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Synthesis of Nanostructured Materials for Photoelectrochemical Oxidation of Organic Compounds

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The present work relates to the use of titanium dioxide nanotubular array (NT) as photoanode for the photoelectrochemical oxidation of phenol used as model of organic compounds. Moreover, surface modification of NT structures has been carried out by deposition of tungsten oxide in order to enhance the response of the system toward wave lengths in the near visible range.

Nanotubular structures were prepared by electrochemical oxidation of Ti foils in a water / organic solution with 0.14 M of NH_4F at room temperature. Tungsten oxide was electrochemically deposited on NTs structures in a hierarchical structure.

The electro- and photoelectro-oxidation of phenol was studied in a typical three-electrode cell equipped with a quartz window. Irradiation of the photoanode was performed by a Xenon lamp (nominal power 300 W).

Different electrochemical techniques, such as potential ramps and potential steps were adopted to investigate the performance of the system.

SEM analysis was also performed to investigate on the morphology of the photoanode. Spectrophotometric analyses have been used to analyse the variation of the organic compound concentration.

1. Introduction

Nowadays, the contamination of natural and drinking water supplies and of the aquatic environment has become a serious environmental problem worldwide. Phenolic compounds are major pollutants of the aquatic environment due to their widespread use in agricultural, petrochemical, textile, paint, plastic, and pesticidal chemical industries. They are well known to be biorecalcitrant and to have acute toxicity with carcinogenic and mutagenic characters (Lathasree et al., 2004).

Titanium dioxide (TiO_2) has been widely studied as a photocatalyst (PC) for environmental applications, such as purification of waters and wastewaters. Actually, its favourable characteristics, such as remarkable charge transport properties and superior oxidation ability, long-term chemical stability, non-toxicity, inertness and low price, make it competitive with respect to other semiconductors (Qin et al., 2012). The TiO_2 features determine to a great extent the efficiency and the performance of the degradation process. Under illumination, the photogenerated holes (free in the valence band or trapped at surface states) are responsible for oxidizing the organic substrates. However, the low utilization efficiency of visible light and the high recombination rate of photoinduced electron–hole pairs, hold back its application in water treatment. Photoelectrocatalysis (PEC) promotes the separation of electron–hole pairs by driving the electron transfer to an external circuit: thanks to the applied potential bias a significant enhance of the PC efficiency, by suppressing the recombination of photogenerated electrons and holes, can be achieved (Zhang et al., 2012). In PEC processes, the degradation rate of organic pollutants depends, to some extent, on the activity of the photoanode; therefore, improving its activity has become a primary research focus.

One of the most studied approaches to increase the activity of TiO_2 is compositional doping with anions or transition metals (Shankar et al., 2009). Another approach is coupling TiO_2 with another metal oxide with narrower bandgap, such as WO_3 (Eg=2.6 eV); this coupling approach is expected to provide a better charge

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separation, which could also increase the charge transport efficiency (Ilieva et al., 2012). After the photons are absorbed and electron-hole pairs (e^-/h^+) are created, the next process is the transport of each of the carriers to other phases or regions before recombination occurs.

Various preparation methods are used to load WO_3 species in TiO_2 nanotubes, including hydrothermal synthesis (Kim et al., 2009) and sol–gel technique (Yang et al., 2010).

The preparation of porous WO_3 structures by anodization is very difficult. In fact, recent studies based on the optimization of the anodization parameters of W foils reported that longer anodization times yielded thicker porous layers, but the pore diameter increased (Reyes-Gil et al., 2013).

Electrochemical methods have been proposed as alternative techniques for the production of semiconductor layers on conducting substrates, since they offer a number of advantages: simplicity of equipment, accurate control of layer thickness and applicability to substrates of complex shapes (Georgieva et al., 2012).

WO_3/TiO_2 composite films have been prepared by Somasundaram et al. following a sequential deposition of WO_3 and TiO_2 from two separate baths containing tungsten and titanium precursor species, respectively (Somasundaram et al., 2006).

In the present work we investigated the use of TiO_2 nanotubes as a skeleton to develop WO_3/TiO_2 nanostructures. Nanostructured WO_3/TiO_2 composites have been prepared following two different steps: anodization of Ti foils was firstly performed to obtain the TiO_2 nanotubular structures (NTs), and then the electrodeposition of WO_3 was realized on NTs using pulse potential techniques. Depending on the deposition time, different morphologies of the deposit were obtained and in turn, different performances were measured in terms of photocurrent responses at the related samples.

Moreover, phenol has been used as sacrificial reagent, to react irreversibly with the photogenerated holes, this resulting in a higher quantum efficiency.

2. Materials and methods

2.1 Synthesis of TiO_2 nanotubes

Ti foils (0.25 mm thickness, 99.7 % metal basis, Aldrich) were used as raw materials to obtain the nanotubular structures by electrochemical oxidation. Prior to the electrochemical oxidation, Ti foils were degreased by sonication in acetone, then in isopropanol and finally in methanol; then, they were rinsed with deionized water and dried in a Nitrogen stream.

The oxidation process was performed in (10%) deionized water / (90%) glycerol organic solution with 0.14 M of NH_4F at room temperature. A potential ramp was imposed from open circuit voltage (OCV) at a fixed potential of 20 V with a scan rate of 100 mVs^{-1}. The applied potential was maintained at this fixed value for 4 h. A final annealing treatment was required in order to transform the amorphous structure into crystalline one and it was performed in air atmosphere at 400°C for 1 h.

2.2 Synthesis of nanostructured WO_3/TiO_2 nanotubes

The electrodeposition of tungsten oxide was performed at room temperature in a classical three-electrode cell in which a saturated calomel electrode (SCE) was the reference, a platinum grid was the counter electrode, while titania was used as working electrode.

A receipt suggested by the literature was adopted to deposit tungsten oxide (Reyes-Gil and Robinson, 2013). Tipically, 25 mL of electrolytic solution, composed by 25 mM Na_2WO_4, 30 mM of concentrated H_2O_2, was used. pH of the solution was adjusted to 1.4 by adding nitric acid. The solution was prepared the day of the deposition experiments.

Preliminary voltammetric study was performed which allowed to individuate the main reductive wave at -0.3 V vs. SCE. This potential value was adopted in the deposition process of tungsten oxide by potentiostatic runs. Pulse potential technique was used in order to obtain the tungsten oxide deposits over the nanotubular structures; the potential was alternately swiftly between opened circuit potential (OCV = 0.4 V) and -0.3 V. A serie of pulses of equal amplitude but different width was performed. Each pulse consisted of an ON-time of 1 s during which -0.3 V was applied, and an OFF-time of 10 s during which the electrode was maintained at OCV. The number of pulses required to reach the final deposition time was calculated according to the ON-time duration. The obtained WO_3/TiO_2 samples were annealed in air atmosphere at 400°C for 2h.

2.3 Characterization of samples

The surface morphology of the deposited films was investigated by high resolution Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-Ray (EDX) detector (Zeiss, Germany). Same analysis allowed also to investigate on the elements present on the deposited layers. Top views of the TiO_2 nanotubes were taken before and after WO_3 eletrodeposition.

A three-electrode cell with a quartz window equipped by a Pt-grid counter electrode and a SCE reference was used for all photoelectrochemical studies.

The light source was a 300W Xe lamp (Lot Oriel) equipped with an IR water-filter. Depending on the runs, suitable optical filters were used in order to select the right wavelength of the light. The characterization of the samples was made using KNO_3 0.1 M as electrolyte.

Electrochemical measurements were recorded using a potentiostat-galvanostat (Amel 7050), controlled by Junior Assist software. Photoactivity of the samples was evaluated at the wave length of 400 nm (band width 10 nm); photocurrent was calculated as the difference between the values recorded under irradiation and in the dark, respectively.

Phenol was used as organic pollutant model and added to the supporting electrolyte in controlled amount of 50 ppm.

During the runs, samples of electrolyte were withdrawn and analysed for the concentration of reactant by 4-aminoantipiryne method (ASTM 5530D) using UV spectrophotometer (Agilent Technologies Cary Series Spectrophotometer).

3. Results and discussion

TiO_2 nanotubular structures were prepared by electrochemical oxidation performed in glycerol/water electrolyte in the presence of fluorides, as pitting agent. Previous studies carried out in our laboratory have shown that different morphologies of the samples can be obtained, depending on the experimental conditions adopted. In particular regular structures were obtained by using glycerol / water electrolyte (Palmas et al., 2012).

Figure 1 shows the morphology of the photoelectrode; TiO_2 nanotubes (Figure 1a) are highly uniform and vertically oriented with a diameter of 50 nm of average size. After the electrodeposition process, WO_3 tubular nanostructures grew on top of the TiO_2 nanotubes developing also a cracked compact layer of WO_3 (Figure 1b and Figure 1c).

WO_3/TiO_2 nanomaterials show a multilayer structure, where the bottom is the TiO_2 nanotube on Ti foil, the middle is WO_3 tubular nanostructure and the top is a WO_3 compact layer. WO_3/TiO_2 composite materials show the same ordered structure of TiO_2 nanotubes with an external layer of WO_3.

Energy dispersive X-ray analysis (Figure 2) confirms that both Ti and W are present on top of the sample. At the moment, no indication about the specific W oxide form was obtained.

However, a study reported by Pauporte (2002) relates on the electrodeposition WO_3 film by exploiting a cathodic reduction of a peroxo precursor, Eq(1), which was obtained by mixing a tungsten precursor with an excess of hydrogen peroxide. The precursor was described as a dimer with the formula $W_2O_{11}^{2-}$ with a peroxide ligand. The oxidation state of W was +6 and the deposition reaction was described as:

$$W_2O_{11}^{2-} + (2+x)H^+ + xe^- \rightarrow 2WO_3 + \frac{2+x}{H_2O} + \frac{8-x}{4O_2} \tag{1}$$

On the bases of these results reported in the literature we can suppose that WO_3 has been obtained on TiO_2 nanotubes in the solution contained a tungsten precursor with an excess of hydrogen peroxide.

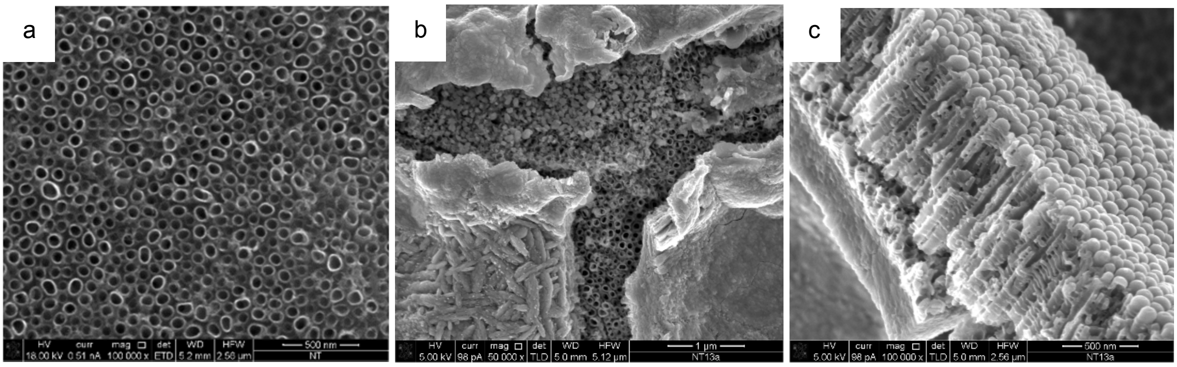

Figure 1: SEM images of TiO_2 nanotubes prepared by anodizing a Ti Foil at 20 V (a) and TiO_2/WO_3 composite materials prepared at -0.3V for 5 minutes using a pulse potential technique (b and c).

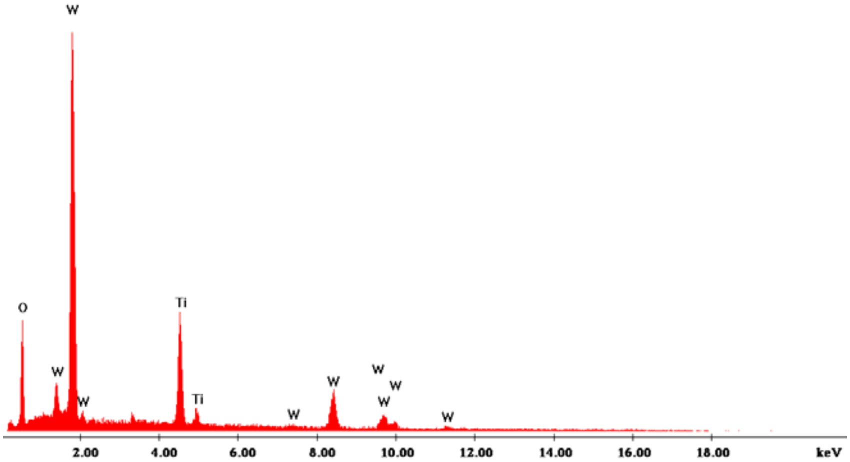

Figure 2: EDX of TiO_2/WO_3 materials prepared at -0.3 V for 5 minutes using a pulse potential technique.

Preliminary cyclicvoltammetric studies have been carried out in order to individuate the deposition potential of WO_3 on TiO_2 nanotube substrates. Figure 3 shows the cyclic voltammogram of TiO_2 nanotube substrates in Na_2WO_4 and concentrated H_2O_2 solution; a reduction peak appears at -0.2 V that can be related to the cathodic reduction of the peroxo precursor.

The electrodeposition test was performed using a pulse potential technique, where each pulse consisted of an ON-time of 1 s, during which -0.3 V was applied, and an OFF-time of 10 s, during which the electrode was maintained at OCV; the final deposition time was calculated according to the ON-time duration and, in this case, was set for 5 minutes.

Photoelectrochemical performance of WO_3/TiO_2 composite materials has been investigated using them as photoanodes in the photoelectrochemical cell. Photocurrent response of pure TiO_2 was also recorded under the same conditions, in order to compare the responses before and after WO_3 assembling.

The photocurrent behaviour of TiO_2 and WO_3/TiO_2 nanotube electrodes was determined from current-potential curves obtained in supporting electrolyte (KNO_3 (0.1 M)) and in the presence of phenol (50 ppm).

Figure 4a shows the photocurrent densities measured in supporting electrolyte, at both TiO_2 and WO_3/TiO_2 nanotube electrodes as a function of the applied potential, using a filter of 400 nm.

It is possible to observe that TiO_2 nanotubes exhibit very small photocurrent densities, if compared to WO_3/TiO_2 nanotube composite-electrodes. Under this conditions only the photooxidation of water is allowed by the photogenerated holes, which may result in some oxidative intermediates, such as OH radicals; these intermediates can recombine with the photogenerated electrons, this decreasing the anodic photocurrent response (Nakamura and Nakato, 2004). The addition of phenol to the electrolyte can scavenge these oxidative intermediates, suppressing the recombination and improving the anodic photocurrent response.

The behavior of WO_3/TiO_2 substrate in the presence of phenol is reported in Figure 4b. As can be seen, WO_3/TiO_2 electrode exhibits a doubling of the photocurrent density when phenol is added to the electrolyte.

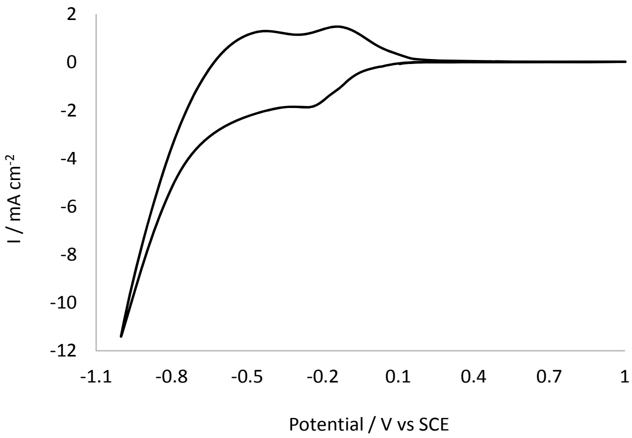

Figure 3: Cyclic voltammogram of TiO_2 substrate in Na_2WO_4 (25 mM) and concentrated H_2O_2 (30 mM) solution.

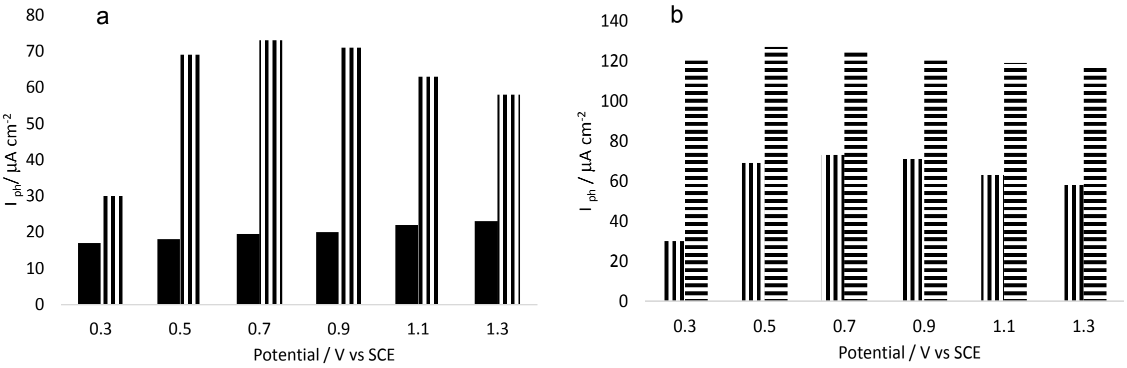

Figure 4: Photocurrent density measured at: a) TiO_2 nanotubes (full bars) and WO_3/TiO_2 nanotubes (vertical lines bars) using KNO_3 0.1 M as electrolyte and b) WO_3/TiO_2 nanotubes using KNO_3 0.1 M with (horizontal lines bars) and without (vertical lines bars) phenol.

The increase in photocurrent could be attributed to a rapid and irreversible consumption of the photogenerated holes by the organic substrate, which suppress the e^-/h^+ recombination at the interface.

Figure 5 compares the catalytic and the photoelectrocatalytic (PEC) oxidation of phenol at WO_3/TiO_2 substrate. All the degradation experiments have been performed for 450 min using a solution containing 50 ppm of phenol. Photo-degradation was carried out at 0.7 V versus SCE, and 400 nm wavelength. Oxidation was also carried out at the same potential in the dark.

As can be noticed, any catalytic activity was recorded at this potential value, neither any appreciable decreasing in the concentration can be attributed to a possible adsorption of phenol at the electrode surface, under these conditions.

Under illumination, a clear decrease in the concentration is measured. Actually, the current value measured in this condition, in the order of 100 µAcm^{-2}, does not account for all the decrease in concentration, indicating a combined effect of adsorption and reaction. The adsorption sites may be activated by the irradiation; at the same time, the applied positive bias can drive the photogenerated electrons through the 1D NTs channels, to the counter electrode; this in turn, increases the lifetime of photogenerated holes and improves the degradation rate of phenol.

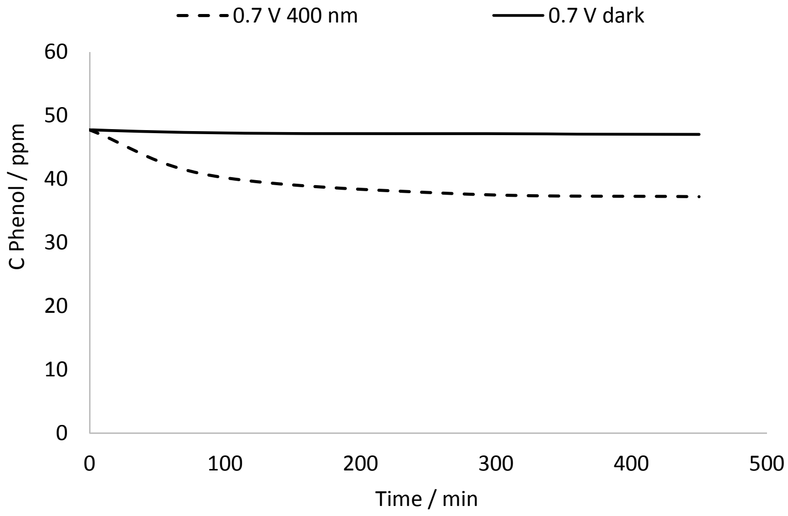

Figure 5: Variation of phenol concentration in PEC oxidation at 0.7 bias at 400 nm and a catalytic oxidation at 0.7 bias at dark by a WO_3/TiO_2 composites.

4. Conclusions

A synthetic method has been proposed to create WO_3/TiO_2 nanotubular structures, that can be used as photoanodes in a photoelectrochemical cell for the degradation of organic compounds.

The combination of WO_3 with TiO_2 nanotubular structures demonstrated to be effective in improving the photocurrent efficiency of the composite materials, if compared to TiO_2 nanotubes alone.

Further study has already been planned, and further experimentation will be carried out in order to optimize the nanostructure and verify the nature and composition of the oxides, and to improve the photogenerated carrier transport.

Further investigation will also be approached on the adsorption of the organic substrate at the electrode surface, in order to derive information on the reaction mechanism.

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