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Study of Well-Structured Titanium Nanotubes AnodeSynthesisfor Solar Cell Applicationby Electrochemical Anodization Method

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Abstract: Well-structuredperpendicularly Titaniumnanotubes anode sample of size of 10×10mm^{2}has been fabricated by the electrochemical anodization method using an electrolyte containing 0.44 wt % NH_4F and 4 vol % DI water. The influence of the technological condition ofanodization high voltage has been studied. It was found that anodizationhigh voltage significantly Influence the diameter and length of a Titanium nanotubes anode. The diameter and the length of a Titanium nanotubes anode have been observed and estimated by using high resolution scanning electron microscopy(HRSEM).It has revealed that the diameter and the length of about 150.05nm and 7.581µm, respectively, were acquiredfor the anodized sample, under a voltage of 70V for 22 minutes, after 19 hours long break then, 35V for 40 minutes condition.The XRD measurement has revealed the anatase phase ofTitaniumnanotubes anode and found neat matching with others investigated works. The sample of nanotubes anode fabricated,have showna maximum absorbance ability at wavelengths around 300 nm to 350 nm, was recorded at room temperature. It is experimental evidence that the manufactured Titanium nanotube anode is an expected material for the nano solar cells
Keywords: *TNA, nanotube arrays, Anodization method,HRSEM*

Introduction

In the modern years, vertically oriented, highly ordered titanium dioxide (TiO_2) nanotube array, had fabricated by anodization of titanium, and had attracted great attention[1-5]. Highly ordered vertically oriented nanotube structure of high surface to volume ratio had revealed unique properties. Nanotube had suggested a larger interface area due to their external and internal surfaces, which had created them suitable for applications in dye-sensitized solar cells[6]. It also had givenwonderful electron pathways for charge transfer between interfaces. TiO_2 nanostructures can be synthesized by different methods like sol gel transcription using organogelator template[6,7], spilled development mechanism[8], hydrothermal techniques[9]. Among these processes, the electrochemical anodization method of titanium in fluorinated electrolytes is an easy method to fabricateporous, highly vertically ordered structures with high aspect ratios. The process of self-organization of nanotube is a complicated mechanism[10-13] and needsimmense study. The properties of self-organized TNA can be fabricated using differentanodizationparameters and post deposition treatment. In the present work, anodizationhigh voltage 70V-35V was applied to observe changes in the morphology of the Titanium nanotubes anode.

Materials and Experiment Method

Titanium foil (99.6% purity, Ti TEK UK LTD, Birmingham, UK) with athickness of 0.45mm was taken for the anodization. Smallpieces of Ti foil of size 10x10 mm^2 were cleaned byseparately in acetone,

ethanol, and finally withde-ionized water (DI), for 15 min each. Electrochemicalanodization of titanium had been carried out using a two-electrodeconfiguration with Ti as working electrode and stainless steel as counterelectrode.

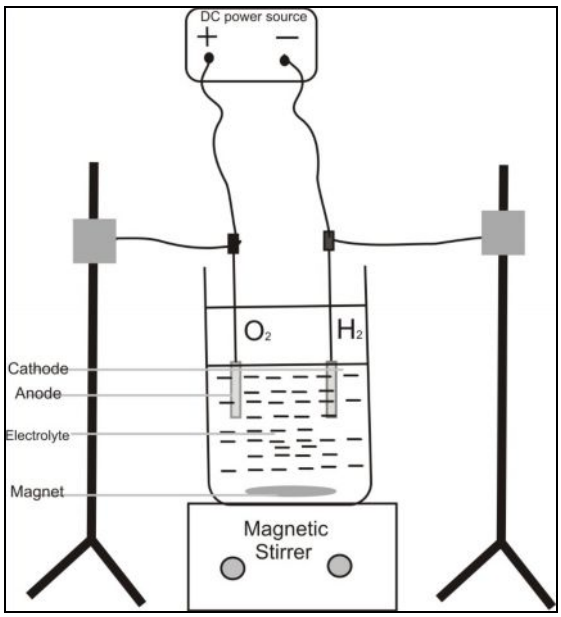

Figure 1. Schematic diagram of Electrochemical anodizing method.

Anodization process was conducted above room temperature under 70V-35V voltage condition using a source meter and the current response of the sample was examined in real time.

The electrolyte solution containedof 0.44 wt % NH_4F salt, 4 vol.% DI water and ethylene glycol. During the electrochemical anodization process,70V was supplied for 22 minutes, then 19 hours long break, again 35V have been supplied for 40 minutes. While anodization temperature range had been maintained from 27°C to 41°C for 70 V. After the 19 hours long break,anodization temperature range had beenmaintained from 27°C to35°C for 35 V.After synthesis of anodized titanium foil was rinsed in deionized water. Then, the sample had been annealed in a muffle furnace at 500°C for 1 hour at the heating rate of 10°C/4minutes and used for characterization test. The electrolyte was stirred at 115RPM continuously during the anodization process.

Figure 2. (A) Electrochemical anodizing method Equipments setup in the Lab. (B) DC regulator (C) Titanium foil and Stainless steel foil.

The syllable architecture of the anodized sample had been examined by High resolution scanning electron microscopy (HRSEM, AU Quanta 250 FEG). Titanium nanotubes anode structural characterization had been analyzed by X-ray diffraction (XRD, Flat stage PW 3050/60) using Cu, Kα incident radiation, a voltage of 40 kV and a current of 30 mA. The scan range was 10.0167° to 79.9767°, 5 minutes with a scanning rate 12.7°/Sec. UV-vis spectroscopy exhibited the maximum absorbance edge at wavelengths (UV-vis

spectroscopy, Erkin Elmer Lambda 750, USA). A small piece of Titanium nanotubes anode thin film had been madefor the cross sectional HRSEM images.

Results and Discussions

The Figure2 represents the anodizationprocess for the Titanium nanotubes anodefabricated at70V for 22 minutes, after 19 hours long break then, 35V for 40 minutes condition. By using electrochemical anodizationof two electrodeconfigurations, well-structured Titanium nanotubes anode had been fabricated and characterized by using EDX Spectra, UV-vis Spectroscopic, HRSEM, and XRD method at room temperature.

Surface Morphology Analysis

The High resolution scanning electron microscopy (HRSEM) images of the Titanium nanotubes anode fabricated at 70V for 22 minutes, after 19 hours long break then, 35V for 40 minutes condition are shown in Figure. 3.and Figure. 4. The average diameter and length of the Titanium nanotubes anode prepared are about 150.05nm and 7.581µm respectively.Figure.4shows the cross section view of a Titanium nanotubes anode at two different magnifications.

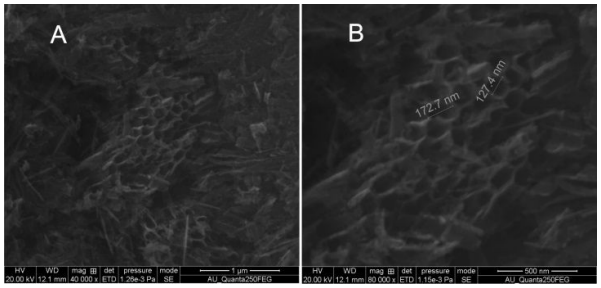

Figure 3.HRSEM images of top view of Titanium nanotubes anode, fabricated at anodization voltage 70V-35V.(A) Low magnification image (B) High magnification image.

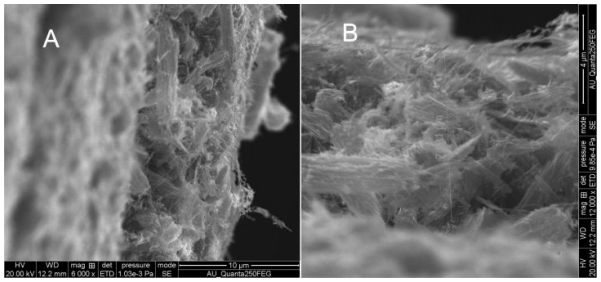

Figure 4.HRSEM images of side view of Titanium nanotubes anode,fabricated at anodizationvoltage 70V-35V.(A) Low magnification image (B) High magnification image.

Schmuki et al,[14] had experimented the diffusion of ion in the electrolyte solution with the blooming of nanotube arrays in the thin foil. In the case of Titanium nanotube arrays bloom in organic electrolyte solution, the impact of DC voltage, stirrer and anodization temperature would also be reviewed into account.Two different diffusion processes were studied that is, the H^+ ion diffusion toward the cathode electrode and F^- ion diffusion toward the anode electrode.

The following chemical reactions had taken position at the anode [14,15,16] in the development of Titanium nanotube arrays.

$$Ti + 2H_2O/2OH^- \rightarrow TiO_2 + 4H^+ / 2H^+ + 4e \quad [1]$$
$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF^{2-}{}_6 + 2H_2O \quad [2]$$

Reaction of chemical one was answerable for field-assisted oxidation process, while the reaction of chemical two had fulfilled to field-assisted dissolution. Nanotubes blooming had taken place, due to tuning between these two chemical reactions. The fluorine ion is basically a very importantfactor in the blooming rate ofthe Titanium nanotubes anode, in the absence of which only a thin titanium oxide layer was created through chemical reaction one[17].

In the current organic electrolyte had wanted hydrogen ions originate mainly from field-assisted oxidation through chemical reaction to nanotube arraysblooming. Emission of gas had been investigated from both titanium foil and stainless steel foil, foil surfaces in the first tens of seconds after initiating the anodization process. This proposed the thing of the achieving desired chemical reactions under DC power supply.

$2H_2O \rightarrow O_2 + 4H^+ + 4e$ (Anode) [3]
$2H_2O + 2e \rightarrow H_2 + 2OH^-$ (Cathode) [4]

We had investigated a potential drop in the electrolyte, ionic flux at the front side of Titanium foil consist of two parts which were ion diffusion reaction under concentration gradient and ion movementreaction under electric fields. In contrast, only ion diffusion reaction withstand at the front side of Titanium foil, as follows:

$J_f = -pD [\partial c/\partial x] + ucE$[5]

Where 'J_f' is the ionic flux at the front side of Titanium foil, 'p' is the porosity of the nanotube arrays surface, 'D' is the diffusion coefficient, c is the concentration, '$\partial c/\partial x$' is the concentration gradient, 'u' is the ion mobility, and 'E' is the strength of electric field in the organic electrolyte. In this anodization method hypothetically, mass transport in the electrolyte had happened by diffusion reaction, convection reaction, or migration reaction.

EDX Analysis

EDEX study had been carried out to investigate the components of the fabricated Titanium nanotubes anode. The result shows that the sample fabricated at 70V for 22 minutes, after 19 hours long break then, 35V for 40 minutes condition, comprised the elements such as Ti and O. From Figure 5, it can be revealed that the atomic ratio of Ti to O was approximately 1 : 2, exhibiting that Ti and O elements have existed with carbon and nitrogen elements as shown in the graph.Ti and O are 65.90 wt% and 25.61 wt% respectively. The existing other elements in the Titanium nanotubes anode such as Carbon and Nitrogen are 03.41 wt% and 05.08 wt% respectively.

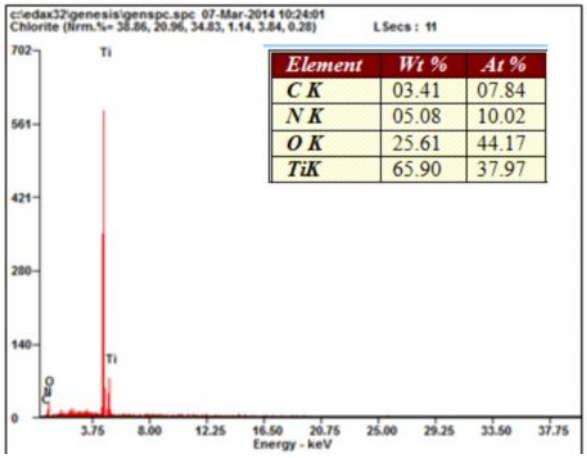

Figure 5.EDEX Spectra of Titanium nanotubes anode at 70V-35V.

XRD Analysis

After annealing titanium nanotubes anode at 500°C for 1 hour in a muffle furnace, the X-ray diffraction analysis had been conducted for crystal phase identification.The diffraction peaks of Titanium nanotubes anode were clearly investigated which could be referred to anatase. The sample of nanotubes anode fabricated at 70V for 22 minutes, after 19 hours long break, 35V for 40 minutes condition, exhibited a presence of anatase TiO_2 with 2θ peaks at 24.96°, 37.47°, 39.78°, 47.76°, 52.65°, 53.64°, 62.45°, 68.62°, 70.34°, 74.82°, and 75.91°. In general, as-fabricated Titanium nanotubes anode are amorphous in nature which can be transformed into anatase or a mixture of anatase and rutile after annealing at temperature 500°C.The average size of particles can be calculated from the XRD pattern of the sample using Schere's equation.

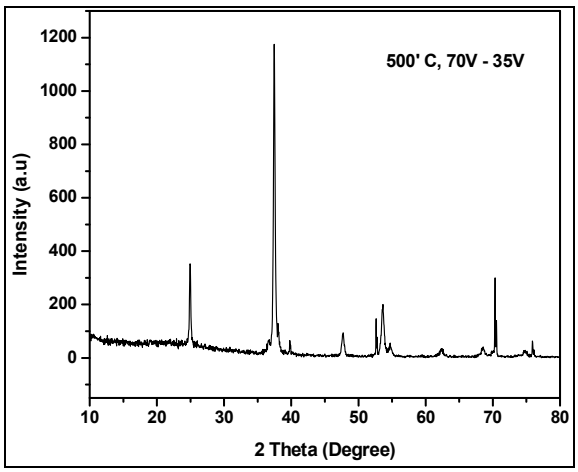

Figure 6.X-ray diffraction of Titanium nanotubes anode at 70V-35V.

UV-VIS Spectroscopy Analysis

Figure 7 shows at room temperature the visible light absorbance of Titanium nanotubes anode had been learned in the range of 300-800 nm. The sample of Titanium nanotubes anode fabricated at 70V for 22 minutes, after 19 hours long break then, 35V for 40 minutes condition had unveiled maximum absorbance ability at wavelengths around 300 nm to 350 nm.

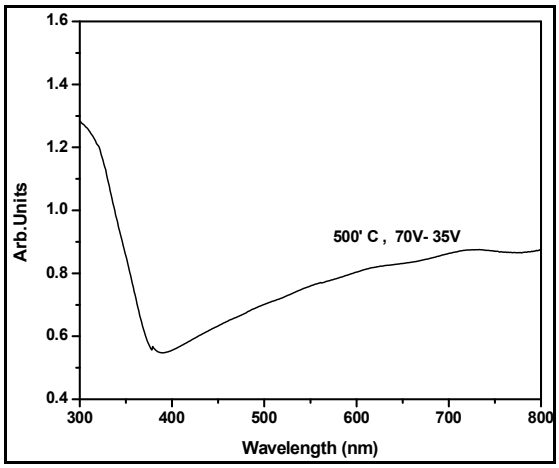

Figure 7.The UV pattern of Titanium nanotubes anode, prepared at 70V-35V.

$E_g = h \times (v/\lambda)$ [6]

'E_g' is the band gap of Titanium nanotubes anode, 'h' is the Plank constant, 'v' is the speed of light and 'λ' is the cut off wavelength of radiation generated by UV-vis spectroscopy.

Conclusions

In conclusion, well-structured perpendicularly Titanium nanotubes anode had been successfully prepared by anodization technique with anodizationhigh voltage ranging from 70V for 22 minutes, after 19 hours long break then, 35V for 40 minutes condition,to study the growth of nanotube dimensions such as diameter and tube length. The study had revealed that increase of anodization voltage induced systematic changes in the morphology of the Titanium nanotubes anode. This gradual morphological change is very useful for fine tuning property that is appropriate for (DSSCs) - dye sensitized solar cell application. In this present investigation, HRSEM measurement confirmed that increase of anodization voltage enhanced diameter of the Titanium nanotubes anode and nanotube length are 150.05nm and 7.581µm respectively. The sample showed maximum absorbance ability at wavelengths around 300 nm to 350 nm from UV-vis spectroscopy result.

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Abbreviations

DSSCs, dye sensitized solar cells; HRSEM, high resolution scanning electron microscope; TNA, Titanium nanotube arrays.

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