

# Direct Growth of TiO<sub>2</sub>-Nanotubes on Ti-Mesh Substrate for Photoanode Application to Dye-sensitized Solar Cell

Min-Woo Park\* · Dong-Hoon Lee · Youl-Moon Sung

## Abstract

Partial anodic oxidation of Ti-mesh with a wire diameter of  $\sim 200[\mu\text{m}]$  produces self-aligned TiO<sub>2</sub> nanotube arrays ( $\sim 50[\mu\text{m}]$  in length) on Ti-mesh substrate. The electrolyte used for anodic oxidation was an ethylene glycol solution with an addition of 1.5 vol. % H<sub>2</sub>O and 0.2 wt. % NH<sub>4</sub>F. A dye-sensitized solar cell utilizing the photoanode structure of TiO<sub>2</sub>-nanotube/Ti-mesh was fabricated without a transparent conducting oxide (TCO) layer, in which Ti-mesh replaced the role of TCO. The 1.93[%] photoconversion efficiency was low, which can be attributed to both insufficient dye molecules attachment and limited electrolyte flow to dye molecules. The optimized nanotube diameter and length as well as the TiCl<sub>4</sub> treatment can improve cell performance.

Key Words : Anodic Oxidation, Dye-Sensitized Solar Cell, TiO<sub>2</sub> Nanotube, Ti-Mesh

## 1. Introduction

Typical dye-sensitized solar cells (DSCs) use a transparent conducting oxide (TCO) layer[1] as both the anode and the cathode electrode due to its low sheet resistance, adequate light transparency, and high photoelectrical response.[2] The most widely used TCO is fluorine-doped tin-oxide (FTO); however, the thin FTO layer deposited on glass has limitations in infrared ray (IR) transmission and

thermal resistance as a transparent conductor. In addition, the FTO layer is commonly prepared by an expensive and somewhat complicate process such as either a physical vapor deposition or a chemical vapor deposition method. Thus, the use of FTO-coated glass for the two DSC electrodes can result in a significant cost increase for the less-effective DSC compared to an Si-based solar cell.[3,4] Therefore, there have been strong demands to replace TCO with a highly-efficient low-cost electrode in the commercial application to DSCs.

A layer of 15~20[nm] sized TiO<sub>2</sub> nanoparticles is coated onto TCO, to which is then bound a large number of dye molecules. Efficient light harvesting is possible by electron injection from the large number of dye molecules to the TiO<sub>2</sub> nanoparticles. The performance of the diffusing electrons can,

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however, be a limiting factor during electron transport via the networks of  $\text{TiO}_2$  nanoparticles. This is due to the structural disorder at the contact between the  $\text{TiO}_2$  nanoparticles, which leads to enhanced scattering of electrons, thus resulting in slow mobility.

The arrays of  $\text{TiO}_2$  nanotubes produced by anodic oxidation are a focus of considerable interest as this can produce highly-ordered nanotube arrays providing unique material architectures of a large internal surface area with very high aspect ratio[5-7]. The arrays of  $\text{TiO}_2$  nanotubes may not possess structural disorder at the contacts between the tubes, resulting in high mobility of electron transport. Partial anodic oxidation of Ti-metal allows fabrication of  $\text{TiO}_2$ -nanotube arrays on the underlying Ti surface, thus a hybrid structure of  $\text{TiO}_2$ -nanotube/Ti-metal can be fabricated. Substrate Ti-metal can replace TCO as an anode electrode, whereas the  $\text{TiO}_2$  nanoparticles are replaced by  $\text{TiO}_2$  nanotube arrays. However, to facilitate the Ti-metal plate as an anode electrode, modification of the photoanode structure is required since the Ti-metal is neither transparent nor permeable to electrolytes. A DSC using this hybrid structure, as schematically shown in Fig. 1, is described further in the next section. In this work, a new type of DSC photoanode replacing the TCO layer is developed to produce highly-efficient low-cost solar cells. The DSC structure using new photoanode electrode is composed of a glass/dye-sensitized  $\text{TiO}_2$  nanoparticle layer/Ti-mesh electrode/electrolyte/metal counter electrode /glass. Processing and electrical characterization of the DSCs using this photoanode cell structure are presented in this study.

## 2. Ti-mesh/ $\text{TiO}_2$ -nanotube Structure of DSC Photoanode

A schematic diagram of a DSC is shown in Fig. 1, in which the photoanode is the layers of  $\text{TiO}_2$ -nanotube arrays directly grown on Ti-mesh substrate. The electron-collecting layer in the photoanode is the  $\text{TiO}_2$ -nanotube arrays (around 20 [ $\mu\text{m}$ ] in thickness) to which dye molecules have been bound. The collected electrons diffuse into the Ti-mesh metal and transport to the counter electrode. The electrons at the counter electrode are transferred to the  $\text{I}^-/\text{I}_3^-$  electrolyte, which subsequently transport electrons to the dye molecules. The Ti-mesh allows the charge-carrying electrolyte to flow to the dye molecules. Ti-mesh was fabricated using powdered Ti mixed with polymer binders as described in the following section. Subsequent anodic oxidation of Ti-mesh fabricates the hybrid structure of the  $\text{TiO}_2$ -nanotube (20 [ $\mu\text{m}$ ] thick)/Ti-mesh layers. A DSC structure in sequence is glass/ $\text{TiO}_2$ -nanotube/Ti-mesh/electrolyte/counter-electrode/glass (Fig. 1).

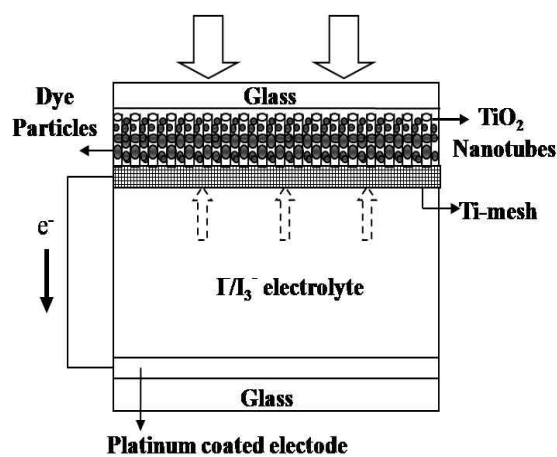


Fig. 1. The schematic of DSC shows the photoanode structure of the  $\text{TiO}_2$ -nanotube/Ti-mesh layers without TCO film

### 3. Experiments

Predetermined amounts of powdered Ti (<45[ $\mu\text{m}$ ] in diameter) were mixed with a polymer binder to produce a homogeneous paste. Three dimensional Ti-mesh scaffolds were fabricated by the direct exclusion of the paste onto a cooled substrate using a robotic deposition device with a heat controlled blowing system. The fabricated Ti-mesh scaffold was then sintered at 1,200[ $^{\circ}\text{C}$ ] in a vacuum ( $5.0 \times 10^{-6}$  torr). Fig. 2 shows a Ti-mesh scaffold with  $\sim 70\%$  porosity. The self-aligned highly-ordered TiO<sub>2</sub> nanotube arrays were grown from the Ti-mesh by potentiostatic anodic oxidation in a two-electrode electrochemical cell. The electrodes were spaced 2[cm] apart. The voltage applied to the Ti-mesh anode and Pt cathode was 60V at  $\sim 22[^{\circ}\text{C}]$ . The electrolyte used was an ethylene glycol solution with an addition of 1.5 vol. % H<sub>2</sub>O and 0.2 wt. % NH<sub>4</sub>F. Prior to anodization, all the Ti-mesh samples were cleaned with ethanol and dried in a nitrogen stream. By tape-masking one face, only the other face of the Ti-mesh was exposed to the electrolyte during anodization. TiO<sub>2</sub> nanotube arrays having lengths up to  $\sim 50[\mu\text{m}]$  were grown vertically to the underlying Ti-mesh. The growth rate of the nanotube was  $5\sim 7[\mu\text{m}]$  per hour. The anodic oxidation of the Ti-mesh metal substrate was partially completed to fabricate the hybrid layer structure of the Ti-mesh/TiO<sub>2</sub>-nanotube arrays for photoanode application to DSCs.

The fabricated TiO<sub>2</sub>-nanotube/Ti-mesh was thoroughly washed with alcohol, and immersed in a 0.1M HCl solution for 20 min followed by washing with deionized water and drying in an 80[ $^{\circ}\text{C}$ ] oven to remove any unwanted deposits and surface impurities introduced during anodic oxidation. The anodized TiO<sub>2</sub> nanotubes were in an amorphous phase and were crystallized into an anatase phase

after annealing at 580[ $^{\circ}\text{C}$ ] for 3 hours in oxygen. This result was obtained by examining the TiO<sub>2</sub> nanotubes anodized from the Ti plate instead of using Ti-mesh in the exact same condition. Prior to use, the annealed sample was placed in a 0.2 M TiCl<sub>4</sub> solution for 60 min at room temperature within airtight bottles and then rinsed in ethanol followed by annealing in air at 450[ $^{\circ}\text{C}$ ] for 30 min.

TiO<sub>2</sub>-nanotube arrays on Ti-mesh were immersed for 24 hours in a N719 dye (Solaronix, Switzerland) solution, 0.035[g] of Ruthenium 535-bisTBA in a mixture of acetonitrile and tert-butanol (v/v=1:1), and kept at room temperature for 48 hours. The electrolyte used in the solar cell contained 0.5mM iodide, 0.005M LiI, 0.0058M 4-tert-butylpyridine, and 5 ml acetonitrile.

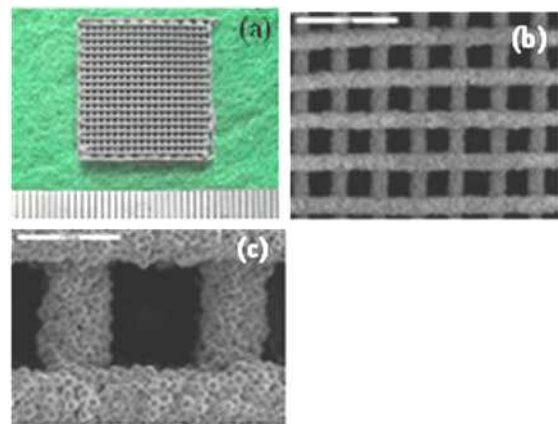


Fig. 2. Optical and scanning electron micrograph of the fabricated three dimensional Ti-mesh scaffold with  $\sim 70\%$  porosity

Counter-electrodes were prepared by coating with a solution of H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O and 2-propanol dihydrate (v/v=1:1) followed by drying at 450[ $^{\circ}\text{C}$ ] for 30 min. Electrode spacing was ensured by the use of Surlynfilm spacers, 60[ $\mu\text{m}$ ] in thickness. The electrolyte was introduced into the clamped electrode by capillary action. The fabricated cell size was 5×5[mm<sup>2</sup>] and the solar cell geometry is

schematically shown in Fig. 1.

#### 4. Results and discussion

A DSC was fabricated without the use of TCO film with a hybrid structure of TiO<sub>2</sub>-nanotube/Ti-mesh as the photoanode. TiO<sub>2</sub>-nanotube arrays grown on Ti-mesh became an electron-collecting layer, in which dye molecules are bound to the nanotubes. The Ti-mesh shown in Fig. 2 (a) is made of ~200[μm] diameter Ti wires (Figs. 2 (b) and (c)). The Ti-mesh has ~70[%] porosity. The pores in the Ti-mesh allow the charge-carrying I<sup>-</sup>/I<sub>3</sub><sup>-</sup> electrolyte to flow toward dye molecules. Subsequent anodic oxidation of Ti-mesh fabricates

TiO<sub>2</sub>-nanotube (50[μm]-thick) arrays on the Ti-mesh substrate, which allows the hybrid roles facilitating electron collection and the anode layer.

Fig. 3 (a) shows a cross-sectional view of TiO<sub>2</sub> nanotube arrays grown on Ti-mesh. Complete conversion of the Ti metal substrate into TiO<sub>2</sub> nanotube arrays is possible. However the anodic oxidation of Ti-mesh substrate is partially completed to fabricate the layer structure of TiO<sub>2</sub>-nanotube/Ti-mesh. The thickness (or length) of the grown TiO<sub>2</sub>-nanotube arrays on underlying Ti-mesh is ~50[μm] (Fig. 3 (a)). The amorphous phase of the anodized TiO<sub>2</sub> is transformed into an anatase structure by subsequent annealing at 580 [°C] for 3 hours in oxygen. Fig. 3 (b) shows the top view of the TiO<sub>2</sub>-nanotubes after annealing at 580 [°C] and TiCl<sub>4</sub> treatment.

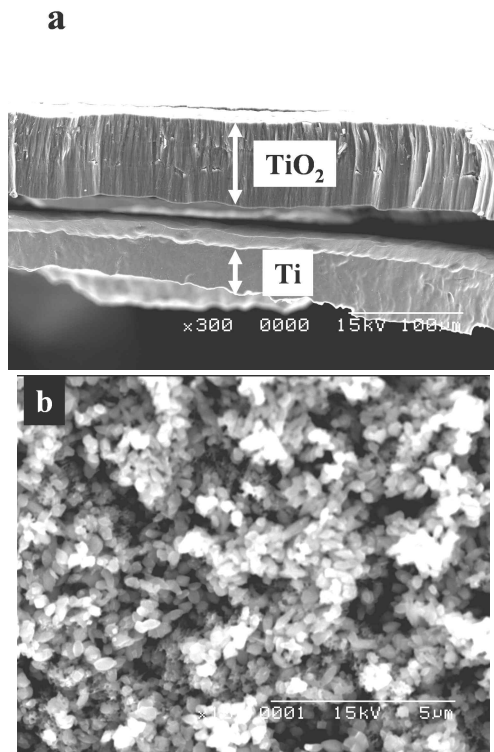


Fig. 3. (a) Lab-grown TiO<sub>2</sub> nanotube arrays on Ti-mesh are shown cross-sectionally after heat treatment at 580[°C], (b) the top view of TiO<sub>2</sub>-nanotubes after TiCl<sub>4</sub> treatment

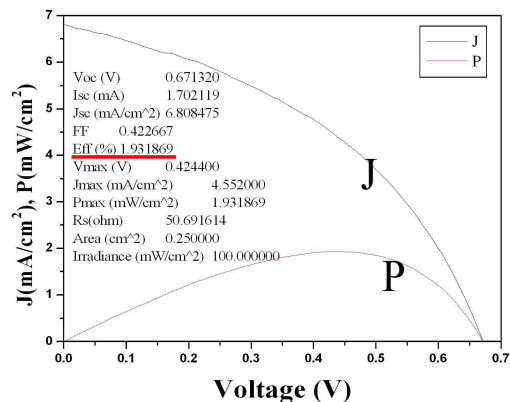


Fig. 4. Photocurrent (I) and photovoltage (V) characteristic of DSC using the photoanode of TiO<sub>2</sub>-nanotube/Ti-mesh under 100[%] AM 1.5 illumination

The photocurrent (I) and the photovoltage (V) of the cell were measured with an active area of 0.2[cm<sup>2</sup>] Ti-mesh using simulated sunlight at AM-1.5 produced by a 150-W Solar Simulator. I-V characteristics of the devices are shown in Fig. 4. the overall photoconversion efficiency is very low

(<1.93[%]), which can be attributed to two major factors. The relatively very large pore size (100[nm] in diameter) of the nanotubes may cause insufficient dye molecules to be bound, thus limiting light harvesting significantly.

G. K. Mor et al. [7] reported the effects of TiCl<sub>4</sub> treatment of nanotubes (360[nm]-thick, 46[nm] pore diameter) on photoconversion efficiency. By placing the annealed TiO<sub>2</sub>-nanotube arrays in 0.2 M TiCl<sub>4</sub> solution, the overall photoconversion efficiency (2.9[%]) increases by 5 times the efficiency of non-TiCl<sub>4</sub> treated nanotubes. The authors hypothesize that the TiCl<sub>4</sub> treatment facilitates improved bonding between the TiO<sub>2</sub> and dye molecules, resulting in improved charge transfer. A similar result was obtained in this study, where the cell efficiency of non-TiCl<sub>4</sub> treated nanotubes is only about 0.5[%].

The Ti-mesh itself may also limit the electrolyte flow to the dye molecules resulting in low photo conversion efficiency. Although the perforated area is ~70[%] of the Ti-mesh, it may still limit electrolyte flow to the dye molecules. Many of the electrons carried by the electrolyte can diffuse through the Ti-mesh to the counter electrode, instead of passing through the mesh holes to the dye molecules. The low value of  $J_{sc}$ , 6.8[mA]/[cm<sup>2</sup>] is also attributed to the two major factors explained above. Since DSC performance is significantly affected by the amount of dye molecules bound to the nanotubes, anodization processing is further studied to yield the optimized nanotube diameter and length as well as the TiCl<sub>4</sub> treatment. The effects of Ti-mesh perforation on electrolyte flow and the area of anodized nanotube arrays are critical issues for on-going research.

## 5. Conclusions

The anodic oxidation of Ti-mesh results in the formation of TiO<sub>2</sub> nanotube arrays on Ti-mesh with pore diameters of 100[nm] and lengths of ~50[μm]. A dye-sensitized solar cell utilizing the photoanode structure of the TiO<sub>2</sub>-nanotube/Ti-mesh was fabricated without a transparent conducting oxide (TCO) layer, in which Ti-mesh replaces TCO. Overall photoconversion efficiency is low (<1.93[%]), which can be attributed to insufficient dye molecules binding and a limited electrolyte flow hindered by the Ti-mesh. The optimized nanotube diameter and length as well as the TiCl<sub>4</sub> treatment can improve cell performance. Sufficient electrolyte flow through control of the area of Ti-mesh perforation and anodized nanotube arrays is the focus of on-going research.

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## References

- [1] Min-Woo Park and Ki-Young Chun, "Effects of Anodization Growth of TiO<sub>2</sub>-Nanotube Array Membrane on Photo-conversion Efficiency of Dye-Sensitized Solar Cell", *Electron. Mater. Lett.* Vol. 5, pp. 7-11, 2009.
- [2] Alan E. Delahoy, Liangfan Chen, Masud Akhtar, Baosheng Sang, and Sheyu Guo, "New technologies for CIGS photovoltaics", *Solar Energy*, Vol. 77, pp. 785-793, 2004.
- [3] Supachai Ngamsinlapasathiana, Thammanoon Sreethawongb, Yoshikazu Suzukia, and Susumu Yoshikawa, "Doubled layered ITO/SnO<sub>2</sub> conducting glass for substrate of dye-sensitized solar cells", *Solar Energy Materials & Solar Cells*, Vol. 90, pp. 2129-2140, 2006.
- [4] T. Kato and S. Hayase, "Quasi-Solid Dye Sensitized Solar Cell with Straight Ion Paths", *J. Electrochem. Soc.*, Vol. 154, pp. B117-B121, 2007.
- [5] M. Paulose, H. E. Prakasam, O. K. Varghese, L. Peng, K., C. Popat, G. K. Mor, T. A. Desai, C. A. Grimes, "TiO<sub>2</sub> Nanotube Arrays of 1,000[μm] Length by Anodization of Titanium Foil", *J. Phys. Chem. C*. Vol. 111, pp.

14992-14997, 2007.

- [6] H. E. Prakasam, K. Shankar, M. Paulose, O. K. Varghese, C. A. Grimes, "A New Benchmark for TiO<sub>2</sub> Nanotube Array Growth by Anodization", *J. Phys. Chem. C*, Vol. 111, pp. 7235-7241, 2007.
- [7] G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, C. A. Grimes, "Use of highly-ordered TiO<sub>2</sub> Nanotube Arrays in Dye-Sensitized solar Cells", *Nano Letters*, Vol. 6/2, pp. 215-218, 2006.

## Biography



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Min-Woo Park was born in Korea in 1957. He received a Bachelor's degree in metallurgical engineering from Inha University in 1984; M.S. and Ph.D. degrees in materials engineering from the Polytechnic Institute of New York University in 1988 and from Arizona State University in 1993, respectively. He joined Hyundai Electronics in 1993. He is currently a professor in the department of materials engineering at Kyungsung University. His research interests include the processing of nanometer-sized metal oxide semiconductors.



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