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Synthesis of Titanium Oxide Nanotubes for Photo Electrochemical Cells and its Characterizations

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ABSTRACT

Nano scale materials have many peculiar properties than the bulk ones and have led to break through in various fields of science and technology. Titanium oxide is one of the excellent and most demanded materials because of its various applications and properties such as such as large surface area. In this paper, Titanium oxide (TiO_2) nanotube arrays were synthesized by electrochemical anodization of titanium foil. Dimension of nanotubes and elemental composition were detected by Field Emission-Scanning Electron Microscope with Energy Dispersive X-Ray Analysis (FESEM- EDAX). From X- Ray Diffraction (XRD) the intensity of peaks, d-spacing values and phase of TiO_2 nanotubes were analyzed. The Energy Bandgap (Eg) of the formed TiO_2 nanotubes was determined by Diffuse Reflectance Spectroscopy from Kubelka-Monk Plot. From the obtained results, the synthesized TiO_2 nanotubes are suitable for Photo Electrochemical Cell applications.

Key words: Energy Bandgap, Electrochemical Anodization, Titanium Oxide Nanotubes, X- Ray Diffraction (XRD);

1. INTRODUCTION

Now-a-days, a wide range of materials are required to design and study modern devices, which are suitable for various possible commercial applications. Nanomaterials play an important role in recent technologies to reach high performance devices. The performance of such devices is significantly based on the geometry, shape, and morphology of nanostructures [1]. The expectation that a better understanding of the 1–100 nm size materials (nanoscale) leads to a seamless integration of theory and models across the size scales that encompass atomic–molecular nanostructure–microstructure behavior, and thereby enable the priori prediction and design of a material's properties. Photo electrochemical cell is a photocurrent-generated device composed of an electrolyte, a photoactive semiconductor electrode. Under irradiation of the interface electrolyte–semiconductor with an energy level greater than the band gap of the semiconductor; electron–hole pairs are generated [2]. During a typical photo-water splitting on the photo anode, generated holes oxidize water to oxygen or other oxygen containing species (OH* radicals, H_2O_2 or HO_2-). Electrons produced via an external circuit are transferred to e.g. metallic cathode and involved in the hydrogen evolution reaction [3], [4]. Many different semiconductors are investigated as the anodes in photo-water splitting [5], but due to an easy synthesis, excellent corrosion resistance in solutions of different pH, titanium dioxide is the most widely studied photo anode materials. In comparison with the bulk TiO_2 materials, the different TiO_2 nanomaterials attracted much more attentions. Because of high surface to volume ratio, TiO_2 nanostructures provide increased surface area at which photo-reactions could occur. Moreover, nanomaterials improved light absorption rate, increase near surface photo induced charge carrier density, improving the photo-reduction rate, and resulting in advanced photo activity. At the same time, the high surface to volume ratio of the nanomaterials increase the surface absorption of OH^- and H_2O, increasing the photocatalytic reaction rate. The TNT with high-specific surface area, ion-exchangeable ability, and photocatalytic property has been considered for various potential applications as catalyst in pool boiling [6], photo catalysis [7]–[12], electro chromic device [13], [14], hydrogen generation [15], [16], corrosion resistance [17], solar cells [18], sensors [19], storage device [20], catalyst support [21] and many.

2. EXPERIMENTAL METHOD

Electrochemical anodization is the widely used method because of its controllable, reproducible results in single process, the feasibility to tune the size and shape of nano tubular arrays to the desired dimensions and meeting the

demands of specific applications by means of controlled anodic oxidation of the metal substrate. Furthermore, it is a cost-effective method and the tubes prepared via this method have good adherent strength. In addition, the thickness and morphology of TiO_2 films can easily be controlled by the anodization parameters [22] , [23].

2.1. Electrochemical Anodization

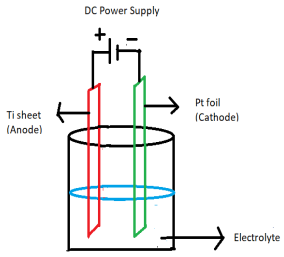

Figure 1: Experimental setup of Electrochemical Anodization

The TiO_2 nanotube array film was fabricated by electrochemical anodic oxidation process. High purity titanium (99.8%) plate of 0.25 mm thickness from Sigma-Aldrich, Bangalore was washed in double distilled (DD) water and then rinsed with acetone for 10 min. The TiO_2 nanotube arrays were fabricated in a cylindrical electrochemical reactor. The experimental setup consist of as a working electrode i.e., anode and Platinum Pt of 0.2 mm thickness as co-electrode (cathode)immersed in an electrolytic solution of 0.25wt% of ammonium fluoride (NH4F) dissolved in 99% of ethylene glycol. The constant DC voltage of 12V is applied to carry out anodization at a particular anodization time of 1 hour and annealed at 480 degree Celsius for 1 hour. The pH of the electrolytic solution used is 4.3 and has the mortality of 0.06M. Schematic diagram of the experimental setup is shown in (Figure 1).The TiO_2 nanostructure formation in an electrolyte is a result of two competing electric field assisted processes: Hydrolysis of TiO_2 and chemical dissolution of TiO_2 at the oxide/electrolyte interface [24], [25]. These two processes lead to the fabrication of vertically aligned titanium oxide nanotubes on the surface of titanium substrate by the anodization of fluorides present in the electrolyte (mixture of ammonium fluoride and ethylene glycol). The TiO_2 nanostructure formation is given as:

$$Ti^{4+} + 2H_2O \rightarrow TiO_2 + 4H^+ \quad (1)$$

$$TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{2-} + 2H_2O. \quad (2)$$

3. RESULTS AND DISCUSSIONS

By using potentiostatic anodization of two electrode configurations, self-aligned TiO_2 nanotube arrays were prepared and characterized.

3.1. Field Emission Scanning Electron Microscope (FESEM)

The Field Emission Scanning Electron Microscope (FESEM) micrograph of the sample is shown in Figure 2 annealed at 480^0 C. The presence of element in the sample was identified with the help of Energy Dispersive X-Ray Analysis (EDAX) shown in Figure 3.Using ImageJ software the outer radius the tube length of the nanotube formed is determined as 25nm and is about 180nm respectively.

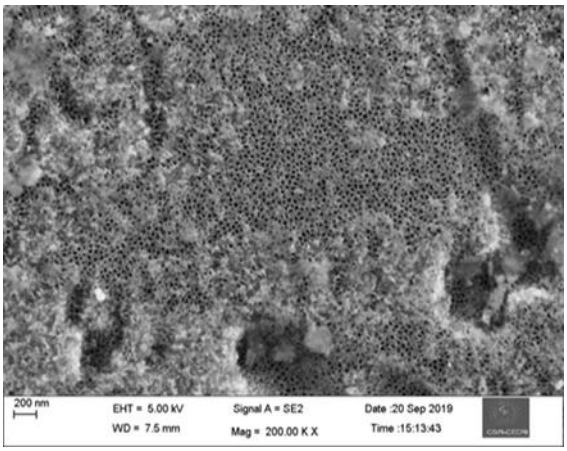

Figure 2: The FESEM image of TiO_2 nanotubes annealed at 480 degree Celsius

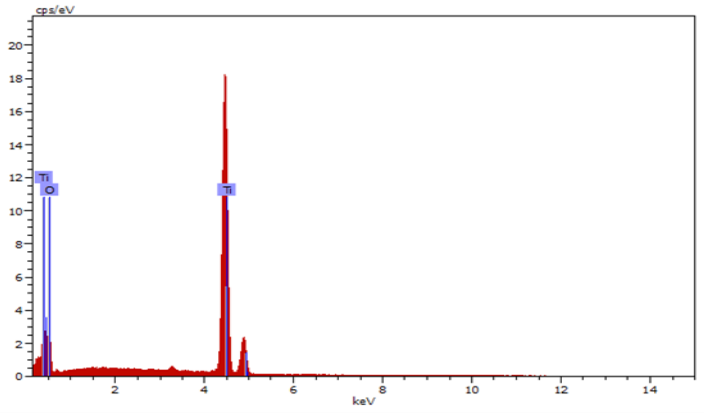

Figure 3: The EDAX pattern of TiO_2 nano particles annealed at 480 degree Celsius

Table 1: Chemical Composition of TiO_2 nano particles

Elements	Weight (%)	Atomic (%)
O	28.19	54.02
Ti	71.81	45.98
Total	100.00	100.00

The Table1indicates the amount of Ti and O present in the TiO_2 nanotube is 71.81% and 28.19% and no characteristic peaks of impurities or other precursor compounds are observed.

3.2. X Ray Diffraction Analysis (XRD)

The X-Ray Diffraction pattern of TiO_2 nanoparticles annealed at 480 degree Celsius is shown in Fig.4. It confirms that the TiO_2 nanoparticles formed are in anatase phase (TiO_2 exists in three phases' anatase, rutile and brookite). The low intensity peaks at 2θ values of 36.24^0, 62.08^0, 76.56^0, 79.71^0 and 82.40^0 are corresponding to the anatase phase.Diffraction peaks observed are well in correlation with standard JCPDS data. (JCPDS card no. 021-1272).

Table 2: XRD parameters of anodic TiO2 nanotube arrays annealed at 480 degree Celsius for 1hour

2θ (degree)	Intensity (counts)	$d_{observed}$ (Å)	d_{jcpds}(Å)	FWHM (degree)	Planes
36.24	433.0	2.51	2.54	0.14	(101)
39.54	294.0	2.31	2.29	0.16	(200)
41.31	222.0	2.20	2.18	0.12	(111)
54.13	151.0	1.70	1.68	0.12	(211)
62.08	109.0	1.47	1.47	0.12	(002)
72.40	102.0	1.32	1.30	0.12	(311)
79.71	400.0	1.24	1.24	0.10	(202)
76.56	58.0	1.21	1.20	0.10	(212)

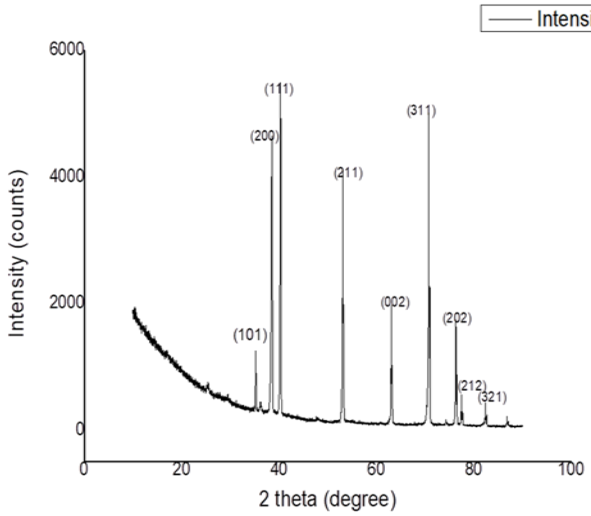

Figure 4: X-ray diffraction pattern of anodic TiO_2 nanotube arrays annealed at 480 degree Celsius

3.3. Diffuse Reflectance Spectroscopy (DRS)

The theory which makes possible to use DR spectra was proposed by Kubelka and Munk [26]. The remission function with respect K-M scattering constant S is given by

$$[F(R_0)h\vartheta]^{\frac{1}{2}} = B(h\vartheta - E_g). \qquad (3)$$

Therefore, by obtaining $F(R_o)$ and plotting the $[F(Ro)h\upsilon]^{1/2}$ against $h\upsilon$, the bandgap E_g of a sample can be extracted.The band gap energy is calculated with Kubelka- Munk function is found to be 3.02 eV. Figure 5. Kubelka- Munk transformed reflectance spectra of TiO_2 nanotubes annealed at 480^0 C.

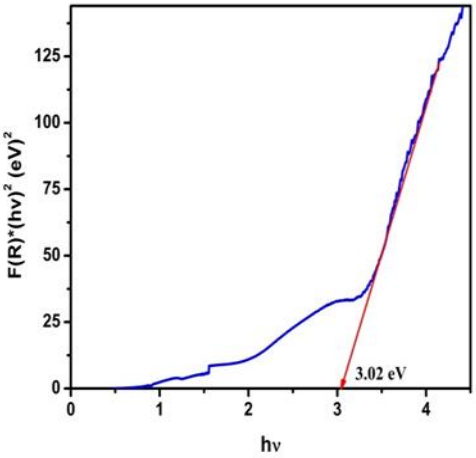

Figure 5: Kubelka- Munk transformed reflectance spectra of TiO_2 nanotubes annealed at 480 degree Celsius

4. APPLICATION

TiO_2 nanotubes are widely used as a photo catalyst in many environment and energy application due to its efficient photoactivity. In Photo Electrochemical Cell TiO_2 plays vital role in water splitting (Hydrogen Generation).

5. CONCLUSION

TiO_2 nanotubes were prepared By Electrochemical Anodization Method. The developed nanotubes were characterized by FESEM- EDAX, XRD and DRS measurements. By FESEM measurement, well aligned formation of nanotube arrays is confirmed with ~25 nm of inner diameter and tube length of ~180nm nm. By XRD measurement, the anatase phase of TiO_2 nanotube arrays is confirmed and the obtained peaks in XRD pattern were found to be consistent with JCPDS Card No. 021-1272. From Kubelka- Munk plot, the band gap energy of TiO_2 nanotubes are found to be 3.02 eV. Finally, the prepared anatase TiO2 nanotube arrays are well aligned and hence, suitable for the application in dye sensitized solar cells due to their higher mobility of charge carriers than rutile TiO_2.

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REFERENCES

1. N. S. Peighambardoust and F. Nasirpouri. **Technol Manipulating morphology, pore geometry and ordering degree of TiO_2 nanotube arrays by anodic oxidation,** *Surf Coat,* Vol. 235, pp.727–734, September 2013.
2. S. Bakardjieva, J. Subrt, V. Stengl, M. J. Dianez and M. J. Sayagues. **Photoactivity of Anatase–Rutile TiO_2 Nanocrystalline Mixtures Obtained by Heat Treatment of Homogeneously Precipitated Anatase,** *Applied Catalysis B: Environmental,* Vol. 58, pp. 193–202, June 2005.
3. A. J. Nozik and R. Memming. **Physical chemistry of semiconductor-liquid interfaces,** *J. Phys. Chem,* Vol.100, pp. 13061-13078, August 1996.
4. T. Bak T, J. Nowotny J, M. Rekas and C. C. Sorrell. **Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects.** *Int. J. Hydrogen Energy,* Vol.27, 6991–1022, October 2002.
5. X. Chen, S. Shen, L. Guo and S. S. Mao. **Semiconductor-based photocatalytic hydrogen generation,** *Chem. Rev,* Vol.110, pp. 6503–6570, November 2010.
6. S. Choudhary, S. Upadhyay, P. Kumar, N. Singh, V. R. Satsangi R., Shrivastav S Dass. **Nanostructur6 6ed bilayered thin films in photo electrochemical water splitting: A review,** *Int. J. Hydrogen Energy,* Vol. 37, pp.18713-18730, October 2012.
7. C. Yue, M. D. Chuan, Z. H. Bin.**Pool boiling on the super hydrophilic surface with TiO_2 nanotube arrays.** *Sci China-Ser E: Technol Sci,* Vol. 52, pp.1596–1600, October 2012.
8. L. L. Costa and A. G. S. Prado.**TiO_2 nanotubes as recyclable catalyst for efficient photocatalytic degradation of indigo carmine dye,** *J Photochem Photobiol A Chem*, Vol. 01, pp. 45–49, January 2009.
9. H. C. Liang and X. Z. Li. **Visible-induced photocatalytic reactivity of polymer-sensitized titania nanotube films,** *Appl Catal B,* Vol. 86, pp. 8–17, February 2009.
10. T. J. Whang, H. Y. Huang and M. T. Hsieh. **Laser-induced silver nanoparticles on TiO_2 for photocatalytic degradation of methylene blue,** *Int J Mol Sci,* Vol.10, pp. 4707–4718, October 2009.
11. S. Liu , Y. R. Smith and M. Misra. **Photocatalytic activities of C-N-doped TiO_2 nanotube array/carbon Nano rod composites,** *Electrochem Commun,* Vol.11, pp.1748–1756, September 2009.
12. Y. S. Sohn, Y. R. Smith and M. Misra. **Electrochemically assisted photocatalytic degradation of methyl orange using anodized titanium dioxide nanotubes.** *Appl Catal B,* Vol. 84, pp. 372–378, December 2008.
13. L. Sun, J. Li and C. L. Wang C. L. **Cells An Electrochemical strategy of Doping Fe^{3+}into TiO_2 nanotube array films for enhancement in photocatalytic activity,** *Sol Energy Mater Sol,* Vol. 6,1875–1880,October 2009.
14. J. M. Macak, H. Tsuchiya and A. Ghicov**. TiO_2 nanotubes: self-organised electrochemical formation, properties and applications.** *Curr Opin Solid State Mater Sci,* Vol.11, pp. 3–18, August 2007.
15. A. Ghicov and P. Schmuki. **Self-ordering electrochemistry: a review on growth and functionality of TiO_2 nanotubes and other self-aligned MOx structures.** *Chem Commun,* Vol.20, pp.2791–802, April 2009.
16. Z. Liu, B. S. K. S. Raja and R. R. Rangaraju. **Self-ordering electrochemistry: a review on growth and functionality of TiO_2 nanotubes and other self-aligned mox structures Hydrogen generation under sunlight by self-ordered TiO_2 nanotube arrays,** *Int J Hydrog Energy,* Vol.34, pp. 3250–57, April 2009.
17. S. Bae, E. Shim and J. Yoon. **Enzymatic hydrogen production by light-sensitized anodized tubular TiO_2 photoanode,** *Sol Energy Mater Sol Cells,* Vol. 92, pp.402–09, April 2008.
18. R. Narayanan and S. K. Seshadri S.K. **Anodic oxide coatings on Ti-6Al-4V produced from electrolyte containing Ca and P-corrosion aspects,** *J Appl Electrochem,*Vol. 36, pp.475–79, January 2006.
19. G. K. Mor, O. K. Varghese and M. Paulose M. **A Review on highly ordered, vertically oriented TiO_2 nanotube arrays: fabrication, material properties, and solar energy applications,** *Solar Energy Mater Solar Cells,* Vol.90, pp.2011–2075, April 2006.
20. W. Chanmanee, A. Watcharenwong and C. R. Chenthamarakshan. **Titania nanotubes from pulse anodisation of titanium foils,** *Electrochem Commun,* Vol.9, pp. 2145–49, August 2007.
21. O. K. Varghese, D. Gong and M. Paulose. **Sensor Actuat B Hydrogen sensing using titania nanotubes,** *Sensor Actuat B,* Vol.93, pp.338–344, 2008.
22. P. Pillai, K. S. Raja and M. Misra. **Electrochemical storage of hydrogen in nano tubular TiO_2 array6s,** *J Power Sour,* Vol. 161, pp.524–530, 2006.
23. Z. Zhang, Y. Yuan, Y. Fang. **Photo electrochemical oxidation behavior of methanol on highly ordered TiO_2 nanotube array electrodes,** *J Electroanal Chem, Vol.* 610, pp. 179–85, December 2007.
24. F. Mura, A. Masci and M. Pasquali. **Effect of a galvanostatic treatment on the preparation of highly ordered TiO_2 nanotubes.** *Electrochimica Acta,* Vol.54, pp. 37946–3798, May 2009.
25. J. M. Macak, H. Tsuchiya, A. Ghicov, K. Yasuda, R. Hahn, S. Bauer and P. Schmuki. **TiO_2 nanotubes: Self-organized electrochemical formation, properties and applications**.

Curr.Opin.Solid St, Vol.11, pp.3–18, February 2007.

26. L. Kavan, M. Grätzel, S. E. Gilbert, C. Klemenz, and H. J. Scheel. **Electrochemical and Photoelectrochemical Investigation of Single-Crystal Anatase,** *J. Am. Chem. Soc*, Vol.118, pp.6716–6723, July 1996**,**