Novel bamboo structured TiO2 nanotubes for energy storage/production applications

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Abstract. Nanostructured TiO$_2$ received much attention owing to its high surface-to-volume ratio, which can be advantageous in energy storage and production applications. However, the increase in energy consumption at present and possibly the foreseeable future has demanded energy storage and production devices of even higher performance. A direct approach would be manipulating the physical aspects of TiO$_2$ nanostructures, particularly, nanotubes. In this work, dual voltage anodization system has been implemented to fabricate bamboo shaped TiO$_2$ nanotubes, which offers even greater surface area. This unique nanostructure would be used in Dye Sensitized Solar Cell (DSSC) fabrication and its performance will be evaluated and compared along other forms of TiO$_2$ nanotubes. The results showed that bamboo shaped nanotubes indeed are superior morphologically, with an increase of efficiency of 107% at 1.130% efficiency when compared to smooth walled nanotubes at 0.546% efficiency.

1. Introduction

TiO$_2$ has been regarded as a suitable anode material in both energy storage and production applications. Many efforts have been poured to enhance the performance of both devices[1–4]. Among them, increasing the surface area of TiO$_2$ would suffice. This leads to the development of TiO$_2$ nanostructures, which offers greater performance while allowing smaller sized device to be made. One of the well-known nanostructured TiO$_2$ would be nanotubes, obtained using anodization method[5–8]. Anodization of Ti foil promises vertically aligned nanotubes with tunable physical aspects based on the anodization parameters such as anodization voltage [9, 10], time,[11, 12] and electrolyte [13, 14].

While nanotubes may offer superior surface area when compared to a flat surface, the length of the nanotubes cannot be increased indefinitely; an optimized length needs to be determined [15]. Hence, innovations of nanostructures manipulation become more important. One plausible way to increase the surface area of the nanotubes could be to decorate them with smaller nanostructures, such as, nanocrystals[16, 17], quantum dots,[18, 19] and nanowires [20]. However, these processes increase the number of steps and time to synthesize the materials, thus a quicker and more facile approach is attempted in this study.

Manipulating the morphology of the nanotubes would be that approach. Nanomaterials have been made with various morphologies, such as nanoribbons [21, 22], nanorods [23–25], nanowires [26–28] and hollow spheres [29]. An increase in surface area to volume ratio can be achieved by carefully choosing the right morphology to be used in each application.
In this work, bamboo-shaped TiO\textsubscript{2} nanotubes were fabricated using a modified anodization process. In lieu of a single potential source, anodization was performed using dual voltage sources of different potential. A careful tailored voltage parameter allowed TiO\textsubscript{2} nanotubes that resembled bamboo structure can be achieved. To demonstrate the superior aspects of bamboo shaped TiO\textsubscript{2} nanotubes in terms of higher surface-area, the said samples were used in DSSC setup.

2. Methodology
2.1 Sample Preparation
2.1.1 Foil cleaning
The titanium foil of 97% purity and 0.127mm thickness was cut into 3 cm by 4 cm pieces of Ti. The pieces were mechanically polished using Silicon Carbide sandpaper and then washed with distilled water. After that, the back of the foil was made electrically resistant by the application of a rubber aerosol paint. The foils were then cleaned by ultrasonic agitation in ethanol, acetone, and then distilled water then finally dried.

2.1.2 Anodizing of Titanium foils
Once dried, the cleaned foils were anodized in an electrolyte solution of 0.10 M ammonium fluoride (\textit{NH}_4\textit{F}) and 5% distilled water in an ethylene glycol solution. Two-step anodization was chosen for higher uniformity and alignment of the TiO\textsubscript{2} nanotubes (TNT). The first step was done with a constant voltage of 60 Volts for 1 hour. The anodized foil was cleaned by ultrasonic agitation in distilled water, followed by drying on a hot plate. Mechanical delamination with the use of cellotape was performed to remove the TNT layer followed by ultrasonic cleaning in ethanol. After a final cleaning in distilled water, the foil was dried, then once again anodized as the second step.

For the second step, the voltage was set to alternate between two voltages, holding a voltage for a set duration before switching, then switching back to the first voltage after another set duration. Each cycle of the first voltage was 30 seconds, while each cycle of the second voltage was 90 seconds. The anodization voltages and durations are as shown in Table 1. The voltage of the first cycle is denoted as Voltage 1 (\textit{V}_1) and the voltage of the second cycle is denoted as Voltage 2 (\textit{V}_2). Sample S3 acts as a control, as the alternating voltage of \textit{V}_1 = 60V and \textit{V}_2 = 0V renders one cycle inactive, thus smooth-walled TNTs are formed.

| Sample | \textit{V}_1 (V) | Duration of one cycle \textit{V}_1 (s) | \textit{V}_2 (V) | Duration of one cycle \textit{V}_2 (s) |
|--------|-----------------|-------------------------------|-----------------|-------------------------------|
| S1     | 60              | 30                            | 40              | 90                            |
| S2     | 60              | 30                            | 20              | 90                            |
| S3     | 60              | 30                            | 0               | 90                            |
| S4     | 60              | 30                            | -60             | 90                            |

After anodizing the second time, once again the samples were cleaned with a brief ultrasonic cleaning in ethanol before being dried on a hot plate at 80°C. Anatase phase TNTs were obtained by annealing of the anodized foils for 3 hours at 500°C.

2.2 DSSC fabrication
The DSSC was fabricated by first coating the TNT layer with a spacer coating to ensure a constant active surface area of 0.25 cm\textsuperscript{2} in all samples. These coated layers were immersed in a 0.5 mM N-719 dye solution for 24 hours to ensure maximum dye adsorption. The samples were then rinsed with an ethanol solution to clean excess dye. Fluorine doped Tin Oxide (FTO) conductive glass was used as an electrode for the TNT foil. Another FTO glass piece was used as a transparent counter electrode. This FTO was
coated with Platinum (Pt) via Magnetron sputtering, then both electrodes were sealed with the active TiO$_2$ and Pt facing each other. A redox electrolyte of 0.5M Sodium Iodide and 0.05M Iodine in acetonitrile was injected between the two electrodes. A cross-section of the DSSC device is shown in Figure 1.

**Figure 1.** Cross-section of the DSSC. The layers from top to bottom are; FTO conducting glass, Platinum coating, Iodine redox solution, TiO$_2$ nanotubes with N-719 dye, FTO Conducting Glass. The two points at both ends of the FTO Conducting glasses are electrical contacts.

After the fabrication of the DSSC for each sample, the samples were tested using a solar simulator. Data was collected with the use of a NIPXie-1073 Source Measure Unit (SMU).

3. Results and discussion

3.1 Morphological properties of the TNT under alternating voltage

Bamboo nanostructures were successfully fabricated using an alternating voltage on the second step of a two-step TNT anodization. The morphological properties of the TNT were observed under a Field Effect Scanning Electron Microscope (FESEM) and is shown in Figure 2.

**Figure 2.** Cross Section of TNT arrays anodized at the alternating voltages of a) $V_1=60V$ $V_2=40V$, b) $V_1=60V$ $V_2=20V$, c) $V_1=60V$ $V_2=0V$, d) $V_1=60V$ $V_2=-60V$. 
From the diagram above bamboo nanostructured ridges can be observed along the TNT surface. The effect is the largest as seen in Figure 2a, where the difference between \( V_1 \) and \( V_2 \) is the least. In Figure 2b, less distinct ridges are formed along the wall surface. This could be due to insufficient etching produced by the 20 V level, which would require a longer time to etch the surface of the oxide. Over etching was noticed in sample S4 in Figure 2d, where the reversed voltage was strong enough that incomplete TNT walls or broken walls from over etching were observed. As expected, smooth nanotube walls were obtained in Sample S3, shown in Figure 2c. Random locations of the TNT were analysed for nanotube dimensions, and the averaged values are listed in Table 2:

| Sample | Anodization Voltage (V) | TNT Length (µm) | TNT Diameter (nm) | Ridges Diameter (nm) |
|--------|------------------------|----------------|-------------------|---------------------|
| S1     | \( V_1=60V \) \( V_2=40V \) | \~3.6          | \~141.6           | \~195.8             |
| S2     | \( V_1=60V \) \( V_2=20V \) | \~3.6          | \~133.4           | \~168.8             |
| S3     | \( V_1=60V \) \( V_2=0V \)  | \~3.3          | \~115.4           | N/A                 |
| S4     | \( V_1=60V \) \( V_2=-60V \) | \~0.7          | \~63.3            | N/A                 |

From the data two factors that are necessary in creating the bamboo ridges are (1) An alternating Voltage (2) The hold time of each level in the alternating voltage. To fabricate bamboo TNT, the levels of voltage need to be sufficiently high that the etching reaction can compete with the oxidation reaction. If the etching rate is insufficient then minor ridges or no ridges may be formed, as seen in the differences of ridges diameter from Table 2. The holding time of each level is also important as the diameter of the TNT depends on the voltage when anodized, if the holding time is too quick uneven nanotubes may form and not a periodic bamboo structure as one would expect.

3.2 DSSC characterization
The DSSC fabricated in this study was successful in showing a drastic increase in photo-energy conversion. Figure 3 shows the J-V curve of the samples obtained from the SMU while Table 3 indicates the sample’s performance.
Figure 3. J-V Characteristics of the various TNT arrays.

Table 3. The performance of DSSCs TiO$_2$ nanotubes fabricated under different two-step anodization conditions.

| Sample | Voltage $(V_1) - (V_2)$ (V) | Open Circuit Voltage $V_{oc}$ (V) | Short Circuit Current Density, $J_{sc}$ (mA/cm$^2$) | Short Circuit current, $I_{sc}$ (mA) | Fill Factor | Efficiency, $\eta$ (%) |
|--------|-----------------------------|-----------------------------------|---------------------------------|-----------------------------------|-------------|----------------------|
| S1     | 60 - 40                     | 0.620                             | 3.60                            | 899.84                            | 0.51        | 1.130                |
| S2     | 60 - 20                     | 0.576                             | 2.32                            | 534.59                            | 0.47        | 0.627                |
| S3     | 60 - 0                      | 0.546                             | 2.18                            | 544.06                            | 0.46        | 0.546                |
| S4     | 60 – (-60)                  | 0.648                             | 0.40                            | 99.95                             | 0.53        | 0.137                |

We can see from the Table 3 that the efficiency of the bamboo TNT outperforms the smooth walled TNT almost two times, from 0.546% of S3 (smooth-walled TNT) to 1.130% of S1. Even with lesser ridges we see an increase of 14.835% from S2 to S3. An interesting note is that while the $V_{oc}$ of sample S4 is larger as compared to the other samples, we see a much smaller $I_{sc}$, which may arise from the imperfect TNT wall integrity, increasing resistance from the collapsed oxide layers. The largest short circuit current of 899 mA from sample S1, with the maximum power output of 557.90 mW, compared to S3 with a maximum power output of 297.06 mW.

The results obtained are consistent with reported findings, where the density of ridges affects the dye loading and thus performance [4]. Sample S1 with larger ridges increased the dye loading, evident by the increase in efficiency between S1 and S2, which differ in ridge diameter, by 80.2% from a 0.627% efficiency to 1.130% efficiency. The increase in efficiency due to dye loading was also reported previously [30]. The ridges play an important role thus for increasing available active surface area for the given nanotube length, which is crucial as longer nanotubes of 10µm or more require much longer anodization time [31].
4. Conclusion
In this study, bamboo structured nanotubes were found to be able to enhance the efficiency of DSSC by increasing dye adsorption. Bamboo nanotubes were successfully fabricated with two voltage levels with the highest efficiency of 1.130% for the bamboo TNT sample, as compared to smooth-walled TNT with a 0.546% efficiency.

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