

TiO₂ and TiO₂/WO₃ porous film electrodes for application in solar energy conversion

Haroldo G. Oliveira, Erika D. Silva, Claudia Longo*
Institute of Chemistry, State University of Campinas – Unicamp, C. Postal 6154
13084-971 Campinas, SP, Brazil

ABSTRACT

TiO₂ and TiO₂/WO₃ porous films were deposited onto transparent conducting glass electrodes, resulting in uniform films consisted of agglomerated particles with average diameters ranging from 50 to 200 nm; Ti, O and W atoms were homogeneously distributed at the surface of hybrid film. Comparable electrochemical properties were observed in the dark, with small capacitive currents and similar potentials for O₂ and H₂ evolution reactions in aqueous solution. Under polychromatic irradiation, the hybrid film electrode, molar ratio WO₃/TiO₂ = 12 %, revealed higher photocurrent and photocatalytic activity for oxidation of phenol and 17- α -ethynylestradiol. The visible light harvesting ability of hybrid film, with band gap energy estimated as 2.3 eV, and the relative position of conduction and valence band edges that inhibits charge recombination, should improve its photocatalytic activity for organic pollutant removal.

Keywords: TiO₂, WO₃, photocatalysis, phenol, endocrine disrupting compound

1. INTRODUCTION

Titanium oxide has been widely investigated in several applications for solar energy conversion, including solar cells, photochromic devices, photo-rechargeable batteries and in photocatalysis for self-sterilizing materials, air and water purification. TiO₂ is a wide band gap, n-type semiconductor (E_g near 3.1 eV) and its photocatalytic activity is observed under UV irradiation that induces a charge separation in electron/hole (e⁻/h⁺) pairs at its surface. Then, several reactions involving the positive hole or reactive species, mainly *OH and O₂* radicals and H₂O₂, result in complete oxidation of organic compounds, assuring the successful performance of this semiconductor in water disinfection.^[1-3]

TiO₂ photocatalysts are used as fine suspended particles or as thin films; films can be deposited onto an electrically conducting substrate, and then application of a positive potential enhances the separation of photogenerated electrons and holes, resulting in higher efficiency for pollutant degradation.^[4,5] Recently, we investigated the degradation of phenol by electroassisted photocatalysis using TiO₂ electrodes connected to a solar cell, in an efficient and low cost method to achieve water remediation.^[5] Phenol photocatalytic oxidation has been extensively studied, and phenol can be considered a “model pollutant”; also, phenolic compounds are carcinogenic to mammals, and are found in the wastewater from several industries.^[6] Heterogeneous photocatalysis with TiO₂ can remove phenol as well as numerous organic pollutants from aquatic environment, including dyes, herbicides and refractory compounds as endocrine disruptor chemicals (EDC). Concerns with water contamination with EDC have increased lately, because they can interact with steroid hormone receptors even at very low concentration, which is extremely hazardous for humans and wildlife.^[7,8]

TiO₂ photoactivity under solar radiation can be improved by increasing its ability to harvest the visible light, since UV region corresponds to less than 10 % of solar spectrum. This is achieved by narrowing the TiO₂ band gap by doping or by sensitizing the semiconductor with a dye that absorbs visible light. Also, the photocatalytic performance of TiO₂ can be intensified by a coupling with another semiconductor, such as WO₃, which exhibits E_g between 2.5-2.7 eV and a lower conduction band edge compared to TiO₂.^[2,9,10] For hybrid TiO₂/WO₃, photoinduced electrons can be transferred to WO₃ conduction band while holes are transferred to TiO₂ valence band, inhibiting electron/hole recombination.^[11-13] This effect can enhance the overall efficiency for pollutant degradation, which motivated us to investigate electrodes consisted of TiO₂/WO₃ films as photocatalyst for removal phenol and the EDC 17- α -ethynylestradiol from aquatic environment.

* clalongo@iqm.unicamp.br; phone 55 19 3521-3114; fax 55 19 3521-3023; www.iqm.unicamp.br/profs/clalongo.html

2. METHODOLOGY

2.1 TiO₂ and TiO₂/WO₃ film electrodes preparation

All the chemicals were of p.a. grade and used without any further purification. Deionized water from a Milli-Q water purification system was used throughout the work. Fluorine-doped tin oxide transparent conducting glass, glass-FTO (TCO22-15, Solaronix, 15 ohm/sq), was ultrasonically cleaned and then used as substrate for TiO₂ and TiO₂/WO₃ film electrodes. TiO₂ electrodes were prepared using an aqueous suspension of TiO₂ particles (Degussa P25, consisted of 80:20 anatase:rutile wt %) and polyethylene glycol. For TiO₂/WO₃ film electrode, tungstic acid powder was previously dissolved in 30 % H₂O₂ and then mixed to the TiO₂ suspension for a resulting WO₃:TiO₂ molar ratio of 12 %. Each suspension was continuously stirred for 24 h and then a small aliquot was spread onto the transparent electrode with a glass rod and adhesive tape as spacer, followed by heating at 450°C for 30 min.

2.2 Characterization of TiO₂ and TiO₂/WO₃

The structure of TiO₂ and TiO₂/WO₃ powder samples, obtained from thermal treatment of the suspensions, was characterized by X-ray diffraction using a XRD Shimadzu 7000 using Cu K α ($\lambda = 1,5406 \text{ \AA}$) radiation. Diffraction peaks of crystalline phases were compared with those of standard compounds reported in JCPDS database. UV-Vis spectroscopy in diffuse reflectance mode was carried out with a Cary SG-Varian UV-Vis recording spectrophotometer. The surface of the films was examined by scanning electron microscope using a SEM JEOL JSM 63601V with energy-dispersive X-ray analysis (EDX).

The electrochemical properties of the TiO₂ and TiO₂/WO₃ films deposited on glass-FTO electrodes were investigated in aqueous solutions with Na₂SO₄ 0.1 mol L⁻¹ as supporting electrolyte. A three-electrode, single-compartment glass cell with optic glass windows was used, with the working electrode (geometrical area = 1.0 cm²) facing the Pt counter-electrode and Ag/AgCl (in aqueous 3 M KCl) as reference electrode (which was placed in a Luggin capillary). The electrochemical measurements were performed with a potentiostat Eco-Chemie Autolab PGSTAT 128-N in the dark and under irradiation. The samples were irradiated with a "homemade" solar simulator, assembled with a metallic vapor discharge lamp (Metalarc Sylvania HIS-YHX 400 W) with polychromatic irradiance intensity estimated as (130 \pm 10) mW cm⁻². The temperature was maintained at (30 \pm 2)°C.

2.3 Photocatalytic activity for organic pollutants removal

The photocatalytic activity of TiO₂ and TiO₂/WO₃ films for organic pollutant degradation were investigated in "heterogeneous photocatalysis" (HP) configuration using samples with an active geometrical area of 1.0 cm² in 10 mL of aqueous pollutant solution in supporting electrolyte. Immediately after the irradiation period, the amount of pollutant removal was estimated. A "blank control" was also carried out for each experimental condition, i.e., a pollutant solution irradiated in similar conditions without a photocatalyst film. The solution was not stirred in any of these studies; nor was it bubbled with any gas.

The studies were performed for phenol aqueous solution with initial concentration C₀ = 50 mg L⁻¹ (0.53 mM), and for aqueous ethynilestradiol solution with initial concentration 0.16; 0.50 and 50 mg L⁻¹ (0.54; 1.7 and 170 μ M, respectively). For solutions that initially contained 50 mg L⁻¹ of pollutant, the dissolved organic carbon concentration was measured with a total organic carbon analyzer (TOC Analytic Jena Multi N/C 2100). Ethynilestradiol was also determined by fluorescence using a fluorimetric spectrometer Varian, Cary Eclipse, with excitation and emission wavelengths at 278 nm and 307 nm, respectively. The hormone remaining concentration was estimated considering the linear relationship previously determined for the intensity of fluorescence peak and the hormone concentration ranging from 0.1 to 1.0 mg L⁻¹ (a calibration curve).

3. RESULTS AND DISCUSSION

3.1 TiO₂ and TiO₂/WO₃ characterization

The crystalline phases of TiO₂ and TiO₂/WO₃ were characterized for powder samples obtained from thermal treatment, 450°C for 30 min, of the respective suspensions. The XRD pattern of TiO₂, Fig. 1a, compared to the JCPDS database, exhibited the characteristic reflections for anatase and rutile phases. Considering the areas under the peaks at $2\theta = 25.3^\circ$, which corresponded to (1 0 1) reflection for anatase, and at $2\theta = 27.4^\circ$, (1 1 0) reflection for rutile, the relative amount of anatase:rutile was estimated as 80:20 wt %, in good agreement with the reported composition of TiO₂ Degussa P25.^[14,15]

For the XRD pattern of TiO_2/WO_3 sample, Fig. 1b, all the peaks observed for TiO_2 sample (Fig. 1a) can be identified, as well as the peaks for triclinic and hexagonal phases of WO_3 , according to JCPDS database.^[16]

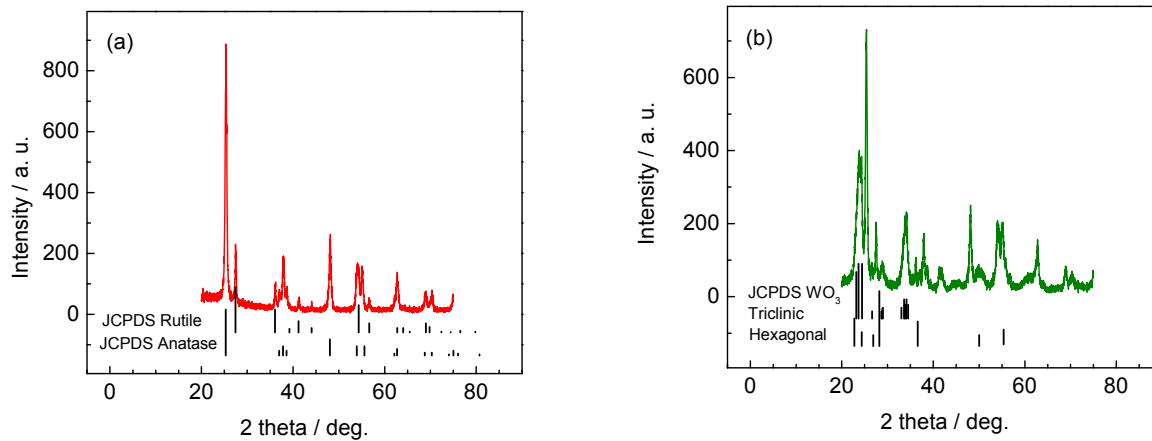


Fig. 1. XRD patterns for TiO_2 (a) and TiO_2/WO_3 (b) samples obtained after annealing the respective suspensions at 450°C for 30 min. The JCPDS data for TiO_2 (anatase and rutile) and for WO_3 (triclinic and hexagonal) were also included.

The optical properties were investigated by diffuse reflectance UV-Vis absorption spectroscopy; the spectra and the respective curves derivative were represented at Fig. 2. The maximum absorption values for TiO_2 and TiO_2/WO_3 were observed at 400 and 446 nm, respectively. Also, at the region of visible light, the reflective intensity of the TiO_2/WO_3 , a slightly yellow sample, was smaller than that observed for white TiO_2 . The absorption edge energy is related to the photon energy required to excite an electron from the top of the valence band to the bottom of the conduction band (E_g), and can be estimated from diffuse reflectance measurements considering the variation of sample and standard reflectance ratio (R_{∞}) with the incident photon energy ($h\nu$) in the Kubelka-Munk function.^[17] Considering direct-allowed electronic transition for TiO_2 and TiO_2/WO_3 samples, the respective E_g was estimated as 3.1 and 2.3 eV. Thus, the smaller E_g for the hybrid sample can be associated to the high dispersion of WO_3 particles on the TiO_2 surface.^[18]

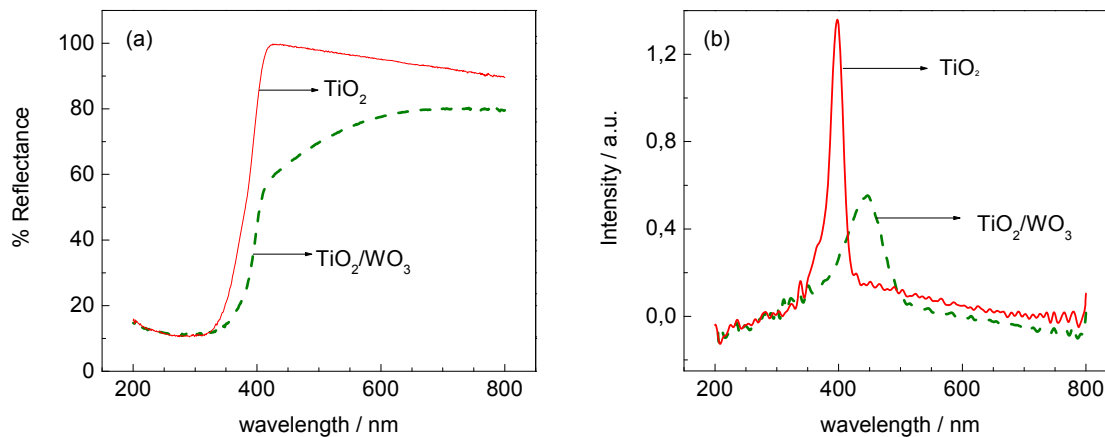


Fig. 2. Diffuse reflectance spectroscopy (a) and respective derivate of the curves (b) for TiO_2 (—) and TiO_2/WO_3 (---).

3.2 Morphological and electrochemical properties of TiO_2 and TiO_2/WO_3 film electrodes

Films of TiO_2 and TiO_2/WO_3 deposited onto glass-FTO electrodes from aqueous suspensions followed by annealing were uniform and mechanically stable. Figure 3 shows typical SEM images of the films, which are consisted of agglomerated particles with irregular sizes and average diameters ranging from 50 to 200 nm. Energy-dispersive X-ray analysis revealed a homogeneous distribution of Ti, O and W atoms at the TiO_2/WO_3 surface.

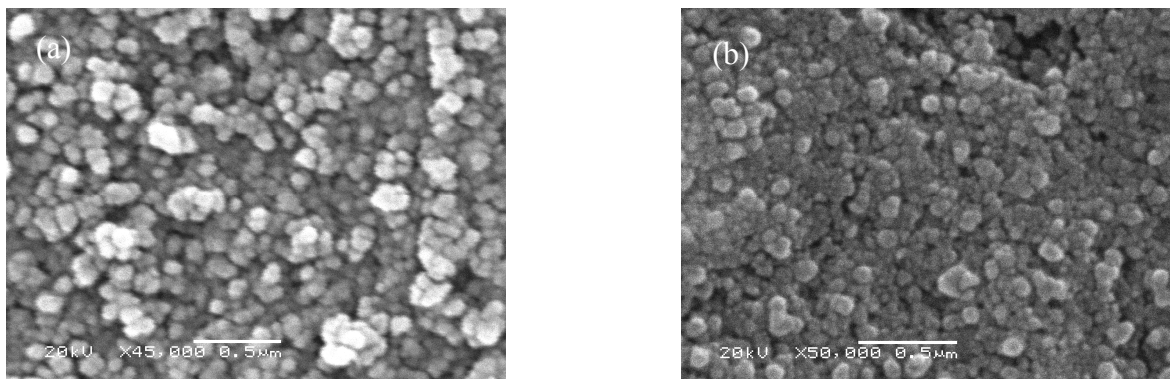


Fig. 3. Scanning electron micrograph of the surface of (a) TiO₂ and (b) TiO₂/WO₃ films deposited on glass-FTO substrate.

The electrochemical properties of TiO₂ and TiO₂/WO₃ film electrodes were investigated for samples with 1.0 cm² in aqueous solutions containing Na₂SO₄ as supporting electrolyte. Figure 4 shows the cyclic voltammetric response registered at 20 mV cm⁻² in the dark and under polychromatic irradiation. For both electrodes, in the dark, a small capacitive current is observed in a wide potential window, limited at -0.2 and +1.2 V (vs Ag/AgCl) due to H₂ and O₂ evolution reactions. Higher currents were observed under polychromatic irradiation; at 0.8 V, the current corresponded to 116 and 147 μA cm⁻² for the TiO₂ and TiO₂/WO₃ film electrodes, respectively. Thus, the photocurrent increased 35 % for the hybrid film electrode containing 12 % of WO₃. Probably, the higher photocurrent is associated with the WO₃ ability to harvest visible light, as well as to the relative position of conduction and valence bands of these semiconductors, that inhibits the charge recombination.^[11-13]

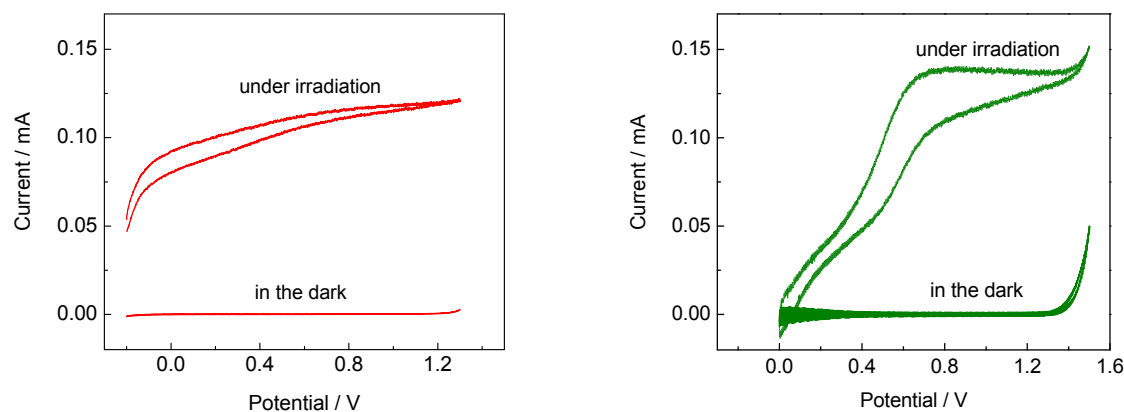


Fig. 4. Cyclic voltammograms in 0.1 M Na₂SO₄ aqueous solution, in the dark and under polychromatic irradiation for (a) glass-FTO|TiO₂ and (b) glass-FTO|TiO₂/WO₃ electrodes (20 mV s⁻¹).

These semiconductor electrodes also exhibited different values for open circuit potential, V_{OC}. In the dark, the V_{OC} determined in supporting electrolyte for TiO₂ and TiO₂/WO₃ electrodes corresponded respectively to 0.18 V and 0.13 V (vs Ag/AgCl). The lower V_{OC} for hybrid film electrode was already reported and can be associated to the smaller zero point of charge of WO₃ (zpc = 2.5) compared to TiO₂ (zpc = 6.25 for TiO₂ P25 Degussa); for TiO₂/WO₃ hybrid zpc = 5.0, which modify the equilibrium of hydroxyl groups at the oxide surface with water and change the V_{OC}.^[19,20] Under irradiation, both electrodes exhibited negative values for V_{OC}, -0.25 V for TiO₂ and -0.01 V for the hybrid film, as expected considering that both oxides are n-type semiconductors and the negative V_{OC} is an indicative of photogenerated electrons accumulation. Similar V_{OC} values were reported for hybrid TiO₂/WO₃ electrodes in literature; however, photocurrent values ranged from 80 to 220 μA cm⁻².^[18,21-23]

3.3 Photocatalytic activity for organic pollutants removal

The photocatalytic performance of electrodes was investigated for phenol and 17- α -ethinylestradiol degradation in “heterogeneous photocatalysis” configuration, for remediation of 10.0 mL of pollutant solution with $C_0 = 50 \text{ mg L}^{-1}$, without stirring, using photocatalyst films (1.0 cm^2) irradiated with a homemade solar simulator. The results represented in Table 1 revealed that, after 3 h under irradiation, for TiO_2 and TiO_2/WO_3 films, TOC measurements indicated respectively 40 % and 51 % of phenol degradation, and 22 % and 34 % of hormone removal. For pollutant solutions irradiated without the photocatalyst, the “blank” control experiments, $(20 \pm 5) \%$ and $(3 \pm 2) \%$ of TOC removal was observed for phenol and ethinylestradiol, respectively. Comparison of these results revealed that, in HP configuration, both the films exhibited higher photocatalytic activity for oxidation of phenol in comparison to 17- α -ethinylestradiol, which can be attributed to the complex structure of the hormone. Also, these results revealed that 12 % of WO_3 enhance the photocatalytic activity of TiO_2 . The hormone degradation was also studied for less concentrated solutions in HP configuration, and hormone concentration was determined by fluorescence measurements. However, for diluted hormone solutions, lower efficiencies were observed.

Table 1. Photocatalytic activity of TiO_2 and TiO_2/WO_3 films (1.0 cm^2) deposited on glass-FTO, irradiated with a solar simulator for 3 h for remediation of 10.0 mL of aqueous pollutant solution.

Pollutant concentration	Pollutant removal with TiO_2	Pollutant removal with TiO_2/WO_3	Pollutant removal - blank control
Phenol, $C_0 = 50 \text{ mg L}^{-1}$	40 %	51 %	$(20 \pm 5) \%$
17- α -ethinylestradiol $C_0 = 50 \text{ mg L}^{-1}$	22 %	34 %	5 %
17- α -ethinylestradiol $C_0 = 500 \mu\text{g L}^{-1}$	21 %	24 %	2 %
17- α -ethinylestradiol $C_0 = 160 \mu\text{g L}^{-1}$	7.5 %	10 %	2 %

Photocatalytic degradation of phenolic compounds using a TiO_2/WO_3 photocatalyst has been reported in literature. The efficiency of TiO_2 , WO_3 and TiO_2/WO_3 catalysts irradiated at 369 or 435 nm for remediation of a solution containing 17 mg L^{-1} of 4-chlorophenol was compared; after 180 min, 65 % of pollutant was removed with TiO_2/WO_3 system, but degradation was insignificant with TiO_2 and WO_3 system.^[24] Studies of hormone removal by advanced oxidative process have also been reported. The estrogenic activity of 17- α -ethinylestradiol and 17- β -estradiol decreased 90% using an UV/ H_2O_2 process;^[25] also, total mineralization of 17- α -ethinylestradiol was achieved by UVA irradiation of TiO_2 deposited on titanium alloy for 2 h.^[26] However, comparison of these results with those reported in literature is not straightforward, since the pollutant removal efficiency can be affected by several parameters in the experimental setup.

4. CONCLUSION

TiO_2 and TiO_2/WO_3 porous films deposited onto transparent conducting glass electrodes exhibited comparable electrochemical properties in the dark, with small capacitive currents and similar potentials for O_2 and H_2 evolution reactions in aqueous solution. Under polychromatic irradiation, the hybrid film electrode, molar ratio $\text{WO}_3/\text{TiO}_2 = 12 \%$, revealed higher photocurrent and photocatalytic activity for oxidation of phenol and 17- α -ethinylestradiol. The visible light harvesting ability of hybrid film, with band gap energy estimated as 2.3 eV, and the relative position of conduction and valence band edges that inhibits charge recombination, should improve its photocatalytic activity for organic pollutant removal.

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