



Enhanced photoelectrocatalytic degradation of an acid dye with boron-doped TiO₂ nanotube anodes



Guilherme Garcia Bessegato, Juliano Carvalho Cardoso, Maria Valnice Boldrin Zanoni*

Departamento de Química Analítica, Instituto de Química, Universidade Estadual Paulista - UNESP, Av. Prof. Francisco Degni, 55, C. P. 355, 14801-970 Araraquara, SP, Brazil

ARTICLE INFO

Article history:

Received 18 January 2014

Received in revised form 23 March 2014

Accepted 28 March 2014

Available online 28 April 2014

Keywords:

TiO₂ nanotube arrays

B-doped TiO₂

Bandgap engineering

Photoelectrochemical degradation

Photoelectrochemistry

ABSTRACT

The present work evaluates the performance of boron-doped TiO₂ nanotubes (B-TiO₂ NTs) prepared by electrochemical anodization in the presence of 70, 140, 280 and 560 ppm of boron when activated by UV/visible irradiation. The presence of boron was characterized by FEG-MEV, XRD, DRS, XPS and photocurrent curves, where the maximum values were obtained for B-TiO₂ NTs. Assessment of the electrodes were conducted in the hair dye degradation (Acid Yellow 1 dye) and the degradation rate was 2 times higher at the doped electrode containing 280 ppm of boron, where the maximum electrode activation was obtained under UV/vis irradiation. The best results indicate 100% of discoloration and up to 95% of TOC removal when 100 ppm of Acid Yellow 1 dye was treated at B-TiO₂ NTs electrode during 120 min at $E_{app} = +1.2$ V in 0.01 mol L⁻¹ of Na₂SO₄ at pH 2. These findings showed that the photoelectrocatalysis is an efficient method to remove hazardous organic compounds from water and B-doped TiO₂ electrodes are an important step in the search for efficient and stable catalysts for photo(electro)catalysis.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The combination of photocatalysis and electrochemical techniques has been successfully explored in the degradation of hazardous organic compounds since the beginning of the 1990s [1,2], although Fujishima and Honda [3] had already used the photoelectrocatalysis technique for water splitting in 1972. The great goal is that under external positive bias potential there is better charges (e⁻/h⁺) separation and minimization due to competitive recombination process. Among several semiconductor materials TiO₂ has promoted high efficiency when activated by UV irradiation ($\lambda \leq 387$ nm). In this condition the photogenerated holes (h⁺) at the photoanode surface can oxidize adsorbed water molecules and/or hydroxyl ions producing hydroxyl radicals (*OH) [4], which are the base to promote efficient degradation of organic compound as a contaminant [4–6]. Nevertheless, the use of sunlight for photoelectrodes activation is limited (because it provides up to 5% of UV light), and in order to extend the absorption onset of TiO₂ with light at longer wavelengths (redshift) several authors have adopted the

insertion of cation or anion into the TiO₂ lattice [7], such as N-doped TiO₂ [8,9], C [10], S [11], B [12], Cr [13], Fe [14] and W [15].

Among them, boron-doped TiO₂ has gained attention since boron atoms can be introduced in the TiO₂ lattice and the p orbital of B is mixed with O 2p orbitals, leading to a shift in the optical response to the visible range [12,16]. Therefore, it is a promising path towards photocatalysis under visible light. B-doped TiO₂ NTs were obtained by chemical vapor deposition treatment [12,17], electrodeposition method [18] and in a one-step process during the electrochemical anodization [19] with addition of boric acid in the electrolyte of growth of nanotubes.

In addition, the doping process coupled to a nanostructured material has improved the interest of this material in photoelectrocatalysis, due to improvement in the active surface area (reaction/interaction can be facilitated between the catalyst and the interacting media) and excellent electric properties, once the charges carriers transfer is mainly governed by the quantum confinement phenomenon [20]. For this purpose TiO₂ nanotube arrays (TiO₂ NTs) have shown high structural organization and excellent electron percolation based on vectorial charge transfer between interfaces [6,21,22], which has been applied in several wastewater treatment.

The present work investigates the fabrication and characterization of boron-doped TiO₂ nanotubes (B-TiO₂ NTs) by electrochemical anodization (one-step doping) using NaBF₄ as a

* Corresponding author. Tel.: +55 1633019619.

E-mail addresses: guilhermebessegato@outlook.com (G.G. Bessegato), boldrinv@iq.unesp.br (M.V.B. Zanoni).

boron source and the application in the wastewater treatment containing acid dyes. For this, our main objective was to investigate the effect of boron doping in the electronic and optical properties when TiO₂ is activated by using a simple commercial lamp (125 W Hg high pressure lamp) as a source of irradiation of UV and visible region. The electrodes were tested in the photoelectrochemical degradation of hazardous dye AY1 (also called Naphthol Yellow S) [23] extensively used in oxidative and semipermanent hair colorants. The dye degradation was optimized and performed by direct photolysis, electrocatalysis, photocatalysis and photoelectrocatalysis. Then, the degradation was evaluated by UV/vis spectrophotometry, total organic carbon (TOC) removal and liquid chromatography coupled to mass spectrometry (LC-MS/MS) with the aim to assess low levels of dye remaining.

2. Material and methods

2.1. Preparation of TiO₂ NTs and boron-doped TiO₂ NTs

Titanium samples (Realum, Brazil) with 5 cm × 5 cm were polished using silicon carbide sandpaper of successively finer roughness (220, 320, 400, 800, 1200, and 1500 grit). Then, the sheets were degreased by successively sonication for 15 min in isopropanol, acetone and ultrapure water and dried in a N₂ stream. TiO₂ NTs were produced by electrochemical anodization using as electrolyte 1.0 mol L⁻¹ (NH₄)SO₄ + 0.5 wt.% NH₄F (Sigma–Aldrich). The applied potential was 20 V for 2 h (room temperature) using a DC power supply (Minipa MPL-1303) in a two-electrode electrochemical cell using a Ti/Ru sheet (25 cm²) as a counter electrode. The boron-doped TiO₂ NTs electrodes were grown using the same conditions, adding NaBF₄ in the electrolyte as a boron source, in the concentrations of 70, 140, 280 and 560 mg L⁻¹. Then, the samples were rinsed with DI water, dried in a nitrogen stream and annealed at 450 °C for 2 h in air, with heating rates of 2 °C min⁻¹ [24].

2.2. Characterization of materials

The prepared TiO₂ NTs and B-doped TiO₂ NTs samples were characterized by X-ray diffraction (XRD) on a SIEMENS D5000, DIFFRAC PLUS XRD Commander X-ray diffractometer with Cu K α radiation. The morphological characterization was carried out by Field Emission Gun-Scanning Electron Microscopy (FEG-SEM) on a JEOL 7500F Microscope. The chemical composition was examined using X-ray photoelectron spectroscopy (XPS, UNI-SPECS UHV).

The optical properties were evaluated by diffuse reflectance spectroscopy (DRS), using an UV/vis/NIR spectrometer (PerkinElmer Lambda 1050) with an Integrating Sphere-150 mm UV/vis/NIR (InGaAs) Module. The equipment was calibrated with a Spectralon standard (Labsphere USRS-99-020, 99% reflectance) and the reflectance was measured in the 250–800 nm range.

The electronic properties were evaluated by photocurrent curves registered by linear sweep voltammetry technique at $\nu = 10 \text{ mV s}^{-1}$ in 0.1 mol L⁻¹ Na₂SO₄ (Sigma–Aldrich) using a potentiostat/galvanostat Autolab PGSTAT302N.

2.3. Degradation of the dye Acid Yellow 1

The degradations were performed in a 500 mL cylindrical glass reactor at a controlled temperature of 25 °C by a thermostatic bath (Quimis, Brazil), as shown in Fig. 1. The anode was irradiated by a commercial Hg high pressure lamp of 125 W (Osram) (without the bulb) vertically inserted in a central quartz tube. The photoelectrochemical reactor consisted of a conventional three-electrode electrochemical cell where a Ti/Ru plate and a saturated

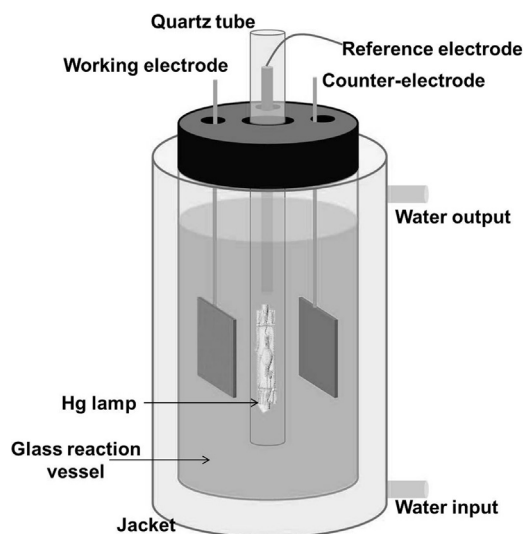


Fig. 1. Scheme of the photoelectrochemical reactor.

Ag/AgCl were used as counter and reference electrodes, respectively. The TiO₂ NTs or the B-TiO₂ NTs electrode were used as working electrodes. The electrolyte was Na₂SO₄ and all the photoelectrochemical experiments were carried out in a potentiostat/galvanostat Autolab PGSTAT302N.

2.4. Evaluation of degradation

In the course of the Acid Yellow 1 degradation, aliquots were taken at controlled times and discoloration was monitored by UV/vis spectrophotometry (Hewlett-Packard 8453 spectrophotometer) and the mineralization of organic matter with a total organic carbon analyzer (TOC-V_{CPN}, Shimadzu).

3. Results and discussion

3.1. Characterization of doped and bare TiO₂ NT electrodes

Images of FEG-MEV (Fig. 2) show the formation of self-aligned and self-organized nanotubes perpendicularly to the metallic substrate when Ti foil is submitted to 20 V for 2 h in 1.0 mol L⁻¹ (NH₄)SO₄ + 0.5 wt.% NH₄F, with an average diameter of 110 nm and a tube wall of 15 nm. Fig. 2B shows a cross sectional image of TiO₂ nanotubes, presenting 800 nm in length. The introduction of boron atoms in the TiO₂ lattice did not cause changes in the morphology of the nanotubes, as can be seen in Fig. 2C–F, for all the boron-doped samples.

However, the XPS analysis confirmed the presence of boron in the TiO₂ NTs lattice, as can be observed in the B 1s spectra in Fig. 3A. For B-TiO₂ samples, the B 1s peak appeared at a binding energy of 191.6 eV. According to earlier reports of Zaleska et al. [25] and Gopal et al. [26] this position is consistent with substitutional boron at Ti sites (Ti–O–B–O–Ti). In the Ti 2p spectrum (not shown) the symmetrical 2p_{3/2} peak is located at 459.0 eV for the doped and undoped samples. As this binding energy is characteristic for pristine TiO₂ phase, no influence of B doping on the peak position was detected, excluding a direct Ti–B interaction. In the case of boron atoms inserted in interstitial positions (also compatible with a binding energy of 191.6 eV) the presence of the Ti³⁺ phase at about 456 eV is expected [27], which was not detected in the Ti 2p spectra. Fig. 3A shows that the intensity of the B 1s peak increases when the concentration of NaBF₄ in the anodization electrolyte increases. The quantitative XPS analysis showed an increase of the boron content from 0.4 to 0.7 at.% when changing the

Download English Version:

<https://daneshyari.com/en/article/54434>

Download Persian Version:

<https://daneshyari.com/article/54434>

[Daneshyari.com](https://daneshyari.com)