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Development of a TiO_2 Nanotube Array-Based Photo-Reactor for H_2 Production by Water Splitting

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We report on the development of an innovative photoelectrochemical (PEC) cell based on the use of TiO_2 nano-engineered array thin films as photo-anode for water splitting and/or ethanol photoreforming processes. The photo-reactor was realized in a highly compact configuration in order to reduce light scattering phenomena due to the water and maximize the photocatalytic efficiency. The separation of the photo-induced process in two physically distinct areas related to water oxidation (to form O_2, protons and electrons) and proton reduction (to form H_2) allowed to overcome some drawbacks of the reaction, by limiting charge recombination and avoiding the fast back-reaction to water. Results in terms of hydrogen production showed Pt-doped TiO_2 nanotubes to be the best photocatalysts used, where their performance depended upon the parameters chosen during the preparation of the samples.

1. Introduction

The issues regarding greenhouse gas emissions and fossil fuel depletion, together with the increase of the world population and growing energy demand, have raised the social and economic pressure to develop clean and safe energy conversion processes and introduce fundamental changes in the present energy supply systems. There is the need on a short-term of new technologies for energy saving and efficiency, and use of biomass. On a medium term, a more rational use of renewable resources is needed, including solving the issue of energy storage and transport, and find a sustainable solution to CO_2 emissions, because the full transition to non-fossil fuels will require longer time. Finally, in a long-term, the renewable energy scenario, based in particular on solar energy, will become predominant (Centi et al., 2011).

The conversion of solar energy into H_2 via water splitting process is one of the most attractive ways to obtain clean and renewable energy. The main work in photochemical water splitting, at present, concerns the increase of the efficiency and stability of the photoactive materials, in the way to achieve the required efficiency benchmark of 10% that will be viable for commercial implementation. In order to perform this aim, two parallel lines of research have been pursued: the former refers to the synthesis of new materials with characteristics suited to be used as photo-catalysts (band gap near to the visible region, stability, non-toxicity, low cost etc.) (Mor et al., 2006); the latter is the correct evaluation of the engineering aspects concerning the photochemical reactor, to achieve an improvement of the process efficiency (irradiation pattern, geometrical

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configuration, material of construction, heat exchange, and mixing and flow characteristics) (Ampelli et al., 2009).

In this work we report on the realization and development of an innovative photoelectrochemical (PEC) cell based on the use of TiO_2 nano-engineered array thin film as photo-anode for water splitting and/or ethanol photoreforming processes. The photo-reactor, built in Plexiglas and equipped with a quartz window, was realized in a highly compact configuration in order to reduce light scattering phenomena due to the water and maximize the photocatalytic efficiency. The separation of the photo-induced process in two physically distinct areas related to water oxidation (to form O_2, protons and electrons) and proton reduction (to form H_2) shows many potential advantages, by limiting charge recombination and avoiding the fast back-reaction to water. For a practical use of the PEC solar cell, its design is quite different from that commonly used in literature: the anode and cathode are in the form of a thin film separated from a proton-conducting membrane and deposited over a porous conductive substrate, which allows the efficient collection/transport of the electrons over the entire film, as well as the diffusion of protons to/from the membrane and an efficient evolution of the gases (Ampelli et al., 2010). The particular configuration of the PEC cell allows also to measure in-situ the photocurrent generated between the electrodes.

2. Experimental

2.1 Preparation of the photocatalyst

The highly ordered TiO_2 nanotube arrays were synthesized by controlled anodic oxidation of Ti foils. The essence of the method may 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 presence of fluoride-based electrolytes. The starting titanium disc (Alfa Aesar, 0.025 mm of thickness) was anodized by using a stirred electrochemical cell working at room temperature, at different voltages in the range of 20–60 V, for times of up to 6 h. Details about the geometry of the cell and the procedure of preparation were described elsewhere (Centi et al., 2007). The voltage was kept constant at the set-up value for the whole anodization time. After preparation, the nano-structured substrates were annealed at 450°C in air for 3 h with heating and cooling rates of 2°C/min in order to induce crystallization in the anatase phase. The structural and morphological characterization of the materials was performed by scanning electron microscopy (Hitachi S4800) with FEG (field emission gun) and by transmission electron microscopy (TEM) (JEOL-JEM 2010). The oxide layer sizes (nanotube length and diameter) were directly obtained from SEM cross-section images. The characteristics of the obtained titania nanotubes, such as size, shape, packing density and length, depend on several synthesis parameters: electrolyte type, applied voltage, pH, anodization procedure, etc (Ampelli et al., 2008). In all cases, the 1D nanostructures are aligned perpendicularly to the metallic substrate and have a cylindrical shape and narrow size distribution (Fig. 1d).

2.2 Apparatus with photo-reactor

The apparatus for the photo-catalytic experiments consists of a solar illuminator source, a photo-reactor and gas chromatographs for on-line analysis (Fig. 1a-c). The lamp housing is furnished with a Xe-arc lamp (ORIEL, 300 W), a set of lenses for light collection and focusing, and a water filter to eliminate the infrared radiation. The PEC reactor, made of Plexiglas and equipped with a quartz window, is homemade. 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 photoanode is the nanostructured TiO_2 thin film supported over the porous Ti foil. The cathode is a carbon cloth (CC) loaded with Pt. The two electrodes are joint together by a Nafion® membrane. 1 M NaOH and 0.5 M H_2SO_4 aqueous solutions were used as electrolytes in the anodic and cathodic compartments respectively. Each solution circulates continuously between the solar cell and an outer reservoir. The simplified process is as follows: (1) light crosses the quartz window and reaches the nanostructured film (photoanode) where photo-generated electron and hole pairs are generated and O_2 evolves, (2) protons pass through the Nafion® membrane, while electrons are collected and reach the cathode through an external wire, and (3) protons recombine with electrons, over Pt nanoparticles supported on CC, to give H_2. A potentiostat–galvanostat (AMEL 2049) was used to measure the generated photocurrent.

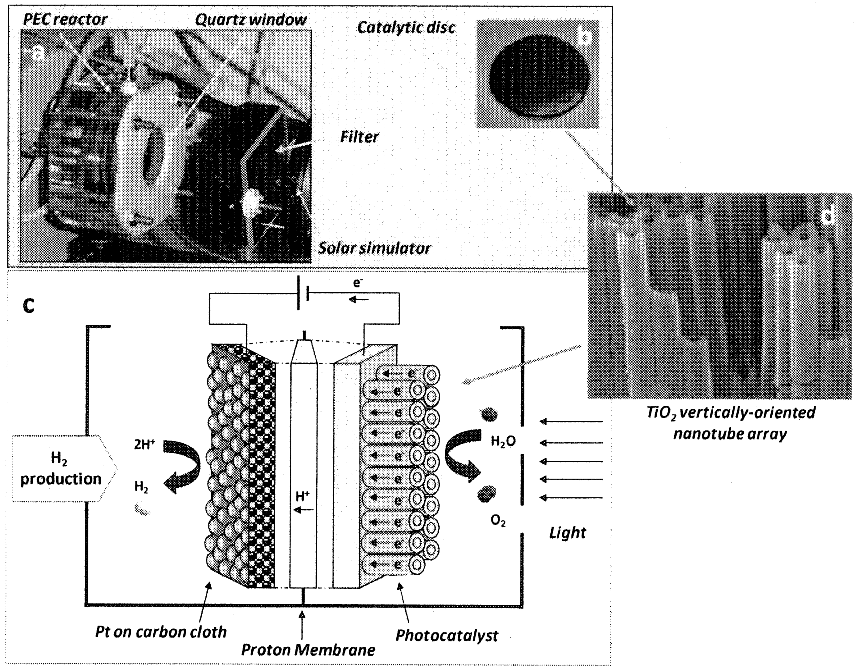

Figure 1: (a) View of the lab-scale PEC photo-reactor. (b) Image of the photo/electro-catalytic disc. (c) Scheme of the PEC device for H_2 production. (d) SEM image of a TiO_2 vertically-oriented nanotube array.

H_2 and O_2 amounts in the gas streams were periodically determined with an on-line gas-chromatograph (GC), equipped with a molecular sieve 5A column and a thermal conductivity detector (TCD). Aqueous solutions of hydrolysis products of lignocellulose or waste solutions from biomass fermentation (e.g. diluted solutions containing bioethanol) can also be used to enhance H_2 formation by photoreforming. For this reason, ethanol was used as model reactant in some testing experiments.

3. Results and discussion

The photoanode in a PEC reactor should be in the form of a porous thin film allowing a good light harvesting, a fast transport of the protons and electrons produced during the water oxidation, and a good contact with both the electron-collector substrate and the proton-conductor membrane. For this aim, anodic oxidation was chosen to synthesize TiO_2 nanotube array thin films to be use as suited photoanode materials in the PEC reactor. Table 1 reports a comparison of the performance in H_2 photoreforming of three different titania films: (a) produced by pressing the commercial P25 Degussa TiO_2, (b) prepared by anodic oxidation of Ti foils and (c) prepared by sol–gel dip-coating method. These results are also compared with those obtained with P25 Degussa in a slurry-type well-mixed reactor which was irradiated with the same solar illuminator. All TiO_2 samples were loaded with 0.5 wt % Pt by wet impregnation.

Table 1: Hydrogen evolution rate for different kinds of TiO_2 samples during photoreforming of 10% ethanol in water.

	TiO_2 sample	**Hydrogen (mmol h^{-1} g^{-1})**
slurry	P25 Degussa powder	3.5
film	pressed powder (P25 Degussa) layer on Ti	7.0
	TiO_2 nanotube array on Ti by anodization	47.8
	layer by sol-gel (dip-coating)	5.3

The data in Table 1 demonstrated well that the specific photoreforming activity (per amount of titania) considerably depends on both the reactor geometry and the nanostructure of the titania thin film. TiO_2 nanotube array thin films (produced by anodic oxidation) showed one-order of magnitude higher activity with respect other samples in terms of hydrogen production. It is thus evident how the nanostructure of TiO_2 has a marked effect, improving light harvesting and limiting charge recombination at the grain boundaries with respect to an assembly of nanoparticles.

The activity of nanostructured TiO_2 films in H_2 production by photoreforming is a factor of about 6–7 higher than that by water splitting, but a similar trend is observed, evidencing that the basic mechanistic factors determining the photoactivity are the same in the two reactions. Fig. 2 shows this concept by comparing the behaviour in H_2 production by photoreforming and water splitting of two nanostructured TiO_2 thin films prepared by anodic oxidation at two different voltages. As reported earlier (Ampelli et al., 2008), the increase of the anodization voltage leads to thicker films, but with a larger diameter of the TiO_2 nanotubes and a less dense packing.

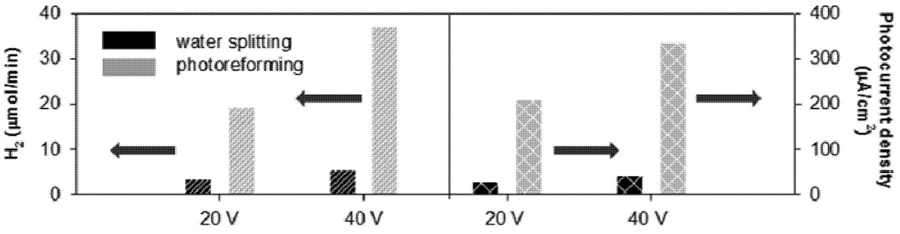

Figure 2: Hydrogen evolution rate and photo-generated current during water splitting and photoreforming for samples anodized at different voltages.

The sample prepared at higher anodization voltage proved to be the most active in H_2 photoproduction. There is a good correspondence between activity increase in water splitting due to the different characteristics of the nanostructured film, and photoreforming activity. Fig. 2 also shows a parallel trend for photocurrent generated during the reaction of H_2 photo-production. This experimental evidence lead us to suggest that it is preferable to indicate the reaction of H_2 production from water on titania as photoelectrolysis instead of water splitting, as it is often termed.

Fig. 3 shows the profiles of H_2 and O_2 production rates and photo-generated current for a water splitting experiment in the PEC reactor with a TiO_2 nanostructured thin film (anodized at 20 V) as photoanode. It may be noted that the maximum in O_2 production occurs previous to that for H_2. However, this could be related to the time necessary to establish the equilibrium through the protonconductive membrane (Nafion®), because H_2 is produced on the cathode side and O_2 on the anode side of the PEC reactor. Constant production of H_2 and O_2 is reached after about 3–4 h of time-on-stream. The photocurrent instead shows a very sharp maximum after a few minutes, and then decreases, reaching a constant value about one order of magnitude lower than the maximum value.

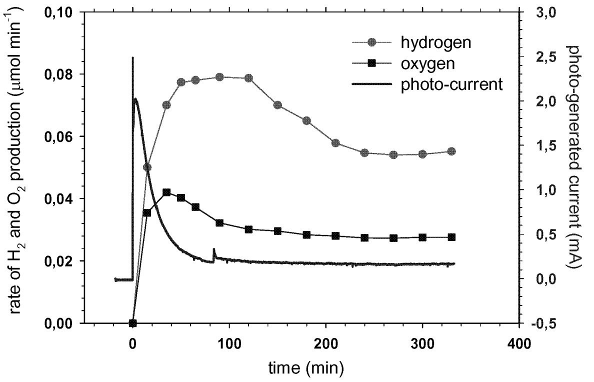

Figure 3: Rate of H_2 and O_2 production and photo-generated current profiles for a water splitting experiment in the PEC reactor with a nanostructured TiO_2 thin film (anodized at 20 V) as photoanode.

The explanation of this effect requires more detailed studies, but it may be suggested that, during the initial part of the reaction, photo-electrons likely react with oxygen produced from water to form O_2^- species which quench the photoanode activity. According to this hypothesis, the potential photoactivity of the system in water splitting is about one order of magnitude higher, but limited by the presence of oxygen adsorbed species which determine partial inhibition of the photo-process.

4. Conclusions

The use of the PEC reactor allowed to maximize light absorption efficiency of vertically-oriented TiO_2 nanotube arrays prepared by anodic oxidation. The H_2 photo-production depended on both the geometry of the photo-reactor and the presence of an nano-ordered photocatalyst. The synthesis of a precise nano-architecture is an example of how it is possible to confine the environment of reaction within a very small volume, changing substantially the mechanism of the whole process. This may be considered as the starting point of the design of nano-confined reactors (microreactors) that, alternatively to a conventional batch reactor, allow to obtain several advantages in terms of energy efficiency, reaction rate, yield, selectivity, safety and reliability, facility of scale-up and high grade of process control.

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