Synthesis and characterization of highly ordered titanium nanotubes with different lengths for highly efficient dye sensitized solar cells

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Abstract- The performance of nanotube (NT) based dye sensitized solar cells (DSSC) depends on the length of the NTs. In this research, we fabricated ordered nanochannel arrays of titanium nanotube (TNT) films at 22.5°C on anodizing titanium (Ti) foil at a constant voltage of 60V. The electrolyte solution contained ammonium fluoride in ethylene glycol (EG). The NT lengths were controlled from 15 to 35µm while varying the anodization time. The NT films were treated with TiCl₄ in two stages. With the increase in NT lengths, the great effective surface area TNT arrays has been shown to increase dye loading and photovoltaic performance of NT. The best performance of the NT-DSSC device was achieved at L ~ 30 µm.

Keywords: Anodization, TiO₂, Dye sensitized solar cell, Nanotube.
1. Introduction

Dye-sensitized solar cells (DSSC) attract attention because of their potential as next-generation photovoltaic devices.[1] The electron collecting layer of a DSSC is composed of randomly packed TiO$_2$ nanoparticles (NP) and the best efficiency (η) of power conversion of a porphyrin-based NP-DSSC device has exceeded 12.3%.[2]

The great advantage of a NP-DSSC is the large surface area of the nanoporous TiO$_2$ films for dye adsorption, but the trap-limited diffusion for electron transport in NP-DSSC limits the efficiency. [3-6]

Vertically oriented arrays of one-dimensional TiO$_2$ nanotubes have been prepared using potentiostatic anodization as a promising advance in DSSC applications because they have superior electron transport and their rate of charge recombination is smaller than that of a conventional NP-based system. [7-10].

The efficiency of charge collection and light harvesting of NT films are much better than those of NP films because of the 1D nature and stronger light scattering effect of the former. [11]

In the present work, we controlled the lengths of NTs from 15 to 35μm with anodization for various periods. The unwanted surface depositions of the films introduced during anodization were removed upon ultrasonic cleaning in ethanol.

The photovoltaic performance of the NT-DSSC devices changed as a function of tube length. The TNT films were treated with TiCl$_4$ and annealed with a two-stage procedure.

2. Experiments

2.1. Synthesis of TiO$_2$ NT arrays

We fabricated ordered titanium nanotube films at 22.5 °C on anodizing titanium (Ti) foil at a constant voltage of 60 V. The electrolyte solutions contained ammonium fluoride (NH$_4$F, 99.9%; 0.4 wt %) in ethylene glycol in the presence of H$_2$O (2 vol %, pH = 6.8) with anodization for varied periods.[12] The sample as anodized was washed in ethanol and annealed at 450 °C for 1 h to convert the amorphous TiO$_2$ to an anatase crystalline phase. To obtain TNT arrays free of debris for DSSC applications, the annealed sample was then ultrasonicated in ethanol for 15 min to remove the bundled impurities on the top openings of the pores of the nanotubes.

2.2. TiCl$_4$ Post treatment

The films as prepared were first immersed in TiCl$_4$ solution (0.073 M) for 30 min at 55 °C. The films were re-immersed in TiCl$_4$ stock solution for 2 h and annealed at 350 °C for 30 min.

3. Devise Fabrication

We immersed the TNT films (size 0.4 × 0.4 cm$^2$) in a solution containing N719 (3×10$^{-4}$ M, Solaronix) at room temperature for 18 h to absorb sufficient dye for light harvesting. The samples were then washed with ethanol to remove the remaining dye. In the fabrication of a NT-DSSC device, the N719/TNT film served as an anode combined with a transparent Pt counter electrode as a cathode. A H$_3$PtCl$_6$ / isopropanol solution was used spin-coated onto a FTO substrate through thermal decomposition at 385 °C for 15 min.

The NT-DSSC devices were simply sealed with a hot-molten film (Solaronix, thickness 60 μm), electrolyte was introduced as a thin layer into the space between the two electrodes.

A typical electrolyte contained lithium iodide (LiI, 0.1 M), diiodine (I$_2$, 0.01 M), 4-tert-buty1pyridine (TBP, 0.5 M), butyl methyl imidazolium iodide (BMII, 0.6 M), and guanidinium thiocyanate (GuNCS, 0.1 M) in a mixture of acetonitrile (CH$_3$CN, 99.9%) and valeronitrile (n-C$_3$H$_7$CN, 99.9%) (v/v = 85/15).
4. Results and discussion

SEM images of the samples, including cross section and top view of NT films are shown in figures 1 and 2. Figure 1 shows different lengths ranging from 15µm to 35µm of NTs. According to the top-view SEM image shown in the Figure 2, the average pore diameter on the top of the film is ~100 nm. Figure 3 shows the X-ray diffraction (XRD) pattern of the NT films reveals anatase phase.

Crystalline structure of the TiO₂ tubes was investigated by Raman spectroscopy. Raman peaks shown in Figure 4 also confirmed anatase phase. In particular, the tetragonal structure of anatase gives rise to six Raman-active transitions: three E_g modes centered at 144, 197, and 637 cm⁻¹, two B_1g modes at 395 and 515 cm⁻¹, and one mode of A_1g symmetry at 513 cm⁻¹ overlapping with the B_1g mode at 515 cm⁻¹. [13, 14].

UV-vis absorption spectra of N719/MeOH aqueous solutions desorbed from the corresponding N719-sensitized TNT to estimate the amount of dye loading for NT-DSSC. Figure 5 presents the UV-vis absorption spectra of NTs with different lengths. The amounts of dye coverage on TNT films shown in the second column of Table 1 were obtained from the measured absorbance of the spectra at 518 nm and the calibrated absorption coefficient of N719 according to Beers’ law.

We selected four anodic TNT films of various tube lengths to assess their photovoltaic properties: the tube lengths were 15, 23, 30 and 35 µm.
The characteristic of photocurrent density (J) versus photovoltage (V) of samples is plotted in figure 6, along with detailed parameters listed in table 1.

### Table 1. Different parameters corresponding to each DSSC

<table>
<thead>
<tr>
<th>Tube Length (µm)</th>
<th>Dye Loading (nmol cm⁻²)</th>
<th>J_S (mA cm⁻²)</th>
<th>V_OC (V)</th>
<th>FF</th>
<th>η (%)</th>
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<tr>
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<td>0.767</td>
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### References