from mulberry that determines the absorption of light and the spectral response of the semiconductor.

2. Experimental

The titanium oxide was prepared by the hydrolytic sol-gel method, while the cyanidin solution was obtained from mulberries by macerating 1 g of the fruit with 12 mL of ethanol and filtering the resulting product. The titanium oxide sol functionalized with raw mulberry (*Morus nigra*) cyanidin extract was prepared by mixing 12 mL of ethanolic solution of dye, 1 mL of acetic acid as a stabilizing agent and 1 mL of titanium (IV) isopropoxide. The resulting blue sol was stirred for 30 minutes at 25 °C. The flowchart in Figure 2 illustrates the experimental procedure.

The sol-gel method was utilized to synthesize TiO_2 because it is carried out at a low temperature, resulting in small particles with a high surface area and a large quantity of superficial Ti-OH groups due to incomplete condensation. Mulberries were used as a dye source because they contain large quantities of cyanidin¹¹.

Deposition of the films was carried out by the dip-coating method using an controller model MQCT 2000-MP microprocessor-controlled syringe pump to deposit the films on glass substrate. The substrates were immersed in the sol at speeds of 50, 70 and 100 mm/min, varying the number of immersions in the sol from 1 to 5 times to obtain films with different thicknesses.

The material left behind by deposition of the films was dried in the form of xerogel for subsequent FTIR, thermal and morphological characterization.

3. Results and Discussion

The absorption spectra in the ultraviolet-visible region were obtained using a HP 8452A diode array spectrophotometer. The cyanidin ethanol solution presented maximum absorption at 545 nm, while the cyanidin-functionalized TiO_2 sol showed maximum absorption at 590 nm and the films at 595 nm. The shift to the infrared region at the absorption maxima of the sol and the functionalized film confirmed the reaction between the TiO_2 and the mulberry cyanidin extract, since the interaction caused a reduction of the electron density in the chromophore group, thus reducing its polarity (bathochromic effect). Figure 3 illustrates the absorption spectra in the UV-visible region.

The surface area and porosity of the TiO_2 and cyanidin-functionalized TiO_2 xerogel were determined by nitrogen adsorption-

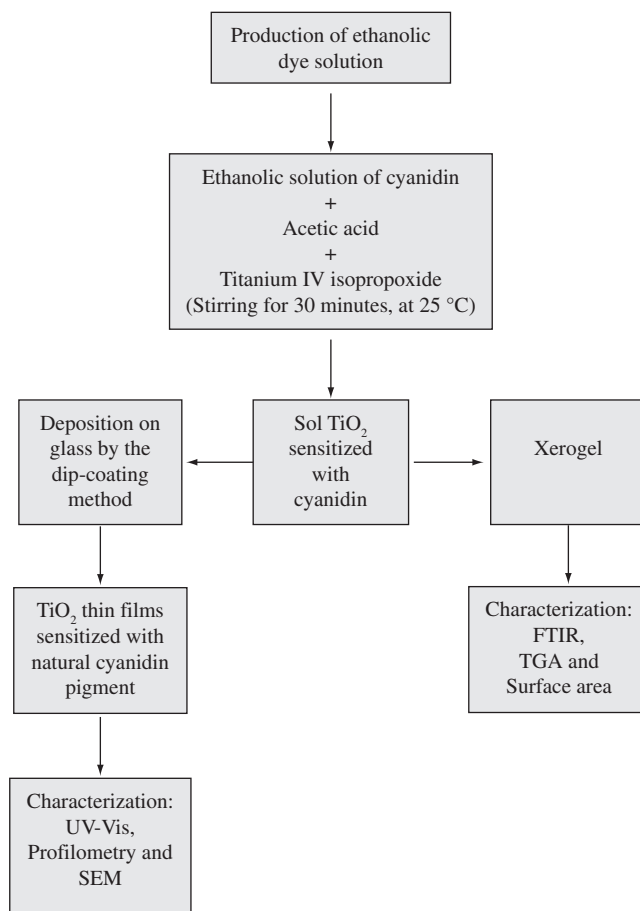


Figure 2. Flowchart of the experimental procedure.

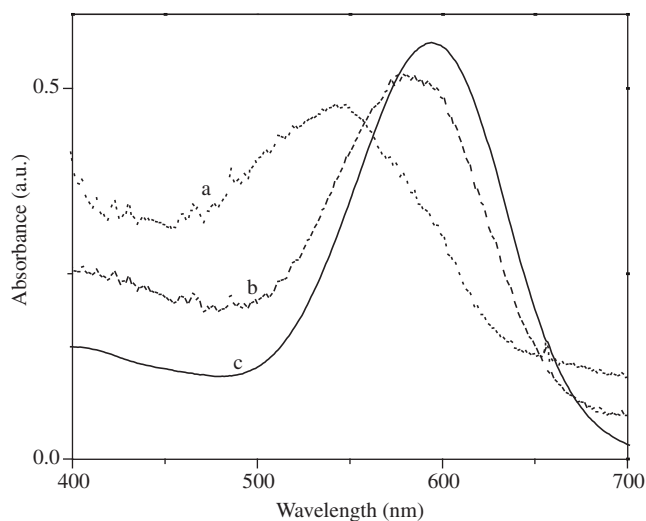


Figure 3. Absorption spectra: a) cyanidin ethanol solution; b) cyanidin-functionalized TiO_2 sol; and c) cyanidin-functionalized TiO_2 film.

desorption isotherms in a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. The TiO_2 xerogel showed a BET surface area of 202.9 $\text{m}^2\cdot\text{g}^{-1}$, a total pore volume of 0.105 $\text{cm}^3\cdot\text{g}^{-1}$, and an average pore size of 20.7 Å, while these values for the cyanidin-functionalized hybrid material were 0.4733 $\text{m}^2\cdot\text{g}^{-1}$, 0.000578 $\text{cm}^3\cdot\text{g}^{-1}$

and 48.9 Å, respectively. Because these measures are based on the adsorption and desorption of nitrogen by OH groups at the surface of TiO₂ particles, the measures will show incorrect values if the OH groups are linked to a molecule, preventing them from interacting with the nitrogen. The alterations in the values of surface area and porosity are attributed to the efficiency of the dye's adsorption by the TiO₂ particles. In a study of TiO₂ R-213 produced by a chemical company, Agnieszka¹⁶ reported values of 39.9 m².g⁻¹, 0.0981 cm³.g⁻¹ and 98.4 Å for BET surface area, total pore volume and average pore size, respectively. The larger surface area of the TiO₂ material presented here was probably due to incomplete condensation of Ti – OH groups and low particle sizes characteristic of materials obtained by the sol-gel process, which allowed for the adsorption of a larger amount of dye per TiO₂ mass. Dye-TiO₂ interactions were confirmed by a shift of Ti-O surface vibration in the FTIR analysis. The conventional methods of solar cell film production require a thick TiO₂ layer (1 to 10 μm) so that a sufficient quantity of dye is adsorbed to allow for the absorption of a significant fraction of the incident light¹⁷. Our films, whose thickness was in the order of 100 nm, presented light absorption in the same order of magnitude as 4 μm thick films produced by the conventional method.

The infrared absorption spectra of the xerogels were obtained with a Perkin Elmer FTIR 1600 infrared spectrophotometer, operating from 400 to 4000 cm⁻¹ using KBr tablets. The absorption spectra in the infrared region of the TiO₂ xerogel and of the cyanidin-functionalized oxide presented bands characteristic of TiO₂, with the bands at 550 and 655 cm⁻¹ attributed to normal TiO₂ stretching. The bands in the regions of 1030, 1425 and 1542 cm⁻¹ observed for non-sensitized TiO₂, were attributed to stretching and vibrations of the Ti – O – Ti group, indicating the formation of the inorganic matrix¹⁸⁻²⁰. The band at 1425 cm⁻¹ in the TiO₂ spectrum shifted to 1445 cm⁻¹ in the spectrum of the functionalized TiO₂. The band ascribed to superficial Ti – O vibrations appeared at 755 cm⁻¹ for TiO₂ and at 790 cm⁻¹ in the cyanidin-functionalized oxide, indicating the oxide was functionalized by the dye¹⁸⁻²⁰ (Figure 4).

The band at 3745 cm⁻¹ in the TiO₂-cyanidin spectrum was attributed to stretching of the OH groups of the glycoside and of the phenolic groups, confirming the presence of the dye in the material²⁰⁻²³.

The TGA curves and the curves of the TiO₂ and cyanidin-functionalized TiO₂ xerogels were obtained with a SDT Q600

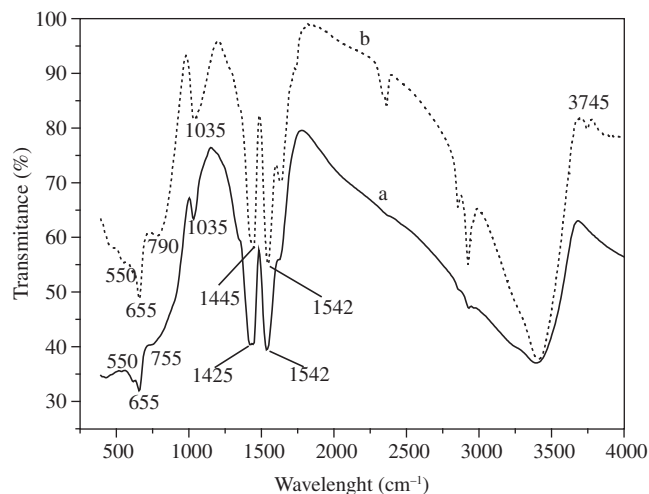


Figure 4. FT-IR spectra: a) TiO₂; and b) cyanidin-functionalized TiO₂.

Simultaneous DTA-TG analyzer (TA Instruments) in a nitrogen atmosphere at a heating rate of 20 °C/min.

The samples showed rapid weight loss at around 100 °C resulting from the evaporation of residual solvent in the xerogel (powder), and another weight loss at around 340 °C corresponding to the decomposition of organic compounds such as acetic acid covalently bonded to TiO₂. The DTG curve of cyanidin-functionalized TiO₂ xerogel presented a peak at around 430 °C, which was not present in the DTG curve of TiO₂ xerogel and which can be attributed to cyanidin linked to TiO₂ decomposition. These results led us to consider that the cyanidin, in this material, reaches thermal stability at around 400 °C (Figure 5 and 6).

The thickness of the films was determined by the profilometry technique, which indicated a thickness of about 100 nm as well as good homogeneity.

The SEM micrographs, obtained with a JEOL JSM T330A scanning electron microscope, revealed that the films were of high density and had a very homogeneous structure devoid of cracks, as indicated in Figure 7.

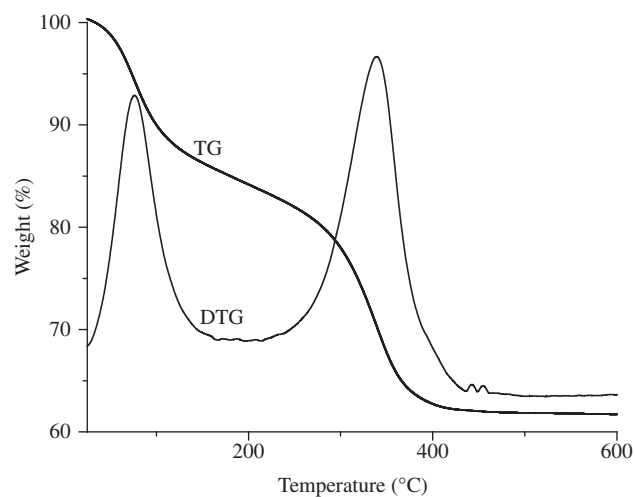


Figure 5. TG curve and DTG of TiO₂ powder.

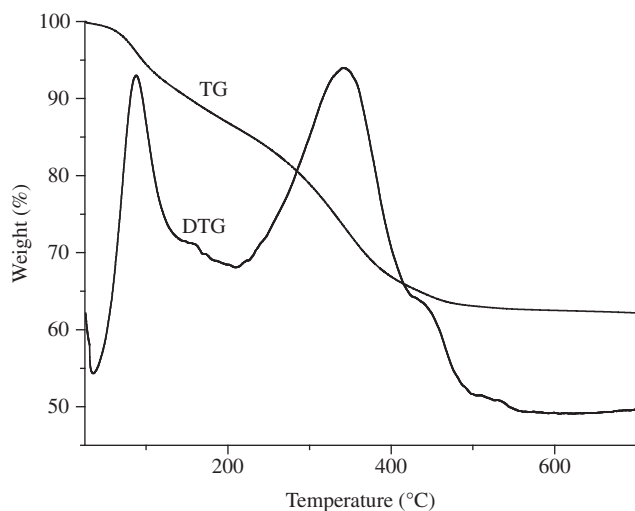


Figure 6. TG curve and DTG of cyanidin-functionalized TiO₂ powder.

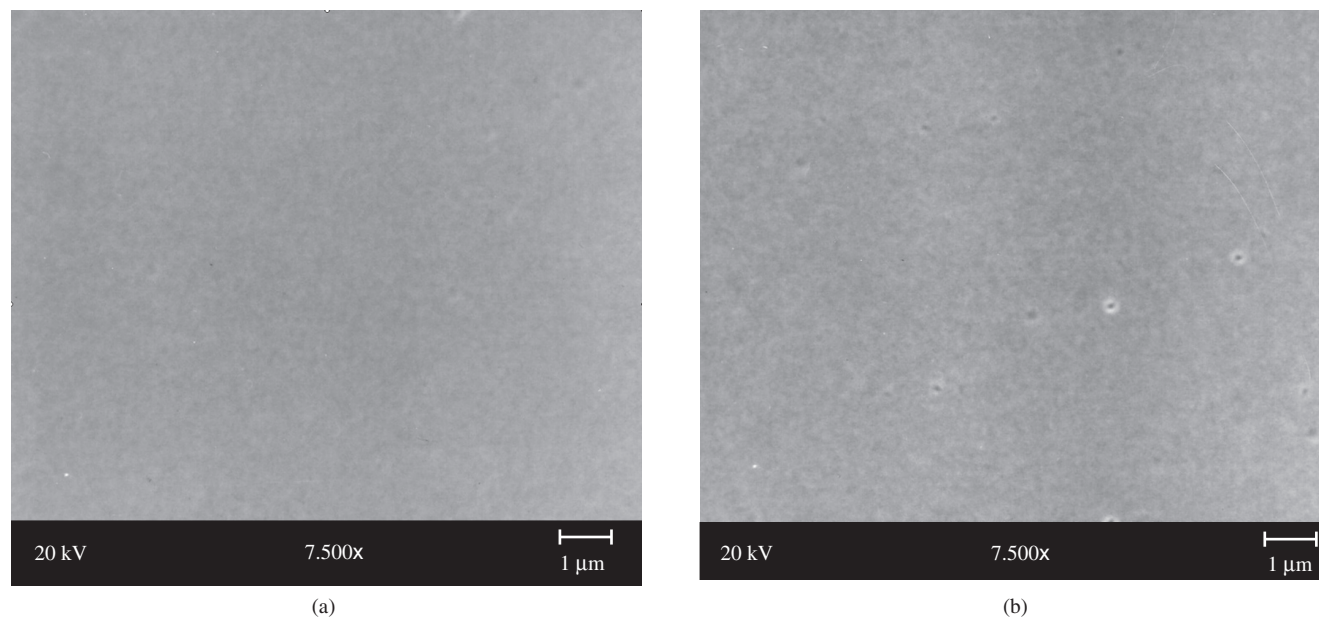


Figure 7. SEM micrograph of films: a) 70 mm/min 3 dips; and b) 50 mm/min 2 dips.

4. Conclusions

Unlike the systems studied previously, in which the interaction between cyanidin and TiO_2 particles occurs after the particles or films have been obtained, in the present work this interaction occurred during the reactions of hydrolysis and condensation, resulting in a material with a larger quantity of adsorbed dye molecules in relation to the number of titanium atoms, possibly leading to the greater efficiency of solar cells obtained by this methodology.

The thin films were transparent, homogeneous, uniform, with a thickness in the order of 100 nm, and presented excellent adhesion to the substrate. These characteristics indicate the possible application of these films in solar cells.

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