

Photocatalytic activity of TiO₂ nanomaterials

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To investigate the effect of calcination temperature on crystal structure, phase, and photocatalytic activity of methylene blue (MB), TiO₂ nanofibers were prepared through sol-gel derived electrospinning, calcination from 500 °C to 650 °C, and subsequent mechanical grinding. XRD results indicated that TiO₂ nanofibers calcined at 500 °C is composed of anatase TiO₂ only. However, mixed crystals of anatase and rutile were observed for TiO₂ calcined above 550 °C. Higher MB degradation was observed for the TiO₂ nanofibers calcined at 550 °C most likely due to the mixed crystals and large surface area. Enhanced photocatalytic activity was achieved for TiO₂ and Nb-TiO₂ nanotubes due to the synergic combinations of mixed crystals and larger specific surface area.

Key words: TiO₂, Nb-TiO₂, Nanofiber, nanotube, Photocatalytic activity, Methylene blue.

Introduction

TiO₂ photocatalysts have been investigated extensively for environmental applications such as air, water treatment, and deodorizer because of its strong oxidizing power, high photocatalytic activity, self-cleaning function, bactericidal and detoxification activity [1-10]. TiO₂ under ultraviolet (UV) illumination has been proposed as the most effective and advanced removal alternative for environmental and biomedical applications for its efficiency of electron-hole pair separation and its optical absorption property [1]. TiO₂ under UV radiation can be excited to organic pollutants into carbon dioxide and water [1-6]. The suitable doping has exhibited the enhancement of TiO₂ photoactivity [2-6]. TiO₂ possessing wide band gap energy of 3.20 ~ 3.56 eV for anatase and 3.00 ~ 3.34 eV for rutile limits its uses to those involving UV radiation [4, 5].

Although suitable doping (Pt, W, Er, Al, Nb) has exhibited the enhancement of photoactivity of the dopant decorated TiO₂ under visible light [1-5], few studies have been done regarding the effect of calcination temperature on the photocatalytic activity of un-doped TiO₂ nanomaterials. In this study, a sol-gel derived electrospinning was used to fabricate TiO₂ nanomaterials. The catalytic properties of TiO₂ nanofibers calcined in the temperature range of 500 °C to 650 °C and TiO₂ and Nb-TiO₂ nanotubes calcined at 500 °C were investigated by using a pyrex cylindrical photoreactor and an UV-vis spectrophotometer (Jasco V-670, Japan) [3].

Experimental

TiO₂ nanofibers

The precursor solution was prepared from titanium tetraisopropoxide (Ti(OCH(CH₃)₂)₄, 98%, Aldrich, USA) in ethanol by stirring. Polyvinylpyrrolidone (PVP, Mw = 1,300,000, Aldrich, USA) dissolved in ethanol. Then, acetic acid was added to the TiO₂ precursor solution by weight [7]. The solutions were mixed and stirred for 1 h at room temperature. The precursor solution was then filtered by using a sintered glass filter (16 ~ 40 μm) to remove possible impurities in the solution. The electrospinning apparatus consisted of a syringe pump (KDS-200, Stoelting Co., USA), a 22 gage BD metal needle, a grounded collector, and a high-voltage supply (ES30P-5W, Gamma High Voltage Research Inc., USA) equipped with current and voltage digital meters. The solution was placed in a 5 mL BD luer-lok syringe attached to the syringe pump and fed into the metal needle at a flow rate of 0.5 mL/h. A piece of flat aluminum foil was placed 10 cm below tip of the needle to collect the nanofibers with a voltage of 10 kV. The as-spun nanofibers were dried in air for 5 hrs to allow the hydrolysis of Ti(OCH(CH₃)₂)₄. Subsequently, annealing for 3 hrs at temperatures in the range of 500 °C to 650 °C in air was performed to remove the PVP and achieve the crystallization of titania. The nanofibers were ground mechanically in a pestle and mortar to produce nanorods. The diameter and the morphology of the nanorods were evaluated using SEM (Hitachi S-3000H, Japan) and TEM (JEM-2000EX, Jeol, Japan). All specimens were coated with Au/Pd to ensure higher conductivity. The crystalline phases of the TiO₂ nanorods were analyzed

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by using an XRD (Mac Science, KFX-987228-SE, Japan).

TiO₂ nanotubes

TiO₂ and Nb-TiO₂ nanotubes were prepared by electrospinning two immiscible liquids through a dual concentric nozzle (17G-23G) followed by selective removal of the cores as described elsewhere [14]. The concentration of Ti(OiPr)₄ precursor and PVP were 0.14 and 0.09 g/mL, respectively [7]. The preparation of Nb-TiO₂ precursor solution was described elsewhere [5, 11, 12]. During the preparation of TiO₂ and Nb-TiO₂ nanotubes, the feeding rates for heavy mineral oil (Sigma-aldrich, USA) and TiO₂/Nb-TiO₂ sol were 0.01 and 0.5 mL/hr, and 0.1 and 1.0 mL/hr, respectively. The electric fields were 1.34 kV/cm and 1.22 kV/cm, respectively. Hollow nanofibers were obtained by immersing the fibers in octane (CH₃(CH₂)₆CH₃, Sigma-Aldrich, USA) for 7 days and the subsequent calcination for 3 hrs at 500 °C.

Photocatalytic activity

A pyrex cylindrical photoreactor enclosed by a blackbody was used in the experiment [3]. A 9-W medium-pressure mercury lamp with a main emission peak at 365 nm (Philips, PL-S 9W/10/2P, Holland) was positioned at the center of the cylindrical vessel with a circulating water jacket to control the temperature at 25 ± 1 °C during the reaction. The reaction suspension was prepared by adding 0.1 g of photocatalyst (0.2 g/L) into 500 mL of methylene blue (MB, Daejung Chemicals & Metals Co., Korea) solution with a concentration of 10 mg/L. Prior to photocatalytic oxidation, the suspension was stirred in a dark condition for 120 min for adsorption and desorption equilibrium, which was considered as the initial concentration (*C*₀) after dark desorption. The aqueous suspension containing MB and photocatalyst was irradiated under UV illuminated with constant aeration. Air at a flow rate of 2 L/min was bubbled through the reaction solution from the bottom to ensure a constant dissolved oxygen concentration [8, 9]. At the given time intervals, the analytical samples were taken regularly from the suspension and immediately centrifuged at 2000 rpm for 20 min, and then filtered through a 0.45 µm Millipore filter to remove the particles. The change of adsorption at 664 nm was applied to identify the concentration of MB using an UV-vis spectrophotometer. The concentration of MB was measured as a function of irradiation time [3, 10-15].

Results and Discussion

Our previous studies reported that uniform, smooth, and continuous fibers with a diameter of 120 nm were observed for the fibers calcined for 3 hrs at 500 °C containing a PVP concentration of 0.09 g/mL and a Ti(OCH(CH₃)₂)₄ concentration of 0.14 g/mL at a flow

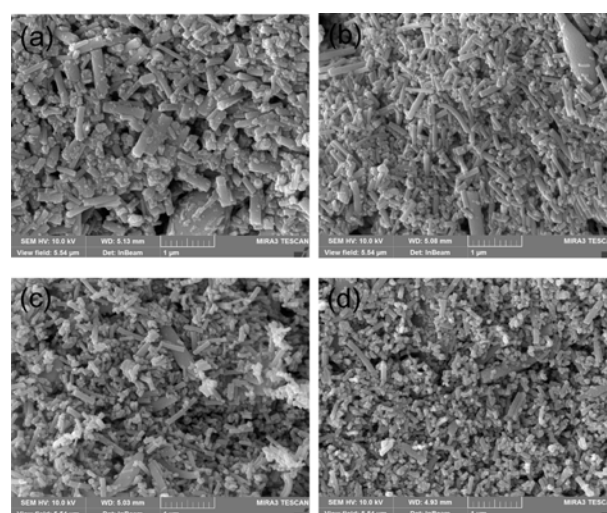


Fig. 1. SEM images of TiO₂ nanorods calcined for 3 hrs at (a) 500 °C, (b) 550 °C, (c) 600 °C, and (d) 650 °C, respectively.

Table 1. Crystallite size and phase fraction of TiO₂ nanofibers, nanotubes, and Nb-TiO₂ nanotubes calcined at various temperatures.

Calcination temperature (°C)	Phase	Content (%)	Crystal-lite size (nm)	Diameter (nm)	BET surface area (m ² /g)
500 (nanorod)	Anatase only	100/0	16/-	108 ± 20	16.75
550 (nanorod)	Anatase/rutile	58/42	15/15	80 ± 14	21.96
600 (nanorod)	Anatase/rutile	50/50	16/17	76 ± 19	20.89
650 (nanorod)	Anatase/rutile	27/73	17/23	74 ± 18	20.40
500 (nanotube)	Anatase/rutile	76/24	11/7.4	130 ± 40	34.21
500 (Nb-TiO ₂)	Anatase/rutile	61/39	4.2/9.1	110 ± 10	73.70

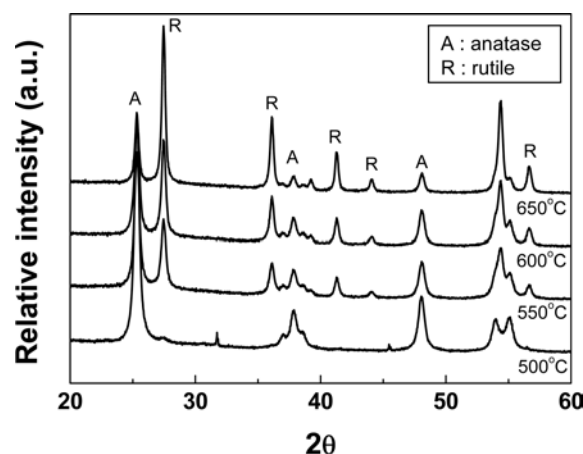


Fig. 2. XRD patterns of TiO₂ nanorods calcined at different temperatures.

rate of 0.5 mL/h and an electric field of 1 kV/cm [7]. In the present study, the TiO₂ fibers were calcined for

3 hrs at temperatures from 500 °C to 650 °C under the above-mentioned condition, followed by mechanical grinding to produce nanorods, as shown in Fig. 1. SEM results revealed that the diameter of TiO₂ nanorods decreased from 120 nm to 74 nm with increasing the calcination temperature from 500 °C to 650 °C. The specific surface area played a key role in the adsorption ability of materials. The larger the surface area of the catalyst, the better the adsorption capacity. The largest specific surface area determined a Barrette-Emmett-Teller (BET) method (ASAP 2010, Micromeritics, USA), as listed in Table 1, is found for the nanofiber calcined at 550 °C (21.96 m²/g). The TiO₂ nanorods possessing mixed crystalline phases (anatase and rutile), as displayed in Fig. 2, showed the largest BET surface area.

XRD patterns for TiO₂ nanorods were presented in Fig. 2. The anatase-to-rutile ratio was calculated according to Parida and Sahu [13], % of anatase phase = $100 / \{1 + (I_R / 0.79I_A)\}$, where I_A and I_R are the intensity of strongest diffraction line (101) of anatase phase and (110) of rutile phase, respectively. The results indicated that the nanorods calcined at 500 °C consisted of pure anatase (JCPDS-21-1272) with no traces of rutile TiO₂ (JCPDS-41-1445). The anatase TiO₂ peak located at 25°, corresponding to the (101) plane, became weaker with increase in the calcination temperature. On the other hand, the rutile peak located at 27.4°, corresponding to the (110) plane, became stronger as depicted in Fig. 2. As the calcination temperature rose from 500 °C to 550 °C, 600 °C, 650 °C, the extent of anatase to rutile phase transformation increased from 0% to 42%, 50%, and 73%, respectively. The TiO₂ nanorods calcined at 550 °C exhibited mixed crystals of 58% anatase and 42% rutile TiO₂. The crystallite size of anatase and rutile TiO₂ determined by the Scherrer formula is summarized in Table 1. The smallest crystallite size of both anatase and rutile TiO₂ was observed for the TiO₂ calcined at 550 °C. Smaller crystallite size may correspond to larger surface area, which is consistent with BET results. Larger specific surface area is likely to be effective to the photocatalytic activity.

In order to enhance catalytic activity, TiO₂ and Nb-TiO₂ nanotubes were prepared by electrospinning two immiscible liquids through a dual concentric nozzle (17G-23G), followed by selective removal of the cores [12, 16]. Increased specific surface area was observed (Table 1). XRD results (Fig. 3) showed mixed crystalline phases of anatase (76%) and rutile (24%) with an average crystallite size around 11 nm and 7 nm, respectively. It is reported that the best ratio for photocatalysis of the anatase to rutile phase is between 70 : 30 and 80 : 20 due to higher porosity, which aligns with our results [17]. TEM image of TiO₂ nanotube (Fig. 4) indicates the formation of tubular structures, uniform in size, with an inner diameter (lighter portion) of 100 nm and wall thickness (darker portion) of 15 nm. Although the ratio of the anatase to rutile phase

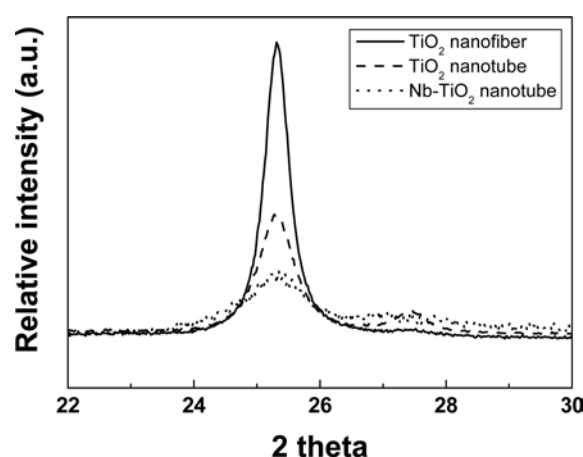


Fig. 3. XRD patterns of TiO₂ nanofiber, nanotube, and Nb-TiO₂ nanotube calcined at 500 °C.

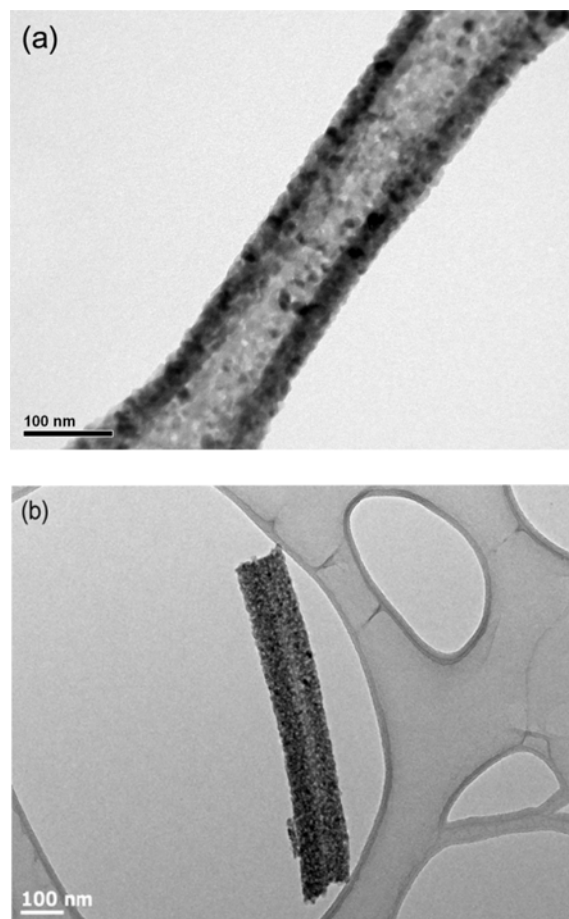


Fig. 4. TEM image of (a) TiO₂ and (b) Nb-TiO₂ nanotube fabricated by electrospinning and subsequent calcination for 3 hrs at 500 °C in air.

decreased from 76/24 to 61/39 for the Nb-TiO₂ nanotube, the BET surface area increased twice higher than that of TiO₂ nanotube. It was reported that nanotubes having larger specific surface area than nanofibers may absorb more oxygen, resulting in the formation of more electrons and holes [17]. For

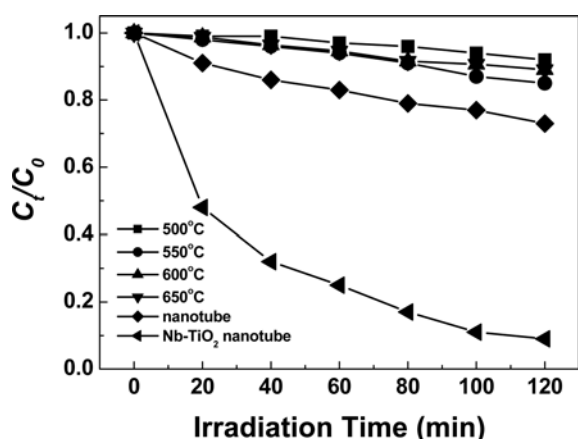


Fig. 5. The photodegradation of MB on different TiO₂ catalysts calcined at different temperatures under UV light. Note that the TiO₂ and the Nb-TiO₂ nanotubes were calcined at 500 °C.

photocatalytic activity, the light-trapping effect inside the nanotube may improve the utilization rate of light. The light enters inside the porous nanotube and is repeatedly reflected inside the nanotube until it is completely absorbed, leading to the improved photocatalytic activity. In addition, the Fermi energies of the two phases had to be the same, leading to both the conduction and valence bands of rutile TiO₂ to lie above that of anatase TiO₂, inducing the electrons and holes to concentrate on anatase and rutile TiO₂, respectively [16]. The separated electrons and holes are likely to participate in the photocatalytic reaction. Larger specific surface area, light-trapping effect, and the greater separation of the photogenerated electrons may be attributed to enhanced catalytic activity.

The photocatalytic activities of TiO₂ catalysts were investigated by the photodegradation of MB under UV light (365 nm) [3]. No degradation of MB without catalysts was observed because the energy of 365 nm was too low to degrade the dye molecule. After 120 min of UV irradiation and aeration with TiO₂ catalysts calcined at 500 °C, ~8% degradation of MB was monitored at 664 nm absorbance measurements, most likely due to the adsorption of dye molecule on the surface of TiO₂. TiO₂ catalysts calcined at 550 °C enhanced MB degradation by ~15%. However, higher calcination above 550 °C was detrimental to the photodegradation of MB. Fig. 5 shows the plot of (C_t/C_0) versus time (t), where C_0 and C_t are the initial concentration of MB and the concentration at any time t , respectively. Since all the curves can be fitted roughly to an exponential relation, the degradation kinetics of MB on various TiO₂ catalysts under UV light can be analyzed by a pseudo-first-order kinetic model. A Langmuire-Hinshelwood type of kinetic model, $-\ln(C_t/C_0) = k_r K_d t = kt$, where k_r , K_d , and k are the degradation kinetic constant, the adsorption equilibrium constant, and the apparent kinetic constant (min⁻¹) [3, 11, 12]. It was reported that the apparent kinetic constant (k) showed a similar

behavior of the degradation constant (k_r), suggesting that the adsorption played an important role in the degradation of MB on TiO₂ [3]. The calculated data for the first-order rate constant (k) of TiO₂ catalyst calcined 500 °C at 10 ppm MB concentration were found to be $6.6 \times 10^{-4} \text{ min}^{-1}$. The degradation kinetic constant (k) increased from $6.6 \times 10^{-4} \text{ min}^{-1}$ to $1.4 \times 10^{-3} \text{ min}^{-1}$ with the temperature rise from 500 °C to 550 °C, but decreased to $1.0 \times 10^{-3} \text{ min}^{-1}$ with further heating, suggesting that the TiO₂ nanofibers calcined at 550 °C may be the best catalyst for the photodegradation of MB. The photocatalytic activity of TiO₂ and Nb-TiO₂ nanotube catalysts was also examined. After 120 min of UV irradiation and aeration with TiO₂ and Nb-TiO₂ nanotubes, ~30% and 90% degradations of MB were monitored (Fig. 5). Their k values were 2.4×10^{-3} and $1.9 \times 10^{-2} \text{ min}^{-1}$, respectively. The k value of Nb-TiO₂ nanotube was hundred times higher than that of TiO₂ nanofibers. The improved catalytic activity may be due to the synergic combinations of mixed crystals, larger BET surface area, and Nb doping effect [4].

Conclusions

Undoped TiO₂ nanorods were synthesized by sol-gel derived electrospinning, calcination from 500 °C to 650 °C, and subsequent mechanical grinding. XRD results indicated that TiO₂ calcined at 500 °C showed anatase TiO₂ only. However, the co-existence of anatase and rutile phases was found for the TiO₂ calcined above 550 °C. The TiO₂ nanorods calcined at 550 °C showed the highest MB degradation. k increased from $6.6 \times 10^{-4} \text{ min}^{-1}$ to $1.4 \times 10^{-3} \text{ min}^{-1}$ with the increase of temperature from 500 °C to 550 °C. It is found that the degradation of MB under UV radiation was more efficient with TiO₂ consisting of mixed crystals. The improved catalytic activity was obtained for the TiO₂ nanotube due to the synergic combinations of mixed crystals and larger BET surface area as well as Nb doping effect. The highest k value of $1.9 \times 10^{-2} \text{ min}^{-1}$ was discovered for the Nb-TiO₂ nanotube most likely due to the mixed crystal phases, larger BET surface area, and Nb doping effect.

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References

1. D.Y. Lee, J.Y. Park, B. Kim, and N. Cho, J. Nanosci. Nanotechnol. 12 (2012) 1599-1603.
2. D.Y. Lee and N. Cho, Physica Status Solidi C 9 (2012)

- 1423-1426.
3. D.Y. Lee, M. Lee, and N. Cho, *Current Appl. Phys.* 12 (2012) 1229-1233.
 4. D.Y. Lee, J. Park, Y. Kim, M. Lee, and N. Cho, *Current Appl. Phys.* 14 (2014) 421-427.
 5. Y. Song, B. Kim, N. Cho, and D.Y. Lee, *J. Nanosci. Nanotechnol.* 15 (2015) 5228-5231.
 6. X.Z. Li, F.B. Li, C.L. Yang, and W.K. Ge, *J. Photochem. Photobio. A: Chem.* 141 (2001) 209-217.
 7. D.Y. Lee, B. Kim, S. Lee, M. Lee, Y. Song, and J. Lee, *J. Korean Phys. Soc.* 48 (2006) 1686-1690.
 8. K. Fujihara, A. Kumar, R. Jose, S. Ramakrishna, and S. Uchida, *Nanotechnol.* 18 (2008) 365709.
 9. J. Shi, J. Zheng, and P. Wu, *J. Hazard. Mater.* 161 (2009) 416-422.
 10. C. Liang, M. Hou, S. Zhou, F. Li, C. Liu, T. Liu, Y. Gao, X. Wang, and J. Lu, *J. Hazard. Mater.* 138 (2006) 471-478.
 11. D.Y. Lee, M. Lee, B. Kim, and N. Cho, *J. Nanosci. Nanotechnol.* 16 (2016) 5341-5344.
 12. D.Y. Lee, S. Son, M. Jeon, M. Lee, and B. Kim, in *Proceedings of SPIE 9798, Electroactive Polymer Actuators and Devices (EAPAD) 2016*, edited by Y. Bar-Cohen and F. Vidal (April, 2016), p. 97982N (doi:10.1117/12.2217884).
 13. K.M. Parida and N. Sahu, *J. Mol. Catal. A: Chem.* 287 (2008) 151-158.
 14. A.L. Linsebiger, G.Q. Lu Jr., and J.T. Yates, *Chem. Rev.* 95 (1995) 735-758.
 15. C.Y.W. Lin, A. Nakaruk, and C.C. Sorrell, *Prog. Org. Coat.* 74 (2012) 645-647.
 16. D. Li and Y. Xia, *Nano Lett.* 4 (2004) 933-938.
 17. B. Lu, C. Zhu, Z. Zhang, W. Lan, and E. Xie, *J. Mater. Chem.* 22 (2012) 1375-1379.