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TiO_2 Nanotubes Photo-anode: an Innovative Cell Design

Francesca A. Scaramuzzo*[a], Mauro Pasquali[a], Francesco Mura[a], Alfonso Pozio[b], Alessandro Dell'Era[a], Antonella Curulli[c]

[a]Department SBAI, University of Rome "La Sapienza". Via A. Scarpa, 14/16 – 00161 Roma (Italy)
[b]Department UTRINN, ENEA-Casaccia R.C., Roma (Italy)
[c] ISMN sez.Roma2, CNR, Roma (Italy)
francesca.scaramuzzo@uniroma1.it

Photocatalytic properties of titanium dioxide make it an extremely useful material in the field of renewable energy. Here we describe an electrochemical cell with an innovative design in which the anode consists of an array of highly ordered TiO_2 nanotubes on porous nickel. Such a combination of materials renders this system able to work both in dark and under solar light exposure, thus opening new perspectives for industrial-scale applications.

1. Introduction

The design of efficient devices for renewable energy requires a continuous effort for the development of new materials able to combine functional properties with both environmental and economic sustainability. In this field, titanium dioxide has been proved to be extremely promising for its high versatility, especially enhanced when used in form of nanotube arrays. Since their architecture is characterized by both a large internal surface area and a geometric and structural order, highly-ordered vertically oriented TiO_2 nanotube arrays allow excellent electron percolation pathways for vectorial charge transfer between interfaces, as reviewed by Frank et al. (2004). Moreover, TiO_2 nanotube arrays have been found to possess outstanding charge transport and carrier lifetime properties enabling a variety of advanced applications, including their use in sensors (Varghese et al. 2004, Mor et al. 2006), dye sensitized solar cells (Shankar et al. 2007 and 2008, Kuang et al. 2008), photocatalytic reduction of CO_2 under outdoor sunlight (Zhang et al. 2012, Habisreutinger et al. 2013), supercapacitors (Fabregat-Santiago et al. 2008), as anodic material in lithium-ion batteries (Dell'Era et al. 2013) and in biomedical related applications including biosensors, molecular filtration, drug delivery, tissue engineering (Popat et al. 2007, Peng et al. 2009). In their use as hydrogen sensors, they showed excellent photocatalytic properties and the ability to self-clean from contamination under exposure to ambient UV light, as described by Mor et al (2003). Mor et al. (2005) also reported that TiO_2 nanotube array based photoanodes, up to 6.4 μm in length, enhance the photocleavage of water, while more recently TiO_2 nanotube arrays have been used as a superior electrocatalyst for methanol oxidation (Liu et al. 2013) and for ethanol photoreforming (Ampelli et al. 2011). Furthermore, moving from the pioneering work published by Fujishima and Honda (1972), who proposed the use of *n*-type TiO_2 as a heterogeneous photoassistance agent for reaction in a wet photoelectric cell, the nanotube arrays have been widely exploited in hydrogen generation by water photoelectrolysis (Mor et al. 2005 and 2008, Grimes et al. 2007a). According to the system described in 1972, the electrode operates with maximum quantum efficiency upon irradiation with near ultraviolet light; the maximum quantum efficiency for the photoassisted electrolysis of water is obtained when an external potential is applied. In this contest, the nanotube array geometry appears to be an ideal architecture: under UV-spectrum illumination (320–400 nm), nanotube arrays 30 μm long demonstrate a photoconversion efficiency of 16.25% with a current density of 25 mA/cm^2. Under visible light AM 1.5 illumination (100 mW/cm^2), the titania nanotube array photoanodes generate hydrogen by water photoelectrolysis at a rate of 175 μL/h, with a photoconversion efficiency of 0.6% and a current density of about 1 mA/cm^2 (Shankar et al. 2007, Grimes et al. 2007a and 2007b, Lai et al. 2012), even enhanced in case of doped systems (Altomare et al. 2013). In the past years,

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our group has been involved in the synthesis of highly-ordered TiO_2 nanotubes for photocurrent generation (Mura et al. 2009). In this work, starting from the good UV photoconversion efficiency we obtained (Mura et al. 2010), we describe an electrochemical cell with an innovative design in which the anode consists of an array of TiO_2 nanotubes on porous nickel. Such a geometry allows to scale up the device and to exploit at the same time the features of a standard cell with the features of a photoelectrochemical device.

2. Experimental Part

2.1 Nanotubes growth

Titanium 99.6% (Goodfellow) with a thickness of 0.5 mm was cut into discs of 1.5 cm diameter. For nanotubes preparation, each disc was etched in a HF 5 vol% for 3 minutes, rinsed with distilled water and mounted in an electrochemical cell to show an active area of 1 cm^2. Anodization was carried out at a 60 V potential generated by a potentiostat/galvanostat (Solartron 1286) for 4 hours in ethylene glycol containing 0.4 wt% NH_4F and 1 wt% H_2O with Pt counter electrode. After the anodization, all the samples were rinsed in distilled water and dried at 60°C for 10 minutes. A heat treatment in a furnace (Lenton) in air at T = 580°C for 1 hour with a heating rate of 1°C min^{-1} allowed the crystallization of nanotubes in anatase form, which shows a higher photosensitivity.

2.2 Surface analysis

The morphology of the nanotubes was investigated by scanning electron microscopy (SEM) analysis performed using an AURIGA Zeiss Field Emission.

2.3 Photoanode preparation and measurements of photocurrent density

For the photocurrent experiments we used the plexiglas cell shown schematically in Figure 1. The cell geometry allowed to use a large photoanode, which was obtained by mounting16 discs of TiO_2 nanotubes (1 cm^2) on a 7 cm side foil of porous Ni (Figure 1), thus obtaining an active area for TiO_2 of 16 cm^2. The discs were simply fixed by applying a small pressure. As a counter electrode we used two foils of porous nickel (1 cm x 7 cm) juxtaposed to the photoanode. The cell, equipped with a plexiglas stopper, has suitable channels for the emission of H_2 and O_2, which do not have been quantitatively determined at this stage of the work. The photoanode was immersed in a KOH 1M solution and exposed to UV-Vis light source (Osram) placed at 5 cm of distance. This source has a spectrum with peak intensity in the UV-A region at 360 and 400 nm. The UV intensity, measured on the sample by a photo-Radiometer HD2302.0 (Delta OHM) over the spectral range 220–400 nm, is 13.0 mW cm^{-2}. Potentiostatic measurements were collected both in dark and under UV light upon 60 seconds of exposure.

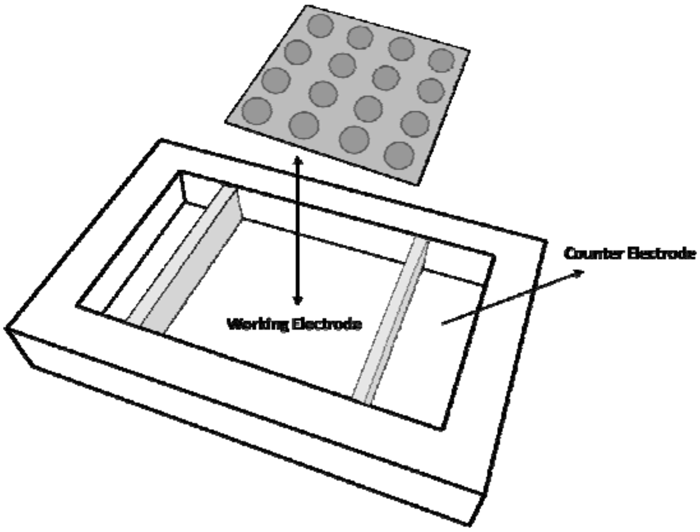

Figure 1: Schematic representation of the plexiglas cell and of the photoanode used for this work. The counter electrode is only 0.5 cm far from the working electrode. The cell has channels for electrical connections and to collect the gas, but they have been omitted in the scheme for simplicity.

3. Results and Discussion

3.1 Growth of the Nanotubes

SEM analysis shows that the nanotubes are highly oriented, well-ordered and separated, even though partially covered by a slight oxide layer, and definitely comparable to those grown in similar conditions (Figure 2), with an internal diameter in the range of 100-150 nm.

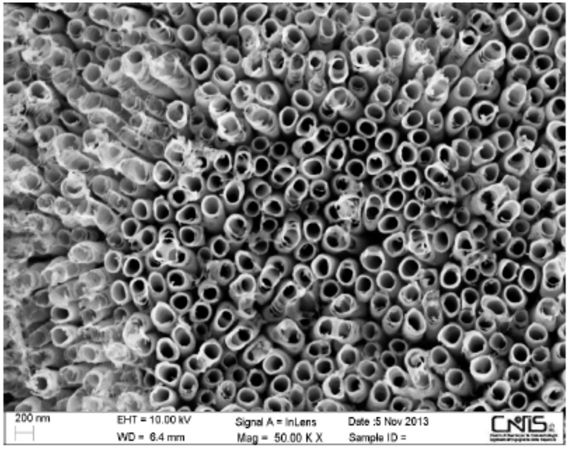

Figure 2: SEM image of the nanotubes obtained.

As reported in Figure 3 and in perfect agreement with our previous results, during the nanotubes growth the anodization current undergoes a sudden decrease, followed by a slight recover and the final achievement of a quasi-steady state value. Such a trend indicates rapid formation of a non-conductive thin oxide layer first, and local enlargement of the pores then. Finally, the system tends to establish an equilibrium between the continuous oxidation of metallic titanium and the dissolution of titanium dioxide, which leads to the nanotubes growth (Figure 3).For details on the nanotubes formation see Macak et al (2007), Grimes et al. (2007a), Mura et al. (2010).

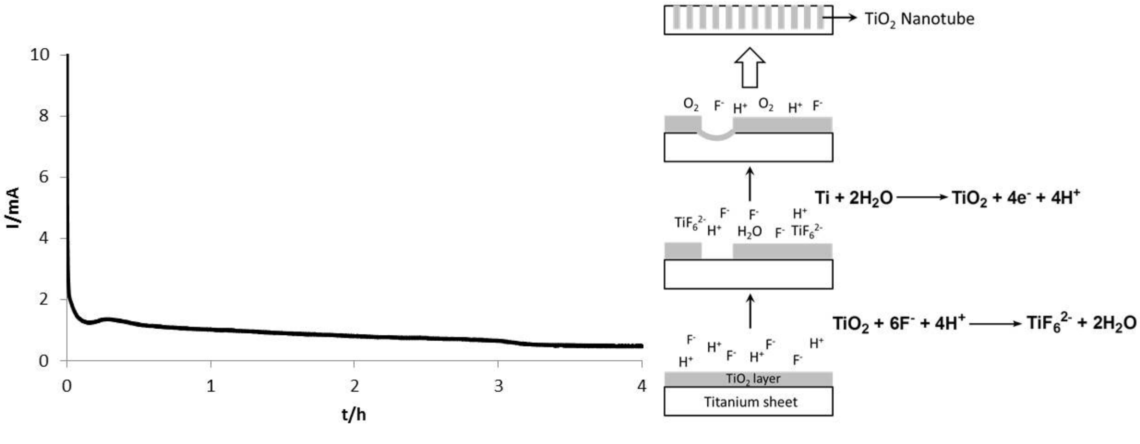

Figure 3: Trend of the current during the nanotubes growth via anodization (left) and schematic representation of the reaction leading to the nanotubes formation (right).

3.2 UV Photoconversion Efficiency and Advantages of the New Cell Design

UV photoconversion efficiency was measured for a single sample in a system similar to the one we previously described (Mura et al 2010). A comparison of the current values obtained in dark and under UV light after 60 seconds is reported in Figure 4. The TiO_2 nanotubes array allows obtaining water splitting at low values of potential. The electrode potential corresponding to the onset of electrolysis (detection of electrolysis products) in the case of single TiO_2 nanotubes array disc in dark is 0.52 V *vs* NHE, while under irradiation it is -0.55 V *vs* NHE. It is important to notice that the oxide layer sometimes observed at the top of the nanotubes does not interfere with the photoconversion and does not influence the anode efficiency.

Such a result, which is in perfect agreement with the results we already obtained in similar experimental conditions, can be considered our reference to quantify the efficiency of the new cell.

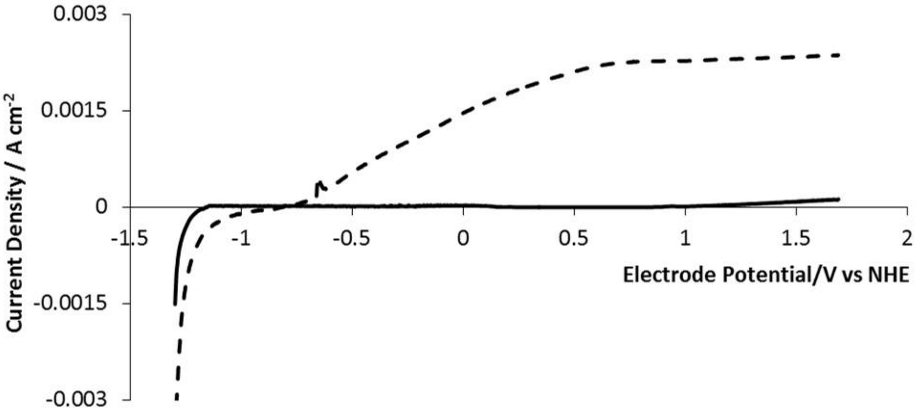

Figure 4: Voltammograms obtained at 20 mVs^{-1} using a single TiO_2 nanotubes array disc (1 cm^2) in dark (solid line) and under UV light (dashed line).

As for the single disc, the multiple photoanode (Figure 1) has been tested both in dark and under the light, applying increasing voltage values and measuring the current generated after the system reached steady state, i.e. after 60 seconds. No electrolysis was detected at voltage values lower than 1.4 V. In the dark, as the voltage increases, a current is generated by the porous nickel. Under UV light exposure a photocurrent is generated by the TiO_2 nanotubes, thus using Ni-TiO_2 electrode it is possible to obtain water splitting working at lower voltage values. In this case we have onset of electrolysis equal to 1.57 V in dark and 1.32 V under irradiation. Such values are of course referred to cell voltage and not to electrode potential, so they cannot be directly compared to the values obtained for the single disc. At this stage of the work, we can deduce that there is no electrolysis at voltage values lower than 1.4 V on the basis of the currents. Obviously, at higher voltage values we observed H_2 and O_2 evolution, but we did not quantified them.

In Figure 5, the comparison of the current values obtained using the multiple photoanode either in dark or under light at increasing voltage (up to 2.0 V) is reported. From the plot it is possible to deduce that the current generated under UV light is always higher than the one generated in the dark. In particular at 1.5 V the current produced is about 10 fold higher than the one obtained in absence of light (0.023971 A *vs* 0.0021 A), thus demonstrating the efficiency of the system. Moreover, at 1.6 V the photocurrent obtained is 16 fold higher than the one produced using a single disc in a small cell. Unfortunately, since for the single disc we consider the electrode potential while for the cell we can only take into account the cell voltage, such a comparison exclusively has a purely qualitative meaning. Actually, for the cell the overall overpotential should be undoubtedly considered, but it is hard to estimate. Nevertheless, this result shows the scale up of the device, as well as the possibility to extend even more the cell size.

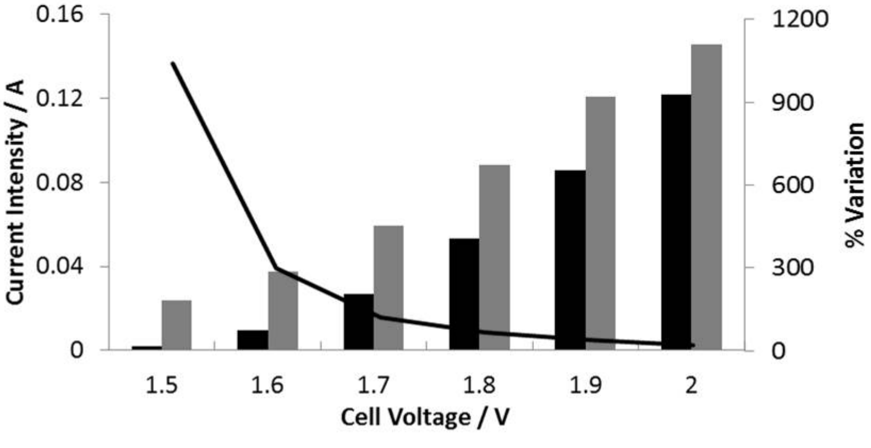

Figure 5: Current intensity vs cell voltage in dark (black bar) and UV (grey bar). The trend of the values percentage variation is reported as well (black line).

4. Conclusions

The fabrication of a cell with an innovative design allowed us to use a photoanode constituted by an array of TiO_2 nanotubes on porous nickel. Here we demonstrated that using this cell a photocurrent can be generated, so that it is possible to obtain water splitting at values lower than in the dark. Showing an active area 16 fold larger than a single disc in a small cell, at 1.6 V it allows obtaining a 16 fold higher photocurrent. This result shows the scale up of the device, as well as the possibility to extend even more the cell size. At 1.5 V the current produced is about 10 fold higher than the one obtained in absence of light, thus demonstrating the efficiency of the system. Moreover, containing both Ni and TiO_2 nanotubes, this anode is able to work both in dark and under solar light exposure, which makes it extremely versatile for industrial-scale applications.

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