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Development of photoanodes for photoelectrocatalytic solar cells based on copper-based nanoparticles on titania thin films of vertically aligned nanotubes

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ABSTRACT

Titania nanotube (TNT)-array thin films well decorated by copper nanoparticles with average size of 3 nm were prepared by spray coating of a solution containing size-controlled Cu^0 nanoparticles. The consecutive calcination at 300 °C and 450 °C leads to the oxidation of these Cu NPs to CuO, with small amounts of Cu_2O at the lower calcination temperature, but maintaining the high dispersion. Analogous materials prepared by copper electrodeposition lead to significantly larger Cu NPs. The TNT-array thin film shows significantly enhanced photocurrent (up to about 90%) with respect to a comparable thin film prepared by spin coating using a commercial TiO_2 P25 sample. The behavior is similar by applying different filters to cut part of solar light simulator radiation. Particularly, using an UV B/C blocking filter, which permits to pass light in the 350–550 nm range, an about two-fold intensification in the current-to-electrical energy conversion (normalized to the same total irradiance) is obtained. The presence of CuO nanoparticles decreases the photocurrent density with respect to the support alone (TNT-array 1h), but enhances the H_2 photogeneration rate in the gas-phase photoreactor experiments. The results indicate that in the tested experimental conditions, the main role of CuO nanoparticles is to act as co-catalyst to improve the H_2 photogeneration rate rather than to promote charge separation or other effects, which promote the photocurrent density.

1. Introduction

The rising word-wide interest on the development of new solutions for producing solar fuels [1–8], due to the increasing quest for alternatives based on renewable energy for the production of fuels and chemicals [9–15], has spurred the research interest on the development of advanced nano-architectured photocatalytic anode thin films [16–19]. For photoelectrochemical (PEC) cells, preferably defined as photoelectrocatalytic devices [20–24], we earlier showed [19,24] that in the development of photoelectrodes in cells suitable for scale-up and industrialization in the production of solar fuels, particularly for liquid fuels from CO_2, the need to develop novel type of PEC cells and related materials is fundamental. This advanced design for PEC solar cells requires preparing a photoactive electrode with characteristics different from those utilized in conventional PEC cells or other types of solar cells such as dye-sensitized solar cells (DSSC). It is necessary to have a thin (nanoporous) semiconductor film over a conductive substrate (necessary for the efficient collection of electrons) and with an optimal interface with the underlying membrane, in order to allow an effective transport of photogenerated charges (H^+, e^-). Furthermore, the photoanode should have a specific nanostructure coupling an effective light harvesting, to optimal charge separation and charge transport. For this reason, we focused attention [25] on the preparation of photoanodes based on vertically aligned TiO_2 nanotube (TNT) thin films, fabricated by anodic oxidation of Ti foils [26–30]. The optimization of the characteristics of these TNT-based thin films is very important to increase their performances in solar-to-fuel conversion [24]. These advanced electrodes find application as photoanodes for PEC solar cells and various other applications such as (i) direct ethanol fuel cells [31–33] and (ii) H_2 production by ethanol gas-phase photoreforming [34]. In addition, it is increasing their relevance to develop advanced sensors and batteries, and novel photocatalytic electrodes or environmental catalysts [35–37].

In all these applications, the performances can be increased by decorating the TNTs with small metal nanoparticles, which catalyze the process, act as heterojunctions and charge trapping elements, or induce plasmonic effects [22,38–41]. The ordered nanotube arrays offer distinct characteristics with respect to equivalent titania thin films formed

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by nanoparticles, because the deposition of the nanoparticles within defined desired locations along the tube wall can influence markedly the properties [39]. This allows an unprecedented level of engineering of these materials, with possibilities to tune their catalytic and other properties.

However, the specific studies on the role of the method of deposition of metal nanoparticles in ordered nanotube arrays thin films are limited, and mostly focused on noble metal nanoparticles [42]. In addition to the general effort to move out from catalysts containing critical raw materials, in photo- and electro-catalysis the use of transition metal oxide nanoparticles widens considerably the possible applications. Copper is among the interesting elements, particularly for its characteristics of p-type semiconductor (Cu_2O) [43], e.g. useful as mediator species in dye-sensitized solar cells (DSSCs) [44], but that was not extensively studied. Wang et al. [45] showed the interesting properties of Cu_2O/TiO_2 composite nanotube arrays for CO_2 reduction to methanol, but they observed an average size of 80–100 nm of these Cu_2O nanoparticles, thus being located out of the titania nanotubes (having average diameter of 80 nm). Xiang et al. [46] reported Cu_2O nanoparticles of average 20 nm size, present both inside and outside of the nanotubes. However, these Cu_2O nanoparticles are still one order of magnitude larger than diameter sizes obtained for noble metal nanoparticles. Even if these authors reported enhanced visible-light photoelectrocatalytic activity, in general properties like heterojunction formation, charge trapping and other properties depending on quantum confinement, become relevant for smaller sizes of the nanoparticles. Yang et al. [47] reported the behavior of Cu_2O flakes and particles deposited on TiO_2 nanotube arrays by electrochemical deposition. Some Cu_2O nanoparticles with diameter of about 20 nm were initially formed, but after more extended electrochemical pulses or deposition, the nanoparticles show a size in the 200–300 nm range. These literature data highlight the difficulty in preparing very-small copper nanoparticles (Cu NPs), below 5–10 nm, which can uniformly decorate the TNTs. We focus here especially on the role of CuO nanoparticles, because reduced copper nanoparticles (Cu_2O, Cu^0) are not stable in longer-term experiments.

The work reported here is thus focused on the development of titania nanotube arrays thin films decorated with very small CuO nanoparticles and the initial evaluation of their behavior as catalytic photoanodes.

2. Experimental

2.1. Synthesis of TiO_2 nanotube array thin films by controlled anodic oxidation

TiO_2-nanotube (TNT) based photoactive layers were prepared by controlled anodic oxidation of Ti foils. The method induces a reconstruction of a thin TiO_2 layer (formed initially by oxidation of a Ti foil) which occurs under the application of a constant voltage in the presence of fluoride-based electrolytes [48,49]. The starting titanium disc (Alfa Aesar, 0.025 mm of thickness, 3.5 cm of diameter) was anodized by using a two-electrode electrochemical cell working at room temperature at 50 V, for times ranging from 1 to 3 h in order to obtain different thicknesses of the photoactive layer. The reaction bath consisted of a solution of ethylene glycol with H_2O (2 wt%) and NH_4F (0.3 wt%). The set voltage was gradually reached by a programmed ramp at 3 V min^{-1} using an Agilent E3612A DC Power Supply, and then kept constant for the whole anodization. This procedure was optimized to obtain a robust TNT layer. Details about the geometry of the cell and procedure of preparation were described elsewhere [50]. After the preparation, the nanostructured amorphous substrates were annealed at 450 °C in air for 3 h in order to induce crystallization into the anatase phase. The non-oxidized Ti layer, remaining after the anodization, acts as an electron-collective layer. The surface area of TNT layer is 68 m^2/g.

2.2. Deposition of Cu nanoparticles

Two techniques were used for the decoration of TNT with Cu nanoparticles (Cu NPs): (i) electrodeposition (ED) and (ii) deposition of preformed nanoparticles.

Electrodeposition technique (ED) was made in a conventional electrochemical cell with a three-electrode configuration using Ag/AgCl as the reference electrode and a Pt wire as the counter electrode. The as-prepared TNTs (working electrode) was subjected to seven cycles of potential changes ranging from 0 V to −0.8 V in an aqueous solution of 0.5 mM $CuSO_4$ at a scan rate of 20 mV s^{-1} and 50 °C temperature. After the electrodeposition of Cu, the sample was dried in air at 200 °C for 2 h (heating rate of 2 °C min^{-1}). The copper loading is 0.32 wt%.

The synthesis of preformed (size-controlled) Cu^0 nanoparticles was made at room temperature and atmospheric pressure using polyethylene glycol (PEG) as spacing agent and sodium borohydride as reducer in a basic solution. To avoid a fast metal oxidation, ascorbic acid was used. Five different aqueous solutions were prepared: 0.01 M of $CuSO_4$ $5H_2O$, 0.02 M of PEG 2000, 0.03 M of l-ascorbic acid, 0.1 M of NaOH, 0.1 M of $NaBH_4$; the volume of each solution was 25 mL. Copper precursor, PEG, ascorbic acid and NaOH solution were mixed together, whereas the $NaBH_4$ solution was then added dropwise. The reduction was completed in 2 h of reaction.

The deposition of the preformed copper nanoparticles on titania nanotubes thin films was then realized by two methods: in situ reduction and spray coating. Regarding the in-situ reduction, the titania support was added into the mixed solution before the $NaBH_4$ addition. The copper loading in this case is small, around 0.15 wt%. By spray coating, on the contrary, the loading can be changed, even if we have maintained low the loading (around 1 wt%), in order to retain a high dispersion. The metal nanoparticles were filtered and redispersed in ethanol in a way to be sprayed on the surface of the titania nanotube layer.

The reference TiO_2 P25 Degussa (now Evonik) thin film, with thickness comparable to that of TNT-array thin films, was prepared by spin coating. The surface area of TiO_2 P25 is 48 m^2/g.

2.3. Characterization

The structural and morphological characterization of the TNT materials was made by Scanning Electron Microscopy (SEM, Philips XL-30-FEG), operated at an accelerating voltage of 5 kV. The oxide layer sizes (nanotube diameter and length) were directly obtained from SEM images. The nanotube structure and the metallic nanoparticles dispersion were also investigated by transmission electron microscopy (TEM) using a Philips CM12 microscope (resolution 0.2 nm), provided with high-resolution camera, at an accelerating voltage of 120 kV.

Ultraviolet-visible diffuse reflectance spectra were recorded by a Jasco V570 spectrometer equipped with an integrating sphere for solid samples, using $BaSO_4$ as the reference in air.

Chronoamperometry measurements were performed by the use of a three-electrode photo-electrochemical cell, with a Pt wire as the counter-electrode and a Ag/AgCl as the 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.

The phase composition and the degree of crystallinity were analysed by X-ray diffraction analysis with a Bruker D2 Phaser diffractometer using a Cu-Kα radiation. Data were collected at a scanning rate of 0.025 s in a 2θ range from 15 to 90°. Diffraction peak identification was made based on the JCPDS database of reference compounds.

The light irradiance data were determined by a spectroradiometer system (Lot Oriel, model ILT950). The probe connected to the spectroradiometer was placed inside the photoreactor replacing the photoactive layer in order to obtain the values of irradiance with the use of the different cut off filters.

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