materials proceedings

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Proceeding Paper

Photovoltaic Performance of TiO_2 Nanotubes Anodized under Different Voltages †

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† Presented at the 6th Conference on Emerging Materials and Processes (CEMP 2023), Islamabad, Pakistan, 22–23 November 2023.

Abstract: The present study was conducted to develop highly ordered facile TiO_2 nanotubes (TiNTs) at two different applied voltages using two-step electrochemical anodization for the application in dye-sensitized solar cells (DSSCs). The nanotube fabrication is carried out in an aqueous electrolyte containing ethylene glycol and ammonium fluoride at 40 V and 60 V fixed applied potentials. Nanotubes synthesized at 40 V are comparatively uniform and smoother, whereas a rough top surface is observed at 60 V. The photovoltaic efficiency achieved for the device based on TiNTs prepared at 40 V is 0.84% which is higher than the efficiency achieved for the 60 V device. This work highlights the importance of ordered nanotubes for efficient devices.

Keywords: TiO_2 nanotubes; anodization; DSSCs; efficiency

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Citation: Ghani, T.; Mehmood, M.; Kanwal, H.; Naz, M.Y.; Bashir, S. Photovoltaic Performance of TiO_2 Nanotubes Anodized under Different Voltages. *Mater. Proc.* **2024**, *17*, 24. https://doi.org/10.3390/materproc2024017024

Academic Editors: Sofia Javed, Waheed Miran, Erum Pervaiz and Iftikhar Ahmad

Published: 22 April 2024

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1. Introduction

The increasing population and global warming have caused an enormous challenge to cope with the increasing demand for clean energy. Renewable energy sources must be utilized abundantly including solar, hydroelectric, wind, geothermal, biomass, and fuel cells. Sun is the source of the most abundant, accessible, and clean energy. The pseudo-infinite source of clean solar energy, the sun, provides more solar energy on earth in one hour than the yearly energy consumption of humankind [1].

Photovoltaic devices include p-n junction cells, photo-galvanic and photo-electrochemical cells, dye-sensitized solar cells, and organic solar cells [2]. Among these, dye-sensitized solar cells (DSSCs) are a third generation, low cost, efficient, and emerging technology. A DSSC typically consists of a dye-sensitized wide band gap metal oxide semiconductor layer on a transparent conductive substrate (photoanode), a redox electrolyte, and a conductive counter electrode. Among wide band-gap semiconductors, TiO_2-based DSSCs have shown the best photoelectrode properties approaching theoretical values [3].

One of the problems is the low charge collection efficiencies due to electron recombination. The main reason for the phenomenon is the longer paths followed by electrons in randomly connected TiO_2 nanoparticles. Modifying the morphology of the TiO_2 to a one dimensional (1D) structure such as nanorods, nanotubes, and nanowires is an alternative to address the problem [4,5]. TiO_2 nanotubes (TiNTs) in comparison to other structures provide a better directional path for the electron transport and orthogonal separation, therefore, they improve the charge collection efficiencies [6–8].

Anodization potential is one of the key parameters that has a direct effect on the TiNTs length (or growth) and pore (or tube) diameter [9–11]. In the present study, we have chosen two voltages for nanotube formation and their effect on the ordered morphology, length,

and consequently on performance of the DSSC device. It is observed that applied voltage strongly effect the ordering of nanotubes.

2. Materials and Methods

2.1. Fabrication of TiO_2 Nanotubes

For the anodization, a Ti sheet (0.5 mm thickness, 99.99% purity, Sigma-Aldrich) was used as working electrode and a stainless-steel plate was used as counter electrode. All of the anodization experiments were performed in ethylene glycol (99% purity; Merck, Rahway, NJ, USA), electrolyte containing 0.5 wt. % NH_4F (Unichem, and 3 wt. % DI water (pH~6) kept at 20 °C and with moderate stirring of the electrolyte. Anodization of samples was performed at two different voltages, 40 V and 60 V. Before anodization, Ti foils were cleaned using ultrasonication in acetone (analytical reagent; Sigma-Aldrich), ethanol (absolute; Sigma-Aldrich), and DI water each for 20 min. A two-step anodization method was used for the preparation of TiO_2 nanotubes (TiNTs). Ti samples were pre-anodized for 3 h. TiNTs formed during the pre-anodization were removed by ultrasonication in DI water to ensure fabrication of highly ordered TiNTs during the subsequent anodization steps. After each step of anodization, samples were immersed in ethanol and DI water to remove the electrolyte. All samples were annealed at 450 °C for 2 h while the heating and cooling rates were maintained at 1 °C/min.

2.2. DSSC Fabrication

For the preparation of DSSCs, annealed TiNT samples were employed as photoanode and soaked in 0.3 mM N-719 solution for 24 h. With the Pt-coated FTO glass as counter electrode, the DSSCs were prepared by assembling the two electrodes in a sandwich-type cell geometry using a hot melt sealant/spacer of a thickness of 25 µm (Meltonix; Solaronix, Oriel Solar Simulator, Model 91160, Aubonne, Switzerland). The electrolyte iodide/triiodide (Iodolyte AN-50; Solaronix) was injected to fill in the spaces between the electrodes through the drilled hole in the Pt counter electrode via vacuum back-filling technique. The active area for the cell was 0.16 cm^2. The cell was illuminated in back illumination mode as the substrate underlying the TiO_2 oxide is Ti metal.

3. Results and Discussion

Figure 1 shows typical SEM images of TiNTs prepared using the two-step anodization approach at a constant voltage of 40 V for 2 h. Figure 1a shows the top surface of the TiNTs. It is evident that the top surface of the TiNTs has a relatively ordered arrangement with open-ended tubes having an inner diameter of 100 nm on average. The tubes were vertically aligned and remained intact, as shown in the cross-sectional image (Figure 1b) with a thickness of 15 µm.

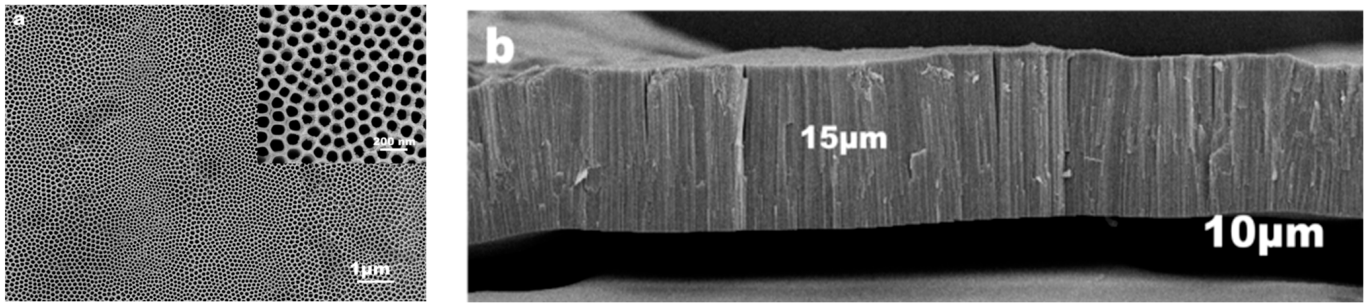

Figure 1. SEM images showing the top surface (**a**) and cross-sectional images (**b**) of TiNTs prepared at 40 V.

The SEM image in Figure 2 presents the top surface and cross-sectional view of TiNTs prepared at 60 V by the two-step anodization method. The top surface is rough, as shown in Figure 2a. Nano-grass and cracks are clearly observable. The inner diameter of the

TiNTs is 150 nm on average, which is increased due to the anodization at a higher voltage (Figure 2).

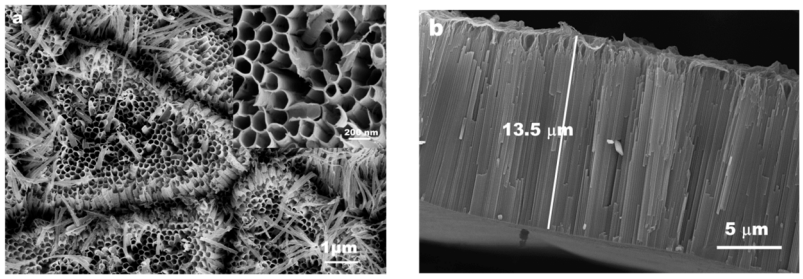

Figure 2. SEM images showing the top surface (**a**) and cross-sectional images (**b**) of TiNTs prepared at 60 V.

However, the thickness of the nanotubes is reduced to 13.5 µm when observed for tubes prepared at 40 V. Nano-grass is formed due to the permanent etching of the tube walls in the fluoride-containing electrolyte [11]. As anodization is performed at a higher applied voltage (60 V), the wall thinning is more prominent and results in the grass (or bundle) formation at the top of the TiNTs. As a consequence of chemical etching and grass formation, the thickness of the nanotubes is decreased.

The performance of TiNTs prepared at two different voltages was investigated in DSSCs. The photovoltaic measurements were performed under A.M. illumination with 100 mW/cm^2 intensity. The performance parameters such as Jsc—short current density, Voc—open circuit voltage, FF—fill factor, and ɳ—photocurrent conversion efficiencies of the two DSSCs are summarized in the table on the right of Figure 3 and the corresponding J-V curves for both DSSCs are shown in Figure 3.

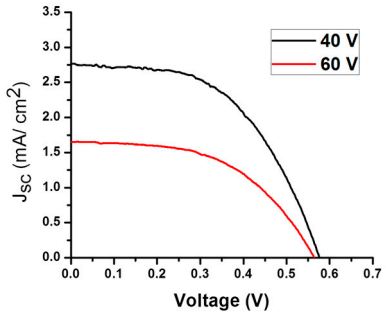

Figure 3. Current–voltage characteristics curves of DSSCs.

The device based on TiNTs prepared at 40 V shows a larger J_{SC} as 2.4 mA/cm^2 and FF as 0.52 than the device prepared with the photoanode consisting of TiNTs fabricated with 60 V applied voltage. As is evident in Table 1, the efficiency of the TiNTs based DSSC is enhanced by 75% when tubes are prepared at 40 V rather than those prepared at 60 V. The higher efficiency was achieved due to the ordered and open-ended morphology of TiNTs. The top surface of the nanotubes prepared at 40 V is homogeneous without any crack or roughness due to nano-grass formation. The open channels allow a better infiltration of dyes as well as electrolytes during device testing. Moreover, the ordered one one-dimensional morphology results in efficient electron transport.

Table 1. Performance Parameters for the prepared TiNTs samples.

Sample	Jsc (Ma cm^2)	Voc (V)	FF	ɳ (%)
TiNTs-40 V	2.74	0.59	0.52	0.84
TiNTs-60 V	1.65	0.59	0.5	0.48

4. Conclusions

In summary, TiNTs are successfully fabricated using the two-step anodization method at two different voltages, 40 V and 60 V. Highly ordered and open-ended with homogenous top surface nanotubes are achieved at 40 V applied voltage. However, tubes have a rough surface when prepared at 60 V. With the increase in voltage, the inner diameter of tubes is increased but the thickness is decreased. The lower thickness at higher voltage is due to the increased chemical etching resulting in nano-grass formation on top surface. The DSSC based on TiNTs prepared by anodization at 40 V is more efficient than the device fabricated by TiNTs prepared at 60 V. This study concludes that well defined tube geometry with smooth surfaces and vertical channels transports the electrons effectively, resulting in more efficient photoanodes in DSSC.

Author Contributions: In this research work, the conceptualization and formal analysis was performed with the original draft preparation by T.G., M.M., M.Y.N., S.B. and H.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: We are pleased to acknowledge the School of Chemical and Materials Engineering, NUST, Islamabad, which is providing an exciting platform for sharing our research. In addition, we wholeheartedly acknowledge the Department of Metallurgy and Materials Engineering, PIEAS, for their administrative and technical support during this whole experimental work.

Conflicts of Interest: The authors declare no conflicts of interest.

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