

## Photo corrosion of titania nanotubes within water splitting reaction

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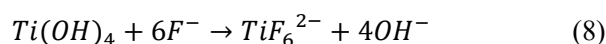
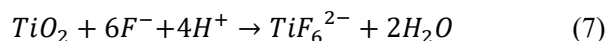
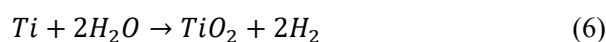
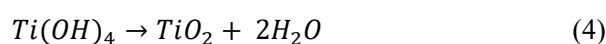
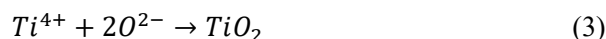
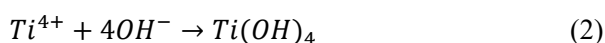
### ABSTRACT

Titania nanotubes (TNT) prepared by anodization of Ti foils were used for water splitting in a standalone cell. The concentration polarization between the anode side (1M NaOH) and cathode side (0.5 M H<sub>2</sub>SO<sub>4</sub>) ensured that the water splitting reaction could take place with no external bias and separate H<sub>2</sub> and O<sub>2</sub> evolution could be achieved. The destruction of TNT structures under 365 nm UV irradiation as well as the absence of the stoichiometry between the anodic and cathodic gas collectors indicates the limits of the stability of TNT structures under these conditions.

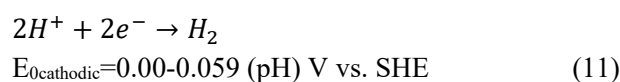
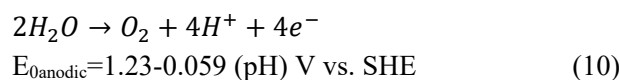
**Keywords:** TiO<sub>2</sub>, Photocatalysis, Solar energy materials, Corrosion, Instability, Surfaces.

### 1. Introduction

TiO<sub>2</sub>-based photocatalysts were widely investigated for water-oxidation and water-reduction half reactions since the first report in 1972, when TiO<sub>2</sub> has been shown to be active in photoelectrochemical water oxidation by Fujishima and Honda [1]. The absence of oxygen evolution during photocatalytic water splitting using TiO<sub>2</sub> has been acknowledged since then [2]. TiO<sub>2</sub> is regarded as stable under mild conditions (*i.e.*, room temperature and near atmospheric pressure). While using TiO<sub>2</sub> as a suspension in water is common [2,3], this method has the drawback of producing a mixture of H<sub>2</sub> and O<sub>2</sub>. In addition to gas separation problems, back reaction of H<sub>2</sub> and O<sub>2</sub> in the suspension to produce H<sub>2</sub>O decreases the efficiency of the photocatalysis. Among many alternative designs, the H cell proposed by Anpo Group [4,5], based on Fujishima and Honda reactor [1], was selected to test the performance of titania nanotubes electrochemically grown on titanium foils in aqueous acidic electrolyte. It is believed that Ti metal oxidizes to form a thin oxide layer and then TNT on the Ti metal at the solid-liquid interface under applied voltage according to reactions 1-9.



In this design, hydrogen and oxygen evolution is separated using a proton conducting membrane and a conducting foil between anodic and cathodic reaction chambers according to reactions 10-12.



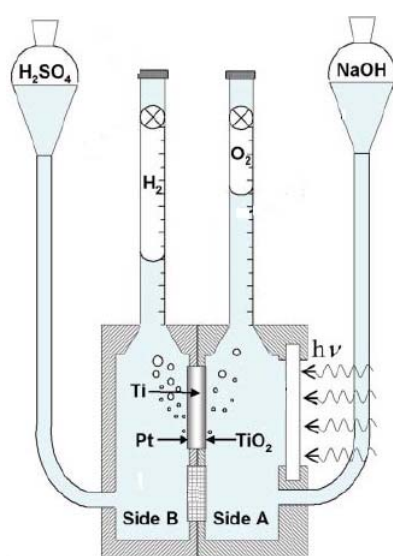
The device is a standalone system (*i.e.*, no external bias applied) with two cells for the separate evolution of H<sub>2</sub> and O<sub>2</sub> and can be considered as a short circuited H-type cell, the electrodes being the two sides of a titanium foil.

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The mechanism by which  $H_2$  and  $O_2$  evolution takes place in separate chambers is depicted in Fig. 1. Photogenerated holes on the illuminated side (anode; reaction 10) of the electrode oxidize  $OH^-$  ions form  $O_2$  while photoelectrons are transported to the cathode side and reduce  $H^+$  ions to form  $H_2$  (in dark side; reaction 11). The excess charge accumulated on one side is compensated by the cation transport through the Nafion membrane (acting like a salt bridge). In this report, we present our results whereby a porous  $TiO_2$  nanotube layer, supported on a Ti foil, is destroyed under conditions designed for water splitting. The results indicated how the efficiency of photo catalysts decreased in reactions in long time applications because of photo corrosion of titania. This phenomenon was not calculated in kinetic and efficiency calculation of other researchers.

## 2. Experimental

A Ti foil ( $40 \times 40 \times 0.25$  mm<sup>3</sup>, with a narrow tail extending out of the solution for electrical contact) was anodized in a 1 M  $NH_4H_2PO_4$  + 0.5 wt%  $NH_4F$  aqueous solution (powder  $NH_4F$ : Merck 98.0%, powder  $NH_4H_2PO_4$ : Merck 99.0%) and a Pt foil ( $35 \times 50$  mm<sup>2</sup>) was used as the counter electrode. A custom-made high voltage DC source was employed in the anodization process. In a two-electrode configuration, +20 V was applied to the anode relative to the cathode. The anodization parameters were thus identical to the ones used by Ghicov *et al.* [6]. The titanium foil was cut from a larger commercial foil (Aldrich 99.7%) using a pair of standard scissors and washed with acetone, ethanol and DI water, respectively.



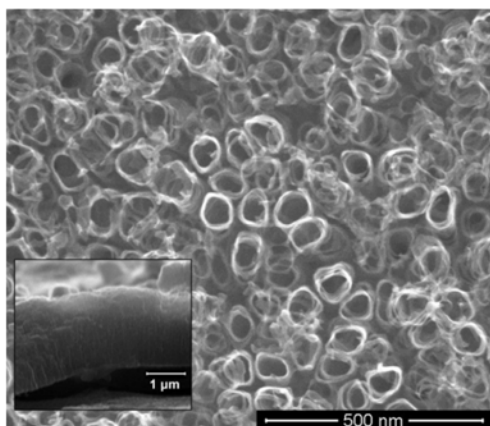
**Fig. 1.** Scheme of the processes that are expected to take place inside the photocatalytic cell.

Anodization was carried out immediately after cleaning. On one side of this anodized and air dried foil, to enhance the efficiency of photoreaction in near UV-Vis range in reactor, Pt was loaded by dropping 1 mL of 0.003 M ( $Pt^{2+}$  ion) solution (prepared using  $Pt(NH_3)_4Cl_2 \cdot H_2O$  salt, 56.4 wt% Pt, Alfa-Aesar). The foil with Pt solution impregnated on one side was annealed in a tubular furnace under air flow with a heating rate of 2 °C/min up to 450 °C for 2 hours, and was slowly cooled inside the furnace. The samples used for XRD were prepared separately. Pt loading per area was approximately one order of magnitude higher for the sample used for XRD than for the sample used in the water splitting cell.

Two-sided electrode prepared as such and a Nafion membrane was placed between two 10 mm thick PMMA plates. The holes allowed 9.1 cm<sup>2</sup> of the foil and 1.5 cm<sup>2</sup> of the membrane to be exposed to the surrounding medium. O-rings were used at the PMMA/membrane and the PMMA/foil contacts to prevent leakage. The PMMA plates were pressed into each other by using metal bolts in order to fasten the electrode and the membrane. On the two sides of this assembly, two identical quartz cells were placed. O-rings were used at the PMMA/quartz contacts as well. The side of the plain  $TiO_2$  nanotubes is identified as the anode and the side of the Pt-loaded  $TiO_2$  nanotubes as the cathode side. The anode side of the cell was filled with 1 M NaOH and cathode side with 0.5 M  $H_2SO_4$ . The Nafion membrane was prepared according to a procedure known in the literature [7]. The volumes of the evolved gases were measured via the displacement of water in 1 mL burettes, connected to the quartz cells with ultra-torr fittings. The cell was illuminated from a ~15 cm distance with a UVP B-100AP model 365 nm long wave UV lamp equipped with a beam directing funnel. Light intensity is specified as 21.7 mW/cm<sup>2</sup> at 2 inches away from the source. A Rigaku X-ray diffraction with a Cu target (30 kV, 15 mA) was used for the XRD measurements with a scan rate of 2 degrees/min. Scanning Electron Microscopy images were taken with a QUANTA 400F Field Emission SEM instrument.

## 3. Results and Discussion

The SEM images of the anodized surfaces are shown in Fig. 2. The size and shape of the nanotubes are very similar to the original report of the method used in this study [6]. The average tube diameter is estimated as 75 nm and the average tube length is ~2 μm. These values correspond to a tube density of  $4.6 \times 10^9$  tubes/cm<sup>2</sup>. The inner surface area of the tubes is calculated to be ~20 times larger than the underlying flat surface.



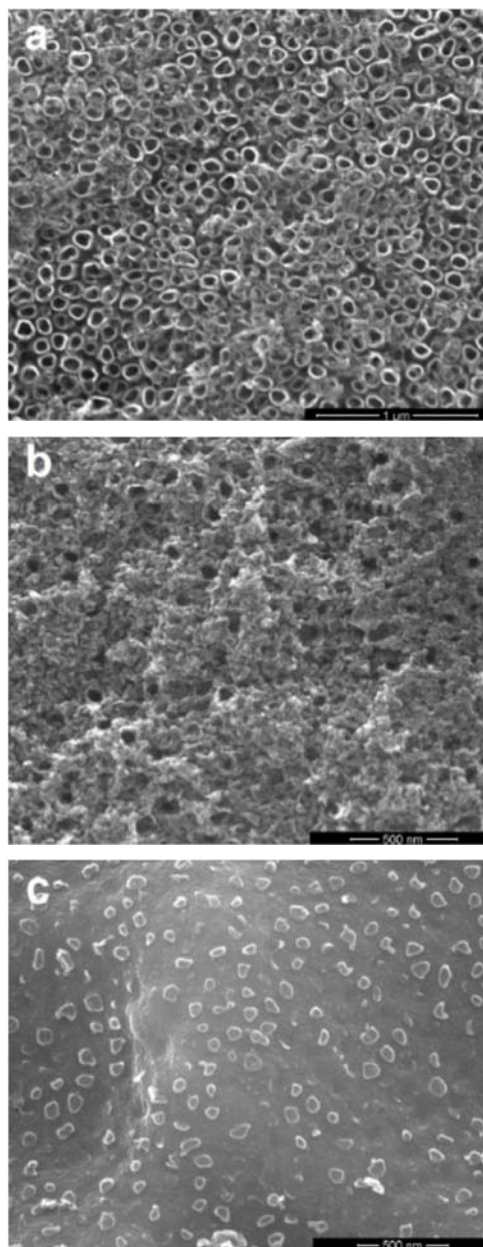
**Fig. 2.** SEM image of synthesized TNT.

The anodized foil, after Pt addition on the anode and the cathode sides, was mounted in the H Cell as described in the method section. The gas evolution upon illumination of the anode side was monitored by measuring the displaced water volume in the attached burettes, without any qualitative analysis. A gas volume ratio close to 1:2 (illuminated side: dark side) is observed during the first ~10 minutes of UV illumination, which is consistent with stoichiometric production of H<sub>2</sub> and O<sub>2</sub> via the splitting of water. The ratio of the evolved gases is reversed after ~10 minutes, indicative of the starting of other reactions/processes that could emanate from factors such as poor ionic conductance of the Nafion membrane or poor electronic conductance of the TiO<sub>2</sub> layer. The unexpected ratio of the evolved gases is accompanied by a physical change of the electrode, clearly observed in the post-reaction characterization.

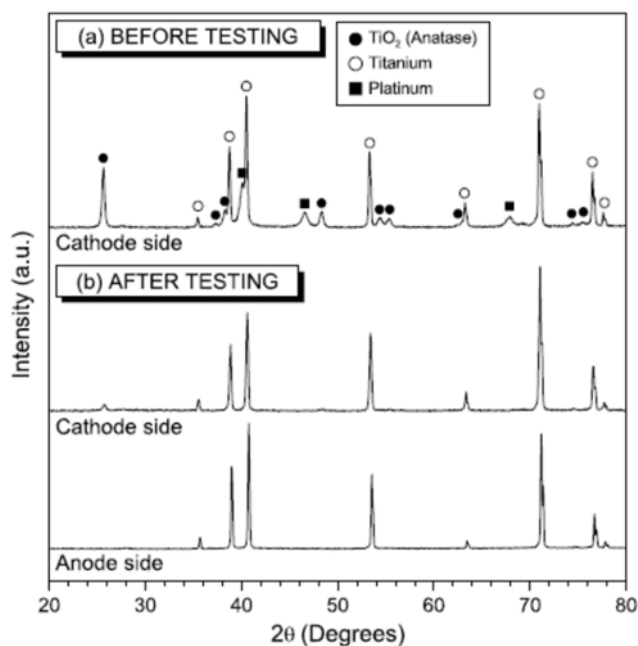
The SEM images of the anode side (Fig. 3) indicate that the oxide layer is structurally destroyed. Image (a) in Fig. 3 was taken from the dry part of the electrode, which was not in contact with the electrolyte; (b) was taken from the region under the o-rings (partially wetted) and (c) from the completely wetted part of the foil. The change in the wetted surface was even clear to the naked eye. This region acquired a purple color which is characteristic of a thinner and flatter film than the nanotube layer. The x-ray patterns of the electrode indicate that the crystalline TiO<sub>2</sub> layer is lost entirely on the anode side.

The x-ray patterns of the platinized surface of the foil is shown in Fig. 4. The peaks that belong to the underlying, metallic titanium can be observed as well as the peaks from TiO<sub>2</sub> and Pt. The phase of the TiO<sub>2</sub> layer is anatase as expected from the relatively low annealing temperature. Results presented in Fig. 4 show that anatase peaks are completely diminished for the anode side while still existing for the cathode side.

Furthermore, no Pt is visible in the cathode side patterns after the reaction, most probably due to the low Pt loading. Removal of TiO<sub>2</sub> on the anode side is likely to be concomitant with the turnaround in the gas evolution ratio. Although the present evidence cannot clearly identify the bottleneck in the mechanism of the water splitting reaction, it is responsible for the dissolution of the TiO<sub>2</sub> layer on the anode side.



**Fig. 3.** SEM images of the anode side of the anodized foil used in the photocatalytic cell. (a) Surface outside the o-ring, not wetted by the aqueous NaOH electrolyte (b) surface under the o-ring, partially wetted by the aqueous NaOH electrolyte and partially illuminated by UV light (c) surface that is totally wetted by the aqueous NaOH electrolyte and illuminated by UV light.



**Fig. 4.** X-ray patterns, taken before and after the photocatalytic test, of anode and cathode sides of the anodized foil used in the photocatalytic cell. The pattern (a) is from a sample different from the one used in reaction. It was prepared in the exact same way, but it contains approximately one order of magnitude more Pt.

Aging of reduced rutile-TiO<sub>2</sub> photo anodes in acidic solutions was studied by Harris and Wilson, as early as 1976 [8]. The instability of the electrodes manifested itself as a decrease in quantum efficiency and a roughening of the surface. However, aging was not observed in the absence of an electric field (i.e. anodic bias). A similar result was also published by Nakamura *et al.*, whereby anodic bias was required for the roughening of TiO<sub>2</sub> electrodes [9].

Dissolution of powder TiO<sub>2</sub> in organic acid containing solutions was quantified by Mukherjee *et al.* [10]. The solubility of TiO<sub>2</sub> in NaCl solutions lies in the range of 10<sup>-6</sup>-10<sup>-9</sup> moles/L [11, 12]. The solubility decreases to ~10<sup>-9</sup> moles/L for neutral conditions. Given the amount of the oxide layer in the cell and the reported solubility values, the present volume of the electrolyte in the cell is roughly one order of magnitude smaller than the amount required for the complete dissolution of the oxide layer. Nevertheless, this analysis suggests that a significant amount of TiO<sub>2</sub> can already be removed even in dark conditions. In the experimental conditions where UV-illumination is present, dissolution may be more significant.

The reports in the literature for successful water splitting in an H cell [13] differ from ours in depositing Pt on Ti metal on the cathode side. The resistance created by the TNT film and detachment of Pt [14]

from the cathode side may be responsible for the dissolution of the TNT on the cathode side. Our results do not diminish the superior performance of the TNT structures for water splitting in photoelectrochemical cells [15], but simply summarize a set of conditions that may lead to titania dissolution during the water splitting process.

#### 4. Conclusion

TiO<sub>2</sub> has been considered as a stable material under photocatalytic conditions, which may involve basic/acidic solutions, UV irradiation and so on. Our results indicate that a porous anatase layer in contact with an alkaline solution can be destroyed under UV light. The loss of the TiO<sub>2</sub> layer might be related to the blocking of one of the steps in the overall reaction scheme. Possible candidates for problematic steps are hindrance of H<sub>2</sub> evolution on Pt via the loss of Pt particles from the cathode side, poor ionic conductance of the Nafion membrane and poor electronic conductance of the TiO<sub>2</sub> layer on the cathode side. Although the exact mechanism of the loss of TiO<sub>2</sub> is not clear, the observation of such a phenomenon demonstrates the distinct possibility of photo corrosion for TiO<sub>2</sub> under conditions relevant for photocatalytic water splitting in the absence of oxygen evolution.

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