

DEVELOPMENT OF TiO₂ NANOTUBES VIA ANODIZATION FOR DEGRADATION OF METHYL ORANGE

Khairul Arifah Saharudin* and Srimala Sreekantan

*School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia
Engineering Campus, 14300 Nibong Tebal, Seberang Perai Selatan,
Pulau Pinang, Malaysia*

Corresponding Author: amui86@yahoo.com

ABSTRACT

TiO₂ nanotubes were prepared by anodization of titanium foil (Ti) in an electrochemical bath consisting fluorinated ethylene glycol/glycerol organic solvents. The pH of the bath was kept constant at pH 7 and the anodization time was varied (1, 15, 20, 30 and 60 min) to study the formation of well ordered TiO₂ nanotubes. The crystal structure was studied by X-Ray Diffraction (XRD) analysis, and the morphology was observed via Field Emission Scanning Electron Microscopy (FESEM). The average tube diameter and tube length was found to be increase with increasing anodization time. Crystallization of the nanotubes to anatase phase occurred at 300 °C while rutile formation occurred at 600 °C. Sintering of the nanotube arrays was observed at 700 °C. Photocatalytic activity of the nanotubes produced in different annealing temperature was also evaluated by the degradation of methyl orange. The detail of the observation is discussed thoroughly in this paper.

Keywords: TiO₂; nanotubes; anodization time;

INTRODUCTION

Environmental contamination which has grown globally has become a serious problem that cannot be neglected. Various types of contaminant that cause global warming including SO_x and NO_x. Apart from global warming, problem with dirty water has also been addressed. Contaminants in water must be removed in order to provide clean water source for human consumption. An advance oxidation process is seemed to be the best ways to performed environmental clean up [1]. This process can be performed by photocatalysis.

Photocatalytic oxidation (or photocatalysis) over UV-illuminated semiconductors constitutes a very promising technique for the destruction of organic and inorganic contaminants. Unlike filtration, which merely transfers contaminants to a different phase and requires the replacement and disposal of depleted treatment units, photocatalytic treatment systems are “self-generating” [2,8]. Photocatalytic processes chemically oxidize (or convert) organic compounds into carbon dioxide and water. Complete oxidation refers to a reaction in which all of the carbon in the target

compound is converted to carbon dioxide. Since the photocatalytic material is not consumed during the oxidation process, photocatalysis is applicable to long-term situations where the supply of consumable materials becomes a major concern [2].

It has been well accepted that TiO₂ nanotubes poses excellent performance due to their one-dimensional (1D) nature which offers high surface area towards photocatalytic reaction. Therefore, number of fabrication methods such as electrochemical lithography [4], photoelectrochemical etching [6], sol-gel processing [3,7], hydrothermal synthesis [25] and template synthesis [9,10] have been used to form nanometer-sized TiO₂ tubules, wires, dots and pillars. Among these processes, electrochemical anodization of titanium in fluorinated electrolytes is a relatively simple method to synthesize porous or tubular structures.

Anodization in an organic solvent or a mixture of organic solvent result in long and very smooth tubes form without any ridges. Poulose et.al, 2009 have introduce the use of ethylene glycol (EG), formamide (FA), dimethyl sulfoxide (DMSO), dimethylformamide (DMF) to form tubes with lengthy range from 10 μm to 1000 μm . Thus in this work, we have reported on the formation of nanotubes in glycerol/ ethylene glycol based electrolyte using conventional mixing in neutral condition which is believed to be viable and competent for robust industrial application.

EXPERIMENTAL PROCEDURE

Ti foils (0.127mm thickness, 99.6% purity, STREM Chemicals) were degreased by sonicating in ethanol for 15 minutes, rinsed with deionized water (DI) and dried in oven. The samples were anodized in glycerol electrolyte containing 6.0 wt% ethylene glycol and 0.7 wt.% NH₄F by using a conventional electrode configuration with platinum as counter electrode and Ti as working electrode. The anodization voltage was kept constant at 30 V and the anodization time was varied to 1, 15, 20, 30 and 60 min. After the experiments the samples were sonicating in acetone for 1 min, rinsed with DI water, dried in oven and subsequently annealed at 400°C in argon for 2 hours.

The second set of the experiment involved Ti foils anodized at 30 V, 60 min for further investigation. The effect of annealing temperature on the surface and crystal structure of TiO₂ nanotube was examined. The annealing temperature varied from 200°C to 700°C for 2 hours in argon.

A scanning electron microscope FESEM SUPRA 35VP ZEISS operating at working distance of 5mm with an accelerating voltage of 5 kV was employed for the structural and morphological characterization of the TiO₂ nanotubes. The cross-section images were taken from the cracked layers after bending the samples. By dividing using $\cos 45^\circ$, the tubes' length was estimated. The crystal phases of the TiO₂ nanotubes were studied by X-ray diffraction using the Philip model PW 1729 which was operated at 40 kV and 40 mA. The sample is placed at the center of the diffraction chamber and exposed to Cu K α_1 radiation ($\lambda=1.5404 \text{ \AA}$) in reflection mode and reflections were

recorded by a detector. The reflection of the X-ray is observed at different angles with respect to the primary beam. The relationship between the wavelength of X-ray beam λ , the angle of the diffraction, 2θ , and the distance between each set of atomic planes of the crystal lattice, d , is given by Braggs Law: $n\lambda = 2d \sin \theta$. In this research work, the step scan mode with the step size of 0.1° in the range of $20-70^\circ$ was used. The step time was 3 s, which capable of obtaining a good signal-to-noise ratio in the main reflections of the TiO_2 nanotube, (101) anatase ($2\theta=25.3^\circ$), and (110) rutile ($2\theta=27.4^\circ$). The weight fractions of the anatase and rutile phases of the nanotube are subjected to various heat treatments estimated from the relative intensities of the strongest peaks corresponding to anatase and rutile respective integrated XRD peak intensities using Equation:

$$X_A = (1 + 1.26 I_R / I_A)^{-1}$$

where X_A is the weight fraction of anatase in powder, and I_A and I_R are the X-ray integrated intensities if the (101) reflection of anatase and (110) rutile, respectively.

Photocatalytic activity of TiO_2 nanotubes were studied by degradation of Methyl Orange (MO) solution. The parameters involved in this part are investigated. After the degradation test, the treated MO solution is then characterized by using UV-Vis spectrophotometer.

A cylindrical glass reactor (35 cm length and 2 cm diameter) together with the tube holder (45 cm length and a stopper) was fabricated by using quartz tube. TiO_2 foil with dimension of 2 cm x 1 cm (2 samples) are attached on the holder and inserted in the quartz tube and fixed into the center of the reactor. To start the experiment, 35 ml MO solution (30 ppm) is poured into the quartz tube. The MO solution together with TiO_2 nanotubes were irradiated by the UV light (germicidal 36 watt) with total duration of 5 hours where each hour the degraded solution is collected into glass bottle and the new MO solution is poured again into the quartz tube. The determination of the MO concentration after degradation is determined by using a UV-Vis spectrophotometer PerkinElmer Lambda 35.

RESULTS AND DISCUSSION

Surface Morphology of the anodized TiO_2 nanotube arrays

The variations of surface morphology of TiO_2 nanotubes during the anodization process are exhibited in Figure 1 to Figure 5 and the diameter and length of TiO_2 nanotubes anodized under different anodization times are shown in Table 1. In the early stage of anodization (Figure 1), compact oxide layer was observed. However, the formations of randomly distributed pits are seen at high magnification (Figure 1(insets)). After 15 minutes of anodization, pore formation was initiated (Figure 2). In the case of the sample anodized for 20 minutes, the formation of nanotubes was observed but the structure was less uniform. Porous oxide structure can be seen underneath the oxide layer (Figure 3 (a) and 3 (b)).

At 30 minutes, a breakdown of the compact TiO_2 layer occurred on the surface, after which a porous TiO_2 layer gradually grows and the TiO_2 nanotubes with average length of 645 nm was obtained (Figure 4). This stage exhibited a fast increase of growth rate 21nm/min and regular nanotubular morphology was obtained. For 60 minutes, the morphology becomes stable and gradually grows up to 1.1 μm with average diameter 85 nm (Figure 5).

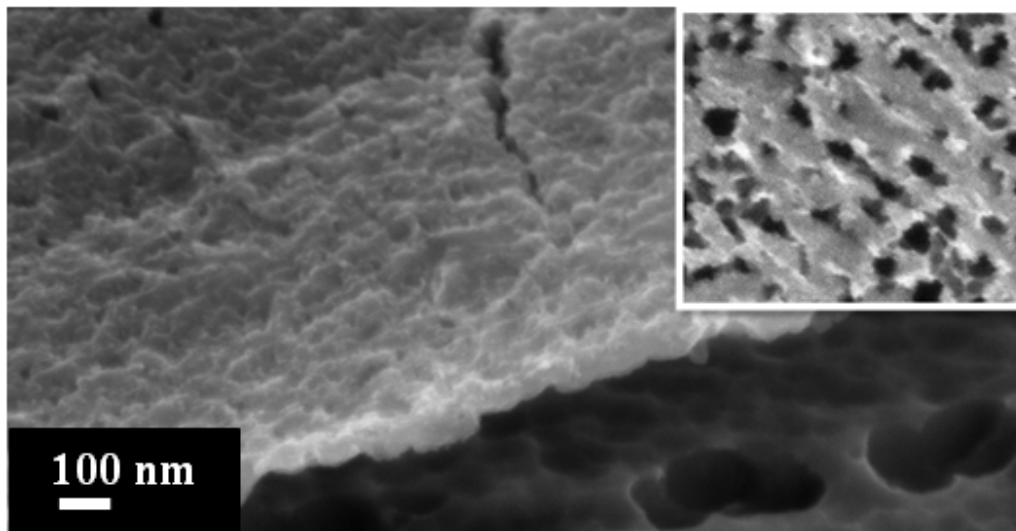


Figure 1: FESEM images of TiO_2 nanotube anodized for 1 minute. The inset shows randomly pits distributed

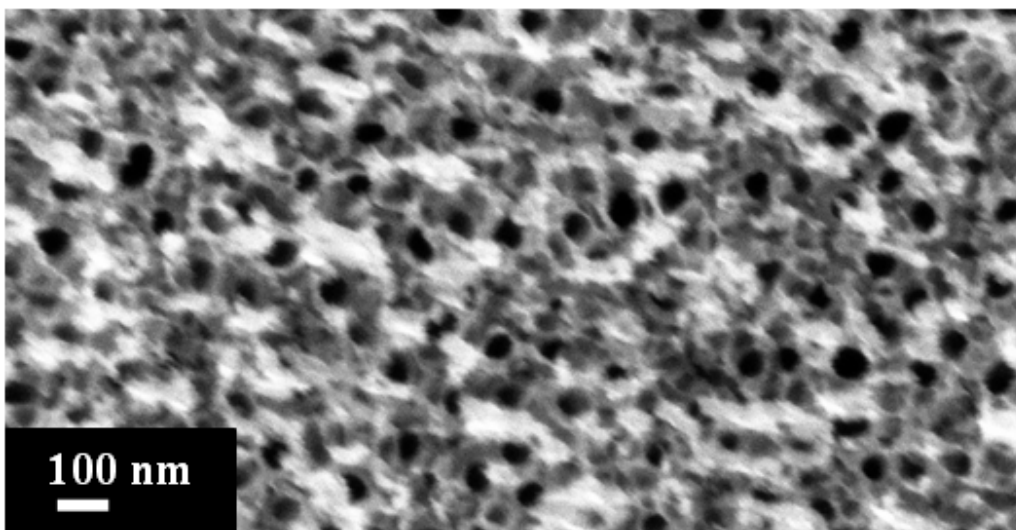


Figure 2: FESEM image of TiO_2 nanotube anodized for 15 minutes

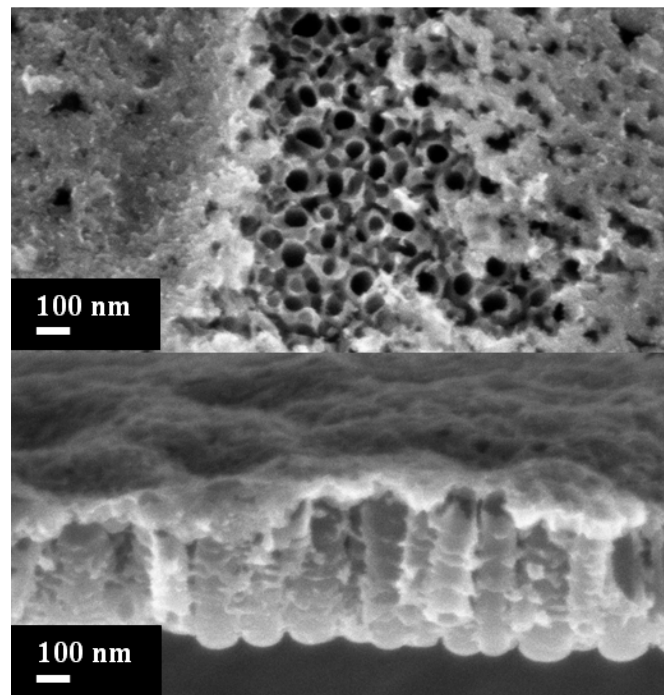


Figure 3: FESEM images of TiO_2 nanotubes anodized for 20 minutes. a) top view
b) cross sectional view

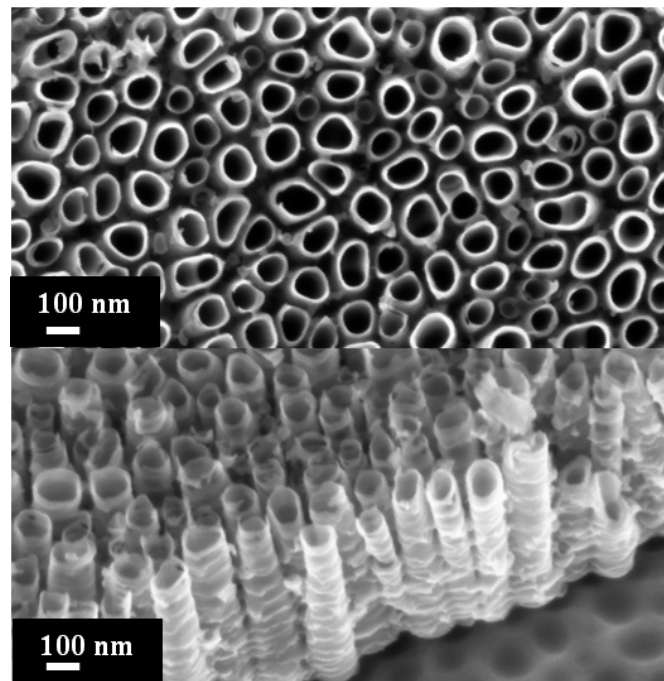


Figure 4: FESEM images of TiO_2 nanotubes anodized for 30 minutes. a) top view
b) cross sectional view

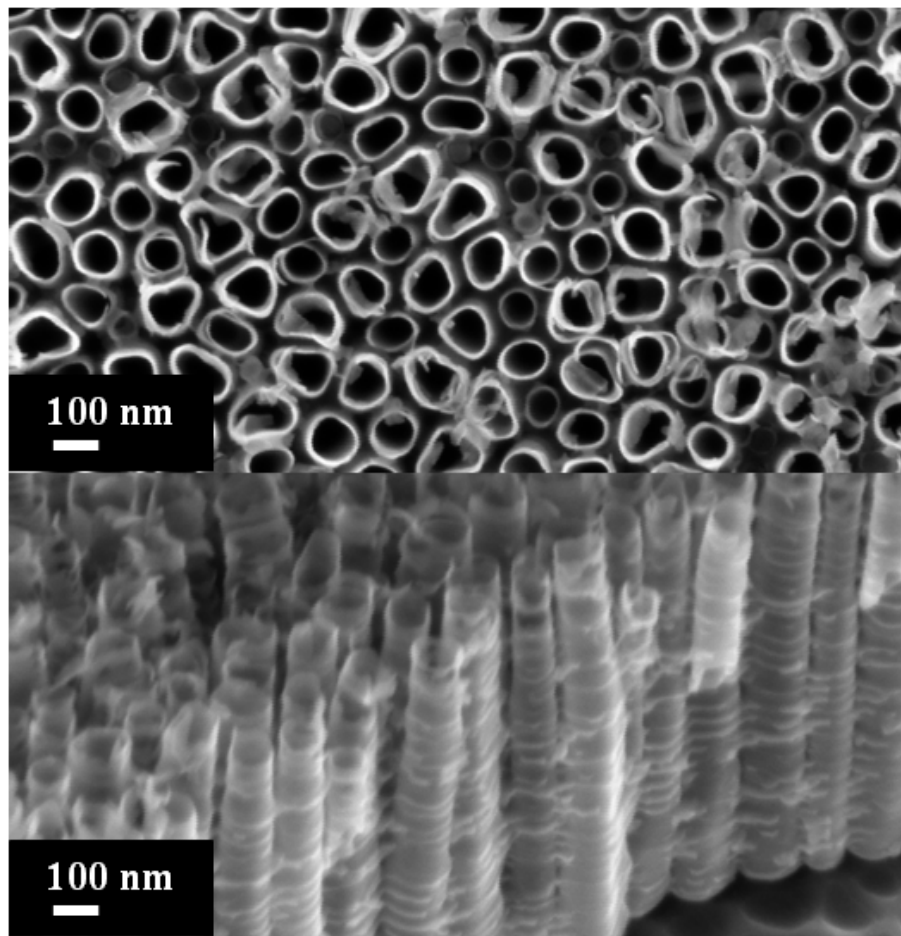


Figure 5: FESEM images of TiO_2 nanotubes anodized for 60 minutes. a) top view
b) cross sectional view

Table 1: Diameter and Length of TiO_2 nanotubes in different anodization time

Time (minutes)	Microstructure	Diameter (nm)	Length (nm)	Aspect Ratio
1	Compact oxide	-	-	-
15	Compact oxide with pits	-	-	-
20	Nanotubes underneath oxide layer	65	561	8.63
30	Nanotubes	85	645	7.59
60	Nanotubes	85	1100	12.94

XRD analysis of the anodized TiO₂ nanotube arrays

The corresponding XRD pattern of the Ti anodized in at different anodization time is shown in Figure 6. The plot shows the Bragg reflections at 2 theta values of 24.96°, 35.54°, 38.54°, 40.25°, 46.11°, 53.33° and 63.22° corresponding to the (101), (100), (002), (101), (102), and (110). Hence, this indicates that the nanotubes anodized at different anodization time and annealed at 400 °C have crystalline structure with Ti peaks.

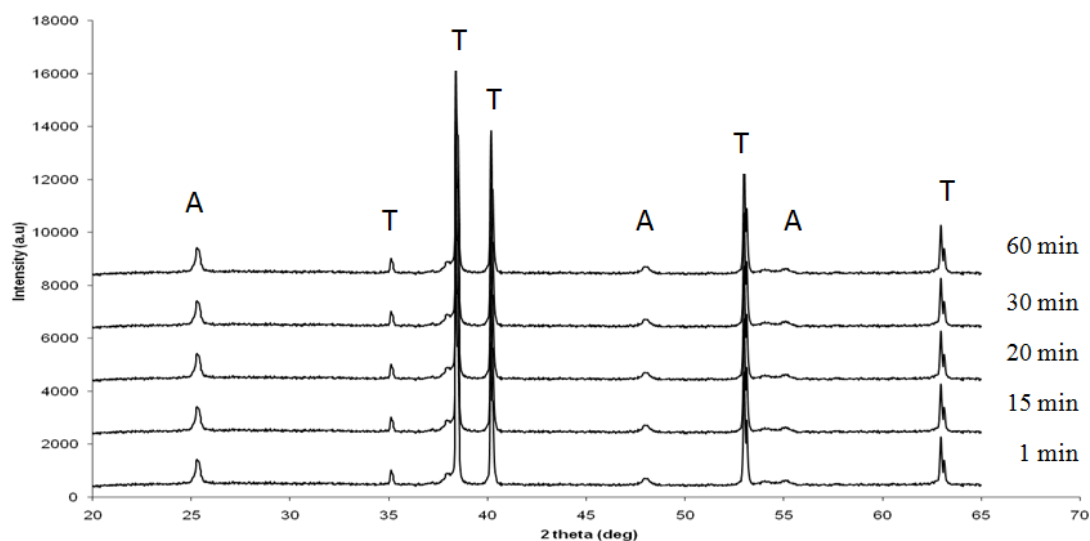


Figure 6: XRD pattern of as anodized TiO₂ nanotubes. A: anatase, T: titanium

Surface morphology of the annealed TiO₂ nanotube arrays

Ti foil anodized at 30 V for 60 minutes was selected and annealed from 200 °C to 700 °C. Figure 7 to Figure 12 shows the FESEM images of the anodized foil annealed at different temperature. The morphology of the sample is significantly altered by the annealing process. The low annealing temperature (200 °C to 500 °C) ensured that the nanotube structure will not be destroyed (Figure 7 - 10). At 600 °C the tubes start to sintegrate at the bottom (Figure 11) and at 700 °C (Figure 12) the sintegration become more prominent whereby the tube structure start to collapse to form porous structure. The change in morphology with annealing temperature is perhaps associated with the excessive diffusion of Ti ion along with the nanotube walls, which induced oxidation and thus thickened the oxide walls.

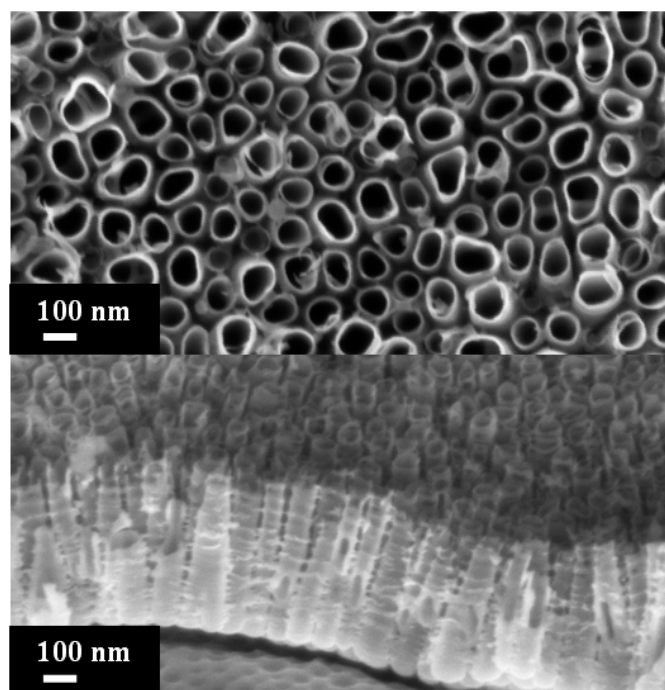


Figure 7: FESEM images of TiO₂ nanotubes annealed at 200°C. a) top view b) cross sectional view

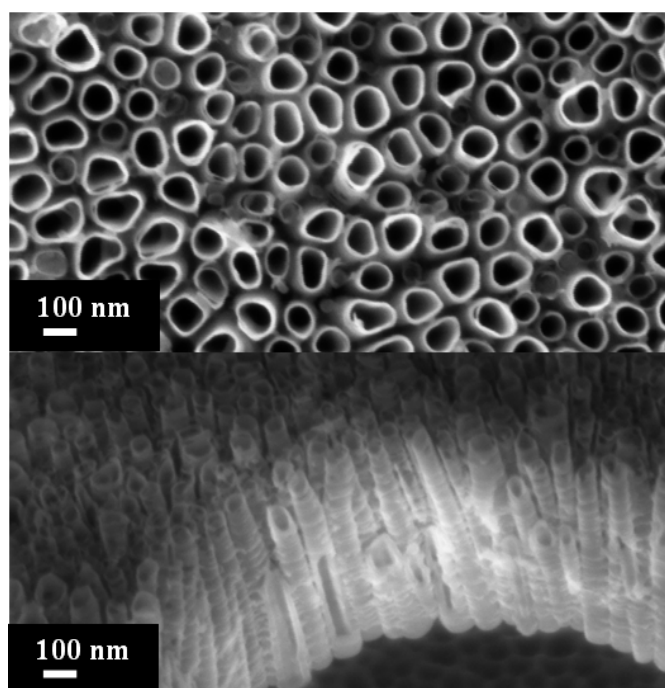


Figure 8: FESEM images of TiO₂ nanotubes annealed at 300°C. a) top view b) cross sectional view

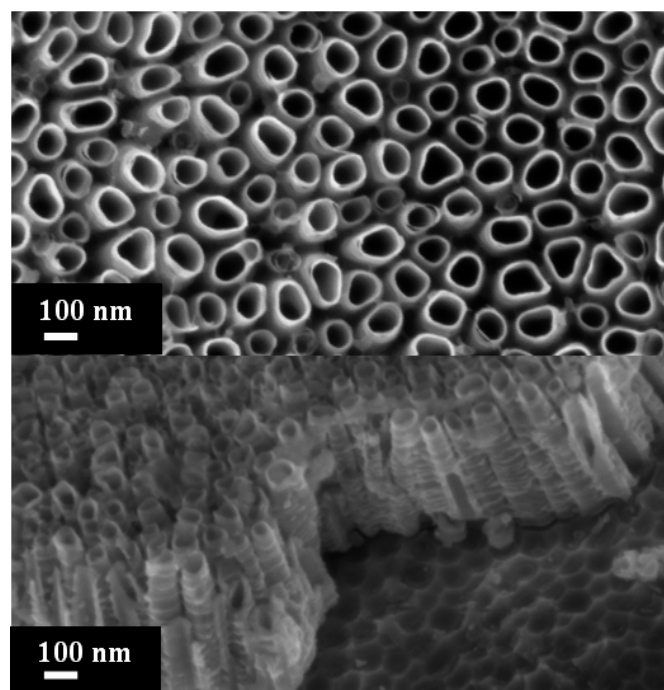


Figure 9: FESEM images of TiO₂ nanotubes annealed at 400°C. a) top view b) cross sectional view

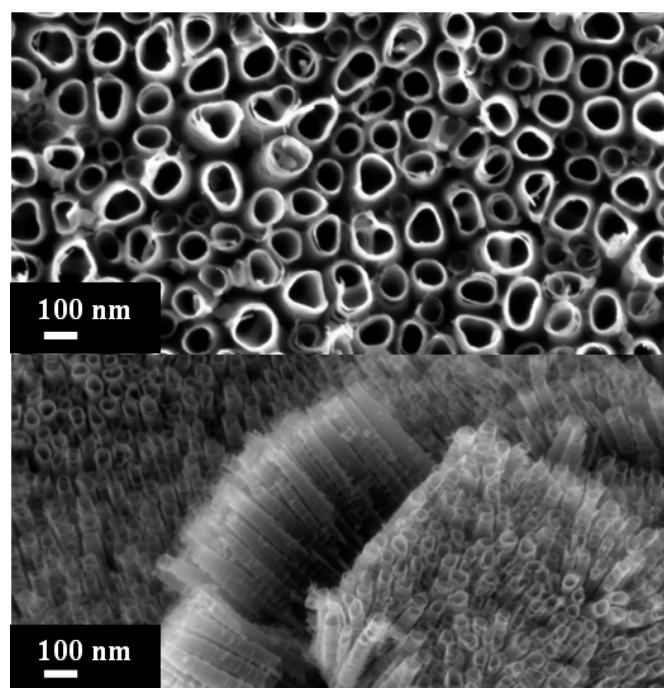


Figure 10: FESEM images of TiO₂ nanotubes annealed at 500°C. a) top view b) cross sectional view

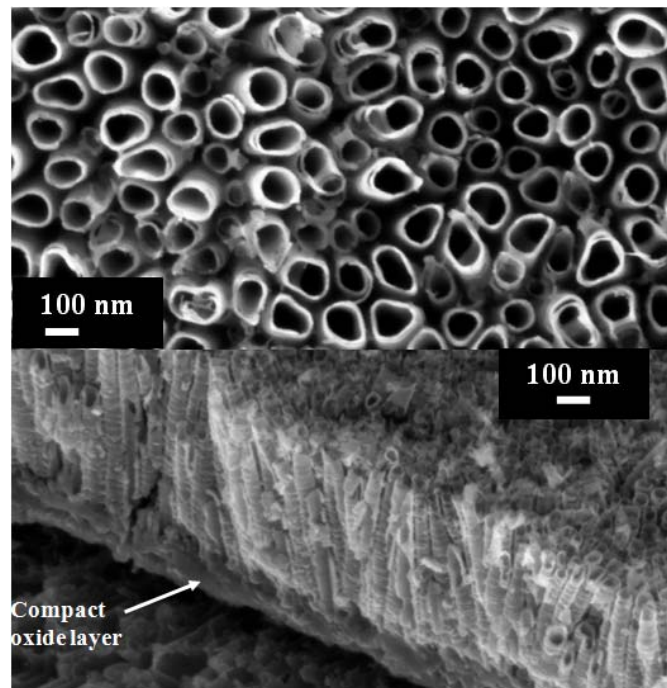


Figure 11: FESEM images of TiO₂ nanotubes annealed at 600°C. a) top view b) cross sectional view

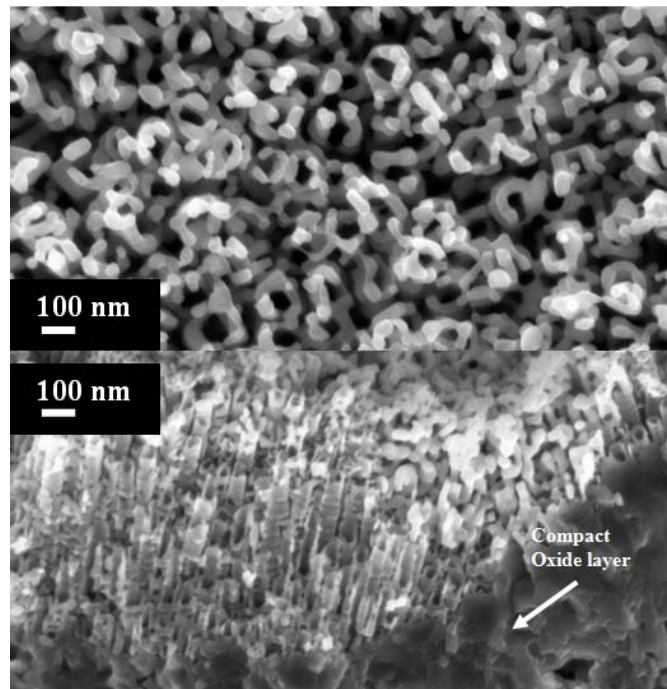


Figure 12: FESEM images of TiO₂ nanotubes annealed at 700°C. a) top view b) cross sectional view

XRD analysis of the annealed TiO₂ nanotube arrays

Figure 13 shows the XRD pattern of the TiO₂ nanotubes arrays annealed at different temperatures. The result clearly shows the crystal structure of TiO₂ depends on the annealing treatment. The XRD of the sample annealed at 200°C indicates the nanotubes have amorphous structure as only Ti peaks were observed. Increasing the temperature to 300°C until 500°C has promoted the crystallization of 100 % anatase phase (101). At 600°C, rutile peak (110) at 27.8° starts to exist. The weight fraction of anatase and rutile was 40 % and 60 % respectively. By increasing the temperature to 700°C, the rutile peak with higher intensity is obtained, indicating the presence of rutile with a high degree of crystallinity. The weight fraction of anatase and rutile was 9 % and 91 % respectively.

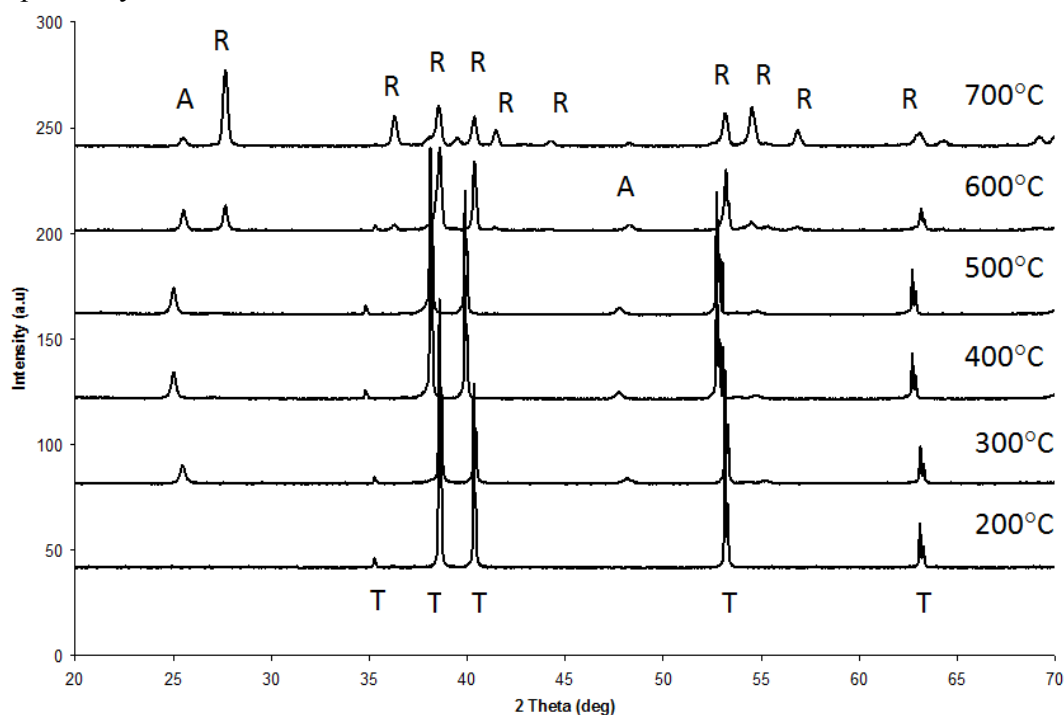


Figure 13: XRD pattern of annealed TiO₂ nanotubes. A: anatase, R: rutile, T: titanium

Photocatalytic activity of the TiO₂ nanotube arrays

Photocatalytic activity of TiO₂ nanotubes was evaluated by photodegradation of Methyl Orange (MO) solution after UV irradiation for 5 hours. In order to evaluate the effect of TiO₂ nanotubes surface structure on its photocatalytic activity, the degradation of methyl orange in presence of Ti foil anodized at 30V and subsequently annealed at different temperatures was carried out and the result is shown in Figure 14. It can be seen that TiO₂ nanotubes annealed at 200 °C and 300 °C showed very poor degradation in which the concentration of MO decreased by 50 %, presumably because of the low degree of crystallinity. On the other hand, the high activity (97 % degradation of mo) shown by TiO₂ nanotubes annealed at 500 °C could be due to the formation of the

anatase phase with enhanced crystallinity and the surface structure as explained previously. TiO₂ nanotubes annealed at 400 °C and 600 °C demonstrates 70 % and 56 % degradation of mo respectively. The decrease in photocatalytic activity of the sample annealed at 600 °C as compared to 400 °C could be explained by the decrease in surface area of the porous structure and the loss of the anatase phase at 600 °C. A similar reason is believed to contribute the low photocatalytic behavior of TiO₂ nanotubes annealed at 700 °C, which possesses a grain structure with 91 % rutile phase.

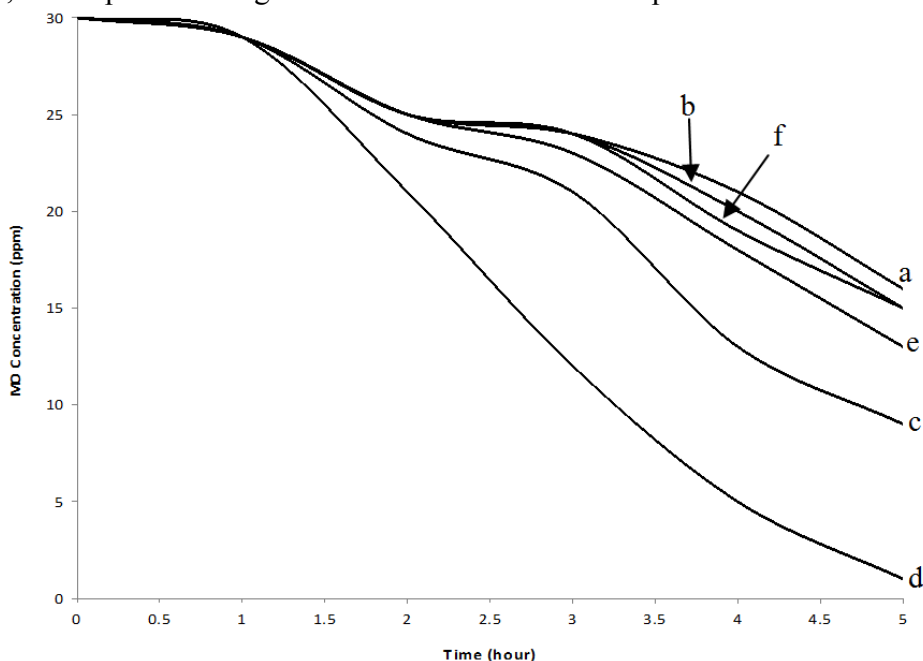


Figure 14: Plots of mo concentration versus time for a) 200 °C, b) 300 °C, c) 400 °C d) 500 °C, e) 600 °C, f) 700 °C

CONCLUSION

TiO₂ nanotubes with different surface structure were prepared in ethylene glycol/glycerol at 1, 15, 20, 30 and 60 minutes. Based on this study, it can be concluded that the length of the nanotubes is increasing with time while the photodegradation of mo show that the crystal structure and the degree of crystallinity the also key factor affecting the photocatalytic activity. TiO₂ nanotubes anodized for 60 minutes and annealed at 500 °C exhibited high photocatalytic activity for the degradation of mo and it is attributed to the dominant anatase phase with high degree of crystallinity. Annealing at 600 °C and above induces thickening of the nanotubes wall and higher proportion of rutile phase and thus decline the photodegradation of mo.

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