Hierarchically organized nanostructured TiO_2 for photoelectrochemical water splitting applications

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Introduction

The production of hydrogen by photoelectrocatalytic (PEC) water splitting represents a promising way to provide a clean and renewable energy resource [1]. Nanostructured TiO_2 films based on highly ordered nanostructures (e.g. tubes, rods, wires) have triggered a lot of research interest because of their controlled structure, electronic and optical properties [2]. More recently novel 3-D architectures consisting of quasi 1-D hierarchical structures received attention for their advantages in combining (i) large surface area, (ii) light scattering, (iii) mesopores for infiltration of molecules and also (iv) anisotropic morphology (similarly to nanotubes or nanowires) to ensure better electron transport to the electrical contact [3].

In this work we investigated in detail TiO_2 hierarchical tree-like assemblies, prepared by reactive pulsed laser deposition (PLD), to be used as photoanodes for the PEC water splitting process. In particulars, the effect of crystalline structure and morphology of the obtained titanium oxide films on the photoelectrochemical response has been investigated, with the aim of selecting the optimal structures for water splitting applications.

Materials and Methods

TiO_2 hierarchically structured films have been deposited, at room temperature, by ablating a TiO_2 target (0.25 mm thick, 99.7 % metal basis, Aldrich) with UV laser pulses (7 ns, 266 nm) from a Nd:YAG laser in the presence of a background O_2 gas pressure (in the 5-15 Pa range). Thermal treatments (400, 650 and 800°C in air) were used to transform the so-obtained amorphous systems into nanocrystalline structures. The morphology and the phase composition of the samples were characterized by BET, SEM and Raman Spectroscopy.

The photoelectrochemical water splitting performances of the TiO_2 nanostructured photoanodes were investigated under illumination in a three-electrodes cell with SCE as reference electrode, a Pt wire as counter electrode and 0.1M NaOH as electrolyte solution. The photocurrent response was analyzed by applying an external bias, provided by a potentiostat both at a constant potential of 0.5V and with potential ramps from OCV to about 1 V, with a scan rate of 5 mV/s.

Results and Discussion

Figure 1 shows a SEM image of typical hierarchical TiO_2 structures grown by PLD, in the 5-15 Pa O_2 range. By increasing the oxygen pressure nanostructured layers develop into tree-like hierarchical nanoparticle assemblies, associated with an increase in the surface area. This results in a strong decrease of the film density. By tuning the deposition parameters an optimal structure can be obtained, where the roughness factor is maximized, so that the highest effective surface area is guaranteed. Post deposition thermal treatments (400-800 °C) assure nanocrystalline structure where the oxide phase (anatase/rutile) can be varied by tuning growth parameters.

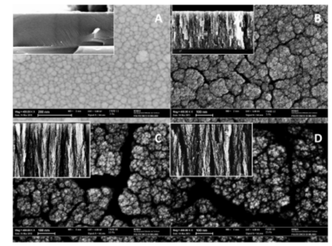

Figure 1.SEM images of as deposited TiO_2 photoanodes produced by PLD at different background O_2 pressure, A) 3 Pa, B) 5 Pa C) 10 Pa and D) 15 Pa.

Photoelectrochemical runs, preformed over the calcined photoanodes revealed that the best performances were associated with the sample prepared using 5 Pa of oxygen, possibly because it allows optimized values of density/surface area, crystallinity and electron transport. Moreover, the effect of the variation in the mass of deposited material, that leads to an increased thickness of the catalytic layers, revealed the existence of an optimal thickness value that can guarantee improved electron transfer. Finally, the effect of the annealing temperature, showed that the best performances are associated with the sample calcined at 650°. According to a previous work carried out on TiO_2 nanoparticles, the obtained results highlighted the importance of a good balance between anatase and rutile phase [4].

Significance

Hierarchical tree-like TiO_2 nanostructures prepared by PLD have been proposed as photoanodes for hydrogen production via water splitting. The structural/morphological properties of the TiO_2 nanostructures have been tuned via a fine control of the growth parameters (e.g., background gas pressure or time), of the mass of catalyst, and of the annealing treatments. A correlation between structural/morphological properties and photoelectrochemical behavior was found, and optimal values of the preparation parameters identified.

References

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