

## Enhanced Visible Light Response of Phosphorus Incorporated TiO<sub>2</sub> Nanotube Arrays Photocatalyst

Khairul Arifah SAHARUDIN<sup>1,a\*</sup> and Srimala SREEKANTAN<sup>1,b</sup>

<sup>1</sup>School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Pulau Pinang, Malaysia.

<sup>a</sup>khairularifah@usm.my, <sup>b</sup>srimala@usm.my

**ABSTRACT.** Titanium dioxide (TiO<sub>2</sub>) nanotubes incorporated with phosphorus (P) were synthesized via anodization of Ti in the electrolyte containing H<sub>3</sub>PO<sub>4</sub> and ethylene glycol (EG) with 0.66 wt.% NH<sub>4</sub>F. The morphology of the TiO<sub>2</sub> nanotubes can be tuned by changing the H<sub>3</sub>PO<sub>4</sub> and EG contents. The TiO<sub>2</sub> nanotubes with 3.1 μm length and approximately 103 nm average diameter were as-anodized in 90 EG:10 H<sub>3</sub>PO<sub>4</sub> at 30 V for 1 hour. The length and average diameter of the nanotubes increased with increasing voltage and water amount. The length of the nanotubes was 5.3 μm and the average diameter was 128 nm under optimized conditions (90 EG:10 H<sub>3</sub>PO<sub>4</sub>:1 H<sub>2</sub>O at 60 V for 1 h). The as-anodized TiO<sub>2</sub> nanotubes were annealed under different atmospheres (argon and nitrogen) at 400 °C. XRD analysis revealed that the TiO<sub>2</sub> nanotubes were anatase. When the TiO<sub>2</sub> nanotubes were annealed in argon or nitrogen, a high photoluminescence (PL) intensity at 2.4 eV was observed in response to the 325nm light excitation. The high PL intensity is due to the increase in the number of defects upon reduction. According to photocatalytic degradation of methyl orange, the P doped TiO<sub>2</sub> nanotubes exhibited enhanced photocatalytic activity compared with carbon doped TiO<sub>2</sub> nanotubes, which might be a result of the P-incorporated induced band gap narrowing.

**Keywords:** TiO<sub>2</sub> Nanotubes, Anodization, Phosphorus doped, Dye Degradation;

*Received:* 15.10.2017, *Revised:* 15.12.2017, *Accepted:* 30.02.2018, and *Online:* 20.03.2018;

**DOI:** 10.30967/ijcrset.1.S1.2018.95-100

*Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.*

### 1. INTRODUCTION

Photocatalysis is not only an important industrial process in wastewater treatment but also in heavy metal remediation, sterilization and others. Recent work on titanium dioxide (TiO<sub>2</sub>) has showed that it is widely used as photocatalyst for its efficiency, low cost and high stability [1]. However, it is activated only under UV light irradiation because of its large band gap (3.2 eV for anatase). As only 3% of the solar spectrum has wavelength shorter than 400 nm, it is very important to develop efficient visible light sensitive photocatalyst by the modification of TiO<sub>2</sub>.

Recently, researchers [2,3] found that modification of TiO<sub>2</sub> by phosphorus seems to be a promising approach to enhance the photocatalytic activity. P-doped TiO<sub>2</sub> prepared by sol-gel method with NaH<sub>2</sub>PO as precursor showed an improved optical absorption in the visible light range [4]. Lv et al. [5] reported that P-doped TiO<sub>2</sub> showed higher photocatalytic degradation of RhB under solar light and UV light irradiation than pure TiO<sub>2</sub>.

In this work, P incorporated TiO<sub>2</sub> NT prepared by anodization in ethylene glycol and phosphoric acid was demonstrated. The morphology, crystal structure and electronic structure of the samples formed at different applied voltage were characterized. In addition, the effect of annealing atmosphere on the chemical

composition was also studied. The effects of the surface properties on the photocatalytic activity were done by degradation of methyl orange (MO).

## 2. MATERIALS AND METHODS

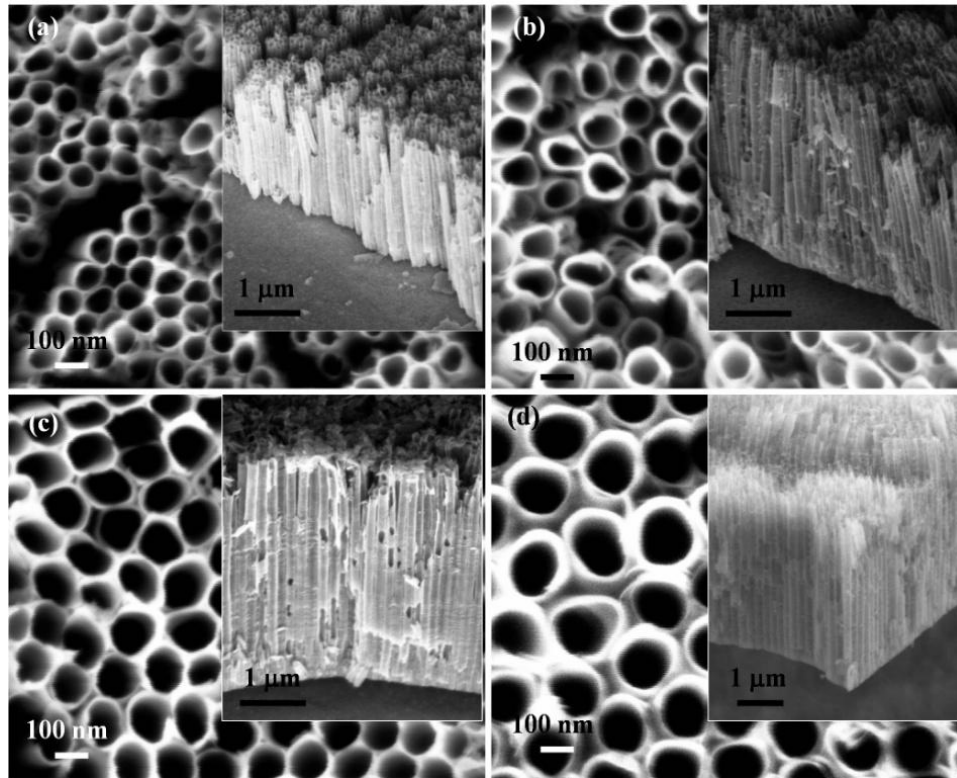
A 1 x 5 cm<sup>2</sup> (Strem Chemicals, 0.27 mm thick) Ti foils were ultrasonically cleaned in acetone for 15 minutes followed by rinsed with deionized (DI) water and then air dried. Highly oriented P-TiO<sub>2</sub> NT arrays were fabricated by anodization in ethylene glycol (EG) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) mixture electrolyte with 0.66 wt.% ammonium fluoride (NH<sub>4</sub>F) using a Keithley Series 2611A potentiostat (60 V) and a conventional two-electrode configuration with platinum as cathode and Ti foil as anode. The anodization process was done for 1 hour. Afterward, the samples were cleaned in ultrasonic bath of acetone for 1 min, followed by rinsed with DI water and dried in a nitrogen stream. The obtained highly ordered CP-TiO<sub>2</sub> NT were annealed in an argon atmosphere at 400 °C for 4 hours with heating and cooling rate of 5 °C min<sup>-1</sup>. The morphology of the CP-TiO<sub>2</sub> NT arrays was characterized using field emission scanning electron microscope (FESEM-EDX, Zeiss, Supra 35VP). X-ray diffraction (XRD, Phillip model PW 1729) were carried out to study the crystal structure of P-TiO<sub>2</sub> NT, while photoluminescence (PL, JovinBr). The photodegradation activities of CP-TiO<sub>2</sub> NT were evaluated by the degradation of methyl orange (MO). The initial concentration of MO was 30 ppm. The experiment was performed under sunlight for 5 hours. The concentration of MO was monitored by measuring the absorbance of samples at 465 nm using UV-Vis spectrophotometer (Perkin Elmer).

## 3. RESULTS AND DISCUSSION

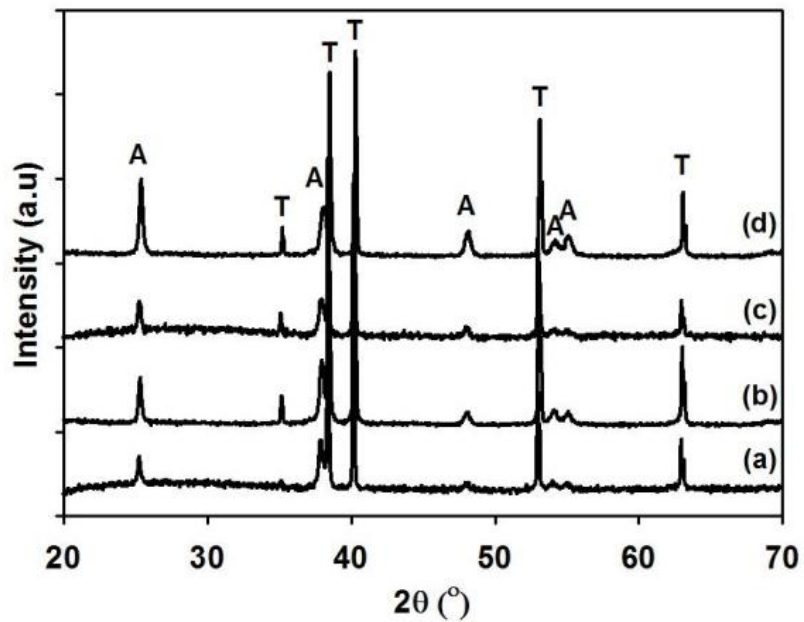
FESEM images in Fig. 1 reveal that Ti anodized at 30V to 60V resulted in a formation of well aligned nanotubes. It is noticeable that the diameter and the length of the nanotubes increase with voltage. At higher anodization voltage, the electric field dissolution at the barrier layer occurs much higher resulting Ti-O bond undergoes polarization and become weakened promoting dissolution of the Ti<sup>4+</sup>. This will lead to greater driving force for ionic transport through the barrier layer at the bottom of the nanotubes favouring formation of [TiF<sub>6</sub>]<sup>2-</sup> complex that will eventually accelerate the pore growth. At the same time, the faster movement of the Ti/TiO<sub>2</sub> interface into the metal [6] resulted in the formation of long nanotubes. Based on the results, sample anodized at 60 V is selected for further investigation due to its higher length and larger diameter which are approximately ~5.3 μm and ~128 nm, respectively. The EDX result of the Ti anodized at 60 V shows that carbon and phosphorus content in the TiO<sub>2</sub> nanotubes are 10.92 At.% and 0.40 At.% respectively.

The XRD pattern of the CP-TiO<sub>2</sub> NT arrays anodized at different voltages are shown in Fig.2. The peaks for samples made in different voltages match well with anatase phase (PDF, No. 96-900-8214). However, the intensity of the anatase peak was different for sample anodized at different voltages. The intensity of anatase peak increases with increasing voltages. Such phenomenon could be related to the formation of more weakly crystalline CP-TiO<sub>2</sub> NT formed by anodic oxidation with increasing voltage. According to Habazaki et al [7], the formation of crystalline TiO<sub>2</sub> is possible when the formation is carried out at a certain threshold voltage where the amorphous to crystalline transformation is made possible. The said work referred 20 V as the voltage which allows this transformation to occur. The formation of the weakly crystalline oxide is believed not uniform throughout the oxide and is localized at certain region in a matrix of amorphous-like oxide. With annealing process, the weakly crystalline nanotubes transform to crystal structure corresponding to better crystallization of nanotube arrays.

The effects of annealing atmospheres were studied by annealing the CP-TiO<sub>2</sub> NT arrays in Ar and N<sub>2</sub>. Both samples were anodized in optimized volume fraction of 90:10 (EG: H<sub>3</sub>PO<sub>4</sub>) with addition of 0.66 wt.% NH<sub>4</sub>F at 60 V for 60 min prior to annealing process. The surface morphology of CP-TiO<sub>2</sub> NT annealed in Ar is shown in Fig.1(d) while CP-TiO<sub>2</sub> NT annealed in N<sub>2</sub> is shown in Fig.3. Annealing in argon atmosphere resulted in a formation of nanotubes with smoother and more uniform tubes whereas the sample annealed in nitrogen atmosphere is more rigid and less uniform. This may be due to the inert properties of argon gas which is less reactive compared to nitrogen gas.

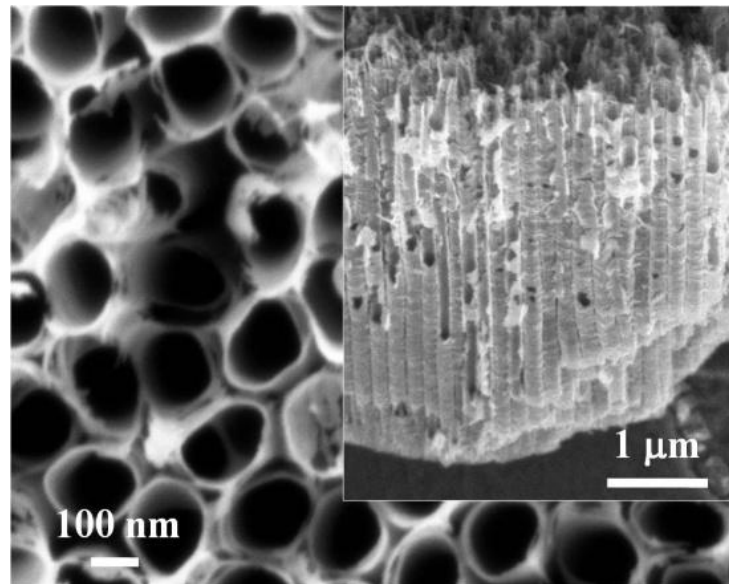


**Fig.1** FESEM images of CP-TiO<sub>2</sub> NT formed in 90:10 (EG:H<sub>3</sub>PO<sub>4</sub>) electrolyte containing 0.66 wt.% NH<sub>4</sub>F for 60 min at (a) 30, (b) 40, (c) 50 and (d) 60 V. The inset shows the cross-section view of respective morphologies. (FESEM images taken after annealing at 400 °C for 4 hours in argon atmosphere)



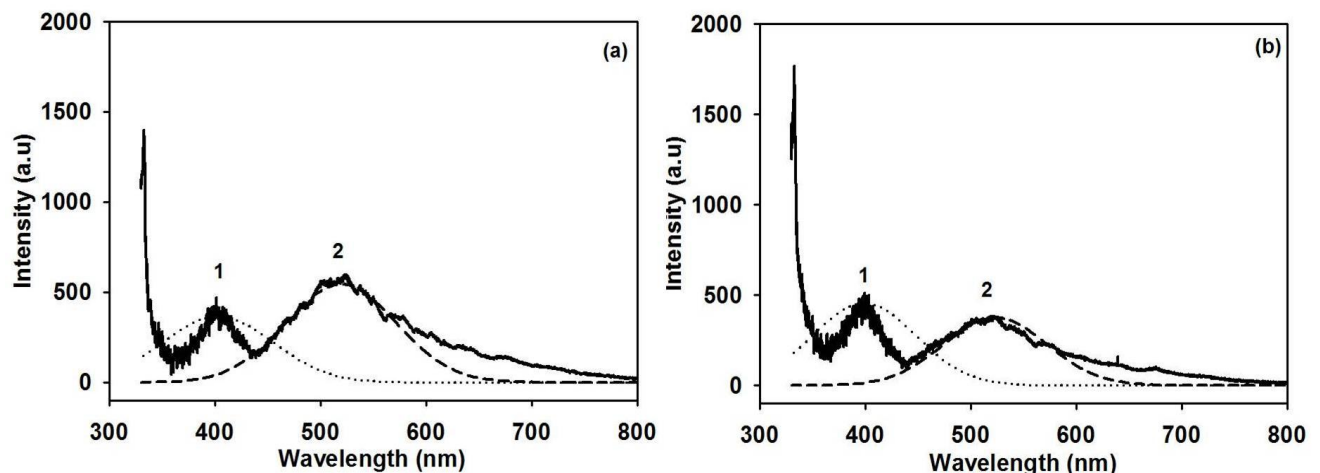
**Fig.2** XRD patterns of CP-TiO<sub>2</sub> NT prepared in 90:10 (EG:H<sub>3</sub>PO<sub>4</sub>) at (a) 30 V, (b) 40 V, (c) 50 and (d) 60 V for 60 min after annealed in argon atmosphere for 4 hours at 400 °C.

However, the dimensions of the tubes annealed in both atmospheres are almost similar; tube length, tube diameter and wall thickness approximately  $\sim 5.3 \mu\text{m}$ ,  $\sim 150 \text{ nm}$  and  $\sim 18 \text{ nm}$  respectively. Besides that, the EDX show that the incorporation of C and P are 10.92 At.% and 0.40 At.% in Ar atmosphere whereas 5.03 At.% and 0.46 At.%, respectively.



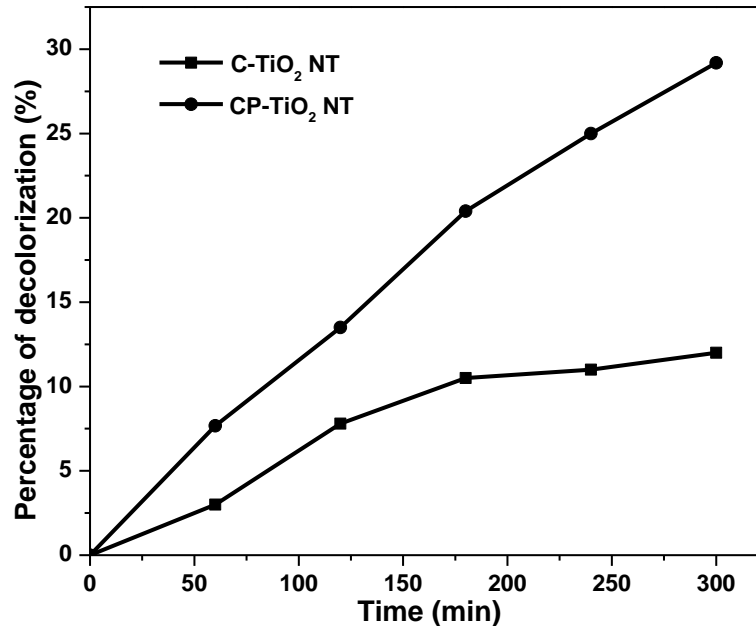
**Fig.3** FESEM images of CP-TiO<sub>2</sub> NT formed in 90:10 (EG: H<sub>3</sub>PO<sub>4</sub>) electrolyte containing 0.66 wt% NH<sub>4</sub>F for 1 hr at 60 V and subsequent annealed at 400 °C for 4 hours in N<sub>2</sub>. The inset shows the cross-section view of respective morphologies

The PL results are shown in Fig.4. The room temperature PL spectra of CP-TiO<sub>2</sub> NT annealed in Ar and N<sub>2</sub> were obtained using the wavelength at the range of 325 nm to 800 nm. Based on Fig.4, the PL signals show there are two peaks at 400 nm and 525 nm appear for both samples. The band gap energy corresponds to peak at 400 nm 3.1 eV and for 525 nm 2.7 eV. This proves that there is an intermediate energy level in the TiO<sub>2</sub> energy band gap. It may be due to oxygen vacancies, defects, C and P dopants present in the TiO<sub>2</sub> NT.



**Fig.4** PL spectra and their Gaussian fit band of CP-TiO<sub>2</sub> NT formed in 90:10 (EG: H<sub>3</sub>PO<sub>4</sub>) electrolyte containing 0.66 wt% NH<sub>4</sub>F for 1 hr at 60 V and subsequent annealed at 400 °C for 1 hours in (a) Ar and (b) N<sub>2</sub> atmosphere (excitation wavelength = 325 nm)

Fig.5 shows the results of MO decolorization by C-TiO<sub>2</sub> NT formed in pure EG and CP- TiO<sub>2</sub> NT formed in EG:H<sub>3</sub>PO<sub>4</sub> (90:10) under visible light irradiation. As seen from Fig.5 C-TiO<sub>2</sub> NT formed in CP-TiO<sub>2</sub> NT formed in EG:H<sub>3</sub>PO<sub>4</sub> (90:10) has high PC activity (29%) as compared to pure EG which has only 12% decolorization rate due to low AR of nanotubes obtained in C-TiO<sub>2</sub> NT.



**Fig.5** Visible light decolorization of MO solution using CP-TiO<sub>2</sub> NT prepared in 90:10 (EG:H<sub>3</sub>PO<sub>4</sub>) electrolyte at 60 V for 60 min and pure EG containing 0.66 wt.% NH<sub>4</sub>F

#### 4. SUMMARY

CP-TiO<sub>2</sub> NT can be successfully formed by anodization process in EG:H<sub>3</sub>PO<sub>4</sub> (90:10) and 0.66 wt.% NH<sub>4</sub>F at 60 V for 60 min with length of 5.4 μm, wall thickness of 32.2 nm and pore diameter of 128.64 nm. The rate of formation was 89.26 nm/min. This allows the effective photocatalytic degradation of MO with degradation rate of 29 % compared to 12% using C-TiO<sub>2</sub> NT.

#### ACKNOWLEDGEMENT

The authors are very much grateful to Universiti Sains Malaysia (USM) for providing the necessary facilities to carry out the research work and funding this work under Research University (RU) grant no. 814281.

#### REFERENCES

- [1] Y. Wang, C. Feng, M. Zhang, J. Yang, Z. Zhang, Enhanced visible light photocatalytic activity of N-doped TiO<sub>2</sub> in relation to single-electron-trapped oxygen vacancy and doped-nitrogen, *Appl. Catal. B-Environ.*, 100 (2010) 84-90.
- [2] R. Zheng, L. Lin, J. Xie, Y. Zhu, Y. Xie, State of doped phosphorus and its influence on the physicochemical and photocatalytic properties of P-doped titania, *J. Phys. Chem. C*, 112 (2008) 15502-15509.
- [3] E. Krasicka-Cydzik, K. Kowalski, A. Kaczmarek, I. Glazowska, K.B. Heltowski, Competition between phosphates and fluorides at anodic formation of titania nanotubes on titanium, *Surf. Interface Anal.*, 42 (2010) 471-474.



- [4] Q. Shi, D. Yang, Z. Jiang, J. Li, Visible-light photocatalytic regeneration of NADH using P-doped TiO<sub>2</sub> nanoparticles, *J. Mol. Catal. B-Enzym.*, 43 (2006) 44-48.
- [5] Y. Lv, L. Yu, X. Zhang, J. Yao, R. Zou, Z. Dai, P-doped TiO<sub>2</sub> nanoparticles film coated on ground glass substrate and the repeated photodegradation of dye under solar light irradiation, *Appl. Surf. Sci.*, 257 (2011) 5715-5719.
- [6] K. Shankar, G.K. Mor, H.E. Prakasam, S. Yoriya, M. Paulose, O.K. Varghese, C.A. Grimes, Highly-ordered TiO<sub>2</sub> nanotube arrays up to 220 μm in length: use in water photoelectrolysis and dye-sensitized solar cells, *Nanotechnology*, 18 (2007) 065707.
- [7] H. Habazaki, M. Uozumi, H. Konno, K. Shimizu, P. Skeldon, G. Thompson, Crystallization of anodic titania on titanium and its alloys, *Corros. Sci.*, 45 (2003) 2063-2073.