

Research Article

Photocatalytic Properties of Nanotubular-Shaped TiO₂ Powders with Anatase Phase Obtained from Titanate Nanotube Powder through Various Thermal Treatments

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Photocatalytic properties of nanotubular-shaped titanate powders, synthesized by hydrothermal treatment of TiO₂, were studied after calcinations at various temperatures and times under O₂, air, and H₂ atmospheres. Their photocatalytic properties were measured with checking decomposition of 4-chlorophenol under UV-A irradiation, together with physical characterizations using SEM, TEM, XRD, BET, and Raman spectroscopy. With increasing calcination temperature and time, nanotubular-shaped titanate particles became short, rod-like, or irregular by oversintering, and their crystalline structure was changed into anatase phase. The photocatalytic ability in decomposition of 4-chlorophenol using the calcined powders showed the highest value due to obtainment of high specific area by maintaining nanotubular shape, together with transformation from titanate to anatase phase having perfect crystallinity in O₂ or air atmosphere.

1. Introduction

Nanostructured TiO₂ powder with the particle sizes under 100 nm has been studied as one of the most important matters in materials industry over the last decades due to its great advantages as unique electrical, chemical, optical, and photochemical properties [1–4]. Recently, for getting around severe agglomeration between nanoparticles in the powder with high quality in their properties, the synthesis researches are mainly focused on the maximization of specific surface area of obtained particles by rearrangement of bulk TiO₂ materials like changing their particle shapes into nanotube [5], nanowire [6], or nanorod [7] with one-dimensional structure. Among them, TiO₂-based nanotube powder which had been firstly reported by Kasuga et al. in 1998 [5] is structurally very similar to carbon nanotube and has been actively used in researches in application fields for solar cell

electrode [8], photoelectrochemical water splitting catalyst [9], secondary battery electrode [10], hydrogen storage [11], photocatalyst [12], and so on [13–15] because it has high chemical stability as well as specific physical properties such as high aspect ratio, high surface area, and fast ionic path.

The TiO₂-based nanotube material synthesized by the hydrothermal process is generally referred to as titanate phase, which has TiO₆ octahedra consisting of a layered structure for H_xTi_yO_z obtained normally with its rearrangement in a strong basic NaOH solution and also has a particular crystallinity that differs from anatase, rutile, and brookite phases [3]. However, large amount of Na⁺ ions existed on the surface of and inside the tubular particles gone through water washing and drying steps after synthesis and it has been already well known that Na⁺ ions significantly decrease photocatalytic activity of TiO₂ [16, 17]. Also, it was reported by Qamar et al. [18, 19] that the photocatalytic activity

of the titanate powder increased due to its transformation into anatase phase with calcination, only when completely removing Na^+ ions on surface of and inside the powder by ion-exchange process compared to that of the powder without ion-exchange process. According to their research, the most excellent photocatalytic property of hydrothermally prepared titanate powder was obtained at the calcination of 400°C for 2 hours after completely removing the Na^+ ions, where their photocatalytic ability were still lower than that of commercial P25 powder. Also, their titanate nanotube powder after calcination had relatively very smaller value in the specific surface area, compared to original ion-exchanged titanate nanotube powder. In general, there is a large amount of H_2O content or moisture in the finally obtained powder with high surface area through the solution-based hydrothermal process. The H_2O content or moisture inside and outside the particles with increasing calcination temperatures causes severe problem that the specific surface area of powders is greatly decreased due to the rapid mass transportation. Therefore, in this study, for high efficient photocatalytic TiO_2 powder from the titanate powder, we quantitatively evaluate the effects on photocatalytic activities of titanate nanotube with variations of particle shape, specific surface area, and crystal structure by controlling the heating time, temperatures, and atmospheres with removing H_2O content or moisture in the powder.

2. Experimental Procedure

For preparing titanate nanotube powder, 0.1 M P25 (Degussa Co.) powder was at first put into 10 M aqueous NaOH (Junsei Chem. Co.) solution, and then the solution was vigorously stirred for 2 hours at room temperature using magnetic stirrer. The solution after complete mixing was poured into nickel-lined stainless steel autoclave, and it was hydrothermally heated at 150°C for 48 hours. After hydrothermal process, white-colored precipitate was obtained and the precipitate was repetitively washed with deionized water until the solution pH became 7. The removal of Na^+ ions on the surface of and inside the obtained precipitated particles was carried out by ion-exchanging process in 0.1 N aqueous HCl solution for 24 hours to have less than 0.1 at % Na^+ . After ion-exchanging process, the precipitate was washed again with deionized water, followed by freeze drying (ALPHA 1-2 LD, Christ) at -57°C for 24 hours. Then, the dried precipitates were calcined with variables in temperature and time using tube furnace-controlled various atmospheres such as oxygen, air and hydrogen (10 vol% H_2 with balanced N_2).

Particle shapes of as-prepared and calcined powders were observed using scanning electron microscope (S-4700, Hitachi), and specific surface area of the powder was measured using BET (KICT-SPA3000, MiraeSI Co.). Crystal structure of the powder was analyzed using X-ray diffractometer (D/MAX-2500/PC, Rigaku) and ambient Raman Spectroscopy (InVia Raman Macroscopy, Renishaw). Finally, to evaluate photocatalytic properties of the calcined powders, 0.1 g of the obtained powders were mixed together with

0.1 mM aqueous 4-chlorophenol (4-CP) solution. Then, UV-A light source (PowerArc UV-100, UV Process Co.) with ~ 400 nm of wavelength and 100 W of power was irradiated on the mixed solution for 3 hours for the photocatalytic reaction. After the reaction, the remaining organic carbon in the mixed solution was measured to check the extent of photocatalytic decomposition of 4-CP using TOC analyzer (TOC-VCPH, Shimadzu Co.).

3. Result and Discussion

Figure 1(a) shows XRD results for the ion-exchanged titanate nanotube (H-TiNT) powders calcined at temperatures from 400°C to 500°C for 30 min in O_2 atmosphere. It can be seen that the diffraction intensities for characteristic peaks of anatase TiO_2 phase at $2\theta = 25.35, 37.84, 48.14, 53.97,$ and 55.18° rise gradually with increasing temperature by transformation of the titanate into anatase phases, when there coexist a peak of the titanate phase at $2\theta = 24.5^\circ$ and other weak anatase peaks at 400°C . Those are well matched with mixed Raman spectra at 400°C of Figure 1(b), which includes the titanate characteristic peaks of 197, 280, and 450 cm^{-1} and the anatase characteristic peaks of 145, 390, 506, and 638 cm^{-1} . It can be also seen that the titanate phase transforms almost perfectly into anatase phase at 450°C , although very small traces of the titanate phase at 280 cm^{-1} undetectable in normal scale exist. On the other hand, Figure 2 shows SEM images of the calcined powders corresponding to the XRD patterns of Figure 1(a), respectively. Well-developed nanotubular shape is observed at $400\sim 450^\circ\text{C}$ but the agglomerations between tubular particles above 450°C become more severe. This observation about tubular shape was also confirmed using TEM as previously reported [20]. It was also observed that they were shortened like nanorod and then became nanoparticles when the heating temperature approached 500°C or higher for 2 hours of calcination [18]. From these results, therefore, it can be said that the nanotubular-shaped TiO_2 powder with perfect anatase phase from the H-TiNT powder was obtained by calcination at 475°C for 30 min in O_2 atmosphere. It was also observed that the calcined powders in air atmosphere showed almost the same results as Figures 1 and 2. However, it was observed in H_2 atmosphere that the fast transformation into anatase phase was occurred with some reduction into TiO_{2-x} on the surface of H-TiNT particle.

Figure 3 shows photocatalytic decomposition abilities in aqueous-mixed solutions of 4-CP and calcined H-TiNT powders of Figure 1. For reference, well-known commercial P25 powder shows 52.50% in the 4-CP decomposition with the same photocatalytic reaction under UV-A irradiation for 3 hours, together with not showing decomposition at all when applying without photocatalyst ("no powder" marked). The photocatalytic decomposition of 4-CP in the mixed solution by the calcined H-TiNT powder increases gradually with increasing calcination temperature and then shows the maximum decomposition of 67.21% at 475°C . Here, it was confirmed that the H-TiNT powder before calcination shows only 2.43% in the 4-CP decomposition.

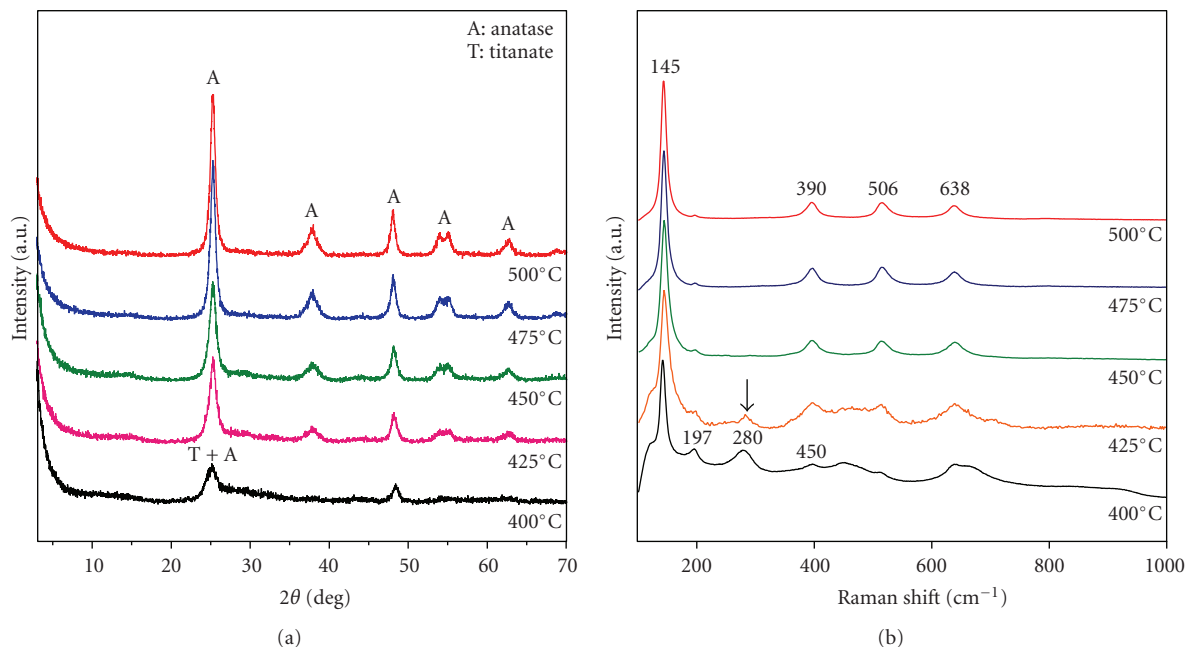


FIGURE 1: X-ray diffraction patterns (a) and Raman spectra (b) of the calcined powders with different temperatures in O_2 atmosphere for 30 min.

It means that the H-TiNT powder with the titanate phase has no photocatalytic ability under UV-A irradiation, and its photocatalytic ability is enhanced as the titanate phase transforms into the anatase phase by the calcination. However, the powder with perfect anatase phase by the calcination at 500°C shows a little higher decomposition ability of 4-CP than P25 powder, although the specific surface area of the powder ($162\text{ m}^2/\text{g}$) is about 3 times larger than that of P25 powder ($\sim 50\text{ m}^2/\text{g}$). Especially, the 4-CP decomposition ability of the calcined powder at 475°C only is as high as 15% compared to that of P25, regardless of having high surface area ($170\text{ m}^2/\text{g}$). When simply grinding the powder calcined at 500°C , its decomposition was measured having almost the same value as that of the powder at 475°C . From these results, it can be said that the effects on the photocatalytic properties of the calcined H-TiNT powders with anatase phase do not depend on the specific surface area alone. Like these, the decrease in the photocatalytic ability at higher calcination temperature results from that the calcined H-TiNT powders might not be dispersed well in the 4-CP solution by severe agglomerations or sintering between the calcined particles as shown in Figure 2. Therefore, the photocatalytic decomposition would be hindered due to the screening or shadow effect by the growth of the particles although their specific surface area for surficial sites was large. Anyway, in order to apply the titanate nanotube particle with anatase phase by simple heating for a photocatalyst with high specific surface area, it can be suggested that the optimized temperature for the calcination for 30 min in O_2 atmosphere should be in the ranges of $450^\circ\text{C}\sim 500^\circ\text{C}$ from particle observations and crystallinity analysis of Figures 1 and 2.

Yu et al. [21] and Qamar et al. [19] had already reported that the particles with well-developed anatase phase obtained by calcining ion-exchanged titanate nanotube particles at 200°C in long time or higher than 400°C were changed into nanorod or nanospherical typed. From our previous works [22–24] and other researcher's reports [25–27], it can be said that the structural changes and particle growth of the H-TiNT powder might be controlled by appropriately controlling the calcination time and temperature.

It can be observed in Figure 4 that the shape of the H-TiNT particle apparently remains unchanged when calcining at 475°C for 10 min but the particles in longitudinal direction are greatly shortened at the same temperature for 60 min when the calcination time increases. Here, the calcination temperature of 475°C was chosen from the condition of the highest photocatalytic activity, as shown in Figure 3. Furthermore, with increasing calcination time to 120 minutes, the particles are more shortened and gradually become larger spherically due to sintering between the particles. With the same photocatalytic reaction of Figure 3, when the effect on the calcination time in the 4-CP decomposition by the photocatalytic reaction was checked, the highest value at the powder obtained at 475°C for 30 min was measured as shown in Figure 5. Compared with the powders calcined at 475°C with the calcination times of 10 and 30 min, it is likely that there is no difference in the particle shape as that of the original H-TiNT but the powder obtained for 10 min might show a little lower decomposition ability due to relatively weak crystallinity. Also, the particles calcined at longer times became severely agglomerated showing decreased photocatalytic ability.

On the other hand, Figure 6 shows the photocatalytic decomposition abilities of the calcined H-TiNT powders

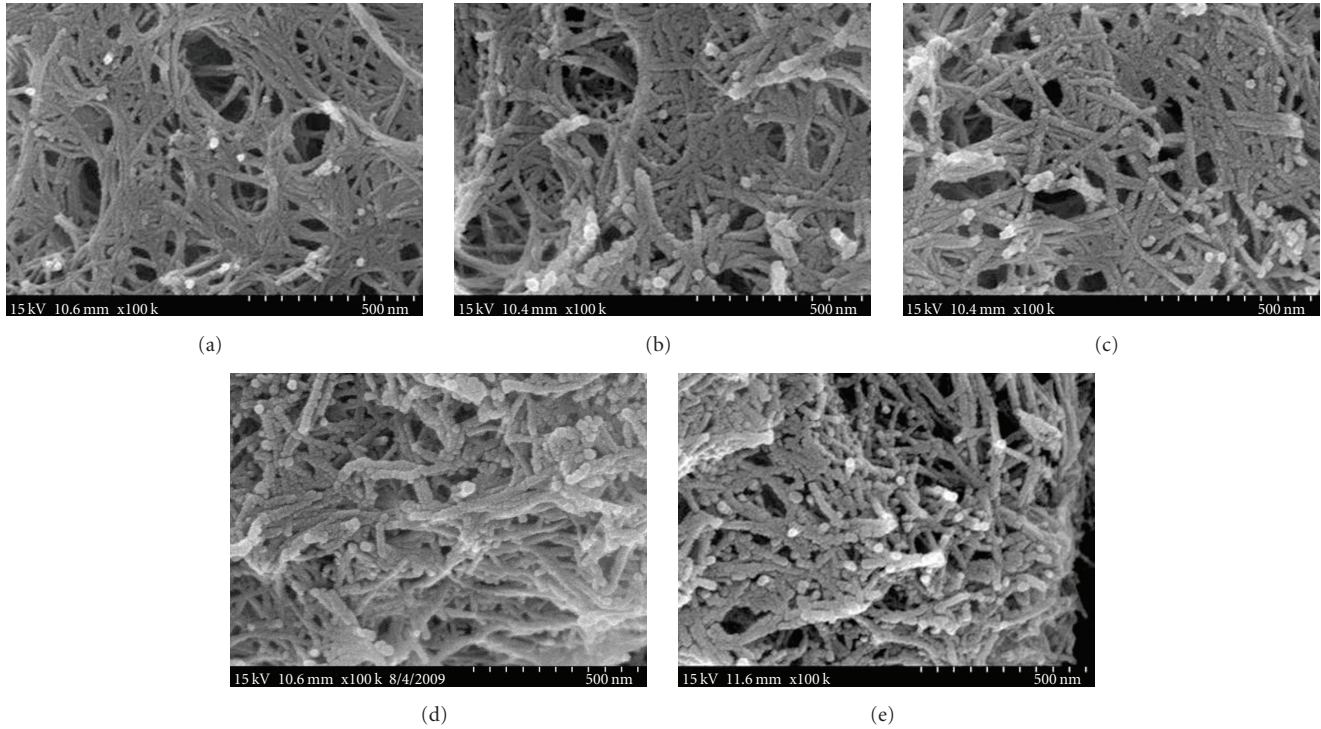


FIGURE 2: Scanning electron microscope images for the calcined powders at (a) 400°C, (b) 425°C, (c) 450°C, (d) 475°C, and (e) 500°C in O₂ atmosphere for 30 min.

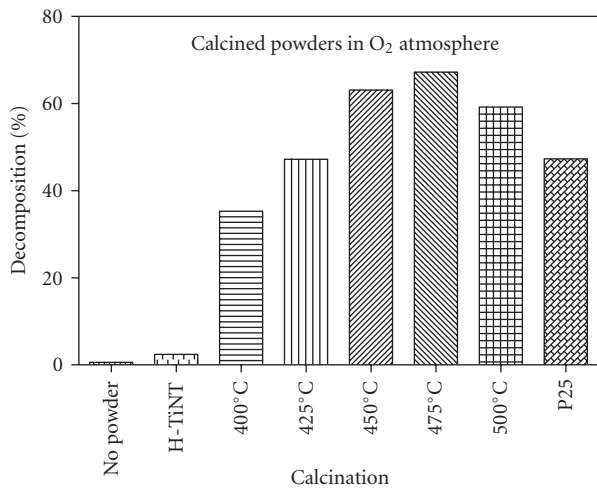


FIGURE 3: Photocatalytic 4-CP decomposition results of the powders calcined at various temperatures for 30 min in O₂ atmosphere and of H-TiNT, comparing with that of P25 powders.

with various heating times under air and H₂ atmospheres. It can be seen that the powders calcined under H₂ atmosphere show relatively low photocatalytic abilities and the maximum ability (45.50%) at 500°C becomes lower at higher temperature compared to other atmospheres. But the powders under air atmosphere have almost the same abilities compared to that under O₂ atmosphere. It was observed that these particles, obtained under H₂ and air

atmospheres, had the same crystallinity with the same calcination temperature and time under O₂ atmosphere, as shown in Figures 1 and 2, through XRD and Raman analysis, and also showed apparently almost the same nanotubular shape in these temperature ranges regardless of different calcination atmospheres. However, as shown in TEM photos in Figure 7 for further investigation on particle shapes with the calcinations, the H₂ atmosphere for the calcination at 500°C made the fast shape change of nanotube into nanorod caused comparatively small surface area of the powder. It could be additionally confirmed that, at temperatures higher than 450°C in H₂ atmosphere, the sintering phenomenon between the nanorod typed particles was locally observed (Figure 7(b)) and was enhanced when phase transformation of anatase into rutile phase occurred at higher temperatures, whereas in the air atmosphere the nanotubular shape of the titanate particles was almost perfectly maintained. Thus, it seems that the low photocatalytic ability of the powder calcined under H₂ atmosphere would be ascribed to the defect formations of TiO_{2-x} with grayed color on the surface of the calcined particles and to the destruction of nanotubular shape by reducing atmosphere. Consequently, for the application of the H-TiNT powder as a high efficient photocatalyst, it can be thought that the powder should be calcined to have fully anatase phase at the condition of an appropriate time and temperature like 30 min at 475°C, under comparatively no severe agglomeration by the calcination of O₂ or air atmosphere. In addition, from the BET data, it could be thought that to obtain a high efficient anatase powder from the H-TiNT, powder should be calcined

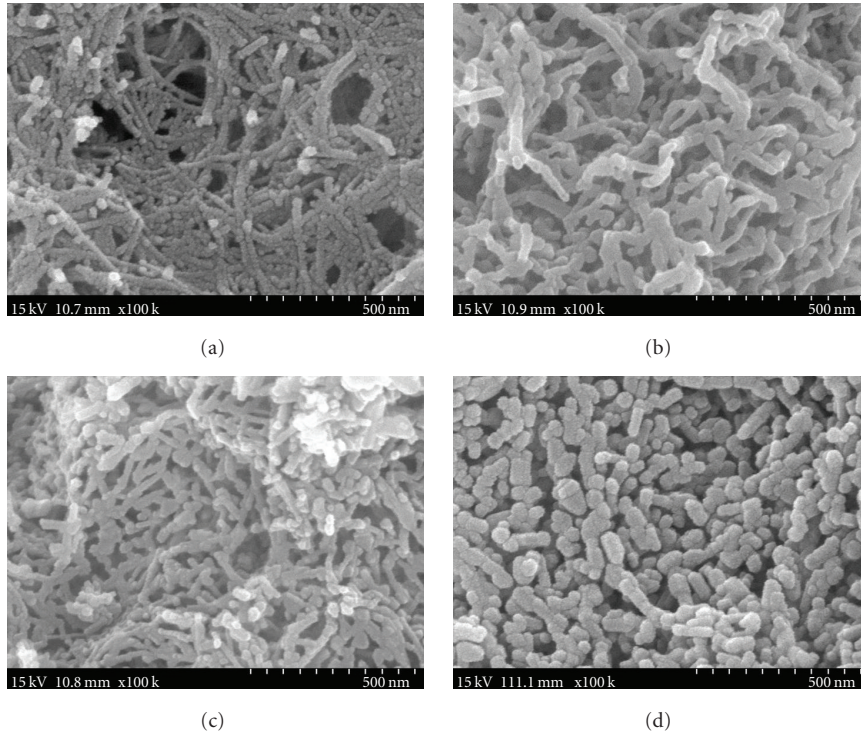


FIGURE 4: Scanning electron microscopy images of the calcined powders at 475°C for (a) 10 min, (b) 60 min, (c) 120 min, and (d) 240 min in O₂ atmosphere.

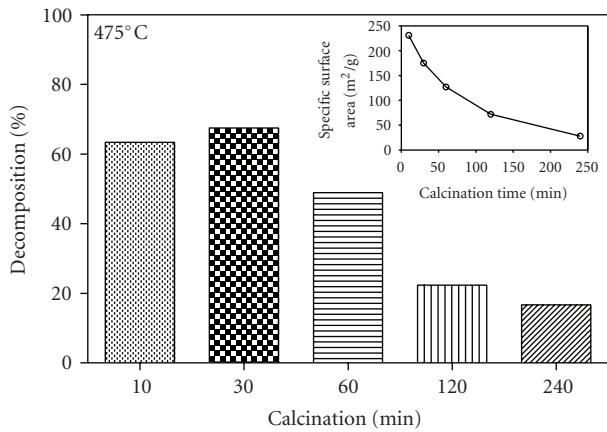


FIGURE 5: Photocatalytic 4-CP decomposition results of the powders calcined at 475°C for various times in O₂ atmosphere and variation of specific surface area shown in inset.

for a short time at the temperature as high as possible because the long time of calcination at lower temperature also makes severe agglomerations between the particles.

4. Conclusions

Photocatalytic activities of H-TiNT powders were characterized by controlling the calcination conditions as the function of times and atmospheres in the ranges of 400~500°C. With increasing calcination temperature and time,

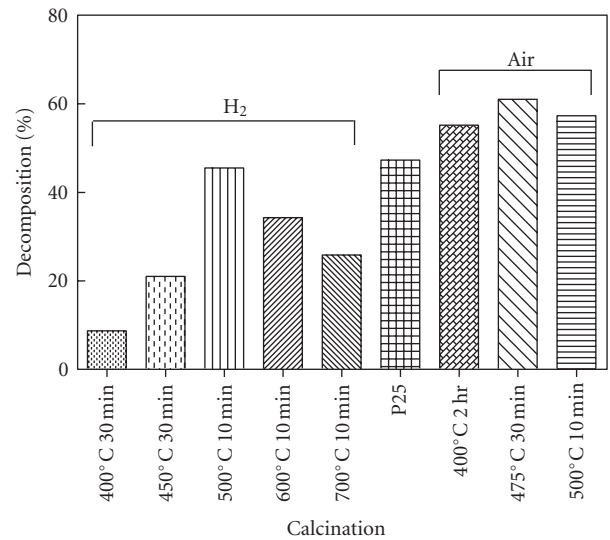


FIGURE 6: Photocatalytic 4-CP decomposition abilities of the powders with various calcination conditions.

the titanate phase in the ion-exchanged H-TiNT was changed into anatase phase and at the same time nanotube-shaped particles were naturally turned into nanoparticles at higher temperature and longer time. The calcined powders at 475°C for 30 min in O₂ or air atmosphere to maintain nanotubular shape with high surface area showed the highest decomposition ability in the photocatalytic reaction, whereas

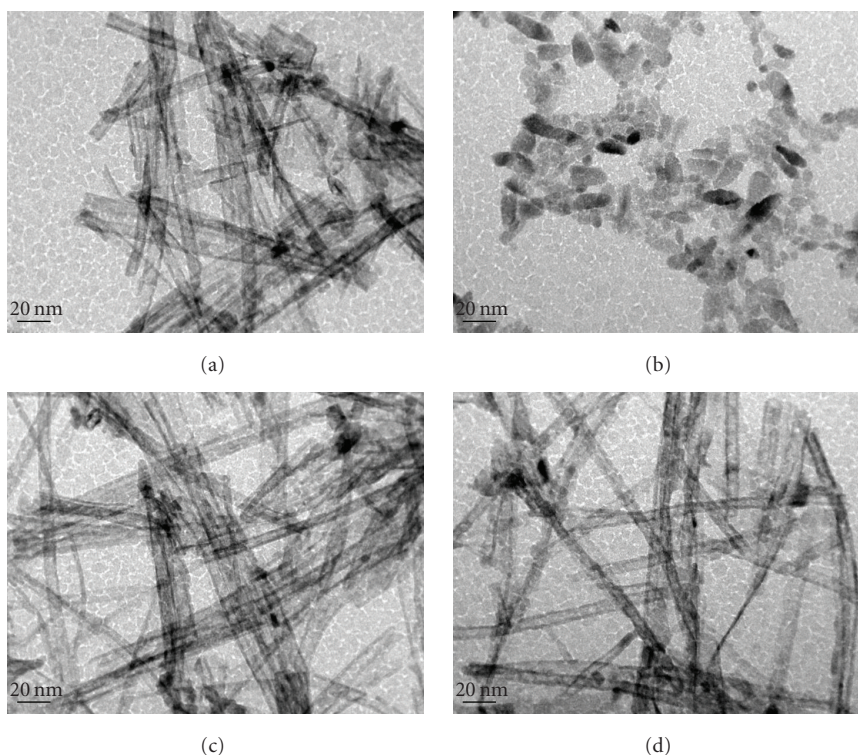


FIGURE 7: TEM photos for some samples in Figure 6; (a) 400°C for 30 min in H₂, (b) 500°C for 10 min in H₂, (c) 475°C for 30 min in air and (d) 500°C for 10 min in air atmosphere.

the powders calcined at 500°C or higher showed low photoactivity due to their severe agglomeration. Therefore, it can be thought that to obtain a high efficient anatase powder from the ion-exchanged H-TiNT powder should be calcined for a short time at a temperature high as much as possible because the long time calcination at lower temperature makes severe agglomerations between the particles.

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References

- [1] T. L. Thompson and J. T. Yates, "Surface science studies of the photoactivation of TiO₂—new photochemical processes," *Chemical Reviews*, vol. 106, no. 10, pp. 4428–4453, 2006.
- [2] X. Chen and S. S. Mao, "Titanium dioxide nanomaterials: synthesis, properties, modifications and applications," *Chemical Reviews*, vol. 107, no. 7, pp. 2891–2959, 2007.
- [3] D. V. Bavykin, J. M. Friedrich, and F. C. Walsh, "Protonated titanates and TiO₂ nanostructured materials: synthesis, properties, and applications," *Advanced Materials*, vol. 18, no. 21, pp. 2807–2824, 2006.
- [4] F. Garin, "Environmental catalysis," *Catalysis Today*, vol. 89, no. 3, pp. 255–268, 2004.
- [5] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, and K. Niihara, "Formation of titanium oxide nanotube," *Langmuir*, vol. 14, no. 12, pp. 3160–3163, 1998.
- [6] X. D. Meng, D. Z. Wang, J. H. Liu, and S. Y. Zhang, "Preparation and characterization of sodium titanate nanowires from brookite nanocrystallites," *Materials Research Bulletin*, vol. 39, no. 14-15, pp. 2163–2170, 2004.
- [7] Y. Lan, X. Gao, H. Zhu et al., "Titanate nanotubes and nanorods prepared from rutile powder," *Advanced Functional Materials*, vol. 15, no. 8, pp. 1310–1318, 2005.
- [8] M. Wei, Y. Konishi, H. Zhou, H. Sugihara, and H. Arakawa, "Utilization of titanate nanotubes as an electrode material in dye-sensitized solar cells," *Journal of the Electrochemical Society*, vol. 153, no. 6, pp. A1232–A1236, 2006.
- [9] J. Jitputti, S. Pavasupree, Y. Suzuki, and S. Yoshikawa, "Synthesis of TiO₂ nanotubes and its photocatalytic activity for H₂ evolution," *Japanese Journal of Applied Physics*, vol. 47, no. 1, pp. 751–756, 2008.
- [10] J. Li, Z. Tang, and Z. Zhang, "H-titanate nanotube: a novel lithium intercalation host with large capacity and high rate capability," *Electrochemistry Communications*, vol. 7, no. 1, pp. 62–67, 2005.
- [11] S. H. Lim, J. Luo, Z. Zhong, W. Ji, and J. Lin, "Room-temperature hydrogen uptake by TiO₂ nanotubes," *Inorganic Chemistry*, vol. 44, no. 12, pp. 4124–4126, 2005.
- [12] J. Yu, H. Yu, B. Cheng, and C. Trapalis, "Effects of calcination temperature on the microstructures and photocatalytic activity of titanate nanotubes," *Journal of Molecular Catalysis A*, vol. 249, no. 1-2, pp. 135–142, 2006.

- [13] M. Grandcolas, A. Louvet, N. Keller, and V. Keller, "Layer-by-layer deposited titanate-based nanotubes for solar photocatalytic removal of chemical warfare agents from textiles," *Angewandte Chemie International Edition*, vol. 48, no. 1, pp. 161–164, 2009.
- [14] S. Fujikawa, R. Takaki, and T. Kunitake, "Nanocopying of individual DNA strands and formation of the corresponding surface pattern of titania nanotube," *Langmuir*, vol. 21, no. 19, pp. 8899–8904, 2005.
- [15] C. H. Han, D. W. Hong, I. J. Kim, J. Gwak, S. D. Han, and K. C. Singh, "Synthesis of Pd or Pt/titanate nanotube and its application to catalytic type hydrogen gas sensor," *Sensors and Actuators B*, vol. 128, no. 1, pp. 320–325, 2007.
- [16] A. Fujishima, K. Hashimoto, and T. Watanabe, *TiO₂ Photocatalyst: Fundamentals and Applications*, BKC, Tokyo, Japan, 1999.
- [17] D. V. Bavykin and F. C. Walsh, *Titanate and Titania Nanotubes: Synthesis, Properties and Applications*, RSC Publishing, Cambridge, UK, 2010.
- [18] M. Qamar, C. R. Yoon, H. J. Oh et al., "Effect of post treatments on the structure and thermal stability of titanate nanotubes," *Nanotechnology*, vol. 17, no. 24, article no. 004, pp. 5922–5929, 2006.
- [19] M. Qamar, C. R. Yoon, H. J. Oh et al., "Preparation and photocatalytic activity of nanotubes obtained from titanium dioxide," *Catalysis Today*, vol. 131, no. 1–4, pp. 3–14, 2008.
- [20] S. J. Kim, Y. U. Yun, H. J. Oh et al., "Characterization of hydrothermally prepared titanate nanotube powders by ambient and in situ Raman spectroscopy," *Journal of Physical Chemistry Letters*, vol. 1, no. 1, pp. 130–135, 2010.
- [21] J. Yu, H. Yu, B. Cheng, X. Zhao, and Q. Zhang, "Preparation and photocatalytic activity of mesoporous anatase TiO₂ nanofibers by a hydrothermal method," *Journal of Photochemistry and Photobiology A*, vol. 182, no. 2, pp. 121–127, 2006.
- [22] N. H. Lee, H. J. Oh, C. R. Yoon et al., "Understanding for controls of particle shape of various titanates with layered structure," *Journal of Nanoscience & Nanotechnology*, vol. 8, no. 10, pp. 5158–5161, 2008.
- [23] Y. Guo, N. H. Lee, H. J. Oh, K. S. Park, S. C. Jung, and S. J. Kim, "Formation of 1-D nanostructures of titanate thin films and thermal stability study," *Journal of Nanoscience & Nanotechnology*, vol. 8, no. 10, pp. 5316–5320, 2008.
- [24] M. Qamar, S. J. Kim, and A. K. Ganguli, "TiO₂-based nanotubes modified with nickel: synthesis, properties, and improved photocatalytic activity," *Nanotechnology*, vol. 20, no. 45, Article ID 455703, 2009.
- [25] W. Li, T. Fu, F. Xie, S. Yu, and S. He, "The multi-staged formation process of titanium oxide nanotubes and its thermal stability," *Materials Letters*, vol. 61, no. 3, pp. 730–735, 2007.
- [26] E. Morgado, M. A. S. de Abreu, O. R. C. Pravia et al., "A study on the structure and thermal stability of titanate nanotubes as a function of sodium content," *Solid State Sciences*, vol. 8, no. 8, pp. 888–900, 2006.
- [27] X. Sun and Y. Li, "Synthesis and characterization of ion-exchangeable titanate nanotubes," *Chemistry: A European Journal*, vol. 9, no. 10, pp. 2229–2238, 2003.



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