Research Article

Electrospinning Preparation and Photocatalytic Activity of Porous TiO$_2$ Nanofibers

Shanhu Liu, Baoshun Liu, Kazuya Nakata, Tsuyoshi Ochiai, Takekoshi Murakami, and Akira Fujishima

1 Photocatalyst Group, Kanagawa Academy of Science and Technology, KSP East 412, 3-2-1 Sakado, Takatsu-ku, Kawasaki, Kanagawa 213-0012, Japan
2 Institute of Environmental and Analytical Sciences, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475001, China
3 Research Institute for Science and Technology, Energy and Environment, Photocatalyst Research Division, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

Correspondence should be addressed to Kazuya Nakata, pg-nakata@newkast.or.jp

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1. Introduction

TiO$_2$-based photocatalysts have been one of the most active areas in heterogeneous catalysis due to their great catalytic abilities for removing environmental pollutants relating to waste water, polluted air, and spilling water [1, 2]. Over the past few years, it has been demonstrated that the photocatalytic activity strongly depends on the specific surface area of photoactive materials [3–5]. Many strategies have been developed to fabricate porous and hollow TiO$_2$ nanostructures to enhance their photocatalytic performance [6–10]. Among these methods for generating porous nanostructures, especially for porous nanofibers, electrospinning is a well-established top-down approach [11–15]. For instance, Li et al. synthesized porous TiO$_2$-based nanofibers via a combined electrospinning and alkali dissolution method; they firstly prepared TiO$_2$/SiO$_2$ composite nanofibers by electrospinning and sintering and then leached out silica with alkaline solution to produce porous TiO$_2$ microstructures [16]. Mesoporous TiO$_2$ nanofibers were prepared by electrospinning TiO$_2$-nanoparticle-containing polymeric spinning solution [17]. Furthermore, in our previous work, TiO$_2$ fibers with interior hollow channels were fabricated via multi-fluidic electrospinning with the obvious improvement of photocatalytic activity [18]. In this paper, porous TiO$_2$ nanofibers were fabricated through an electrospinning method with carbon nanospheres as sacrificial template. Firstly, the spinning solution containing carbon nanospheres was prepared. Our aim was to retain the carbon nanospheres in the as-spun nanofibers, followed by calcination leading to the thermal decomposition of carbon nanospheres, leaving behind a porous TiO$_2$ nanofiber structure.

2. Experimental

2.1. Preparation of Carbon Nanospheres. Carbon nanospheres were synthesized via a hydrothermal method by
using glucose as reagents as previously reported [19]. In brief, 3.5 g glucose (Wako, Japan) was dissolved in 40 mL of water to form a clear solution, which was placed in a teflon-sealed autoclave (50 mL) and maintained at 170 °C for 5 h. The black or puce products were isolated by centrifugation, washed several times under sonication with water and ethanol, then oven-dried at 60 °C for characterization and subsequent application.

2.2. Preparation of Porous TiO₂ Nanofibers. In the typical electrospinning procedure, 0.3 g of carbon nanospheres was dissolved in 10 mL of ethanol to form a homogeneous solution, followed by adding 1.0 g of polyvinylpyrrolidone (PVP, Mw = 130,000, Aldrich) and 3 mL of acetic acid (Wako, Japan). After stirring for one hour, this solution was added to 1.0 mL of titanium tetraisopropoxide (Ti(OiPr)₄, Aldrich) (Wako, Japan) and stirred for another hour. The mixed solution was fed through a nozzle at a feeding rate of 4 mL min⁻¹. The applied voltage was 22 kV and the working distance was 15 cm. After electrospinning process, the obtained fibers were calcined in air at 500 °C for 2 h at a heating rate of 5 °C min⁻¹ to form porous TiO₂ nanofibers, which were denoted as P-TiO₂ nanofibers. For comparison, we have prepared TiO₂ nanofibers in the absence of carbon nanospheres. The morphology of these nanofibers was examined using scanning electron microscopy (JSM-5400, JEOL, Japan). X-ray diffraction (XRD) patterns were recorded using a Rigaku RINT 1500 diffractometer with the use of Cu Kα radiation. Nitrogen adsorption isotherms were measured at −196 °C using a Micromeritics system (Gemini V, Shimadzu, Japan). UV-vis absorption was performed on UV-1700 (Shimadzu, Japan) spectrophotometer.

3. Results and Discussion

The crystalline structure and phase composition of the products were characterized by XRD. As shown in Figure 1, all of the obtained products matched well with the standard pattern of anatase (JCPDS no. 21-1272), with four reflections at 25.3, 37.9, 48.1, and 54.2, corresponding to (101), (004), (200), and (105), respectively. More importantly, no impurity peaks were observed in the XRD patterns of P-TiO₂ nanofibers.
nanofibers, suggesting that the crystal phase is not changed
during the process of generating pores.

Carbon nanospheres were investigated by SEM analyses. Figure 2 represents SEM image and the corresponding histogram of the diameters of carbon nanospheres. The nanospheres are monodispersed and uniform on a large scale. A statistical analysis yields an average size of 320 nm in diameter. In this paper, carbon nanospheres could be removed by calcination simultaneously during the process of removing PVP, without needing an additional removing
Figure 3 shows SEM images of TiO$_2$ nanofibers and P-TiO$_2$ nanofibers before and after calcination. It was observed that the surface of nanofibers without carbon nanospheres was smooth (Figure 3(a)) while the surface of nanofibers with carbon nanospheres was lumpy at places where the nanospheres were present (Figure 3(c)). After calcination, the average diameters of the nanofibers decreased slightly (Figures 3(b) and 3(d)). This is because the organic components (PVP or carbon nanospheres) were removed by combustion and the inorganic component had crystallized. The carbon nanospheres were removed via calcination leaving behind pores in the nanofibers. The diameters of nonporous TiO$_2$ nanofibers and P-TiO$_2$ nanofibers were statistically determined to be 230 and 330 nm, respectively.

The porous structure within the P-TiO$_2$ nanofibers was further confirmed by the N$_2$ physisorption experiments. Despite its larger diameter, P-TiO$_2$ nanofibers have larger specific surface area (33 m$^2$/g) than TiO$_2$ nanofibers (9 m$^2$/g). As shown in Figure 4, the pores volume of P-TiO$_2$ nanofibers was larger than that of nonporous TiO$_2$ nanofibers. However, the P-TiO$_2$ nanofibers possess wide pore size distributions from several nanometers to tens of nanometers because of the complex interplay between the shrink of the nanofibers and the decomposition of organics during calcination.

More evidence on crystallinity of P-TiO$_2$ nanofibers was obtained from the TEM analysis. As shown in Figure 5, the distinct contrast derived from the difference of electron density in TEM image further confirms the porous structure of the nanofibers. The crystal lattice fringes indicates that the nanofibers are formed by geometrically random TiO$_2$ nanograins, which exhibit high crystallinity after calcination.

4. Conclusion

In conclusion, porous TiO$_2$ nanofibers were prepared via an efficient and simple electrospinning method by using carbon nanospheres as sacrificial template. Carbon nanospheres together with PVP could be removed at the same time during calcination.
during calcination. Microstructural analysis and properties evaluation revealed that porous TiO₂ nanofibers have higher surface area and enhanced photocatalytic activity compared to nonporous TiO₂ nanofibers. In addition, the method for synthesis of porous TiO₂ nanofibers presented here can be extended to synthesize other one-dimensional porous nanostructures.

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