Research Article

Rapid Formation of 1D Titanate Nanotubes Using Alkaline Hydrothermal Treatment and Its Photocatalytic Performance

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One-dimensional (1D) titanate nanotubes (TNT) were successfully synthesized using alkaline hydrothermal treatment of commercial TiO_2 nanopowders in a Teflon lined stainless steel autoclave at 150°C . The minimum time required for the formation of the titanate nanotubes was 9 h significantly. After the hydrothermal processing, the layered titanate was washed with acid and water in order to control the amount of Na^+ ions remaining in the sample solutions. In this study, the effect of different reaction durations in a range of 3 h to 24 h on the formation of nanotubes was carried out. As the reaction duration is extended, the changes in structure from particle to tubular shapes of alkaline treated TiO_2 were obtained via scanning electron microscope (SEM). Also, the significant impact on the phase transformation and crystal structure of TNT was characterized through XRD and Raman analysis. Indeed, the photocatalytic activity of TNT was investigated through the degradation of methyl orange aqueous solution under the ultraviolet light irradiation. As a result, TNT with reaction duration at 6 h has a better photocatalytic performance than other samples which was correlated to the higher crystallinity of the samples as shown in XRD patterns.

1. Introduction

Nowadays, various kinds of environmental contaminants are around all of us, especially organic and inorganic pollutants from industrial textile [1]. In fact, textile industry with the discharge of synthetic dyes-containing effluents into the water system can cause considerable environmental pollution which would gravely impact the quality of life of humans [2–4]. For instance, methyl orange acts as one of the major chemical classes of azo dyes that is normally carcinogenic, toxic, and mutagenic in nature [5, 6]. Thus, the treatments of such wastewater have become a major concern and it is urgent to develop a sustainable and cost-effective treatment technology to solve the discharge of toxic chemicals into water systems [6–8]. Lately, photocatalytic oxidation treatment has attracted much attention from science community as one of the effective treatments applied for dye removal from textile effluents [9, 10].

In this case, titanium dioxide (TiO_2) based nanomaterials have been studied extensively as a cheap and promising photocatalyst for environmental remediation [2, 4, 6]. The

reason for using TiO_2 is mainly attributed to its ability to break down complex molecules in the pollutant into simple and non-toxic substances during the photocatalytic oxidation treatment; thus, no second treatment was involved for processing the sludge. Furthermore, the catalyst remains unchanged and can be reused which results in a significantly lower operating expense [7–9].

To date, designing one-dimensional (1D) nanostructure assemblies with precisely controllable nanoscale features has gained significant scientific interest, such as nanotubes, nanowires, and nanorods [11–15]. Of such properties, the large surface-to-volume ratio, good ion-changeable ability, and the tube-like structures of TNT have become the major interest of study [3, 8, 16–18]. In addition to this, a few studies showed that TNT exhibits a better photocatalytic activity than the titania nanopowders which have been summarized in Table 1. TNT consists of edge- and corner-sharing TiO_6 octahedral with the Na^+ ions that existed between the TiO_6 layers which are capable of good ion-changeable ability effective for photocatalysts applications [7, 9, 11].

TABLE 1: Comparison of photocatalytic performance between TiO_2 nanopowders and TNT.

Types of photocatalyst	Applications	Efficiency	References
TiO_2	Degradation of methylene blue	65%	[9]
TNT		95%	
TiO_2	Degradation of tobacco smoke	0.5 : 1	[10]
TNT			
TiO_2	Degradation of methyl orange	46.8%	[11]
TNT		57.2%	
TiO_2	Degradation of methylcyclohexane (MCH)	72%	[12]
TNT		95%	

Throughout the studies, alkaline hydrothermal method provides a relatively simple, easy, low energy consuming, and cost-effective method for attaining TNT with high purity in terms of phases and morphology [19–21]. Essentially, this method also allows for the green synthesis of TNT in the fact that the reaction was carried out in an autoclave under controllable temperature and pressure within a closed system. Therefore, the as-prepared TNT in this manner was considered as an attractive material for photocatalytic systems [22, 23].

Up to now, most of the studies performed on titanate nanotubes have focused on hydrothermal temperature and concentration of NaOH, and most of the experiments were carried out under the same reaction duration, typically at 24 h. However, information on the effects of reaction duration on the rapid formation of TNT is still lacking in the literature.

In this work, systematic studies and analytic approaches on the transformation of TiO_2 nanoparticles into nanotubular structure TNT were carried out by using a chemical treatment with highly concentrated NaOH under hydrothermal conditions. In general, hydrothermal durations played a crucial factor influencing morphological characteristics of the TNT. At this point, the effect of various reaction durations in a range of 3 h to 24 h on the formation of nanotubes and their photocatalytic activity upon methyl orange was studied. With respect to this, the yield of nanotubes increased with the hydrothermal duration and the rapid formation of nanotubes at only 9 h.

2. Materials and Methods

2.1. Materials. Commercial titania nanopowders (97%), hydrochloric acid, HCl (37%), sodium hydroxide, NaOH (97%), and methyl orange (85%) with the molecular formula of $\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$ (Figure 1) were purchased from Sigma-Aldrich, USA. All chemicals were used as received without further purification. Deionized water was used throughout the whole experiment.

2.2. Hydrothermal Treatment of TNT. In a typical synthesis, TNT was prepared via an alkaline hydrothermal treatment and commercial TiO_2 nanopowders were used as a starting material. An appropriate amount of TiO_2 nanopowders was mixed with 10 M NaOH in Teflon lined stainless steel

FIGURE 1: Structural formula of methyl orange.

autoclave and heated at 150°C for 24 h [24]. Ou and Lo (2007) reported that higher inner diameter and specific area of TNT were produced at 150°C . After hydrothermal processing, the mixture was first cooled to room temperature. Then, the white precipitate obtained was separated through centrifugation and washed with diluted HCl aqueous solution followed by deionized water until a pH 7 of washing solution was obtained. The purpose of acid treatment after the hydrothermal process is to control the amount of Na^+ ions remaining in the sample solution. Finally, the sample was dried overnight in an oven at 100°C . Moreover, the reaction durations of TNT at 3, 6, 9, and 21 h were prepared by following the same procedure as stated above. The schematic diagram of TNT formation was represented in Figure 2.

2.3. Characterization. X-ray diffraction (XRD) was used to study the crystal structure and the degree of crystallinity of TNT. The XRD was performed at 40 kV and 30 mA at a scanning rate of $0.01^\circ/\text{s}$ with a Cu $\text{K}\alpha$ radiation ($\lambda_{\text{K}\alpha 1} = 1.5406 \text{ \AA}$) on a Bruker axs D8 Advance diffractometer from 10° to 80° . The morphology and particle size were determined by using a scanning electron microscope (SEM) operating at 5.00 kV and high vacuum with a magnification of 30 000x, using a Hitachi Tabletop Microscope. Raman spectra were used for determining the changes in the phase and morphology of the TNT using Raman spectroscopy (Renishaw in Via) with a 514.5 nm Ar^+ laser as an excitation source.

2.4. Photocatalytic Activity of Alkaline Treated TNT. Photocatalytic degradation of methyl orange was evaluated under ultraviolet (UV) light irradiation of a 96 W UV lamp. Typically, 0.05 g of TNT photocatalysts was added into 100 mL of methyl orange aqueous solution (concentration: 15 mg/L). Initially, the solution was stirred in darkness for 30 minutes to reach adsorption before UV lamp was switched on to initialize the photodegradation of methyl orange solution. The solutions were collected at certain time intervals and then centrifuged to separate the photocatalyst from the solution. The concentration of methyl orange was then determined by using a UV-Vis spectrophotometer.

3. Results and Discussions

3.1. Morphological Studies and Elemental Analysis. Figure 3 shows the FESEM images of the starting material, commercial

FIGURE 2: A schematic representation on the preparation of TNT.

TiO₂ nanopowders, and the as-prepared TNT with different time durations. From Figure 3(a), it can be seen that the as-received TiO₂ nanopowders with spherical shape have an average particle size of 10–20 nm. Figure 3(b) displays a partial formation of hollow tubular structure and a micron-sized titanate in sheets forms after the hydrothermal treatment at 150°C for 3 h. The FESEM images revealed that TiO₂ particles were not fully transformed into nanotubes and some parts of TiO₂ particles were transformed into nanosheets. Generally, the reaction formation of nanotubes involves the delamination of TiO₂ nanoparticles in an alkali solution followed by the exfoliation of layered sodium titanates to form TiO₂ nanosheets [5, 6]. The nanosheets were curled, rolled up, and scrolled into nanotubes. Eventually, the formation of TNT was primarily due to the hydrothermal treatment with strong NaOH aqueous solution which breaks the Ti-O-Ti bond and forms the Ti-O-Na and Ti-OH bond [24–26]. As the reaction duration is longer, an increase in the number of randomly tangled TNT formed was observed. This finding is in agreement with the findings of [20] (2010) which indicated the yield of nanotubes increased with the hydrothermal duration [27]. The average diameter size of the TNT is in a range of 15–30 nm.

Basically, two reaction steps were involved during the hydrothermal treatment, namely, (i) formation of layered titanate and (ii) dissolution-crystallisation along with the ion exchange that occurred. At first, TiO₂ reacts with concentrated NaOH forming layered titanate and then was followed by washing with HCl and distilled water. During the washing process, ion exchange occurred with the small radius of H⁺

acting as a free proton and it reacts chemically with the exchanged Na⁺ [9, 11]. The overall hydrothermal reactions can be elucidated as follows:

where the first step is the formation of layered titanate, while the second step corresponds to the dissolution of layered structure and the following steps represent the ion exchange reaction and finally the crystallization of titanate formation.

Further observation on the morphology of the as-obtained material is carried out through TEM as shown in Figure 3(b). The TNT are hollow tube-like structure with the diameter being about 10 nm and length in the range of micrometres.

Figure 4 shows one of the EDX spectra of TNT with the confirmation of the elements present which included Ti and O. From the EDX spectra, the impurities such as Na and Cl do not exist which reveal that they have been removed and exchanged with hydrogen ions during the washing process [12]. The effect of reaction durations does not show any significant impacts on the EDX spectra. This may be due to all samples being equally reacted with 10 M NaOH and

FIGURE 3: FESEM images of (A) starting material, TiO_2 nanopowders, and formation of nanotubes with different reaction duration: (B) 3 h, (C) 9 h, and (D) 24 h; (b) TEM image of the as-prepared TNT.

completely washed with HCl and distilled water until the pH reached 7.

3.2. Phase Studies. Powder X-ray diffraction (XRD) is used to characterize the crystal structure and the degree of crystallinity of the nanotubes. The XRD patterns of the as-prepared TNT with different reaction durations are shown in Figure 5. When the TiO_2 nanopowders were hydrothermally treated with NaOH, the anatase phase of TiO_2 disappeared and the XRD diffraction peaks at $2\theta = 24^\circ$, 28° , and 48° corresponded to (110), (211), and (020) phases of the layered titanate, respectively [3, 5, 7]. It was interesting to observe

that, as the reaction duration increases, the peak width becomes broader along with the decreasing of the intensity of the characteristic peaks. This indicated that the TNT have poor crystallinity and a very small crystallite size. This might be due to the completely disappeared anatase crystallinity and is replaced by the formation of layered protonic titanates [9].

3.3. Raman Studies. Raman spectroscopy is an important characteristic tool used to further confirm the changes in the phase and morphology of TNT. Figure 6 illustrates the Raman spectra of TNT with various reaction durations. From the study, the TiO_2 nanopowders show the four main peaks

FIGURE 4: EDX spectra of TNT.

FIGURE 5: XRD patterns of hydrothermal formation of nanotubes with different reaction duration: (a) 3 h, (b) 6 h, (c) 9 h, (d) 21 h, and (e) 24 h.

FIGURE 6: Raman spectrum of hydrothermal formation of nanotubes with different reaction duration: (a) 3 h, (b) 6 h, (c) 9 h, (d) 21 h, and (e) 24 h.

(141.85, 396.53, 517.12, and 641.86 cm^{-1}) which indicated the presence of anatase mode as Eg (1), B1g (1), A1g, and Eg (2), respectively [8, 10]. However, for TNT with different reaction durations, three main peaks exist (280.87, 449.76, and 654.18 cm^{-1}) in Raman spectrum which determined the presence of layered titanate structure. The absence of anatase phase within the samples indicated that TiO_2 nanopowders have been reacted with the NaOH aqueous solution to

FIGURE 7: The photocatalytic activity of nanotubes with different reaction duration: (a) 3 h, (b) 6 h, (c) 9 h, (d) 21 h, and (e) 24 h for the degradation of methyl orange.

form TNT. The Raman peaks at 280.87 cm^{-1} were typically belonging to the phonon mode of titanate structure. In addition, the peaks at 449.76 cm^{-1} were assigned for Ti-O bending vibration in the layered titanate structure while the peaks at 654.18 cm^{-1} are believed to be attributed to the Ti-O-H vibration [11, 13, 28]. Mostly, the nanotubes samples will consist of minor variations in terms of peaks shifts and intensities which represent the sample phases. Hereby, some study found out that the changes in the Raman spectra are so-called titanate-influenced [9]. As a conclusion, the Raman results in this study were in accordance with the XRD results obtained.

3.4. Photocatalytic Activity. The effect of the reaction duration on the TNT photocatalytic activity was studied through the methyl orange dye photodegradation by using UV-Vis spectroscopy with C being the concentration of methyl orange after different light irradiation times and C_0 being the initial concentration of methyl orange before light irradiation. Methyl orange with a major absorption peak at 464 nm was considered as one of the major organic contaminants in wastewater [11]. Figure 7 displays the photocatalytic activity of TNT with different reaction duration. As can be observed, all the TNT samples show photocatalytic activity. It was obvious that the TNT with reaction duration at 6 h has a better photocatalytic performance than other samples. This finding can be attributed to the higher crystallinity of the samples as shown in XRD patterns which can lead to the lower recombination rate of electron-hole pairs and, hence, increase the photocatalytic performance of TNT.

The kinetics of photocatalyzed degradation of MO is illustrated in Figure 8. The linearity of the curves suggests that the photocatalytic decolorization of MO can be described by the first-order kinetic model, $\ln(C_0/C) = kt$, where C_0 is the initial concentration and C is the concentration at time t . The plots of the concentration data gave a straight line. The results

FIGURE 8: Pseudo-first-order kinetics for methyl orange photodegradation using nanotubes with different reaction duration.

TABLE 2: Rate constants for catalytic photodegradation of MO.

Reaction duration	Rate constant (k)	R^2
3 h	0.0132	0.9941
6 h	0.0172	0.9836
9 h	0.0109	0.9911
21 h	0.0073	0.9869
24 h	0.0061	0.9823

of fitting experimental data to pseudo-first-order kinetics are given in Table 2.

The rate constant firstly increases with increasing TiO_2 nanotubes reaction duration up to 6 hours but then decreases with further increasing reaction duration. This shows that the TiO_2 nanotubes with 6 hours reaction duration demonstrated the best photocatalytic activity for the degradation of MO among the samples produced.

4. Conclusions

A hollow tube-like TNT has been successfully synthesized using alkaline hydrothermal method. The effect of reaction durations on the formation of TNT has been carried out. The changes in phase, surface morphology, and elemental determination of hydrothermally treated TNT were investigated through XRD, FESEM, EDX, and Raman analysis.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] V. C. Ferreira, M. R. Nunes, A. J. Silvestre, and O. C. Monteiro, "Synthesis and properties of Co-doped titanate nanotubes and their optical sensitization with methylene blue," *Materials Chemistry and Physics*, vol. 142, no. 1, pp. 355–362, 2013.
- [2] K. Hu, X. Xiao, X. Cao et al., "Adsorptive separation and photocatalytic degradation of methylene blue dye on titanate nanotube powders prepared by hydrothermal process using metal Ti particles as a precursor," *Journal of Hazardous Materials*, vol. 192, no. 2, pp. 514–520, 2011.
- [3] S. Kim, M. Kim, S. H. Hwang, and S. K. Lim, "Effects of hydrothermal temperature and acid concentration on the transition from titanate to titania," *Journal of Industrial and Engineering Chemistry*, vol. 18, no. 3, pp. 1141–1148, 2012.
- [4] N. Liu, X. Chen, J. Zhang, and J. W. Schwank, "A review on TiO_2 -based nanotubes synthesized via hydrothermal method: formation mechanism, structure modification, and photocatalytic applications," *Catalysis Today*, vol. 225, pp. 34–51, 2014.
- [5] I. A. Santos-López, B. E. Handy, and R. García-de-León, "Titanate nanotubes as support of solid base catalyst," *Thermochimica Acta*, vol. 567, pp. 85–92, 2013.
- [6] L. Shi, L. Cao, W. Liu, G. Su, R. Gao, and Y. Zhao, "A study on partially protonated titanate nanotubes: enhanced thermal stability and improved photocatalytic activity," *Ceramics International*, vol. 40, no. 3, pp. 4717–4723, 2014.
- [7] C. L. Wong, Y. N. Tan, and A. R. Mohamed, "A review on the formation of titania nanotube photocatalysts by hydrothermal treatment," *Journal of Environmental Management*, vol. 92, no. 7, pp. 1669–1680, 2011.
- [8] S. Kim, M. Kim, S.-H. Hwang, and S. K. Lim, "Enhancement of photocatalytic activity of titania-titanate nanotubes by surface modification," *Applied Catalysis B: Environmental*, vol. 123–124, pp. 391–397, 2012.
- [9] K.-C. Huang and S.-H. Chien, "Improved visible-light-driven photocatalytic activity of rutile/titania-nanotube composites prepared by microwave-assisted hydrothermal process," *Applied Catalysis B: Environmental*, vol. 140–141, pp. 283–288, 2013.
- [10] M. S. Meor Yusoff, M. M. Masliana, W. Paulus, P. Devi, and M. E. Mahmoud, "Fabrication of titania nanotubes by a modified hydrothermal method," *Journal of Science and Technology*, vol. 2, no. 2, 2011.
- [11] M. N. An'amt, N. M. Huang, S. Radiman, H. N. Lim, and M. R. Muhamad, "Triethanolamine solution for rapid hydrothermal synthesis of titanate nanotubes," *Sains Malaysiana*, vol. 43, no. 1, pp. 137–144, 2014.
- [12] H.-L. Li, W.-L. Luo, T. Chen et al., "Preparation and photocatalytic performance of titania nanotubes loaded with Ag nanoparticles," *Acta Physico-Chimica Sinica*, vol. 24, no. 8, pp. 1383–1386, 2008.
- [13] M. Q. Yang, N. Zhang, M. Pagliaro, and Y. J. Xu, "Artificial photosynthesis over graphene-semiconductor composites. Are we getting better?" *Chemical Society Reviews*, vol. 43, no. 24, pp. 8240–8254, 2014.
- [14] N. Zhang, Y. Zhang, and Y.-J. Xu, "Recent progress on graphene-based photocatalysts: current status and future perspectives," *Nanoscale*, vol. 4, no. 19, pp. 5792–5813, 2012.

- [15] B. Weng, S. Liu, Z.-R. Tang, and Y.-J. Xu, "One-dimensional nanostructure based materials for versatile photocatalytic applications," *RSC Advances*, vol. 4, no. 25, pp. 12685–12700, 2014.
- [16] Z.-R. Tang, F. Li, Y. Zhang, X. Fu, and Y. J. Xu, "Composites of titanate nanotube and carbon nanotube as photocatalyst with high mineralization ratio for gas-phase degradation of volatile aromatic pollutant," *Journal of Physical Chemistry C*, vol. 115, no. 16, pp. 7880–7886, 2011.
- [17] T. A. Saleh, M. N. Siddiqui, and A. A. Al-Arfaj, "Synthesis of multiwalled carbon nanotubes-titania nanomaterial for desulfurization of model fuel," *Journal of Nanomaterials*, vol. 2014, Article ID 940639, 6 pages, 2014.
- [18] Y. Zhang, Z.-R. Tang, X. Fu, and Y.-J. Xu, "TiO₂-graphene nanocomposites for gas-phase photocatalytic degradation of volatile aromatic pollutant: is TiO₂-graphene truly different from other TiO₂-carbon composite materials?" *ACS Nano*, vol. 4, no. 12, pp. 7303–7314, 2010.
- [19] W. Liu, J. Gao, F. Zhang, and G. Zhang, "Preparation of TiO₂ nanotubes and their photocatalytic properties in degradation methylcyclohexane," *Materials Transactions*, vol. 48, no. 9, pp. 2464–2466, 2007.
- [20] S. Sreekantan and L. C. Wei, "Study on the formation and photocatalytic activity of titanate nanotubes synthesized via hydrothermal method," *Journal of Alloys and Compounds*, vol. 490, no. 1-2, pp. 436–442, 2010.
- [21] H. Y. Niu, J. M. Wang, Y. L. Shi, Y. Q. Cai, and F. S. Wei, "Adsorption behavior of arsenic onto protonated titanate nanotubes prepared via hydrothermal method," *Microporous and Mesoporous Materials*, vol. 122, no. 1-3, pp. 28–35, 2009.
- [22] S. Uchida, R. Chiba, M. Tomiha, N. Masaki, and M. Shirai, "Hydrothermal synthesis of titania nanotube and its application for dye-sensitized solar cell," *Studies in Surface Science and Catalysis*, vol. 146, pp. 791–794, 2002.
- [23] M. A. Khan and Y.-M. Kang, "Catalytic properties of titania nanotube prepared by simple refluxing method," *Materials Letters*, vol. 116, pp. 160–163, 2014.
- [24] H. H. Ou and S. L. Lo, "Review of titania nanotubes synthesized via the hydrothermal treatment: fabrication, modification, and application," *Separation and Purification Technology*, vol. 58, no. 1, pp. 179–191, 2007.
- [25] B. Erjavec, R. Kaplan, and A. Pintar, "Effects of heat and peroxide treatment on photocatalytic activity of titanate nanotubes," *Catalysis Today*, vol. 241, pp. 15–24, 2014.
- [26] Z.-Y. Yuan and B.-L. Su, "Titanium oxide nanotubes, nanofibers and nanowires," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 241, no. 1-3, pp. 173–183, 2004.
- [27] S. Thennarasu, K. Rajasekar, and K. Balkis Ameen, "Hydrothermal temperature as a morphological control factor: preparation, characterization and photocatalytic activity of titanate nanotubes and nanoribbons," *Journal of Molecular Structure*, vol. 1049, pp. 446–457, 2013.
- [28] C. M. Rodrigues, O. P. Ferreira, and O. L. Alves, "Interaction of sodium titanate nanotubes with organic acids and base: chemical, structural and morphological stabilities," *Journal of the Brazilian Chemical Society*, vol. 21, no. 7, pp. 1341–1348, 2010.