



Stable TiO₂ nanotube arrays with high UV photoconversion efficiency

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ABSTRACT

This work is intended to define an optimal methodology for preparing highly ordered TiO₂ nanotube arrays by a 60-V anodization in a glycol ethylene solution. In order to obtain a mechanically stable structure with a high UV photoconversion efficiency, it is necessary to carefully control the growth mechanism through the anodization process. For this reason, the nanotube arrays have to be formed upon a compact titanium dioxide layer with well-defined thickness. Besides, both the fluoride concentration and anodization time are strictly correlated, because elevated concentrations and/or a long anodization time produce unstable structure with low photoconversion efficiency. The best result in the terms of reproducibility has been obtained previously for a three-minute galvanostatic oxide growth on the pickled titanium sheet, and anodic growth in ethylene glycol solution containing 1 wt.% H₂O and 0.20 wt.% NH₄F for a period lower than 4.5 h. The UV photoconversion efficiency was measured and a maximum value of 28.3% has been obtained, which is the highest result in the literature.

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1. Introduction

The necessity to face the global economical crisis and the alarms about climate changes have led many important governments to stimulate investments on the energy production through renewable sources, like the solar generation of hydrogen by water photoelectrolysis [1]. Titanium dioxide is regarded as the most promising photoelectrode for this application [2] and, since the work by Fujishima and Honda [3], the research on the efficiency improvement for this material has received an important turning point with the methodology proposed by Gong et al. [4]. Their article introduced a new way to obtain titania nanotube arrays via anodic oxidation of titanium foil in fluoride-based solutions, which offers a remarkable simplification of the entire procedure, avoiding the presence of a template like alumina [5] or an organo-gelator [6], because the nanotube growth is produced directly on the titanium substrate. Firstly, the TiO₂ anodic growth was operated in a fluoride-based aqueous bath containing electrolytes like HF [4,7], chromic acid–HF mixtures [8] and H₂SO₄–HF mixtures [9], the so-called first generation nanotubes. Then, a second generation was produced using KF or NaF electrolytes [10], but the real step forward in the growth of such nanotube arrays was made in the work of Paulose et al. [11],

who found out the key to obtain long nanotubes to minimize the water content to less than 5% and to operate in polar organic solvents (formamide, dimethyl sulfoxide [12] and ethylene glycol [13]), the so-called third generation. Another important feature for these systems is that it is possible to control their morphology [7,14], length and pore size [10], and wall thickness [15] by varying the three main parameters of the process: (1) the applied voltage [16,17]; (2) the anodization time [13,18]; (3) the components and concentration of the electrolyte solutions [19,20]. Varghese et al. [21] reported the first utilization of these highly-ordered TiO₂ arrays for water photo-electrolysis application, due to their particular geometric shape, which is well suited for application in water photo-electrolysis, allowing a better absorption of the incoming light and an efficient charge transfer in combination with a high surface area accessible to electrolyte percolation [1]. A very important result in terms of photoconversion efficiency values under an UV source was reached by Shankar et al. [13], who obtained a value of 16.25%. In our previous work [22], we sustained the necessity to have a fixed starting titanium dioxide layer operating a galvanostatic treatment before the anodization growth, in order to obtain a good reproducibility. In this article, we analyzed and optimized different parameters that influence the growth of the highly ordered titania nanotube arrays: concentration of ammonium fluoride in the glycol ethylene solution in the anodization bath, duration of the anodization process, and heat treatment. The final result is the achievement of stable and compact samples showing very high photoconversion efficiency under UV sources higher than those reported in the literature [13].

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Table 1

List of titanium samples for 60 V × 6 h anodization with different bath compositions.

Sample	Anodization bath composition
F0	Glycol ethylene + 1% H ₂ O
F01	Glycol ethylene + 1% H ₂ O + 0.10 NH ₄ F
F015	Glycol ethylene + 1% H ₂ O + 0.15 NH ₄ F
F020	Glycol ethylene + 1% H ₂ O + 0.20 NH ₄ F
F025	Glycol ethylene + 1% H ₂ O + 0.25 NH ₄ F

2. Experimental

2.1. Materials and photoelectrode preparation

Small sheets of commercially pure grade-3 titanium (Titania, Italy) have been used as substrate for the nanotube growth. The samples have dimensions of 55 mm × 15 mm with a thickness of 0.5 mm, and were arranged to show an active area of 1 cm². After 3 min pickling in a HF (Carlo Erba)/HNO₃ (Carlo Erba) solution made by a volumetric ratio of 1:3 and diluted in deionised water until to 100 ml, all the titanium sheets have been set in a three-electrode cell containing a 1 M KOH solution (Carlo Erba) and subjected to a prefixed and optimized density current (1 mA/cm²) generated by a potentiostat/galvanostat (Solartron 1286) for 3 min. The counter-electrode is a platinum sheet, while the reference is a standard calomel electrode (SCE). The study of the fluoride concentration in the anodization bath has been analyzed. The growth of the nanotube arrays has been operated in the system described in our previous work [22], using a glycol ethylene solution with 1 wt.% H₂O and 0–0.25 wt.% NH₄F for 6 h at 60 V (Table 1) and using a glycol ethylene solution with 1 wt.% H₂O and 0.20 wt.% NH₄F for a variable period ranging from 45 min to 6 h at a fixed voltage of 60 V (Table 2). After the anodization, all the samples were washed in glycol ethylene and left overnight in a dry room. In order to transform amorphous TiO₂ nanotubes, obtained by anodic growth after a pre-heat treatment at 80 °C in vacuum for 3 h, into the anatase phase, which shows a higher photosensitivity [23], all the samples have been placed in a tubular furnace (Lenton) for 1 h at 580 °C with a slope of 1 °C/min in air.

2.2. Surface analysis

The morphology of some samples was investigated by scanning electron microscopy analysis performed in a JEOL mod. JSM5510LV equipment.

2.3. Measure of photocurrent density

The photocurrent density was measured using a system similar to the one described by Shankar et al. [13], and the entire scheme of the photocurrent density has been previously described [22]. Briefly, it is made of a pyrex cell with a 1.5 cm diameter quartz window, where the light, emitted by UV source (Ultravitalux Osram) and placed at 4.5 cm of distance, moved through it. This source has a spectrum with peak intensity in the UVA region at 360 and 400 nm.

Table 2

List of the titanium samples in a glycol ethylene + 1% H₂O + 0.20% NH₄F bath at 60 V and different anodization times.

Sample	Anodization time
H45	45 min
H90	90 min
H180	180 min
H270	270 min
H360	360 min

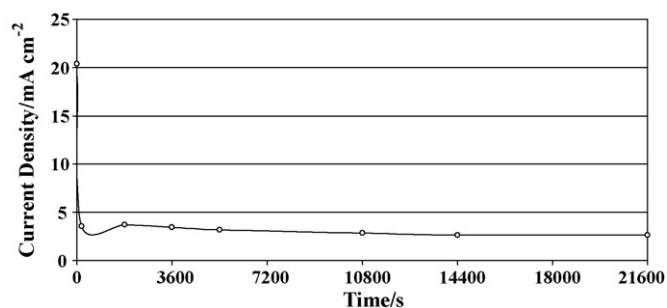


Fig. 1. General trend for the curve current density versus time at 60 V for samples listed in Table 1.

The radiation angle is 30° and the UV intensity, which is measured on the sample by a photo-Radiometer HD2302.0 (Delta OHM) over the spectral range 220–400 nm, is 13.0 mW/cm². The active surface of the sample (1 cm²) was immersed in a KOH 1 M solution and placed at 0.5 cm from the quartz window.

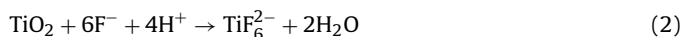
3. Results and discussion

3.1. Analysis of fluoride concentration

The general trend of the anodization growth (current density versus time) for samples F0–F25 is reported in Fig. 1. All the samples listed in Table 1 have curves similar to the ones described in the literature [13,24]. In the early stages of the process (Fig. 1), the rapid decrease of the current density is due to a non-conductive thin oxide layer, which is formed on the surface of the titanium sheet according to the following chemical reaction:



In the next stage, before reaching a quasi-steady state value, a slight increase in the current density can appear, due to the local growth of the pores [25]. This constant current is due to an equilibrium between a continuous dissolution of titanium dioxide according to the following reaction and the oxidation of metallic titanium (Eq. (1)) (Fig. 2):



According to the theory proposed by Grimes et al. [1], the formation of the titania nanotube happens in this part of the anodization because of the combined processes described in Eqs. (1) and (2).

Besides, for sample F0 (absence of fluoride) the current density is near to the zero, which means that the presence of the F⁻ ions in the composition of the anodization bath is absolutely necessary to

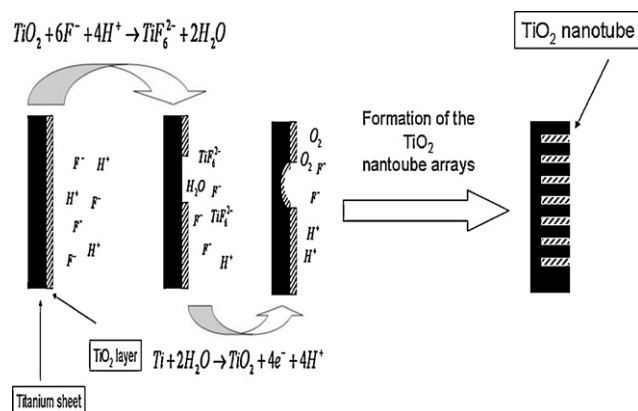


Fig. 2. Scheme of the nanotube anodization growth.

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