Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 61 (2014) 2608 – 2612

Energy Procedia

The 6th International Conference on Applied Energy – ICAE2014

The fabrication of barrier layer free TiO_2 nanotube arrays and its application for highly efficient dye-sensitized solar cells

Wang Yuanhao, Lu Lin, Yang Hongxing *

The Renewable Energy Research Group, Building Service Engineering Department, The Hong Kong Polytechnic University, Hong Kong

Abstract

This paper reports a novel method to fabricate barrier layer free TiO_2 nanotube arrays and its application for dye-sensitized solar cells. Through two-step anodization and utilization of surface stress, the TiO_2 nanotube arrays were detached from the Ti foil and stick onto the FTO glass to fabricate DSSCs. Through the optimization of film thickness, the highest conversion efficiency of 8.12% was achieved.

Peer-review under responsibility of the Organizing Committee of ICAE2014

Kyewords: Dye-sensitized solar cells, TiO_2 nanotube, barrier layer free, anodization

1. Introduction

Currently, most of the research for the application of TiO_2 nanotubes on DSSCs has been limited to the backside illumination configuration because of the opacity of Ti foil. Although recently [1] Grimes' group has optimized the overall conversion efficiency up to 6.89% by using the 20-μm-long TiO_2 nanotubes in the backside illuminated DSSCs, the efficiency is still much lower than that of the front-side illuminated DSSCs. The main reason is that when the sunlight irradiates from the counter electrode side, some of the light is first reflected by the counter electrode substrate, and then nearly 40% of the photons is absorbed by the Pt layer on the counter electrode and the iodine in the electrolyte. Consequently, the best choice to increase the upper limit of efficiency is to realize the front-side illumination by synthesis TiO_2 nanotubes from the transparent TCO glass. With this as motivation, Grime and his coworkers have fabricated a transparent TiO_2 nanotubes-based photoanode by anodizing a pre-sputtered Ti layer on TCO glass and the DSSC with 17.6-μm-long titania nanotubes yielded an overall conversion efficiency of 6.9%

* Corresponding author. Tel.: +0-000-000-0000 ; fax: +0-000-000-0000 .
E-mail address: author@institute.xxx .

Peer-review under responsibility of the Organizing Committee of ICAE2014
doi:10.1016/j.egypro.2014.12.259

[2]. However, due to the high fabrication cost of RF sputtering technology, it is not applicable for large-scale production. Another approach is to detach the TiO_2 nanotubes layer from Ti foil and transfer it to TCO glass [3]. This process is usually divided into three steps: First the TiO_2 nanotubes layer is detached from the Ti foil by physical or chemical methods. Second, the closed bottom barrier layer of the TiO_2 nanotubes arrays is opened by using etching agents. This step is not essential but very important as the opened-ended titania nanotubes layer would have less resistance for the dye solution and electrolyte to fill in than the closed-bottom titania nanotubes layer. Finally the opened-ended TiO_2 nanotubes layer is fixed onto the transparent TCO glass by using titanium-bearing adhesive. For the first step, as the TiO_2 nanotubes layer is thin and brittle, how to detach the TiO_2 nanotubes layer without damage is a key factor. In addition, the time of detachment should not be too long, especially from the viewpoint of industrial application. For the second step, due to the complicated and time-consuming process, most of the relevant studies omitted this step. Until now only a little research group adopted oxalic acid solution or HF vapors as the etching agents, which were complicated and toxic. As a result, it is requested to find more suitable method to prepare transparent TiO_2 nanotubes-based photoanode.

2. Experiment

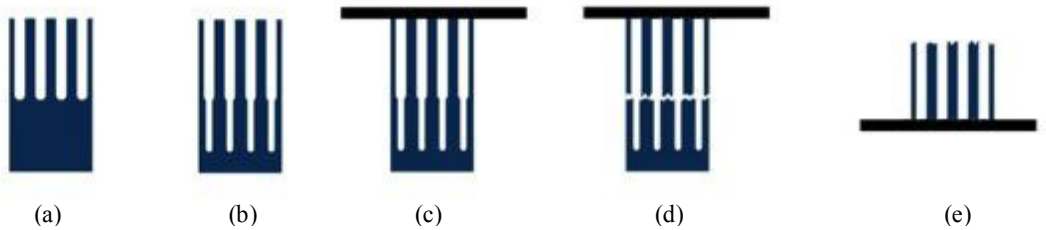

Figure 1. The schematic diagram of the TiO_2 nanotubes layer detachment process: (a) the synthes of upper layer of TiO_2 nanotubes film. (b) the lower layer of TiO_2 nanotubes film. (c) Attach the TiO_2 bilayer onto the FTO glass (d) the detachment of upper layer. (e) the final barrier layer free TiO_2 nanotube photoanode

In the present work we report a facile and cost-effective method to fabricate transparent open-ended TiO_2 nanotubes-based photoanode by combining the original three steps into one step. During the whole process, the TiO_2 nanotubes layer is protected safely. The toxic etching step is also replaced by the two-step anodization under different voltages, which means it is environment friendly. The schematic diagram of this detachment process is summarized in Figure 1. A 500 μm thick Ti foil was first cleaned with ethanol and distilled water in ultrasonic bath to remove surface contaminants, then anodized at 40 V in the fluoride-containing electrolyte. A self-organized TiO_2 nanotubes layer was in situ grown on Ti foil by anodic oxidation, as shown in Figure 1 (a). After 20h, the voltage was changed into 20V and then anodized secondly for 2h, which is shown in Figure 1 (b). As describe elsewhere [4], since the average diameter of the tube increases monotonically with the increasing of the anodization voltage, an apparent interface could be clearly observed between the two nanotubes layers with different diameters corresponding to the different voltages, as shown in Figure 2.

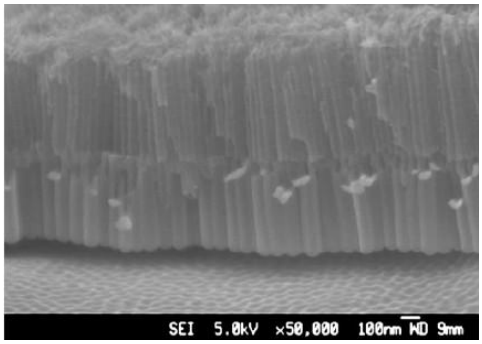

Figure 2 Bilayer structure of TiO_2 nanotubes formed by anodization under two different potential.

After the two-step anodization, a piece of FTO glass was stick to the anodized Ti foil by using titanium isopropoxide as the binder. A hot press was also introduced to compress them tightly with the heating temperature and compressive pressure about 250 °C and 1.5 MPa, respectively. Then both of them were under thermal annealing at 525 °C for 3 h with heating rate of 3 °C/min. After the temperature had cooled, the FTO glass together with the anodized Ti foil was put into the 0.1 M HCl solution for 30 minutes. It could be seen that some bubbles were firstly produced between the FTO glass and Ti sheet and then split them from the middle. The reasons for this phenomenon can be explained as follows: As mentioned above, there was an apparent interface between the two nanotubes layers. Due to the different diameters of the nanotubes in each layer, it was easy to produce stress at the interface, which would finally split these two layers. The environment of high temperature treatment and aqueous HCl solution could help the detachment process [5]. When the two layers were separated, the TiO_2 nanotubes in the upper layer were penetrated which meant they were open-ended (Figure 1 (d)), while the lower layer was still connected with the Ti sheet on which there was a barrier layer. The titanium ixopropoxide connected the top of the upper layer with the FTO glass. As a result, a thin layer of TiO_2 nanotubes film was covered on the FTO surface (Figure 1 (e)), and then dip into the dye solution for 24 hours. After being rinsed with ethanol to remove nonchemisorbed dyes, the TiO_2 nanotubes film was sensitized into pink color Figure 3.

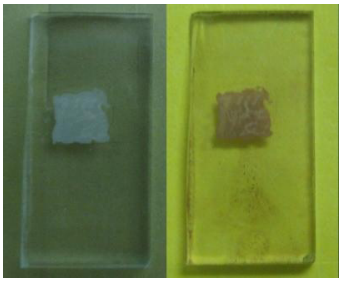

Figure 3 The TiO_2 nanotubes film coated on the FTO surface. (a) before (b) after sensitization.

The fabrication process of DSSC based on TiO_2 nanotubes layer is similar to that of the conventional DSSC based on TiO_2 nanoparticles. For brief, a piece of Surlyn 1702 hot melt film was sandwiched between the as prepared photoanode and counter electrode, and then pressed by the hot press for 100 seconds with positive press of 1.5 MPa under 100°C. The electrolyte, consisting of 0.6 M BMII (butylmethylimidazolium iodide), 0.03 M I2, 0.5 M 4-tert-butylpyridine and 0.1M GuSCN (guanidinium thiocyanate) in the mixture of valeronitrile and acetonitrile (volume ratio: 85/15), was introduced through the hole of counter electrode employing vacuum backfilling method. Finally the hole in the counter electrode side was covered with a piece of glass and then sealed by the Surlyn 1702 film and resin.

3. Result

The cross-sectional SEM image of the as prepared photoanode is shown in Figure 4. There were 4 sections in the image. Section (a) represents the open-ended TiO_2 nanotubes layer with the thickness of 7 μm. The TiO_2 nanotubes arrays were vertically connected with the substrate. Section (b) is the binder layer formed by the titanium ixopropoxide. It connected the section (a) with section (c), which is the conductive layer of FTO glass. Section (d) is the bulk glass substrate. It is further demonstrated from Figure 5 that the TiO_2 nanotube arrays were firmly rooted in the binder layer. Here the binder layer could

not only ensure the transportation of the photo generated electrons from the TiO_2 nanotubes layer to the FTO glass, but also as the compact layer to prevent the direct contact between the substrate and the electrolyte.

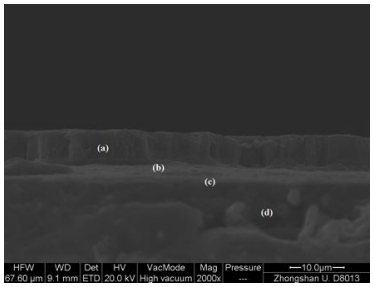

Figure 4 Cross-sectional SEM image of the FTO glass covered with TiO_2 nanotubes layer: (a) the TiO_2 nanotubes layer; (b) the binder layer formed by titanium isopropoxide; (c) the conductive layer of FTO glass; (d) The glass substrate

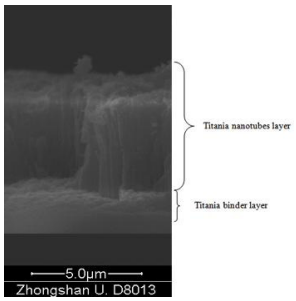

Figure 5. The joint between the TiO_2 nanotubes layer and the TiO_2 binder layer.

We investigated a series of photoanodes based on different thickness of TiO_2 nanotubes layer by control the time of first anodization. As shown in Table 1, the optimal thickness fell in the range of 20–25 µm. By optimizing different parts of the device, the champion cell in our laboratory could achieve the photovoltaic conversion efficiency up to 8.7% in a piece of 5mm × 6mm square TiO_2 nanotubes layer in the thickness of 23 µm, which was a bit higher than the nanoparticle based DSSC (P25 type TiO_2 particles, η = 7.79%) in the nearly same size. The exceeded 0.91% conversion efficiency might attribute to the higher charge-collection efficiency of the highly ordered TiO_2 nanotube arrays.

Film thickness （µm）	V_{oc} (V)	J_{sc} (mA/cm^2)	*ff*	η (%)
5.2	0.80	6.35	0.73	3.71
10.6	0.79	10.06	0.73	5.80
14.8	0.79	12.37	0.72	7.04

21.1	0.77	14.65	0.72	8.12
25.6	0.75	14.88	0.68	7.59
32.4	0.68	16.54	0.63	7.08

Table 1. The photovoltaic parameters of DSSCs based on different thickness of titania nanotubes layer.

4. Conclusion

In summary, the DSSCs based on FTO glass with open-ended TiO_2 nanotubes layer was developed. By changing the anodization voltage, a bilayer TiO_2 nanotubes film was synthesized and finally parted in the middle. The champion cell based on open-ended TiO_2 nanotubes achieved conversion efficiency of 8.7% with the device size of 0.3 cm^2. However, the conversion efficiency dropped dramatically when the device size increased to 4 cm^2. Consequently the size effect is unavoidable for the DSSC based on FTO glass.

Acknowledgements

The work described in this paper was supported by a grant from the PolyU Postdoctoral Fellowships Scheme (G-YX4X) and the support from the Sun Hung Kai Properties Group based in Hong Kong.

References

1. G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, and C. A. Grimes, Use ofhighly-ordered TiO2 nanotube arrays in dye-sensitized solar cells. Nano Lett, 2006. 6: 215-18.
   - K. Varghese, M. Paulose, and C. A. Grimes, Long vertically aligned titania nanotubes on transparent conducting oxide for highly efficient solar cells. Nat Nanotechnol, 2009. 9: 592-97.
2. H. Park, W. R. Kim, H. T. Jeong, J. J. Lee, H. G. Kim, and W. Y. Choi, Fabrication of dye-sensitized solar cells by transplanting highly ordered TiO2 Nanotube arrays. Sol Energ Mat Sol C, 2011. 1: 184-89.
3. N. K. Allam, S. Karthik, and A. G. Craig, A general method for the anodic formation of crystalline metal oxide nanotube arrays without the use of thermal annealing. Adv Mater, 2008. 20: 3942-46.
4. J. H. Park, T. W. Lee, and M. G. Kang, Growth, detachment and transfer of highly-ordered TiO2 nanotube arrays: use in dye-sensitized solar cells. Chem Commun, 2008. 25: 2867-69.
5. X. Y. Wang, S. Zhang, and L. D. Sun, A Two-step anodization to grow high-aspect-ratio TiO2 nanotube. Thin Solid film, 2011.