# Annealing Induced Crystallinity, Photoelectrochemical Response and Hydrogen Evolution of $TiO_2$ Nanotube Arrays as Photocatalyst in Water Splitting

Min Min Thein[a], Nyein Nyein[b], Nyein Wint Lwin[c], Than Zaw Oo[c] *

[a]*Department of Physics, Monywa University, Monywa, Myanmar*
[b]*Department of Physics, Meiktila University, Meiktila, Myanmar*
[c]*Department of Physics, University of Mandalay, Mandalay, Myanmar*

Received 14 April 2018; Revised 25 April 2018; Accepted 26 April 2018

## Abstract

The titanium dioxide nanotube ($TiO_2$-NT) arrays were developed by electrochemical anodization. Scanning electron microscopy investigation showed that the $TiO_2$-NTs have well-defined morphology with average inner diameter of 100 nm and length 2 μm. The crystallinity of anatase phase $TiO_2$ is more pronounced at higher annealing temperature 500 ºC demonstrated by X-ray diffraction. We investigated the photoelectrochemical response of $TiO_2$-NTs annealed at 300 ºC, 400 ºC and 500 ºC in KOH aqueous solution under light illumination with different wavelengths by linear sweep voltammetry. A significant increase in peak current densities is observed (i) under UV light and (ii) in $TiO_2$-NTs annealed at 500 ºC with highest peak current density of 0.782 mA $cm^{-2}$. Former one is attributed to more energetic UV light activation to wide band gap $TiO_2$ and latter one is ascribed to better crystallinity at higher temperature. In the photocatalytic water splitting experiment using white light illumination, hydrogen evolution rate increases with increasing annealing temperature of $TiO_2$-NTs and is as high as 0.347 mL $min^{-1}$ for $TiO_2$-NTs at 500 ºC. It is noted that the crystallinity of photocatalyst plays a key role in determining the electrochemical current generation and hydrogen evolution in photoelectrochemical water splitting.

*KEYWORDS*: $TiO_2$ nanotubes; crystallinity; water splitting; hydrogen evolution

## Introduction

Titanium dioxide ($TiO_2$) is a promising semiconductor material for photoelectrochemical water splitting because of its favorable band-edge positions, high photocorrosion resistance, superior chemical stability and low-cost [1, 2]. Solar water splitting provides an effective route for sustainable hydrogen generation using photoelectrochemical platform where only inputs are sunlight and water. Semiconductor materials are required as photocatalyst in water splitting and they would be able to support rapid charge transfer at a semiconductor/aqueous interface, exhibit long-term stability, and efficiently harvest a large portion of the solar spectrum [3]. As compared to the semiconducting materials in bulk or thin film form, the nanosized materials would offer much higher surface area for a given volume which enhances the catalytic reactions and increases the interactions with surrounding media. In addition, quantum confinement effects in nanosized materials would influence on the charge transport or band gap energy shifts which can determine the light harvesting capacity of semiconductor material [4]. Among $TiO_2$ nanostructures, $TiO_2$ nanotubes have attracted more attention due to their excellent electronic and photonic properties. The oriented nanotube arrays provide not only a high surface area but also the electron transfer channels along the tube walls. The one-dimensional $TiO_2$ nanotubes can therefore offer good oriented charge-transport properties and can alleviate the intrinsically short carrier diffusion length owing to the intimate connection between the nanostructured $TiO_2$ and electrolyte [5].

Prior reports demonstrated that one-dimensional nanostructured $TiO_2$ photoelectrode such as nanotubes and nanowires enabled the water splitting cells to increase their efficiency which is due to an increase in light harvesting and charge transport [6]. The functional properties of nano-$TiO_2$ can be modulated upon varying particle size,

---

* Corresponding authors; e-mail: thanzawoo06@gmail.com, than0031@e.ntu.edu.sg

surface area, synthesis method and conditions, and crystallinity [7]. While a larger surface area with nano-$TiO_2$ increases the concentration of surface active sites for higher photocatalytic activity, it also increases the number of surface defects (lowering the crystallinity) resulting in charge trapping [8]. High crystallinity of the semiconducting material is one of the key factors determining the charge transport, eventually the photoelectrochemical cell efficiency. It is well documented that the crystallinity of the semiconducting materials including $TiO_2$ can be improved by annealing and their high crystalline structure would facilitate a decrease in grain boundaries, thereby increasing the electrical conduction and charge mobility [9, 10]. The present work involves the development of $TiO_2$ nanotube arrays by electrochemical anodization, examination of its crystallinity upon annealing, investigation into spectral dependent photoelectrochemical response of $TiO_2$ nanotubes and hydrogen evolution via water splitting. The principal focus of this study is to understand the correlation among the annealing induced crystallinity and electrochemical current density and hydrogen evolution rate of $TiO_2$ nanotubes in water splitting cell.

## Materials and Methods

Titanium (Ti) sheet (99.7% purity) with a thickness of 0.2 mm was taken for the electrochemical anodization. Small pieces of Ti-sheet of size 25 × 20 $mm^2$ were ultrasonically cleaned in acetone and ethanol for 10 minutes each and then rinsed with distilled water and finally dried under air blow. For electrolyte solution, the volume ratio of ethylene glycol (EG) to distilled water (DW) was fixed at 9:1 and the ammonium fluoride ($NH_4F$) content was 0.5 wt%. Anodization was performed at room temperature in a standard two-electrode electrochemical cell with Ti foil as the working electrode and platinum rod (diameter: 1mm; purity: 99.9%) as the counter electrode connected to a dc power supply. The applied voltage between the Ti sample and the pt cathode (2 cm apart) was 30 V and the anodization time was 1 hour. The as-anodized $TiO_2$ nanotubes ($TiO_2$-NTs) samples were rinsed with distilled water and dried in air. Anodized samples were annealed at 300 ºC, 400 ºC and 500 ºC in a digital muffle furnace (DMF 05) for 2 hr.

The surface morphology and size of $TiO_2$-NTs were investigated by Scanning Electron Microscopy (SEM ZEISS EVO 60) and its crystal phase by using X-ray diffractometer (Bruker D8 Advance). The photoelectrochemical properties of $TiO_2$-NTs were investigated using a three electrodes photoelectrochemical cell with $TiO_2$ nanotubes array as the working photoelectrode, platinum rod as the counter electrode and Ag/AgCl was used as the reference electrode. 1 M potassium hydroxide with 1 wt% of ethylene glycol solution was used as the electrolyte in this experiment. The 100 W LED light with different wavelengths (665 nm, 590 nm, 515 nm and 370 nm) were used as the light sources. Then, a linear sweep potentiometry was sweeped from –0.5 to 1V at a scan rate of 5 mV $s^{-1}$ using the Potentiostat/Galvanostat electrochemical analyzer (CS350). The hydrogen evolution experiment using $TiO_2$-NTs as catalyst in water splitting was carried out using homemade photoelectrochemical (PEC) cell where the $TiO_2$-NTs sample was used as photoanode and a platinum rod as cathode. Water splitting experiments were carried out in 1 M aqueous KOH electrolyte with addition of ethylene glycol (EG) applying an external bias of 30 V. A 100 W LED white light was used as the light source to irradiate the photoanode.

## Results and Discussion

### *Morphology, size and crystalline phase of $TiO_2$-NTs*

First, the size of morphology of anodized $TiO_2$ nanotube ($TiO_2$-NTs) were examined by scanning electron microscopy (SEM). Fig. 1 depicts the SEM images (top view and cross-sectional view) of $TiO_2$ nanotube arrays. It is clear that the $TiO_2$-NTs were well-defined and uniform morphology over large area. The average inner diameter of $TiO_2$-NTs is 100 nm and the length is around 2 µm estimated by cross-sectional view of $TiO_2$-NTs (Fig.1 b). Upon annealing the sample at 300, 400 and 500 ºC, the crystalline phase of $TiO_2$-NTs was identified by X-ray diffraction (XRD). Fig. 2 shows the XRD patterns of $TiO_2$-NTs annealed at 300 – 500 ºC. The major diffraction peaks were examined with standard diffraction data of pure Ti and anatase phase $TiO_2$. The diffraction peaks corresponding to anatase phase $TiO_2$ were found at 25.28º, 48.05º and 53.89º. The peaks were more intensified at higher annealing temperatures (400 ºC and 500 ºC), suggesting an improved crystallinity of $TiO_2$-NTs. The pure Ti peaks still existed in the obtained XRD patterns because of the pure Ti base on which $TiO_2$-NTs were formed.

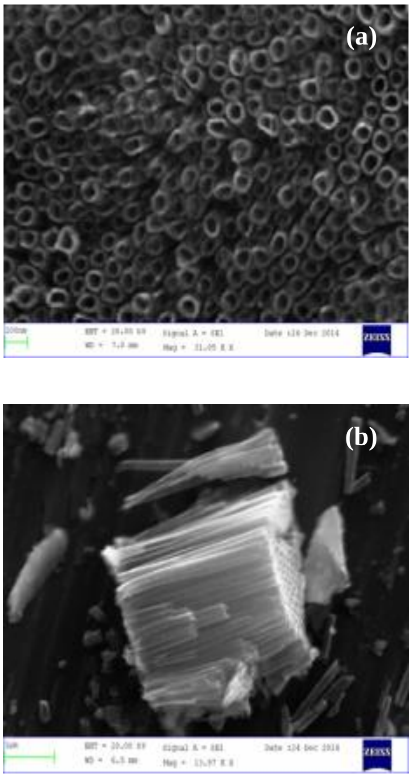

**Fig. 1** SEM images of $TiO_2$ nanotube arrays (a) Top view and (b) Cross- sectional view

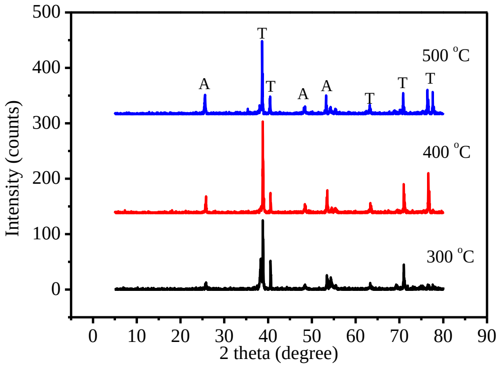

**Fig. 2** XRD patterns of $TiO_2$-NTs annealed at 300°C, 400 °C and 500 °C (“A” and “T” stand for - Anatase phase and pure Titanium respectively)

*Photoelectrochemical response of $TiO_2$-NTs: Varying annealing temperatures of $TiO_2$-NTs*

The photoelectrochemical response of $TiO_2$-NTs annealed at 300 °C, 400 °C and 500 °C in KOH aqueous solution was investigated by evaluating the electrochemical peak current densities from linear sweep voltammograms (–0.5 to 1.0 V) under light illumination with different wavelengths (665 nm, 590 nm, 515 nm and 370 nm) (Fig. 3). Using the measured peak current densities, we calculated the spectral dependent incident-photon-to-current-efficiency (IPCE) of $TiO_2$-NTs which is a better parameter reflecting the spectral dependent photoresponse of $TiO_2$-NTs. The spectral dependent IPCE was calculated by using the equation: IPCE (%) = 1240 $J(\lambda)$ / $\lambda$ $I(\lambda)$ × 100% where $J(\lambda)$ is the current density and $I(\lambda)$ is the light intensity at a particular wavelength ($\lambda$). The peak current densities and IPCE values are plotted against the illuminated light wavelength and depicted in Fig. 4.

It is observed that for all annealed temperatures, the peak current densities of $TiO_2$-NTs are almost unchanged under red and yellow light and increased under green and UV light. It is obvious that increase in peak current is more pronounced under more energetic light (UV) which is attributed to the wide band gap of $TiO_2$ [11, 12]. When we see the annealing effect on current densities, at the particular wavelength of light, the current densities increased with increasing annealing temperature which is ascribed to the increased crystallinity of $TiO_2$-NTs at higher annealing temperatures. The peak current density is as high as 0.782 mA $cm^{-2}$ for $TiO_2$-NTs annealed at 500 °C under UV. In order to visualize clearly the effect of annealing temperature and light illumination on IPCE, we plot the IPCE against the wavelength as seen in Fig. 4. A pronounced increase in IPCE is found under high energetic UV illumination and in high temperature annealed $TiO_2$-NTs. The reason is the same as mentioned previously. The maximum IPCE of 33.1% is realized for $TiO_2$-NTs annealed at 500 °C under UV illumination.

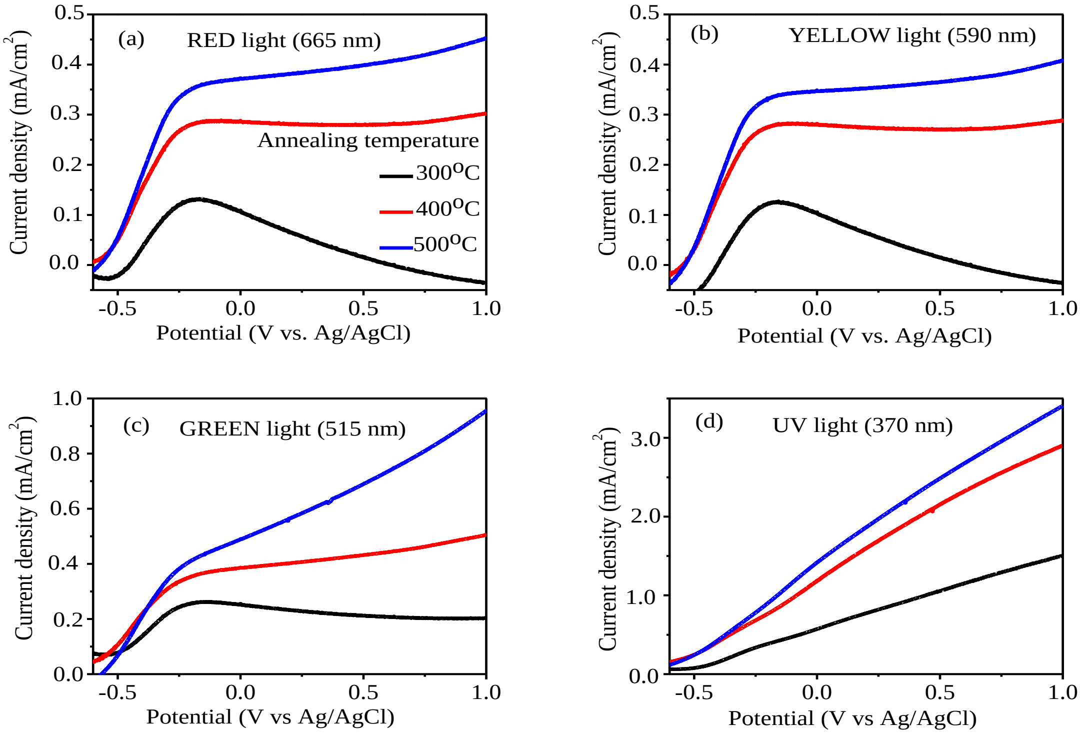

**Fig. 3** Linear sweep voltammograms of $TiO_2$-NTs annealed at 300 °C, 400 °C and 500 °C under (a) red, (b) yellow, (c) green and (d) UV light illumination

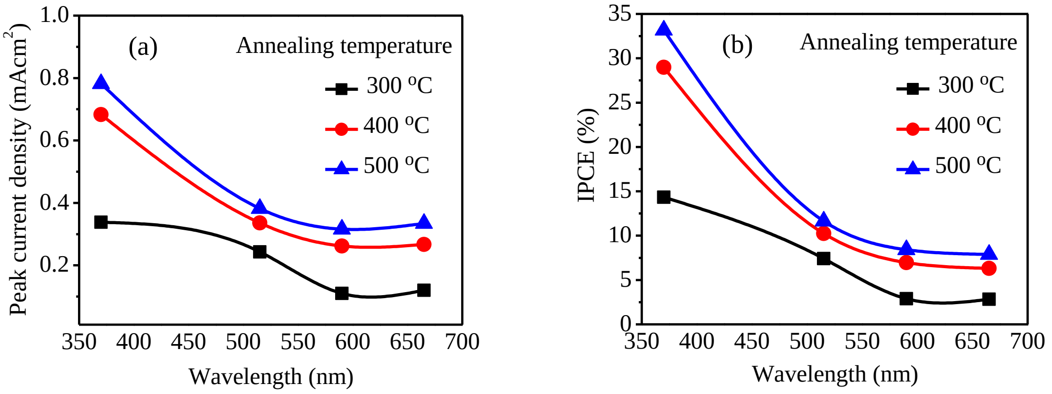

**Fig. 4** Plots of (a) peak current density and (b) IPCE (%) against the illuminated light wavelength for $TiO_2$-NTs

### *Hydrogen evolution rate of $TiO_2$-NTs in water splitting : Varying annealing temperatures of $TiO_2$-NTs*

The photoelectrochemical activity of $TiO_2$-NTs was evaluated by measuring quantitatively the amount of hydrogen ($H_2$) and oxygen ($O_2$) separately produced through water splitting in the photoelectrochemical (PEC) cell. The principle of photoelectrochemical water splitting is based on the conversion of light energy into chemical energy. Measurement was carried out with $TiO_2$-NTs annealed at 300 ºC, 400 ºC and 500 ºC as the photoanode in the KOH aqueous solution using an external bias of 30 V. Upon white light illumination, hydrogen gas was evolved at Pt electrode and collected in the syringe. The volume of hydrogen gas collected was plotted against the collected time in Fig. 5. It is seen that $TiO_2$-NTs annealed at 500 °C generated a larger volume of hydrogen in short time compared to those annealed at 300 °C and 400 °C. The hydrogen evolution rate was found to be 0.042 mL $min^{-1}$, 0.071 mL $min^{-1}$ and 0.347 mL $min^{-1}$ for $TiO_2$-NTs annealed at 300 °C, 400 °C and 500 °C respectively. Higher hydrogen evolution rate in higher temperature annealed $TiO_2$-NTs is attributed to the increased crystallinity and current generation in $TiO_2$-NTs annealed at higher temperatures. We also performed the control experiments such as the testing of hydrogen evolution using (i) as-anodized $TiO_2$-NTs (before annealing) and (ii) pure Ti sheet (before anodization) both of which only show pure Ti peaks (not showing the crystalline anatase peak of $TiO_2$) in XRD profiles. Apart from changing the photocatalyst sample, all other experimental conditions are identical in these control experiments. Extremely low hydrogen evolution was observed in the former case and no hydrogen evolution in the latter case. It supports the fact that only crystalline $TiO_2$ based photocatalysts enable an effective hydrogen evolution via water splitting.

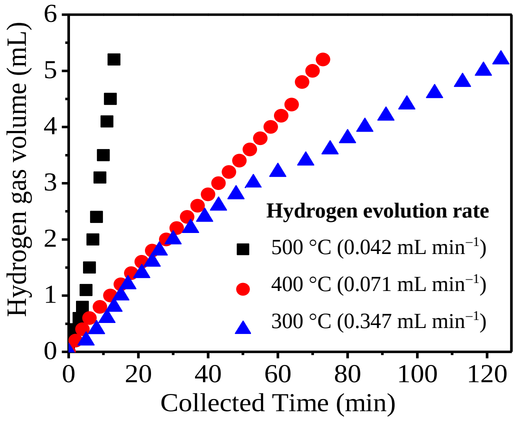

**Fig. 5** Collected hydrogen gas volume vs. time for $TiO_2$-NTs water splitting

## Conclusion

The $TiO_2$-NTs with diameter of ~100 nm and length of 2 μm were developed by electrochemical anodization. X-ray diffraction study indicates that improved crystallinity is exhibited in $TiO_2$-NTs annealed at higher temperature 500 °C. The photoelectrochemical measurements show that the electrochemical peak current density of $TiO_2$-NTs in KOH aqueous solution is higher under energetic UV light activation. Moreover, it is observed that the electrochemical current and hydrogen evolution rate increase with increasing annealing temperature of $TiO_2$-NTs and is as high as 0.347 mL $min^{-1}$ for $TiO_2$-NTs at 500 °C with applied bias of 30 V. Increased hydrogen generation in water splitting is attributed to the increased current generation stemmed from the improved crystallinity of photocatalyst $TiO_2$-NTs which is induced by high temperature annealing. Thus the crystallinity of photocatalyst plays a key role in determining the electrochemical current generation and hydrogen evolution in photoelectrochemical water splitting.

## Acknowledgements

The authors acknowledge the research grant supported by University of Mandalay [Project No. 80 (2016-17)].

## References

[1] C. Hao, W. Wang, R. Zhang, B. Zou, H. Shi, Enhanced photoelectrochemical water splitting with $TiO_2@Ag_2O$ nanowire arrays via p-n heterojunction formation, Sol. Energy Mater Sol. Cells. 174 (2018) 132 – 139.

[2] G. Wang, H. Wang, Y. Ling, Y. Tang, X. Yang, R.C. Fitzmorris, C. Wang, J.Z. Zhang, Y. Li, Hydrogen-Treated $TiO_2$ Nanowire Arrays for Photoelectrochemical Water Splitting, Nano Lett. 11 (2011) 3026 – 3033.

[3] M.G. Walter, E.L. Warren, J.R. McKone, S. W. Boettcher, Q. Mi, E.A. Santori, N.S. Lewis, Solar Water Splitting Cells Chem. Rev. 110 (2010) 6446 – 6473.

[4] M.I. Baraton, Nano-$TiO_2$ for Solar Cells and Photocatalytic Water Splitting: Scientific and Technological Challenges for Commercialization, The Open Nanoscience Journal. 5 (2011) 64 – 77.

[5] H.S. Kim, K.S. Ahn, S.H. Kang, Enhancing photoelectrochemical water splitting performance of $TiO_2$ nanotube arrays by controlling morphological properties, Electron. Mater. Lett. 10 (2) (2014) 345 – 349.

[6] I.S. Cho, Z.B. Chen, A.J. Forman, D.R. Kim, P.M. Rao, T.F. Jaramillo, X.L. Zheng, Branched $TiO_2$ nanorods for photoelectrochemical hydrogen production, Nano Lett. 11 (2011) 4978 – 4984.

[7] S. Pavasupree, J. Jitputti, S. Ngamsinlapasathian, S. Yoshikawa, Hydrothermal synthesis, characterization, photocatalytic activity and dye-sensitized solar cell performance of mesoporous anatase $TiO_2$ nanopowders, Mater. Res. Bull. 43 (2008) 149 – 157.

[8] X. Chen, S.S. Mao, Titanium dioxide nanomaterials: Synthesis, properties, modifications and applications. Chem. Rev. 107 (2007) 2891 – 2959.

[9] Z.W. Zhao, B.K. Tay, Study of nanocrystal $TiO_2$ thin films by thermal annealing, J. Electroceram. 16 (2006) 489 – 493.

[10] A.S. Wochnik, M. Handloser, D. Durach, A. Hartschuh, C. Scheu, Increasing Crystallinity for Improved Electrical Conductivity of $TiO_2$ Blocking Layers, ACS Appl. Mater. Interfaces. 5 (12) (2013) 5696 – 5699.

[11] H. Kiziltas, T. Tekin, Increasing of Photocatalytic Performance of $TiO_2$ Nanotubes by Doping AgS and CdS, Chem. Eng. Commun. 204 (8) (2017) 852 – 857.

[12] S. Noothongkaew, J.K. Han, Y.B. Lee, O. Thumthan, K.S. An, Au NPs decorated $TiO_2$ nanotubes array candidate for UV photodetectors, Progress in Natural Science: Materials International. 27 (6) (2017) 641 – 646.