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Effect of Anodization Duration in the TiO_2 Nanotubes Formation on Ti Foil and Photoelectrochemical Properties of TiO_2 Nanotubes

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Abstract
In this work, the effect of anodizing duration on the morphology and photoelectrochemical properties of TiO_2 nanotubes arrays (NTAs) has been investigated The samples were characterized by X-ray diffraction (XRD) and energy dispersive X-ray (EDX) to characterize their crystalline structure and compositional. Surface morphological and their dimensional variation was examined by field emission scanning electron microscopy (FESEM). The anodizing duration played a significant role in the formation of TiO_2 nanotubes arrays. Moreover, the photoelectrochemical properties (PEC) were studied through photocurrent measurements. Optimum anodizing duration of 60 min at 40 V exhibited maximum photocurrent of 0.03 mA cm^{-2} under illumination of halogen light.

Keywords: Anodization duration, TiO_2 nanotube, Photoelectrochemical.

الخلاصة
في هذا العمل ، تم التحقق من تأثير مدة الأنودة على المورفولوجيا والخصائص الكهروكيميائية الضوئية لصفائف الأنابيب النانوية (TiO_2 NTAs). شخصت العينات بحيود الأشعة السينية (XRD) والأشعة السينية المشتتة للطاقة (EDX) لتوصيف تركيبها البلوري. تم تشخيص الأشكال السطحية وأبعادها بواسطة المجهر الإلكتروني الماسح (FESEM). لعبت مدة الأنودة دورًا مهمًا في تشكيل صفائف أنابيب النانو TiO_2. علاوة على ذلك ، تمت دراسة خواص الكهروكيميائية الضوئية (PEC) من خلال قياسات التيار الناجم عن الضوء. أظهرت مدة الأنودة المثلى خلال ٦٠ دقيقة وفي ٤٠ فولت أقصى تيار ضوئي يبلغ ٠٫٠٣ مللي أمبير سم -٢ تحت إضاءة ضوء الهالوجين.

Introduction
Photoelectrochemical (PEC) cells based on several metal oxides such as CuO_2, Fe_2O_3, ZnO, and TiO_2 are commonly investigated [1] [2] [3] [4]. Self-organized TiO_2 nanotube arrays (NTAs) have been regarded as potential nanodevices for a photoelectrochemical cell [5], sensor [6], and photocatalysis [7][8], due to their large internal surface area, high adaptability, exceptional electron percolation for a vectorial charge transfer between the interface surfaces, and uniformly stable structure [9][10]. Furthermore, the tubular symmetries with one-dimensional nanostructure have a lower recombination of electron-hole pairs and higher photocurrent conversion efficiency [11]. In recent years, many researchers have paid their attention to promoting new methods for fabrication of TiO_2 NTAs, such as hydrothermal syntheses [12], template method [13], and anodization [14]. The chemical dissolution rates and electrochemical oxidization of TiO_2 were the keys to produce TiO_2 NTAs by anodization technique. The thin film of TiO_2 was formed on the titanium surface at the beginning of anodization. The small pits could be shown on the surface of the TiO_2 layer after the localized dissolution of TiO_2 via fluorine ions. These small pits act as pore-forming centers. The electric field at the bottom of the pores was increased to improve electrochemical oxidization and chemical dissolution rates of TiO_2 to form TiO_2 NTAs structure. A dynamic balance between chemical dissolution and electrochemical oxidization leads to length of

TiO_2 NTAs stays constant [15]. Zwilling *et al.* fabricated TiO_2 NTAs in chromic acid solution without and with hydrofluoric acid addition by anodization of titanium [16]. Grimes et al produced the highly ordered and uniform TiO_2 NTAs by anodic oxidation of a pure titanium foil in an aqueous solution containing HF [14]. Thenceforth, a variation of electrolytes was being studied to check the probability of producing TiO_2 NTAs with controllable dimensions such as KF/NaF [17], NH_4F/H_3PO_4 [18], polar organic electrolyte [19] [20] and H_2SO_4/HF [21]. Many studies suggested the electrochemical anodization and electrolyte composition condition play a necessary function in influencing the structure and formation of TiO_2 NTAs film. Therefore, in this study, we display the results of an experimental investigation of titanium anodization in NH_4F dissolved in anhydrous ethylene glycol especially the influence of anodization duration on the geometrical aspect and morphology of resulting TiO_2 NTAs and its photocurrent response.

Materials and Methods

Preparation titania nanotube arrays (TiO_2 NTA)

Sheets of Ti foil (thickness 0.127 mm, 99.7% purity) were first cut into pieces of 2 x 1 cm^2. Then, the pieces of Ti foil were chemical decreasing by ultra-sonication for 15 minutes in acetone, isopropanol and deionized water (DI) respectively. Next, they followed by etching in 6 M HNO_3 to form a smooth surface. Anodization technique on Ti foil was achieved in a dual-electrode cell with the high-density graphite as the counter electrode while Ti foil acts as the working electrode. The distance between two electrodes was preserve at 2 cm. The two electrodes were connected to a power supply and they immersed in electrolyte consisted of 95 ml of anhydrous Ethylene Glycol, 5ml of DI water, and 0.5g of NH_4F. Anodization technique was executed by applying a 40 voltage with different anodization duration (1, 15, 30, 60, and 120) minutes to investigate the effect of anodization duration in the formation of TiO_2 NTAs. As-prepared samples were rinsed with DI water. The amorphous samples were converted to anatase at 500^{o}C in the air atmosphere (heating rate: 2 ^{o}C/min, annealed time: 2 h.

Material characterizations of TiO_2 NTAs

Crystal phases and the morphology of the synthesized TiO_2 NTAs photoelectrodes were analyzed using X-ray diffractometry (Panalytical X, Pert Pro MPD diffractometer by using CuKa radiation, k = 1.5406 A °) and field emission scanning electron microscopy (FESEM, JOEL JSM-7600F, Japan) respectively. The elemental analysis was studied using the energy dispersive X-ray (EDX) spectrometers. While the photocurrent measurements of samples were carried out with an (Autolab PGSTAT204/ FRA32M module) potentiostat, with a TiO_2 NTAs as the working electrode (WE), Ag/AgCl as the reference electrode (RE), and Pt wire as the counter electrode (CE).

Results and Discussion

Morphological and structural of TiO_2 NTAs

The diameter of tube plays the most significant factor in determining the performance of the material. As shown in Table 1 and the FESEM images in Figure 1 (b, c, d, e, and f) the tube diameter of the TiO_2 samples varied with anodization duration used. The tube diameter of the samples was analyzed using image analysis software (Image J). FESEM images at chosen time period are shown in Figure 1. The bare Ti plate showed a flat and smooth surface (Figure 1(a)) and in the initial step of anodization, an only a porous layer was formed within 1 minute as can be seen in Figure 1 (b). Over 15 minutes of anodization, the porous layer converted into a tube-like surface morphology with several precipitates (Figure 1(c)). At increasing the duration of anodization to 30 minutes, reduced surface precipitates with well-separated tubes were obtained as shown in Figure 1 (d)). After 60 minutes, the surface was quite filled with self-organized and well-ordered TiO_2 NTAs (Figure 1(e)). The tube diameter range becomes larger by increasing the anodizing time to 120 minutes, as shown in Figure 1(f), while the top of the

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TiO_2 NTAs is gradually broken due to over-dissolution of the top of the tubes [22].

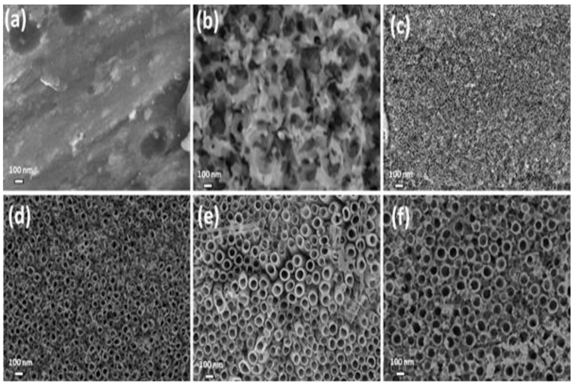


Figure 1: FESEM images showing the (a) Ti foil and different stages of TiO_2 NTAs film formation at 40 V in $NH_4F/EG/H_2O$ solution for (b) 1 min (c) 15 min (d) 30 min (e) 60 min and (f) 120 min

Table 1: diameter range of TiO2 NTAs prepared at different anodization duration in NH4F/EG/H2O solution

Time (min)	Diameter (nm)
1	-
15	5-10
30	16-42
60	60-90
120	72- 108

Figure 2 shows the XRD patterns of Ti foil and TiO_2 NTAs prepared at various anodization duration, only peaks for anatase phase are found (JCPDS: 21-1272) at 2θ (25.8°, 37.6°, 48.05°, 54.0° and 55.0°) corresponding to [101], [004], [200], [105], and [211] respectively. The extra peaks that at 35.45°, 38.8°, 40.5°, and 53.4° was produced from titanium substrate. It is also observed that the [101] reflections presented the highest intensity as a contrast to another anatase peaks for all samples that confirm which this plane is the best orientation for the nanotubes. Moreover, it is clearly seen that the intensity of the peak [101] increase with increasing anodization duration to 60 minutes due to the enhancement in the crystallinity of the TiO_2 NTAs. Furthermore, the intensity of the peak (101) decreases when anodization duration was 120 minutes (Figure 2 (f)) that was ascribed to the non-homogenous TiO_2 NTAs structure.

Figure 3 shows the EDX spectrum that demonstrated the presence of titanium and oxygen elements. The ratio of Ti to O element is about 1:2 thereby confirmed the formation of stoichiometry TiO_2 NTAs.

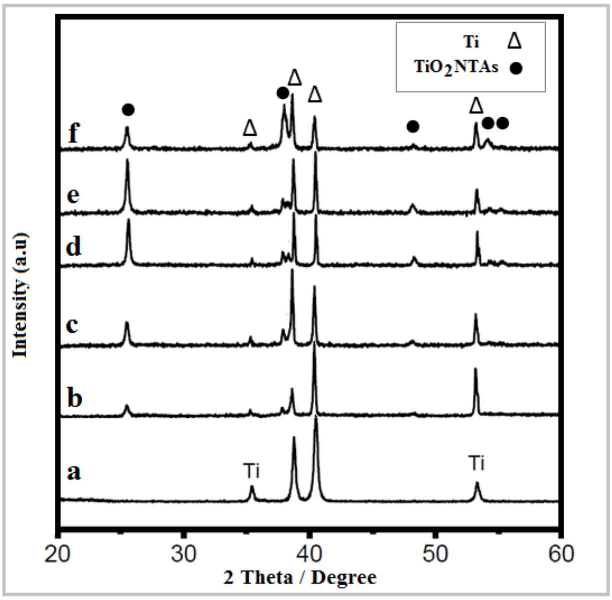
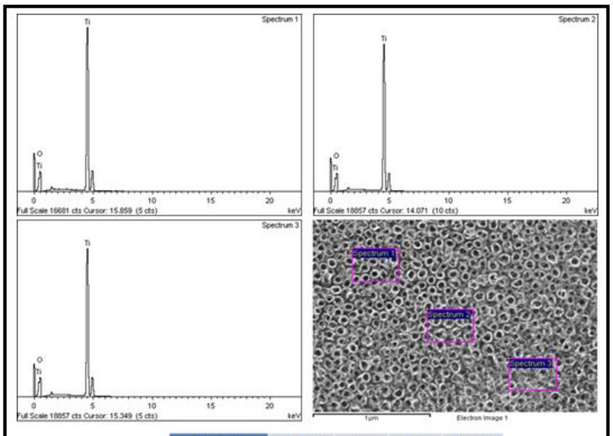


Figure 1: XRD patterns showing the (a) Ti foil and different stages of TiO_2 NTAs film formation at 40 V in $NH_4F/EG/H_2O$ solution for (b) 1 min (c) 15 min (d) 30 min (e) 60 min and (f) 120 min.



Spectrum	In stats.	O	Ti	Total
Spectrum 1	Yes	38.13	61.87	100.00
Spectrum 2	Yes	39.12	60.88	100.00
Spectrum 3	Yes	39.75	60.25	100.00

Figure 3: EDX spectra of TiO_2 NTAs prepared at 60 min anodization duration.

Photoelectrochemical cell performance of TiO_2 NTAs:

A comparison between the photo-electrochemical cell (PEC) performances of the TiO_2 NTAs was conducted in a three-electrode PEC cell with intermittent illumination. Figure 4 shows the current-voltage (I–V) curves that obtained from the TiO_2 NTAs photoelectrode which was synthesized at different anodization duration. The photocurrent response increases when anodization duration increased from 1 to 60 minutes, while the photocurrent response decreased when the anodization duration reached to 120 minutes. This result means that photogenerated electrons have been transferred easily from TiO_2 NTAs to the counter electrode under illumination by the external circuit when prepared the sample at 60 minutes anodization duration.

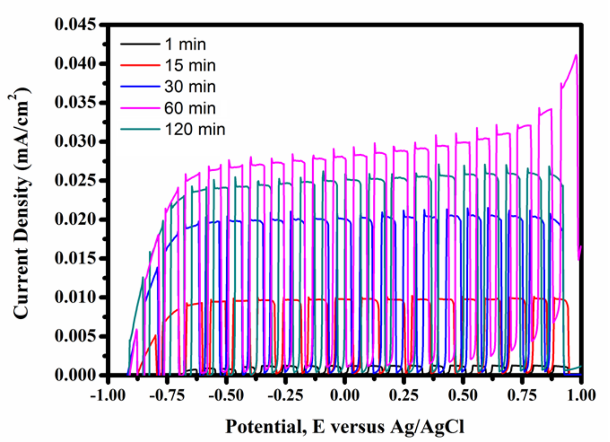


Figure 4: photocurrent responses of TiO_2 NTAs prepared at different anodization duration

Conclusion

In summary, anodization technique was successfully applied to obtain well-ordered and uniform TiO_2 NTAs films. The anatase phase of the TiO_2 NTAs occurred under the annealing temperature of 500 ^oC. This study exposes that optimal anodization duration of 60 minutes is required to get maximum the photoresponse of TiO_2 NTAs. The morphology of the TiO_2 NTAs is very significant and obviously, a variation in behaviour once the change from a porous layer to well-defined TiO_2 NTAs is achieved. Furthermore, extended anodization duration to 120 minutes at 40V causes some damage to TiO_2 NTAs and their photocurrent decreases.

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References

[1] T. G. Kim, H. B. Oh, H. Ryu, and W. J. Lee, “The study of post annealing effect on Cu_2O thin-films by electrochemical deposition for photoelectrochemical applications,” J Alloys Compd, vol. 612, pp. 74–79, 2014.

[2] M. C. Huang, W. S. Chang, J. C. Lin, Y. H. Chang, and C. C. Wu, “Magnetron sputtering process of carbon-doped α-Fe_2O_3 thin films for photoelectrochemical water splitting,” J Alloys Compd, vol. 636, pp. 176–182, 2015.

[3] A. M. Holi, Z. Zainal, Z. A. Talib, H.-N. Lim, C.-C. Yap, S.-K. Chang, and A. K. Ayal, “Enhanced photoelectrochemical performance of ZnO nanorod arrays decorated with CdS shell and Ag_2S quantum dots,” *Superlattices Microstruct*, vol. 103, pp. 295–303, 2017.

[4] A. K. Ayal, Z. Zainal, H.-N. Lim, Z. A. Talib, Y.-C. Lim, S.-K. Chang, and A. M. Holi, “Photocurrent enhancement of heat treated CdSe-sensitized titania nanotube photoelectrode,” Opt Quantum Electron, vol. 49, no. 4, pp. 1–11, 2017.

[5] A. Kadim, Z. Zainal, H. Ngee, Z. Abidin, Y. Lim, S. Chang, and A. Mebdir, “Fabrication of CdSe nanoparticles sensitized TiO_2 nanotube arrays via pulse electrodeposition for photoelectrochemical application,” Mater Res Bull, vol. 106, no. December 2017, pp. 257–262, 2018.

[6] P. Roy, S. Berger, and P. Schmuki, “TiO2 nanotubes: Synthesis and applications,” Angew Chemie - Int Ed,

vol. 50, no. 13, pp. 2904–2939, 2011.

[7] W. Wang, F. Li, D. Zhang, D. Y. C. Leung, and G. Li, "Applied Surface Science Photoelectrocatalytic hydrogen generation and simultaneous degradation of organic pollutant via CdSe / TiO_2 nanotube arrays," Appl Surf Sci, vol. 362, pp. 490–497, 2016.

[8] S. G. Ghugal, S. S. Umare, and R. Sasikala, "Enhanced photocatalytic activity of TiO_2 assisted by Nb , N and S multidopants," Mater Res Bull, vol. 61, pp. 298–305, 2014.

[9] K. Shankar, J. I. Basham, N. K. Allam, O. K. Varghese, G. K. Mor, X. Feng, M. Paulose, J. a Seabold, K. Choi, and C. a Grimes, "Recent Advances in the Use of TiO_2 Nanotube and Nanowire Arrays for Oxidative photoelectrochemistry," J Phys Chem C, vol. 113, no. 16, pp. 6327–6359, 2009.

[10] O. K. Varghese, M. Paulose, T. J. LaTempa, and C. A. Grimes, "High-rate solar photocatalytic conversion of CO_2 and water vapor to hydrocarbon fuels," Nano Lett, vol. 9, no. 2, pp. 731–737, 2009.

[11] J. M. Macák, H. Tsuchiya, A. Ghicov, and P. Schmuki, "Dye-sensitized anodic TiO_2 nanotubes," Electrochem commun, vol. 7, no. 11, pp. 1133–1137, 2005.

[12] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, and K. Niihara, "Formation of Titanium Oxide Nanotube," Langmuir, vol. 14, no. 12, pp. 3160–3163, 1998.

[13] P. Hoyer, "Formation of a Titanium Dioxide Nanotube Array," Langmuir, vol. 12, no. 6, pp. 1411–1413, 1996.

[14] D. Gong, C. a. Grimes, O. K. Varghese, W. Hu, R. S. Singh, Z. Chen, and E. C. Dickey, "Titanium oxide nanotube arrays prepared by anodic oxidation," J Mater Res, vol. 16, no. 12, pp. 3331–3334, 2001.

[15] G. K. Mor, O. K. Varghese, M. Paulose, K. Shankar, and C. a. Grimes, "A review on highly ordered, vertically oriented TiO_2 nanotube arrays: Fabrication, material properties, and solar energy applications," Sol Energy Mater Sol Cells, vol. 90, no. 14, pp. 2011–2075, 2006.

[16] V. Zwilling, D. David, M. Y. Perrin, and M. Aucouturier, "Structure and Physicochemistry of Anodic Oxide Films on Titanium and TA6V Alloy," Surf. Interface Anal., vol. 637, no. October 1998, pp. 629–637, 1999.

[17] Q. Cai, "The effect of electrolyte composition on the fabrication of self-organized titanium oxide nanotube arrays by anodic oxidation," 230 J Mater Res, vol. 20, pp. 230–236, 2005.

[18] M. S. Su, F. Alamgir, P. Scardi, and A. Ahmad, "Morphological Studies of Vertical Arrays TiO_2 Nanotubes by Electrochemical Anodization Technique for Dye Sensitized Solar Cell Application," AIP Conf Proc, vol. 1571, no. 2013, pp. 835–842, 2013.

[19] H. E. Prakasam, K. Shankar, M. Paulose, O. K. Varghese, and C. A. Grimes, "ARTICLES A New Benchmark for TiO_2 Nanotube Array Growth by Anodization," J Phys Chem C, vol. 111, pp. 7235–7241, 2007.

[20] M. Paulose, K. Shankar, S. Yoriya, H. E. Prakasam, O. K. Varghese, G. K. Mor, T. J. LaTempa, A. Fitzgerald, and C. a Grimes, "Anodic growth of highly ordered TiO_2 nanotube arrays to 134 microm in length.," J Phys Chem B, vol. 110, no. 33, pp. 16179–16184, 2006.

[21] X. Chen, X. Chen, J. Tang, and S. Chen, "Energy Procedia Preparation of Self-organized Titania Nanotubes Electrode and Its Electrochemical Properties," Energy Procedia, vol. 16, pp. 1206–1210, 2012.

[22] D. Regonini and F. J. Clemens, "Anodized TiO_2 Nanotubes : Effect of anodizing time on film length, morphology and photoelectrochemical properties," Mater Lett, pp. 1–5, 2014.