Research Paper

GROWTH AND CHARACTERIZATION OF TITANIUM NANOTUBES ANODE FOR SOLAR CELL APPLICATION BY ELECTROCHEMICAL ANODIZATION METHOD

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ABSTRACT

TiO_2 is recognized as one of the most needed material for its extensive scope of industrial applications. In this work, the development of TiO_2 nanotube arrays by using unproblematic and low-cost electrochemical anodizing method of a titanium thin film foil had been presented. The vertically tailored TiO_2 nanotube arrays had been made in an electrolyte solution of 0.44 wt % NH_4F salt, 4 vol.% DI water and ethylene glycol at a constant DC voltage of 60V for 1 hour for the first sample and 75V for 45 minutes for a second sample. The UV absorbance ability, crystallinity and surface morphology of fabricated nanotube arrays were investigated by UV-vis Spectroscopy, XRD and HRSEM. XRD measurement revealed the anatase phase of TiO_2 nanotube arrays and found neat matching with others investigated works. HRSEM measurement revealed comfortably aligned formation of nanotube arrays at 60V is 108.35 nm of mean diameter and nanotube arrays at 75V is 157.5 nm of mean diameter. Formation of titanium nanotube arrays at 60V has 4.177µm of mean length and nanotube arrays at 75V has 17.02µm of length. The first sample of nanotube arrays fabricated at 60V condition had showed maximum absorbance ability at wavelengths around 300 nm to 572 nm than, the second sample of nanotube arrays fabricated at 75V condition had showed maximum absorbance ability at wavelengths around 300 nm to 545 nm.

KEYWORDS : TNT arrays, Titanium anode, Anodizing method, Electrochemical process,HRSEM.

INTRODUCTION

Nowadays, an essential work to our society is the development of efficient devices, comprehensively for energy storage and energy conversion. Among all, the conversion of energy by dye sensitized solar cells (DSSCs) and storage of energy in lithium-ion batteries have been receiving the tremendous attention of researchers. Titanium nanotube arrays have significant properties such as charge transport and carrier lifetime unique property serving a one important application in the dye sensitized solar cells. One-dimensional metal-oxide nanostructures have got attraction due to their excessive electron mobility, deficient carrier recombination rate, excessive surface-to-volume ratio and great surface activity. One of their significant applications is in dye sensitized solar cells, as a thing of fact the electron scattering length in the anodic TiO_2 based DSSCs could be up to 100 µm which is nearly four times longer than in case of popular TiO_2 nanoparticles used in DSSCs. This peerless charge transport property had received a comprehensive research on anodic titania nanotubes for DSSCs. TiO_2 1D-tubular pattern has light scattering power and improved electron charge transport which is the dangerous issues in photoelectrochemical and photocatalysis applications. Due to electronic and good chemical properties, TiO_2 is an appropriate candidate as vital materials in electrochemical devices[1]. Anodic TiO_2 nanotube arrays had received the enormous attention of scientific community due to their comport development with tunable necessary properties. In 2013, Dubey et al. had explained the vertically oriented TiO_2 nanotube arrays preparation in the electrolyte solution of 3 wt % HF (40%) and dimethyl sulfoxide (DMSO) at constant DC voltage of 30 V for 17 hours.[2] Ammar Elsanousia et al. had explained the significant photo conversion efficiencies may be obtained from the front-side illuminated DSSC with an increase of the nanotube arrays length to several micrometers.[3] In first generation, Zwilling et al. had explained the growth of nanoporous anodized titanium nanotube arrays, however, D. Gong et al. had first examined work on anodized titanium nanotube arrays by using a dilute hydrofluoric (HF) acid as an electrolyte[4,5]. The achieved thickness of anodic layer had been ended upto 0.5µm due to employed HF which etched and fluxed most of the developing oxide. In the second generation of nanotubes, the fast rate of titania dissolution had been lowered by substituting the HF acid with lessvigorous solutions comprising fluoride salts and had examined the anodic layer thickness from 2-3µm[6,9]. Even though, the use of water produces irregularities (ripples) along the walls of the nanotubes. In the third generation of nanotubes, plain tubes without ripples along the wall of nanotubes had been produced in the electrolytes which aid to lower the dissolution rate of oxide growth rate. J. M. Macak et al. had investigated the growth rate of titanium nanotube arrays by using organic electrolyte and revealed anodic layer thickness about 7µm[10].

The fabrication of TiO_2 nanotube arrays can be performed by using hydrothermal and electrochemical anodization methods[11,12]. The electrochemical anodization method is considered to be the famous one due to its simple method and great controllability on structural properties of nanotubes. Anodic oxidation method is one which can be stimulated for large area uniform nanotube arrays on the Titanium foil with the relatively great specific surface. Feng Zhou et al. had examined the fabrication of TiO_2 nanotubes with tunable morphologies by modifying the reaction parameters during anodization. By changing the process parameters such as reaction temperature, applied DC voltage and HF concentration level either nanoporous TiO_2 nanotubes or freestanding nanotubes had been achieved with tunable tube diameter size, tube length and tube wall thickness[13]. P. Schmuki et al. had examined the self-organized TiO_2 nanotube layer growth rate in different types of electrolytes such as glycerol/water/ammonium fluoride electrolytes. They revealed that with the use of these types of electrolytes, it is attainable to develop nanotubes of 20-300 nm with the applied DC voltage in the range of 2-40V [14]. F. Durstock et al. were successfully fabricated clear structured TiO_2 nanotubes by employing a nanoporous alumina template process method. The average tube external diameter, tube lengths and tube wall thickness of TiO_2 nanotube arrays were 295 nm, 6-15 µm, and 21-42 nm

respectively. The produced nanotubes had been used as working electrode in dye-sensitized solar cells and obtained power conversion efficiency as high as 3.5% [15]. Jun Wang et al. had investigated the effects of electrolyte temperature and anodization potential on the growth rate of TiO_2 nanotube arrays by employing aqueous and nonaqueous electrolytes. In case of aqueous electrolyte, they had revealed that the anodization potential used significant impact on the growth rate of highly ordered TiO_2 nanotube arrays while lesser effect of the temperature of the electrolyte. However, with nonaqueous electrolyte, the electrolyte temperature clearly impacted the TiO_2 nanotube dimensions[16]. The effect of modification of applied anodization DC voltage ranging from 50V to 57 V on the morphology of the TNA had been investigated using FESEM and XRD pattern by Swati Bhardwaj et al[17].

Patrik Schmuki et al. had reported the development of TiO_2 nano bamboo tubes by employing alternating-voltage anodization of Ti in fluoride containing electrolytes. They had revealed that by a mere change in the electrochemical parameters, the geometry and surface properties of the nanotube layers can be modified over a broad scope. Key to the maximum efficiency is the considerable increase in dye loading of the material that can be obtained because of the bamboo rings[18]. Mahendra A. More et al. had reported the great aligned TiO_2 nanotubes prepared by anodization method of the Titanium foil. The tube inner diameter had been revealed to be 60–80 nm with the average tube wall thickness about 30 nm. A good correlation was revealed between the photo-enhanced field emission (FE), results of photoluminescence and the photoconductivity of the well aligned TiO_2 nanotube arrays[19]. Balasundaramet al. hadanalysed about Study of Well-Structured Titanium Nanotubes Anode Synthesis for Solar Cell Application by Electrochemical Anodization Method[26].Balasundaramet al. had evaluated about Development and Morphology of Titanium Nanotubes Anode for New Generation Solar Cell by Electrochemical Anodizing Method[27]. In this paper, self, great aligned titanium nanotube arrays fabricated by electrochemical anodization method had been examined.

MATERIALS AND METHODS

For anodization process, the electrochemical setup of two electrode configuration had been used. For fabrication, the Titanium thin film foil (99.6% purity, 0.45 mm thickness, Ti TEK UK LTD, Birmingham, UK.) sample size ($10\times10\times0.45mm^3$) have been used as a working electrode and a stainless steel foil as the counter electrode under constant potential at above room temperature. Before the process, titanium foil was degreased in an ultrasonic bath for 15 min. with ethanol and acetone sequentially. The electrolyte solution of 0.44 wt % NH_4F salt, 4 vol.% DI water and ethylene glycol at constant DC voltage of 60V for 1 hour for the first sample and 75V for 45minutes for the second sample.Anodization temperature range was maintained from 27° C to 36° C for the first sample and for the second sample from 27°C to 45° C. After synthesis, anodized titanium foil was rinsed in deionized water. Then, the both the samples had been annealed in a muffle furnace at 470° C for 1 hour at the heating rate of 10°C/4minutes and used for characterization.

Figure 1. (A) Electrochemical anodizing method Equipments setup in the Lab. (B) DC regulator (C) Titanium foil samples.

The syllable structure of the anodized samples had been analyzed by High resolution scanning electron microscopy (HRSEM, AU Quanta 250 FEG). Titanium nanotubes structural characterization had been examined 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° to79.9767°, 5 minutes with a scanning rate 12.7°/Sec. UV-vis spectroscopy showed the maximum absorbance edge at wavelengths (UV-vis spectroscopy, Erkin Elmer Lambda 750, USA). A small piece of Titanium oxide thin film had been prepared for the cross sectional HRSEM images of nanotube arrays.

RESULTS AND DISCUSSION

By using electrochemical anodization of two electrode configurations, self-aligned TiO_2 nanotube arrays had been made and characterized by using HRSEM, EDX Spectra, UV-vis Spectroscopic and XRD method at room temperature.

SURFACE MORPHOLOGY ANALYSIS

Figure 2shows the typical surface morphology titanium nanotube arrays measured by HRSEM. Figure 3 shows the cross sectional view of Titanium nanotube arrays and its mean length. The mean diameter of Titanium nanotube arrays of first sample fabricated at 60V was 108.35 nm and its tube length was about 4.177µm. The approximate mean diameter of Titanium nanotube arrays of the second sample fabricated at 75V was 157.5 nm and its mean tube length was about 17.02µm. The HRSEM result revealed that the second sample at 75V synthesized titanium nanotube arrays had more surface area than the first sample.

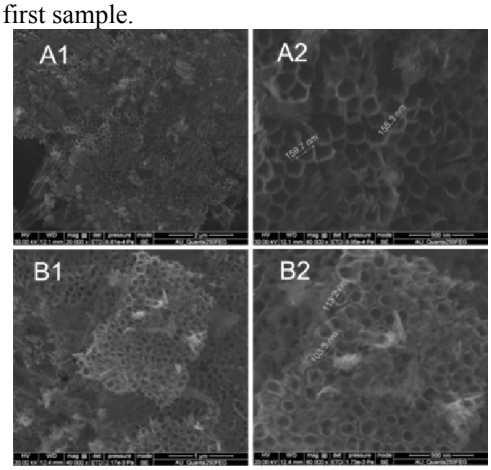

Figure 2. HRSEM images of TiO_2 nanotube arrays at two different magnifications (A1,A2), fabricated at 75V for 45 minutes and (B1,B2), 60V for 1 h and heat treated at 470°C and 470°C for 1 h respectively.

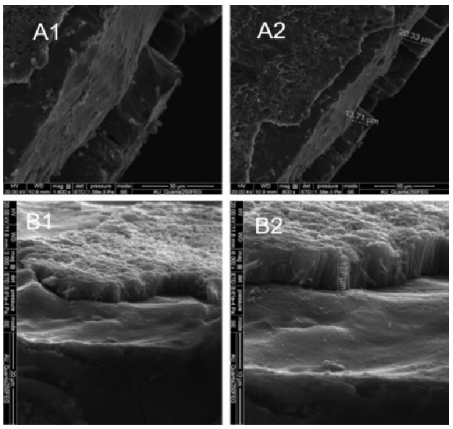

Figure 3. HRSEM cross section images of TiO_2 nanotube arrays at two different magnifications (A1,A2), fabricated at 75V for 45 minutes and (B1,B2) 60V for 1 h and heat treated at 470°C and 470°C for 1 h respectively.

Schmuki et al,[20] investigated the ion diffusion in the electrolyte with the development of nanotube arrays in the thin foil. In the case of Titanium nanotube arrays grown in organic electrolyte, the influence of DC voltage, magnetic stirrer and anodization temperature would also be considered into account. Two kinds of diffusion processes are examined that is, the H^+ ion diffusion toward the cathode and F^- ion diffusion toward the anode electrode.

The following chemical reactions had taken position at the anode [20,21,22]. in the development of Titanium nanotube arrays.

$$Ti + 2H_2O/2OH^- \rightarrow TiO_2 + 4H^+ / 2H^+ + 4e \quad [1]$$

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF^{2-}{}_6 + 2H_2O [2]$$

Chemical reaction one was liable for field-assisted oxidation process, while chemical reaction two served to field-assisted dissolution. Nanotube development had taken place, due to regulation between these two chemical reactions. The fluorine ion is essentially a very significant factor in the development rate of nanotube arrays, in the absence of which only a thin titanium oxide layer was developed through chemical reaction one[23].

In the current organic electrolyte had needed hydrogen ions originate mainly from field-assisted oxidation through chemical reaction to nanotube arrays development. Emission of gas had been examined from both titanium thin film foil and stainless steel thin film, foil surfaces in the first tens of seconds after inaugurating the anodization method. This recommended the thing of the succeeding chemical reactions under DC power supply condition.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \quad \text{(Anode)} \quad [3]$$

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \quad \text{(Cathode)} \quad [4]$$

We had studied a potential drop in the electrolyte, ionic flux at the front side of Titanium thin foil comprised of two sections which were ion diffusion process under concentration gradient and ion migration process under electric fields. In contrast, only ion diffusion process survived at the front side of Titanium foil, as follows:

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

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 process theoretically, mass transport in the electrolyte solution happened by diffusion process, convection process, or migration process. In this work, all the experiments had been held out under above ambient temperature with magnetic stirrer.

EDX ANALYSIS

EDEX analysis had been carried out to study the components of the fabricated Titanium nanotube arrays. The result shows that the first sample fabricated at 60V contain the elements such as Ti and O.From Figure 4, it can be resulted that the atomic ratio ofTi to O was approximately 1 : 2, revealing that only Ti andO elements were existent without any impurities.

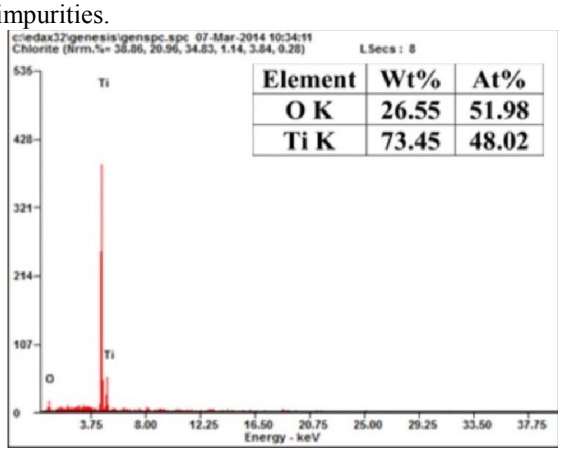

Figure 4. EDEX Spectra of TiO_2 nanotube arrays at 60V of the first sample.

UV-VIS SPECTROSCOPY ANALYSIS

Figure 5 shows at room temperature the visible light absorbance of TiO_2 nanotube arrays had been read in the range of 300-800 nm. The first sample of Titanium nanotube arrays fabricated at 60V condition had showed maximum absorbance ability at wavelengths around 300 nm to 572 nm. The second sample of Titaniumnanotube arrays fabricated at75V condition has showed maximum absorbance ability at wavelengths around 300 nm to 545 nm.

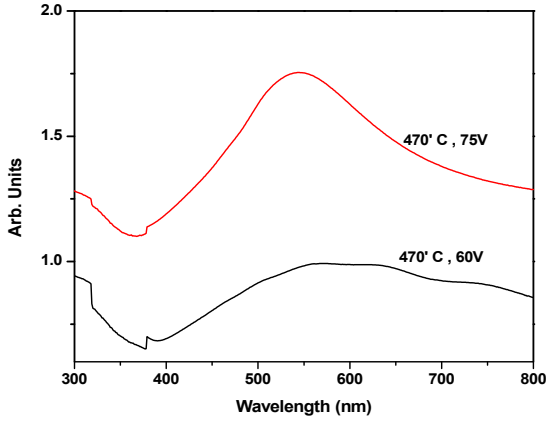

Figure 5. The UV pattern of the TiO_2 nanotube arrays fabricated at 75V for 45 minutes and 60V for 1 h and heat treated at 470°C and 470°C for 1 h respectively.

The firstsample of nanotube arrays fabricated at 60V condition had showed a maximum absorbance ability than second sample.

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

E_g' is the band gap of TiO_2 nanotube arrays, 'h' is the Plank constant, 'v' is the speed of light and 'λ' is the cut off wavelength of radiation produced by UV-vis spectroscopy.

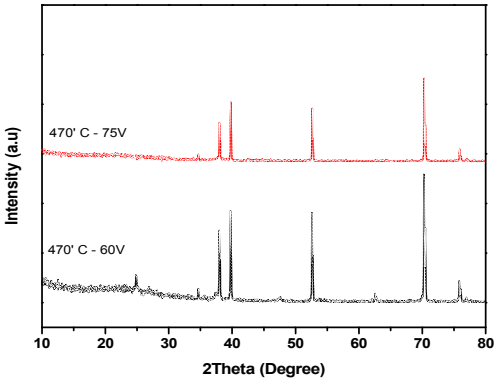

Figure 6. The XRD pattern of the TiO_2 nanotube arrays fabricated at 75V for 45 minutes and 60V for 1 h and heat treated at 470°C and 470°C for 1 h respectively.

XRD ANALYSIS

It is remarkable that then broad peaks in the XRD pattern confirm the existence of amorphous phase[24]. The X-ray diffraction analysis had been conducted for crystal phase identification. After annealing, diffraction peaks of TiO_2 were clearly examined which could be referred to anatase. The first sample of nanotubes fabricated at 60V condition exhibited a presence of anatase TiO_2 with 2θ peaks at 24.93°, 34.66°, 38.03°, 39.78°, 52.62°, 62.61°, 70.31° and 75.88°. The second sample of nanotubes fabricated at 75V condition exhibited a presence of anatase TiO_2 with 2θ peaks at 34.72°, 38.02°, 39.82°, 52.67°, 70.32° and 75.92°. In general, as-prepared TiO_2 nanotube arrays are amorphous in nature which can be converted into anatase or a mixture of anatase and rutile after annealing at temperature 470°C and above. Not even high temperature, but other parameters is also important such as structure, admixture, geometrical size etc. To produce the desired properties of TiO_2 nanotube arrays, A. Grimes et al. had investigated an approach to prepare crystalline (anatase) nanotube arrays without post annealing through an anodization of pre-heated crystalline layer of TiO_2[25]. The average size of particles can be estimated from the XRD pattern of samples using Schere's equation. Figure 5shows the X-ray diffraction analysis of annealed samples of Titanium nanotube arraysat the same temperature. XRD patterns recorded at ambient temperature of the Titanium nanotube arrays, after annealing process.

CONCLUSION

Titanium oxide nanotube arrays had been synthesized successfully by electrochemical anodization process. Hence, HRSEM measurement revealed well aligned growth of nanotube arrays at 75V had 157.5 nm of mean diameter and nanotube arrays at 60V had 108.35 nm of mean diameter. Fabricated titanium nanotube arrays at 75V had 17.02µm of mean length and nanotube arrays at 60V had 4.177µm of length. The first sample of nanotube arrays fabricated at 60V condition had showed maximum absorbance ability at wavelengths about 572 nm compared to the second sample, Finally the prepared anatase TiO_2 nanotube arrays second sample is well adjusted and hence, suitable for the application in dye sensitized solar cells due to their higher surface area and maximum absorbance ability.

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ABBREVIATIONS

DSSCs, dye sensitized solar cells; HRSEM, high resolution scanning electron microscope

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