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Role of CuO in the modification of the photocatalytic water splitting behavior of TiO_2 nanotube thin films

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ABSTRACT

The role of CuO nanoparticles decorating TiO_2 nanotubes (TNT) thin film photoanodes in the behavior of photoelectrocatalytic (PEC) cells for water splitting reaction is investigated. CuO is present mainly as small nanoparticles of few nanometer decorating the internal walls of the TiO_2 nanotubes. Their presence improves i) the photocurrent behavior, ii) the H_2 generation rate by water splitting in a full PEC device (without application of a bias) and iii) the solar-to-hydrogen (*STH*) efficiency. The increase is about 20% with respect to parent TNT photoanodes using open spectrum light from a solar simulator and about 50% increase using AM 1.5G filtered light from a solar simulator. An *STH* efficiency over 2% in the full PEC cell is observed in the best conditions. *IPCE* (incident photon to current conversion efficiency) measurements clearly evidence that the presence of CuO nanoparticles induce an enhanced *IPCE* in the 300–340 nm region. The increase in the performances in water splitting is mainly associated to the transient generation of a p–n junction between the Cu_xO nanoparticles and TNT upon illumination, which enhances photocurrent density by promoting charge separation.

1. Introduction

Hydrogen production by water oxidation has received increasing interest to move towards cleaner and sustainable energy sources [1]. Hydrogen can provide a clean and safe energy storage and can be applied as an effective energy carrier for transportation and portable application. In addition, hydrogen is an important chemical for industrial processes like ammonia production, refined fossil fuels by hydrocracking and to produce different chemicals [2].

While a large variety of systems are under investigation, photoelectrocatalytic (PEC) technology for hydrogen generation is one of the most attractive routes, especially when H_2 is produced with simultaneous degradation of organic pollutants [3]. The function of a PEC device is based on the oxidation of an organic or an inorganic sacrificial agent (including water) and the reduction of water, protons or oxygen [1]. The photo-generated electrons and protons can also be used to reduce CO_2 to higher value-added liquid fuels, gaining a double environmental benefit by energy/fuel production and greenhouse gas emission reduction [4,5]. However, the development of photoanodes for practical PEC devices imposes a series of constrains that greatly limit the range of the possible materials and their characteristics. For example, it is necessary to have thin films with a specific ordered nanostructure to transport the photo-generated charges (H^+/e^-) during water oxidation to the other side of the cell, where they may combine to generate hydrogen or reduce CO_2 to fuels and chemicals [6,7]. For this reason, thin films based on an ordered array of vertically-aligned TiO_2 nanotubes still represent an important sector of development of PEC devices, even though a further engineering [8] is needed to optimize their performances. On the other hand, a great interest still exists on titania-based photocatalysts for water splitting, particularly in optimizing their behavior with visible light through different mechanisms [9–15].

Deposition of metal particles to improve the performances of titania thin films by heterojunction, co-catalysis, co-alloying or plasmonic effects has been widely investigated [16–19], with recent studies remarking also the role of one-dimensional nanoarchitecture (e.g. nanotubes) [20–23]. The synergy between one-dimensional nanoarchitecture and doping with metal nanoparticles, however, has been less investigated [15,24]. In addition, often noble metal nanoparticles (Au, Pt, etc.) have been used [25–28], while for both cost and sustainability motivations (use of non-critical raw materials) it would be preferable to use earth-abundant elements for the development of photoanodes. Among the interesting transition metals to improve semiconductor photocatalytic properties, one is copper oxide. CuO and

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Cu_2O are attractive due to their photoactive properties, good environmental acceptability, low thermal emittance, non-toxicity, simple and low-cost production process [29–32]. CuO is a p-type semiconductor that absorbs light in the visible spectral region, evidencing a bandgap energy between 1.2 and 1.7 eV [33]. Copper oxides are good materials for junctions due to their ability to act simply as an electron trap. Moreover, the electrons have to be consumed in some way, otherwise there will be an accumulation of charge on the surface [34]. Recently, some authors studied the modification of TiO_2 nanotubes with copper oxides (CuO and Cu_2O) and metallic copper in order to improve the photo-response of the system [35–37]. It should be commented, however, that while Cu_2O is interesting for the possibility to promote by semiconductor–semiconductor junction the visible-light response, the stability of this reduced species under the strong oxidizing conditions of the photoanode (nascent oxygen) is questionable. The role of CuO nanoparticles is also unclear. Teng et al. [38], studying Pt@CuO/TiO_2 photocatalysts, but testing in methanol/water solution under UV-light irradiation, indicated that stable p–n heterojunctions form at the interface between CuO and TiO_2 nanosheets, owing to the strong interaction of CuO with the {001} facets of the TiO_2 sheets. This effect decreases the recombination rate of electrons and holes. Hua et al. [39] indicated that CuO reduces to Cu_2O during the initial stage of photocatalytic reaction, and the latter is responsible for the improved photocatalytic activity. However, tests were made in a 10% aqueous solution of methanol, and thus the reduction of copper is likely induced by the organic solvent oxidation. Xu et al. [40] observed a high activity of TiO_2 nanotubes decorated with CuO nanoparticles, but again testing behavior was evaluated in a 10 vol% methanol-water mixture. No indication has been given about the physico-chemical role of copper oxide nanoparticles in promoting the behavior. Ho et al. [41] studied ternary hybrid TiO_2/CuO/Cu materials and indicated that the heterojunctions among the TiO_2, CuO, and Cu interfaces enhance the space separation and transfer of the photogenerated charge carriers. Even in this case, tests were made in water-methanol solution. Yu et al. [42] investigated CuO-deposited TiO_2 rod composites again in water-methanol mixtures. They interpreted the promotion effect of CuO in general terms of synergistic effects of high surface area, specific energy band structure, and enhanced light harvesting at the interface of CuO and porous TiO_2 rods. Kumar et al. [43] studied CuO–TiO_2 nanocomposites in a water–glycerol mixture indicating that CuO nanoparticles facilitate the charge separation and electron transfer.

This short survey of recent results on CuO-TiO_2 photocatalysts evidences the lack in understanding the behavior of these materials without the presence of sacrificial agents (organic molecules) and about the specific role of CuO in promoting the behavior in water splitting of titania thin film photoanodes based on TiO_2 nanotube ordered arrays. This study is thus focused at these aspects to develop advanced photoanodes for solar photo-electrochemical reactors [44–46] for sustainable production of hydrogen by water splitting or CO_2 reduction to fuels/chemicals using light as power supply.

The water splitting reaction, in addition, was studied in a compact PEC solar cell characterized by the photoanode and the cathode joint on the two sides, respectively, of a Nafion® thin proton membrane. This PEC solar cell design represents a state-of-the-art for practical development of this type of cells, with production of H_2 and O_2 in separate compartments, continuous operations, minimization of electrolyte volume, easy scale-up and sealing, possibility of operations either in water splitting or CO_2 reduction [45]. Many literature results in H_2 photoproduction, besides to use sacrificial agents (as indicated above for CuO-TiO_2 photocatalysts), are made in slurry photoreactors without separating H_2/O_2 production, or in PEC reactors with characteristics very different from those required for practical implementation. The results reported here, thus, refer to performances obtained under relevant experimental conditions (no extra bias, no sacrificial donors used, easy separation of products) for utilization of nanostructured TiO_2-based photoanodes modified with non-noble metal/metal oxide (such as CuO and Cu_2O) in order to increase their photocatalytic efficiency in PEC water splitting for a sustainable production of clean and renewable hydrogen.

2. Experimental

2.1. Synthesis

TiO_2 nanotube (TNT) array electrodes were prepared as earlier described [8]. Briefly, titanium plate (Alfa Aesar, 0.025 mm of thickness, 3.5 cm of diameter) was cleaned by 30 min sonication with isopropanol at 40 °C and then with ultrapure water. Electrochemical anodization was performed in a two-electrode cell using platinum as counter-electrode and a solution of ethylene glycol with 0.3% ammonium fluoride and 2.3% water as supporting electrolyte. The applied potential was initially ramped from 0 to 50 at $5\ V\ min^{-1}$ and then kept constant at 50 V for 1 h. After the anodization, the electrode was cleaned by sonication with a 37% HCl solution (1 min) and annealed at 450 °C for 3 h. A thin Ti layer remained non-oxidized, thus acting as an electron-collective layer in the PEC experimental apparatus.

The TNT thin films were decorated with CuO nanoparticles (CuO-TNT) by dip coating using an adapted methodology [47]. The solution used for dip coating was prepared with copper nitrate hydrate ($8.4 \times 10^{-3}\ mol\ L^{-1}$ of metal) as copper oxide precursor, citric acid and ethylene glycol in molar ratio of 1:4:16, respectively. The electrode, after drying, was annealed at 450 °C for 3 h.

2.2. Characterization

Field emission scanning electron microscopy (FE-SEM) images were recorded using a Zeiss model Supra 35 equipped with an energy dispersive X-ray (EDX) spectrometer. High resolution transmission electron microscopy (TEM) images were recorded using a CM200 transmission electron microscope (TEM) (Philips/FEI, Netherlands) operated at 200 kV.

The total copper concentration was evaluated by atomic absorption spectroscopy (AAS) using an AAnalyst 200 spectrometer by PerkinElmer. For the analysis, the CuO-TNT sample was sonicated in concentrated HF aqueous solution (48 wt%) to dissolve Cu and the resulting solution was analyzed after proper dilution. The calibration curve was obtained by means of three standard solutions in the range 1–5 ppm by diluting Copper Standard for AAS ($1000\ mg\ L^{-1}$ in nitric acid) supplied by Sigma Aldrich.

X-ray diffraction patterns were recorded on a Bruker Model D2 Phaser.

X-ray photoemission spectra were collected using PHI VersaProbe II analyzer. Cu_{2p} binding energies (BE) were recorded using AlKα (1486.6 eV) as the excitation source and a pass energy of 23.5 eV. The XPS spectra were recorded with setting of 100 μ100W20kv_HP. Position of XPS peaks of the corresponding element is referred to the C_{1s} peak of carbonaceous contamination, whose energy is taken equal to 284.80 eV.

An UV/Vis spectrometer (Jasco V-570PerkinElmer Lambda 1050) was used for diffuse reflectance measurements in order to obtain the optical band gap.

The photocurrent response was evaluated by linear sweep voltammetry in $1.0\ mol\ L^{-1}$ Na_2SO_3 using a scan rate of $100\ mV\ s^{-1}$ obtained by using a potentiostat/galvanostat (AMEL 2049).

2.3. H_2 production by water splitting

The water splitting was carried out using a photo-electrochemical reactor made of Plexiglas and equipped with a quartz window. It has a two-electrode configuration with two compartments for separated evolution of H_2 and O_2 [8,44,48]. The photoanode consisted of the TiO_2 nanotubes with CuO nanoparticles supported over the Ti foil, while the