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Short communication

Branched titanium oxide/vanadium oxide composite nanofibers formed by electrospinning and dipping in vanadium sol

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Abstract

Titanium oxide/vanadium oxide composite nano-fibers were fabricated *via* a novel method involving electrospinning and dipping in vanadium sol. The fibers were developed to photocatalyze the degradation of pollutants from wastewater. Phases, morphologies, and chemical compositions of the nanofibers were characterized by X-ray diffraction (XRD), scanning electron microscopy, energy dispersive spectrometry (EDS), and X-ray photoelectron spectroscopy (XPS). The XRD patterns indicated an anatase structure, while imaging revealed branched morphologies due to sintering at 550 °C in a N_2 atmosphere. EDS and XPS indicated the presence of TiO_2, Ti_2O_3, V_2O_5 and VO_2. The formation of V^{4+} and surface Ti^{3+} improved the photocatalytic activity because they narrow the band gap and reduce electron–hole recombination rates. Specifically, the 3 h methyl orange decomposition rate photocatalyzed by the composite nanofibers increased by 95.8% relative to the catalysis by unmodified TiO_2 nanofibers.

Keywords: Branched structure; Electrospinning; Nanofibers; Photocatalytic property; Titanium oxide/vanadium oxide

1. Introduction

Because of its excellent chemical stability and photocatalytic properties, titanium dioxide has wide-ranging applications such as sewage treatment and air purification [1,2]. However, many applications of TiO_2 are limited because of fast electron–hole recombination rates near the surface, and because its wide bandgap (3.2 eV) requires ultraviolet light (<387 nm) [3–5]. Efforts to improve the photocatalytic properties include doping, composites with other semiconductors, or surface modification [6–8]. Recently, TiO_2 nanofibers fabricated by electrospinning have exhibited advantages over nanoparticle morphologies that are difficult to disperse and recover [9]. Patterned nanofibers with porous, beaded, or dendritic structures have been prepared *via* combinations of electrospinning and surface modification [10,11]. These structures could significantly increase the TiO_2 specific surface area and thereby increase the adsorption of organic matter [12,13]. Additionally, photocatalytic properties can be improved by doping with metal ions and noble metals, which increase the separation of photogenerated electrons and holes [14,15].

Doping TiO_2 with multivalent vanadium has many advantages [16]. The radius of V^{5+} is smaller than that of Ti^{4+}, and the distance between Ti^{4+} and O^{2-} decreases when V^{5+} replaces Ti^{4+} in the TiO_2 lattice. The latter causes the band gap to narrow, shifting the absorption spectrum [17]. Additionally, Kiriakidou et al. [18] reported that doping of high-valence metal ions in TiO_2 increases the Fermi level and the surface barrier. The space charge region is also narrowed, effectively separating photogenerated electrons and holes and thus enhancing photocatalysis. Ostermann [19] reported on TiO_2/V_2O_5 composite fibers with higher photocatalytic efficiency compared with that of pure TiO_2 nanofibers. The composites were formed by electrospinning isopropanol vanadyl and butyl titanate. V^{5+} provides deep-level doping relative to the top of the TiO_2 valence band, and improves the effectiveness of photons and trapped photogenerated holes [20]. It has also been reported that more oxidation centers and

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oxygen vacancies are obtained if Ti^{3+} or V^{4+} is present in TiO_2-based photocatalytic materials [21,22].

Here, we discuss a new method of fabricating titanium oxide/vanadium oxide composite nanofibers *via* electrospinning and dipping in vanadium sol. The fibers contain Ti_2O_3, TiO_2, VO_2, and V_2O_5. This method binds vanadium sol to TiO_2 fibers and calcines the mixture in an inert atmosphere to obtain Ti^{4+} directly, which is easier than the existing method of calcining vanadium salt in a reducing atmosphere. The phases, morphologies, and chemical compositions of branched titanium oxide/vanadium oxide composite nanofibers are characterized. Additionally, the photocatalytic properties are analyzed in terms of methyl orange decomposition rates. The results indicate that the composite nanofibers could be used for large-scale removal of pollutants in wastewater.

2. Experimental procedure

Butyl titanate (AR, Tianjin Kermel Chemical Reagent Co., Ltd., Tianjin, China) was used as a titanium precursor, and ethanol (AR, Anhui Ante biochemistry Co., Ltd., Suzhou, China) was used as a solvent. Polyvinylpyrrolidone (PVP, MW=1,300,000) was purchased from Sigma Aldrich (Milwaukee, Wisconsin, USA). Acetic acid (AR, Tianjin Shuangchuan Chemical Reagent Co., Ltd., Tianjin, China) was used as a chelating agent and to reduce the degree of cross-linking. Vanadium pentoxide powder (AR, Henan Coal Science Research Institute Co., Ltd., Zhengzhou, China) and deionized water were used to produce vanadium sol.

A solution of PVP in ethanol was prepared by stirring for 2 h. A mixture of butyl titanate and acetic acid was added to the PVP solution, and then stirred for 5 h. The mixture was then aged for 12 h to yield a precursor solution containing 8 wt% PVP and a butyl titanate/PVP mass ratio of 1. The precursor solution was placed in the micro-pump of an electrostatic jet apparatus (KH-08, Beijing Kangsente Co. Ltd, Beijing, China), equipped with a 0.9-mm-diameter metal injector nozzle. A voltage of 20 kV was used together with a flow rate of 0.2 mL/h, and the distance from the nozzle tip to the collector was 12 cm. PVP/butyl titanate composite fibers were thus obtained by electrospinning on the plate collector, followed by drying at 60 °C for 2 h to remove residual ethanol. The fibers were then calcined at 550 °C at a heating rate of 5 °C/min for 2 h to yield titanium dioxide nanofibers. Vanadium sol was made by heating 3 g of V_2O_5 powder at 850 °C for 10 min and then quenching it in 50 ml of water. TiO_2 nanofibers were immersed in the vanadium sol and then dried at 170 °C for 30 min after being pulled out. The immersion process was repeated three times, after which the titanium oxide/vanadium oxide composite nanofibers were annealed at 550 °C for 2 h in a N_2 atmosphere.

X-ray diffraction (XRD; Model 7000, Shimadzu Corporation, Tokyo, Japan) analysis with Cu Kα radiation (operating at 40 kV and 40 mA) was used to identify phases in the samples. Morphologies were characterized by scanning electron microscopy (SEM) operated at 20.0 kV (JSM 6700, OLYMPUS, Tokyo, Japan), while detailed microscopic and crystal structures were characterized by transmission electron microscopy (TEM, JEM-3010, JEOL, Tokyo, Japan). Energy dispersive spectrometry (EDS), in conjunction with SEM, was used to determine compositions. Chemical compositions and spatial distributions were also analyzed with X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD, Shimadzu Corporation, Tokyo, Japan), over the range 0–1200 eV, using Al Kα radiation.

Photocatalytic activity was determined by dispersing the titanium oxide/vanadium oxide composite nanofibers (100 mg) in 50 ml of methyl orange solution (5 mg/L). Photocatalytic decomposition of the methyl orange was carried out in a quartz cuvette under ultraviolet light (365 nm) for 180 min, and then analyzed *via* absorption changes at 460 nm using a UV–visible absorption spectrometer. The photodecomposition rate D of the methyl orange was calculated from

$$D = [(C_o - C)/C_o] \times 100\% \quad (1)$$

In Eq. 1, C_0 is the initial concentration of methyl orange and C is its concentration at different irradiation times.

3. Results and discussion

XRD patterns of TiO_2 nanofibers sintered in air, and those of titanium oxide/vanadium oxide composite nanofibers sintered in N_2, are displayed in Fig. 1. Sharp diffraction peaks from TiO_2 nanofibers are observed at 25.28°, 37.86° and 48.04°, which correlate with anatase TiO_2 (JCPDS 89-4921). Diffraction peaks from the titanium oxide/vanadium oxide composite nanofibers are mostly consistent with anatase TiO_2, while other, weaker, peaks are also observed. This data probably indicates that oxides of both Ti and V are present in the composite nanofibers.

Fig. 2 shows morphologies of TiO_2 and titanium oxide/vanadium oxide composite nanofibers. TiO_2 nanofibers [Fig. 2 (a)] are smooth, with an average diameter of 298 ± 24 nm.

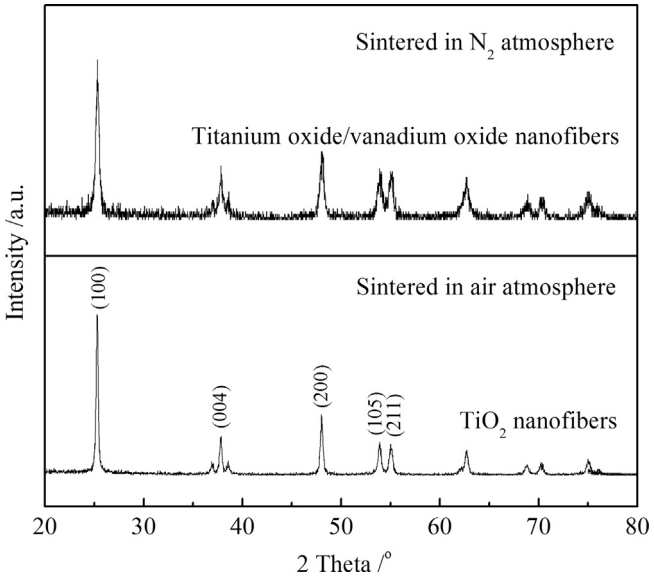

Fig. 1. XRD patterns of (bottom) TiO_2 nanofibers sintered in air, and (top) titanium oxide/vanadium oxide composite nanofibers sintered in N_2.