



# Hydrogen production and simultaneous photoelectrocatalytic pollutant oxidation using a TiO<sub>2</sub>/WO<sub>3</sub> nanostructured photoanode under visible light irradiation



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## ABSTRACT

Photoelectrochemical (PEC) hydrogen production and simultaneous organic waste degradation is a re-emerging field. The main challenge of this technique has been the synthesis of new photoanode materials that are active towards visible light. Coupling close band gap energy oxides can be used to obtain materials with new optical and electronic properties. For this purpose, Ti/TiO<sub>2</sub>/WO<sub>3</sub> electrodes were prepared by electrochemical anodization followed by templating and cathodic electrodeposition. The nanostructured bicomponent material was used as a photoanode for simultaneous hydrogen generation and organic dye degradation. A good photoactivity response (11 mA cm<sup>-2</sup>) was obtained under UV and visible light irradiation, when compared to pure TiO<sub>2</sub> (8 mA cm<sup>-2</sup>). Optimization of photoelectrochemical conditions revealed that pH optimization had a major impact on H<sub>2</sub> production, resulting in satisfactory hydrogen generation efficiency (46%) and dye removal (100% discoloration and 85% reduction in TOC). A dye oxidation mechanism is proposed, based on LC-MS/MS analyses. The TiO<sub>2</sub>/WO<sub>3</sub> photoanode could potentially be used for environmental remediation and hydrogen generation under solar irradiation.

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## 1. Introduction

The potential expansion of the use of TiO<sub>2</sub> as a semiconductor has been held back by its limited absorption in the ultraviolet region. Among the methods reported to produce photoactive TiO<sub>2</sub> in the visible light region, a promising strategy involves the coupling of semiconductor materials [1,2]. The coupling of two semiconductors presenting complementary optical properties can enhance electrode performance by improving charge separation (e<sup>-</sup>/h<sup>+</sup>), minimizing charge recombination, and increasing photoactivity [3]. The coupling of WO<sub>3</sub> and TiO<sub>2</sub> can be especially useful for the photoelectrocatalytic oxidation of organic species [4–9]. There are considerable benefits derived from the coupling of oxide materials containing close band gap energies, such as TiO<sub>2</sub> (3.2 eV) and WO<sub>3</sub> (2.8 eV). The valence and conduction band energy diagrams for WO<sub>3</sub> and TiO<sub>2</sub> bicomponent materials indicate electron injection from the TiO<sub>2</sub> conduction band to WO<sub>3</sub> is favored, while hole transfer between valence bands occurs in the opposite direction [4]. This can increase the number of holes across the TiO<sub>2</sub> surface and enhance the flow of electrons towards the counter electrode, kept under bias potential, hence improving photoelectrocatalysis efficiency. In addition, bicomponent films have shown greater photochemical activation than individual arrays of WO<sub>3</sub> or TiO<sub>2</sub> [4].

Most studies of TiO<sub>2</sub>/WO<sub>3</sub> photoanodes have concerned coatings prepared by electrodeposition and electrosynthesis [8,10], while the preparation of templated TiO<sub>2</sub>/WO<sub>3</sub> nanostructured films has received a reduced amount of attention [7]. Considering recent advances in photoelectrocatalysis is directly related to the morphologies of nanostructured semiconductors, the use of templates could offer a simple and versatile approach for the preparation of dimensionally controlled nanostructured TiO<sub>2</sub>/WO<sub>3</sub> bicomponent films. Advantages of template synthesis include the ability to increase catalyst surface area, improve reaction/interaction between the semiconductor and the electrolyte, consequently enhancing charge transfer efficiency and reducing electron-hole recombination, and extend the absorption spectrum of the catalyst [3].

The cost of wastewater treatment is a major concern in industry, and there is a continual search for effective and inexpensive solutions. One attractive option is to employ photoelectrocatalytic techniques in order to explore a useful strategy by recovering the hydrogen generated at the counter electrode. In these methods, electrons are driven from the photoanode during the photoelectrocatalytic oxidation of organic compounds. Thus, in an ideal system, the organic pollutant is oxidized at the photoanode surface and photogenerated electrons move through an external circuit to the cathode, where reduction of protons occurs under anaerobic conditions. Therefore, the twin environmental benefits of waste material elimination and hydrogen generation could be an attractive way of adding value to wastewater treatment.

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In this work, we report the preparation of Ti/TiO<sub>2</sub>/WO<sub>3</sub> bicomponent material by coating nanocavities with WO<sub>3</sub> film deposited by cathodic electrodeposition onto organized TiO<sub>2</sub> nanotube arrays obtained by electrochemical anodization. The aim was to enhance photoelectrocatalytic performance during irradiation from a commercial lamp that emitted UV and visible light. The photoanode was employed in the photoelectrocatalytic oxidation of Reactive Black 5 azo dye (RB5), used as an organic pollutant model, with simultaneous hydrogen generation at the Pt cathode. The dye oxidation was monitored together with the hydrogen production efficiency.

## 2. Experimental

### 2.1. TiO<sub>2</sub>/WO<sub>3</sub> photoanode synthesis

The electrode materials were prepared following a sequence of four steps: TiO<sub>2</sub> nanotube formation, polystyrene templates self-assembly, WO<sub>3</sub> film formation, and templates removal. Titanium foils were submitted to a cleaning and polishing sequence, as described previously [7]. Formation of nanotubes was achieved by electrochemical anodization (30 V, 50 h) in 0.25 wt.% NH<sub>4</sub>F in glycerol/water (90:10, v/v) [11]. The electrodes were fired at 450 °C for 30 min in a furnace (Model 650-14 Isotemp Programmable Muffle Furnace, Fisher Scientific).

In the next step, the surface was coated with monodispersed polystyrene nanoparticles used as templates (460 nm, Sigma Aldrich), diluted to 0.5% in  $1.0 \times 10^{-7}$  mol L<sup>-1</sup> Triton X-100, according to the procedure described previously [7,12]. Electrodeposition of the WO<sub>3</sub> film was performed at -0.45 V bias potential for 45 min [7,13]. The template was chemically removed under magnetic stirring in toluene (Synth) for 24 h. The electrode was then washed in Milli-Q water, dried in an N<sub>2</sub> atmosphere, and the WO<sub>3</sub> film was fired again at 450 °C for 30 min in a furnace.

The TiO<sub>2</sub>/WO<sub>3</sub> bicomponent photoanode was compared to pure TiO<sub>2</sub> electrodes, where TiO<sub>2</sub> nanotubes were prepared by anodization according to the procedure described above [11].

### 2.2. Characterization of electrodes

All the synthesized electrodes were characterized by X-ray diffraction (XRD) using a Siemens D5000 X-ray diffractometer with Cu K $\alpha$  radiation, controlled using Diffrac Plus XRD Commander software. Morphological examination was performed by field emission gun scanning electron microscopy (FEG-SEM, EDS), using a JEOL 7500F microscope.

In order to evaluate the photocurrent response, linear scanning voltammograms were recorded in 0.1 mol L<sup>-1</sup> sodium sulfate solution in the range from -0.5 to 2.0 V, using a scan rate of 10 mV s<sup>-1</sup>. The measurements were conducted in the absence and presence of irradiation from a commercial 125 W high-pressure mercury lamp (irradiance of 12.55 mW cm<sup>-2</sup>) with emission in the UV and visible regions [14].

### 2.3. Chemicals

Reactive Black 5 dye (55% purity) was purchased from Sigma Aldrich. This compound is used commercially as a textile dye. It is classified as harmful to humans according to US and EU legislation and its specifications are CAS 17095-24-8 and C.I. 20505. Dye solutions were prepared by direct dissolution of the powder in ultrapure water. All other reagents were used without previous treatment.

### 2.4. Photoelectrochemical reactor

All the photoelectrochemical measurements were performed in a PEC reactor consisting of two 25 mL compartments separated by a Nafion membrane and fitted with a quartz window (2.5 cm<sup>2</sup>) (Fig. 1). The PEC reactor was externally irradiated. All the experiments were

performed at room temperature (25 °C) using the previously prepared materials as working electrodes, Ag/AgCl as the reference electrode, and a Pt mesh as the counter electrode. The distance between the counter and working electrodes was 4.5 cm. All the photoelectrochemical measurements were carried out using an Autolab PGSTAT 302 potentiostat/galvanostat.

### 2.5. Hydrogen generation and dye degradation at TiO<sub>2</sub>/WO<sub>3</sub> bicomponent, TiO<sub>2</sub>, and WO<sub>3</sub> electrodes

Nitrogen was purged through the PEC reactor for 15 min prior to irradiation, in order to remove oxygen from the solution in each compartment. The amount of H<sub>2</sub> produced under irradiation was determined using a Thermo TRACE GC Ultra gas chromatograph equipped with TCD and FID detectors. A Carboxen-1006 PLOT column was used (30 m  $\times$  0.53 mm) and the carrier gas was Ar at a flow rate of 60 mL min<sup>-1</sup>. A 1 mL syringe was used for sample injection, and the oven, injector, and TCD temperatures were all kept at 150 °C. The analysis time was 8.5 min. Calibration curves were constructed using injection volumes of 20, 40, 60, 80, 100, 200, 300, 400, and 500  $\mu$ L. The hydrogen evolved was collected in an inverted burette.

The photoelectrochemical dye degradation was monitored by means of spectrophotometry (Model 8453, Hewlett-Packard), total organic carbon analysis (TOC-VCPN, Shimadzu, Japan), and high performance liquid chromatography (LC-MS/MS).

Prior to the chromatographic analysis, all the samples were submitted to solid phase extraction, using 3 mL Phenomenex cartridges, in order to remove the electrolyte from the degradation solutions. The extraction procedure used the following sequence: 3 mL methanol, 3 mL pure water, 500  $\mu$ L sample, 3 mL pure water, 2 mL ACN/MeOH (50:50), and 1 mL dichloromethane. After extraction, the samples were resuspended in water (150  $\mu$ L) before injection.

The analysis of the dye and its degradation products was performed by full scan enhanced mass spectrometry (EMS), with ion product analysis (EPI) for structural elucidation. Before injection, all samples were diluted in MeOH/H<sub>2</sub>O (50:50, v/v) containing 0.1% formic acid. The analytes were separated on a Phenomenex Kinetex C-18 column (5  $\mu$ m, 150 mm  $\times$  4.6 mm) coupled to an automatic injector (Model 1200, Agilent) and an HPLC pump (Model 1200, Agilent). Gradient mode was employed for the elution of byproducts, with 0.1% formic acid as a phase modifier in the eluent, over a period of 22 min. The solvents used were CH<sub>3</sub>COONH<sub>4</sub> (50 mM in water) (A) and ACN (B), following the sequence: 90% A, 10% B (0–2 min); 100% B (2–17 min); 90% A, 10% B (17–22 min). The eluent flow rate was 1.0 mL min<sup>-1</sup> and the injection volume was 20  $\mu$ L.

The LC-MS/MS analysis was performed using a Model 1200 high performance liquid chromatograph (Agilent Technologies) coupled to a 3200 QTRAP quadrupole/linear ion trap mass spectrometer (AB Sciex Instruments) operated in negative ion mode with Turbolon Spray ionization. The spectral data were obtained at a vaporizer temperature of 550 °C, and nitrogen was used as the collision gas.

## 3. Results and discussion

### 3.1. Ti/TiO<sub>2</sub>/WO<sub>3</sub> photoanode characterization

Fig. 2 shows the complete bicomponent electrode synthesis process and the FEG-SEM micrographs obtained for Ti/TiO<sub>2</sub>/WO<sub>3</sub> photoanodes prepared using the electrochemical deposition and template method [7]. The image of the electrode prepared under optimized conditions (Fig. 2, image 2A) showed the surface completely covered by TiO<sub>2</sub> nanotubes 100 nm in diameter and with thickness of 30–40  $\mu$ m (measured by profilometry). The final electrodeposited WO<sub>3</sub> structure after template removal showed the presence of nanopores 500 nm in diameter and with thickness of 40–45  $\mu$ m (Fig. 2, image 2C). As previously reported [7], the XRD spectra (Fig. 2, images 3A and 3C) revealed diffraction

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