

SYNTHESIS OF PHOTOCATALYTIC ACTIVE TITANIUM DIOXIDE NANOTUBES AND THE EFFECT OF CALCINATION

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Abstract

Photocatalytic active, well-ordered TiO₂ nanotubes (TNTs) were synthesized using electrochemical anodization of a Ti substrate. A third generation electrolyte comprising mixture of ethylene glycol and ammonium fluoride in water was used to grow the TNTs at 60 V and 2 h deposition time. The effect of post-annealing on the physical properties and the photocatalytic activity of the TNT samples at two different temperatures, 300°C and 400°C was investigated. Further, the effect of pre-annealing of Ti substrate foil before growth of TNTs between 250°C and 650°C was investigated. Calcining at 300°C and 400°C for 1 h transformed the TNTs from amorphous to anatase phase. SEM images reveal dense and self-organization of TNTs for Ti foils annealed at 350°C and 440°C. The photodegradation rate of MB was twice as high for samples annealed at 400°C compared to those annealed at 300°C. The length of the TNT reached a maximum of 8.85 μm on Ti foils pre-annealed to 440°C for 1 h, after which a drastic reduction to 4.87 μm and 4.24 μm was observed on Ti foils pre-annealed to 525°C and 625°C respectively. The wall thickness systematically decreased as 32 nm, 31 nm, 29 nm, 21 nm, and 20 nm, respectively, when TNTs were grown on Ti foils heated at 250°C, 350°C, 440°C, 525°C, and 625°C.

Keywords: *Anodic, Titanium dioxide, Nanotubes, Photocatalytic*

1. Introduction

Titanium dioxide nanotubes (TNTs) prepared by electrochemical anodization have a high surface to volume ratio with size dependent physicochemical properties (Rani, 2010). TNTs with controlled dimensions have shown promising properties in many applications such as dye sensitized solar cells, photocatalysis, gas sensing, biomedical and antimicrobial applications (Rani, 2010). Titanium dioxide (TiO₂) photocatalysts were first used for remediation of environmental pollutants in 1977, when Frank and Bard reported the reduction of CN⁻ in water (Frank and Bard, 1977), leading to a dramatic increase in research in this area (Fujishima, 1999). Other binary semiconductors that have been studied as photocatalysts include ZnO, WO₃, Fe₂O₃, CdS and ZnS but hitherto TiO₂ stands out as superior for most practical applications. TiO₂ photocatalysis works at room temperature with supply of low intensity UVA light (< 390 nm); practically of the order 1 mW/cm² or higher. Photo-generated electrons in the conduction band of TiO₂ are reducing enough to produce superoxide from dioxygen (Fujishima et al., 2000), and the holes in the valance band are sufficiently low (with respect to the vacuum level) for oxidation reactions. Moreover, TiO₂ is resistant towards photo-corrosion, it is chemically stable in aqueous solutions, and it is non-toxic (Hsien et al., 2000). However, the large band gap of TiO₂ limits its application for efficient solar energy utilization. The most commonly used crystalline structures of TiO₂ are anatase and rutile with energy band gaps of about 3.2 eV and 3.0 eV, respectively. This means that only about 4% of the entire solar spectrum can be utilized by TiO₂. Anatase TiO₂ films are reported to have higher conversion efficiency, photocurrent and electron diffusion length than rutile films of same thickness (Park et al., 2000; Tanaka et al., 1991). Preparation and post-treatment methods can further enhance the photocatalytic activity. For example TiO₂ nanotubes and

nanowires are reported to have high photocatalytic activity because of a large surface area to volume ratio and efficient collection of charge carriers at their interfaces. The photocatalytic efficiency of TiO₂ films has been improved by pre-heat treatment, post-heat treatment and doping. For films made by electrochemical anodization, spray pyrolysis, hydrothermal, dip coating, impurities arising from chemical solutions used during deposition can be removed by heat treatment. TNTs made by anodic oxidation are generally amorphous with high recombination centers limiting their photocatalytic activity (Li et al., 2012; Ghicov et al., 2006), although ways to promote crystallization have been reported by (Grimes et al., 2009). TNTs can however readily be crystallized upon calcination. Anatase TiO₂ has previously been prepared by calcining amorphous TNTs between 300°C and 400°C (Regonini et al., 2010). Annealing amorphous TiO₂ nanotubes at temperatures between 450 °C and 750 °C was shown to yield mixtures of anatase and rutile phases (Li et al., 2012). The effect of substrate annealing on the TNT structure has also been studied and shown to influence the growth mode (Weizhen et al.2011; Zheng et al., 2015).

In this study, electrochemical anodization of Ti foils has been performed to fabricate TNTs using a so called third generation electrolyte with the purpose of investigating the effect post-annealing on the TNT structure and photocatalytic activity. Further, the effect of pre-annealing the Ti substrate foil on the TNT physical properties is also investigated.

2. Experimental

2.1. Preparation and electrodeposition of TNTs on non-annealed Ti foils

Ti foils with dimension 15mm×15mm×0.25 mm were used as anode materials (purity 99.7%, Sigma Aldrich) in a two electrode setup. A Pt foil with size 25mm×25mm×0.25 mm was used as counter electrode (purity 99.9%, Sigma Aldrich). Prior to use the electrode foils were cleaned by sonication in ethanol for 5 minutes, and then rinsed in distilled water and dried in a stream of nitrogen gas. Anodization was performed using a constant DC voltage of 60 V. All chemicals used in this work were purchased from VWR chemicals Sweden with stated purity 99.9 % or better. Electrolyte solutions with the following compositions were used to prepare TNTs on non-annealed Ti foils: (i) 95 vol% ethylene glycol, 5 vol% water, and 0.37 g ammonium fluoride (NH₄F) corresponding to 0.1 M, and (ii) 47.5 vol% ethylene glycol, 2.5 vol% water and 0.37g NH₄F corresponding to 0.2 M. Anodization was done for 2 h. The as prepared TNT samples were rinsed in distilled water and dried in a stream of nitrogen. The as prepared TNTs were subsequently annealed in air for 1 h. The morphology of as prepared samples was characterized by scanning electron microscopy (SEM; Zeiss 1550, Jena, Germany) employing 1 to 10 kV acceleration voltages with an in-lens secondary electron detector. The TNT length was measured by profilometry (DektakXT, Bruker, Germany). The crystallinity and phase composition was measured using X-ray diffraction (XRD) with 2θ between 20 and 80° using a Philips D5000 diffractometer employing averaged Cu K_{α1} (λ = 1.5418 Å) radiation. The photocatalytic activity of the samples was measured using a homebuilt photocatalytic reactor, which continuously can measure the methylene blue (MB) concentration in the reactor as a function of UV illumination by recording the calibrated transmittance of the 670 nm absorption band due to MB in the well-stirred solution with a diode laser (Bozhidar, 2011). A concentration of 1 ppm MB in 100 mL water was used in the experiments.

2.2 Preparation and electrodeposition of TNTs on pre-annealed Ti foils

Prior to anodization the Ti foils were heated in an oven at varying temperatures between 250°C to 625°C in steps of about 100°C in a stream of nitrogen for 1 h. After annealing, the Ti substrates were cleaned by sonication in ethanol for 5 minutes, rinsed in distilled water, and finally dried in a stream of nitrogen gas. The anodization electrolyte comprised of 93 vol% ethylene glycol, 7 vol% water and 0.15 M NH₄F. Anodisation was done in 100 mL Teflon beaker using electrode separation distance of 3 cm at 55VDC for 2 hours. Samples were prepared using an optimized electrolyte preparation procedure where ammonium fluoride was first mixed with water and magnetically stirred. The solution was then added to ethylene glycol and magnetically stirred. The TNTs were then calcined at 400°C to obtain anatase crystalline structure after which characterization of the samples was done.

3. Results and discussion

3.1 Post-annealed TNTs on non-annealed Ti foils

Figure 1 shows SEM images of two samples, TNT07 and TNT08 measured at different magnification, but grown under the same electro-deposition conditions as described section in 2.1. Both TNT sample have tube diameters 120 nm and 10 nm wall thickness, and the TNTs are arranged in hexagonal structure.

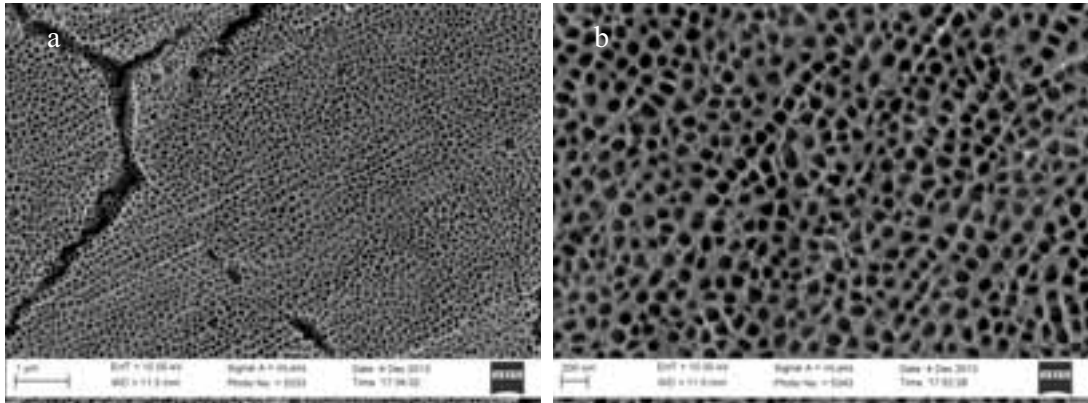


Fig. 1: SEM images for sample TNT 07 and TNT 08 with different magnifications prepared by anodisation for 2hours in 0.2 M NH_4F , 95% Ethylene glycol and 5% H_2O

The as-prepared TNTs were amorphous but on calcining samples TNT07 and TNT08 at 400°C and 300°C, respectively, for 1 h, the TNTs crystallized as shown Fig. 2 XRD diffractograms. It is seen that both samples exhibit predominately the anatase phase, with minor reflections from rutile crystals. The XRD diffractogram in Fig. 2 show that the intensity ratio of the <004> to the <001> reflection is higher for the sample annealed at 400°C than the sample annealed at 300°C. Rutile <111> and <211> reflection peaks are also observed which are more intense in the sample annealed at 400°C.

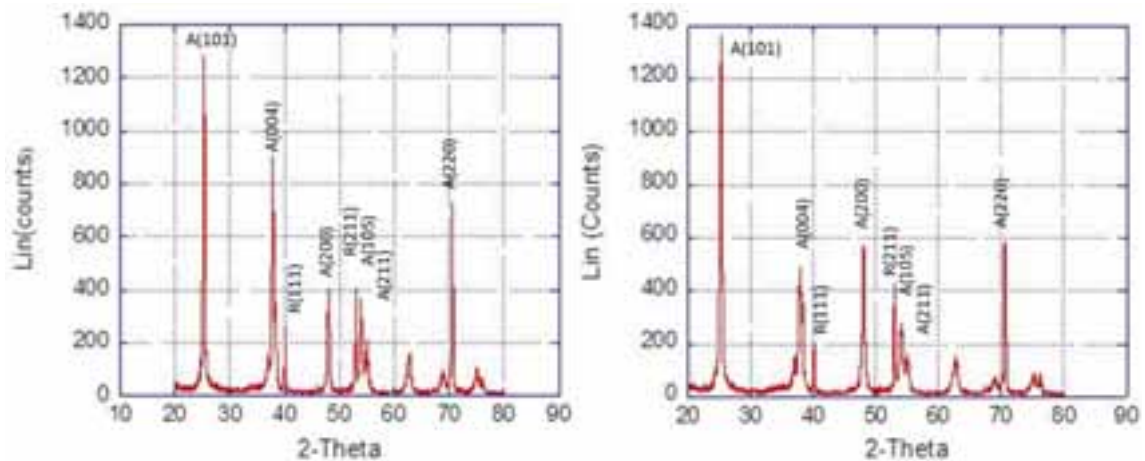


Fig. 2: XRD diffractograms of samples (a) TNT07 calcined at 400°C and (b) TNT08 calcined at 300°C.

Scherrer analysis of the <101> reflection peak was used to obtain a rough estimate of the crystallite size, d , viz.

$$d = \frac{0.94\lambda}{\beta \cos\theta}$$

where $2\theta = 25.27^\circ$ and $2\theta = 25.25^\circ$ for the sample annealed at 400 °C and 300 °C, respectively, β is the FWHM corrected for the instrumental line broadening, yielding $d = 37$ nm and 32 nm, respectively, indicating a crystallite growth with increasing annealing temperature, as expected.

The photocatalytic properties of the samples, where measured in 1 ppm MB solutions. The calibrated MB concentration, as measured by the 670 nm laser intensity integrated in the reactor, is shown in figure 3a, and shows a linear decrease of transmittance in the solution as a function of increasing MB concentration, thus validating the performance of our experimental setup. The photocatalytic degradation rate of sample TNT08 post-annealed at 300°C (Fig. 1b) is $k_{dec} = 0.0019 \text{ min}^{-1}$, while that of TNT07 post-annealed at 400°C (Fig. 1a) is $k_{dec} = 0.0035 \text{ min}^{-1}$. We attribute this to a higher degree of crystallinity after post-annealing at 400°C, and possibly due to the increased rutile content which has been reported to enhance the photocatalytic activity due to synergetic bandgap matching of rutile and anatase particles that are in physical contact to each other (Su et al., 2011)

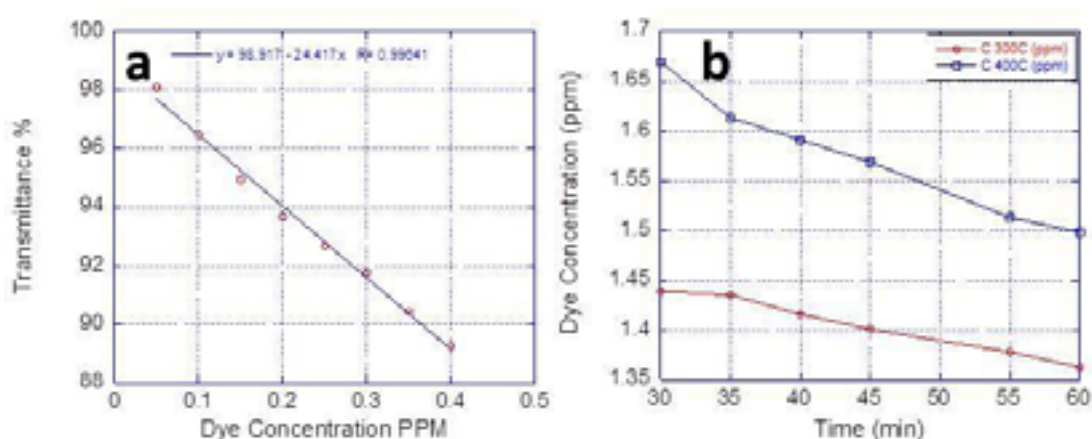


Fig: 3 (a) MB calibration curve for photocatalytic measurements (b) Methylene blue degradation for samples TNT 07 and TNT 08 calcined at 400°C and 300°C. The illumination time in (b) started at time = 30 min.

3.2 TNT on pre-annealed Ti foils

SEM images of a pristine non-annealed Ti foil and annealed Ti foil are shown in Fig. 4. It is seen that the micro-structure and surface morphology are changed upon annealing. Heating of Ti foils brings about rearrangement, crystal growth, as well as surface oxidation of the Ti foil that can facilitate TNT nucleation by providing new reactive sites. The pristine Ti metal foils are polycrystalline in nature and characterized by randomly distributed grain boundaries which act as defect sites for TNT nucleation (Grimes and Mor, 2009). Thus the defect sites act as templates for TNT growth. Substrate heating influences the crystal structure and mechanical behavior of the Ti foils which influences the TNT nucleation and growth. Annealing smoothens the Ti foil which and improves the order and arrangement of TNTs, as we now discuss.

SEM images of TNTs grown on annealed Ti foils pre-annealed between 250°C and 625°C are shown in figure 5 (a-e). SEM images taken from the bottom side of the TNTs are shown in figure 5f. For the non-annealed TNT bottoms, the TNTs have clear grain boundaries. The distribution and size of TNTs is irregular. Some are pentagonal, others are hexagonal, some are small others are large. This irregular distribution and size effects are inherent in the Ti foil and come about during processing of the Ti foils and are transferred to TNTs during the growth process in electrochemical anodization. Pre-heating treatment rearranges the atoms

within the Ti foil through diffusion and smoothen the surface. The inset in figure 5f shows TNTs grown on annealed Ti foils. Here the bottom parts of the TNTs are more densely packed and almost cylindrical

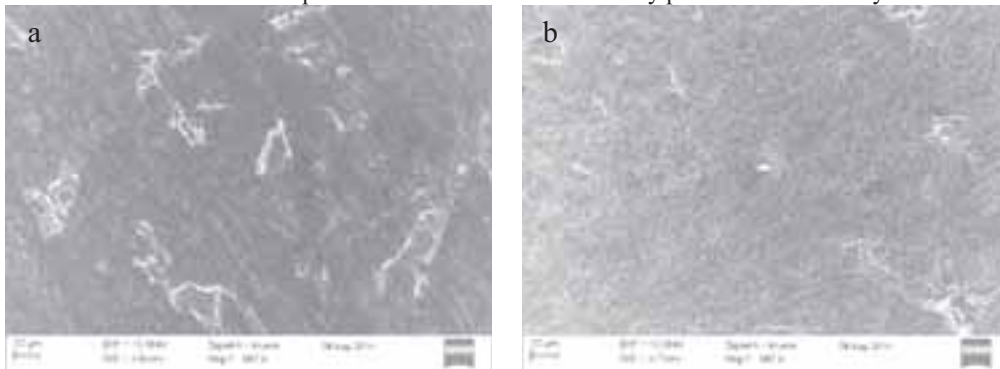


Fig. 4: SEM Images of (a) non annealed Ti foil, and (b) annealed Ti foil.

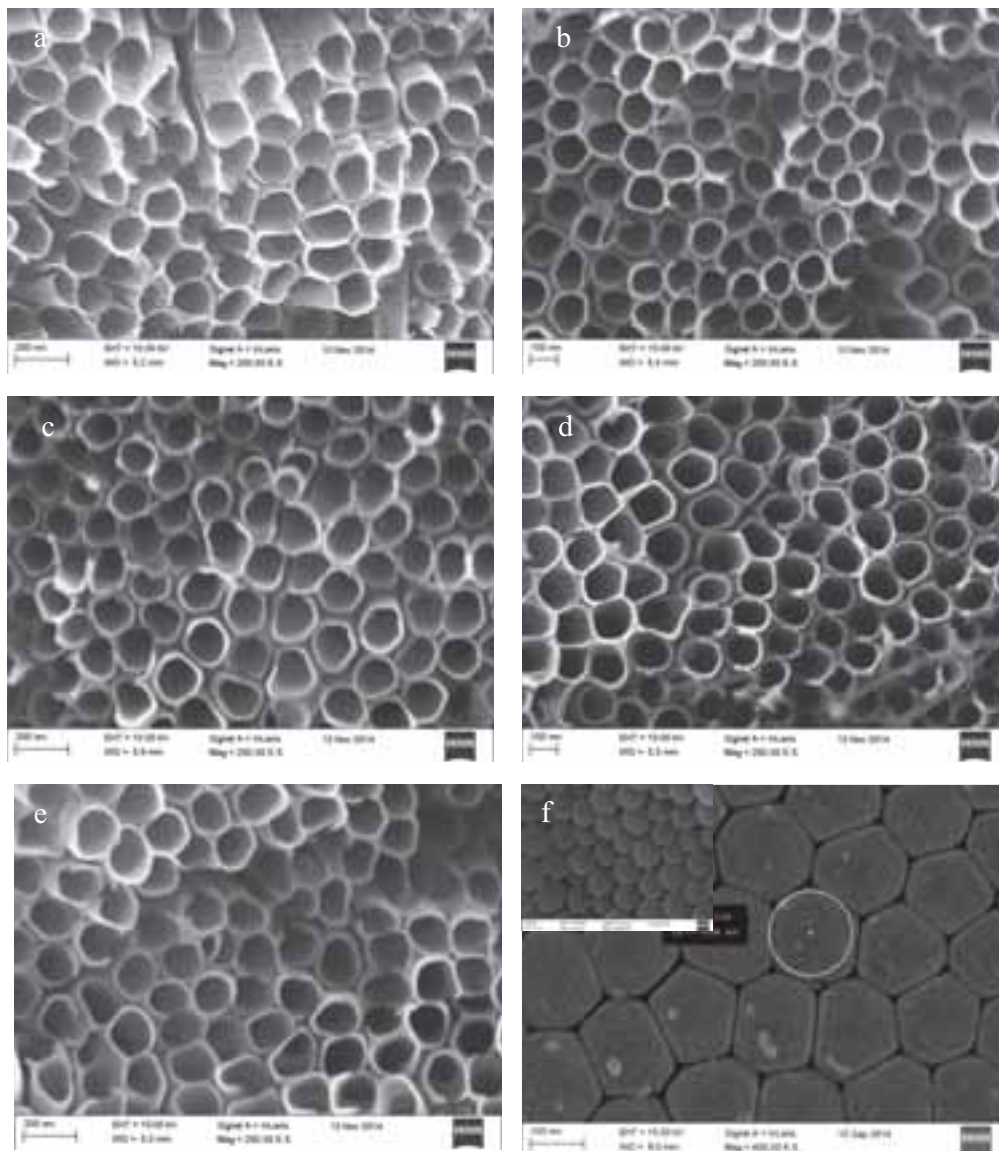


Fig. 5: SEM top-down images of TNTs grown on pre-annealed Ti foils at (a) 250°C (b) 350°C (c) 450°C, (d) 525°C (e) 625°C, and (f) SEM images from scraped off TNT bases grown on non-annealed, and in the inset, annealed Ti foils.

Annealing helps to reduce residual stresses developed during the process of fabricating the Ti foils (Zheng et al., 2015). Heat treatment changes the structure, mechanical properties of the Ti foils improving the structural and mechanical properties of the annealed of the Ti foil which affect the growth of TNTs during the process of anodization as reported by Xialong et al. (Xialong et al, 2010). In the latter study it was noticed a change in microstructure in Ti foil through the formation of V- like structures with ultrathin walls as a result of rearrangement of atoms within the Ti foil. Annealing causes atoms to migrate in a crystal lattice reducing defects and dislocations in the material which in turn changes hardness and ductility of material. While by preheating Ti foil we induce superior properties, it should be noted that from the findings of Zheng and colleagues (Zheng et al., 2015), Ti foil has been shown to exhibit different stages when heated in a so called microforming process. Temperatures below 300°C brought about elastic and work hardening stages. At 450°C the material exhibited elastic, work hardening and softening periods. Fracture strain set in at 450°C and increased thereafter because of the occurrence of the softening behavior with deformation setting in when the temperature was increased (Zheng et al., 2015). With increasing annealing temperature stress on Ti foil is reduced and when the foil is used to grow TNTs, the initiation of TNT growth is affected. A compromise has to be attained where pre-annealing gives desirable TNT growth, structure and high-order with good characteristics.

Figure 6a shows the influence of physical properties of TNTs of Ti foils pre-heated at 250°C, 350°C, 440°C, 525°C, and 625°C. Nanotube inner diameter significantly drops by 18 nm from 158 nm to 140 nm when Ti foils are heated to 350°C. At higher annealing temperatures the inner diameter of the TNTs exhibits only a slight decrease of inner diameter. A similar trend is noticeable for the outer diameters of the TNTs. These results show that most of rearrangement of the crystal atoms within the Ti foil that act as nucleation sites for TNT takes place when the Ti foil is heated between 250°C and 350°C. Packing of the TNTs continues at higher annealing temperatures. This difference in packing of TNTs is seen in the SEM images in figure 5, and the dramatic change of TNT packing above 250°C is clearly evident.

The wall thickness for Ti foils pre-heated at 250°C, 350°C, 440°C, 525°C, and 625°C reduces as 32 nm, 31 nm, 29 nm, 21 nm, and 20 nm, respectively. In fluoride containing electrolytes, wall thickness is a function of electrolyte concentration, water content and anodizing voltage. At high fluoride contents, thin walls are produced because of effects of chemical etching. As seen in figure 6b only short nanotubes were grown on Ti foils annealed at 525 °C and 625 °C. This means with all other anodizing parameters kept constant in growing all the TNTs, the effect of etching of tube walls is most pronounced for the short nanotubes. Short TNTs means disorder, since the metal\oxide base interface is etched away in the fluoride containing electrolyte leaving spacing between growing TNTs. Longer TNTs protect the electrolyte from reaching the metal\oxide base interface. This explains why we have drastic reduction in wall thickness from 29 nm to 21 nm in TNTs grown on Ti foil heated at 440 °C and 525 °C, respectively, together with the use of already deformed electrode with reduced stress. As seen in figure 6b the TNT length drastically reduces by almost twice from about 8850 nm to 4870 nm.

When Ti foils were heated from 250°C to 625°C, the TNT length first increased as 7490 nm, 7970 nm, 8850 nm, for the pre-heat treatment at 250°C, 350°C and 440°C, respectively, after which the length was observed to decrease at higher temperatures beyond 450°C (Fig. 6b). At 525°C and 625°C, the TNT length decreased as 4870 nm and 4240 nm, respectively. Several factors have been reported to influence the growth of TNT, among them being pH of electrolyte, diffusion, temperature of solution and stress induced effects. In ethylene glycol containing electrolytes, high ammonium fluoride content means high pH. This increases the rate of chemical dissolution hindering TNT growth. High temperatures of electrolyte in ethylene glycol containing electrolytes means reduced viscosity of the bulk ethylene glycol solution leading to fast migration of the fluoride ion which diffuses at twice the rate of oxygen ion thereby affecting growth of TNT. This explains why viscous electrolytes such as glycerol and ethylene glycol have been known to produce well-ordered and long nanotubes because the rate of diffusion of F⁻ is reduced enabling growth (Paulose et al., 2007). Aqueous electrolytes only produce TNTs only a few um long because of chemical dissolution\oxidation (Beranek et al. 2003). Stress builds up during oxidation of Ti foil in electrochemical anodization and is present in the growing nanotubes (Macak; 2008). Heating Ti foils at temperatures between 250-450°C reduces stress on Ti foil (Zheng et al., 2015). In this work, the proposition is that the remaining

stress on Ti foil after annealing at this temperature coupled with stress induced effects during anodization can influence the oxidation\ dissolution behavior in the anodization set up initiating growth, self-organization and cause an increase in nanotube growth length as shown in figure 6b for TNTs grown on Ti foil pre-annealed at 250°C, 350°C and 440°C. The reduction in nanotube length in figure 6b, when Ti foils are heated at 525 °C and 625 °C, can be explained by the fact that at temperatures above 450°C stress on Ti foil is minimal, fracture and deformation has set in on the Ti foil (Zeng et al., 2015). The formation of tube bottom (TiO₂) layer at the metal\oxide interface is permanently exposed to compressive stress (Macak; 2008). A reduction in nanotube length as shown in figure 6b means that the fluoride containing electrolyte easily penetrated to the lower part of the nanotube bottom base eroding the nanotube bottoms, and at the same time hinder oxidation\ dissolution behavior at the metal\oxide layer. Eventually this leads to reduced growth. We conclude that a mechanically deformed Ti foil, when used as anode electrode in the electrochemical anodization, will perform poorer than a normal working anode which has not undergone deformation. Since the formation of TNTs takes place at the anode and it is the working electrode, care should be taken not to anneal Ti foils above 440°C.

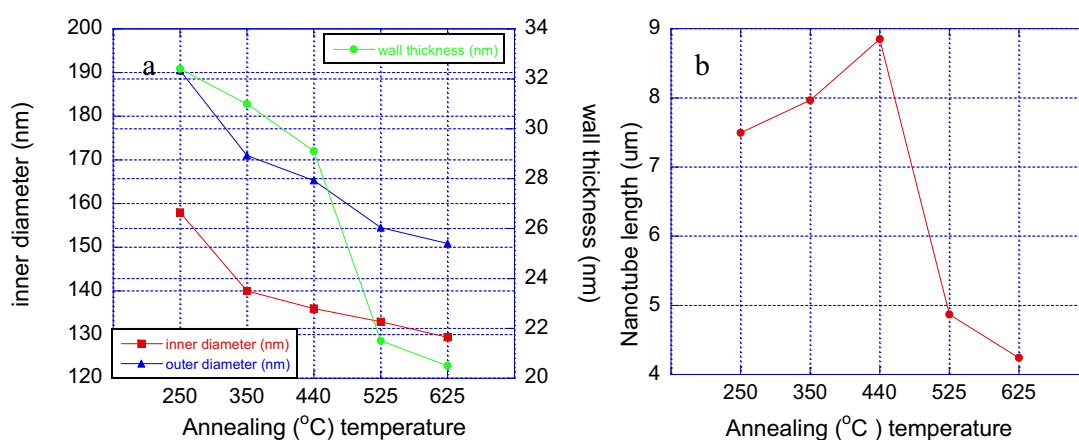


Fig. 6: (a) A graph of physical parameter (inner, outer and wall) dimension (b) Nanotube length of TNTs anodised on preheat treated Ti foils at different temperature in 93% ethylene glycol, 7% vol water and 0.15 M NH₄F for 2 hours in 55VDC

4. Conclusions

The effect of Ti annealing temperature on already grown amorphous titanium dioxide nanotubes has been explored. Heat treatment on the as-prepared amorphous TNTs at 300°C and 400°C gives predominantly TNTs with anatase phase, with minor reflections from rutile crystals. The grain sizes as deduced from Scherrer analysis of XRD diffractograms yield $d = 37$ nm and 32 nm for the TNT07 and TNT08 samples, respectively, demonstrating larger grain sizes with increasing calcination temperature of the amorphous TNTs, and a tendency for alignment along the <004> direction. The rate of photodegradation of methylene blue is higher for the sample annealed at 400°C than that annealed at 300°C which is attributed to increasing crystallinity, and possibly higher percentage of inter-mixed rutile phase. The effect of Ti foil annealing before growth of TNTs is further explored and found to influence nanotube growth, the nanotube structure, and optical properties of the nanotubes. Ti foils annealed between 250°C and 625°C gave an increase in nanotube length up to 440°C, beyond which there was a great reduction in nanotube length from about 8850 nm at 440°C to 4870 nm for Ti foil heated at 525 °C. Nanotubes wall thickness reduced systematically up to about 29 nm at 440°C after which the wall thickness reduced to 21 nm for nanotubes grown on Ti foil heated at 525°C. The outer diameter reduces from 165 nm at 440°C to 154 nm at 525°C. There is structural rearrangement of nanotube structure with better and closer hexagonal packing of the TNTs achieved at 440°C, but beyond this temperature, disorder sets in due to shortening of TNTs which are due to effects of chemical etching as a result of exposure to electrolytes. In this work we propose titanium foils for growing TNTs using electrochemical anodization in ethylene glycol and ammonium fluoride electrolytes should be heated in an atmosphere of nitrogen for one hour at 440°C. The as prepared amorphous nanotubes should

further be calcined at 400°C to get pure anatase for photocatalytic applications since it is the best phase for photocatalytic applications.

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References

- Bozhidar, I. S., Nina, V. K., Gianluca, L. C., 2011. Novel integrated reactor for evaluation of activity of supported photocatalytic thin films: Case of methylene blue degradation of TiO₂ and nickel modified TiO₂ under UV and visible light Colloids and surfaces, A: Physicochem. Eng. Aspects 382: 219-225.
- Frank, S. N., Bard, A. J., 1977. Heterogeneous Photocatalytic Oxidation of Cyanide Ion in Aqueous Solutions at TiO₂ Powder, Journal of the American Chemical Society 99: 303–330.
- Fujishima, A., Hashimoto, K. Watanabe, T. (1999). TiO₂ photocatalysis: fundamentals and applications, Tokyo Bkc.
- Fujishima, A., Rao, T. N., Tryk, D. A., 2000. Titanium Dioxide Photocatalysis. Journal of Photochemistry and Photobiology C Photochemistry Reviews 1: 1-21.
- Ghicov, A., Tsuchiya, H., Macak, J.M., Schmuki, P., 2006. Annealing effects on the photoresponse of TiO₂ nanotubes. Physica Status Solid A Applied Research, 203 (4): 28-R30Grimes C. A. Mor G. K., (2009). TiO₂ Nanotube Arrays Synthesis, Properties, and Applications Springer Science Business Media, LLC.
- Hsien, Y. H., Wang, K. H., Ko, R. C., and Cang, C. Y., 2000. Photocatalytic degradation of wastewater from manufactured fiber by titanium dioxide suspensions in aqueous solution: a feasibility study. Water Sci. Tech.42: 95–99.
- Li, D., Shiwei, L., Li, S., Huang, X., Cao, X., Li, J., 2012. Effects of geometric and crystal structures on the photoelectrical properties of highly ordered TiO₂ nanotube arrays. J. Mater. Res. 27, 1029–1036.
- Park, J.H., Kim, S., Bard, A.J., 2006 . Novel Carbon-Doped TiO₂ Nanotube Arrays.
- Rani, S., Roy S. C., Paulose, M., Varghese O. K., Mor, G. K., Kim, S., Yoriya, S., LaTempa, T. J., Grimes, C. A., 2010. Synthesis and applications of electrochemically self-assembled titania nanotube arrays. Phys. Chem. Chem. Phys. 12, 2780.
- Regonini D., Jaroenworarluck A., Stevens R., Bowen C. R. 2010. Effect of heat treatment on the properties and structure of TiO₂ nanotubes: phase composition and chemical composition. Surf. Interface Anal. 42: 139–144.
- Sarmad 2010. Annealing Effect on the growth nanostructured TiO₂ thin films by pulsed laser deposition (PLD). Journal of Eng. & Tech, No: 3291. 921-929.
- Shiqi, L., Zhang, G., Guo, D., Yu, L., Zhang, W., 2009. Anodization Fabrication of Highly Ordered TiO₂ Nanotubes. J. Phys. Chem., 113, 12759–12765..
- Tanaka, K., Capule, M. F. V, Hisanaga, T., 1999. Effect of crystallinity of TiO₂ on its photocatalytic action. Chemical Physics Letters. 187 : 73-76.
- Weizhen, H., Park, S., Shin, D., Yoon, S., 2011. Effect of Annealing Ti Foil on The Structural Properties of Anodic TiO₂ Nanotube Arrays. Journal of the Korean Physical Society, Vol. 58, No. 3, 575_579.
- Zheng, Q., Shimizu, T., Ming, Y., 2015. Ti foil annealing at different temperatures on properties of thin pure titanium foils Manufacturing Rev. 2015, 2, 3.

