Enhanced-Surface-Area TiO$_2$-Based Nanotube for Photocatalytic Applications

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Abstract. This study utilized chemical method to reform titania nanopowder into larger surface area titania-based nanotubes (NTs). Various factors, such as reaction temperature, concentration, time, and aging time were investigated to determine their effects toward NT properties. The formation of the titania-based NTs was carried out under the conditions of 10N NaOH reaction medium, at reaction temperature and time of 116°C and 23 hours, respectively. Subsequent aging was done at 40°C for 24 hours. The NTs were further resintered at 400°C for 1 hour to improve their crystallinity and photocatalytic efficiency. Result indicates that aging process is significant for NT synthesis process. The treated titania-based NT has a surface area of 247.91 m^2/g with nearly 100% photodecomposition of (MB) in 15 minutes.

1. Introduction

Since Fujishima discovered TiO$_2$ nanotube (NT) in 1991, many other types of NT have been developed, such as BN [1], B$_x$C$_y$N$_2$ [2], WS$_2$ [3], MoS$_2$ [4], W$_x$Mo$_y$C$_2$S$_2$ [5], VO$_x$ [6], and titania [7]. Among these materials, titania has been used most extensively in the fields like pollution control, photocatalysis, gas sensor, and solar energy battery [8] with excellent properties. Many researchers have taken the advantage of the large surface area titania-based NTs and developed various manufacturing methods. Kobayashi [9] used trans-(1R, 2R)-1,2-cyclohexanedi(1l-aminocarbonylundecylpyridi- nium)hexafluorophosphate as a self-assembled flat plate. As this compound has a cation edge, it can combine with Ti through electrostatic effect, and react to form tubular structure. Zhang [10] prepared a mixture of isopropantol titanium oxide, acetoacetic acid (acac), water, and ethyl alcohol with a molar ratio of 1:1:3:20. A porous material formed by anode oxidation was introduced to this solution. Titania-based NTs were produced upon completed reaction. However, the aging effect and the resintering effect for the NT synthesis process of titania was not reported in detailed.

This study deals with the chemical reformation method for titania-based NT preparation. It has the advantage of simplicity. In this report, operating conditions for nanotubalization, and change of crystallinity after resintering are investigated. In addition, its photocatalytic ability is also assessed through the use of surface morphology analysis, material structure analysis, and photocatalytic reaction.

2. Experimental

Photocatalytic reaction works by absorbing photocatalyst onto the surface, and decomposing pollutants by OH radicals from electron and hole separation. Hence, our focus is on enhancing titania surface area and increasing crystallinity by resintering for improved photocatalytic efficiency. The preparation methods and formula for the titania nanopowder and titania-based NT were as follows:

2-1 Titania powder prepared by sol-gel method

Tetrabutyl titania [$Ti(OC_4H_9)_4$] was used as the starting material, whereas isopropyl alcohol (IPA), acetylacetone (acac), and hydrochloric acid (HCl) were used as solvent, particle growth inhibitor, and acid catalyst, respectively. The composition ratio was $Ti(OC_4H_9)_4$: IPA: HCl: H_2O = 1:17:0.08:4:0.01 (molar ratio). While maintaining at 30°C, IPA and acac were added in a 250 ml Erlenmeyer flask. After mixing, $Ti(OC_4H_9)_4$ was slowly poured into the flask and kept mixing for another hour until uniform. HCl solution (0.6 mL/s) was then introduced gently and allowed hydrolysis reaction to proceed.

The titania gel was let sit for 5 days for maturity which lead to a milky white appearance. During the maturity process the released IPA and n-butanol should be removed, hence the gel was left in an oven (70°C, 24 hours) for water removal followed by residual solvent removal in a vacuum oven at 70°C. The obtained dried yellow gel was then subjected to high temperature sintering by heated slowly to 250°C for one hour, and further increased the temperature to 500°C and remained for three hours. The dried gel was then ground to obtain white titania nanopowder.

2-2 Titania-based nanotube preparation

The titania nanopowder was first reformed by adding 1.6 g of nanopowder into 100 ml of NaOH(aq) at 100°C. The reaction conditions [temperature (90 – 116°C) NaOH concentration (8 – 11N) and time (18 – 25 hours)], and aging conditions [temperature reduction (110 – 40°C) and time (12 – 48 hours)] were investigated to determine their effects on NT formation. Then the samples were washed with diluted HCl until pH=7 and then air-dried afterward. In addition, titania NT was resintered at 200 - 600°C for 1 hour under N_2 environment to increase its crystallinity.

2-3 Developed nanotube property analyses

Brunauer–Emmett–Teller surface area analyzer (BET)(ASAP 2000 micromeripics) was used for measuring the surface area change. X-ray diffraction (XRD)(MAC SCIENCE MXP3) was used to observe changes in crystallinity. Field emission scanning electron microscope (FE-SEM)(JEOL J6700) and high-resolution transmission electron microscope (HR-TEM)(JEOL JEM2010) were employed for morphological change observation. Ultraviolet-visible spectrometer (UV-vis)(Cary 50 Installation) and spectrophotometer (SPECTRONIC 20 GENESYS) were used for analyzing its ability to decompose methylene blue (MB) which determined the heterogeneous photodecomposition efficiency of the titania-based NT.

MB solution was prepared at 1 L of 2×10^{-5} M and mix it at 25°C for 1 hour. After the initial absorption is determined, 0.1 g of the sample was added to the MB solution. The MB solution was under UV irradiation with a wavelength of 365 nm, and measured every 30 minutes for MB absorption changes.

A solid-gas phase photocatalytic test was carried out with acetaldehyde. 70 mg of titania-based NT was weighed, coated on nylon material, and placed in a reaction chamber connecting to a Gas Chromatography-Flame Ionization Detector (GC-FID). Acetaldehyde was injected and let fully evaporate in the reaction chamber. The nylon material was UV irradiated and the gaseous acetaldehyde was flowed into the gas tube for analysis.

3. Results and Discussion

3-1 Aging temperature and time

The aging time of titania NTs have a profound effect on surface area and XRD peak height.

The prepared nanopowder was reformed in 10N NaOH and heated at 110°C for 20 hours, and followed by different aging conditions. The changes in XRD patterns of titania are shown in Fig. 1. S-0 is the as-prepared anatase phase titania nanopowder which shows high crystallinity. Nevertheless, after it is chemically reformed [without temperate decrease (S-1), temperature decrease to 60°C (S-2), decrease to 40°C (S-3), decrease to 40°C and set for 12 hours (S-4), 24 hours (S-5), 36 hours (S-6), and 48 hours (S-7)], crystallinities are weakened significantly. Although there are many challenges associated with the surface characterization of titania NT, it is credible that the weakened anatase peak (2θ = 25.28) and appearance of the new peaks (2θ = 24.4, 28.42) are attributed to the formation of amorphous NT structure (Fig. 2) [12]. As the nanopowder reformed, temperature reduced, and aging time extended, greater surface area is obtained (Fig. 3). The stabilization of titania NT surface area and anatase phase peak intensity at 40°C for 24 hours is also observed in Fig. 3 (S-5~7). Longer aging time allows titania particles to reduce (data not shown), and to form longer NTs as shown in SEM and TEM images (Fig. 4).

3-2 Reaction temperature, NaOH concentration and reaction time

According to the results in 3-1, optimal aging conditions can be obtained by XRD, FE-SEM and BET. Thus, similar measures can be taken to optimize the reaction conditions. Consistent surface area change with respect to anatase phase crystallinity (2θ = 25.28) is also shown in Fig. 5. An increase in NT surface area occurs with increasing reaction temperature in 10N NaOH (Fig. 5a). The absence of granular structure (unreacted titania particles) can also be observed as the temperature increases (Fig. 6). Reaction at 10N NaOH (Fig. 5b) and at 23 hours (Fig. 5c) shows the highest surface area and the most stabilized surface area, respectively. Lower NaOH concentration (Fig. 7a) and longer reaction time (data not shown) yield shorter NTs, while less NT is observed in excessive NaOH concentration (Fig. 7c).

3-3 Discussion on nanotube synthesis reaction conditions

As described in literature, nanotube synthesis process involves two steps [13]. NaOH breaks the bonds between particles, and forms a plane structure. The broken bonds nearby then form new bonds, and turns into a tube structure. Our results show that there are many unreacted titania particles remained if temperature is not reduced. When temperature is reduced during aging, the remaining particles disappear gradually. A feasible explanation for this phenomenon is that after bonds breaking bond-reforming time falls in the aging period. During the reaction time, titania particles simply fall apart into plane structure through bond breaking. Hence, if temperature is not reduced after reaction, the broken bonds cannot proceed to NT formation because of the rapid bonds forming and leads to titania particles accumulation.

The effect of reaction temperature, NaOH concentration and reaction time can be further explained by the Arrhenius equation, i.e. higher temperature leads to higher reactivity whereas longer reaction time gives better reaction result:

$$K = A \, e^{-E_a / RT}$$

where K is reaction rate constant, A is constant, E is activation energy, R is gas constant, and T is temperature.

Therefore, the more complete the broken bond plane, the longer the NT with high integrity can be obtained. NaOH concentration also has significant effect on NT formation. Our results reveal that when concentration is too high, it not only causes titania particle to undergo bond breaking and fragmentation, it also forms numerous small broken bond plane. We attempted to substitute 10N NaOH with NaOH-KOH molten salt for similar reaction [14]. Result shows that the surface area decreases from 77.38 to 21.49 m^2/g indicating adverse effect can occur if reaction concentration is excessive.

3-4 Solid-liquid phase photocatalysis test

Photocatalysis of MB is done for analyzing adsorption and photodecomposition abilities of titania-based NT. 0.1 g of titania-based NT was used in this experiment, while 0.15g of SiO_2 –TiO_2

[15](1:9) nanocomposite material was used for comparison under the same experimental condition. Result shows that reformed titania NTs have an adsorption–decomposition efficiency of 89% removal in 5 minutes (Fig. 8). On the other hand, the SiO_2 –TiO_2 nanocomposite material with the surface area of 166.47 m^2/g reaches 69% removal 30 minutes after the initial contact. The former can achieve 100% removal in 15 minutes, which we can conclude its adsorption and photodecomposition performances are far superior to the SiO_2-TiO_2 nanocomposite material.

3-5 The effect of re-crystallization of titania-based nanotube on photocatalysis

Although the prepared titania-based NT has large surface area and high adsorption ability, its crystal structure is not satisfactory. Therefore, an approach of high temperature sintering is proposed to investigate the change in crystallinity and photocatalytic efficiency. Fig. 9 demonstrates the enhancement of titania NT crystallinity after re-sintering. With improved crystallinity, more electron-electron holes can be formed in the post-photocatalysis process. However, high sintering temperature results in poor surface area (Fig. 10). Surface area is decreased to 50 m^2/g as temperature is raised to 500°C. 400°C is thought to be more acceptable as surface area reduces while maintaining good crystallinity. Fig. 11 shows that tube structure has no apparent change when temperature is around 200~300°C. At 400°C, tube length is shortened (Fig.11c). When temperature is further increased to 500°C a rod-type structure is formed (Fig. 11d). A granular structure is obtained at 600°C sintering temperature (Fig. 11e). The change in structure is because of the temperature increase which leads to vigorous atoms vibration. It also causes OH bond to form condensation resulting in the formation of new nucleus and crystal growth.

3-6 Solid-gas phase photocatalytic test

Fig. 12 demonstrates different level of decomposition efficiency by NTs of various preparation methods. Degraded photocatalytic efficiency is obtained from the low surface area NT (sintered at 500-600°C) regardless of its high crystallinity. Low sintering temperature produces NT of low crystallinity, which also results in unfavorable photocatalysis. It is worth noting that, although the as-prepared titania-based NT has faster photocatalytic efficiency, 400°C sintered NT surpasses the efficiency after 30 minutes and reaches 93% removal 120 minutes after the initial contact.

5. Conclusion

This study focuses on the preparation of titania-based NT from titania nanopowder derived by sol-gel method. NTs are reformed in the reaction conditions of 10N NaOH at 116°C for 23 hours, and in the aging conditions of 40°C for 24 hours. Then the crystallinity is further improved by re-sintering at 400°C for 1 hour. The treated titania-based NT has a large surface area of 247.91 m^2/g, and its outstanding adsorption and photocatalytic efficiency allows photodecomposition of 93% acetaldehyde in 120 minutes and 100% MB in 15 minutes.

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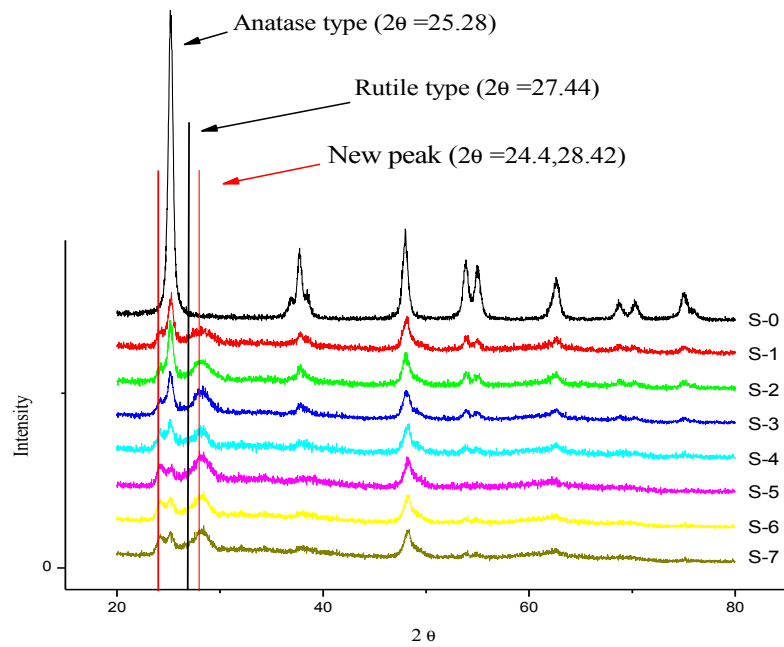
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Figures

Fig. 1. XRD pattenrs of the as-prepared nanopowder and NTs at various aging conditions.
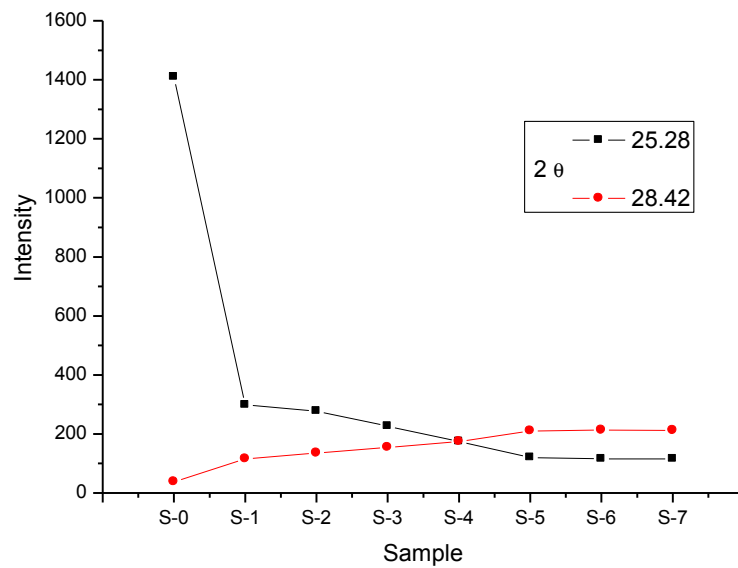
Fig. 2. XRD peaks (2θ = 25.28, 28.42) of the as-prepared nanopowder and NTs at various
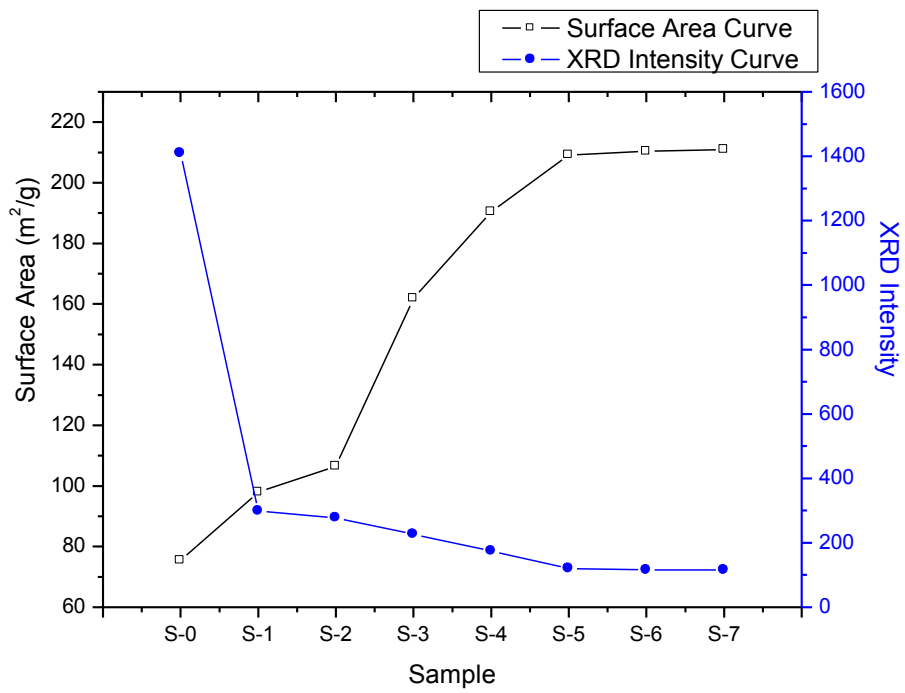
aging conditions.

Fig. 3. The crystallinity and surface area changes of the as-prepared nanopowder and NTs at various aging conditions.
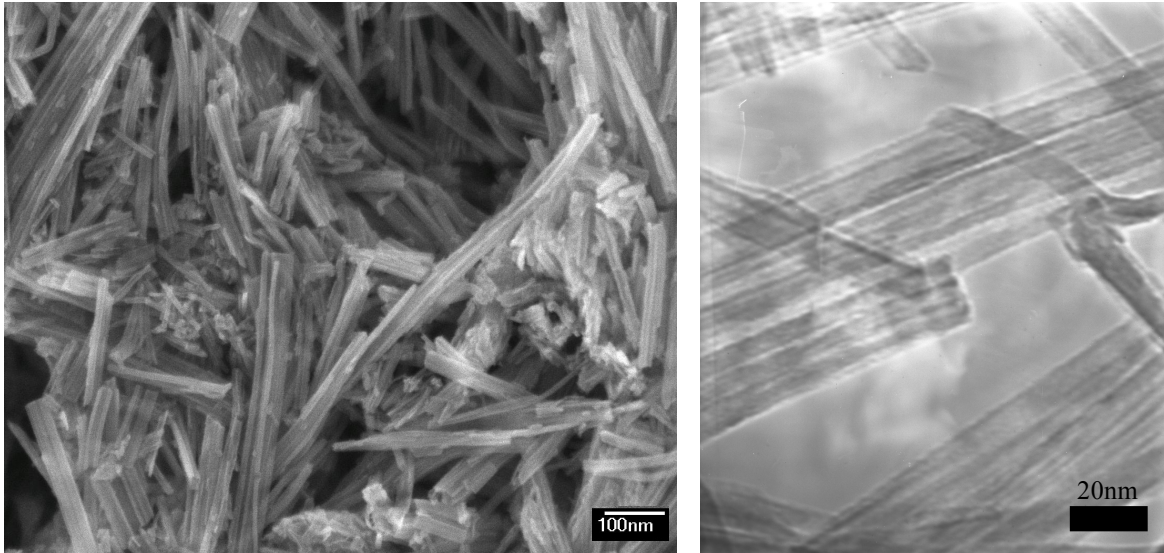
Fig. 4. SEM (L) and TEM (R) images of titania NTs at the aging time of 24 hours.
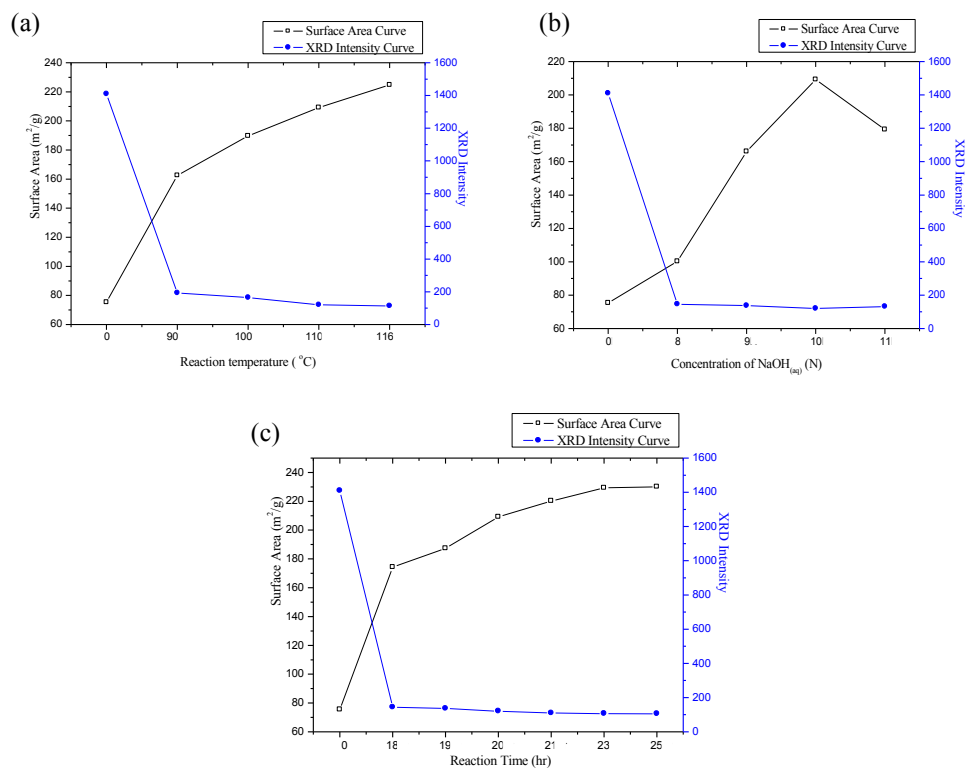
Fig. 5. The effect of (a) reaction temperature, (b) NaOH concentration, and (c) reaction time on optimal titania NT formation.
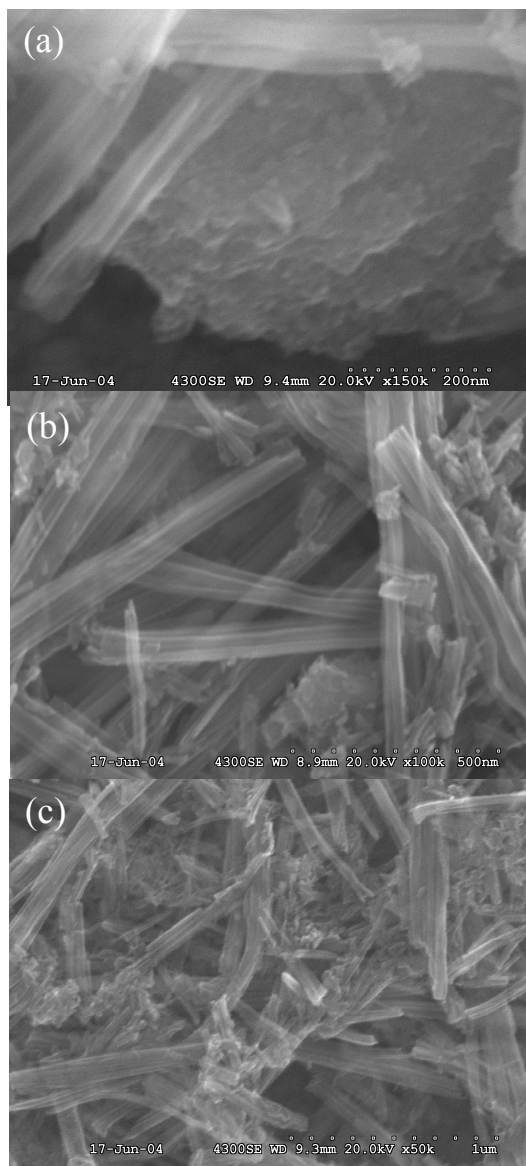
Fig. 6. SEM images of titania NTs at reaction temperature of (a) 90°C, (b) 100°C, and (c) 116°C.
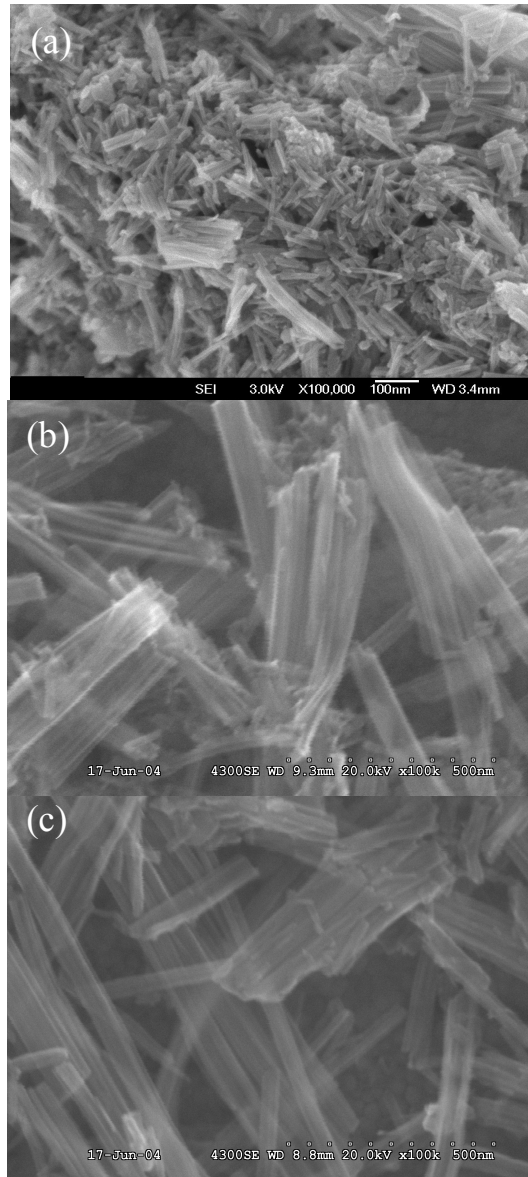
Fig. 7. SEM images of titania NTs in NaOH concentration of (a) 8N, (b) 9N, and (c) 11N.
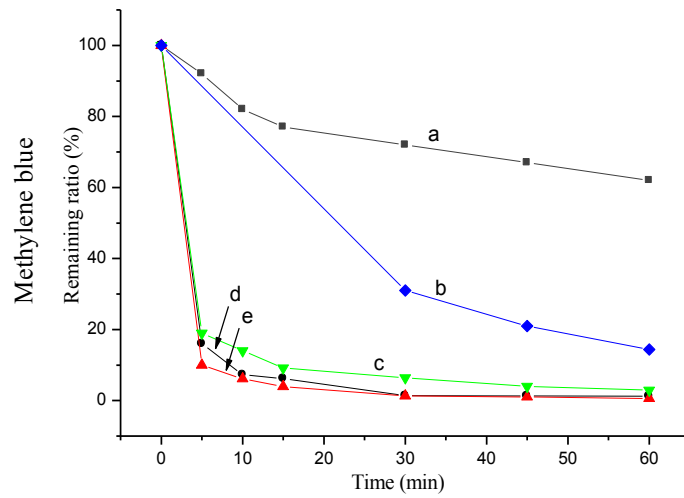
Fig. 8. Photodecomposition efficiency of (a) titania nanopowder, (b) SiO_2-TiO_2 (1:9) nanocomposite material, and titania-based NTs prepared at reaction condition of (c) 10N NaOH at 110°C for 23 hours followed by cooling to 40°C and set for 24 hours, (d) 10N NaOH at 116°C for 23 hours followed by cooling to 40°C for 24 hours (without UV light), and (e) 10N NaOH at 116°C for 23 hours followed by cooling to 40°C and set for 24 hours (with UV light).
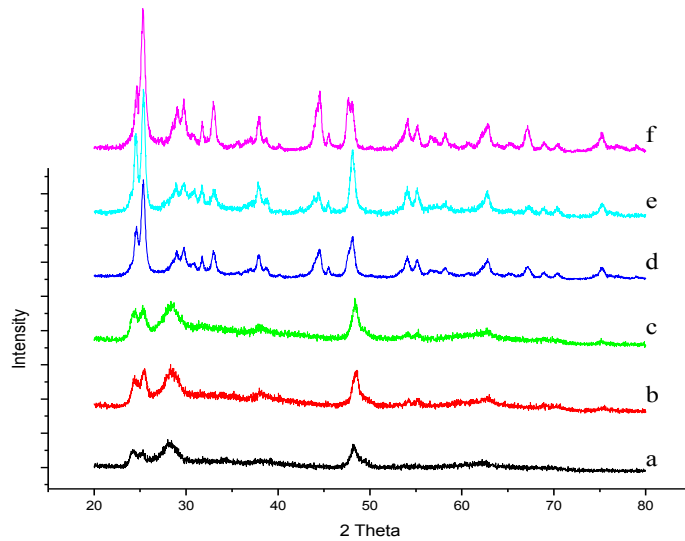
Fig. 9. XRD patterns of the titania-base NTs at the sintering condition of

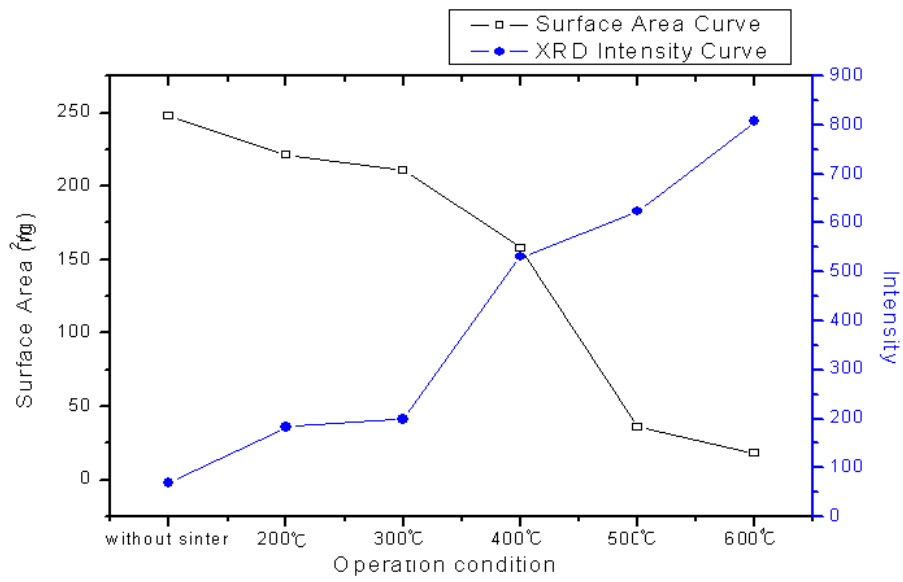(a) not sintered, (b) 200°C, (c) 300°C, (d) 400°C, (e) 500°C, and (f) 600°C.

Fig. 10. Decrease in titania-based NT surface area as crystallinity is enhanced with increasing sintering temperature.
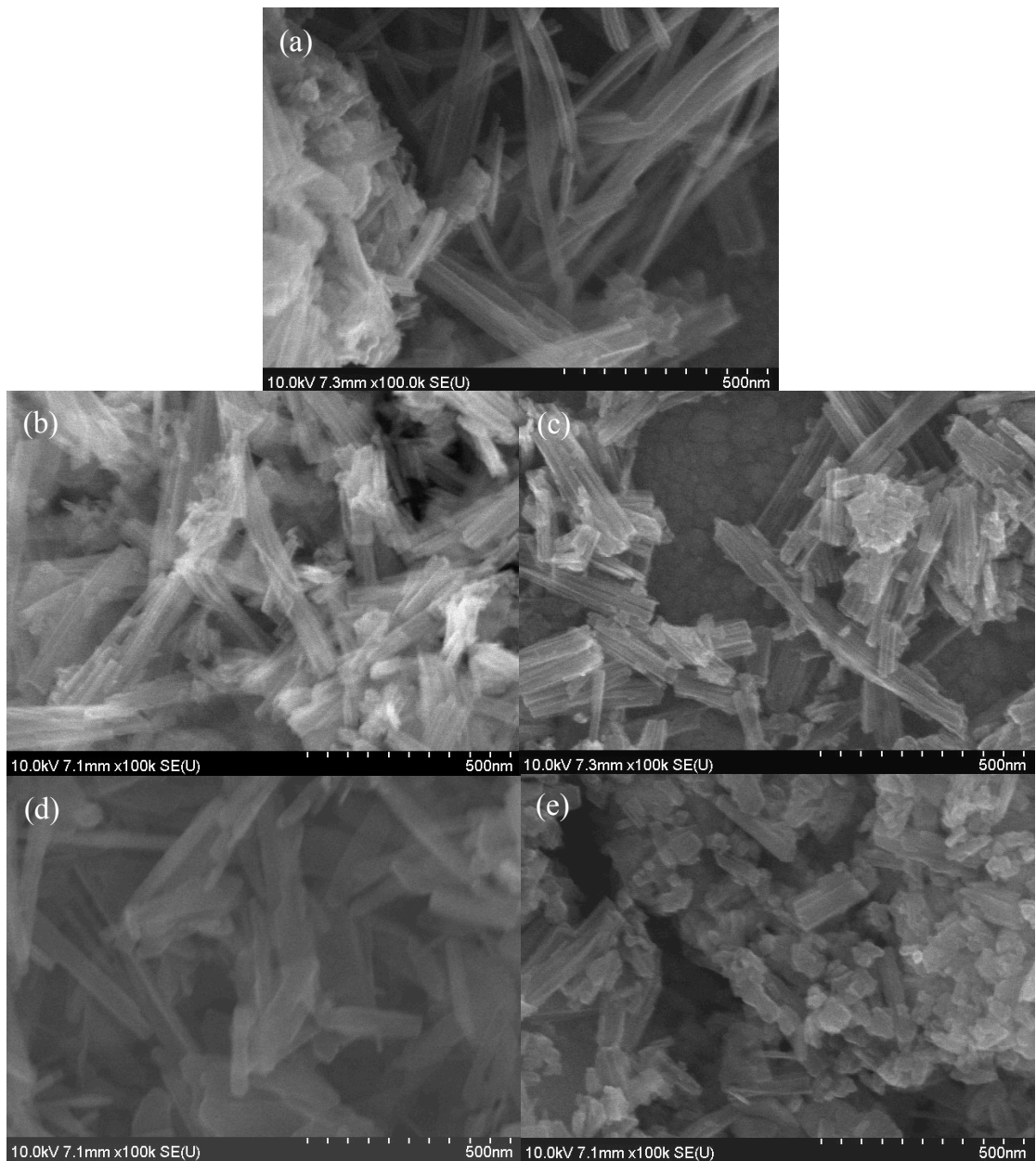
Fig. 11. SEM images of titania-based NTs after re-sintering for 1 hour at the temperature of (a) 200°C, (b) 300°C, (c) 400°C, (d) 500°C, and (e) 600°C.
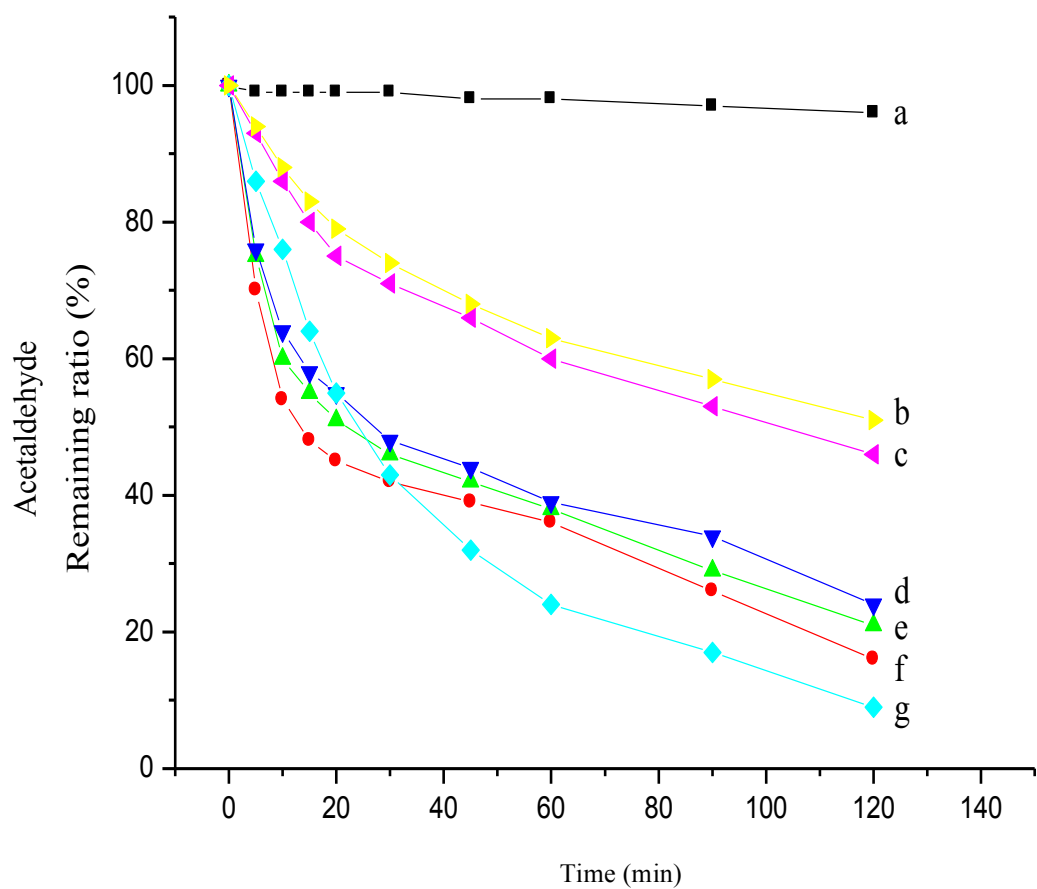
Fig. 12. Photodecomposition efficiency of nylon material with (a) no coating, titania-based NT (b) sintered at 600°C, (c) sintered at 500°C, (d) sintered at 300°C, (e) sintered at 200°C, (f) as-prepared, and (g) sintered at 400°C.