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Assembling of TiO_2 Nanotube Photoelectrodes with Enhanced Visible Properties for a Sustainable Production of H_2

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In this contribution we report on the preparation of advanced TiO_2/Ti photoelectrodes to be used in photoreactors for H_2 production by water photoelectrolysis and ethanol photoreforming. The highly ordered TiO_2 nanotube arrays were synthesized by anodic oxidation of Ti foils applying a constant voltage in the range 40-70 V. Metal nanoparticles of noble (Au) and non-noble (Cu) metals were deposited on the TiO_2 surface by photodeposition method to enhance visible light photoresponse. The TiO_2/Ti photoelectrodes were fully characterized by Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy (SEM-EDX), UV-Visible Diffusive Reflectance Spectroscopy and Chronoamperometry. Then, they were tested within our homemade photoreactors (a gas photoreactor and a photoelectrochemical reactor) in water photoelectrolysis and ethanol photoreforming for H_2 production. A solar simulator, equipped with a set of filters, was used to evaluate their photoresponses in different light absorption regions (ultraviolet or visible part). The results showed high performances of these photoelectrodes under visible light irradiation, depending on the nature of the doping nanoparticles onto the titania surface, opening the route of a feasible implementation of these solar devices in the sustainable production of energy.

1. Introduction

In the last years, the global scientific community has been looking for renewable alternative energy as a sustainable solution to replace fossil fuel resources in the future (Höök and Tang, 2013). Solar energy, as a clean and abundant energy resource, is one of the most promising renewable routes (Ampelli et al., 2012a). So far many technologies have been developed to convert solar energy into an exploitable energy form, such as: solar thermal heat, photovoltaic power, concentrating solar power, etc. (Ampelli et al., 2015).

In this context, the processes of solar water splitting and photoreforming of organics are some of the most attractive and sustainable ways to obtain clean and renewable energy (Genovese et al., 2013). The main efforts are currently focused on the increase of efficiency and stability of the photoactive materials used in solar photoelectrochemical (PEC) devices: the challenge is to develop a robust semiconductor capable of absorbing the visible part of the solar spectrum. Titania (TiO_2) has been the best photocatalyst used so far, for its well known characteristics (high quantum yield, resistance to photocorrosion, no toxicity), but showing two serious drawbacks: i) it only works in the ultraviolet region for its high band gap and ii) charge recombination is very fast (Passalacqua et al., 2012).

Gong et. al. (2001) discovered an amazing method to synthesize ordered nanotube arrays of TiO_2 by anodizing pure Ti foils at high voltage in the presence of fluoride species. The presence of a nano-architecture in TiO_2 facilitates a fast vectorial transport of electrons with respect to a random assembly of nanoparticles (NPs), increasing light harvesting and greatly limiting the recombination of the photogenerated charge carriers

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(Ampelli et al., 2009). Moreover, doping the surface of TiO_2 nanotubes with metal NPs may enhance the visible properties of TiO_2 (Ampelli et al., 2014a).

In this contribution, we have integrated those two aspects (structuring TiO_2 at the nanoscale and decorating its surface with metal NPs) in the preparation of TiO_2 nanotube photoelectrodes with enhanced visible properties and investigated their application in solar PEC devices. The photoactive substrates were synthesised by controlled anodic oxidation of Ti foils at high voltages (40-70 V) in the presence of fluoride anions and ethylene glycol. Then, we decorated the titania surface with metal NPs in order to enhance the visible response through the effect of localized surface plasmon resonance (LSPR); we used gold (Au) and also non-noble metals such as copper (Cu).

The TiO_2 nanotube photoelectrodes were tested within our homemade photoreactors (Ampelli et al., 2011b; Ampelli et al., 2014b) in water photoelectrolysis as well as in photoreforming of ethanol for H_2 production.

2. Experimental

2.1 Synthesis of TiO_2/Ti photoelectrodes

TiO_2 nanotube photoelectrodes were synthesized by controlled anodic oxidation of Ti foils. The essence of the method can be described as 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 (Mor et al., 2006). The starting titanium disc (Alfa Aesar, 0.025 mm of thickness) was anodized by using a two-electrode electrochemical cell working at room temperature, at different voltages in the range of 40-70 V. The reaction bath consisted of a solution of ethylene glycol with H_2O (2 wt.%) and NaF (0.3 wt.%). The set voltage was gradually reached by a programmed ramp at 3 V min^{-1} and then kept constant for the whole anodization (5 h). Details about the geometry of the cell and procedure of preparation were described elsewhere (Ampelli et al., 2008). After the preparation, the nano-structured amorphous substrates were annealed at 450 °C in air for 3 h in order to induce crystallization into the anatase phase. A thin Ti layer remained non-oxidized, thus acting as an electron-collective layer during the photocatalytic process.

Au and Cu NPs were deposited by a photoreduction method starting from $HAuCl_4 \cdot 3H_2O$ and $Cu(NO_3)_2 \cdot 2.5H_2O$, respectively, as metal salt precursors. The thin TiO_2/Ti layer was first immersed into the metal precursor solution, filling the nanotubes by the capillary forces. Then it was exposed to an UV-visible lamp under a low inert-gas flow to form the NPs in a photoreduction process (Ampelli et al., 2012b). By properly adjusting the precursor concentration, very small and dispersed metal NPs can be obtained.

2.2 Characterization

The structural and morphological characterization of the materials was performed by scanning electron microscopy (SEM) with high resolution field emission gun (Zeiss SUPRA 35 VP), operated at a primary beam acceleration voltages of 5 kV, equipped with an energy-dispersive x-ray (EDX) analyzer. The oxide layer sizes (nanotube diameter and voids) were directly obtained from SEM images. Ultraviolet-visible diffuse reflectance spectra were recorded by a Jasco V570 spectrometer equipped with an integrating sphere for solid samples using $BaSO_4$ as reference and in air. Chronoamperometry measurements were performed by the use of a three-electrode photoelectrochemical cell, with a Pt wire as counter-electrode and a saturated KCl-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 Photoreactors

The experimental apparatus for the photocatalytic experiments consists of a solar illuminator, a photoreactor and a gas chromatograph for the analysis. The solar illuminator is a Xe arc lamp (ORIEL, 300 W) equipped with a set of lenses for light collection and focusing, a water filter to eliminate the infrared radiation and a set of filters to evaluate the photoresponse in different light-absorption regions (ultraviolet or visible regions).

Depending on the photocatalytic process, water photoelectrolysis or ethanol photoreforming, we used two different homemade photoreactors: i) a fuel cell type photoelectrochemical reactor (PEC) and ii) a gas phase photoreactor (GP), respectively. The PEC is 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. The irradiated area is 5.7 cm^2. The principle of working of the PEC device was previously reported (Ampelli et al., 2011a). The GP is made in Pyrex and equipped with a quartz window which allows irradiating a photocatalytic area of ~10 cm^2. The substrate, prepared as thin film, was suspended within the reactor headspace and irradiated perpendicularly by light coming from the external lamp. An aqueous ethanol solution, having a controlled temperature (60 °C) and composition, was present on the bottom of the reactor and maintained the gas phase in equilibrium with the liquid phase. Details about the GP were reported elsewhere (Ampelli et al., 2013).

A gas chromatograph (GC) with a Thermal Conductivity Detector (TCD) was used to analyse the permanent gases (H_2, O_2, CH_4 and CO) by a molecular sieve column (5A Plot). Carbon dioxide, ethanol and acetaldehyde were instead analysed by a fused silica column (Rt-Qbond).

3. Results and discussion

Anodic oxidation of Ti foils is an attractive method to synthesize size-controlled TiO_2 nanodimensional arrays, for its easiness, potential scale-up and high degree of control of size and morphology. For instance, by varying the bias applied during the synthesis in the range 40-70 V, we obtained different nanotube diameters, as it is shown in Figure 1. Particularly, the internal average nanotube diameter becomes higher by increasing the voltage from 40 to 60 V (39.1 and 59.8 nm, respectively); then it decreases again at 70 V (36.7 nm), probably because of the higher electromagnetic field in the first stage of nanotube formation when small pits originate on the early oxide layer (Passalacqua et al., 2012). Due to its good properties in terms of nanotube array order and photocurrent response, we chose to anodize all the samples at 50 V before doping with metal NPs.

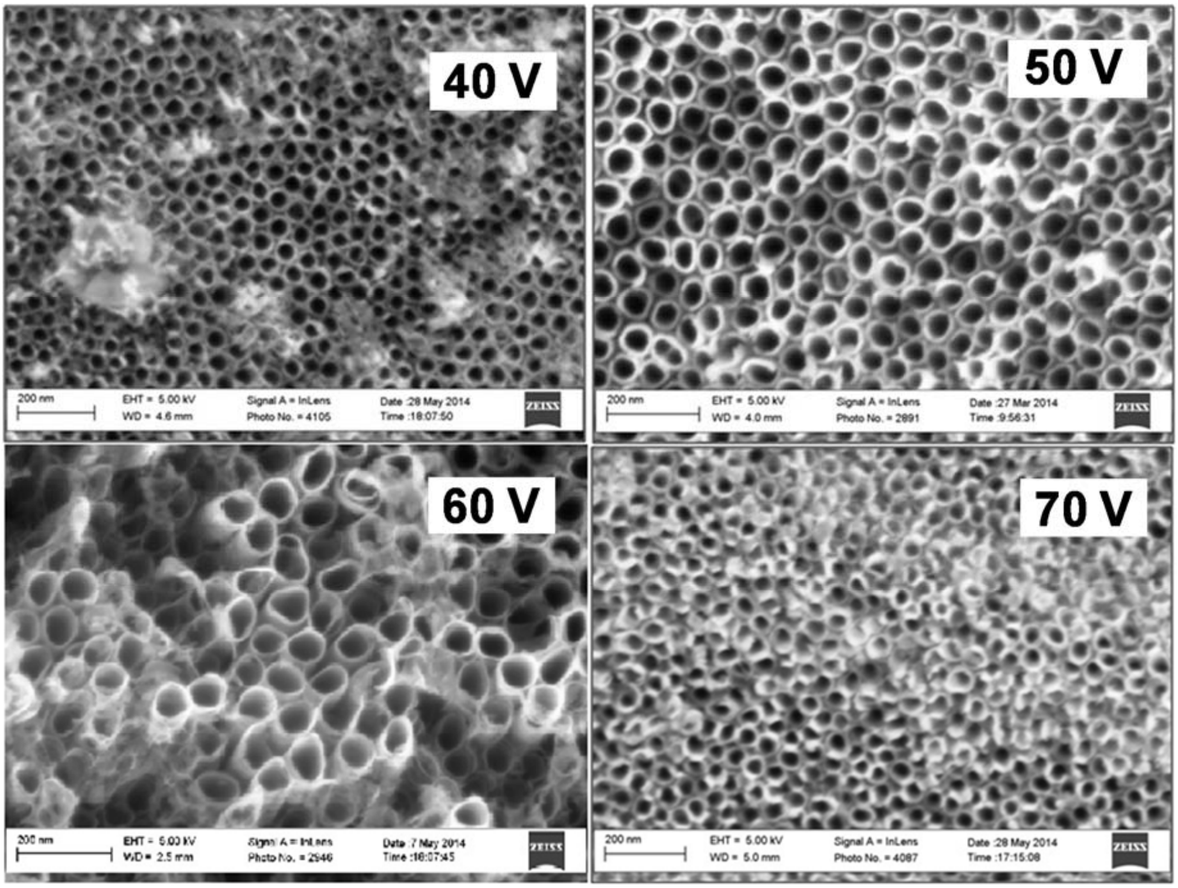

Figure 1: SEM images of the TiO_2/Ti photoelectrodes prepared at different voltages from 40 to 70 V

Figure 2 shows the UV-visible diffuse reflectance spectra of the doped TiO_2/Ti nanotube photoelectrodes. The spectra of TiO_2 P25 Degussa (non-doped) is also shown as a comparison. The intense band below 400 nm is due to the typical absorption of the TiO_2 semiconductor, while the broad band in the visible region is attributable to the presence of the deposited species on the surface of TiO_2. It is well known that Au and Cu NPs absorb light in the visible region due to the Localized Surface Plasmon Resonance (LSPR) effect. Furthermore, Au and Cu can accept the photogenerated electrons from TiO_2, thus significantly improving its photocurrent response (Pan et al., 2014). Samples were then exposed to light irradiation for chronoamperometric measurements, using different filters to select the wanted wavelength region. Figure 3 shows the typical photocurrent vs. time profile, referred to non-doped TiO_2 nanotube arrays. The ON/OFF illumination (no filter) displayed an instantaneous rise in photocurrent and quick recovery to the original photocurrent value through multiple ON/OFF cycles.

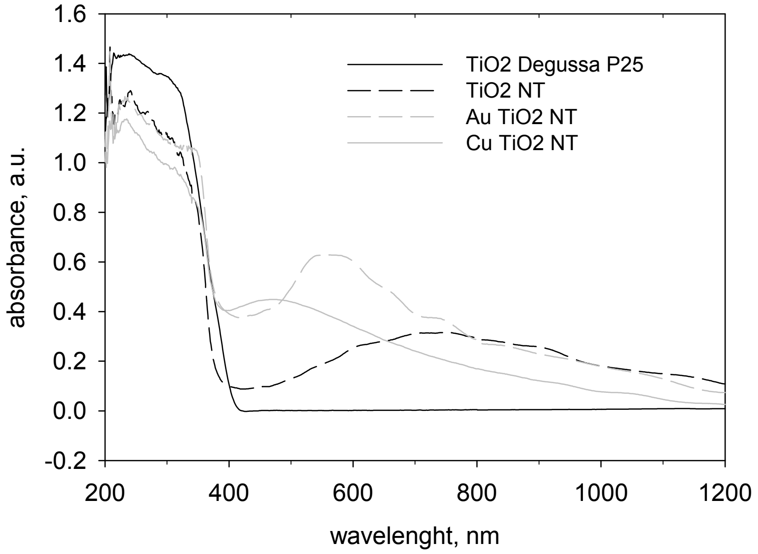

Figure 2: UV-visible diffuse reflectance spectra of the TiO_2 and M/TiO_2 nanotube samples (M = Au, Cu)

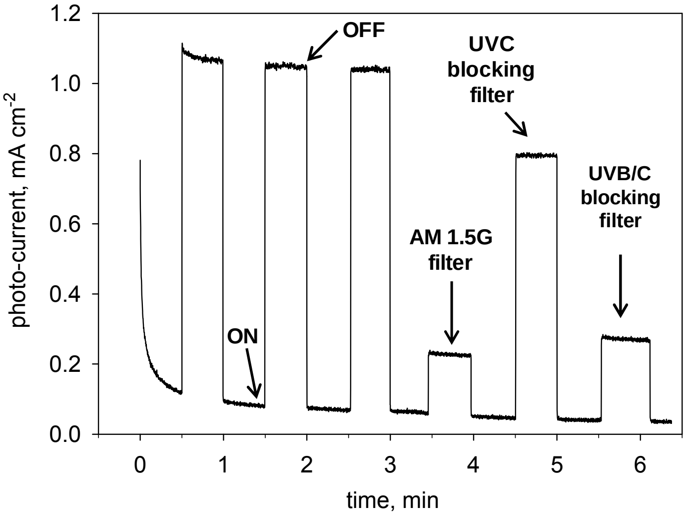

Figure 3: Chronoamperometric measurements for the TiO_2/Ti photoelectrode (0.1 V, 1 M KOH)

The monitoring during discontinuous illumination revealed stability and reproducibility of the photocurrent in all the tested samples. However, one of the most important results was the high photocurrent obtained when an AM 1.5G filter (simulating standard terrestrial solar irradiance distribution) was used for the doped TiO_2/Ti photoelectrodes than for the un-doped ones, especially for $Au/TiO_2/Ti$ layers (not shown in the figure).

Finally, the TiO_2/Ti photoelectrodes were tested in H_2 production in GP and PEC reactors. Different photoreactor using TiO_2 as photoabsorbent materials have been explored in the literature (Scaramuzzo et al., 2014). In recent years, in fact, increasing concern is directed to not only the development of new photocatalytic materials but also to the importance of technologies for the production of hydrogen and oxygen separately (Horiuchi et al., 2013). Both our homemade photoreactors show peculiar characteristics: the GP reactor allows for minimizing light-scattering phenomena, while the PEC reactor allows for limiting the charge recombination and avoiding back reactions. Furthermore, the presence of organics can strongly increase the H_2 productivity for ethanol dehydrogenation or photoreforming. Thus, it may represent a good opportunity for recovering of waste streams coming from biomass processing (agro-food or agro-chemical) which are too dilute to be processed by conventional catalytic routes, i.e. to produce H_2 by catalytic processes or methane by anaerobic digestion, or to be used as feed in the new generation of fuel cells.

Table 1 reports the values of H_2 productivity obtained when irradiating the various photoelectrodes in water photoelectrolysis and ethanol dehydrogenation (10 vol. % ethanol) processes, respectively. The values of H_2 production refer to ~10 mg of photocatalytic materials.

Table 1: Hydrogen productivity for the TiO_2/Ti photoelectrodes in different photoreactors and processes

process	**photoreactor**	**dopant**	**H_2 μmol h^{-1}**
ethanol photo dehydrogenation	gas-phase (GP)	-	82.8
		Au	153.2
		Cu	134.2
water photo electrolysis	photoelectrochemical (PEC)	-	31.5
		Au	58.7
		Cu	52.1

The presence of metal nano-particles on the TiO_2 surface strongly enhanced the H_2 productivity with respect to the bare TiO_2, due to their high capabilities of electron attraction allowing them to behave as active sites for proton reduction and H_2 production. The Au/TiO_2/Ti photoelectrode was the most efficient photocatalyst tested, but also the Cu/TiO_2/Ti sample showed a high H_2 productivity (only 12-13% lower than Au/TiO_2/Ti).

4. Conclusions

TiO_2/Ti nano-structured photoelectrodes were prepared by controlled anodic oxidation starting from Ti foils under the application of a constant voltage (in the range 40-70 V) in the presence of a fluoride-based electrolyte. After a proper modification by depositing metal nanoparticles (Au, Cu) onto the surface of theTiO_2 nanotubes, the samples were characterized to obtain information about their properties in terms of i) UV-visible light absorption and ii) charge separation (electron-hole formation). The TiO_2/Ti photoelectrodes were then tested for H_2 production in water photoelectrolysis and ethanol photoreforming processes in a gas-phase photoreactor and in a photoelectrochemical cell, respectively.

The results showed high performances of these photoelectrodes in terms of H_2 productivity, especially for the Au/TiO_2/Ti photolayer. As for non-noble metals, the Cu/TiO_2/Ti photoelectrode also showed good performances (only 12-13 % lower than Au) and its use may be advantageous in terms of both H_2 production and costs.

Moreover, nanocomposite materials (based on nanocarbons) are very attractive for the new design of semiconductor photoelectric materials (Ampelli et al., 2014c). In this context, our future efforts will be focused on the preparation of graphene oxide quantum dots (GOQDs) to be deposited onto the surface of TiO_2 nanotubes (Li et al., 2011; Favaro et al., 2014a), as a valid alternative to the visible organic sensitizers typically used in dye-sensitized solar cells, for their unique properties (high aqueous solubility, low toxicity, environmentally friendly nature, upconverted photoluminescence behavior and photoinduced electron transfer) (Favaro et al., 2014b). The results obtained in this work, as well as the preliminary results obtained in GOQD doping, are very promising in terms of light harvesting, visible light absorption enhancement and less charge recombination, opening the route of a feasible implementation of these solar devices in the sustainable production of energy.

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