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Hydrogen-treated hierarchical titanium oxide nanostructures for photoelectrochemical water splitting

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ABSTRACT

Hierarchical titanium oxide nanostructures were synthesized by Pulsed Laser Deposition (PLD) and investigated as photoanodes for photoelectrochemical water splitting. An explorative combined approach to enhance TiO_2 performance was based, on the one hand, on the employment of hydrogenation treatments with the aim of improving quantum efficiency and extending light absorption to the visible range; on the other hand, on the optimization of morphology and structure, to increase light harvesting and charge separation/transport. This approach was pursued by depositing at a fixed background pressure with variable oxygen content (to control the growth morphology and structure) and by annealing in a Ar/H_2 mixture (in substitution of or in combination with air annealing), in order to induce crystallization to the anatase structure and reduction/hydrogenation of the material. Morphology, structure and optical properties were investigated by SEM, Raman spectroscopy, X-ray diffraction and UV–visible-IR spectroscopy. An optical absorption tail towards the visible range appeared after Ar/H_2 annealing, without any significant modification of the nanoscale structure after the different thermal treatments. Photocurrent measurements under solar simulator illumination showed a noteworthy increase of photoresponse for Ar/O_2-deposited samples with air annealing followed by Ar/H_2 annealing. These findings can be ascribed to the combination between an improved charge transport of TiO_2 deposited in low-O_2 atmosphere and a hydrogenation effect on the nanostructures surface layers, leading to improved quantum efficiency.

1. Introduction

Hydrogen has been suggested as a possible alternative energy carrier to fossil fuels, since its combustion reaction leads only to water vapor; additionally, it is possible to produce it without greenhouse gases as byproducts exploiting the energy of solar radiation [1]. One promising way in this direction, although far from commercial application, is by means of the so-called photoelectrochemical (PEC) water splitting, in which, most commonly, a photoanode semiconductor material, immersed in water and electrically connected to a cathode, is illuminated by solar light and promotes the decomposition of water into molecular oxygen and hydrogen [2].

This phenomenon was firstly reported in 1972 by Fujishima and Honda using a titanium dioxide (TiO_2) photoanode [3]. Today, nanostructured TiO_2 is still the most investigated material thanks to its activity, low-cost, non-toxicity and high chemical stability [4]. Nevertheless, it suffers from two main limitations: poor light absorption in the visible region and limited quantum efficiency for the water splitting process [4]. To overcome these issues, two main strategies have been proposed so far in literature: i) tuning the material structure and morphology at the nanoscale, in order to enhance the active surface, improve light harvesting and minimize charge recombination, and/or ii) doping or sensitization, to shift the absorption towards the visible light [2,4].

Investigations concerning the first approach have been undertaken in several ways. Notably, one-dimensional (1D) or quasi-1D nanostruc-

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tures have been recently considered to the anisotropic morphology, desirable for a preferential electron transport towards the electrical contact, and, at the same time, the large surface area with tunable porosity at the nanoscale, favoring the infiltration of molecules as well as effective light scattering [5–7]. For instance, extensive research has been devoted to TiO_2 nanotube arrays, thanks to their high surface-to-volume ratio, ordered geometry and simple production process by electrochemical anodization [5], and to quasi-1D hierarchical nanostructures, due to their increased light trapping capability [8]. The latter can be prepared, for instance, by controlling the process parameters of pulsed laser deposition (PLD), an effective and versatile physical vapor deposition technique able to produce thin films of several materials with controlled morphological, structural and functional properties [9,10]. Indeed, TiO_2 hierarchical nanostructures prepared by PLD have been studied by some of us as photoanodes for the oxidation of organic molecules [11], for dye-sensitized solar cells [12,13] and, recently, for photoelectrochemical water splitting [14].

Research aimed at shifting absorption to the visible range has also been extensively developed. Typically, the solar absorption of TiO_2 increases by adding a controlled amount of metal or non-metal impurities capable to generate donor or acceptor states in the bandgap [2]. Recently, a different strategy has been proposed by Chen and Mao [15] by producing a modified form of TiO_2 with a narrowed bandgap. This material, called *"black titania"*, was obtained by treating anatase nanocrystals in a pure hydrogen atmosphere at high temperature and pressure. As black titania showed a significantly increased photocatalytic activity for water splitting with respect to pure TiO_2, several works have been devoted to the synthesis and control of this material. In most of them, TiO_2 nanopowders have been considered and various experimental methods have been employed in order to obtain black titania; accordingly, the results depend on the experimental procedure [16]. Moreover, despite some theoretical investigations [17], an accurate and complete comprehension of the atomic-scale structural changes and of the physical mechanisms involved in hydrogenation and leading to the striking functional properties of black titania has not been achieved yet.

Recent investigations have shown encouraging results in the attempt to combine a suitable morphology with extension of the photoresponse to the visible range, some example being hydrogen treatment on rutile nanowires [18], vacuum annealing of wire-in-tube nanostructures [19] and hydrogen treatment on nanotube arrays [20]. However, many open questions still need to be addressed to reach a full control of morphology and composition to develop this combined approach as a reliable strategy for the realization of effective TiO_2 photoanodes.

Here we develop photoanodes based on titanium oxide hierarchical nanostructures and we study in detail the effect of the deposition atmosphere and of thermal treatments in a Ar/H_2 mixture at atmospheric pressure on the photoelectrochemical water splitting performances, with the aim of investigating and understanding the relation between structural properties and photoresponse.

2. Experimental

2.1. Synthesis of TiO_2 photoanodes

TiO_2 nanostructured films have been deposited by ablating a TiO_2 target with a ns-pulsed laser (Nd: YAG, 2nd harmonic, $\lambda = 532$ nm, repetition rate 10 Hz, pulse duration 5–7 ns). The laser fluence on the target was set at about 3.5 J/cm^2 and the laser pulse energy was 170 mJ. Silicon (100), soda-lime glass and titanium plates were used as substrates, mounted on an off-axis rotating sample holder at a fixed target-to-substrate distance of 50 mm. All the substrates were kept at room temperature and titanium plate substrates of 2×1 cm^2 were half masked during deposition to leave a clean surface for electrical contacts for photoelectrochemical measurements. The deposited mass was fixed at about 0.3 mg/cm^2, as estimated from quartz microbalance measurements; the deposition rate ranged between 6 and 16 nm/min. The depositions were performed at a fixed background gas pressure of 5 Pa in three different gas atmospheres: pure oxygen, Ar/O_2 mixture (50–50%) and Ar/H_2 mixture (97–3%). We selected a deposition pressure of 5 Pa, with a nominal thickness of about 1.4 µm, according to the best results obtained in a previous work [14], in which some of us investigated the morphology dependence of the photoelectrochemical response of TiO_2 nanostructured films deposited by PLD.

Post deposition annealing treatments were performed in a Lenton muffle furnace in air at 500 °C (4 °C/min heating ramp, 2 h dwell). This "standard" air annealing was either followed by or substituted with a thermal treatment in a Ar/H_2 (97–3%) mixture at atmospheric pressure performed in a home-made furnace at 500 °C (10 °C/min heating ramp, 3 h dwell).

2.2. Morphological and structural characterization

SEM analyses (top view and cross-sectional) were performed on samples grown on silicon substrates with a ZEISS Supra 40 FEG-SEM without any sample preparation.

Raman spectra were collected from samples grown on silicon or glass substrates using a Renishaw InVia micro Raman spectrophotometer with 514.5 nm laser excitation wavelength and power on sample of about 1 mW.

X-Ray diffraction patterns were collected using a Bruker D8 Adavance X Ray diffractometer, operating in reflection mode with Ge-monochromated Cu Kα1 radiation ($\lambda = 1.5406$ Å) and a linear position-sensitive detector; with a 2θ range 10–70°, a step size 0.038° and time/step 1.5 s. Samples were mounted in sample holder with motorized z-position (4.3 mm). Diffraction patterns were collected at room temperature. The peak position and the full-width at half maximum (FWHM) of the peaks were then obtained using TOPAS software (Bruker). The crystallite sizes were estimated through the Scherrer formula [21].

Optical transmittance (in the range 250–2000 nm) and reflectance spectra (in the range 290–600 nm) were evaluated with a UV–vis–NIR PerkinElmer Lambda 1050 spectrophotometer with a 150 mm diameter integrating sphere. All the acquired spectra were normalized with respect to the glass substrate contribution by setting to 1 the intensity at the glass/film interface.

2.3. Photoelectrochemical experiments

Photoelectrochemical (PEC) measurements were carried out in aqueous KOH solution (0.1 M) with a three-electrode cell equipped with a flat quartz window. TiO_2 films on Ti substrate photoanodes (working area of 1 cm^2) were used as the working electrode while a platinum grid and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. The light source was a solar simulator (Lot Quantum Design LS0306) equipped with a 300 W xenon arc lamp and AM1.5G filter (Lot Quantum Design LSZ389). A light intensity of 100 mW/cm^2 was measured prior to the experiments using a light meter HD2302.0 (Delta OHM). The performance of the TiO_2 photoanodes was evaluated by measuring the photocurrents under an external bias [22–25], provided by a potentiostat (Amel 7050) performing potential ramps from -0.8 V to about 0.5 V, with a scan rate of 5 mV/s. PEC measurements were also performed under constant light illumination and fixed bias potential (0.4 V) for 6 h, in order to evaluate the photoanodes stability [26–28].

Photocurrent spectral quantum efficiency was measured in the range 300–600 nm at an applied potential of 0.5 V using a three electrode arrangement (Ag/AgCl, 3 M KCl, as reference and Pt as counter electrode) in an electrochemical cell equipped with a quartz glass window in 0.1 M Na_2SO_4 solution. The illumination setup consisted of an Oriel 6356 150 W Xe arc lamp as a light source and an Oriel XCornerstone 7400 1/8 monochromator.