TiO$_2$ - based systems for photoelectrochemical generation of solar hydrogen

Teofil D Silipas$^1$, Emil Indrea$^1$, Simina Dreve$^1$, Ramona-Crina Suciu$^1$, Marcela Corina Rosu$^1$, Virginia Danciu$^2$, Veronica Cosoveanu$^2$ and Violeta Popescu$^3$

$^1$National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath, 400293 Cluj-Napoca, Romania

$^2$Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos, 400028 Cluj-Napoca, Romania

$^3$Technical University of Cluj-Napoca, Department of Materials Science and Engineering, 103-105 Muncii, 400641 Cluj-Napoca, Romania

E-mail: dan.silipas@itim-cj.ro

Abstract. In the present work our attention was focused on the obtaining photoelectrodes for photoelectrochemical cell that incorporate two electrodes, one of which has been titania (TiO$_2$) coated on a transparent conducting oxide (TCO), referred to as the primary electrode and the other, the counter electrode, a non-corrosive metal such as a thin layer of platinum. A thin layer of a nanoporous TiO$_2$ semiconductor was deposited onto a sheet of ITO conducting glass (sheet resistance ~ 30 $\Omega$ cm$^{-2}$). Several complementary investigation techniques like BET, SEM and XRD were used to follow the influence of the reactants molar ratio and thermal treatment on the TiO$_2$ photoanode. The nanocrystalline TiO$_2$/ITO conducting glass electrode seems to be a promising photoanode in a photoelectrochemical cell for hydrogen generation by water splitting.

1. Introduction

Hydrogen generated from the splitting of water using solar energy, termed solar-hydrogen, represents a sustainable fuel that is environmentally safe [1]. There is a growing awareness that titania (TiO$_2$) and TiO$_2$-based oxide systems are the most promising candidates for the development of photoelectrodes for photoelectrochemical cell (PEC) for solar-hydrogen production [1]. The PEC cell is equipped with a single photoelectrode (photoanode) and cathode, both of which are immersed in an aqueous electrolyte. Exposure of the photoanode to sunlight results in charge transport within the PEC and evolution of gases at the photoanode and cathode. The oxygen energy level (O$_2$/H$_2$O) should be above the valence band of the photoanode in order to allow electron transfer and, for the same reason, the hydrogen energy level (H$^+$/H$_2$) should be below the Fermi level of the metal cathode (or the conduction band of a semiconducting photocathode).

The most critical issue in the development of solar-hydrogen is the development of a special class of new photosensitive materials for efficient and clean conversion of solar energy [2]. The development of these materials, which must exhibit sophisticated functional properties, will require
the application of the most recent progress in the science of material interfaces and the solid state science. Because of their ultra low density and high surface area, TiO$_2$ aerogels are attractive for applications in solar energy conversion [3, 4].

In this work, we investigate the preparation of a novel nanocrystalline TiO$_2$/ITO conducting glass electrode that seems to be a promising photoanode in a PEC for generation of solar hydrogen. Nanocrystalline semiconductor films are constituted by a network of mesoscopic TiO$_2$ particles which are interconnected to allow for electronic conduction to take place. The nanoporous TiO$_2$ film was investigated by several complementary techniques like SEM and XRD.

2. Experimental

2.1. Samples preparation

TiO$_2$ gels were prepared with the acid (HNO$_3$)-catalyzed sol-gel method by using titanium isopropoxide (TTIP), HNO$_3$, EtOH and H$_2$O with different molar ratios. The gels were allowed to age in the mother liquor for a week to several months. Before drying, the gels were successively washed with excess of fresh alcohol, at least four times. TiO$_2$ aerogels were obtained by supercritical evacuation of solvent from gels prepared by acid-catalyzed sol-gel method [5].

2.2. Electrodes preparation

The nanocrystalline titania films photoelectrodes for PEC preparation involves the production of a titanium dioxide suspension and then the application of this suspension onto conducting ITO glass. The titania slurry was made from a mixture of: 2 g TiO$_2$ powder, 4 ml of distilled water, 5 drops of Triton X-100 (Sigma-Aldrich) and 0.2 ml of acetylacetonate (Sigma-Aldrich). By adjusting the quantity of Triton X-100 and water the desired viscosity was obtained. This slurry was mixed using a mortar and pestle until uniform. The solution was then applied to a piece of ITO conducting glass (sheet resistance ~ 30Ω cm$^{-2}$) and a semiconductor film was produced. The application technique was the doctor blade method. Greater thickness of the TiO$_2$ film is produced by repeating the doctor blade method with drying at 50°C in between coats. Repeating the doctor blade method with calcining between each coat can produce multiple coats. This is called repetitive combustion coating technique.

In our case the first layer was produced utilizing commercial nanostructured TiO$_2$ (Degusa P25) and the second one utilizing TiO$_2$ aerogel suspensions. The TiO$_2$/ITO conducting glass electrode is then dried at room temperature for 45 min and cut with a scalpel into a 0.5 x 0.5 cm square. The working electrode is then calcined at 450°C for 2 h.

2.3. Samples measurements

The SEM images were collected with a JEOL 7601F electronic microscope with a field emission tip that operated at 10 kV.

The specific surface area of the as prepared samples was determined using Brunauer-Emmett-Teller (BET) method, in a partial pressure range of 0.05 < P/P$_0$ < 0.3. Krypton adsorption was carried out at 77 K. Before each measurement, the samples were heat-cleaned at 333 K for 2 h.

The X-ray diffraction patterns were obtained using a standard BRUKER D8 Advance X-ray diffractometer, working at 40 kV and 40 mA. The Cu K$_\alpha$ radiation was monochromatized with a germanium monochromator placed in the incident X-ray beam. The data of the X-ray diffraction patterns were collected in a step-scanning mode with $\Delta$2θ = 0.01$^\circ$ steps.

3. Results and discussion

3.1. TiO$_2$ aerogels

Titanium dioxide is the most commonly used wide band-gap semi-conductor as photoelectrodes for solar-hydrogen [1]. The nanoporous TiO$_2$ aerogel layer has a high specific surface area. The increases of the contact area of the photoelectrodes with light raise the light energy conversion efficiency of the
cell. Through scanning electron microscopies (SEM) the morphology of the TiO$_2$ aerogel was determined to have two length scales, one for crystalline nanoparticles and other for mesoaggregates constituted by anatase closely packed (figure 1) [6].

![Figure 1. SEM image of the as prepared TiO$_2$ aerogel (sample T5). Note that the mesospheres dimension is of about 30 nm.](image)

The TiO$_2$ aerogels were heat-treated at 400, 500 and 600ºC for 2 h under argon atmosphere and these aerogels were referred to as T4, T5, and T6, respectively. The X-ray powder diffraction technique was used for structural characterization of the TiO$_2$ heat-treated aerogels.

The microstructural information obtained by the single X-ray profile Fourier analysis of the TiO$_2$ heat-treated T4, T5, and T6 TiO$_2$ aerogels are: the D$_{\text{eff}}$ (nm) effective crystallite mean size, the $\langle \varepsilon^2 \rangle_{\text{hkl}}^{1/2}$ root mean square (rms) of the microstrains averaged along [hkl] direction, and dislocation density $\rho$ [7, 8]. Dislocation density $\rho$ (lines m$^{-2}$), as defined by Hirsch [9] is the length of dislocation lines per unit volume of the crystal.

Since both the crystallite size and residual strain are effects of the dislocation networks in the structure, the dislocation density can be expressed as [9]:

$$\rho = \frac{\sqrt{12} \langle \varepsilon^2 \rangle_{\text{hkl}}^{1/2}}{(D_{\text{eff}} \cdot d)}$$

where $\langle \varepsilon^2 \rangle_{\text{hkl}}^{1/2}$ is the rms of the microstrains, D$_{\text{eff}}$ (nm) is the effective crystallite mean size and d(nm) the interplanar spacing.

The Warren-Averbach X-ray profile Fourier analysis of the (200) and the (220) TiO$_2$ anatase peak profiles were processed by a XRLINE [8] computer program. Table 1 summarizes the microstructural parameters of the T4, T5, and T6 samples. It can be observed that higher temperature treatment favor the growth of larger crystallite size and lower crystalline imperfections.

| TiO$_2$ aerogel sample | D$_{\text{eff}}$ [nm] | $\langle \varepsilon^2 \rangle_{\text{hkl}}^{1/2} \times 10^3$ | $\rho \times 10^{14}$ [lines m$^{-2}$] | BET surface area [m$^2$/g] |
|------------------------|------------------------|---------------------------------|---------------------------------|-------------------|
| T4                     | 4.9                    | 3.432                           | 13.63                           | 685               |
| T5                     | 9.1                    | 0.819                           | 1.75                            | 593               |
| T6                     | 14.8                   | 0.609                           | 0.81                            | 466               |

3.2. TiO$_2$ nanocrystalline electrode

The nanocrystalline TiO$_2$/ITO conducting glass electrode for photoelectrochemical generation of solar hydrogen was prepared by repetitive combustion coating. The first compact layer was produced utilizing commercial nanostructured TiO$_2$ (Degussa P25) and the second one utilizing TiO$_2$ aerogel suspensions. The TiO$_2$/ITO conducting glass electrode is then dried at room temperature for 45 min and annealed at 450ºC for 2 h.

The X-ray powder diffraction technique was used for structural characterization of the nanocrystalline TiO$_2$/ITO conducting glass annealed photoelectrode [10].
X-ray diffraction pattern of the nanocrystalline TiO$_2$ photoelectrode suggests the formation of a major anatase-like crystalline network structure (83.77 vol %) with $a = b = 0.378(4)$ nm and $c = 0.951(4)$ nm lattice parameters and a minor rutile-like crystalline phase (16.23 vol. %) with $a = b = 0.459(9)$ nm and $c = 0.295(6)$ nm lattice parameters, quite close to the ASTM reported values. Unit cell parameters and TiO$_2$ anatase/rutile crystalline phase composition were calculated through Rietveld refinement using the PowderCell software [11].

The microstructural parameters of the nanocrystalline TiO$_2$ photoelectrode after heating two hours at 450ºC showed an average size of the TiO$_2$ anatase of 5 nm and a root mean square of the microstrains $<\varepsilon^2>^{1/2} = 8.2 \times 10^{-2}$.

4. Conclusions
The common strategy of research on photoelectrodes for photoelectrochemical generation of solar-hydrogen involves the application of TiO$_2$-based materials that are modified using several procedures, including TiO$_2$ aerogels that combine the aerogel properties with the photocatalytical property of the titania.

The nanocrystalline TiO$_2$/ITO conducting glass electrode seems to be a promising photoanode in a PEC for hydrogen generation by water splitting.

Structural and dimensional investigations of TiO$_2$ aerogels heat-treated for two hours at temperatures between 400 and 600ºC have been performed by means of XRD techniques. Correlations between the morphology and spectral characteristics of the annealed aerogels have been evidenced by assuming the occurrence of the finite size effect of nanocrystallites.

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