

Nano-engineered materials for H₂ production by water photo-electrolysis

C. Ampelli, R. Passalacqua, S. Perathoner, G. Centi

Department of Industrial Chemistry and Materials Engineering, University of Messina
Salita Sperone, 31 - I-98166 MESSINA (ITALY)

Nano-engineered materials based on TiO₂/Ti are proposed as suitable photo-catalysts in studies of novel processes for energy production by renewable and non-polluting sources. The samples, prepared by anodic oxidation, were tested in a laboratory scale photo-reactor, designed on purpose to maximize the catalytic performance of thin substrates in H₂ evolution by water splitting. The voltage applied during the anodization influences the mean dimension of the nanostructures, their wall thickness and degree of packing, and also their photo-catalytic performance. The surface characterization (made by FESEM, TEM, GAXRD, UV-Vis diffuse reflectance and current-time transients during the anodization process) revealed amorphous titania in the nano-structured thin films, the anatase phase appearing only after annealing up to 500°C. Photo-catalytic results showed that H₂ production strongly depends on the quantity of titania anodized on the Ti substrate.

1. Introduction

In the last decades photo-catalysis studies have been increased for their potential applications in energy production by renewable and non-polluting sources. The interest in photo-catalysis became more concrete when the direct conversion of solar energy into chemical energy via photochemical routes has been found to be more effective in heterogeneous systems. The industrial application of these photochemical reactions, however, requires not only the scientific knowledge of the photochemistry of the reaction, but also a rational understanding of the engineering aspects of the photochemical process (Yue, 1985).

In this work a modular photochemical system was developed in order to evaluate the photo-catalytic performance of nano-structured titania (TiO₂) thin films, prepared by anodization, in hydrogen evolution by water splitting. The photo-reactor was designed by taking into account the particular heterogeneous essence of the process: photo-catalytic substrates, prepared as thin films, should have well designed characteristics, such as good absorption of photons of right energy, a long lifetime of activated states, a good adsorption of reactants, and a relatively easy desorption of products; but in order to maximize the photo-catalyst activity, a correct design of the photo-reactor should also be adopted, in terms of geometrical configuration and operating conditions. The photo-reactor (150 ml), constructed in Pyrex, was equipped with a side quartz window in the

way of UV-visible rays, coming from an external lamp, reaching on radial direction the photo-catalytic-film hanging from the reactor head and immersed into the water.

The highly ordered nano-structured titania thin films were prepared by controlled anodic oxidation of titanium foils. The essence of method may be described as a reconstruction of a thin titania layer (formed initially by oxidation of a titanium foil) which occurs under the application of a differential potential which creates also strong local electrical fields at the surface. The 1D nano-structured array obtained, in shapes of nanotubes or nanocoils, may significantly modify the adsorption of reactants and stabilization of transition state complexes. The possibility to control of the catalyst multi-functionality through the ability of controlling the nano-architecture represents an interesting opportunity to bridge the material gap in catalysis between ordered crystals used in surface studies and real catalysts (Ampelli et al., 2008).

2. Photo-reactors

The design of a photo-reactor is based on a careful evaluation of the factors which can influence the reactor performance: light source, geometrical configuration, material of construction, heat exchange and mixing and flow characteristics (Yue, 1985).

The irradiation source determines the range of wavelengths of the radiation in the electromagnetic spectrum. The choice of the most suitable lamp can be made by evaluating the reaction energy requirement with respect the specification of the lamps. If solar energy use is being considered, it should be noticed that the ultraviolet percentage in sunlight is quite limited (<4%). Moreover the light source must be mounted within a glass sheath or some suitable optical assembly to give a certain pattern of irradiation.

In choosing the reactor geometrical configuration it is necessary to determine the optical path of the light within the reactor, in a way to attain the maximum benefit from the pattern of irradiation and a good absorption of light photons. In conventional reactors the conversion for a given reactor volume is independent of geometry, if the effects due to flow characteristics are neglected. However, for photo-reactors, reactor geometry and the spatial relation between reactor and light source are vitally important. The three most commonly used geometries are: cylindrical, parallel and annular. In all the cases the irradiation occurs normal to the reactor surface.

The choice of material of construction for photo-reactors is severely limited by the requirement of light transmission. The choice of the designer is usually limited to different types of glass: optical glass, Pyrex glass, Vycor glass and quartz. The last generally gives the best performance in terms of light transmission, but is the most expensive. At short wavelengths, under 300 nm, quartz is the only appropriate material. The thickness of the reactor wall also diminishes the light transmission; this fact limits both the size of the reactor and the range of operating temperature and pressure.

Heat exchange is another important factor to take into account, specially in gas-solid systems. Since glass has low thermal conductivity, suitable devices must be designed to remove the heat generated by the lamp.

Mixing and flow characteristics must be carefully considered; they strongly depend on the phases involved in the process. For heterogeneous photo-reactions, contact between reactants, photons and catalysts must be facilitated, for example with agitation of the

reacting mixture by means of a stirrer, in a way to attain a high degree of back-mixing (Cassano et al., 2005).

3. Experimental

3.1 Preparation of the catalysts

Nano-structured thin films were prepared by anodizing titanium foils (Alfa Aesar, 30 x 40 mm) of thickness 2.0 mm or 0.025 mm and purity 99.5% and 99.2% respectively. Prior to any electrochemical treatment the foils were sonicated in distilled water, and then in isopropyl alcohol for 10 min each. Then they were dried in air. Anodic oxidation was carried out in a stirred electrochemical cell working at room temperature. An Autolab PGSTAT30 potenziostat/galvanostat in a two-electrode set-up was used to apply different anodizing voltages 10, 15 and 20 V for times ranging from 20 to 45 min, typically 45 min. The electrolyte consisted of 0.5-3.5% wt. HF in double distilled water and a platinum electrode served as the cathode. The geometry of the cell was optimized to obtain the formation of a titania nano-structured array. The cell was characterized from an electrolyte volume of about 200 ml maintained under continuous stirring, a distance of 5 cm between the electrode with the anode in the form of a slabs of 30 mm x 40 mm and the cathode of a Pt wire. The initial voltage (6 V) was maintained for 1 s and then a linear ramp of about 1 V/min was applied up to the final voltage (in the 10–20 V range) which was maintained constant. The pH was 4.0 in all tests and adjusted using NH_4OH aqueous solution. AA and XRF were used to check the purity of the solutions and analyze the amount of Ti dissolved in solution after anodization. The samples were cleaned with deionized water at the end of the anodization process and then dried overnight. The annealing of the nano-structured substrates was made at 450°C in air for 6 h with heating and cooling rates of 2°C/min.

3.2 Testing experimental apparatus

The apparatus constructed for the photo-catalytic experiments consists of an UV-visible light source, a photo-reactor, a magnetic stirrer, a flow mass controller and a gas chromatograph.

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, which serves to remove the heat coming from the lamp. The photo-reactor (150 ml), constructed in Pyrex and equipped with a side quartz window, is placed on a magnetic stirrer at a fixed distance from the lamp housing (~ 20 cm). The nano-structured film was hanged by a glass rod and immersed into the reacting solution parallel to the side quartz window. The lamp is kept constant at 300 W using either a cut-off below 400 nm filter or a solar light-simulating filter. The analysis system consisted of a gas chromatograph (GC Agilent 7890) equipped with a molecular sieve 5A column and a TCD detector. Samples were automatically injected into the gas chromatograph every 30 min to determine the H_2 concentration of the gas stream. Argon was used as carrier gas. Before the experiment the photo-reactor was purged with a 100 ml/min of Ar for 30 min. Then the flow was diminished to 10 ml/min and the irradiation was started.

This configuration permits the determination of the evolved H_2 from photo-induced H_2O splitting. Aqueous solutions of hydrolysis products of ligno-cellulose or waste

solutions from biomass fermentation (e.g. diluted solutions containing bioethanol) can also be used to enhance H_2 formation by photo-reforming. For this reason ethanol was used as model reactant in some testing experiments.

By substituting the photo-reactor with a particular photo-electrolytic cell, a new configuration can be obtained, in order to separate H_2 and O_2 into two different gas streams (Matsuoka et al., 2007). The new system also contemplates the in-situ measurement of the generated current by the photo-electrolytic cell. The cell, constructed in Plexiglas and equipped with a quartz window, is divided in two semi-cells by a photo-catalytic disc formed by three layers: a layer of nano-structured TiO_2/Ti prepared by anodization, a Nafion membrane for separation and H^+ transport and a layer of carbon cloth with 20% of platinum. Water circulates continuously between each semi-cell and the outer water reservoirs, immersed in a constant temperature bath. The reaction mechanism is the following: the light rays cross the quartz window and reach the nano-structured layer where photo-generated electrons and holes are formed and O_2 can evolve (anode); the protons pass through the Nafion layer and reach the other semi-cell (cathode) where the production of H_2 occurs on Pt. The potentiostat-galvanostat (AMEL 2049) is used to measure the photo-current generated between the two semi-cells. The principle of operation of the system is illustrated in Fig.1.

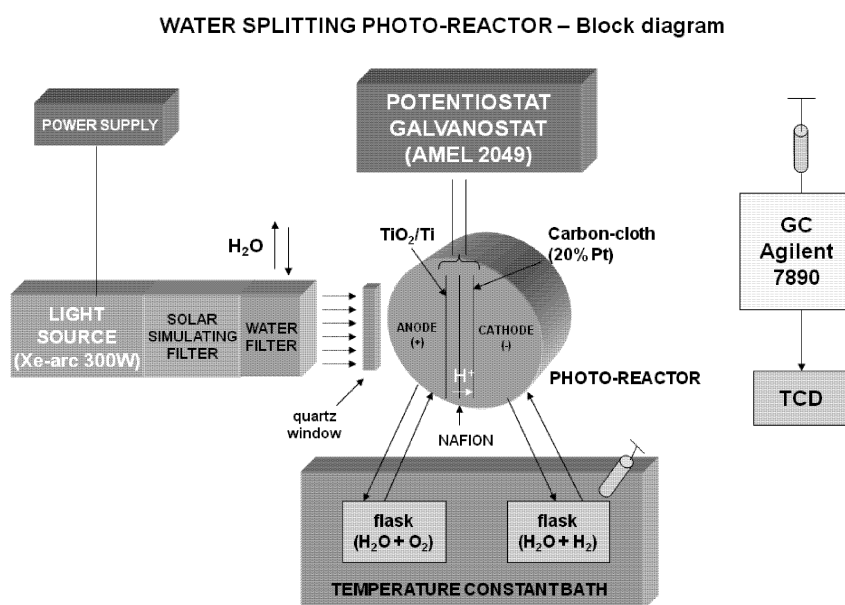


Figure 1: Water splitting PhotoElectroChemical (PEC) Reactor – Block diagram.

4. Results and discussion

The influence of the anodization voltage on the nano-structure of titania films is shown in Fig. 2 which reports FESEM images at lower and higher magnification of three samples prepared by anodization. Images a1–a2 refer to the sample prepared at bias voltage of 10 V, images b1–b2 at 15 V and images c1–c2 at of 20 V. The images at lower magnification (a1, b1, c1) show that large uniform nano-structured areas could be obtained and that TiO_2 particles are not present on the surface. The surface of the Ti foils used was not perfectly flat and thus a moon-like surface could be observed with relatively large depressions. However, an uniform nanostructure (ordered array of titania nano-tubes) is present in all these regions. No preferential orientations at grain boundaries could be observed. The images at higher resolution in Fig. 2 (a2, b2, c2) evidence in all cases the presence of an ordered array of nano-tubes. Increasing the anodization voltage, the mean diameter of these nano-tubes increases from about 30 nm (10 V) to 50 nm (15 V), and 70 nm (20 V). The diameter of nano-tubes is rather uniform. Wall thickness of these nano-tubes is few nanometers and slightly increases on increasing the anodization voltage. The density of packing also slightly increases. A closer inspection reveals that these nano-tubes are separated each other, with reduced contact points between them (see Fig. 2c2).

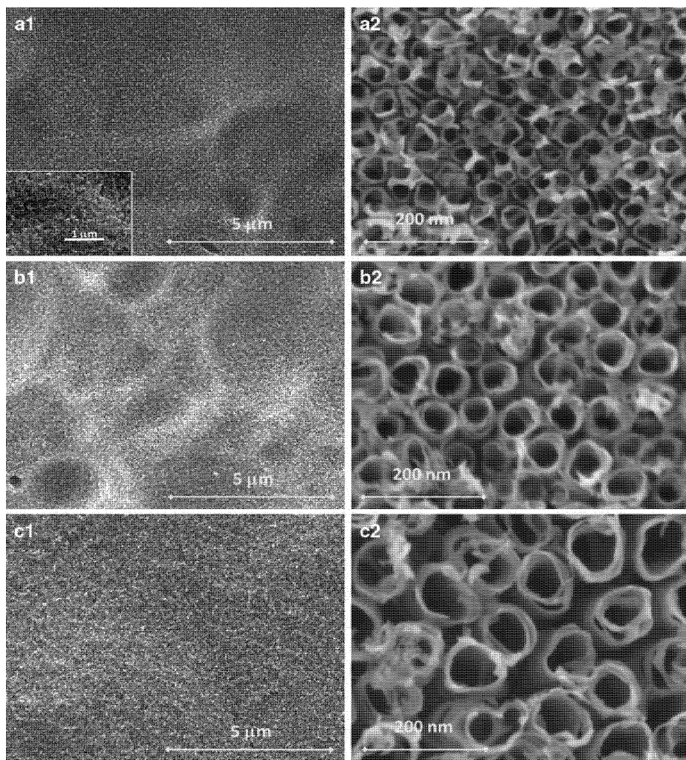


Figure 2: FESEM images at low and high magnifications of nano-structured samples synthesized under different voltages: (a1,a2) 10 V, (b1,b2) 15 V, and (c1,c2) 20 V.

All the substrates were tested using the Pyrex photo-reactor in order to evaluate the H₂ evolution in the photo-reforming of an initial water solution of 10% vol. ethanol. Results showed a dependence of the H₂ production on the potential of anodization during the preparation. Fig.3 shows a comparison between the performance of a nano-structured titania thin film anodized at 20 V and a not-ordered substrate of titania powder deposited on Ti.

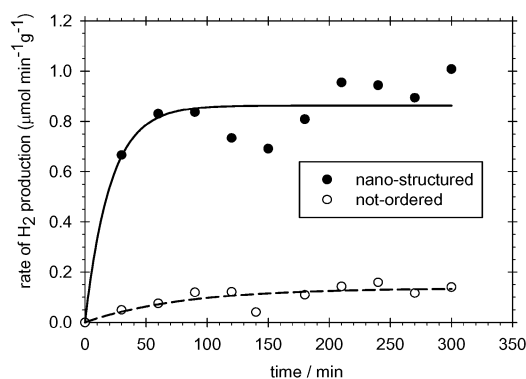


Figure 3: Rate of H₂ production vs. time for a nano-structured titania thin film anodized at 20 V and a not-ordered titania film.

It is possible to note that the use of a nano-structured substrate increases the H₂ production of about 1 order of magnitude. The nano-tubular structures, in fact, increase the light harvesting and the efficiency of charge separation by minimizing the grain boundaries, so that they not only increase the light absorption, but also show a much higher conversion efficiency than standard films formed by TiO₂ nano-particles. Photocatalytic results also showed that hydrogen evolution strongly depends on the film thickness of titania anodized on the Ti substrate. Work is in progress to synthesize a thicker or a multi-layer nano-structured film by anodizing at higher voltage (60-100 V) and for a longer period of time.

Acknowledgments: Financial support from the EU under the project NATAMA (NMP3-CT-2006-032583) is gratefully acknowledged.

References

- Ampelli C., Passalacqua R., Perathoner S., Centi G., Su D.S. and Weinberg G., 2008, Synthesis of TiO₂ Thin Films: Relationship Between Preparation Conditions and Nanostructure, *Top. Catal.*, 50 (1-4), 133-144.
- Cassano, A., Alfano E. and Orlando M., 2005, Design and analysis of homogeneous and heterogeneous photoreactors, *Chem. Eng.*, 125-169.
- Matsuoka M., Kitano M., Takeuchi M., Tsujimaru K., Anpo M. and Thomas J.M., 2007, Photocatalysis for new energy production, *Catal. Today*, 122(1-2), 51-61.
- Yue P.L., 1985, Introduction to the modelling and design of photoreactors, *Photoelectrochemistry, Photocatalysis, and Photoreactors: Fundamentals and Developments*, 527-548, Ed. Schiavello, M., Kluwer.