



# Enhancement of photoelectrochemical activity for water splitting by controlling hydrodynamic conditions on titanium anodization



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## HIGHLIGHTS

- TiO<sub>2</sub> nanosponges were obtained by anodizing under hydrodynamic conditions.
- Electron–hole separation was facilitated in the nanosponges compared with nanotubes.
- TiO<sub>2</sub> nanosponges enhanced the photoelectrochemical activity for water splitting.
- TiO<sub>2</sub> nanosponges synthesized at Reynolds number (Re) > 0 were stable over time.

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## ABSTRACT

This work studies the electrochemical and photoelectrochemical properties of a new type of TiO<sub>2</sub> nanostructure (nanosponge) obtained by means of anodization in a glycerol/water/NH<sub>4</sub>F electrolyte under controlled hydrodynamic conditions. For this purpose different techniques such as Scanning Electronic Microscopy (SEM), Raman Spectroscopy, Electrochemical Impedance Spectroscopy (EIS) measurements, Mott–Schottky (M–S) analysis and photoelectrochemical water splitting tests under standard AM 1.5 conditions are carried out. The obtained results show that electron–hole separation is facilitated in the TiO<sub>2</sub> nanosponge if compared with highly ordered TiO<sub>2</sub> nanotube arrays. As a result, nanosponges enhance the photoelectrochemical activity for water splitting.

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## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) is widely used as a pigment, as a catalyst support and as a photocatalyst, among others [1]. The latter has attracted a great scientific and technological interest over the last years [1–38] due to the exclusive set of properties of TiO<sub>2</sub>, such as high chemical stability, resistance to photocorrosion and favorable band-edge position relative to the redox potentials for the decomposition of water, allowing the use of light for effective direct water splitting.

TiO<sub>2</sub> is habitually used in the form of nanostructures, such as nanoparticles [24,30,37], nanorods/nanowires [20,26,37] or nanotubes [1,6–9,13–15,17–19,22–36,38], to obtain high specific

surfaces areas and, thus increasing its photocatalytic activity. In recent years, TiO<sub>2</sub> nanotubes have gained increasing attention since they have several advantages with respect to other nanostructures due to their perfectly defined geometry (highly ordered nanotube arrays and a very precise control of their dimensions using the process of anodization for their synthesis) [1]. Furthermore, as the oxide nanotubes formed by anodization are grown directly on the metal substrate (back contact), they can be used directly as photoanodes, thus avoiding compaction or sintering of TiO<sub>2</sub> nanoparticles on the metallic substrate.

In recent publications, the influence of hydrodynamic conditions on the anodization process has been evaluated [31], and it has been observed that under flux conditions the geometry of the formed nanostructures is different from that obtained under stagnant conditions, i.e., nanotubes. This new nanostructure, called nanosponge, provides better performance than tube morphologies, for example, for the water splitting process [31].

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In the present work, TiO<sub>2</sub> nanotubes and nanosponges have been obtained by anodization in a glycerol/water/NH<sub>4</sub>F mixture using different hydrodynamic conditions. The morphology and electronic properties of both nanostructures have been studied through different techniques, such as Scanning Electronic Microscopy (SEM), Raman Spectroscopy, Electrochemical Impedance Spectroscopy (EIS) measurements and Mott–Schottky (M–S) analysis. These properties have been correlated to the performance of both nanostructures as photocatalysts for water splitting.

## 2. Materials and methods

Anodization under hydrodynamic conditions was performed in a 2-electrode electrochemical cell with a rotating electrode configuration. The anode was a Teflon coated titanium rod (8 mm diameter, 99.3% purity) in a rotating electrode setup (Metrohm Autolab B.V., Utrecht, The Netherlands). For all experiments, 0.5 cm<sup>2</sup> of the sample was exposed to the electrolyte. Prior to the anodization process, the titanium rod surface was abraded with 500–4000 silicon carbide (SiC) papers (Struers, Denmark), in order to obtain a mirror finish. After this, the sample was sonicated in ethanol (96% v/v, J.T. Baker, Deventer, The Netherlands) for 2 min and dried in a N<sub>2</sub> stream. For anodization a voltage source (EA-PS-2384-05B, EA Elektro-Automatik, Viersen, Germany) was used, where the titanium rod served as working electrode and a platinum mesh acted as counter electrode. The electrolyte for these experiments was a mixture of glycerol/water/ammonium fluoride at a concentration of 0.27 M NH<sub>4</sub>F (>98% purity, Sigma–Aldrich, Germany) in glycerol (99% purity, Panreac, Barcelona, Spain)/water (60:40 vol.%). Different rotation speeds were used: 0, 654, 1307, 1961 and 2614 rpm corresponding to Reynolds numbers (Re) of 0, 100, 200, 300 and 400. The Reynolds numbers (Re) were calculated as follows:

$$Re = \frac{\omega \cdot r^2 \cdot \rho}{\mu} \quad (1)$$

where  $\omega$  is the rotation speed expressed in rad s<sup>-1</sup>,  $r$  is the radius of the working electrode in cm and  $\rho$  and  $\mu$  are the density in g cm<sup>-3</sup> and the dynamic viscosity in g cm<sup>-1</sup> s<sup>-1</sup> of the solution, respectively [39].

The specimens were anodized at 30 V by increasing the potential from zero to the desired value at a rate of 200 mV s<sup>-1</sup>, followed by keeping the end potential for 3 h. To compare the electrochemical and photoelectrochemical behavior of TiO<sub>2</sub> nanostructures with that of a compact TiO<sub>2</sub> layer, this layer was obtained anodizing the titanium rod in the same electrochemical cell, i.e., using platinum as counter electrode in 1 M H<sub>2</sub>SO<sub>4</sub> (98% purity, J.T. Baker, Deventer, The Netherlands) at 30 V for 20 min under stagnant conditions.

After each test, the morphology of the obtained samples was characterized by means of a field-emission scanning electron microscope (FE-SEM, Zeiss Ultra55, Zeiss, Germany). For electrochemical (EIS and M–S measurements) and photoelectrochemical water splitting tests, the as-formed TiO<sub>2</sub> layers were annealed in a furnace (Carbolite, Hope Valley, UK) at 450 °C (heating at 30 °C s<sup>-1</sup>) in air for 1 h. The materials were also examined by Raman spectroscopy (Witec Raman microscope ALPHA300 M+, Witec, Germany) after the heat treatment, in order to evaluate their crystalline structure. For these measurements, a 632 nm neon laser with 420 μW was used.

For the electrochemical and photoelectrochemical water splitting tests, a three-electrode configuration was used. The area of the TiO<sub>2</sub> nanostructures (working electrode) exposed to the test solution was 0.13 cm<sup>2</sup>. A saturated Ag/AgCl (3 M KCl) electrode was the

reference electrode, and a platinum tip was the counter electrode.

The electrochemical measurements were conducted in a 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution using an Autolab PGSTAT302N potentiostat (Metrohm Autolab B.V., Utrecht, The Netherlands) under dark conditions (without irradiation). EIS experiments were conducted at the open circuit potential (OCP) over a frequency range from 100 kHz to 10 mHz with a 10 mV (peak to peak) signal amplitude. Mott–Schottky plots were subsequently obtained by sweeping the potential from the OCP in the negative direction at 10 mV s<sup>-1</sup> with an amplitude signal of 10 mV at a frequency value of 10 kHz.

The photoelectrochemical experiments were carried out under simulated sunlight condition (LOT-QuantumDesign, Darmstadt, Germany) AM 1.5 (100 mW cm<sup>-2</sup>) in a 1 M KOH (>85% purity, J.T. Baker, Deventer, The Netherlands) solution. Photocurrent vs. voltage characteristics were recorded by scanning the potential from –0.8 V to +0.5 V with a scan rate of 2 mV s<sup>-1</sup>. Photocurrent transients as a function of the applied potential were recorded by chopped light irradiation (60 s in the dark and 20 s in the light). Samples were left at +0.5 V in the light for one hour, in order to evaluate their stability to the photocorrosion attack.

## 3. Results and discussion

Fig. 1 shows the scanning electron microscope (SEM) images of the TiO<sub>2</sub> nanostructures obtained under stagnant conditions (Re = 0, Fig. 1a) and under hydrodynamic conditions (Re 100, 200, 300 and 400, Fig. 1b–e, respectively). Under stagnant conditions, organized nanotubes of 1.3 μm in length with pore diameters of 130 and 224 nm in inner and outer diameter were formed. On the other hand, the hydrodynamic conditions changed the morphology of the formed nanostructures from nanotubes to nanosponges, i.e., a connected and highly porous TiO<sub>2</sub> structure. Fig. 2 shows that the thickness of the nanosponges is enhanced in comparison to that obtained for the nanotubes. Additionally, an increase in the rotation rate made nanosponges thicker (from 2 to nearly 3.5 μm). The formed nanosponges have pore openings of roughly 50 nm.

### 3.1. Raman spectra

As an example, Fig. 3 shows the spectra of as-prepared and annealed TiO<sub>2</sub> nanostructures for Re = 0 and Re = 300. Raman peaks originate from the molecular bond and provide useful information such as crystal structure, phase purity and crystallinity. The as-prepared TiO<sub>2</sub> does not clearly show defined peaks and only a single baseline is present. According to other studies [40,41], there are six active RS bands for anatase, i.e.: 144 cm<sup>-1</sup> (E<sub>g</sub>), 197 cm<sup>-1</sup> (E<sub>g</sub>), 399 cm<sup>-1</sup> (B<sub>1g</sub>), 513 cm<sup>-1</sup> (A<sub>1g</sub>), 519 (B<sub>1g</sub>) and 639 (E<sub>g</sub>). For the samples after annealing, the specific bands were recorded in the range of 149 cm<sup>-1</sup>, 197 cm<sup>-1</sup>, 398 cm<sup>-1</sup>, 516 cm<sup>-1</sup>, 637 cm<sup>-1</sup>. These results show that the heat treatment improves the crystallinity of TiO<sub>2</sub> and the peaks obtained correspond to TiO<sub>2</sub> anatase phase.

### 3.2. EIS measurements

Fig. 4 shows the experimental Nyquist and Bode plots for the compact TiO<sub>2</sub> film and TiO<sub>2</sub> nanostructures formed at different Re, measured in a 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution at open circuit potential under dark conditions and at 25 °C. In the case of the compact TiO<sub>2</sub> film, Nyquist and Bode plots exhibit the typical passive state behavior characterized by a semicircular shape and high impedance values in the Nyquist and Bode-module plots (Fig. 4(a) and (d)), as well as phase angles close to 90° (Fig. 4(c)), suggesting the formation of a highly stable TiO<sub>2</sub> passive film on the Ti electrode [42]. The presence of a shoulder in the Bode-phase plot at intermediate

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