

Formation of Poly(vinyl alcohol)-Titanium Lactate Hybrid Nanofibers and Properties of TiO₂ Nanofibers Obtained by Calcination of the Hybrids

Koji Nakane, Kaori Yasuda, Takashi Ogihara, Nobuo Ogata, Shinji Yamaguchi

Materials Science and Engineering Course, Graduate School of Engineering, University of Fukui, Bunkyo 3-9-1, Fukui 910-8507, Japan

Received 14 February 2006; accepted 4 November 2006

DOI 10.1002/app.25769

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: New organic-inorganic hybrid nanofibers, poly(vinyl alcohol) (PVA)-titanium lactate (TL) hybrid nanofibers, were formed by electrospinning employing water as a solvent. Anatase-type TiO₂ nanofibers were obtained by calcination of the hybrid nanofibers in air. The fiber diameters of the PVA-TL hybrid nanofibers was 200–350 nm, and the fiber diameter of the TiO₂ nanofibers was 70–80% of that of the PVA-TL hybrid nanofibers. The specific surface area and av-

erage pore diameter of the TiO₂ nanofiber calcined at 500°C for 5 h were 21.0 m²/g and 7.4 nm, respectively. The photocatalytic decomposition of methylene blue using the TiO₂ nanofibers was also investigated. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1232–1235, 2007

Key words: electrospinning; nanofiber; poly(vinyl alcohol); titanium lactate; titanium oxide

INTRODUCTION

Recently, much attention has been paid to the formation of polymeric nanofibers by electrospinning.^{1–4} The average diameter of the fibers produced by this method is at least one or two orders of magnitude smaller than those of conventional fiber production methods like melt or solution spinning.⁵ As a result, the electrospun fibers have larger specific surface area.⁴ These nanofibers are well-suited to be used as chemical reaction fields.⁶

Inorganic nanofibers can be obtained by the calcination of organic-inorganic hybrid precursor nanofibers formed by electrospinning.⁷ Many kinds of inorganic nanofibers (Al₂O₃, ZrO₂, NiCo₂O₄, and so on) have been formed from organic-inorganic hybrid precursor nanofibers.^{8–11} Li et al. formed anatase-type titanium oxide (TiO₂) nanofibers by the calcination of poly(vinyl pyrrolidone)-Ti tetraisopropoxide hybrid nanofibers in air at 500°C.⁸ The TiO₂ nanofibers would be a useful material for a photocatalytic reaction, but their usage has not been investigated. Ethanol has been used as the solvent of the spinning solution to form the hybrid precursor nanofibers.⁸ Therefore, a spinneret could be stopped up by a solid material because ethanol will evaporate from the tip of the spinneret during the spinning. Furthermore, Ti tetraisopropoxide is very easily hydrolyzed, and thus

a water-free condition is required for the use of Ti tetraisopropoxide.

In the present study, we formed new organic-inorganic hybrid nanofibers, poly(vinyl alcohol) (PVA)-titanium lactate (TL) hybrid nanofibers, using water as a solvent during electrospinning, and TiO₂ nanofibers were formed by calcination of the hybrid nanofibers. TL is a water-soluble titanium compound¹² and mixes well with PVA aqueous solution. The PVA-TL mixed aqueous solution was used as the spinning solution to form the hybrid nanofibers. Many kinds of organic-inorganic hybrid materials have been formed using water as a solvent,^{13–19} but the formations of their nanofibers have not been reported. Therefore, our process provides a simple and convenient method to form organic-inorganic hybrid nanofibers by means of electrospinning. The photocatalytic reaction using the obtained TiO₂ nanofibers was also investigated.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) (degree of polymerization: 1500) was obtained from Wako Pure Chemicals Ind., Japan. Titanium lactate (TL) [(OH)₂Ti(C₃H₅O₂)₂] was kindly gifted from Matsumoto Chemical Industry Co., Japan (TC-310, content: TL 35–45%, 2-propanol 40–50%, water 10–20%).

Formation of PVA-TL hybrid nanofibers by electrospinning

PVA (10 wt %) aqueous solution was prepared. TL (TC-310, 5 g) was added to the PVA solution (10 g) to

Correspondence to: K. Nakane (nakane@matse.fukui-u.ac.jp).

produce transparent PVA-TL mixed solution (spinning solution).

The mixed solution was loaded into a plastic syringe (2 mL) equipped with a needle. The solution extrusion rate was 0.015 mL/min. A voltage of 25 kV was applied to the needle, and the PVA-TL hybrid nanofibers were then deposited on a collector. The collector (copper plate) was grounded, and the distance between the tip of the needle and the collector was 10 cm. The PVA-TL hybrid nanofibers obtained were used as a precursor of TiO₂ nanofibers.

Formation of TiO₂ nanofibers by calcination of PVA-TL hybrid nanofibers

The PVA-TL hybrid nanofibers were calcined up to a given temperature in an electric furnace at 400–700°C in air, and TiO₂ nanofibers were obtained.

Apparatus and procedure

The structure of the nanofibers was observed by scanning electron microscope (SEM) (Hitachi S-2400, Japan).

Thermogravimetric (TG) analysis was performed in air at a heating rate of 10°C/min (Shimadzu DTG-60, Japan).

X-ray diffraction (XRD) measurement was taken using a Cu K α with a Ni filter (40 kV, 30 mA) (Shimadzu XRD-6100, Japan).

The nitrogen adsorption isotherms (–196°C) of the TiO₂ nanofibers were measured by Micromeritics TriStar 3000, USA.

The photocatalysis of the TiO₂ nanofibers was evaluated using the photocatalytic decomposition of methylene blue (3,7-bis(dimethylamino)phenothiazin-5-ium chloride; C₁₆H₁₈ClN₃S).²⁰ The TiO₂ nanofibers

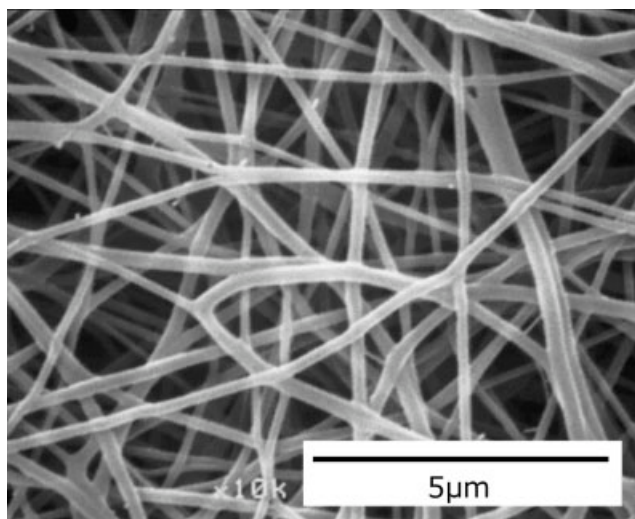


Figure 1 SEM image of PVA-TL nanofibers.

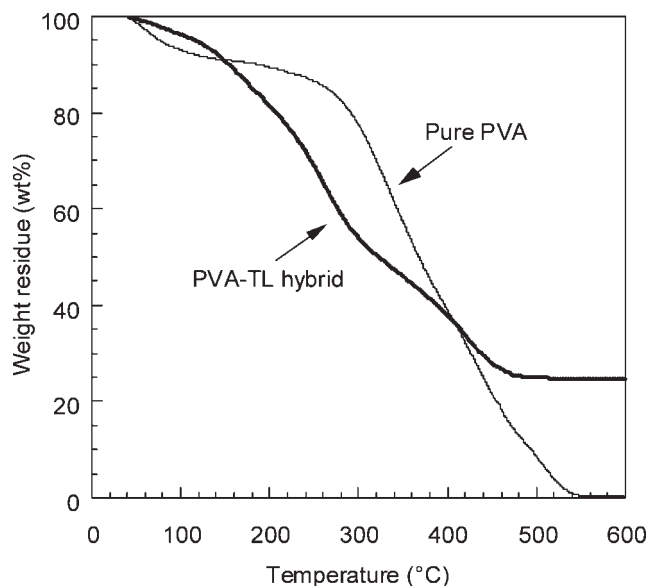


Figure 2 Thermogravimetric analysis curves of PVA-TL hybrid and pure PVA nanofibers.

formed (5 mg) were dispersed in methylene blue (1×10^{-5} mol/L) aqueous solution (50 mL). Three milliliters of test liquid was taken from this solution and fed in a quartz cell. The test solution was irradiated with white light using an extra-high pressure mercury vapor lamp (Ushio, Japan), and the absorbance at 665 nm, which is the maximum absorption wavelength of methylene blue, was measured by an absorptiometer (JASCO, CT-109, Japan). The decomposition rate of methylene blue was calculated from the absorbance.

RESULTS AND DISCUSSION

Figure 1 shows the SEM image of PVA-TL hybrid nanofibers formed by electrospinning. The fiber diameters of the PVA-TL nanofibers are 200–350 nm, and the fibers have a smooth surface without macropores. The specific surface area and the pore volume of the hybrid nanofiber are 1.80 m²/g and 0.00764 cm³/g, respectively. Thus, the hybrid nanofiber is considered a nonporous material.

The viscosity of the PVA-TL mixed aqueous solution (spinning solution) increased very slowly. This phenomenon is due to the interaction between PVA and TL. But the diameters of the nanofibers obtained from the spinning solutions stored within 3 days showed no change.

Figure 2 shows TG curves of the pure PVA and the PVA-TL hybrid nanofibers. The weight residue of pure PVA becomes zero at 550°C, and that of the PVA-TL hybrid is 25% at 600°C. White residues (TiO₂) were obtained after measurement for PVA-TL hybrid.

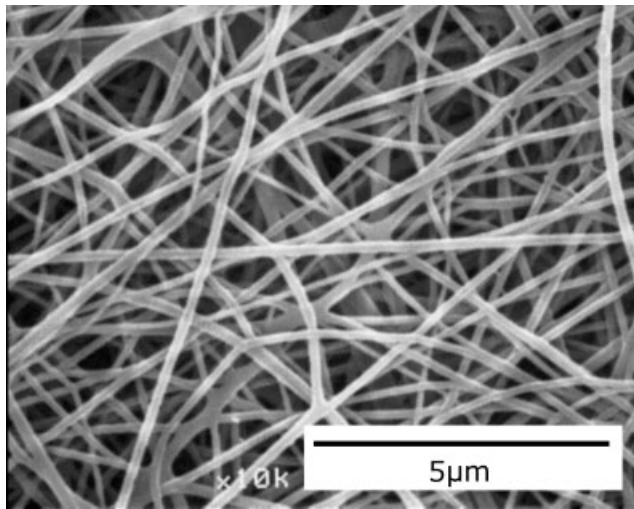


Figure 3 SEM image of TiO₂ nanofibers obtained by calcination of PVA-TL hybrid nanofibers at 400°C for 5 h in air.

Figure 3 shows a SEM image of the TiO₂ nanofibers obtained by the calcination of PVA-TL hybrid nanofibers at 400°C for 5 h. Compared with the images shown in Figure 1, the fiber diameter of the TiO₂ nanofibers is 70–80% of that of the PVA-TL hybrid nanofibers, with the space between the fibers made denser by calcination. The residues are brittle, but maintained the shape of the PVA-TL hybrid nonwoven mat, although shrinkage occurred due to the calcination.

Figure 4 shows XRD curves of the TiO₂ obtained by calcination of the PVA-TL nanofibers at 400–700°C for 5 h. Anatase-type TiO₂ is formed at 400–600°C, and

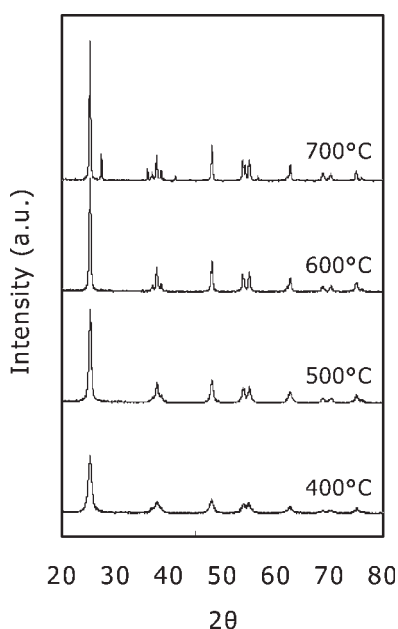


Figure 4 XRD curves of TiO₂ nanofibers obtained by calcination of PVA-TL hybrid nanofibers at various temperatures for 5 h in air.

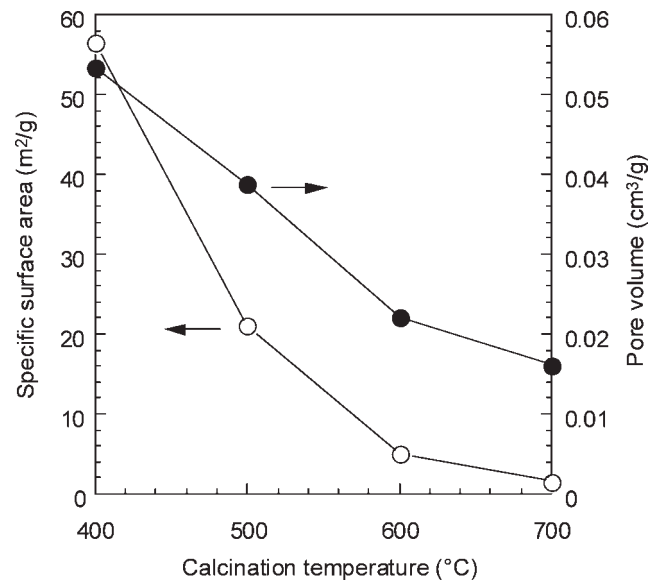


Figure 5 Effect of calcination temperature of nanofibers upon specific surface area and pore volume of TiO₂ nanofibers obtained.

the peak intensity increases with calcination temperature. Rutile-type (rutile-anatase mixed) TiO₂ is formed at 700°C. It is well known that anatase is superior to rutile for photocatalysis. Thus, a calcination temperature of 600–700°C would be an effective condition when using the TiO₂ nanofibers as a photocatalyst.

Figure 5 shows the relationship of the calcination temperature of the hybrid nanofibers and the pore

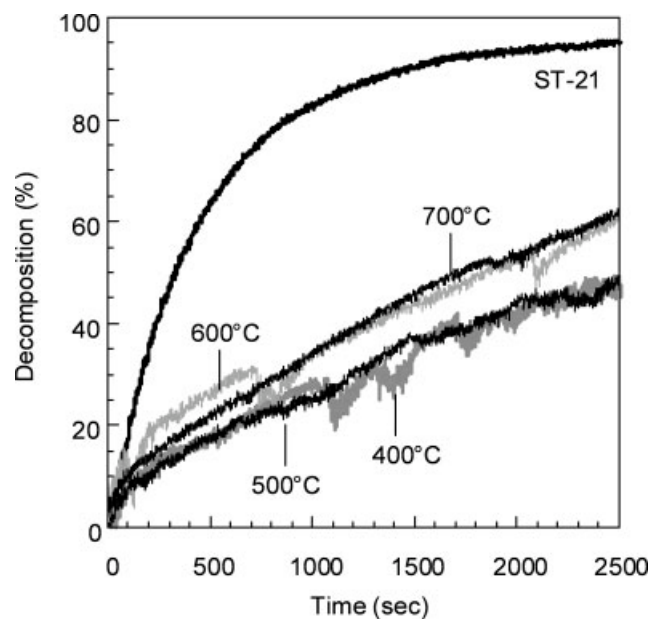


Figure 6 Effect of irradiation time of white light upon the photocatalytic decomposition rate of methylene blue for the TiO₂ nanofibers obtained from PVA-TL hybrid nanofibers at various calcination temperatures and commercially available TiO₂ nanoparticles (ST-21).

characteristics (specific surface area and pore volume) obtained from the nitrogen adsorption isotherms (-196°C) of the TiO_2 nanofibers. The specific surface area and pore volume of the TiO_2 nanofibers decrease with the calcination temperature. This is due to the sintering of the TiO_2 by the calcination. The average pore diameters (d_p), which were assumed to be cylindrical in shape, were based on the specific surface area (S) and pore volume (V) for each TiO_2 nanofiber: $d_p = 4V/S$. The d_p of the TiO_2 nanotubes were 3.8 nm (calcination temperature: 400°C), 7.4 nm (500°C), 17.5 nm (600°C), and 44.0 nm (700°C). Consequently, the TiO_2 nanofibers obtained in this study are classified as mesoporous materials.²¹

The photocatalysis of the TiO_2 nanofibers and commercially available anatase type TiO_2 nanoparticles (Ishihara Sangyo Kaisha: ST-21, particle size: 20 nm, specific surface area: *ca.* $50\text{ m}^2/\text{g}$) was investigated. Figure 6 shows the relationship between the decomposition rate of methylene blue and the irradiation time of white light for each TiO_2 . The photocatalysis of the TiO_2 nanofibers calcined at 600°C and 700°C is higher than those of the TiO_2 nanofibers calcined at 400°C and 500°C , but the major differences between each TiO_2 nanofiber are not observed. The crystallinity of anatase-type TiO_2 increases with calcination temperature, though the specific surface area becomes lower. The photocatalysis of the TiO_2 nanofibers would be affected by both the crystallinity and pore characteristics of the TiO_2 nanofibers. The TiO_2 nanofibers have good photocatalysis, but the properties of the TiO_2 nanofibers are inferior to that of ST-21. The specific surface area of the TiO_2 nanofiber calcined at 400°C ($56.4\text{ m}^2/\text{g}$) is higher than that of ST-21, but the ST-21 excels in photocatalysis. This would be due to the difference of the crystallinity of anatase. However, the TiO_2 nanofibers have the advantage of being easily fixed on other materials, such as a stainless-steel woven fabric, without a binder by the fiber length (ST-21 requires a binder to be fixed on other materials.).

CONCLUSIONS

PVA-TL hybrid nanofibers were formed by electrospinning using water as a solvent. Anatase-type TiO_2 nanofibers were easily obtained by calcination of the PVA-TL hybrid nanofibers. The TiO_2 nanofibers obtained had a high specific surface area and showed good photocatalysis. By optimizing the calcination conditions, TiO_2 nanofibers with higher photocatalysis could be formed.

References

1. Doshi, J.; Reneker, D. H. *J Electrostatics* 1995, 35, 151.
2. Buchko, C. J.; Chen, L. C.; Shen, Y.; Martin, D. C. *Polymer* 1999, 40, 7397.
3. Huang, Z.-M.; Zhang, Y.-Z.; Kotaki, M.; Ramakrishna, S. *Comp Sci Tech* 2003, 63, 2223.
4. Ochi, T. *Sen'i Gakkaishi* 2004, 60, P-266 (in Japanese).
5. Srinivasan, G.; Reneker, D. H. *Polym Int* 1995, 36, 195.
6. Nakane, K.; Ogihara, T.; Ogata, N.; Yamaguchi, S. *Sen'i Gakkaishi* 2005, 61, 313.
7. Chronakis, I. S. *J Mater Proc Tech* 2005, 167, 283.
8. Li, D.; Xia, Y. *Nano Lett* 2003, 3, 555.
9. Larsen, G.; Velarde-Ortiz, R.; Minchow, K.; Barrero, A.; Loscertales, I. G. *J Am Chem Soc* 2003, 125, 1154.
10. Shao, C.; Guan, H.; Liu, Y.; Gong, J.; Yu, N.; Yang, X. *J Cryst Growth* 2004, 267, 380.
11. Guan, H.; Shao, C.; Liu, Y.; Yu, N.; Yang, X. *Solid State Commun* 2004, 131, 107.
12. Kakihana, M.; Tomita, K.; Petrykin, V.; Tada, M.; Sasaki, S.; Nakamura, Y. *Inorg Chem* 2004, 43, 4546.
13. Suzuki, F.; Onozato, K.; Kurokawa, Y. *J Appl Polym Sci* 1990, 39, 371.
14. Nakane, K.; Suzuki, F. *Sen'i Gakkaishi* 1996, 52, 143.
15. Wu, Q. Y.; Wang, H. B.; Yin, C. S.; Meng, G. Y. *Mater Lett* 2001, 50, 61.
16. Wu, Q. Y.; Xie, X. F. *Mater Chem Phys* 2003, 77, 621.
17. Wu, Q. Y.; Sang, X. G.; Deng, L. J.; Pang, W. Q. *J Mater Sci* 2005, 40, 1771.
18. Feng, W. Q.; Wang, J. Q.; Wu, Q. Y. *Mater Chem Phys* 2005, 93, 31.
19. Zhao, S. L.; Wu, Q. Y.; Liu, Z. W. *Polym Bull* 2006, 56, 95.
20. Kinbara, A. Graduation Thesis, Faculty of Engineering, Fukui University, 1999.
21. IUPAC. *Pure Appl Chem* 1972, 31, 578.