

Application of TiO₂ Nanotubes for Photocatalytic Water Splitting

Osman KARSLIOGLU¹, Sadig KULIYEV² and Deniz UNER^{1*}

¹Middle East Technical University, Dept. of Chemical Engineering, Ankara, 06531 (Turkey)

²Vestel Defence Industries, Ankara, (Turkey)

*uner@metu.edu.tr

Introduction

Efficient splitting of water into H₂/O₂ photocatalytically is probably the most desired pathway to convert abundant solar energy into 'hydrogen', the energy carrier of near future. Titanium dioxide is one of the most popular materials of this area owing to its stability in aqueous environment, benign nature and cheapness. It has been employed in many different systems to accomplish water splitting, starting from 1972 [1].

Nanotubes of TiO₂ have been introduced to the literature about a decade ago [2]. Three main strategies are reported in the literature for synthesis [2-4]. The most popular by far is the electrochemical anodization of a titanium foil in a fluoride containing electrolyte, because it's fast, easy and readily applicable to commercial applications. It is now almost verified that one-dimensional structure decreases electron-hole recombination as compared to nanocrystalline films of similar thickness, while preserving the surface area.

In this study, we are going to present the results obtained from photocatalytic water splitting experiments carried out in an H-type cell.

Materials and Methods

Titanium foil of 0.25 mm thickness (Aldrich, 99.7% purity) was anodized in a solution of 1M (NH₄)H₂PO₄ with 0.5 wt% NH₄F added, in a two electrode system with a Pt foil cathode and at 20 V potential difference for 400 minutes. Electrolyte composition is taken from the literature [5]. One side of the foil was wetted with Pt(NH₃)₄Cl₂ solution to introduce platinum and calcined at 450 °C for 3 hours by heating with 2 °C/min heating rate. In the H-cell, which was made of quartz, we used a 4 cm diameter anodized foil and acidified nafion membrane. Electrolyte solutions were 1N NaOH on anode side and 1N H₂SO₄ on the cathode side. pH of electrolytes was as such in order to impose a chemical bias for charge transfer. Illumination was done with a mercury UV lamp. Design of the cell can be found in the literature [6,7]. Evolved gases were not analyzed but just quantified volumetrically.

Results and Discussion

The morphology of plain anodized foil (a), platinized side (b) and the surface after reaction in H-cell (c) are given in Figure 1. Desired stoichiometry of H₂/O₂ = 2 was not observed in the evolved gases. Amounts of evolved gases are illustrated in Figure 2. Destruction of morphology indicates that the surface itself is oxidized in the anode side and probably reduced in the cathode side. Highly basic electrolyte and the UV illumination is thought to cause etching in the anode side, however reactions on the cathode side could not be well understood.

In order to get rid of the corroding environment in the H-cell, similar experiments are being carried out in a photoelectrochemical cell, the bias being applied as electrical potential. This will allow the evaluation of the material performance for water splitting.

Significance

This work gives an idea for the limitations that may be encountered in the utilization of an H-type cell for the splitting of water under UV illumination.

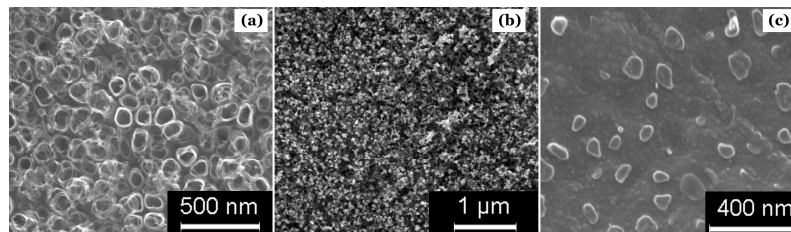


Figure 1. SEM images of (a) plain anodized titanium foil, the anode side, (b) platinized form of 'a', the cathode side, (c) 'a' after reaction in H-cell.

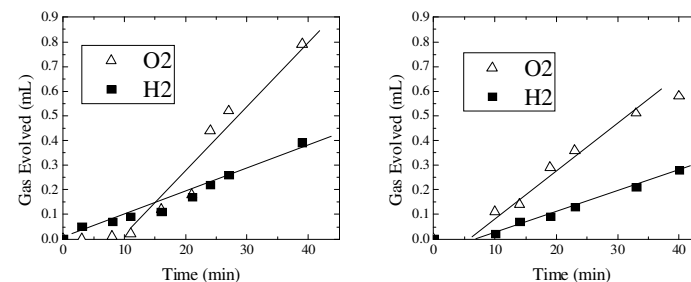


Figure 2. Amount of evolved gases in the H-cell type photolytic device. O₂ and H₂ indicate the anode and cathode side gas respectively, not necessarily the type of gas. Lines are drawn to guide the eye. Two graphs represent two consecutive runs.

References

1. Fujishima, A. and K. Honda, *Nature* 238, 37 (1972)
2. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, and K. Niihara, *Langmuir* 14, 3160 (1998)
3. D. Gong, C. A. Grimes, O. K. Varghese, W. C. Hu, R. S. Singh, Z. Chen, and E. C. Dickey, *J. Mater. Res.* 16, 3331 (2001)
4. W. Z. Wang, O. K. Varghese, M. Paulose, C. A. Grimes, Q. L. Wang, and E. C. Dickey, *J. Mater. Res.* 19, 417 (2004)
5. A. Ghicov, H. Tsuchiya, J. M. Macak, and P. Schmuki, *Electrochem. Commun.* 7, 505 (2005)
6. M. Kitano, K. Tsujimaru, and M. Anpo, *Appl. Catal., A* 314, 179 (2006)
7. M. Kitano, M. Takeuchi, M. Matsuoka, J.M. Thomas, and M. Anpo, *Catal. Today* 120, 133 (2007)