Short Time Synthesis of Titania Nanotubes: Effect of Pre-Mixing Prior Hydrothermal

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Abstract: *The effect of pre-mixing by mechanical stirring before hydrothermal and hydrothermal time on the crystalline phases and morphology of titania has been studied. It was shown that nanotubes titania can be obtained after 5 h hydrothermal at 150 °C. The XRD patterns and Raman spectra of the produced powders showed the existence of anatase and titanate crystalline phases. At the longest stirring, TiO_2 (B) was observed. High textural coefficient for [200] plane of anatase (TC_{200}) confirmed oriented growth of one-dimensional anatase along [200]. All powders resulted at various stirring time were nanotubes, as confirmed by Transmission Electron Microscope (TEM). It was found that the longer the stirring, the higher the surface area of the nanotubes. All powders showed type-IV isotherm for nitrogen gas adsorption/desorption, indicating the existence of mesoporous materials. However, long hydrothermal induced the nanospheres formation, hence reducing the surface area. The band-gap of the resulted titania nanotubes were ranging from 3.11–3.16 eV. The photocatalytic performance toward the degradation of methylene blue of the titania nanotubes was higher (~50%) compared to the bulk TiO_2 (~5%) under visible-light and was comparable under UV-light (~60%). These results pave a way of producing visible-sensitive TiO_2 photocatalyst by altering the morphology.*

Keywords: *nanotube; titanium dioxide; hydrothermal; stirring; photocatalyst; visible-sensitive*

■ INTRODUCTION

Titania or titanium dioxide (TiO_2) has been semiconductor material's focus of interest due to its physical- and chemical properties which are environmentally benign, photochemical- and chemically stable, as well as moderate cost material. Recently, the research focusing on one-dimensional titania nano structures such as nanorods, nanowires, and nanobelts is grown exponentially [1-2]. By the need of having the large specific surface area, titania nanotube has received much attention as the surface area may reach up to 478 m^2/g [3-4], whereas nanorods or nanofibers only reach up to 50 m^2/g [3]. High surface area semiconductor will be beneficial for application involving reactions on the semiconductor surface such as photocatalysis [5], solar cell [6-7], water splitting [8], and adsorbent [9]. Nanotube morphology also provides fast electron transfer at a long distance [10].

Titania nanotubes can be achieved via several methods, such as anodization [1], hydrothermal [3,11], and sol-gel [3]. In comparison to other techniques, the alkaline hydrothermal method was the most promising as it offers simpler, cheaper route, and environment-friendly way with the ability to control the chemical composition and morphology of the synthesized products [3]. In common route, titania source was mixed with excess concentrated alkaline (10 M NaOH) and then heated at low-temperature of 110–150 °C for a typical range of 14 to 48 h to obtain sodium titanate nanotubes. The anatase crystalline phase could be obtained by washing the materials with dilute acid to acquire hydrogen titanate, and with consecutive heating, the titanate acid will transform to anatase through TiO_2 (B) [3]. This conventional hydrothermal route is so time-consuming that the effort to shorten the preparation time is necessary.

Thu et al. [4] have synthesized titania nanotubes at very short-time by employing the one-step dynamic hydrothermal method. The nanotubes were achieved after 3 h heating of the titania precursor in an alkaline medium at 130 °C. It is proven that stirring during hydrothermal can reduce the hydrothermal reaction time needed for morphology transformation from spherical nanoparticles to nanotubes. Anatase crystalline phase with nanotubes morphology was obtained after calcination at 400 °C for 2 h. However, this method requires a hydrothermal reactor with stirring control, which is capital-intensive. Wen et al. [9] achieved titanate nanostructures using TiS_2 as the precursor under static hydrothermal for 6 h at 150 °C. Shorter hydrothermal time was made by utilizing weaker Ti-S bonds instead of Ti-O bonds of TiO_2 precursors for the conventional hydrothermal synthesis of titania nanotubes. Ma et al. [12] used a combination of sonication and hydrothermal to reduce the preparation time to prepare titania nanotubes. The hydrothermal time can be reduced to 4 h. The crystalline phase of the resulted titania nanotubes is titanate which is less photochemically active than anatase crystalline phase. In this study, titania nanotubes with titanate and anatase crystalline phase were synthesized using commercial TiO_2 powders as the precursor. Instead of using dynamic hydrothermal stirring, pre-mixing mechanically prior hydrothermal is introduced to reduce the hydrothermal time. It is shown that titania nanotubes can be obtained hydrothermally at 150 °C for 5 h by applying 30-120 min stirring before hydrothermal treatment. Excellent photocatalytic activity towards degradation of methylene blue was demonstrated under both UV and visible-light illumination.

■ EXPERIMENTAL SECTION

Materials

TiO_2 powder was purchased from Merck (~99% of anatase crystalline phase), as well as sodium hydroxide (NaOH) pellet and hydrochloric acid (HCl, 37%). The chemicals were used as received. Distilled water was used as the solvent for all solutions.

Procedure

Synthesis of titania nanotubes

Typically, 2 g of TiO_2 powder was mixed with 40 mL of 10 M NaOH in a Teflon vessel. The highly concentrated alkaline medium was used to ensure morphology transformation from particles to nanotubes [3-4]. The mixture was stirred by magnetic stirring for the various stirring time of 30, 45, 60, 90, and 120 min. The mixtures were then heated hydrothermally at 150 °C for 5 h. Mixtures stirred for 60 min was heated at 150 °C for the various hydrothermal time of 5, 12, and 24 h. The as-hydrothermal samples were left overnight inside the vessel. The resulted powders were then separated from the liquid and washed using 0.1 M HCl until the filtrate pH reaching 2 (acid-washing). The powders were dried in the oven at 120 °C. The dried powders were subjected to calcination at 400 °C for 4 h. Some samples were washed with distilled water after acid-washing until the pH of the filtrate reaching 7 (neutral washing).

Characterization

As-calcined powders were characterized by using X-Ray diffraction (XRD, Shimadzu XRD 6000) and Raman spectrometer (Senterra) to identify the crystalline phases. The XRD (Shimadzu XRD 6000) analysis was performed by using Cu Kα irradiation (λ = 1.54178 Å) at a scanning rate of 5°/min. Transmission Electron Microscope (TEM, JEOL JEM 1400) was used to access the morphology. N_2-gas adsorption/desorption technique (Quantachrome 1200e) was used to evaluate the porosity and surface areas. The band-gap was determined using the absorption edge method of the

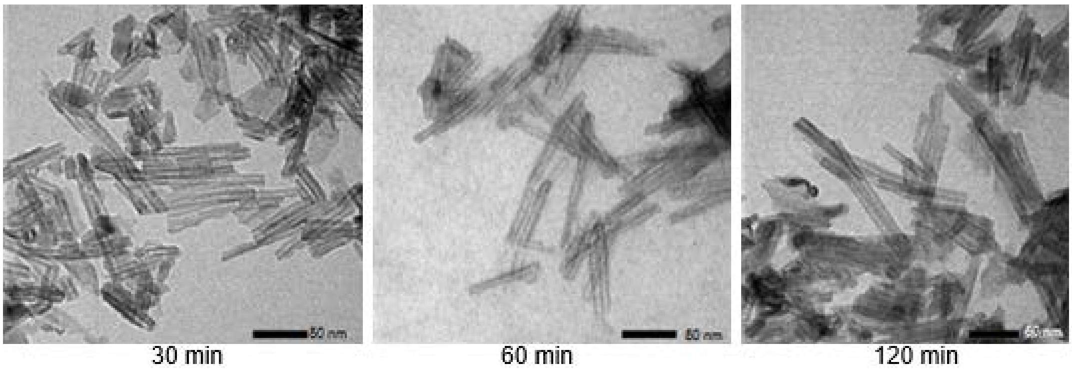


Fig 1. TEM images of the resulted TiO_2 at a various stirring time after static hydrothermal for 5 h at 150 °C

absorption spectra analyzed by the diffuse-reflectance UV-Vis spectrophotometer (Shimadzu type UV-2450). Semiconductors absorb light below a threshold wavelength, the fundamental absorption edge (λg), related to the band gap energy (Eg) is calculated according to the following equation [13]:

$$Eg(eV) = 1240/\lambda g\ (nm) \quad (1)$$

Photocatalytic tests

The photocatalytic test was performed for titania powders resulted from 60 min stirring prior hydrothermal at 150 °C for 5 h and 24 h with and without neutral washing. Commercial TiO_2 as the precursor was used as a comparison. Typically, 5 mg of titania was mixed with 50 mL of 5 ppm methylene blue at a solution pH of 11 in beaker glass. The mixed solution was stirred and irradiated by UV light and visible light (Xenon lamp with UV-filter) for 90 min after 30 min dark-equilibrium. The solution was then separated from the photocatalysts and analyzed by UV-Vis spectrophotometer at 663 nm. The photocatalytic activity was calculated as the percentage difference of the analyzed absorbance before and after the photocatalytic test [13].

■ RESULTS AND DISCUSSION

Synthesis of Titania Nanotubes

The effect of stirring time prior static hydrothermal

The effect of stirring time prior static hydrothermal. Fig. 1 shows the TEM images of the calcined TiO_2 powders resulted from 30, 60, and 120 min stirring time. It can be seen that generally, all stirring time resulted in nanotube morphology with an inner diameter of 1.5–3.5 nm and the outer diameter of 7–12 nm. The consistent morphology obtained at various pre-mixing time confirms that the transformation from nanoparticles to nanotubes hydrothermally is facilitated by mechanical stirring as the pre-treatment. Mechanical stirring is supposed to assist the completeness of the reaction through the efficient collisions among the more energetic particles. At 30 min stirring, the morphology of the resulted titania is a mixture of nanoparticles, nanosheets, and nanotubes, indicating incomplete transformation. It is assumed that when the reaction rate was insufficient, termination of the entire morphology evolution may occur at the intermediate stage, and intermediate products besides the final morphology were also produced. At 60 and 120 min stirring prior hydrothermal, entirely nanotubes were achieved. A similar

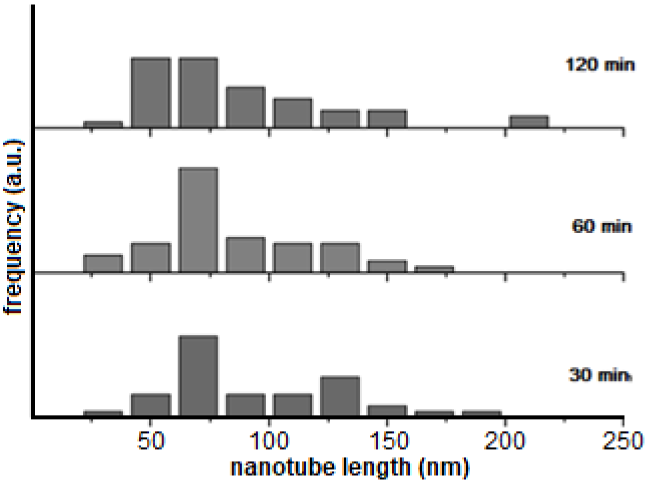


Fig 2. Nanotube length distribution derived from TEM images of the resulted TiO_2 at a various stirring time after static hydrothermal for 5 h at 150 °C

Table 1. Textural coefficients of the resulted TiO_2 prepared at a various stirring time prior static hydrothermal for 5 h at 150 °C

Stirring time (min) prior hydrothermal	The textural coefficient at specified d_{hkl} of anatase TiO_2					
	d_{101}	d_{004}	d_{200}	d_{105}	d_{211}	d_{204}
30	1.216	1.216	1.320	0.942	1.034	1.042
60	0.333	-	1.667	-	-	-
90	0.519	-	1.481	-	-	-
120	0.699	-	1.885	-	-	0.416

phenomenon is observed for the formation of titania nanotubes [4] and Bi_2Te_3 nanoplates [14] using dynamic hydrothermal process. The length of the tubes is also affected by the pre-treatment stirring, as shown in Fig. 2. It is increasing from 30 to 60 min stirring and decreasing at 120 min stirring. At 120 min pre-treatment stirring, the tube length distribution is also wider compare to the 30 and 60 min pre-treatment stirring.

The crystalline phases of the resulted titania were confirmed by XRD (Fig. 3). It can be seen that at 30 min pre-treatment stirring, the strong anatase (PDF 21-1272) peaks of the titania precursor are observed. These support the occurrence of spherical nanoparticle in the product as a result of partial morphology transformation. Diffraction peak for d_{200} of anatase crystalline phase increases as the pre-treatment stirring time increasing, indicating the formation of oriented anatase structure. The orientation is confirmed by the high textural coefficient at a diffraction plane of [200] (TC_{200}) for anatase (Table 1). The TC represents the texture of the particular plane, as the TC value at specified *hkl* exceeding 1, it implies the preferred growth at the corresponding plane [15]. This oriented structure detected in (200) plane is supposed to be responsible for the nanotubes formation.

Titanates polymorphs of sodium titanate ($Na_2Ti_3O_7$) and hydrogen titanate ($H_2Ti_3O_7$) are also contributing phases to the nanotubes morphology. It is confirmed by the broad peaks at around 2θ (°) of 10 from (001) and (200) planes of sodium titanate (PDF 31-1392) and hydrogen titanate (PDF 47-0561), respectively. Diffraction patterns of the resulted titania synthesized using 60 and 90 min pre-treatment stirring are similar to the one observed by Thu et al. [4]. At 120 min stirring, the resulted titania was composed by anatase and titanates. Raman spectra (Fig. 4) are shown to confirm the occurrence of titania polymorphs of the resulted titania nanotubes and to support the XRD data.

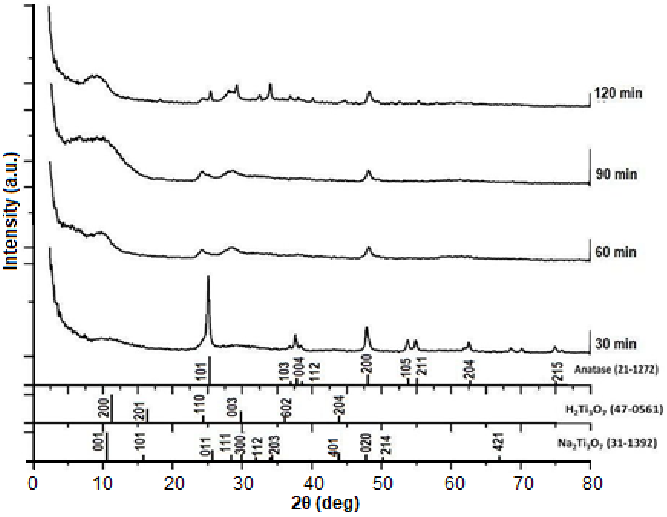


Fig 3. XRD patterns of the resulted TiO_2 at a various stirring time after static hydrothermal for 5 h at 150 °C. Line diffraction patterns of the possible crystalline phases are included

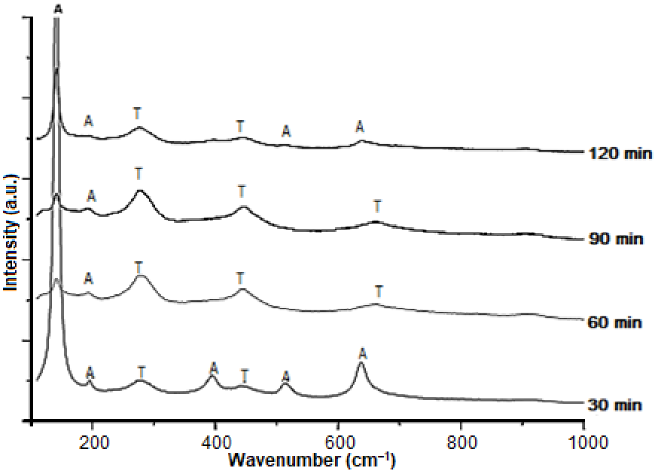


Fig 4. Raman spectra of the resulted TiO_2 at a various stirring time after static hydrothermal for 5 h at 150 °C

Table 2. Textural properties of the resulted TiO_2 prepared at a various stirring time prior static hydrothermal for 5 h at 150 °C

Stirring time (min) prior hydrothermal	Textural properties			
	ϕ_{inner} (nm)	ϕ_{outer} (nm)	S_{BET} (m^2/g)	V_p (cm^3/g)*
30	1.644	11.276	96.198	0.471
60	1.630	8.077	109.159	0.361
90	1.509	7.861	113.191	0.352
120	1.498	7.846	38.357	0.107
TiO_2 precursor			33.450	

* From desorption branch

Based on the Raman spectrum (Fig. 4), anatase crystalline phase of the titania precursor is the predominant phase for the resulted titania preparing using 30 min pre-treatment stirring. It is confirmed by strong peaks at ~138 and 638 cm^{-1}, weak peaks at 191, 393, and 513 cm^{-1}, and a very weak broad peak ~796 cm^{-1} [16]. There is no indication of the presence of others TiO_2 polymorphs, such as rutile, brookite or TiO_2 (B). The peaks at ~290 cm^{-1} are assigned to the vibration of Ti–O stretching [17] of titanate nanostructure, as well as the peak at ~448 cm^{-1} of internal vibration of TiO_6 octahedral. The very weak broad bands around 930 cm^{-1} assigned to a four-coordinate Ti–O vibration in the titanate structure [17] was appeared at titania resulted from 60 to 120 min pre-treatment stirring time. These results suggest that the structure of the synthesized titania is a mixture of anatase and $H_2Ti_3O_7$ titanate nanostructure, which is consistent with the XRD result. Transformation of the anatase nanoparticle precursor to the nanotube seems to occur for titania resulted from longer pre-treatment stirring time. Peaks responsible for titanate nanostructures (~290 and 448 cm^{-1}) are increasing as the pre-treatment stirring time increases. It is also supported by the peaks at 680 and ~930 cm^{-1}, for Ti-O-Ti stretching of edge-shared TiO_6 [17]. The anatase crystalline phase starts to reform at 120 min pre-treatment stirring, as confirmed by the intense Raman band at ~138 cm^{-1}.

The nitrogen adsorption-desorption isotherms of the resulted titania are shown in Fig. 5. The isotherm has an apparent hysteresis loop at P/P_0 = 0.4–1.0, indicating the presence of mesoporosity in the materials. The specific surface area (S_{BET}) are ranging from 38 to 113 m^2/g, while the pore diameters are about 7.8 to 11.3 nm. Those textural properties are listed in Table 2. The peaks shown in the inserted pore size distribution graph may correspond to the dimension of the nanotubes, the inner and outer diameter of the tubes. These are in coincidence to the TEM data (Fig. 1). The presence of spherical morphology, as observed in the resulted titania prepared at 30 and 120 min pre-treatment stirring, seems to decrease the surface area. However, all the nanostructures achieve higher surface area compared to the titania precursor. The trend on the pore volume also follows the diameter. It decreases as the stirring time increases. Then 60 min stirring was applied to study the effect of the hydrothermal time since the morphology of the resulted titania is completely nanotubes.

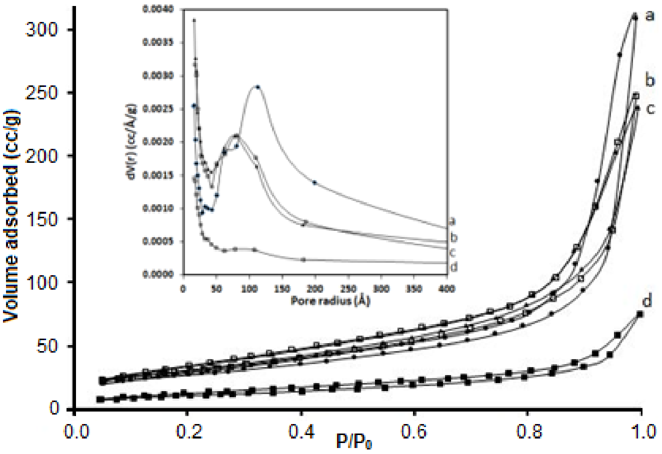
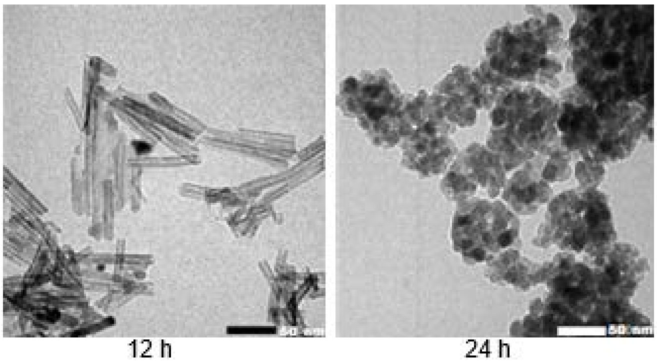


Fig 5. N_2 gas adsorption/desorption isotherm of the resulted TiO_2 at 30 min (a), 60 min (b), 90 min (c), and 120 min (d) stirring time after static hydrothermal for 5 h at 150 °C. The inset shows the corresponding pore size distribution from the desorption branch

The effect of hydrothermal time

Fig. 6 displays TEM images of the resulted titania synthesized by applying 60 min pre-treatment stirring for 5, 12, and 24 h hydrothermal treatment. It can be seen that nanotubes morphology can still be obtained up to 12 h hydrothermal. At 24 h hydrothermal, the resulted titania has transformed into nanospheres. The length distribution of the tubes depicted in Fig. 7 shows that 12 h hydrothermal shorten the nanotube. The XRD patterns of the resulted titania (Fig. 8) show that the anatase crystalline phase is getting very sharp at 24 h hydrothermal indicating high crystallinity of anatase. The Raman spectra (Fig. 9) have confirmed the predominant anatase crystalline phase for titania powder resulted from 24 h hydrothermal time. There is only a weak Raman band at ~290 cm^{-1} assigned for titanate (T). The Raman band at ~144 cm^{-1} for anatase vibration [16] is so strong that it is off-axis. Based on the factor group analysis, the 400 cm^{-1} peak is assigned to the B_{1g} mode; 640 cm^{-1} peaks can be attributed to the E_g mode; 520 cm^{-1} peaks can be attributed to the A_{1g} + B_{1g} modes, while the peaks at 195 and 144 cm^{-1} are assigned to the E_g modes [18].

The textural parameters of the resulted titania after 5 and 24 h hydrothermal are listed in Table 3. It can be



12 h 24 h

Fig 6. TEM images of the resulted TiO_2 at 150 °C for a various hydrothermal time after 60 min stirring prior hydrothermal. The image for 5h hydrothermal time has been presented in Fig. 1

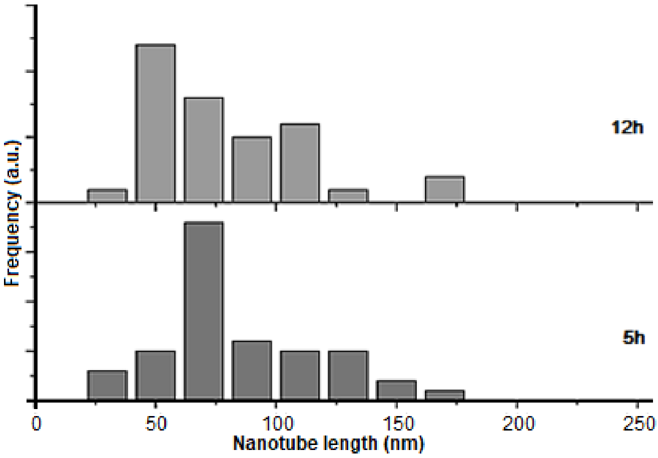


Fig 7. Nanotube length distribution derived from TEM images of the resulted TiO_2 at 150 °C for 5 h and 12 h hydrothermal time after 60 min stirring prior hydrothermal

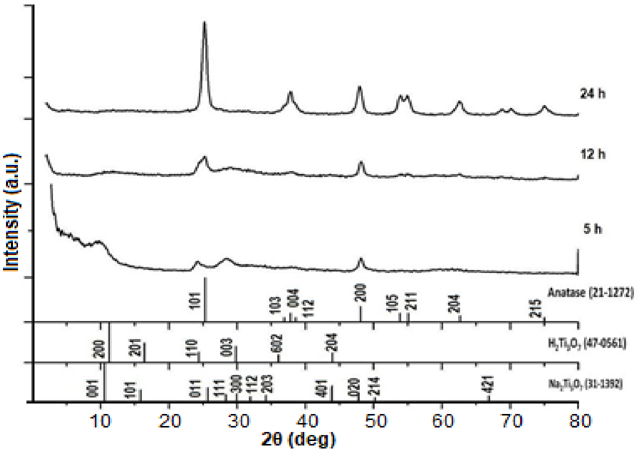


Fig 8. XRD patterns of the resulted TiO_2 at 150 °C for a various hydrothermal time after 60 min stirring prior hydrothermal. Line diffraction patterns of the possible crystalline phases are included

Table 3. Textural properties of the resulted TiO_2 prepared at 60 min stirring time prior static hydrothermal at 150 °C for 5 and 24 h hydrothermal time

Hydrothermal time (h)	Textural properties			
	ϕ_{inner} (nm)	ϕ_{outer} (nm)	S_{BET} (m^2/g)	V_p (cm^3/g)
5	1.634	8.077	109.159	0.361
24	1.806	2.903	78.395	0.171

seen that long hydrothermal time reduces the surface area, the outer diameter of the tubes, and the pore volume, as well. It is clear that nanotubes morphology contributes to high surface area titania. The N_2 adsorption/desorption isotherms depicted in Fig. 10 confirm the decrease porosity for the sample treated hydrothermally for 24 h. An apparent explanation could be due to the presence of prominent aggregation of the irregular titania spheres.

The effect of acid-washing only and acid- then neutral-washing of the as-synthesized titania powder is also compared. Fig. 11 shows the XRD patterns of the calcined samples. It can be seen that the combined acid- and neutral-washing of the as-synthesized titania powder resulted in higher anatase to titanate ratio compared to the acid-washing only powder. From the intensity of the XRD peaks corresponding to anatase and titanate, the percentage ratio of anatase to titanate was obtained. The ratio is 47 to 53% of anatase to titanate for the sample with acid-washing only and 57 to 43% for the combined washing sample. The specific surface area is also improved for the combined washing powder (Table 4).

Photocatalytic Activity

Photocatalytic activity of the nanotubes titania was tested toward photodegradation of methylene blue (MB) under illumination of UV- and Visible-light for 90 min under gentle stirring. The results are listed in Table 4 along with the corresponding calculated band gap and surface areas. Commercial TiO_2 used as the titania precursor was also tested for comparison. Samples tested were titania powders resulted from pre-treatment stirring for 60 min and hydrothermal treatment for 5 h applying acid- and combined acid-/neutral-washing and sample hydrothermally treated for 24 h after combined washing. Samples after combined washing treatment are denoted as neutral-washing samples.

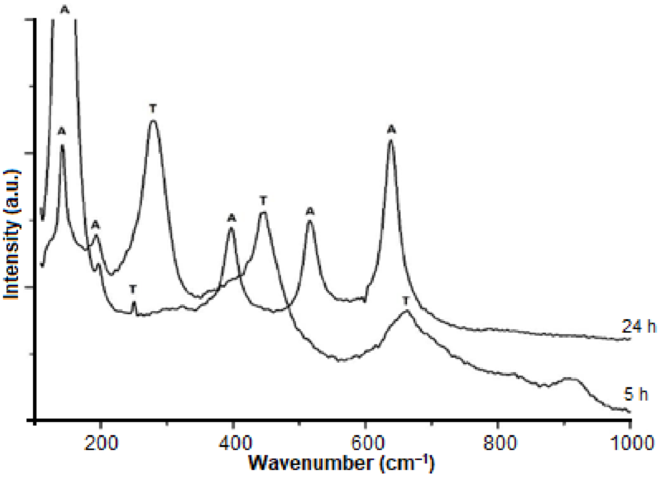


Fig 9. Raman spectra of the resulted TiO_2 at 60 min stirring time after static hydrothermal for 5 h and 24 h at 150 °C

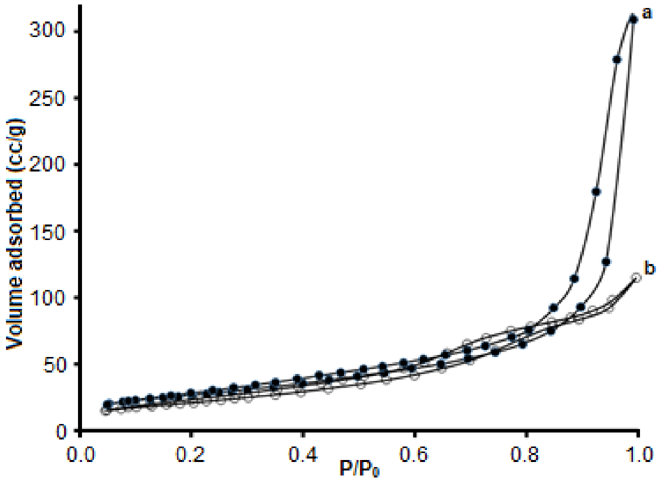


Fig 10. N_2 gas adsorption/desorption isotherms of the resulted TiO_2 at 150 °C for 5 h (a) and 24 h (b) hydrothermal time after 60 min stirring prior hydrothermal

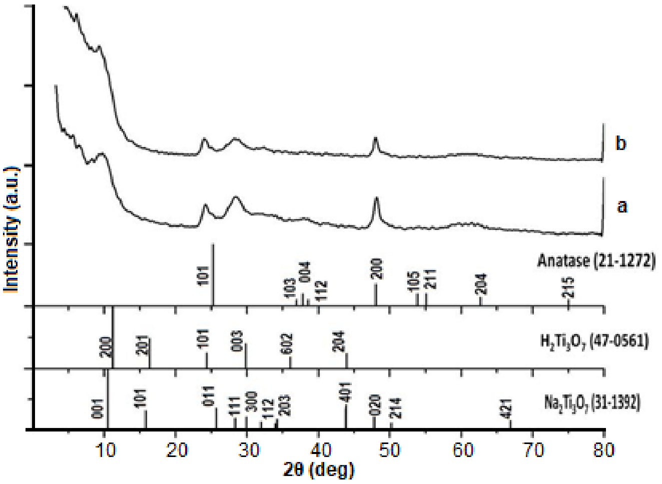


Fig 11. XRD patterns of the synthesized TiO_2 at 150 °C for 5 h by applying 60 min pre-treatment stirring and: (a) acid-washed, (b) acid- and neutral-washed

Table 4. Photocatalytic activity of some resulted TiO_2 under UV and Visible irradiation

Sample	S_{BET} (m^2/g)	Eg (eV)	Photocatalytic activity (%) Under UV illumination	Photocatalytic activity (%) Under Visible illumination
TiO_2 (commercial)	33.450	3.21	74.81	4.58
TiO_2 60 min stirring, 5 h hydrothermal	109.159	3.11	62.60	49.62
TiO_2 60 min stirring, 5 h hydrothermal neutral washed	116.023	3.15	54.96	36.64
TiO_2 60 min stirring, 24 h hydrothermal neutral washed	74.695	3.16	44.27	31.30

Based on the photocatalytic test, it is clear that the nanotubes titania comprising of anatase and titanate crystalline phases has comparable performance to the commercial titania which has fully anatase domain. All the synthesized titania resulted in photoactivity of about 44 to 63% under UV illumination compared to the commercial titania of ~75%. It is widely known that anatase is the most photoactive crystalline phase of TiO_2 [19-20]. However, it is worthy to note that the nanotubes titania demonstrates reasonable photoactivity under visible-light irradiation. The synthesized titania with nanotube morphology have shown higher photoactivity under visible irradiation (Table 4 for TiO_2 60 min stirring, 5 h hydrothermal (~50%) and TiO_2 60 min stirring, 5 h hydrothermal neutral washed (~37%)) than those of titania nanoparticle with irregular spheres morphology (TiO_2 60 min stirring, 24 h hydrothermal neutral washed) of ~31% and commercial TiO_2 (~5%). These results are in accordance with recent results of some researchers [21-23]. The photoactivity can be ascribed due to the red-shifted band-gap of the morphology engineered titania nanostructures. All the tested titania powders exhibit narrower band-gap compare to the commercial TiO_2 powders. The variability of the photoactivity is then may be related to the variability on the surface area. The higher the surface area, the higher the photoactivity of the resulted in nanostructured titania to degrade MB [24].

■ CONCLUSION

To conclude, it has been shown that pre-treatment stirring before hydrothermal reduces the hydrothermal time to produce nanotube titania. Nanotube morphology along with nanosheets and nanospheres can be obtained by applying 30 min pre-treatment stirring prior hydrothermal treatment at 150 °C for 5 h. It has also revealed that 60 min pre-treatment stirring is sufficient to obtain only nanotubes morphology with a mixture of crystalline phases of anatase and titanate. Longer hydrothermal time induced the morphology transformation back to the nanospheres, resulting in a significant decrement of the titania surface area. The photocatalytic test under UV- and Visible-light has shown that the nanotubes titania exhibit excellent photoactivity under both irradiation sources. Hence, these results inspire a route to derive visible-photosensitive catalyst by altering the morphology of titania in nanoscale.

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