Research Article

Electrospinning Preparation and Photocatalytic Activity of Porous TiO₂ Nanofibers

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Porous TiO₂ nanofibers were prepared via a facile electrospinning method. The carbon nanospheres were mixed with the ethanol solution containing both poly(vinylpyrrolidone) and titanium tetraisopropoxide for electrospinning; and subsequent calcination of as-spun nanofibers led to thermal decomposition of carbon nanospheres, leaving behind pores in the TiO₂ nanofibers. The morphology and phase structure of the products were investigated with scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). Furthermore, the photocatalytic activity of porous TiO₂ nanofibers was evaluated by photodecomposition of methylene blue under UV light. Results showed that the porous TiO₂ nanofibers have higher surface area and enhanced photocatalysis activity, compared to nonporous TiO₂ nanofibers.

1. Introduction

TiO₂-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 TiO₂ 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 TiO₂-based nanofibers via a combined electrospinning and alkali dissolution method; they firstly prepared TiO₂/SiO₂ composite nanofibers by electrospinning and sintering and then leached out silica

with alkaline solution to produce porous TiO₂ microstructures [16]. Mesoporous TiO₂ nanofibers were prepared by electrospinning TiO₂-nanoparticle-containing polymeric spinning solution [17]. Furthermore, in our previous work, TiO₂ fibers with interior hollow channels were fabricated via multifluidic electrospinning with the obvious improvement of photocatalytic activity [18]. In this paper, porous TiO₂ 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 TiO₂ nanofiber structure.

2. Experimental

2.1. Preparation of Carbon Nanospheres. Carbon nanospheres were synthesized via a hydrothermal method by

FIGURE 1: XRD patterns of TiO₂ nanofibers (a) and P-TiO₂ nanofibers (b).

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, and the rest of the synthesis conditions were kept the same as those described above in the typical experiment.

2.3. Characterization. The morphology of the 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.

FIGURE 2: SEM image (a) and the corresponding histogram of the diameters (b) of carbon nanospheres.

2.4. Photocatalysis Measurement. The photocatalytic activity of these nanofibers was evaluated as their ability to decompose the aqueous suspension of methylene blue (MB) under UV-light at room temperature. Prior to the light irradiation, 20 mL of MB solution (20 mg mL⁻¹) was mixed with the catalyst (20 mg) and kept in the dark for 200 minutes to establish an adsorption-desorption equilibrium. The concentration of dye solution was measured with UV irradiation time by using a UV-vis spectrometer. To monitor the change in concentration of MB, the absorbance spectra of MB were recorded at its maximum absorption.

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

FIGURE 3: SEM image of nanofibers prepared without (a, b) and with carbon nanospheres (c, d); SEM images of nanofibers before (a, c) and after (b, d) calcination.

FIGURE 4: Pore size distributions of the TiO_2 nanofibers (a) and P- TiO_2 nanofibers (b).

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

FIGURE 5: HRTEM image of P- TiO_2 nanofibers.

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 6: Liquid-phase photocatalytic degradation (a) and photocatalytic degradation reaction kinetics (b) of MB against TiO₂ nanofibers, TiO₂ P25, and P-TiO₂ nanofibers.

step. Moreover, during the calcination carbon nanospheres only release nontoxic CO₂ and H₂O but not toxic gases.

Figure 3 shows SEM images of TiO₂ nanofibers and P-TiO₂ 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 TiO₂ nanofibers and P-TiO₂ nanofibers were statistically determined to be 230 and 330 nm, respectively.

The porous structure within the P-TiO₂ nanofibers was further confirmed by the N₂ physisorption experiments. Despite its larger diameter, P-TiO₂ nanofibers have larger specific surface area (33 m²/g) than TiO₂ nanofibers (9 m²/g). As shown in Figure 4, the pores volume of P-TiO₂ nanofibers was larger than that of nonporous TiO₂ nanofibers. However, the P-TiO₂ 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-TiO₂ 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 TiO₂ nanograins, which exhibit high crystallinity after calcination.

To determine the photocatalytic activity of P-TiO₂ nanofibers, the degradation experiments of MB against P-TiO₂ nanofibers, TiO₂ P25 (AEROXIDE), and TiO₂ nanofibers were carried out. In the dark (−200~0 min), the relative concentration of MB in the solution is slightly decreased owing to the adsorption of MB on the catalysts; the concentration decrease is slightly greater for P-TiO₂ nanofibers than for TiO₂ nanofibers, which reflects that the surface area is greater for P-TiO₂ nanofibers. As shown in Figure 6(a), 90% of MB could be decomposed by P-TiO₂ nanofibers within 60 min and was degraded completely after 110 min. Although the most of MB was also decomposed in the presence of the P25 after the same period, the photocatalytic activity was lower than P-TiO₂ nanofibers. In contrast, the photocatalytic activity of TiO₂ nanofibers was lowest; about 50% MB remained after 60 min irradiation. The reaction rate constant of the MB degradation against P-TiO₂ nanofibers (0.035 min^{-1}) is three times higher than that of TiO₂ nanofibers (0.011 min^{-1}) (Figure 6(b)). The results indicate that P-TiO₂ nanofibers have greater photocatalytic activity than nonporous TiO₂ nanofibers, suggesting that the surface area is an important factor for adsorption and catalysis.

4. Conclusion

In conclusion, porous TiO₂ 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. 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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