Preparation and Characterization of Porous TiO_2 Fibers and Their Photocatalytic Activity

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ABSTRACT

TiO_2 fibers were successfully prepared by combining electrospinning and calcination processes without using the conventional sol-gel method. Polymethyl methacrylate (PMMA) and tetrabutyl titanate (TBT) were used as TiO_2 precursor blended with chloroform to form a homogeneous solution for preparing PMMA/TBT composite fibers. The electrospun fibers were calcinated at 500 ºC for 4 h in air atmosphere to obtain TiO_2 fibers. XRD, SEM TEM and Brunauer-Emmett-Teller (BET) were used to study structures and morphology of the PMMA/TBT and TiO_2 fibers. The photocatalytic property of TiO_2 fibers was evaluated by photocatalytic degradation of methyl orange (MeO) under UV irradiation. The results demonstrate that mesoporous TiO_2 fibers with larger specific surface area possessing pure anatase phase were successfully prepared and the average diameter of PMMA/TBT fibers decreased from 1.5 μm to 1.0 μm after calcination. The TiO_2 fibers show high photocatalytic reactivity in photodegradation of MeO solutions.

INTRODUCTION

One-dimensional (1D) nanostructures of semiconductor materials have attracted particular attention over the past few years, because of their potential in the preparation of optical signal processors, switches, and anodes of lithium-ion [1-4]. Titanium oxide (TiO_2) is an important semiconductor material for use in a wide range of applications, including photocatalysis, environmental pollution control and solar energy conversion [5,6]. However, the shortcomings of conventional powder catalysts include low efficiency of light use and difficulty of separation after reaction [7-10]. These disadvantages of TiO_2 powders result in low efficiency of photocatalytic activity. In order to obtain better TiO_2 catalysts for rapid and efficient decomposition of organic pollutants and easy manipulation in a whole photocatalytic process, it is desirable to use integrated TiO_2 catalysts with high surface areas. Therefore, much recent work has focused on the preparation of pure TiO_2 fibers with high surface area [11]. It has been reported that the TiO_2 fibers showed high surface area and the efficient degradation of some organic compounds in the photocatalytic process [12]. Most of the reported TiO_2 fibers or TiO_2 composite fibers were produced by combining sol-gel method and electrospinning techniques [13,14]. The process of sol-gel during fiber formation makes the electrospinning solution unstable and needs more time due to hydrolysis of the precursors.

To overcome these problems, PMMA/TBT composite fibers were successfully prepared via electrospinning technique without the sol-gel process. The resulting porous TiO_2 fibers were obtained by the subsequent calcination. Photocatalytic degradation of TiO_2 fibers on methyl orange (MeO) in aqueous solution was investigated. The results show that the degradation rate reached almost 90% after 5 hours.

EXPERIMENTAL

Fibers Preparation

A homogeneous solution containing 1 g PMMA (Mw~191,700), 3 g TBT mixed with 20 g chloroform were prepared at room temperature for 24 h. The positive voltage, working distance, and flow rate were 15 kV, 15 cm (the distance between the needle tip and the collection foil), and 2.0 mL/h, respectively.

The resulting composite fibers produced by electrospinning were placed in a tube furnace and incubated at 500 ºC for 4 h (heating rate: 5 ºC min^{-1}) in an air atmosphere.

Characterization

X-ray powder diffraction (XRD) patterns were obtained using a Philips MPD-18801 diffractometer. The morphology of the fiber was analyzed using scanning electron microscope S-4800 and

transmission electron microscope (TEM, Philips, CM120). Surface characterization of the porous TiO_2 fibers was carried out using Brunauer-Emmett-Teller (BET) nitrogen adsorption method (Micromeritics Gemini 2360).

Photocatalytic Activity Test

Photocatalytic experiments were conducted using porous TiO_2 fibers to degrade MeO in water solution. The photocatalytic degradation reactions were carried out under atmospheric condition using a 300 W high pressure mercury lamp (Philips 254 nm) as the irradiation source at ambient temperature. The irradiation distance between the lamp and the sample was 15cm. One milligram of TiO_2 fibers was added into a cylindrical glass vessel containing 16 g of 1 ppm MeO aqueous solution. The aqueous solution was dispersed in the dark by ultrasonic treatment for 30 minutes to reach adsorption equilibrium of MeO on the fibers, and then exposed to UV light. At a certain time interval, the degradation reaction was ceased and the solution was centrifuged. The MeO concentration was measured on a UV-vis spectrometer (Lambda850, PerkinElmer).

RESULTS AND DISCUSSION

XRD Pattern

The X-ray diffraction pattern of the TiO_2 fibers prepared by annealing the PMMA/TBT composite fibers at 500 ºC for 4h is shown in *Figure 1*. The sample exhibited XRD peaks corresponding to the (101), (004), (200), (105), (211), (204), (116), (204) and (215) planes for the anatase structure of TiO_2 (JCPDS 89-4921). The annealed TiO_2 fibers possessed pure anatase phase. The absence of diffraction peaks at 27o and 31o indicated that this sample was free from the rutile and brookite structures of TiO_2.

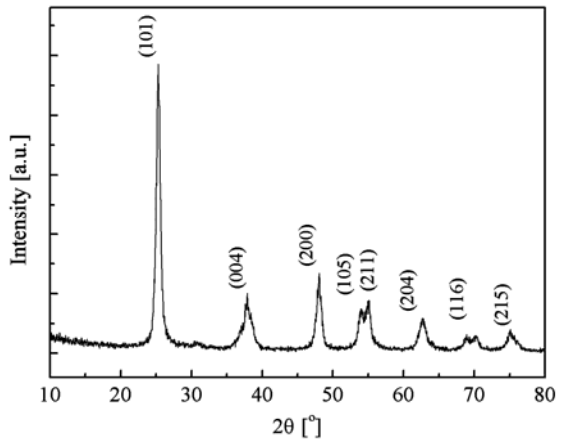

FIGURE 1. The XRD pattern of TiO_2 fibers.

The anatase lattice parameters a and c calculated from the XRD spectrum for the TiO_2 nanocrystals were a=b=0.375 nm and c=0.951 nm. The most predominate peak at 2θ=25.3o was representative of the (101) anatase phase reflections. By applying the Scherrer equation to peak (101), the original crystal size of porous TiO_2 fibers was found to be ca. 15 nm.

SEM And TEM Images

Figures 2a-b show scanning electron micrographs of the electrospun PMMA/TBT composite fibers containing TiO_2 precursor. It is clear that the continuous fibers were very uniform along the length of the fibers and the relatively even distributed pores were formed because of the quick evaporation of chloroform. The morphologies of the TiO_2 fibers after calcinations are presented in *Figure 2c* and *Figure 2d*, respectively.

The original microstructure of the fibers was well preserved after the high-temperature treatment. The theoretical yield of the TiO_2 fibers is 17.6 wt%, however, its diameter only decreased from ca. 1.5 μm to 1.0 μm compared with the PMMA/TBT composite fibers. The reason may be explained as follows: firstly, decomposition of PMMA and TBT at high temperature led to fiber diameter decrease. Secondly, TBT was uniformly distributed in the PMMA matrix, so after complete pyrolysis of PMMA the phase of TBT (TiO_2) was preserved better. Hence, the morphology of fiber was well retained and the fiber diameter showed slight decrease.

The detailed microstructure and crystallinity of TiO_2 fibers was further invested by SAED pattern and TEM imaging as shown in *Figure 2e* and *Figure 2f*. It is clearly indicated that the TEM observations of the TiO_2 fibers were in accordance with the results from the SEM. From *Figure 2e*, it can be seen that TiO_2 fibers possessed a very rough surface due to a great deal of mesopores distributed on the surface of TiO_2 fibers. The selected-area electron diffraction (SAED) on the TiO_2 fibers (inset *Figure 2e*) shows the apparent ring diffraction patterns from the crystallinity of polycrystalline anatase, in good agreement with the XRD results. *Figure 2f* displays a TEM image recorded from the white circle of *Figure 2e*. The fringes spacing is ca. 0.384 nm, corresponding to the (101) plane of anatase crystal structure of TiO_2.

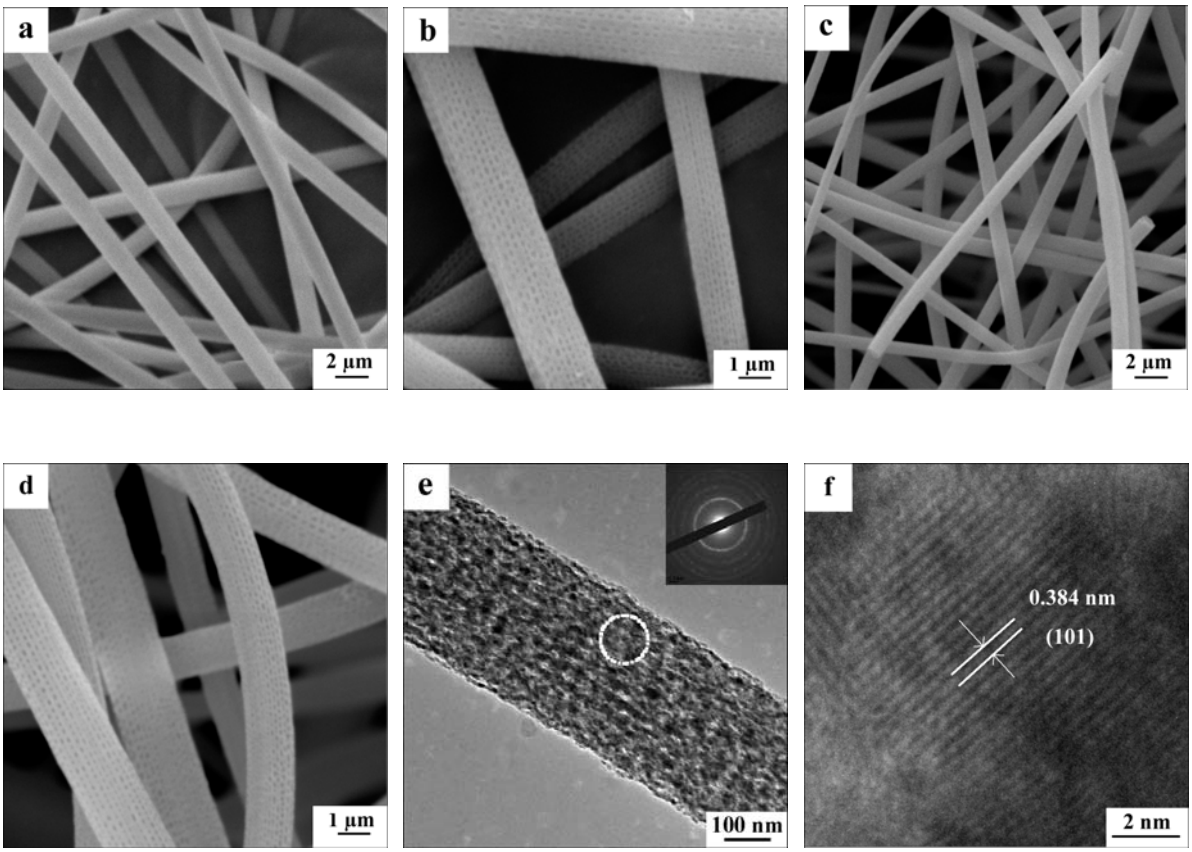

FIGURE 2. SEM (a) and higher resolution (b) images of PMMA/TBT fibers; SEM (c) and higher resolution (d) images; (e)TEM image of TiO_2 fibers and SAED pattern of TiO_2 fibers ;(f) HR-TEM image of TiO_2 fibers (as the circle pointed in e).

Nitrogen Sorption and Photocatalytic Activity

The nitrogen adsorption-desorption isotherms and pore size distribution curves of TiO_2 fibers are shown in *Figure 3*. It exhibited type II isotherms according to IUPAC classification [15], which are typical characteristics of mesoporous materials. The average pore size and BET surface area of TiO_2 fibers were found to be about 11.86 nm and 13.85 m^2/g, respectively. The mesopores were produced by the volatization of chloroform and decomposition of PMMA and TBT during high-temperature processing.

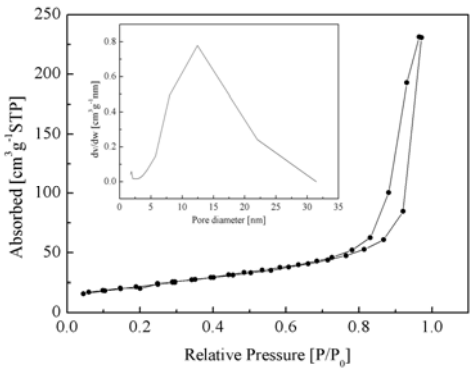

FIGURE 3. Nitrogen adsorption-desorption isotherms and pore size distribution curves of TiO_2 fibers.

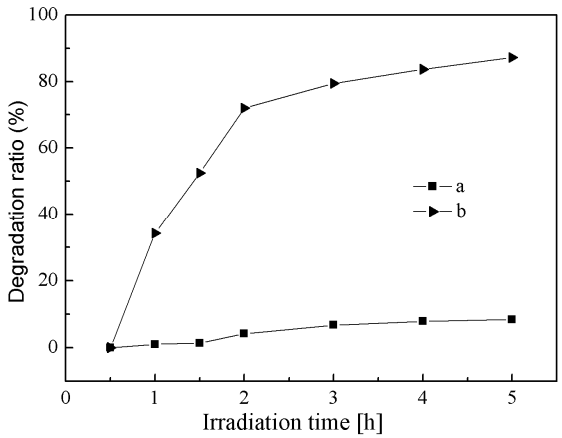

FIGURE 4. Photocatalytic degradation rates of MeO aqueous solutions (a) containing TiO_2 fibers; (b) without TiO_2 fibers.

For evaluation of photocatalytic properties, TiO_2 fibers were distributed into MeO solution using ultrasonic. To determine the change in MeO concentration in solution during the process, a few milliliters of the solution was taken from the reaction mixture, subsequently centrifuged to separate the suspended TiO_2 fibers. TiO_2 parallel degradation reactions of MeO aqueous solution without TiO_2 fibers under the same conditions were conducted for the same time intervals in order to further confirm the photocatalytic activity of the TiO_2 fibers. The changes in MeO concentrations were estimated from the changes in absorption of the absorption maximum at 465 nm.

As can be seen from *Figure 4*, 80% of MeO was decomposed by TiO_2 fibers in 3 h. After 5 h of UV irradiation, the MeO degradation achieved nearly 90%. TiO_2 fibers presented excellent photocatalytic properties for organic dye because of the following reasons. The first reason was that porous fibers with high specific surface area led to the large generation of OH• free radical on the surface of TiO_2 fibers in solution, which had successive attacks by oxidation of the dyestuff. The second was that H_2O was easily absorbed on the TiO_2 fiber surface and reacted with valence-band hole to produce a great deal of OH• free radical and the photogenerated holes had direct reaction with the dyestuff. The third was that fibers with high surface area worked well to concentrate MeO around the TiO_2 fibers, which also facilitated the photocatalytical degradation.

CONCLUSIONS

Mesoporous anatase TiO_2 fibers with highly photocatalytic activity were prepared successfully by combining the electrospinning and calcination methods. TiO_2 fibers possessed pure anatase phase. The diameters were distributed with the average diameter of about 1.0 μm. TiO_2 fibers exhibited excellent photocatalytic properties for MeO and the degradation rate almost 90% after 5 h due to its high specific surface area. TiO_2 fibers can also be potentially used in energy storage devices and this fabrication can also be extended to other type of metal or metal oxides as well.

ACKNOWLEDGEMENTS

The work was financially supported by National High-tech R&D Program of China (863 Program) (No.2012AA030313), the National Natural Science Foundation of China (No.51006046), Changjiang Scholars and Innovative Research Team in University (No.IRT1135) and the Priority Academic Program Development of Jiangsu Higher Education Institutions.

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