การศึกษาผลกระทบของการแอโนไดเซชั่นสองครั้งต่อประสิทธิภาพของท่อนาโนไททาเนียมไดออกไซด์สำหรับผลิตเซลล์แสงอาทิตย์สีย้อมไวแสง

The Investigation of the Impact of Double-anodization on the Performance of TiO_2 Nanotubes for Dye-sensitized Solar Cells

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บทคัดย่อ

ในงานวิจัยนี้ เราได้สังเคราะห์ท่อนาโนไททาเนียมไดออกไซด์บนแผ่นฐานรองไททาเนียมโดยวิธีการแอโนไดเซชั่นด้วยไฟฟ้ากระแสตรงที่ 50 โวลต์ เพื่อทำเป็นขั้วทำงานสำหรับเซลล์แสงอาทิตย์สีย้อมไวแสง (DSSCs) ท่อนาโนไททาเนียมไดออกไซด์ถูกสังเคราะห์ในสารละลายอิเล็กโทรไลต์ที่ประกอบด้วยเอทาลีนไกคอล แอมโมเนียฟลูออไรด์ และน้ำบริสุทธิ์เป็นเวลา 3 ชั่วโมง เซลล์แสงอาทิตย์สีย้อมไวแสงถูกประกอบขึ้นโดยการประกบกันระหว่างแผ่นแก้วโปร่งแสงนำไฟฟ้ากับแผ่นขั้วไฟฟ้าท่อนาโนไททาเนียมไดออกไซด์ที่ดูดกลืนสีย้อมไวแสง N719 เราศึกษาผลกระทบของการบำบัดความร้อนและการสังเคราะห์สองครั้งต่อประสิทธิภาพของท่อนาโนไททาเนียมไดออกไซด์ในเซลล์แสงอาทิตย์สีย้อมไวแสงประสิทธิภาพของเซลล์แสงอาทิตย์สีย้อมไวแสงจากการสังเคราะห์สองครั้งลดลงจาก 3.36% เป็น 0.88% ประสิทธิภาพเซลล์แสงอาทิตย์สีย้อมไวแสงที่ทำจากท่อนาโนไททาเนียมไดออกไซด์ที่สังเคราะห์แต่ไม่ได้ผ่านการบำบัดความร้อนลดลงเป็น 1.95% กลไกของคู่อิเล็กตรอนและโฮลเคลื่อนย้ายจากแถวของท่อนาโนไททาเนียมไดออกไซด์สู่ชั้นของออกไซด์และรูพรุนของท่อนาโนไททาเนียมไดออกไซด์ถูกทำลายเมื่อทำการแอโนไดเซชั่นสองครั้งส่งผลทำให้ประสิทธิภาพของเซลล์แสงอาทิตย์สีย้อมไวแสงต่ำลง

คำสำคัญ : เซลล์แสงอาทิตย์สีย้อมไวแสง การแอโนไดเซชั่นสองครั้ง ท่อนาโนไททาเนียม การบำบัดความร้อน

Abstract

In this research, we have synthesized TiO_2 nanotubes on titanium metal substrates by DC anodization at 50 V to be used as working electrodes for dye-sensitized solar cells (DSSCs). The TiO_2 nanotubes were fabricated in an electrolyte consisting of ethylene glycol, ammonium fluoride and deionized water for 3 hours. DSSCs were assembled by sandwiching the N719 dye - coated TiO_2 nanotubes electrode and transparent conducting oxide glass electrode. We investigated the impact of heat treatment and double-anodization on the performance of the titania nanotubes in the dye sensitized solar cells. The performance of the double-anodization TiO_2 nanotubes greatly reduces when compared with single anodization in DSSCs from 3.36% down to 0.88%. The performance of anodization without heat treatment also reduces to 1.95%. The mechanism of electron - hole pairs was favor and transits from TiO_2 nanotubes arrays to the oxide layer. The crack and destroyed pore tubes on these specimens appeared by double-

anodization. Hence, the low performance of the dye sensitized solar cells was found in this experiment.

Keywords : dye-sensitized solar cells; double-anodization; titania nanotubes; heat treatment

Introduction

Semiconducting titania - Titanium dioxide (TiO_2) has attracted greatly attention in scientific research because of its excellent electrical, chemical and optical properties. Currently, its applications increase in many areas such as photovoltaic [1], photocatalysis [2], humidity sensing [3] and hydrogen generation [4]. Solar absorption in titania is limited to the ultra-violet region of the solar spectrum due to its wide band gap of about 3.2 eV for anatase phase. Another problem encountered during titania applications is that of charge recombination. These problems, together with others lower the efficiency of titania devices for commercial applications. The development of titania nanotubes - TNT [5] and introduction of foreign ions through doping [6], are some of the ways being used to enhance the performance of titania devices.

Several methods have been used to prepare TNT. These include hydrothermal method [7], solvothermal method [8], co-sputtering techniques [9] and anodization method [10]. Anodization is more commonly used because its cheaper and the apparatus is simple and easy to set up. A number of different parameters such as anodization conditions, electrolyte conditions, cleaning methods, and calcination conditions have been investigated during the fabrication process.

In 2011, S. Bauer et al [11] investigated the effects of types of electrolyte and annealing time on the size (diameter and length) of titania nanotubes. The different electrolytes used were: H_3PO_4 /HF (with varying fluoride content), Glycerol/Water/NH_4F, Na_2SO_4/NaF and NaH_2PO_4/HF. The annealing was carried out at 450 ℃ for 5 minutes and 60 minutes. They found out that size effect determined the phase transformation of the TNT upon annealing. The results found the small pore diameters of titania nanotubes were formed when it was synthesized in the varying fluoride content. The rutile phase was found when this specimen was annealed at 450 ℃ for 5 minutes. On the other hands, Glycerol mixed with varying fluoride content electrolytes were used for the large diameters of formation and anatase phase was formed at 450 ℃ for 5 minutes annealing. R. Liu et al [12] in 2011 reported on the influence of electrolyte concentration, anodization voltage, and annealing temperature on TNT size and morphology. Pore diameter was decreasing because of the increasing of electrolyte concentration.

Materials and Methods

TiO_2 nanotubes were grown by DC anodization method at 50 V for 3 hours at room temperature. Titanium sheets of 0.25 mm thickness and 99.7% purity purchased from Sigma Aldrich were first polished by abrasive papers. After being polished, the Ti

foils were degreased ultrasonically in isopropanol, de-ionized water and ethanol. The electrolyte was composed of ethylene glycol (EG), ammonium fluoride (0.3% wt NH_4F). Sources of the chemicals were put properly and deionized water (4% vol D.I. H_2O) [13]. For the homogenous in electrolyte, the electrolyte was kept for 5 hours before anodization. The anodization apparatus is a two-electrode configuration with a piece of highly pure platinum counter electrode. Figure 1 shows the schematic diagram of the anodization process. This set up allows only one face of the Ti foil to be in contact with the electrolyte. The samples studied in the experiment consisted of (a) anodized without annealing (b) anodized once and annealed at 450 °C and (c) re-anodized after annealing at 450 °C. Characterization was done using XRD, SEM, AFM and performance test of DSSCs. For DSSCs, TiO_2 nanotubes working electrodes were immersed in 0.5 mM solution of N719 dye in a mixture of acetonitrile/tert-butanol (1:1) at 25 °C for 24 hours. A transparent conducting oxide glass (TCO) is used as a counter electrode. A platinum catalyst was deposited on the TCO glass by coating with drop of platinum solution (H_2PtCl_6). The TCO glasses were heated for 30 min at 80 °C. Then, TiO_2 nanotubes photoelectrode and Pt counter electrode were assembled into a sandwich. The TiO_2 nanotubes arrays were finally assembled into DSSCs and their IV characteristics were measured. And then the photovoltaic parameters of the DSSCs were measured by the four most important parameters, which were the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and the conversion efficiency (η). The equations of DSSCs are shown as follows: [14]

$$FF = \frac{V_m I_m}{V_{oc} I_{sc}} \quad (1)$$

$$\eta = \frac{V_m I_m}{P_{in}} = \frac{V_{oc} I_{sc} FF}{P_{in}} \quad (2)$$

where I_m and V_m are the current and voltage at the optimal operation point that gives the maximum output power or power at maximum power point and P_{in} is the power of the incident light.

Results and Discussion

Figure 2 shows XRD patterns of anodized TiO_2 nanotubes for samples (a) anodized without heat treament (b) anodized once and annealed at 450 °C and (c) re-anodized after annealing at 450 °C. The anodized without heat treament sample (a) shows anatase phase. Whereas, the annealed samples (b) and (c) clearly indicate presence of anatase phases A with the most prominent peak at 2θ = 25.27°, corresponding to the phase A (101). The TiO_2 transformed from an amorphous phase to a crystalline anatase phase all samples. This result is in good excellent agreement with the report in [15], which explains that heat treament or annealing is essential for phase transfomation to occur in titania.

Figure 3 shows the SEM images of the prepared samples. From the images (C), we can see that the morphology and top surface of the nanotubes become crack and destroyed pore tubes as non-nanotubes arrays when the specimens were re-anodized. This

crackness and non-arrays could have the effect to the formation of additional oxide layers [16]. The average of pore size is 83 nm that appears in the once anodization. For the re-anodization, the average of pore size is 45 nm. Figure 4 shows the AFM immages of the once anodization (b) and re-anodization (c) the pore of tubes average is 77 nm and 88 nm respectively. The thickness of tube was increased at re-anodization. Therefore, The thickness of tubes is one of factors in photoresponse and the electron transportation. Moreover, in the Figure 3 (c) and Figure 4 (c) show the creackness of titanium nanotubes layer. Consequently, the electron-hole pairs recombination in the oxide layer is more increasing than the nanotubes. Although all pore tubes are decresed [17].

Figure 5 shows the current-voltage characteristic curves for the different samples in the DSSCs. Figure 6 shows a schematic of the photo-response for the DSSCs. From the curves, we calculated current-conversion efficiencies of the DSSCs for the different samples. This is displayed in table 1. The performance of the anodized once and annealed sample shows the best with efficiency of 3.36%. This is almost double that of the anodized without heat treament sample with efficiency of 1.95%. On the other hand, the re-anodized sample gives the worst performance with efficiency of 0.88%. This is less than half the efficiency of the anodized without heat treament sample. As seen from the XRD results, the presence of anatase phase is responsible for the higher efficiencies for samples (a) and (b). However, as observed from the SEM images, poor uniformity and high surface roughness in the sample (c), strongly accounts for its very low efficiency. These results are in agreement with the works of P. Roy et al [18], which stated that in homogeneity of morphology of nanotubes was detrimental to their performance.

Conclusion

Titania nanotubes were prepared on titanium metal substrates by DC anodization at 50 V. The nanotubes were anodized in an electrolyte consisting of ethylene glycol, ammonium fluoride and deionized water for 3 hours. We investigated the impact of heat treatment and double-anodization on the performance of the samples in DSSCs with N719 dye. Our findings suggest that double-anodization greatly reduces the performance of the nanotubes, while heat treatment enhances the performance of DSSCs due to phase transformation. The best case scenario is to achieve longer tubes. Longer tubes will offer larger surface area for photon capture. But as we have found out in this work, the probability of that happening is very low. Nonetheless, the results of this research are important for future researchers.

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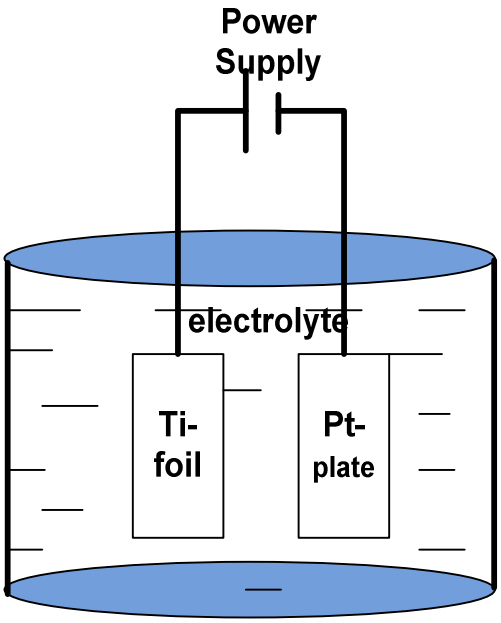


Figure 1. The schematic diagram of a single-face anodization process.

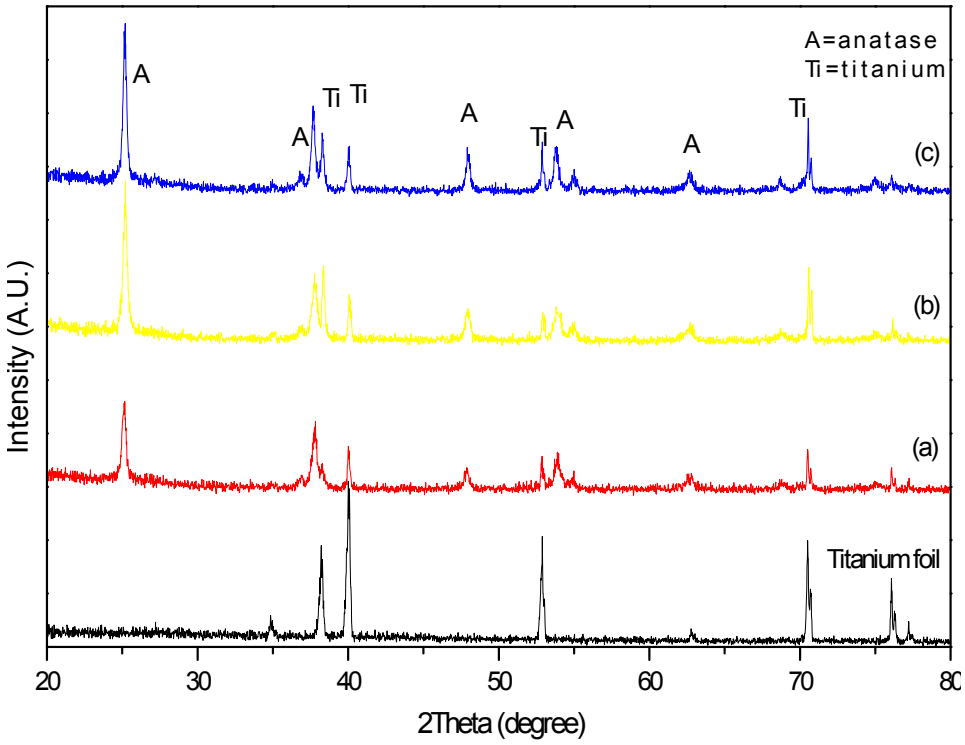


Figure 2. XRD patterns of anodized TiO_2 nanotubes for samples (a) anodized without heat treament (b) anodized once and annealed at 450 ℃ and (c) re-anodized after annealing at 450 ℃.

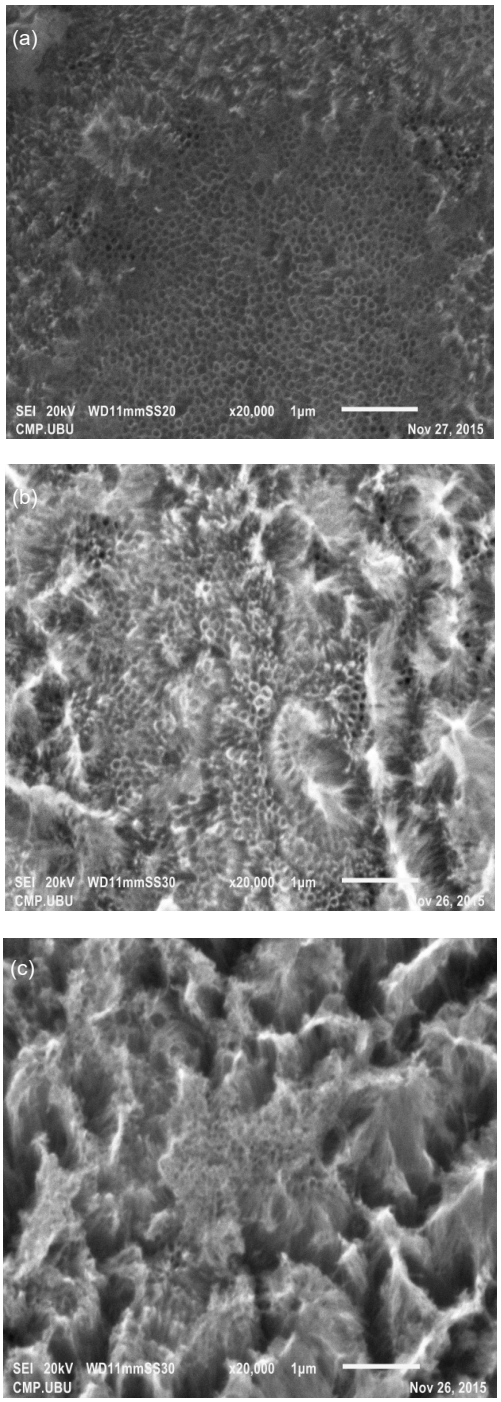


Figure 3 SEM image (top surface views) of TiO_2 nanotubes with different tops (a) anodized without heat treament (b) anodized once and annealed at 450 °C and (c) re-anodized after heat treatment at 450 °C.

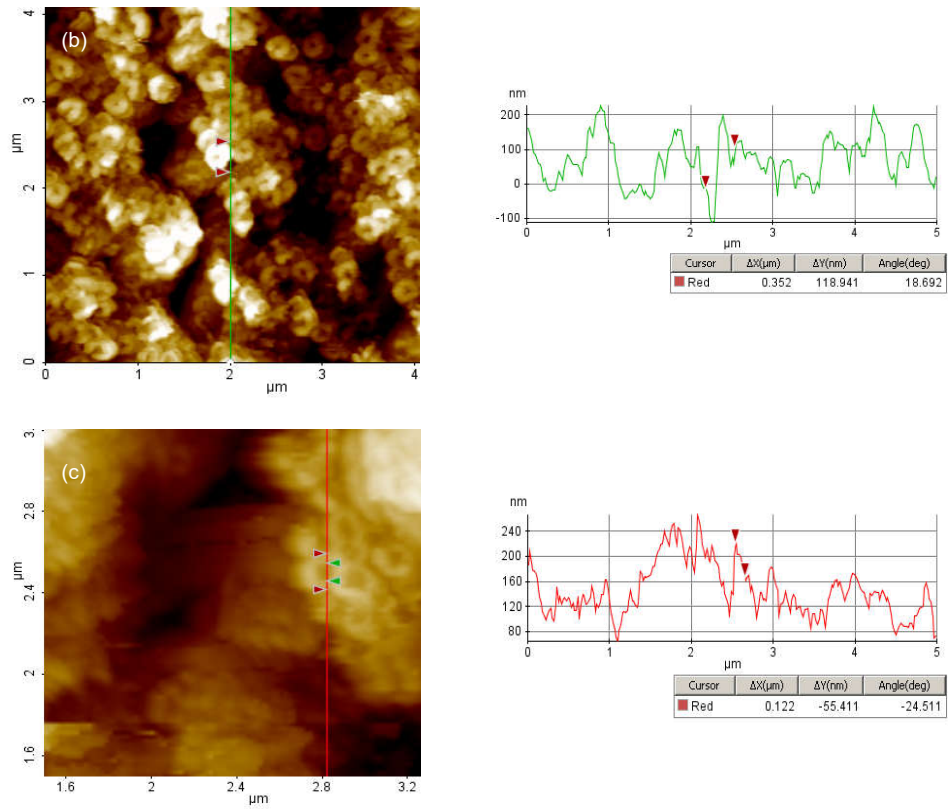


Figure 4 AFM image of anodized TiO_2 nanotubes (b) anodized once and annealed at 450 °C and (c) re-anodized after heat treatment at 450 °C.

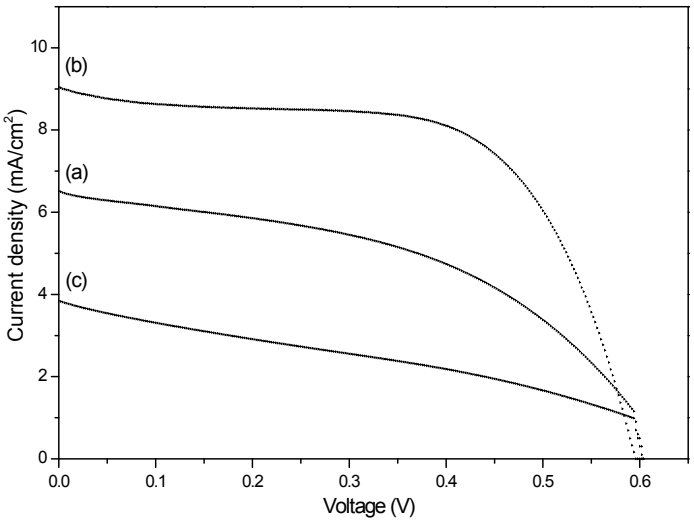
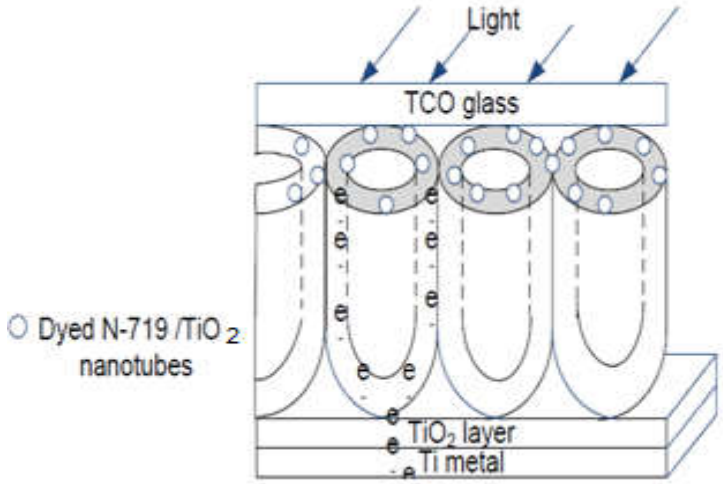
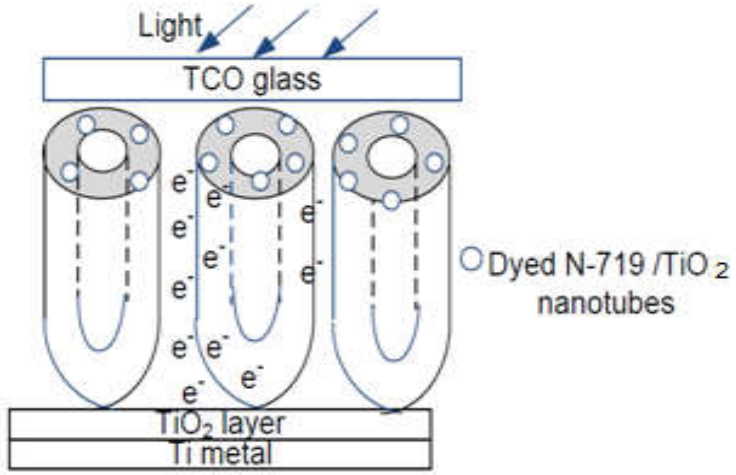


Figure 5 I-V characteristic curves of DSSCs for the samples (a) anodized without heat treatment (b) anodized once and annealed at 450 °C and (c) re-anodized after heat treatment at 450 °C.



(b)



(c)

Figure 6 A schematic diagram of photo-response for dye-sensitized solar cells (b) anodized once and annealed at 450 °C and (c) re-anodized after heat treatment at 450 °C.

Table 1 The efficiencies of dye-sensitized solar cells (a) anodized without heat treatment (b) anodized once and annealed at 450 °C and (c) re-anodized after heat treatment at 450 °C.

Samples	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	**η** (%)
(a) without heat treatment	6.52	0.61	0.49	1.95
(b) single anodization	9.04	0.59	0.63	3.36
(c) re-anodization	3.85	0.60	0.38	0.88

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