Research Article

An Analysis and Research on the Transmission Ratio of Dye Sensitized Solar Cell Photoelectrodes by Using Different Etching Process

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Classical photoelectrodes for Dye Sensitized Solar Cells (DSSCs) were fabricated by using the electrochemical method on the titanium (Ti) template, for that the fabrication process would influence the characteristics of the DSSCs. In this study, at first three different methods were used to etch Ti templates from 10 to 17 min, (1) polishing-chemical etching: Ti template was annealed at 450 °C for 1 h, abraded using number 80 to 1500 SiC sheet, and then etched in a solution of 5% HF + 95% H2O; (2) electrochemical polishing-chemical etching: Ti template was annealed at 450 °C for 1 h, electrolytic polishing with 42% CH3OH + 5% HClO4 + 53% HOCH2CH2OC(CH3)9 solution, and the chemical-etching in a solution of 5% HF + 95% H2O; (3) chemical etching: Ti template was etched in a solution of 5% HF + 95% H2O and annealed at 450 °C for 1 h. When the etching time was changed from 10 to 17 min, the thicknesses of Ti templates decreased from 75.3 μm to 14.8 μm, depending on the etching method. After etching process, the TiO2 nanotube arrays were fabricated as the photoelectrode of DSSCs by electrochemical process, in which the Ti as anode and platinum (Pt) as cathode. The electrolyte solution included C2H4(OH)2, NH4F, and deionized water. After annealing the grown TiO2 nanotube arrays at 450 °C for 3 h, we would show that the etching process had large effect on the structure and transmittance ratio of the TiO2 nanotube arrays.

1. Introduction

Tubular inorganic nanostructures offer great potential for use in heterojunction solar cells, fuel cells, molecular filtration, tissue engineering, and Dye Sensitized Solar Cells (DSSCs). In contrast to random nanoparticle systems where slow electron diffusion typically limits device performance [1, 2], the precisely oriented nature of the crystalline (after annealing) nanotube arrays makes them excellent electron percolation pathways for vectorial charge transfer between interfaces [2, 3]. Highly ordered vertically oriented nanotube arrays fabricated by different metal-oxide can be used as photoelectrode materials of the DSSCs, which include titanium dioxide (TiO2) [4], ferric oxide (Fe2O3) [5], zinc oxide (ZnO) [6], and so forth. Among those proposed photoelectrode materials, TiO2 is best because it has the merits of low cost, chemical stability, and good charge transport [7].

As numerous major advances in research and technology over the past decade have been made possible by the successful development of nanostructures, various avenues have been used to fabricate a diversity of TiO2 nanostructure photoelectrodes, including the sol-gel method [8], metalorganic...
chemical vapor deposition (MOCVD) [9], templating [10], and electrochemical method [11]. Although many of those fabrication routes are complicated due to the use of templates or the nature of the involved chemical processes, it has been demonstrated that self-organized vertically oriented titanium dioxide (TiO$_2$) nanotube arrays can be fabricated using a simple anodization technique. Using electrochemical method to fabricate the TiO$_2$ nanotube arrays as photoelectrodes is first one using hydrofluoric acid (HF) electrolyte by Zwilling et al. [12]. After that, many electrolytes are also developed to fabricate the TiO$_2$ nanotube arrays as photoelectrodes, such as HF/H$_2$O, HF/H$_2$SO$_4$/H$_2$O [13], and EG (ethylene glycol)/NH$_4$F/H$_2$O [14]. When the EG/NH$_4$F/H$_2$O electrolyte is used to fabricate TiO$_2$ nanotube arrays, the length of TiO$_2$ photoelectrodes has the value between 10 $\mu$m and 100 $\mu$m [14].

When using as the photoelectrodes, the property of the anatase phase TiO$_2$ is believed to be superior than that of the rutile phase TiO$_2$. Because the band gap of anatase phase TiO$_2$ is 3.2 eV and rutile phase TiO$_2$ is 3.0 eV, the light absorption edge of anatase phase TiO$_2$ is located at lower wavelength. When the ultraviolet light is irradiated, the photoelectrodes of TiO$_2$ nanotube arrays are proceeded photocatalytic activities to make light through photoelectrodes to dye layer [15]. Except the crystalline phase, when the TiO$_2$ nanotube arrays are used as the photoelectrodes, the transmission ratio of TiO$_2$ nanotube arrays has large effect on the efficiency of the fabricated DSSCs. In this study, Dye Sensitized Solar Cells (DSSCs) photoelectrodes, TiO$_2$ nanotube arrays, were fabricated by using electrochemical method and using UV-Vis examination transmission ratio in the DSSCs structure. Therefore, the purpose of this study was to investigate the effect of etching process on transmission ratio of the TiO$_2$ nanotube arrays after treating by using different etching methods.

2. Experimental

The Ti metals were cut into Ti-plates with a size of 2.5 cm × 2.5 cm and thickness of ~142 $\mu$m. The flow chart for the different etching process, the process for formation of TiO$_2$ nanotube arrays, and the characteristic measurements of the TiO$_2$ nanotube arrays was shown in Figure 1 and described below.
2.1. Preprocess

2.1.1. Polishing-Chemical Etching. A pure Ti plate with 99.7% purity was used as the template for the polishing-chemical etching process. The template was first annealed 1 h at 450°C and cooled in air, then the template was abraded using SiC sheets (Nos 80 to 1500), and then it was ultrasonicated for 30 min in distilled water. After that, the mixture of 5% HF + 95% H₂O was used as the etching solution and the etching time was changed from 10 to 17 min.

2.1.2. Electrochemical Polishing-Chemical Etching. Another titanium plate with higher purity 99.995% was also used as the template, too. The sample was first annealed 1 h at 450°C and then it was ultrasonicated for 30 min in distilled water. The polishing electrolytic solution was mixed with 42% methanol (CH₃OH) + 5% perchloric acid (HClO₄) + 53% ethylene glycol monobutylether (HOCH₂CH₂OC₄H₉), and the etching solution was mixed by 5% HF + 95% H₂O; the etching time was changed from 10 to 17 min.

2.1.3. Chemical Etching. A pure titanium plate with 99.7% purity was also used as the template for the chemical etching process. The mixture of 5% HF + 95% H₂O was used as the etching solution and the etching time was changed from 10 to 16 minutes. After the etching process the titanium plate was annealed at 450°C for 1 h.

2.2. Preparation of Photoelectrodes. We fabricated ordered nanochannel TNT arrays at 25°C on the prepared titanium (Ti) square foils (2 cm × 2 cm) at a constant voltage of 50 V and Ti foils as an anode. The electrolyte solutions contained 0.2 M ammonium fluoride (NH₄F) + 2% H₂O + ethylene glycol (C₂H₄(OH)₂) with anodization. Ti foils were degreased by ultrasonication in acetone and then isopropanol, respectively, for about 30 min, followed by rinsing with deionized (DI) water, and finally dried in the air before used. Highly ordered TiO₂ nanotube arrays over large area were prepared by a potentiostatic anodization in a two-electrode electrochemical cell with a platinum (Pt) sheet as counter electrode. All anodization experiments were carried...
out at room temperature. After the electrochemical process, the foils were annealed at 450°C for 3 h.

3. Results and Discussion

3.1. Morphologies for the Cross-Section of Nonetched and Etched Ti Specimens. Figure 2 shows the cross-section of the nonetched and annealed Ti specimen, the nonetched Ti specimen showed a densified structure and no defect and porous were observed. After different etching processes were used, the etch-treated Ti plates were thoroughly rinsed with distilled water for clean at room temperature and morphologies for the cross-section were observed. In Figures 3–5, a series of micrographs of titanium plate after various etching processes and at different etching time, from 10 to 17 min, are observed. From Figures 2 and 5, the thickness of titanium plates linearly decreased with etching time and, however, the nonuniformity in thickness became apparently at a longer etching time. For the polishing-chemical etching specimens, as the etching time was equal to and longer than 13 min, the thickness become obviously asymmetrical. As shown in Figure 3, the polished surface of Ti plate was changed to be a porous structure after alkali treatment. Apparently, the porosity of the structure was observed to be increased after chemical etching treatment.

For the electrochemical polishing-chemical etching specimens, as Figure 4 shows, asymmetrical in the thickness was not observed even the etching time was 17 min. Figure 4 also shows that even with the electrolytic publishing and chemical etching the Ti plate had a smooth surface. For the results shown in Figure 5, after annealing treatment, the porous structure seemed to become more compact and rigid than before the annealing treatment, and asymmetrical in the thickness was not observed even the etching time was 17 min. A cross-section of the etched Ti plates was observed by using scanning electron microscope (SEM) and the thickness of the Ti plates was measured by SEM. The variation in the thickness of Ti plates under different etching processes as a function of etching time is displayed in Figure 6.

When the etching time was increased from 10 to 17 min, the thicknesses of the polishing-chemical etching, electrochemical polishing-chemical etching, and chemical etching Ti plates decreased from 75.3 µm to 33 µm, from 60.4 µm
to 23.6 \mu m, and from 50 \mu m to 14.8 \mu m, respectively. As Figure 6 shows, as the same etching time is used, the thicknesses of the chemical-etching Ti plates are thinner than those of the other two processes-treated Ti plates, and the abrading process is the reason to cause this result. From the results shown in Figures 3–5, the porous structure on the surfaces of Ti plates only existed in polishing-chemical etching Ti plates but not existing in electrochemical polishing-chemical etching and chemical etching Ti plates. A similar porous structure was reported to be produced by the alkali (KOH) treatment of a commercial Ti plate; the porous structure was composed of nanowires with a diameter of less than 30 nm, and the thickness of nanowire layer was estimated to be approximately 500 nm on the Ti substrate [16]. For that, the different etching processes would have large effect on the formation of the TiO\textsubscript{2} nanotube arrays. If the thickness of Ti plates is too thin, the photoelectrodes of the TiO\textsubscript{2} nanotube arrays are not easy to be grown; therefore, the 11 min treated Ti plates are chosen for producing the TiO\textsubscript{2} nanotube arrays.

3.2. Morphology of TiO\textsubscript{2} Nanotube Arrays. From the X-ray diffraction patterns (not shown here), the main crystalline phase of the as-prepared TiO\textsubscript{2} nanotube arrays was amorphous, the diffraction peaks of Ti and rutile TiO\textsubscript{2} phases

Figure 5: Cross-section morphologies of chemical etching under different times (a) 10 min, (b) 11 min, (c) 12 min, (d) 13 min, (e) 14 min, (f) 15 min, and (g) 16 min.

Figure 6: Titanium plates thickness curve chart of different methods and etching times.
could be found, and these diffraction peaks were not enhanced as the TiO$_2$ nanotube array length was changed. It is noted that the anatase TiO$_2$ peaks are much worse than the Ti and rutile TiO$_2$ peaks, so it is reasonable to neglect the influences of such trace anatase TiO$_2$ content in the as-prepared TiO$_2$ nanotube arrays. As TiO$_2$ nanotube arrays were annealed at 450°C for 1 h, the diffraction peaks of anatase TiO$_2$ were clearly observed. Figures 7–9 show the top view and side view of TiO$_2$ nanotube arrays. The top views in Figures 7(a), 8(a), and 9(a) show that all of the TiO$_2$ nanotube arrays had the diameters between 100 nm and 140 nm. The surfaces of TiO$_2$ nanotube arrays with electrochemical polishing-chemical etching and chemical etching processes were smoother than that of TiO$_2$ nanotube arrays with polishing-chemical etching process. The side views in Figures 7(b), 8(b), and 9(b) show that the lengths of TiO$_2$ nanotube arrays with the polishing-chemical etching, electrochemical polishing-chemical etching, and chemical etching processes are 19.6 μm, 18.2 μm, and 22.6 μm, respectively. From the side views in Figures 7–9 TiO$_2$ nanotube arrays with the polishing-chemical etching process are not as good as the photode-}


trodes of DSSCs because TiO$_2$ nanotube arrays are easily peeled off. Figures 8(b) and 9(b) show that the TiO$_2$ nanotube arrays with polishing-chemical etching and chemical etching processes are not easily to be peeled off. Figure 7(b) also shows that the TiO$_2$ nanotube arrays reveal an unsmooth surface, which will influence the transmission ratio and will be proven in Figure 10.

### 3.3. Transmission of Photoelectrodes Nanotubes

The transmission ratios of TiO$_2$ nanotube arrays are shown in Figure 10 as a function of different polishing process and optical wavelength. The measured structure includes the layers of TiO$_2$ nanotube arrays (photoelectrode), dye, electrolyte, and counter electrode. When the sunlight passes through the photoelectrode layer to dye layer, the transmission ratio has no apparent change. The results in Figure 10 show that the structures with the polishing-chemical etching (70–75%) and electrochemical polishing-chemical etching processes (80–85%) have high transmission ratio in the range of visible light. The structure with the polishing-chemical etching process has the lower transmission ratio which is caused by the being peeled off and unsmooth surfaces. Because TiO$_2$ nanotube arrays with the chemical etching process have the thicker thickness, the transmission ratio (20–25%) is very low. From those results, the electrochemical polishing-chemical etching and chemical etching processes are the better for formation of TiO$_2$ nanotube arrays than polishing-chemical etching.
Figure 9: Morphologies of the TiO$_2$ nanotube arrays grown on chemical etching Ti plates (a) top view and (b) side view.

Figure 10: Transmission ratio curves of the TiO$_2$ nanotube arrays grown on etching Ti plates.

process because they have the better structure and morphology factors to get the better characteristics of TiO$_2$ nanotube arrays as the photoelectrodes of DSSCs.

4. Conclusions

In this study, three different methods were used to etch Ti template from 10 to 17 min, the experimental results were summarized as follows.

(i) The thicknesses of the polishing-chemical etching, electrochemical polishing-chemical etching, and chemical etching Ti plates decreased from 75.3 $\mu$m to 33 $\mu$m, from 60.4 $\mu$m to 23.6 $\mu$m, and from 50 $\mu$m to 14.8 $\mu$m, respectively.

(ii) The TiO$_2$ nanotube arrays with polishing-chemical etching, electrochemical polishing-chemical etching, and chemical etching processes have the lengths of 19.6 $\mu$m, 18.2 $\mu$m, and 22.6 $\mu$m, respectively, and their diameters were between 100 nm and 140 nm.

(iii) In the range of visible light, the TiO$_2$ nanotube arrays with polishing-chemical etching (70–75%) and electrochemical polishing-chemical etching (80–85%) processes had the higher transmission ratio than that of the TiO$_2$ nanotube arrays with chemical etching process (20–25%).

(iv) The electrochemical polishing-chemical etching and chemical etching processes were better for formation of TiO$_2$ nanotube arrays than the polishing-chemical etching process because they could fabricate TiO$_2$ nanotube arrays with the better characteristics to be used as the photoelectrodes of DSSCs.

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References


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