

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of Titania Nanotubes (TNTs)

4.1.1 Effect of Reaction Time and Acid Shaking Process

Titania precursors were microwave heated for 30, 60, 90, and 120 min at 150 °C. SEM images (Figure 4.1) show the development of TNTs synthesized without shaking in 0.1 M HCl, meaning that there were still Na⁺ ions in the tubes. Ma *et al* (2004) described that 1D nanotube structure was achieved by rolling 2D nanosheet structure. The intercalation of Na⁺ ions created the stacking of unilamellar nanosheets that further exfoliated to independent sheets stabilized by the Na⁺ ions. Rolling of nano sheets into nanotubes was formed due to the reducing of the Na⁺ ions in the system by washing process (Wu *et al.*, 2007). During 30 min microwave irradiation (Figure 4.1(a)) the sample exhibited fusing of primary particles of the precursor and started to form stacking of nanosheets since there was not enough time for the Na⁺ ions to fully intercalate the titania layers. While increasing the reaction time, the random oriented tube-like structure was formed after 60 min and beyond. The tubes length was inspected increasing (Figure 4.1(b)). At 90 min heating, the nanosheet structure no longer existed. The length of the nanotubes was greatly extended, resulting in a random woven-like structure spread throughout the particle (Figure 4.1 (c)). Finally, 120 min reaction time resulted in fusing nanotubes and agglomerate particles (Figure 4.1 (d)).

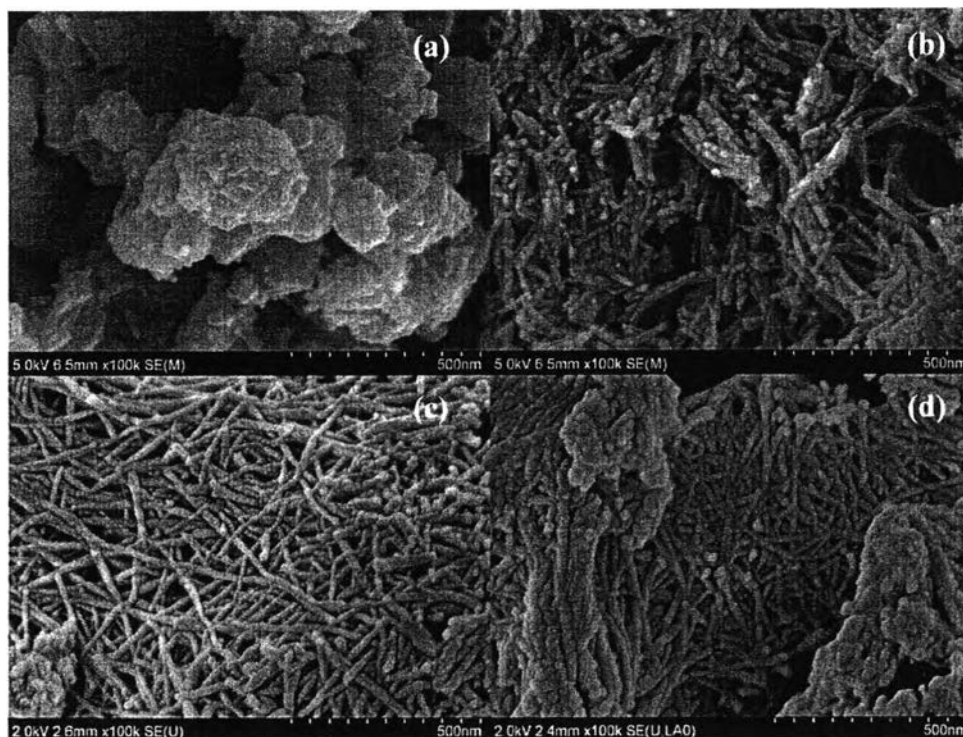


Figure 4.1 SEM images of Na-TNTs samples prepared for various reaction times: (a) 30, (b) 60, (c) 90, and (d) 120 min.

X-ray diffraction spectra (Figure 4.2) revealed sharp peaks of anatase phase and small amount of rutile phase at 30 min heating time. The longer reaction time resulted in gradual reduce of anatase and rutile titania phases while new peaks at $2\theta \sim 10^\circ$, 24° , 28° and 48° were observed. The peaks were resembled to the monoclinic $\text{Na}_2\text{Ti}_3\text{O}_7$ (100), (011), (300), and (020), respectively (Qamar *et al.*, 2008), indicating the changing process from anatase particles to titanate tube structure. The atomic percent of Na^+ ion from EDX measurement was found between 5.12 – 8.55% (Table 4.1) lower than theoretical Na content calculated from the chemical formula (16.66%). The lowered Na atomic content resulted in the occurrence of ion exchange process during washing precipitate with distilled water.

Table 4.1 Summary of sodium content in TNTs from the acid-shaken and unshaken samples

Reaction Time (min)	HCl Shaking	% Na ⁺ content (each point)
30	yes	0.04,-0.09,-0.01
60	yes	-0.01,-0.19
90	yes	-0.05,0.01
120	yes	0.05, 0.24, 0.50
90	-	8.50, 7.44
120	-	6.34, 7.87, 8.55, 7.97, 7.02, 5.12

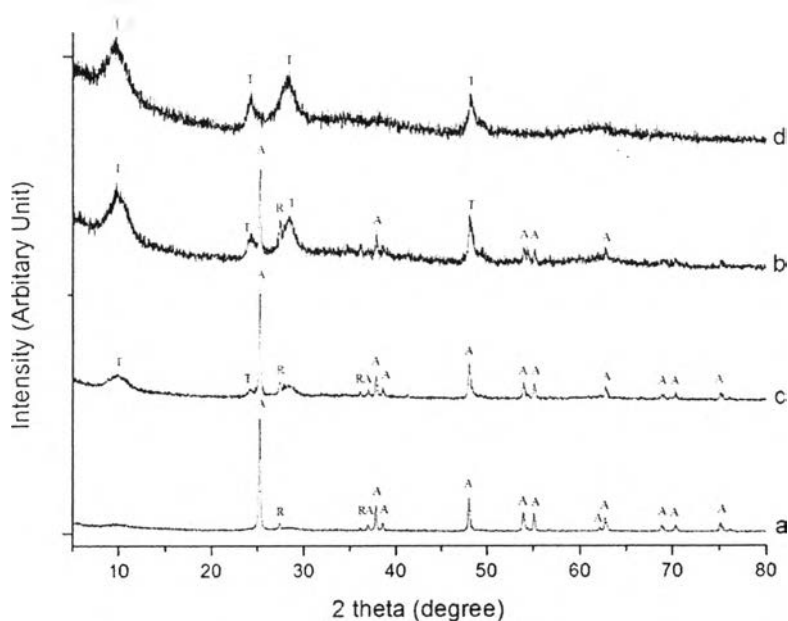


Figure 4.2 X-ray diffraction spectra of Na-TNTs samples synthesized for various times: (a) 30, (b) 60, (c) 90, and (d) 120 min (annotation A; anatase, R; rutile, and T; titanate).

The samples synthesized by shaking in 0.1 M HCl solution exhibited different results. The tube structure could be seen at 30 min reaction time along with agglomerated particles (Figure 4.3 (a)), indicating the influence of acid shaking in the nanotube formation by removing all Na⁺ ions from the sample, as confirmed by

the EDX results (Table 4.1), Na^+ ion was all exchanged by H^+ ion during the acid shaking process. This was in accordance with Kasuga *et al.* (1999) who indicated that the washing process was a factor to obtain the tubular structure. Fewer particles were formed in the 60 min reaction time sample and vanished in 90 min sample probably due to enough time for the tubes to be formed. The nanotubes grew longer toward random woven-like structure (Figure 4.3 (b), (c)) similar to non shaking samples. At 120 min, the nanotubes were fused together and formed a ribbon-like structure (Figure 4.3 (d)). For XRD spectra of the as synthesized acid shaking samples (Figure 4.4), anatase and rutile titania phases were absent. Only titanate phase appeared in all reaction time samples. It can be observed the weakened intensity of peaks at 10° (100) and 28° (300) since, both peaks are formed by the diffraction of planes along a axis, indicating that the acid shaking changes the structure of the nanotubes. This change is due to the ion exchange process where the Na ions were substituted by smaller size H ions (Qamar *et al.*, 2008).

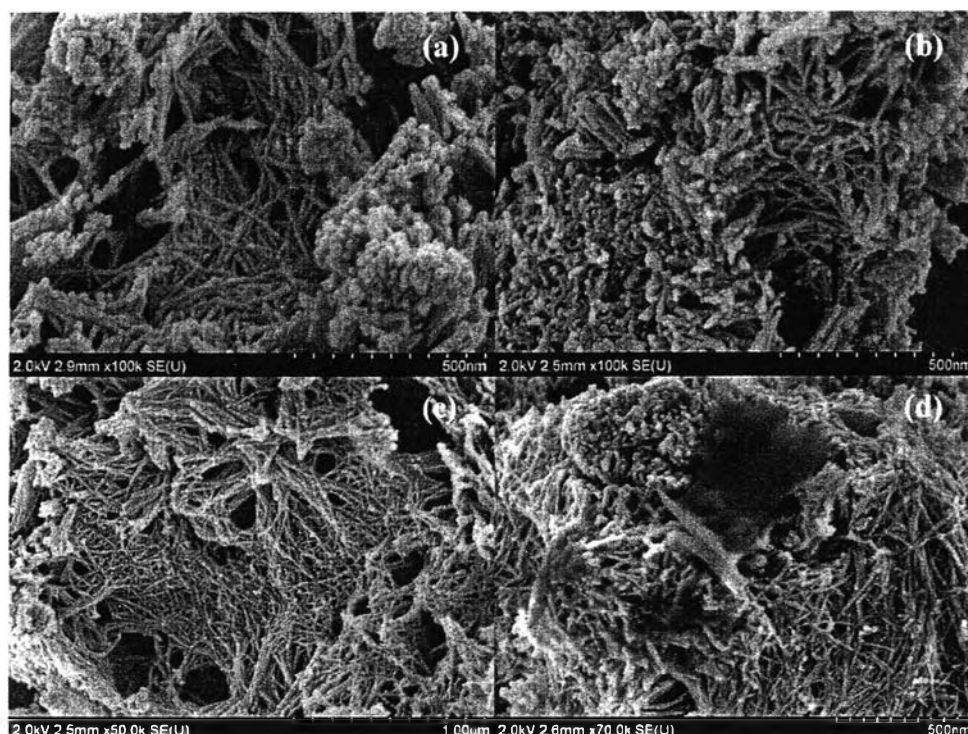


Figure 4.3 SEM images of H-TNTs samples prepared for various reaction times: (a) 30, (b) 60, (c) 90, and (d) 120 min.

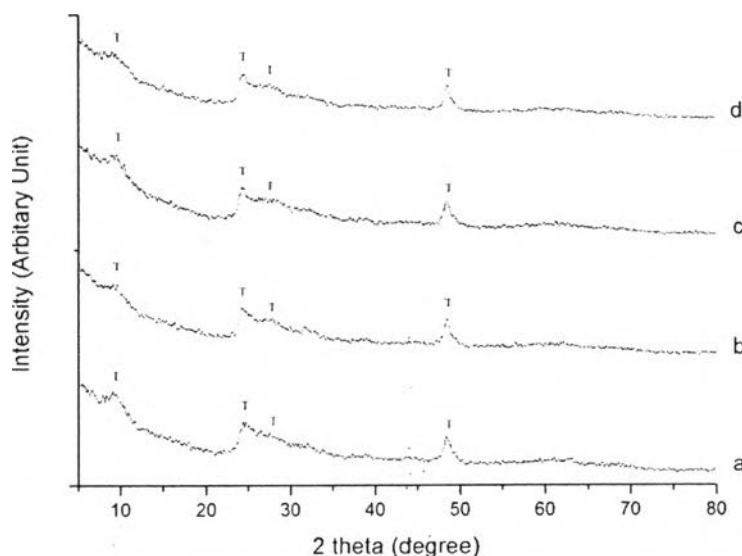


Figure 4.4 X-ray diffraction spectra of H-TNTs samples synthesized for various times: (a) 30, (b) 60, (c) 90, and (d) 120 min (annotation T; titanate).

4.1.2 Effect of Reaction Temperature

It is believed that the formation of the nanotubes would form at adequate thermal energy (Seo *et al.*, 2008). The reaction temperature was varied from 120° to 180 °C with 30 °C intervals for 90 min to observe its effect on the nanotubes formation. It was found a great effect on the nanotubes formation. There were only agglomerate particles present in the 120 °C sample (Figure 4.5 (a)) due to deficient energy provided for the tubes to be formed. The nanotubes were clearly presented at 150 °C while 180 °C exhibited dense and fused nanotubes (Figure 4.5 (a), (b)). This was similar to the samples carried out for 120 min reaction time (Figures 4.1 (d) and 4.3 (d)), exhibiting the changing of the nanotubes to another form.

From XRD results in Figure 4.6, 150 ° and 180 °C showed the same pattern as the acid shaking samples, exhibiting peaks corresponded to the titanate phase at 2θ around 10°, 24°, 28° and 48°. At the 120 °C condition, the anatase titania phase could be observed along with the titanate phase, referring the anatase transformation to the titanate.

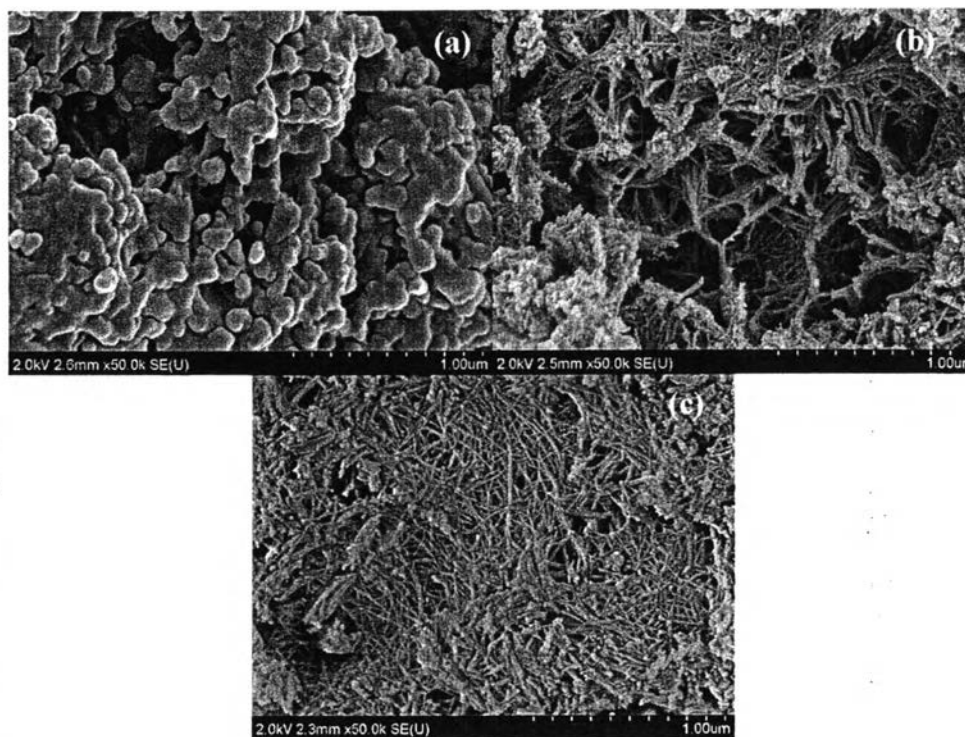


Figure 4.5 SEM images of H-TNTs samples synthesized at various reaction temperatures: (a) 120°, (b) 150°, and (c) 180 °C.

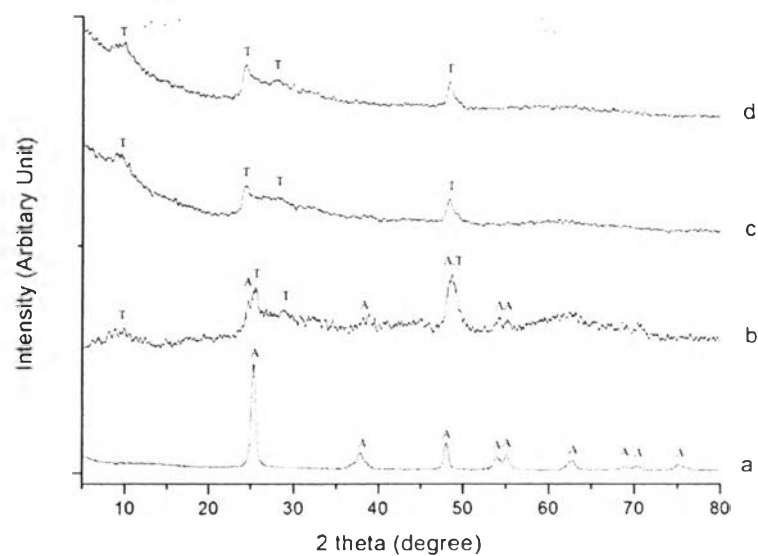


Figure 4.6 XRD spectra of titania precursor (a) and H-TNTs samples synthesized at various reaction temperatures: (b) 120°, (c) 150°, and (d) 180 °C.

4.2 Structure of Synthesized Titania Nanotubes

Transmission electron microscope was employed to investigate nanotube dimension in Na-TNTs and H-TNTs synthesized at 150 °C for 90 min due to the nanotube formation and uniformity according to SEM and XRD results. The images presented open ended hollow tubular structure in both samples. However, the close ended tubes can also be observed in Na-TNTs sample (Figure 4.8(a)). Together with SEM and XRD results, it could be confirmed the formation of the nanotube. The acid shaken and unshaken samples exhibited random groups (Figures 4.8 (b) and (d)). Na-TNTs (Figure 4.8 (a)) had multiple shells of 3 layers inspected from TEM showing both inner and outer diameters around 5 and 9 nm, respectively. The inter-shell spacing of Na-TNTs was calculated to be 7.4 Å resemble with the spacing between $(\text{Ti}_3\text{O}_7)^{2-}$ layers of 7.8 Å. (Ou *et al.*, 2007). The H-TNTs obtained from ion exchanged Na-TNTs (Figure 4.8 (c)) exhibited a larger outer diameter (12 nm) while still keeping the inner diameter at 5 nm consistent with the work by Morgado *et al.* in 2006. This can be explained by SAED patterns of Na-TNTs and H-TNTs (Figure 4.7), showing that the ion-exchange increases the spacing from 1.79 Å to 1.84 Å, resulting in the enlargement of H-TNTs outer diameter. The H-TNTs spacing of 1.84 Å was in accordance with the $(\text{Ti}_3\text{O}_7)^{2-}$ octahedral interlayer spacing of 1.875 Å.

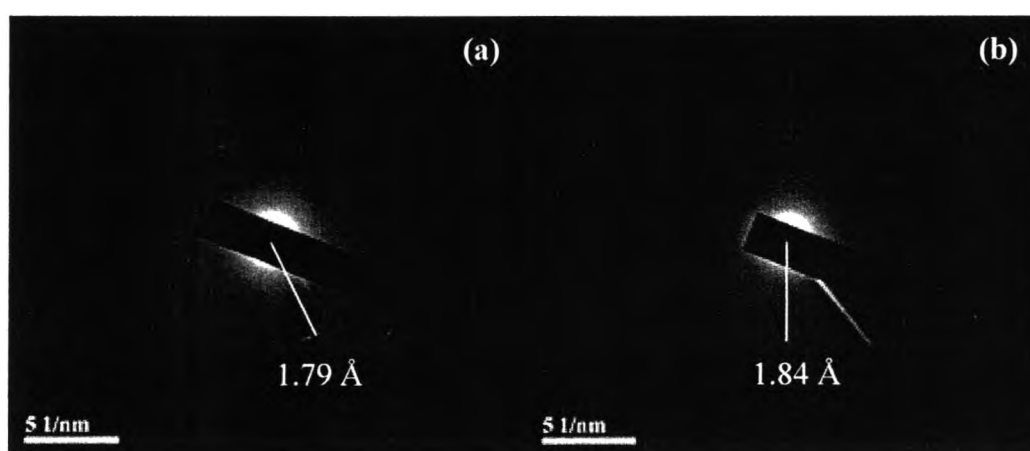


Figure 4.7 Selected area of electron diffraction (SAED) of Na-TNTs (a) and H-TNTs (b).

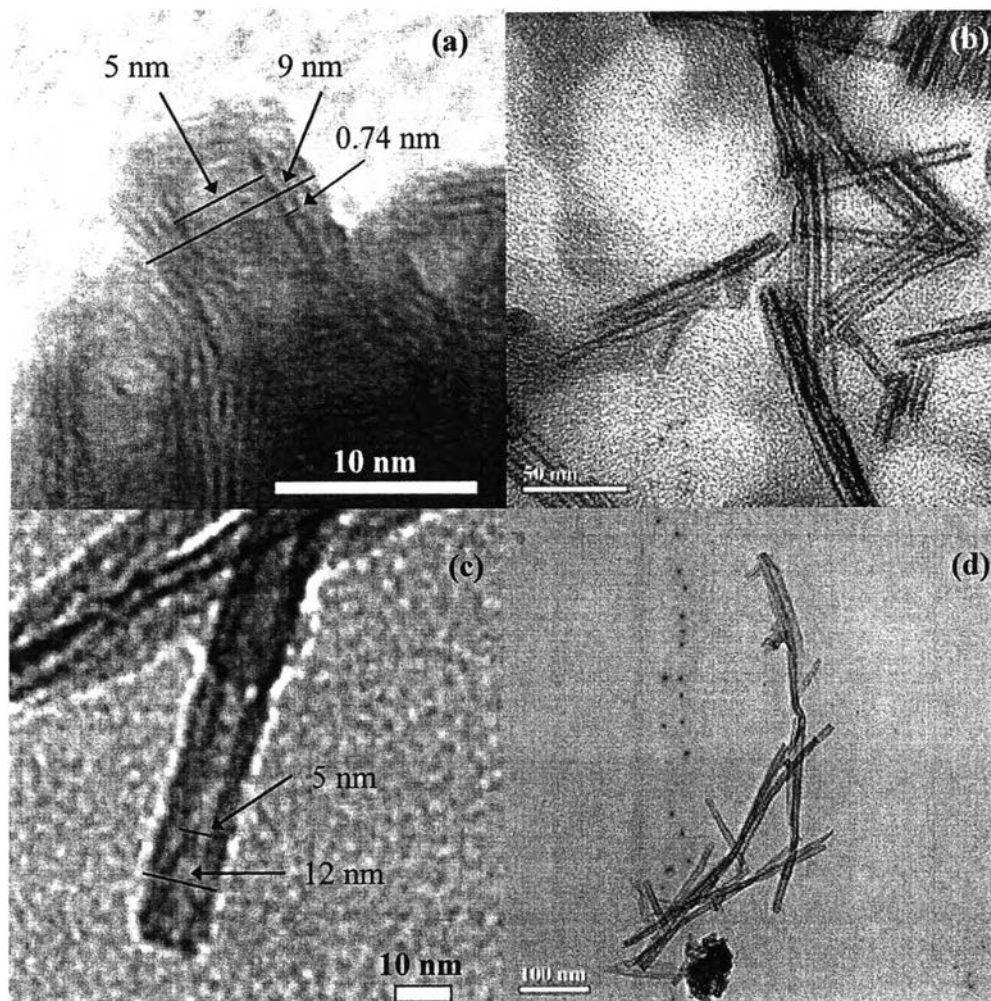


Figure 4.8 TEM micrographs of Na-TNTs (a), (b) and H-TNTs (c), (d).

BET surface area, pore volume, and pore size were given by analysis of nitrogen adsorption-desorption isotherms (Table 4.2). N_2 adsorption-desorption isotherm of titania precursor, H-TNTs, and Na-TNTs (Figure 4.9) were classified as a type H3 hysteresis loop (IUPAC classification), corresponding to almost formation of multilayer adsorption. The surface area of the titania precursor was $81.97 \text{ m}^2/\text{g}$. As can be seen from the table, the surface area, the pore volume, and the pore diameter increased with the reaction time. It is worth noticed that the surface area and the pore volume were lower for the 90 min sample, attributed to the weak nanotubular structure, causing the destruction of layered titanate structure (Lee *et al.*, 2010). However, the 90 min sample showed the most nanotube content in SEM micrographs

(Figures 4.1 and 4.3). Pore diameter data of Na-TNTs irradiated for 90 min (2.891 nm) did not exceed the inspected inner diameter (5 nm), as can be seen from TEM micrograph (Figure 4.8). However, the H-TNTs pore diameter was 7.420 nm larger than the inner diameter. This was presumably due to the differences in nanotubes dimensions, resulting from the ion-exchange of large sodium cations with small protons, as also mentioned by Ribbens *et al.* (2008). However, there should be further studies in this relation to prove the assumption. The pore size distribution of the titania precursor in Figure 4.10 (a) presented the diameter in a range between 10-100 nm. After hydrothermal process, the samples were improved in uniformity, showing mono-dispersion of nanotubes having maximum diameter around 10 nm in the samples synthesized for 60, 90, and 120 min (Figure 4.11 (c), (d), (e)). This was in line with the outer diameter of H-TNTs obtained from TEM around 12 nm. While 30 min sample exhibited maximum diameter around 7 nm, confirming the low nanotube formation. The acid shaking process affected very much to the pore size distribution, showing a shift of the peak from 5 nm to 10 nm for 90 min Na-TNTs sample (Figure 4.10 (f)), consistent with the increase of the outer diameter observed by TEM (Figure 4.8).

Table 4.2 Specific surface area, pore volume, and pore diameter of titania precursor and TNTs samples.

Reaction time (min)	BET surface area (m ² /g)	Pore volume (mL/g)	Pore diameter (nm)
0 (precursor)	81.97	0.3008	8.885
30	277.5	0.7472	3.632
60	370.6	1.142	6.162
90	313.6	0.9116	7.420
120	396.1	1.218	6.163
90 (non acid shaking)	175.6	0.8350	2.891

The results also presented that the acid shaking process increased the surface area, the pore volume, and the pore diameter in 90 min sample. According to the literature (Morgado *et al.*, 2006), the possible reasons for increasing in the surface area and the pore volume with a decrease in the Na content of TNTs were an increase in nanotube yield and average internal diameter and/or a decrease in wall thickness and skeletal density of the TNTs structure.

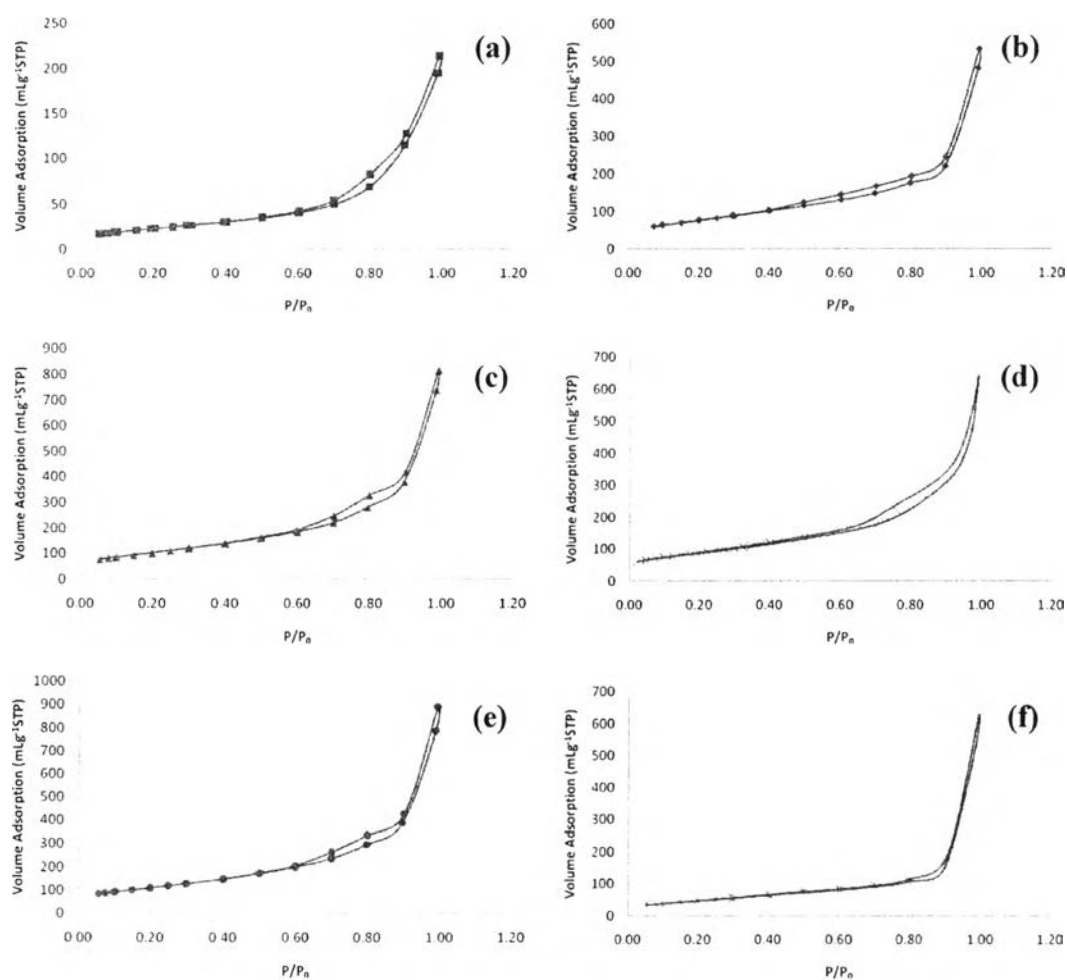


Figure 4.9 The N₂ adsorption-desorption isotherms of titania precursor (a), H-TNTs synthesized at 150 °C for 30 (b), 60 (c), 90 (d), 120 min (e), and Na-TNTs synthesized at 150 °C for 90 min (f).

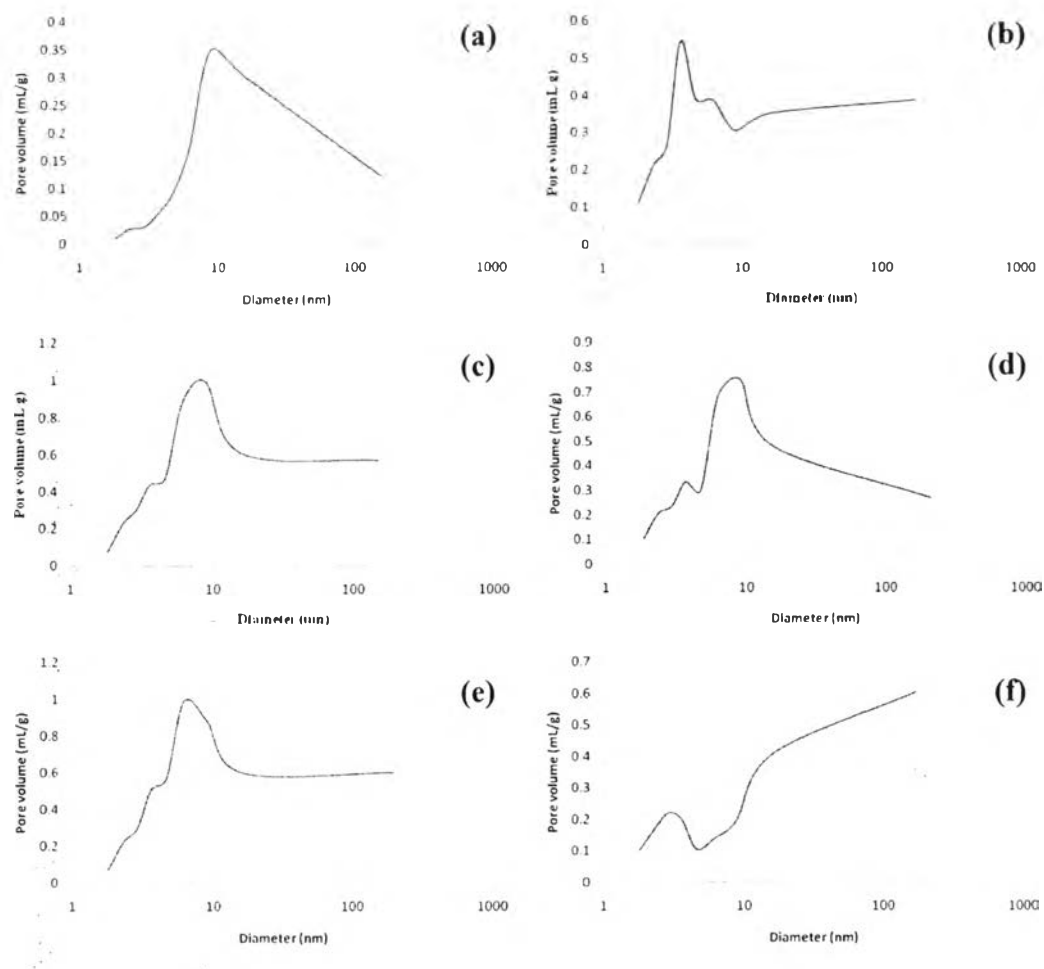


Figure 4.10 Pore size distributions of titania precursor (a), H-TNTs synthesized at 150 °C for 30 (b), 60 (c), 90 (d), 120 min (e), and Na-TNTs synthesized at 150 °C for 90 min (f).

4.3 Photocatalytic Degradation of 4-Nitrophenol

The photocatalytic activity of TNTs, annealed TNTs, and titania (anatase) precursor was studied with the UV-irradiated degradation of 4-nitrophenol. The selected TNTs was from the 150 °C 90 min acid shaking sample, in which some of it went through annealing at 400 °C for 1 h to obtain the TNTs having the anatase phase because this phase is well known as a good photocatalyst (Ribbens *et al.*, 2008).

The annealing process successfully provided anatase titania (Figure 4.11 (b)) while maintaining nanotube structure (Figure 4.11 (a)). Adsorption-desorption isotherm and poresize distribution were the same pattern. However, the surface area and the pore diameter were decreased significantly (Table 4.3) owing to the collapsing of the nanotube shell and growing of the anatase titania.

However, the results exhibited non photocatalytic activity, as compared with a blank batch (Figure 4.12) while the titania precursor showed a gradual decreasing of 4-nitrophenol concentration (34–12 ppm in 4 h). This could be explained by 2 reasons, first, the H-TNTs structure was ascribed to $H_2Ti_3O_7$ which had a band gap energy 3.52 eV higher than anatase titania 3.22 eV (Wang, 2006), resulting in harder electron excitation, and the other is the high electron-hole recombination process of the nanotube structure due to the fact that the nanosize structure exhibited inefficient electron-hole separation (Carp *et al.*, 2004).

Table 4.3 Specific surface area, pore volume, and pore diameter of H-TNTs synthesized at 150 °C for 90 min before and after annealing.

Sample	BET surface area (m^2/g)	Pore volume (mL/g)	Pore diameter (nm)
H-TNTs	313.6	0.9116	7.420
Annealed H-TNTs	196.3	0.9061	2.891

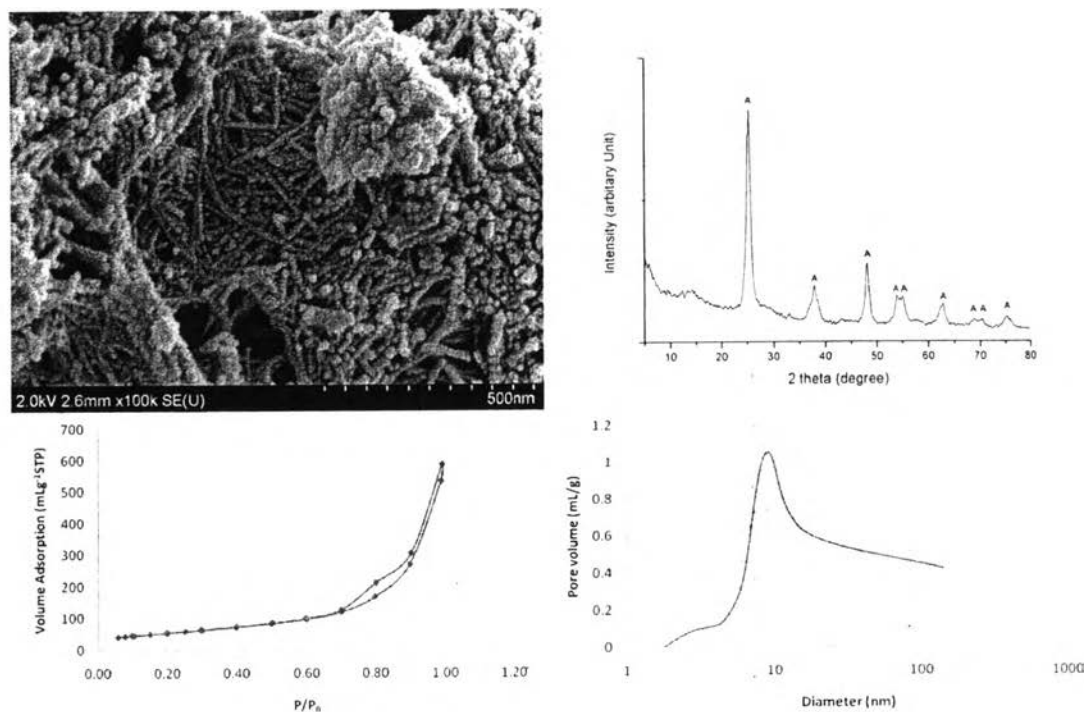


Figure 4.11 Instrumental results of the annealed H-TNTs; SEM (a), XRD (b), BET isotherm (c), and pore size distribution (d).

Table 4.4 The concentration of 4-nitrophenol in samples sampling at a given UV irradiation time.

Time (min)	Concentration (ppm)			
	blank	anatase	TNTs	Anneal TNTs
Initial	35.38	34.42	36.71	36.18
Start	34.32	33.77	37.30	31.98
30	35.31	31.81	37.60	37.25
60	34.28	28.91	38.07	37.33
90	35.38	25.20	37.83	37.48
120	35.09	22.67	39.42	32.45
150	34.66	19.96	38.18	37.45
180	35.08	17.17	39.22	33.16
210	34.68	14.55	39.35	34.94
240	34.32	12.05	39.55	36.32

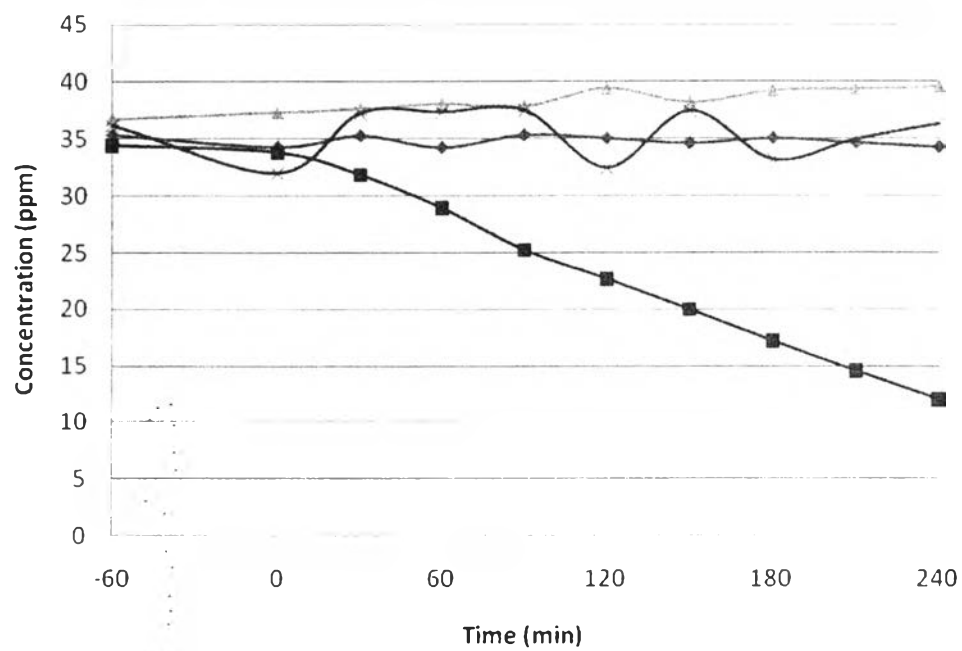


Figure 4.12 Photocatalytic degradation of 4-nitrophenol using various catalysts: (◆) blank, (■) titania precursor, (▲) TNTs and (×) Annealed TNTs.