



## Water splitting on 3D-type meso/macro porous structured photoanodes based on Ti mesh



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### ABSTRACT

The behaviour of photoanodes based on TiO<sub>2</sub> nanotubes (TNTs) grown on Ti gauze (80 mesh) by controlled anodic oxidation was studied in a compact photo-electrocatalytic (PECa) device for H<sub>2</sub> production by water photo-electrolysis. The 3D-type structured TNTs-Ti meshes evidenced: i) a mesoporosity due to the presence of highly ordered TiO<sub>2</sub> nanotube arrays grown on the round surface of the regularly woven wires of the Ti gauze and ii) a macroporosity due to the open area (36%) of the mesh. The resulting hierarchical porous 3D structure allowed the TNTs-Ti meshes to act both as photoactive materials for efficient light absorption and as porous substrates for fast mass diffusion of protons. The synthesis of TNTs was investigated by varying the applied voltage (in the range 40–60 V) and the anodization time (from 20 min to 7 h). Results showed that two main opposite aspects influenced their performances in the PECa cell: i) the inner diameter and ii) the length of TNTs. While the increase of the inner diameter with the anodization time should favour H<sub>2</sub> productivity, longer nanotubes negatively influence the catalytic activity due to increasing charge recombination phenomena. The result is an initial decreasing profile of H<sub>2</sub> evolution vs. anodization time, reaching a minimum at 3 h and then increasing again for the 5 h-anodized sample (H<sub>2</sub> production rate: 1.4 L m<sup>-2</sup> h<sup>-1</sup>). The maximum photo-conversion efficiency (0.7%) was obtained, instead, for the 20 min-anodized sample. It is to remark that tests of water splitting were performed with no applied bias and without adding sacrificial donors, opening the route for a sustainable use of these 3D-type meso/macro porous structured photoanodes in the production of solar fuels.

### 1. Introduction

Photo-electrochemical (PEC) cells are considered as an attractive technology for the sustainable production of clean and renewable fuels [1–3], as well as for environmental remediation [4,5]. Taking advantage of PEM (Proton Exchange Membrane) fuel-cell technology, these PEC systems exhibit several advantages over “conventional” photo-catalytic approaches [6,7]: i) the cell has a compact design, useful for a delocalized energy production, ii) the two redox half-reactions occur in two separate zones (avoiding back reactions, safety problems and eliminating the costs for product separation) and iii) the cell works at convenient and continuous flow operating conditions (ambient pressure, room temperature or slightly higher temperatures). The combination of these design aspects with the development of

suitable catalytic electrodes is a key strategy for PEC systems to pass the lab-scale stage and be implemented into the future energy scenario [8–10]. For that reason, PEC cells for production of solar fuels have been also indicated as PECa (Photo-ElectroCatalytic) cells, to remark the role of catalysis in the engineering design of these systems.

Beside the above mentioned advantages, there are still some issues that currently limit PECa performances. They mainly deal with the electron and proton transport inside the cell, whose limitations lead to high overpotential and low photo-catalytic efficiency. These aspects have been scarcely investigated in literature, as most of the papers generally focus on how to improve the single properties of the electrocatalytic materials without taking into account the characteristics of the whole system where these materials should be used [11].

More in detail, the overall efficiency of a PECa cell depends on the

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individual efficiencies of the following three processes: i) light absorption by the photo-anode; ii) long lifetime charge separation (electrons and holes) and iii) conversion of electrical energy into chemical energy at the cathode side (production of solar fuels). To assure a high overall conversion efficiency, all these single steps should proceed with a fast rate/kinetics. Unfortunately, the mobility of charges within the cell is not enough effective. All the charges involved in the photo-catalytic process should easily move inside the cell, but the presence of many interfaces between the electrodic layers constituting the MEA (the Membrane Electrode Assembly, in analogy to fuel cells) may provoke a considerable resistance contrasting the normal pathway of the charges within the electrochemical compartments of the cell [12].

The general objective of this paper is to contribute at limiting these overpotential phenomena by developing photoactive materials with novel 3D-type structural characteristics to be adapted in solar PECa cells. In particular, we have studied the behaviour of highly ordered TiO<sub>2</sub> nanotubes grown on Ti mesh in the process of water photo-electrolysis.

TiO<sub>2</sub> nanotubular mesoporous materials produced by controlled anodic oxidation of Ti plates have attracted significant interest in recent years [13–15]. Despite having similar surface area with respect to conventional TiO<sub>2</sub> powder (40–60 m<sup>2</sup> g<sup>-1</sup>), these self-organized TiO<sub>2</sub> nanotube films (with an inner diameter in the range of 40–120 nm) can be grown with a high-aspect ratio by modulating the anodization conditions (i.e. by increasing voltage or anodization time). However, they suffer from a poor mass diffusion performance, mostly linked to the high-aspect ratio (necessary to increase the active area). Therefore, creating a macroporosity in these mesoporous TiO<sub>2</sub> electrodes is a priority requirement in order to improve the diffusion properties and enhance the photoconversion efficiency. The presence of macropores may also improve light harvesting properties and reactivity, especially when a multifunctional behaviour is needed. For example, it was observed that in Dye-Sensitized Solar Cells (DSSCs), the incorporation of macropores or particles of several hundred nanometers in diameter can induce Mie scattering of the incidents photons enhancing the light absorption, particularly at infrared wavelengths where the extinction coefficients of dyes are low [16].

In this context, we have investigated the electrocatalytic performances of 3D-type meso/macro porous structured substrates based on highly ordered TiO<sub>2</sub> nanotubes grown on Ti mesh. The synthesis of TiO<sub>2</sub> nanotubes on Ti mesh substrates and their application as flexible electrodes for dye-sensitized solar cells (DSSCs) were already reported [17–23], also in combination with transition metals (i.e. Nb) to further improve light absorption properties [24]. However, the main scope of this paper is to evaluate the performances of these 3D-type photoanodes in the production of hydrogen without applying any bias in the PECa cell (i.e. with the energy power coming only from light source), without doping the TNTs with heteroatoms or decorating their surface with other transition metals and without using other artifices (e.g. adding sacrificial donors in the reacting bath). To the best of our knowledge, there is no evidence in literature of similar papers on Ti mesh, as most of the studies focus on the behaviour of photoactive materials in presence of at least one of the artifices mentioned above.

It is evident that the dimensions and morphology of TNTs are crucial in determining their activity in PECa cells [25]. In this work, the influence of both length and internal diameter of the nanotubes on the PECa performances is investigated, providing useful indications to understand the relationship between the hierarchical meso/macro porosity in TiO<sub>2</sub> and the overall electron transport and proton diffusion, with the aim of minimizing the overpotential phenomena inside the cell.

The control over the macropore and mesopore morphology and size (by developing hierarchical porous structures) may improve the electrolyte diffusion efficiency and light absorption in TiO<sub>2</sub>-based photoanodes. This solution is in line with the recently reported hierarchical porous structures of zeolites [26–28], which evidence versatile

structural properties, such as high surface area and large pore volume, with the option of incorporating metal nanoclusters inside the micropore cavity. At the same time, the presence of bigger pores (macropores) can alleviate the diffusional limitations with solely microporous framework.

## 2. Experimental

### 2.1. Preparation of TNTs-Ti mesh photoanodes

Highly ordered TiO<sub>2</sub> nanotube arrays were prepared by controlled anodic oxidation of a macroporous Ti substrate (TNTs-Ti mesh). The method can be described as an electrochemically-induced growth of a thin TiO<sub>2</sub> layer on the external surface of a commercial Ti mesh, due to the application of a constant oxidizing voltage in the presence of fluoride-based electrolytes [13,29]. The starting metallic substrate (supplied by Alfa Aesar) consists of Ti wires (0.13 mm diameter) regularly woven to form an 80 mesh (i.e. 0.177 mm) gauze with an open geometric area of 36%. Prior to the anodization, the Ti gauze was sonicated for 30 min in isopropyl alcohol to remove any organic impurities and dried in air. Then, the clean substrate was located in a stirred electrochemical cell to act as the working electrode, while a platinum wire was used as the cathode. A potentiostat (Agilent E3612A DC Power Supply) and a multimeter (Keithley 2000) interfaced to a personal computer were used to apply a constant bias between the two electrodes (in the range 40–60 V) for times of 1–7 h and save the current profile data. The constant set voltage was gradually reached by a programmed ramp rate of 5 V min<sup>-1</sup>. The electrolyte bath was a 100 mL ethylene glycol solution with 2 vol% distilled H<sub>2</sub>O and 0.3 wt% ammonium fluoride (Sigma Aldrich). At the end of the anodization process, the TNTs-Ti mesh was annealed at 450 °C for 3 h under air with heating and cooling rates of 3 °C min<sup>-1</sup>, in order to induce crystallization of the amorphous TiO<sub>2</sub> nanotubes to the anatase phase. The internal part of the Ti wires, remaining non-oxidized after the anodization, acts as a conductive metallic mesh for the collection of the electrons, which are then transferred to the cathode side through an external circuit.

### 2.2. Characterization of TNTs-Ti meshes

The structural and morphological characterization of the TNTs were performed by a scanning electron microscope (SEM) with Quanta 250 FEG FEI high resolution field emission gun, equipped with energy dispersive x-ray (EDX) analyser, at the “Centre Technologique des Microstructures” (CTμ, Villeurbanne, France). Nanotube length as well as pore diameter were obtained directly from SEM images. The degree of crystallinity was analysed by X-Ray Diffraction (XRD) using a D2 Phaser Bruker diffractometer equipped with a Cu-Kα radiation source and operated at 30 kV and 10 mA. Data were collected at a scanning rate of 0.025° s<sup>-1</sup> in a 2θ range from 12° to 80°. Ultraviolet-visible diffuse reflectance spectra were recorded in air by a Jasco V570 spectrometer equipped with an integrating sphere for solid samples using BaSO<sub>4</sub> as reference. Chronoamperometry measurements were performed by the use of a three-electrode photo-electrochemical cell, with a Pt wire as counter-electrode and a saturated Ag/AgCl reference electrode. All the tests were performed at room temperature in 1 M KOH solution at 0.1 V using a 2049 AMEL potentiostat-galvanostat.

### 2.3. PECa device

The experimental apparatus for the water photo-electrolysis tests consists of a solar illuminator source, a photo-electrocatalytic (PECa) device and a gas chromatograph for on-line analysis. The lamp housing is furnished with a Xe-arc lamp (ORIEL, 300 W), a set of lenses for light collection and focusing, and a water filter to eliminate the infrared radiation. In particular, the following filters were used to select the

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