

Rapid synthesis of TiO₂ nanotubes via microwave-assisted hydrothermal method

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Microwave irradiation was used as a tool for shortening the reaction time in the hydrothermal process for the fabrication of TiO₂ nanotubes. The variation of microwave hydrothermal treatment time from 1 h to 4 h was implemented to investigate the effects of microwave reaction time on the nanotubes formation. Many different spectroscopic and physicochemical analysis, such as X-ray diffraction (XRD), Raman spectroscopy (RS), Transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) and UV-Vis DRS spectroscopy, were performed to characterize the microwave hydrothermally synthesized TiO₂ nanotubes (TNTs). The results demonstrated that the TNTs preparation time can be significantly reduced to 4 h by the use of microwave hydrothermal process under the optimized microwave conditions of 150 °C, 195 W and the rotation speed of 300 rpm. The obtained nanostructured TiO₂ products with chemical formula Na_{2-x}H_xTi₂O₅·H₂O indicated larger BET surface area over 200 m²·g⁻¹ as compared to 56 m²·g⁻¹ of the TiO₂-P25 precursor. The study revealed the high degree of dye adsorption by TiO₂ nanotubes during the photocatalytic dye degradation experiments.

Key words: TiO₂, Nanotubes, Hydrothermal method, Microwave, Photocatalytic activity.

Introduction

In recent years, TiO₂ nanotubes (TNTs) have been widely studied and drawn much attention because of their unique properties such as high surface area, low cost, chemical stability, and non-toxicity [1, 2]. There are three common approaches to prepare TNTs such as templating, anodic oxidation, and hydrothermal method [1-3]. Out of these methods, hydrothermal treatment process has revealed a considerable attention because of its simple route to obtain the relatively large amount of the product and easy modification to enhance the applicability of the synthesized nanostructured materials [1, 3, 4]. However, one of the main drawbacks of this method is the prolonged hydrothermal processing time. In a traditional hydrothermal method, thermal energy is to be supplied via sand bath or oil bath so that the heat is transferred to the walls of the reactor and then passes to the reaction mixture. In other words, hydrothermal method requires much longer time (usually several days) and higher energy (over a thousand Watts) to achieve the desired conditions for the reaction [2, 4-12]. In addition, another disadvantage of the conventional hydrothermal method is the difficulty in controlling the reaction temperature of the sample container to reach the thermal equilibrium. The reason is that the heat source used in this process needs to be taken out to decrease the internal temperature. Consequently, the local overheating phenomenon may occur and break down the structure of

the products [6].

Recently, many groups of researchers have used microwave assisted hydrothermal process to reduce the reaction time significantly [13, 14, 15]. In the microwave irradiation process, power is not wasted to heat all oven or bath, the reactants and solvents get energy through the interaction of molecules with the electromagnetic field [6]. Using a microwave hydrothermal method, therefore, consumes lower power (hundreds of Watts) and shortens the reaction time [4].

In this study, TiO₂ nanotubes were successfully prepared via hydrothermal reaction by using the microwave as an internal heating source. This research is expected that it would be helpful for further understanding the microwave hydrothermal process to shorten reaction time for the synthesis of TNTs.

Experimental Procedure

Precursors used to prepare TNT were TiO₂-P25 Degussa consisting of 20% rutile phase and 80% anatase phase with an average particle size of 20 nm, and NaOH (98% purity, Samchun chemical). All chemicals were of analytical grade and used without further purification. The synthesis process was started by adding 2 g of TiO₂-P25 in 100 ml of 10 M NaOH aqueous solution. And then, the obtained mixture was stirred by a magnetic stirrer at room temperature for 15 min to form a suspension. Next, this suspension was put in ultrasound for 10 min to break any agglomeration. After that, it was transferred into a Teflon vessel reactor to begin for the microwave assisted hydrothermal treatment at 150 °C, 195 W and rotation speed 300 rpm for 1 h to

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4 h. The suspension obtained after completion of hydrothermal process was adjusted to pH 7 with 5 N HCl aqueous solution [13]. Then, the solid products were repetitively washed with distilled water and centrifuged to eliminate any residual NaCl. Finally, the samples were dried in a freeze dryer (EYELA, FDU-2100) for 24 h at -80°C . The products were denoted as TNT1, TNT2, TNT3, and TNT4 for 1 h, 2 h, 3 h, and 4 h of the microwave hydrothermal treatment time, respectively.

The crystal structure of all samples was analyzed by X-ray diffraction (XRD, RINT-2200, Rigaku) patterns from 5° to 70° using a monochromatized Cu-K α ($\lambda = 1.54 \text{ \AA}$) radiation. The microstructure and morphology were determined by FESEM (JSM-7000F, Jeol) and transmission electron microscopy (TEM, JEM-2100F, Jeol). Raman spectroscopy (LABRAM HR800, Horiba coupled to an Olympus BX41 optical microscope) was used to measure Raman spectra. The specific surface area of TNTs was characterized by N_2 adsorption-desorption using Brunauer-Emmett-Teller (BET) method (ASAP 2010 Micromeritics Instrument Corporation). The band gap was measured by UV-Vis diffuse reflectance spectroscopy (UV-VIS, V-500, Jasco).

Photocatalytic activity of the prepared samples was evaluated in 20 ppm aqueous methylene blue (MB) dye solution with 0.02 g TiO_2 nanotube under simulated solar light irradiation. Firstly, a suspension of 20 ml MB solution and 0.02 g prepared samples was stirred in the dark for 60 min to determine the adsorption degree of TiO_2 nanotubes. After that, this suspension was irradiated under the simulated solar light source (portable solar simulator PEC-L01, Pecell 200 W) (Am 1.5G) for 240 min. All the experiments were carried out at the atmospheric temperature and pressure. The change in the concentration of MB solution within the reaction time was measured by a UV-Vis spectrophotometer (Optizen-2120UV, Mecasys) and the total organic carbon (TOC) was analyzed by TOC-L CPH/CPN (Shimadzu).

Results and Discussion

Fig. 1 shows FE-SEM images of TiO_2 -P25 and the synthesized TNT samples. It is observed that the microwave irradiation time in a hydrothermal process strongly effected to the structure changes of the precursor P25. Fig. 1(a-d) show the morphological changes of the precursor TiO_2 -P25 after 1 h to 4 h of microwave hydrothermal reaction, respectively. The particle morphology of pristine TiO_2 material was disappeared and transformed into a mixture of different TiO_2 nanostructures. The distinct nanostructural morphologies TiO_2 products were not clearly observed by FE-SEM, therefore, TEM investigation was performed to identify the TiO_2 nanostructures formed at the different time in the microwave hydrothermal process.

The TEM images of TNT samples are shown in Fig. 2. The TEM images show more precisely the changes of the TNT structures as a function of microwave hydrothermal process time. It is clearly observed that the TNT1, TNT2 and TNT3 samples have a nanowire-like shape. The length of these nanowires ranges about several hundreds of nanometers. For TNT4, non-

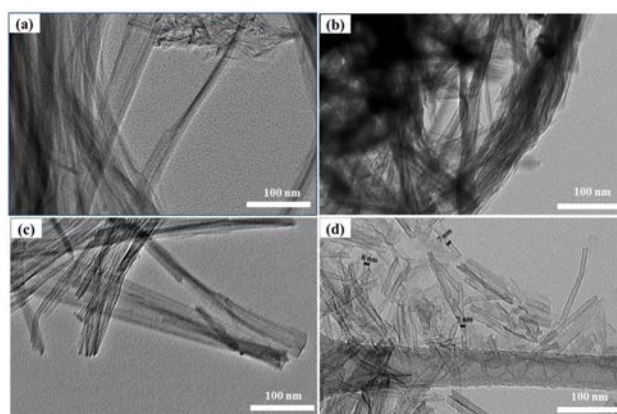


Fig. 2. TEM images of samples: (a) TNT1, (b) TNT2, (c) TNT3, and (d) TNT4.

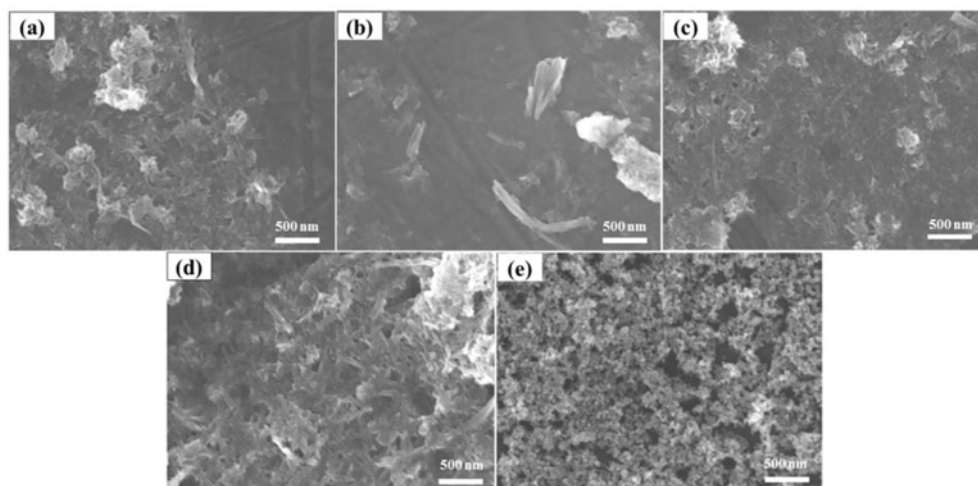


Fig. 1. FE-SEM images of samples: (a) TNT1, (b) TNT2, (c) TNT3, (d) TNT4, and (e) TiO_2 -P25.

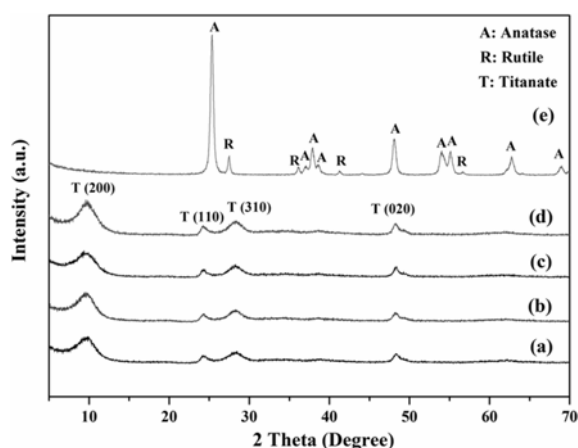


Fig. 3. XRD patterns of samples: (a) TNT1, (b) TNT2, (c) TNT3, (d) TNT4, and (e) TiO₂-P25.

Table 1. The spacing between diffraction planes (d) and the incident angle (θ) of synthesized TNTs samples with reference to H₂Ti₂O₅ · H₂O (JCPDS card No. 47-0124).

	hkl	(200)	(110)	(310)	(020)
H ₂ Ti ₂ O ₅ · H ₂ O	2 θ (°)	9.7	24.0	27.8	48.0
	d (Å)	9.04	3.70	3.20	1.89
TNT1	2 θ (°)	9.8	24.3	28.5	48.3
	d (Å)	8.98	3.66	3.13	1.88
TNT2	2 θ (°)	9.50	24.4	28.3	48.3
	d (Å)	9.30	3.64	3.15	1.88
TNT3	2 θ (°)	9.36	24.3	28.3	48.4
	d (Å)	9.44	3.66	3.15	1.88
TNT4	2 θ (°)	9.6	24.3	28.4	48.2
	d (Å)	9.20	3.66	3.14	1.89

uniformed nanotubes were observed with a distinct reduction in length and diameter of the nanotubes in comparison to TNT3. The measured length and diameter of the formed nanotubes are around 100 nm and 8 nm, respectively in TNT4.

Fig. 3 shows the XRD patterns of TiO₂-P25 precursor and the prepared TNT samples. The precursor TiO₂-P25 powder consisted of a mixture of rutile and anatase phases with high crystallinity. However, the obtained TNT products demonstrated a low degree of crystallinity and looked like an amorphous. In addition, the anatase and the rutile phases of precursor material were entirely disappeared. The proposed crystal structures of nanotubular TiO₂ products, prepared by alkaline hydrothermal method, by different authors in the past include Na_xH_{2-x}Ti₃O₇·*n*H₂O [5, 16], H₂Ti₃O₇ [17, 18], Na₂Ti₂O₄(OH)₂ [19], and H₂Ti₄O₉ [20]. In our XRD patterns, all obtained samples have four main diffraction peaks at around 9°; 24.3°; 28.4° and 48.3°. According to the literatures [5, 19], these main peaks indicate the layered titanates of TNTs. In particular, the strong broad peak at around 9° [i.e. (100) plane] is attributed to the enlarged interlayer distance. Detailed analysis (see Table 1) demonstrated that the peaks of synthesized

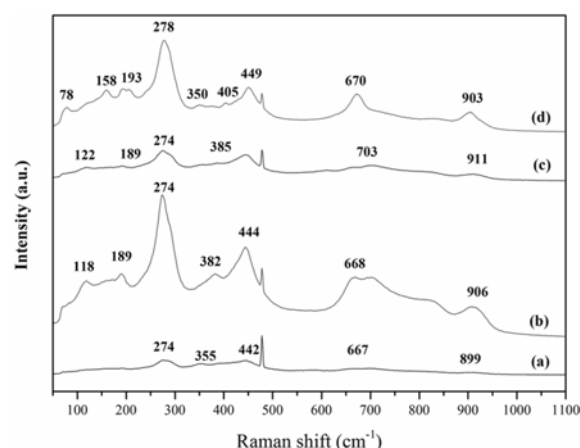


Fig. 4. Raman spectra of different samples: (a) TNT1, (b) TNT2, (c) TNT3, and (d) TNT4.

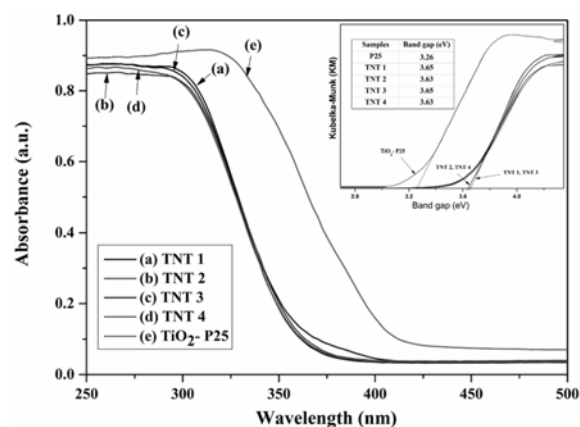


Fig. 5. UV-vis DRS spectra of different samples (inset shows the modified Kubelka-Munk plot vs band gap energy plot).

products have a good agreement with (200), (110), (310), (020) planes of H₂Ti₂O₅ · H₂O (JCPDS card No. 47-0124), similar to the results obtained by Jiang et al. [2] and Tsai et al. [9].

A slight variation in the characteristic peak intensities among the prepared TNTs samples are observed. This might be due to the difference in microwave irradiation time and the formation of different intermediate nanostructures. It has been observed from FESEM and TEM images that the transformation of nanoparticles into nanosheets, wires or nanotubes occurred within 3 h of microwave hydrothermal processing. However, nanoparticles, nanosheets, or nanowires almost disappeared and those structures changed into the nanotubes at 4 h of microwave processing. Therefore, the structure of TNT4 is more stable than TNT1, TNT2 and TNT3. As a result, the intensity of characteristic peaks of samples that were prepared with synthesis time range 1 h to 3 h was lower than the sample obtained at 4 h.

The Raman spectra of all synthesized samples are shown in Fig. 4. Pristine TiO₂-P25 has five peaks corresponding to 138 cm⁻¹, 391 cm⁻¹, 463 cm⁻¹, 512 cm⁻¹, and 634 cm⁻¹. According to Qian et al. [7], the Raman

peaks of TiO_2 at 144 cm^{-1} , 197 cm^{-1} , 399 cm^{-1} , 513 cm^{-1} , 519 cm^{-1} and 639 cm^{-1} were assigned to anatase phase, while the peaks at 143 cm^{-1} , 447 cm^{-1} , 612 cm^{-1} and 826 cm^{-1} were of rutile phase. Therefore, in our TiO_2 -P25 material, the peak at 463 cm^{-1} is attributed to rutile phase and the others belong to anatase phase.

For TNT1, TNT2, TNT3, TNT4 samples, the raman modes at 703 cm^{-1} and 442 cm^{-1} to 449 cm^{-1} are related to the bending and stretching vibration of Ti-O bond in the layer structure of TiO_2 nanotubes [8]. Meanwhile, peaks at 78 cm^{-1} , 118 cm^{-1} , 122 cm^{-1} , 158 cm^{-1} , 189 cm^{-1} , 193 cm^{-1} , 274 cm^{-1} to 278 cm^{-1} , 350 cm^{-1} , 355 cm^{-1} , 667 cm^{-1} to 670 cm^{-1} , 899 cm^{-1} to 911 cm^{-1} were originated from Ti-O bond of sodium titanate in layer structure [7, 8, 13]. It has been previously proposed that during the washing process by acid or distilled water, Na^+ ion of the T-O-Na bond is substituted by H^+ ion, that results the formation of Ti-O-H bond [1, 4]. However, the emergence of Ti-O bond of sodium titanate has proved that the substitution of ion H^+ for Na^+ is incomplete. Therefore, the nanotubular walls consisted of not only $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ but also of $\text{Na}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$. As a result, it is possible to conclude that the chemical formula of TNT is $\text{Na}_{2-x}\text{H}_x\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$, with reference to the results presented by Tsai et al. [9]. It is worth pointing out that the band at 274 cm^{-1} of TNT1, TNT2 and TNT3 shifted toward higher wave number 278 cm^{-1} of sample TNT4. Besides, the new peak at 78 cm^{-1} also appeared in only TNT4. Thus, it is concluded that peaks at 78 cm^{-1} and 278 cm^{-1} are characteristics of TiO_2 nanotubes.

Fig. 5 shows the UV-Vis diffuse reflectance spectra and band gap energies of TiO_2 -P25 and synthesized TNT samples. The band gap energies were evaluated by modified Kubelka-Munk method [21]. The results indicate that the band-gap energies of all TNTs samples are higher than that of TiO_2 -P25 (see inset of Fig. 5). According to N. Satoh et al. [22] and T. Sekino et al. [23], the effect of quantum-size results in higher band gap energy of TiO_2 nanotubes than TiO_2 -P25 sample. This means as being formed, the diameter of nanotubes (about 8 nm) decreases as compared to P25 (about 25 nm) leading to an increase in the band gap values of nanotube samples.

Fig. 6 shows that all prepared samples have a much higher MB dye adsorption than TiO_2 -P25. The significant difference in the adsorption is probably due to larger BET surface area of TNTs as compared to pristine TiO_2 -P25 (see Table 2). Furthermore, another possible reason may be due to the difference in surface charge of TiO_2 -P25 and synthesized TNT nanostructures. The surface charge of TiO_2 -P25 and synthesized TNT samples are neutral and negative [2, 24, 25], respectively. Thus, MB as a cationic dye, a large amount of MB from an aqueous solution was easily adsorbed on the negative surfaces of TNTs by electrostatic attraction.

The kinetic plot (C/C_0) for the decolorization of MB

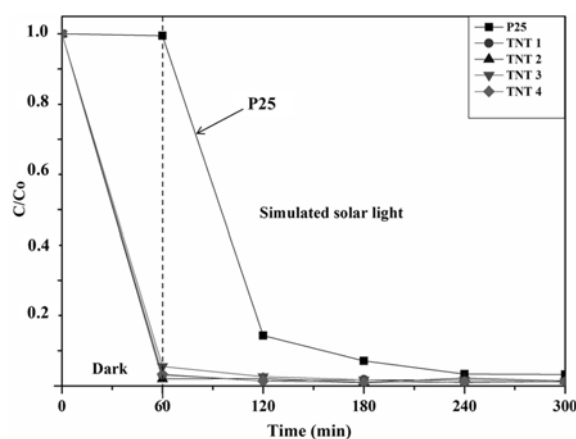


Fig. 6. Kinetics (C/C_0) plot of the photocatalytic decolorization of MB aqueous solution in the dark and under simulated solar light.

Table 2. BET surface area and the percentage mineralization of MB aqueous solution after 4 h of irradiation under the simulated solar light.

Samples	P25	TNT1	TNT2	TNT3	TNT4
BET surface area [$\text{m}^2 \cdot \text{g}^{-1}$]	45	128	186	232	230
% Mineralization of MB	80.70	41.39	47.50	50.68	60.05

dye after 60 min adsorption in the dark, as shown in Fig. 6, reveals that the decolorization degree of MB by four different TNT samples stood at over 90% whereas TiO_2 -P25 was less than 2%. Under the irradiation in simulated solar light, the decolorization by TiO_2 -P25 reduced rapidly in the first 1 h and reached to an equilibrium (more than 90% color of methylene blue was decreased) for 3 h, while with TNT samples, the color of the dye solution slightly changed.

In addition, to evaluate the actual mineralization degree of MB by TNTs, total organic carbon (TOC) of the aliquot, after 4 h of illumination, was measured as shown in Table 2. The figures showed that the mineralization percentage of TiO_2 -P25 is still higher than the prepared TNT products. Jiang et al. [2] explained earlier that the low crystallinity of the synthesized TiO_2 nanotubes was the cause for lower photocatalytic activity. Furthermore, the fast rate of the recombination of electron-hole pairs in nanotubular structure might be an another reason for decreasing photocatalytic activities [13]. Besides, the presence of anatase phase in the structure of TiO_2 -P25 is also one of the important reasons to enhance dye degradation than the titanate phase of TNTs.

The mineralization percentages are 41.39%, 47.50%, 50.68%, and 60.05% by TNT1, TNT2, TNT3, and TNT4 samples, respectively. The significant differences in TOC values may be attributed due to the larger BET surface area of as synthesized samples (in Table 2). Larger the surface area, the greater the chances of adsorption of MB dye on

the TNT. In the paper [26], authors demonstrated that the dye adsorption on the semiconductor material is directly proportional to the photocatalytic degradation. Therefore, TNT3 and TNT4 samples with higher surface area showed better photocatalytic activities in comparison with TNT1 and TNT2. Although the BET surface area of TNT3 is almost similar to the TNT4, the TOC value of TNT3 is lower. This is because of the slightly larger band gap energy of TNT3 in comparison to TNT4. Thus, the study revealed that the microwave hydrothermal processing time significantly affects the structures and the properties of the TNT products.

Conclusions

The importance of the microwave irradiation to shorten reaction time in synthesis of TiO₂ nanostructures by the hydrothermal method was investigated. The optimized microwave hydrothermal treatment time to obtain TiO₂ nanotubes has been found to 4 h. The results revealed that the chemical formula of synthesized samples was identified as Na_{2-x}H_xTi₂O₅ · H₂O. The TNT products with the structure of titanate phase interpreted lower photocatalytic activity than P25 precursor for methylene blue dye degradation. However, much larger BET surface area and higher MB adsorption of TNTs were observed in comparison to the TiO₂-P25 precursor. Hence, the TiO₂ nanotube is one of the potential materials to attract scientists in the field of semiconductor photocatalysis.

Acknowledgments

This research was supported by the Global Research Laboratory Program of the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (MEST) of Korea (Grant number: 2010-00339).

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