

Growth and Optimization Processes Towards Self-organized and Highly Ordered Titanium Dioxide Nanotubes for Photocatalytic Applications

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Abstract

Highly- ordered and self-organized titanium dioxide nanotubes (TNT) for photocatalytic activity were fabricated by anodization method, and characterized using scanning electron microscopy, X-ray diffraction, UV-Vis spectrophotometry, and profilometry. Anodization electrolyte preparation and growth conditions were studied towards the growth of ordered TNTs by systematically varying electrolyte composition and mixing procedures. TNTs were grown by anodizing pure titanium foils in a third generation electrolyte consisting of 0.2 M ammonium fluoride and water. For optimization purposes, the samples were anodized at a constant DC voltage of 60 V for two hours while varying the electrolyte composition by employing different ways of mixing the electrolyte so as to achieve a homogeneous solution. The concentration of fluoride was varied between 0.005 M to 0.3 M, while the water content was varied between 3 and 50 vol %. Introducing a two-step anodization procedure, improved TNT structures were achieved. The as-prepared TNTs between 87 nm and 170 nm; and wall thickness between 20 nm to 40 nm depending on anodizing conditions were amorphous, and were found to transform into highly crystalline anatase structure upon calcination at 400°C. The physical dimensions of the TNTs varied with length between about 7.2 nm to 46 nm; inner diameter. The TNTs were shown to be active for methylene blue photo-degradation, and that reaction rate was shown to be more than twice as high on the two-step anodized TNTs.

Keywords: *Anodization, TiO₂, nanotubes, photocatalysis.*

1. Introduction

Titanium dioxide nanotubes (TNT) have attracted considerable interest due to its wide applicability in a variety of fields such as gas sensing, photocatalytic pollutant degradation, dye sensitized solar cells, self-cleaning surfaces, antibacterial coatings and biomedical application (see Rani, 2010, and references therein). Various ways to prepare TNTs have been reviewed by Macak et al, (2007) and Rani et al (Rani, 2010). Anodic oxidation of Ti foils has been shown to yield high quality TNTs (Mizukoshi et al., 2013), by judicious control of parameters such as electrolyte concentration, applied voltage, pH and temperature. Several different types of electrolytes have been reported over the years to grow ordered TNTs. This includes the so-called first, second, third and fourth generation of electrolytes (Raja, 2010). The nature of electrolyte (aqueous or non- aqueous) plays a key role, and has been found to influence the TNT growth. In viscous organic electrolytes TNTs with smooth walls are obtained at low water concentrations (Macak et al, 2007). In such electrolytes high order is achieved because of reduced rate of dissolution. High water content favors transition to sponge like structures rather than nanotubular structure (Kiyong et al., 2013). Aqueous electrolytes give rise to high chemical dissolution rates causing dissolution of the oxide, thus resulting in short TNTs of just a few micrometers. Nanotube dimensions have been tailored by controlling the concentration of electrolyte (Paulose et al., 2007), voltage (Regonin et al., 2013), water content (Macak et al., 2005), anodizing time (Choi et al., 2006; Crawford et al., 2007), and temperature (Prida et al., 2007;

Varghese et al., 2005). In fluoride containing electrolytes the structure of TNT depends on the amount of the fluoride content. Increasing the fluoride content increases the pH, which in turn affects the oxidation/dissolution behavior due to fast etching of the Ti substrate. Low concentrations are required to obtain uniform nanotubular structures since they minimize oxide dissolution into the electrolyte.

In this work, TNTs were grown using electrochemical anodization employing a so called “third generation” electrolyte containing ammonium fluoride, ethylene glycol and water, and optimum processes parameters were established. A second anodization step was adopted and shown to result in TNTs with improved physical properties. Finally, the photocatalytic activity of the TNTs towards photo-degradation of methylene blue in water solution was demonstrated.

2. Experimental

2.1 Titanium dioxide nanotube preparation

2.1.1 Materials

Ti foil with dimensions 8 mm × 8 mm × 0.25 mm was employed as anode material (purity 99.7%, Sigma Aldrich). Prior to use the Ti foils were cleaned by sonication in ethanol for 5 min, and then rinsed in distilled water and dried in a stream of nitrogen gas. A Pt counter electrode with size 25 mm × 25 mm × 0.25 mm (Sigma Aldrich, purity > 99.7%) was used. The electrolyte mixing procedure was varied to see the effect on the TNT morphology and order of nanotubes. A mixture of ethylene glycol (Ethane-1, 2-diol, C₂H₆O₂, Sigma Aldrich, purity > 99.8%), ammonium fluoride (NH₄F, Sigma Aldrich, purity >99.99%), and distilled water was used for the reaction. The relative amounts of the chemicals were varied, as described below. All anodisation experiments were done with a two-electrode system a constant voltage of 60 V using 100mL Teflon reaction cell. The electrode separation was fixed at 30 mm.

2.1.2 Electrolyte mixing conditions

NH₄F is a white solid which is immiscible in ethylene glycol but very soluble in water. Proper mixing of the electrolyte solution is crucial to obtain homogenous mixtures with proper NH₄F concentration. Here three sets of mixing procedures were adopted, which differed in how NH₄F was mixed with ethylene glycol: (A) All chemicals were simultaneously mixed in a teflon reaction beaker with a magnetic stirrer for 30 min. (B) NH₄F was first dissolved in H₂O and vigorously hand shaken. The solution was then added to ethylene glycol to yield the desired composition, while constantly stirred with a magnetic stirrer. The solution was then ultrasonicated for 3 minutes. (C) NH₄F was first dissolved in water and mixed with magnetic stirring. The solution was then transferred to the teflon reaction beaker containing ethylene glycol and magnetically stirred. In all three cases, the as prepared samples were cleaned by immersing them in deionized water for 3 min and dried in a stream of nitrogen gas. Anodization was done for 2 h.

2.1.3 Water concentration

TNT were grown using 3 vol%, 5 vol%, 7 vol%, 10 vol%, 15 vol%, 20 vol%, 30 vol% to 50 vol% in all set of experiments to investigate the effect of water content on TNT growth. The concentration of NH₄F was kept constant at 0.1 M. Anodization was done for 3 h using method (C) of electrolyte preparation.

2.1.4 Fluoride concentration

The NH₄F concentration was varied between 0.05 M to 0.3 M while keeping the ethylene glycol (95 vol%) and H₂O concentration (5 vol%) fixed. Anodization was done for 2 hours.

2.1.5 Two-step anodization

A two-step anodization was employed using an electrolyte consisting of 0.1 M NH₄F in 95 vol% ethylene glycol and 5 vol% H₂O. The electrolyte mixing procedures in (A), (B) and (C) were employed to study their effect on TNT Growth. In the first step of anodization, TNTs were grown in 0.1M NH₄F, 95 vol % Ethylene glycol and 5 vol % H₂O for 4 hours in 60V DC after which they were removed by ultra sonicating the samples in ethanol for 5 minutes, and rinsed in deionized water. The samples were finally dried in a stream of nitrogen prior to a second 1.5 h anodizing step at 60 V using the same electrode separation distance was

30 mm.

2.2 Characterization

The TNT were characterized by scanning electron microscopy (SEM) using a Zeiss microscope (Zeiss 1550, Jena, Germany). An acceleration voltage of 10 keV and an in-lens secondary electron detector were employed. X-ray diffraction (XRD) was performed with a Philips D5000 diffractometer employing averaged Cu K α ($\lambda = 1.541056 \text{ \AA}$) radiation. A profilometer (DektakXT, Bruker, Germany) was used to measure the thickness of the opal and inverse opal films. Reflectance measurements were performed in UV/Vis/NIR transmittance spectra taken in the 300–1000 nm range with a Perkin-Elmer Lambda 900 spectrophotometer. Photocatalytic measurements were performed in a reactor described in detail elsewhere (Stefanov, 2011) consisting of a continuously stirred reaction cell with a 670 nm laser to measure the absorbance of methylene blue (MB) in situ during UV illumination. A standard 4 W BLB tube lamp (4W F4T5/BLB, OSRAM, Germany) operated at $\lambda = 365 \text{ nm}$ was used as a light source. The lamp intensity was measured with a calibrated thermopile detector (Ophir, North Andover, MA, USA) and was measured to be 2.44 mW cm^{-2} at the UV tube wall. The intensity distributions at the position of the film in the reactor was estimated to be 0.38 mW cm^{-2} . A concentration of 1 ppm methylene blue in 100 mL deionized water was employed in all experiments. The absorbance of MB at 670 nm was continuously monitored during UV illumination. The absorbance of the water solution without methylene blue was used as a reference for the absorbance measurements.

3. Results and discussion

3.1. Electrolyte preparation

Figure 1 shows top-view SEM images of TNTs obtained from a one-step anodization process employing different electrolyte mixing conditions. Figure 1a shows an image of TNTs grown using an electrolyte prepared by method A in Section 2.1.2, using 0.2 M NH $_4$ F, 95 vol% ethylene glycol and 5 vol% H $_2$ O, whereby all chemicals were simply mixed in the Teflon reaction beaker and mixed with a magnetic stirrer. Deposition of un-reacted NH $_4$ F is visible as particles and non-porous layers on top of the TNTs. Figure 1b shows a SEM image of TNTs grown from electrolyte prepared by dissolving NH $_4$ F in water, and shaking till it was fully dissolved in the water (method B). Adding NH $_4$ F solution to the ethylene glycol results in less amounts of unreacted NH $_4$ F which is visible as non-porous layer on top of the TNTs. Small amounts of NH $_4$ F are however deposited on top of TNT layer, meaning that it was not fully mixed. In Figure 1c shows a SEM image from TNTs grown from uniformly mixed electrolyte where NH $_4$ F was added in water and carefully mixed with a magnetic stirrer to ensure that all the fluoride ions fully dissolved (methods C). Only after complete pre-mixing, the NH $_4$ F solution was added to bulk ethylene glycol solution under stirring to obtain a homogeneous solution. This procedure produced densely packed and well-ordered TNTs with 120 nm diameter, 20 nm wall thickness and length of about 23 μm . The as prepared TNTs were immersed in distilled water for 3 minutes and dried in a stream of oxygen, followed by ultrasonication in isopropyl alcohol to remove top non-porous yielding well organized nanotubes.

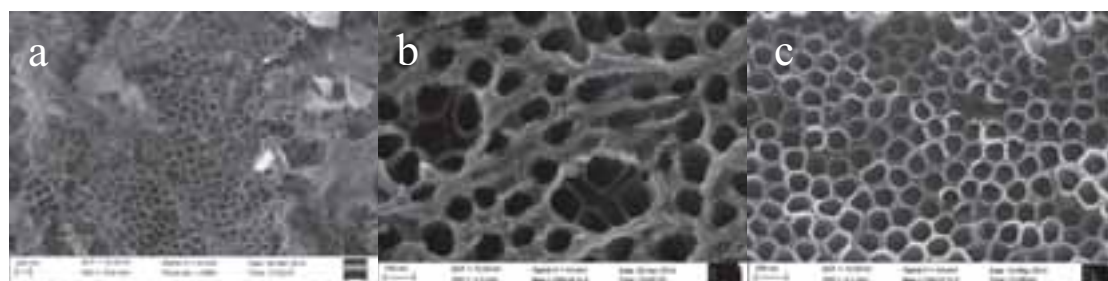


Fig. 1 Dependence of mixing condition: TNT prepared from anodization of Ti foil in a freshly prepared electrolyte consisting of 95% ethylene glycol, 5% H $_2$ O and 0.2 M NH $_4$ F at 60 V for 2 hours, according to mixing procedures (a) method A, (b) method B, and (c) method C (see Section 2.1.2).

Figure 2 shows SEM images from a batch of TNTs grown with different water concentrations between 3

vol% and 50 vol% at a fixed concentration of 0.1 M NH_4F . Compact and smooth nanotubes are grown at low water contents because of reduced chemical dissolution rates on the oxide layer. At high water content

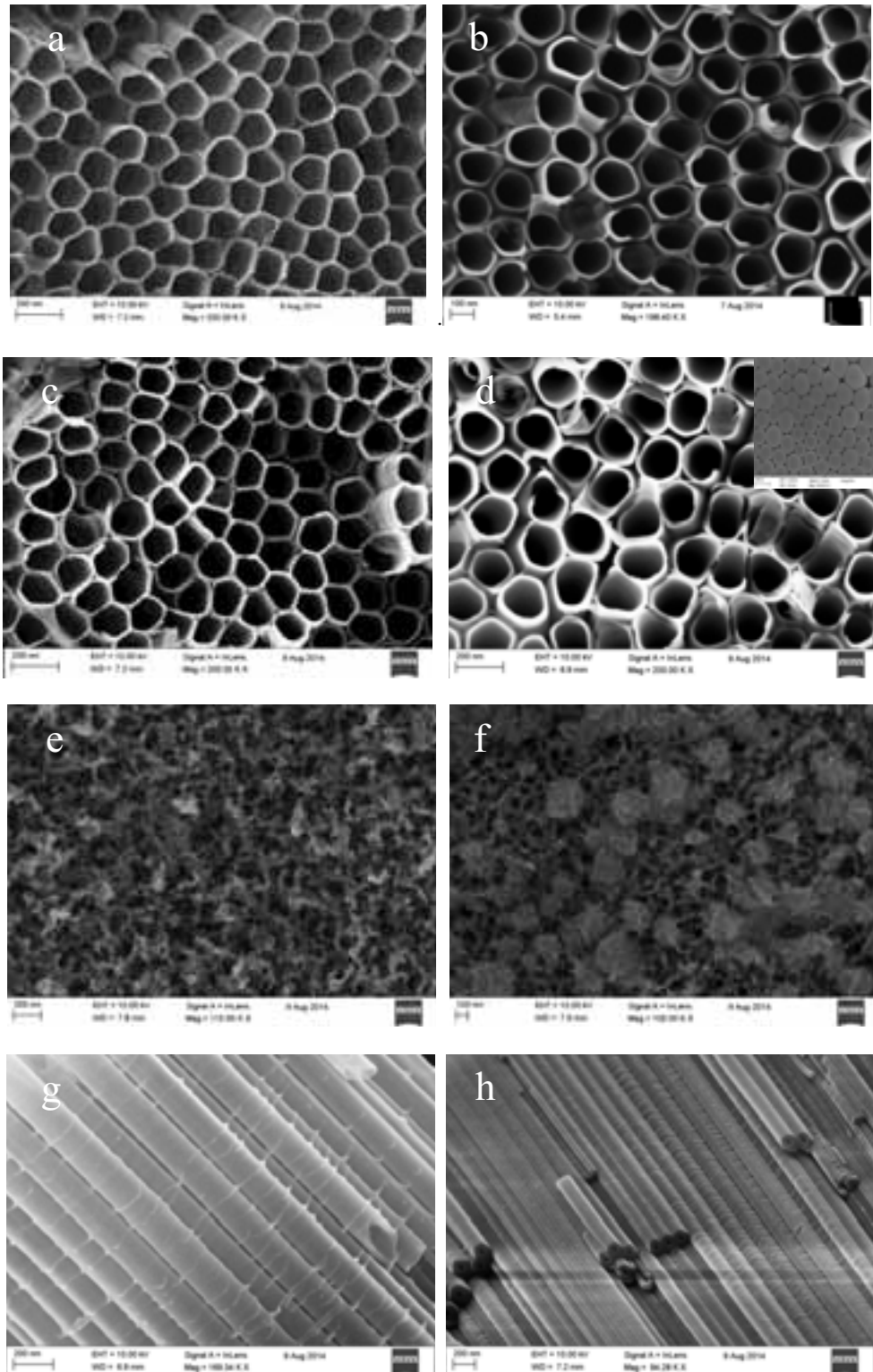


Fig. 2 SEM images showing TNTs prepared from an electrolyte in 0.1 M NH_4F with varying H_2O concentrations: (a) 3 vol%, (b) 10 vol%, (c) 7 vol% (d) 10 vol% (e) 15 vol% (f) 50 vol%. (g) and (h) show cross sections showing 10 % H_2O and 3% H_2O respectively. The anodization was carried out at 60 V for 3 hours.

(>10%), ripples are formed as seen in the cross-section image in Fig. 2g. due to etching of the nanotube walls by the F⁻ ions. The minimum water content for growth of well-ordered structure has been reported to be 0.18 vol% employing 20 V anodizing potential (Raja et al. 2007). When the water content is less than 1 vol%, the formation of long nanotubes (> 300 nm) is impossible no matter the applied voltage (Yin et al., 2010). In our case, well-ordered TNTs were grown at low water contents between 3% H₂O and 7 % H₂O. At higher concentration exceeding 10 vol % less ordered sponge-like structures were formed (Fig 2e and f). At high concentrations the viscosity of electrolytes is decreased leading to an increasing dissolution rate and disordered growth.

The water concentration affects the crystallinity of the nanotubes. Figure 3a shows XRD diffractogram from samples made with different water concentrations, which were post-annealed at 400°C in an oven for 1 h. All TNTs exhibit anatase structure but the anatase peaks diminish with increasing water concentrations at 10%. The most developed crystalline TNTs are obtained at < 10 vol% H₂O.

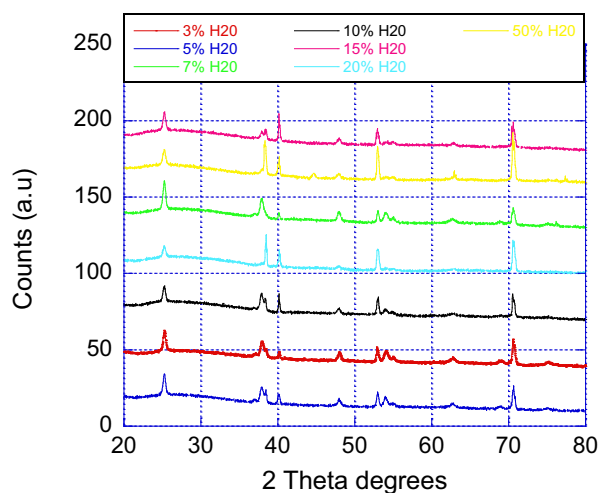


Fig. 3 XRD diffractograms of TNTs prepared with varying water concentrations in 0.1 M NH₄F anodized at 60 V for 3 hours.

3.3 Fluoride concentration

Figure 4 shows top-view SEM images of TNTs obtained from a one-step anodization process with varying NH₄F concentration between 0.05 M and 0.3 M.

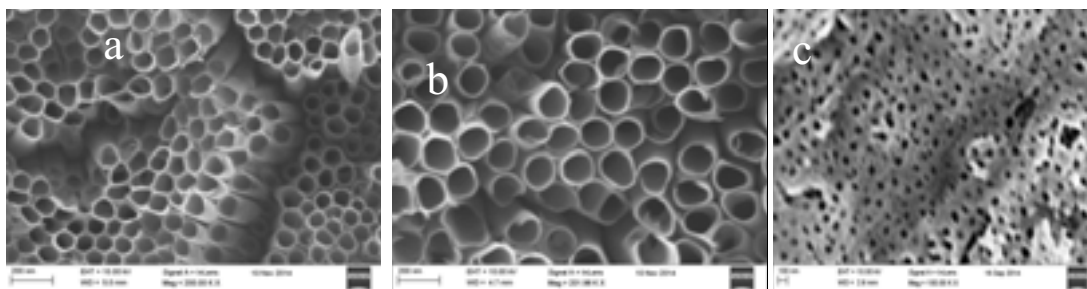


Fig. 4 Selected SEM images of TNTs obtained with varying NH₄F: (a) 0.3M, (b) 0.1M (c) 0.05M, respectively, in 95 vol% ethylene glycol and 5 vol% H₂O. (d) XRD diffractograms at varying NH₄F concentrations of 0.05M, 0.1M, 0.15M, 0.2M and 0.5M. Anodization was done at 60 V for 2 h using electrolyte prepartion method C.

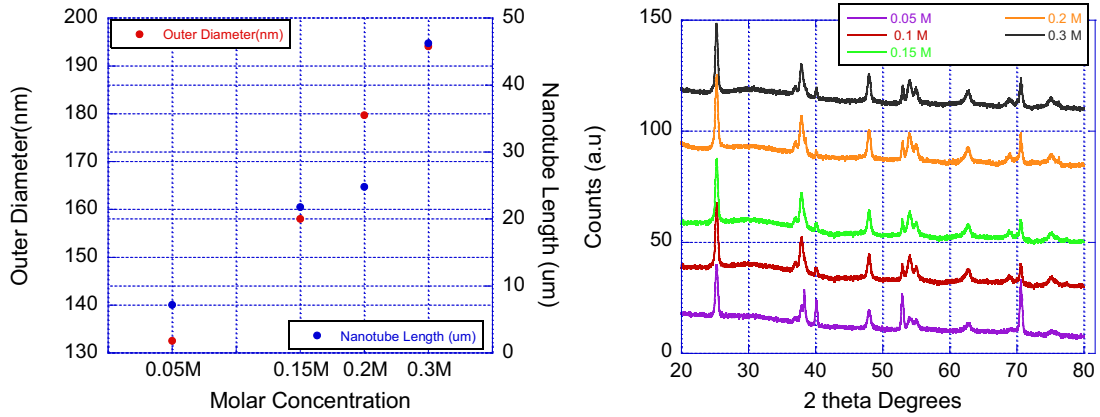
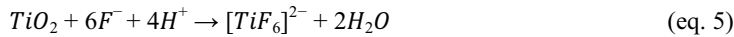


Fig. 5 Outer diameter and length of TNTs versus NH_4F molar concentration prepared by anodization at 60 V for 2 h in an electrolyte containing 95 vol% ethylene glycol and 5 vol% H_2O at varying molar concentrations using method C of electrolyte preparation.

The F^- ions act as powerful oxidants of the Ti plate leading to formation of TiO_2 . The fluoride ions react to form Ti fluoride complexes as shown in reaction 3 from which TNTs are formed according to reaction 4 (Macak et al., 2007), viz.



Increasing the fluoride content in the electrolyte increases the rate of nanotube formation. For example the length of the nanotubes as measured by profilometry is increased as 7.2 μm , 22.6 μm , 24.8 μm and 46.2 μm for concentrations 0.05 M, 0.1 M, 0.2 M and 0.3 M, respectively. By increasing the amount of F^- ions, the rate of chemical etching on the nanotubes also increases causing thinner walls, as evident from figure 4 (a) and (b). Fig. 4d shows XRD diffractograms for TNTs prepared at different NH_4F concentrations between 0.05M and 0.3M. A well-developed anatase phase structure is obtained in all cases. The distribution of the reflections was however observed to change as a function of F^- concentration, with the $\langle 101 \rangle$ orientation slightly increasing with F^- concentration, which correlates with the decreasing wall thickness and suggests that (101) planes develop perpendicular to the growth direction. At 0.3 M the intensity of the $\langle 101 \rangle$ reflection is reduced. This may be explained due to the effect of increased etching rates on the surfaces of the TNTs. From these results, it appears that a NH_4F concentration around of 0.2 M in the 95 vol% ethylene glycol and 5 vol% water electrolyte yields optimum growth conditions for long, well-ordered TNTs.

3.4 Second step anodization

In Figure . 6 a-d SEM images of TNTs formed after the two-step anodization procedure described in Section 2.1.5. It is evident that the TNT array is more ordered and uniform than those formed in the corresponding one step anodization (Figure 1).

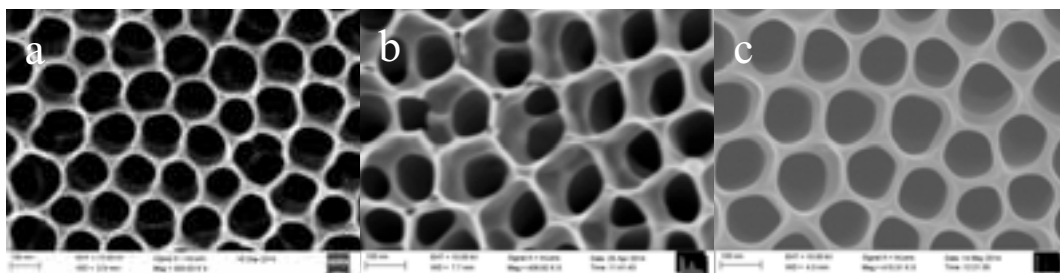


Fig. 6 SEM images of TNTs formed after two-step anodization procedure, employing (a) method A, (b) method B, and (c) method C, respectively, in the second anodization step. The electrolyte composition was 0.1 M NH_4F in 95 vol% ethylene glycol and 5 vol% H_2O .

Superior order and structure are obtained when the electrolyte is thoroughly mixed (method C), thus enhancing reaction between the participating species in anodization reactions. The crystallinity is poor as seen in XRD in Fig 7 (a) because TNTs were grown from un-optimized electrolyte conditions procedure (A) with impurities of unreacted species in electrolyte being trapped as nanotubes grow thus introducing defects and affecting crystallinity. Image (b) is from procedure (B). In the two-step anodization procedure, TNT grow from a pre-textured surface from the first anodization step, and this has been reported to cause fast initiation of pore nucleation and ordering (Zhao et al. 2007). The TNTs are seen to be arranged in a hexagonal super lattice.

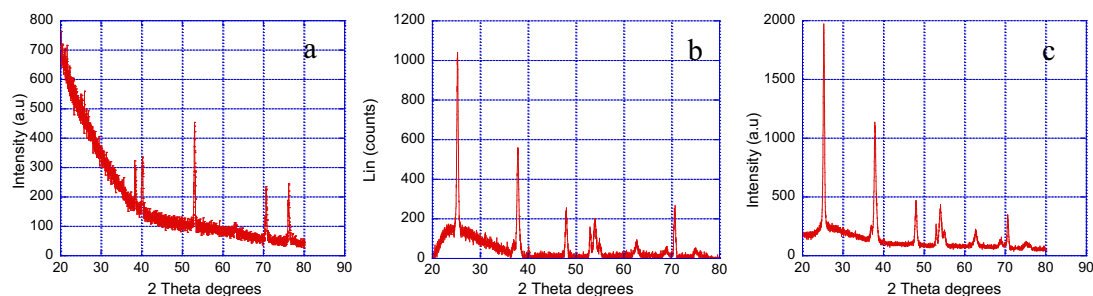


Fig. 7 XRD diffractograms TNTs formed after two-step anodization obtained after different electrolyte mixing protocols to prepare the first anodization step. (a) Prepared according to method (A), (b) method (B), and (c) method (C) respectively.

It is evident that well-developed crystalline anatase TNT were obtained for samples which were prepared according to methods B and C in the first anodization step.

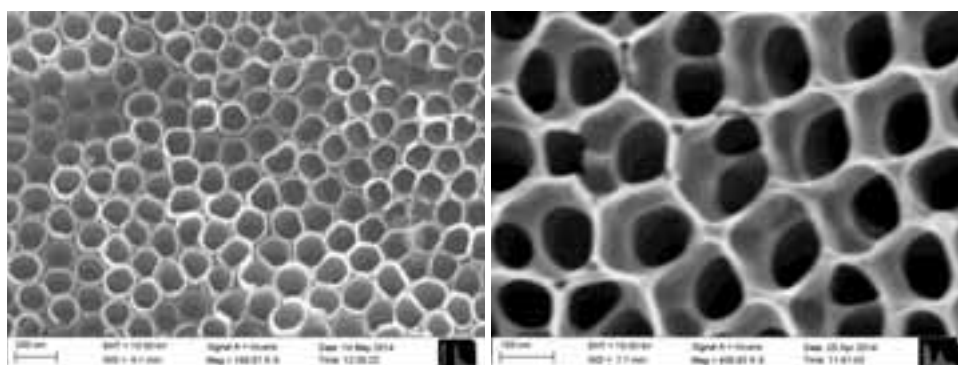


Fig. 8 SEM images of nanotubes anodized using different electrolyte mixing conditions. (a) Sample R21 from Optimized process in first step anodisation method (C) (b) SEM images of sample 14 after second step anodization using method (A).

When the optimized electrolyte preparation procedure (C) is applied to prepare electrolyte for growing TNTs in a second step anodization, a more crystalline well developed anatase phase is obtained (Figure) 7 c. The particle size of ammonium fluoride is reduced in every step of magnetic stirring exposing large area for the electrolyte to oxidize of the Ti plate during anodization. This leads to faster formation of the complex

$[TiF_6]^{2-}$ from which TiO_2 is formed. It also ensures that the concentration of ammonium fluoride participating in the reaction is as expected since all the fluoride particles take place in the chemical reaction due to reduced size. The crystallinity of the sample is dependent on the electrolyte preparation procedures. The presence of unreacted particles in the formation of any material in our case TiO_2 film will be an impurity and introduce defect sites on TiO_2 film reducing crystallinity.

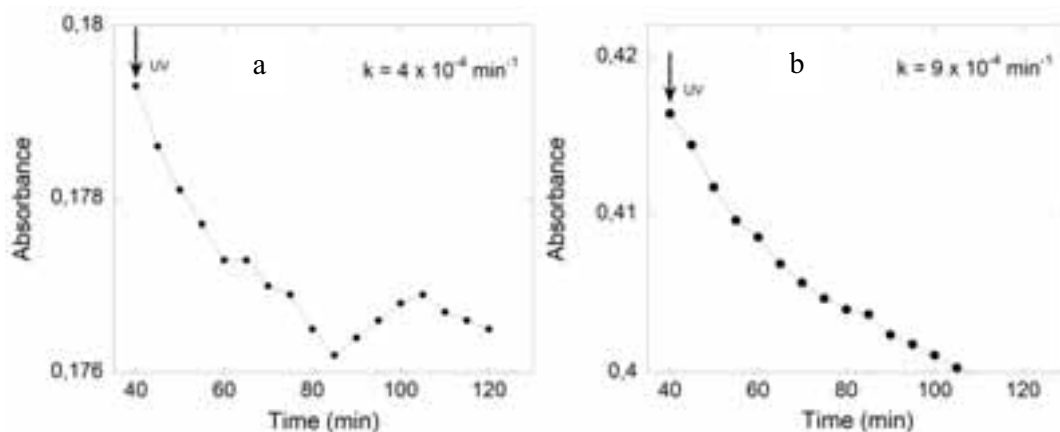


Fig. 9: Photocatalytic degradation of methylene blue (1 ppm) in deionized water by TiO_2 nanotube samples (a) prepared according to the 1-step method C, and (b) two-step method A, respectively. Illuminations was done with a 370 nm BLB lamp with lamp power of about 0.4 m W cm^{-2} at the position of the sample surface. The pseudo-first order rate constants are shown as insets in the figures.

Figure 8 a shows top-view SEM images of Sample R 21 of TNTs obtained from optimized one-step anodization process described in section 3.1, while Figure 8 b show SEM image from a two-step anodization process. A well-ordered uniform nanotubular structure is obtained after the second step of anodisation. We attribute the improved nanotube properties to template assisted nucleation on top of the nanotube structures formed after the first anodization step. During a one-step anodization on a Ti foil, nucleation and nanotube growth takes place at random sites. By introducing a template through a first anodization step, a pre-defined pattern for nanotube nucleation is made. Nanotubes grow on already ordered imprints and retain the order as they grow. The intermittent cleaning and electrolyte exchange removes impurities and improves the quality of subsequent nanotube growth.

Finally, the photocatalytic activity of the porous TNT structures was determined by measuring the decomposition of MB. The photocatalytic degradation rates for one sample from the 1-step and one from the 2-step anodization procedure were measured and determined to be $k = 4 \times 10^{-4} \text{ min}^{-1}$ and $k = 9 \times 10^{-4} \text{ min}^{-1}$, respectively, from a pseudo-first order kinetic analysis (Figure. 9). The rate constant for the (non-optimized electrolyte) TNTs from second step anodisation was found to be more than twice as large compared to the one from the 1-step anodization procedures, confirming the microscopy results that the 2-step process yields higher quality TNTs.

4. Conclusion

The preparation procedures of highly ordered and self-organized titanium dioxide nanotubes for photocatalytic application have been presented. Optimized growth conditions including electrolyte preparation, water content, ammonium fluoride concentration and second step anodization have been explored. Water content and ammonium fluoride concentrations are known to influence the order and self-organization through high chemical dissolution and fast etching rates. Here we show that although NH_4F is an essential component in the formation of TiO_2 by oxidation of Ti plate and formation of $[TiF_6]^{2-}$ complex. Increasing ammonium fluoride beyond 0.2 M in this work causes thinning of nanotube walls, and introduces disorder in the nanotube structure. Increasing the water content increases the rate of chemical dissolution causing ripples on the nanotubes. Beyond 10 vol% a sponge-like structure is obtained. An optimized

electrolyte preparation procedure where NH_4F is first dissolved in water followed by magnetic stirring to fully dissolve the NH_4F particles and subsequent transferring the NH_4F solution in ethylene glycol ensures that all participating species in the electrolyte are intimately mixed forming a homogeneous solution. Magnetic stirring in both stages of electrolyte mixing reduces the particle size; which is an important parameter in determining how fast the reaction will proceed. Furthermore, ensuring all particles are intimately mixed improves the crystallinity by reducing impurities and defects on the TiO_2 nanotube structure as nanotubes grow. A second step of anodization improves the order and self-organization of the nanotubes, and hence the photocatalytic activity. Growing nanotubes employing a second step anodization and using the optimized electrolyte preparation procedure is expected to further enhance the photocatalytic activity. We propose that the two-step anodization method, followed by use of optimized electrolyte procedure, a water content of 3 vol% and ammonium fluoride of between 0.1 M and 0.2 M can be used to fabricate well-ordered TiO_2 nanotubes which are photocatalytic active.

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