سنتز و مشخصه یابی نانولوله های بسیار منظم دی اکسید تیتانیم با طول های مختلف جهت استفاده در سلول های خورشیدی رنگدانه ای با بازده بالا

زهرا صیدالی لیر و رسول ملک فر
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چکیده – عملکرد سلول های خورشیدی رنگدانه ای بر پایه نانولوله، به طول نانو لوله ها بستگی دارد. در این تحقیق نانولوله های دی اکسید تیتانیم با طول های ۱۵ تا ۳۵ میکرومتر را با روش آندیزیشن در دمای $22.5\ ^{\circ}C$ ، با استفاده از الکترولیت حاوی آمونیوم فلوراید در اتیلن گلیکول و ولتاژ ثابت ۶۰ولت در زمان های مختلف سنتز گردید. نانو لوله های تیتانیم در دو مرحله تحت محلول تتراکلرید تیتانیم قرار گرفتند. با افزایش طول نانولوله ها میزان جذب رنگدانه افزایش و فعالیت فوتوولتائیک بهبود یافته است. بهترین بازده سلول های خورشیدی در طول حدود ۳۰ میکرومتر بوده است.

کلید واژه- آندیزیشن، دی اکسید تیتانیم، سلول های خورشیدی رنگدانه ای، نانولوله.

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 $TiCl_4$ 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, TiO_2, 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_4F, 99.9%; 0.4 wt %) in ethylene glycol in the presence of H_2O (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_2PtCl_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-butylpyridine (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_3CN, 99.9%) and valeronitrile ($n\text{-}C_4H_9CN$, 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.

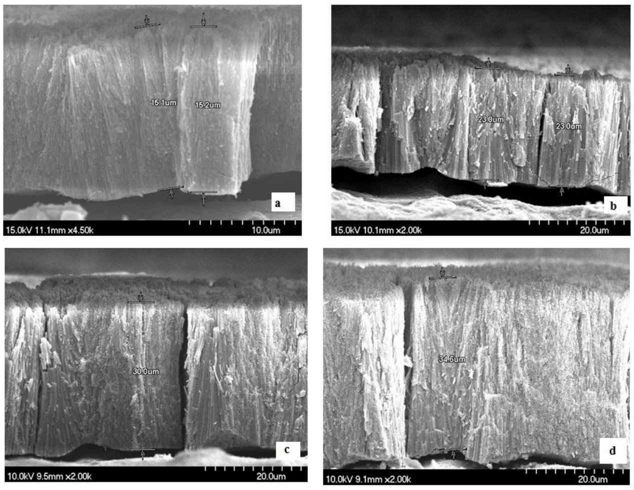

Fig1. SEM images of NTs grown on Ti foil showing various NT lengths (a:L=15µm, b:L=23µm, c: L=30µm and d: L=35µm) after anodization

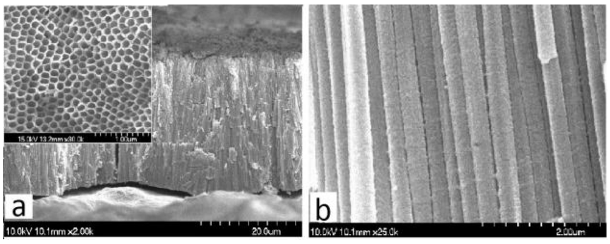

Fig2. SEM images of the TNT film with 30 µm length. (a) side view and the inset shows top-view image of the corresponding TNT arrays (b) cross-section view of straight tube.

Crystalline structure of the TiO_2 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]

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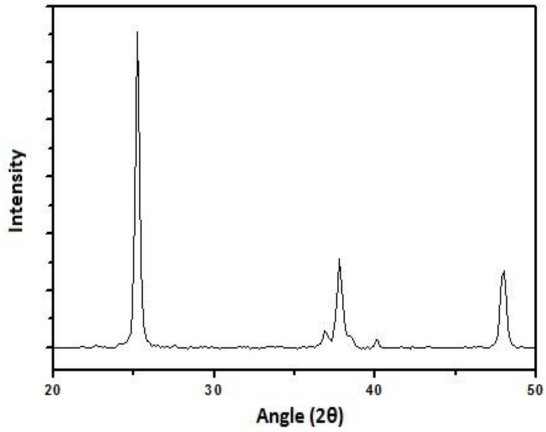

Fig3. (XRD) pattern of the synthesized NT films

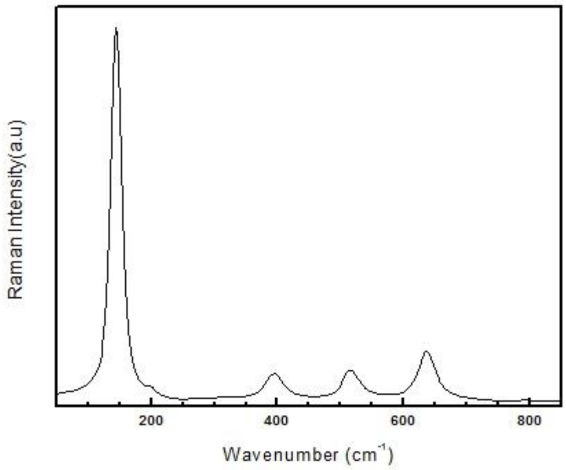

Fig4. Raman Spectrum of the synthesized TiO_2 NTs

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 Table1 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.

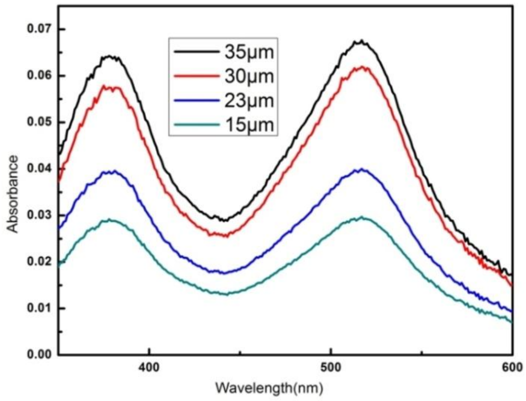

Fig5. Absorption spectra of TNT films sensitized with N719 dye at various tube lengths

The characteristic of photocurrent density (J) versus photovoltage (V) of samples is plotted in figure 6, along with detailed parameters listed in table 1.

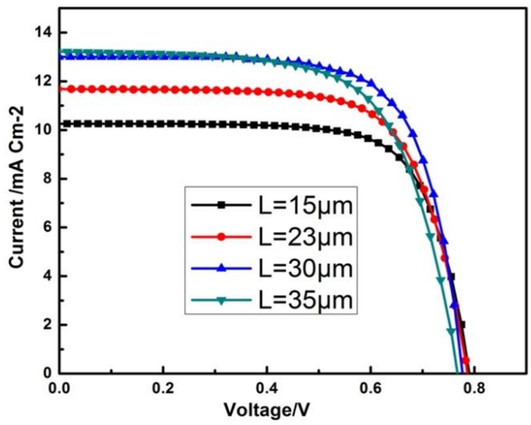

Fig6. Current–voltage characteristics of the NT-DSSC devices fabricated using the anodic TNT films with tube lengths (L/µm) of 15 (■), 23 (●), 30 (►) and 35 (◄).

We summarize the corresponding photovoltaic parameters in Table 1, which demonstrates that the current density at short circuit (J_{SC}/mA cm^{-2}), the voltage at open circuit (V_{OC}/V), the filling factor (FF), and the efficiency ($\eta= J_{SC}V_{OC}FF/P_{in}$ with P_{in}= 100mWcm^{-2}) of power conversion vary as a function of the tube length.[1] The results display a systematic increase for J_{SC} which confirmed that longer tubes offer a larger surface area on which dye molecules adsorb. Our results show also a systematic trend for both V_{OC} and FF decreasing with increasing tube length. The devices with shorter tube length give higher V_{OC} and FF because of good adhesion of NTs to Ti substrate. The optimum length is 30µm. For tubes with 35µm length the quality and adhesion to Ti substrate was very poor, therefore V_{oc} and FF decreased compare to 30µm length.

Table1. Different parameters corresponding to each DSSC

TNT length(µm)	Dye loading/ nmol cm^{-2}	J_{sc}/mAcm^{-2}	V_{oc}/V	FF	η/%
15	114	10.26	0.79	72	5.83
23	153	11.68	0.785	70	6.42
30	237	13.01	0.777	71	7.18
35	257	13.16	0.767	67	6.76

5. Conclusion

Dye-sensitized solar cells based on working electrodes made of highly ordered anodic titanium oxide nanotube arrays of varied tube length formed on Ti foil were fabricated successfully. The NTs were characterized using SEM, XRD and Raman spectroscopy. The lengths of these NT were controlled from 15 to 35 µm. The cell performance of the device was optimized to reach η=7.18% at the tube length ~30 µm, which is the best efficiency presented for a back illumination NT-DSSC using N719 as sensitizer and simple potentiostatic anodization method for NT preparation.

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