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Highly porous SnO_2/TiO_2 electrospun nanofibers with high photocatalytic activities

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Abstract

Highly porous SnO_2/TiO_2 composite nanofibers were prepared by electrospinning based on water/oil phase separation effect, and their photocatalytic degradation abilities of Rhodamine B (RhB) under UV–visible light irradiation was assessed. Results indicated that the porous SnO_2/TiO_2 nanofibers show a significantly improved reaction rate (about 99% RhB dye degraded in 30 min), which is about 2.7 times higher than that of the pure TiO_2 nanofibers (about 97% RhB dye in 80 min). The specific surface area of porous SnO_2/TiO_2 nanofibers is 55.6 m^2/g, which is 2.85 times larger than that of pure TiO_2 nanofibers (19.5 m^2/g). The SnO_2 addition into TiO_2 suppressed the recombination of photo-generated electron–hole pairs, and highly porous structures within the nanofibers improved the utilization efficiency of light due to multiple photon reflections. In addition, it is worth being mentioned that more than 60% RhB dye was degraded during the first 10 min by the highly porous SnO_2/TiO_2 nanofibers. The high photocatalytic activity of porous nanofibers was rooted from changed energy level structure due to addition of Sn and to lots of bulk oxygen vacancies formed in SnO_2/TiO_2 nanofibers.

Keywords: Electrospinning; Phase separation; Porous nanostructures; Photocatalysis; Multiple reflections

1. Introduction

Since Fujishima and Honda first reported the electrochemical photolysis of water, the semiconductor photocatalysis technology has been regarded as one of the most effective and economical ways to solve the environmental problems caused by the industry pollution and human beings daily lives [1–3]. Among the semiconductors used in the photocatalysis technology, TiO_2 is the most frequently used in various fields including water splitting, environmental purification, self-cleaning/superhydrophilic surfaces, sensors, and disinfection etc. [4–6]. In particular, TiO_2 nanomaterials have been extensively studied due to its low cost, non-toxicity, environmental friendliness, and chemical stability.

However, the practical applications of TiO_2 nanomaterials in photocatalytic fields meet enormous limitation because of its wide band gap (anatase: Eg=3.2 eV, rutile: Eg=3.0 eV) i.e. TiO_2 nanomaterials can only be excited under the ultraviolet (UV) irradiation. To dissolve this problem, up till now, two main strategies have been put forward to improve the photocatalytic performance of TiO_2 nanomaterials. One strategy was to change the energy structure of TiO_2, in other words, to extend optical absorption range of the materials, and decrease the recombination of photo-generated electron–hole pairs. In this case, TiO_2 materials were often doped with various metals [7–12], non-metal elements [13–18], or self-impurities [19,20]. The other one was to improve the specific surface area of TiO_2 nanomaterials by fabricating various nanostructured TiO_2 nanomaterials, such as nanoparticles, nanofilms, nanofibers, nanotubes and porous nanostructures etc. [21–27]. Among them, fibrous TiO_2 nanomaterials draw much attention due do their high aspect ratio and

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good dispersion in pollutant aqueous during photocatalytic progresses. It was demonstrated that the combination of these two strategies would give a high sight to the improved photocatalytic activity of TiO_2 based nanomaterials. Liao et al. prepared a TiO_2/Ti mesh electrode with 3D nanotubular arrays and investigated its ability to photo-degradate Methyl Orange [20], Leary et al. have observed the enhancement of photocatalysis from the carbonaceous TiO_2 nanomaterials [28], Yu et al. synthesized TiO_2/Ag nanosponge composites based on natural cellulose-template and also observed improved photocatalytic properties [29], and Mu et al. have fabricated In_2O_3–TiO_2 nanofibers heteroarchitectures and found that their visible-light photocatalytic activities were enhanced etc. [30]. Particularly, semiconductor/TiO_2 systems attracted much more interest due to their unique energy structure, and SnO_2 was considered as one of the most promising material due to its high conductivity and the good lattice matching with TiO_2. Some correlative studies have been reported, such as, Lee et al. electrospun TiO_2/SnO_2 nanofibers for the study of photocatalytic H_2 generation [4], Pan et al. prepared the SnO_2–TiO_2 core–shell nanowires and investigated their solid state reactivity and photocatalytic behavior [26]. Although those new SnO_2/TiO_2 composite materials and structures showed improved photocatalytic properties, the complicated preparation progress and/or low effective specific surface areas of materials limited their practical application, and the methods above are hard to be extended to the preparation of other nanomaterials. Therefore, it is important to open a simple and versatile way to fabricate unique nanostructure TiO_2 nanomaterials with high photocatalytic activity will promote the practical applications of TiO_2 materials in photocatalytic field.

Herein, we prepared the porous SnO_2/TiO_2 nanofibers by electrospinning technology based on the water/oil phase separation effect. The photocatalytic activities of the as-prepared porous SnO_2/TiO_2 nanofibers were investigated by the degradation of Rhodamine B (RhB) aqueous solution under UV–visible light. Our strategy used here would provide a simple and low cost way to the preparation of other porous photocatalytic materials.

2. Experimental section

2.1. Preparation of porous SnO_2/TiO_2 nanofibers

The solid SnO_2/TiO_2 nanofibers were prepared by electrospinning technique. Firstly, 2.0 g of tetrabutyl titanate ($C_{16}H_{36}O_4Ti$) was mixed with 3 ml of ethanol, 1 ml of acetic acid, and 0.06 ml of 0.02 mol/L ($SnCl_4 \cdot 5H_2O$), followed by vigorous stirring for more than 30 min, the obtained solution was marked as Solution 1 (S1). Secondly, 1.0 g of polyvinylpyrrolidone (PVP, $Mw = 1{,}300{,}000$, Sigma-Aldrich Chemical Inc.) was dissolved in 4.5 ml of N, N-dimethylformamide (DMF) and 2 ml of ethanol, after being stirred vigorously for 20 min, a homogeneous transparent solution was obtained, marked as Solution 2 (S2). And then, 2 ml of plant oil was added into the mixture of S1 and S2 with Sn–Ti mass ratio of 0.5%. After stirred vigorously for more than 12 h, a type of mixture solution containing well-dispersed oil was finally obtained, marked as Solution for Electrospinning (SE), and then sent for electrospinning process. The electrospinning experimental system contained a glass syringe with a metal spinneret (inner diameter of 0.5 mm) and a collector made by stainless steel. A DC of 16 kV was applied between spinneret tip and collector with distance of 15 cm, the flow rate of SE was fixed at 0.7 ml/h and controlled by a peristaltic pump. After electrospinning, the as-spun nanofibers were placed in ambient atmosphere for about 24 h to complete hydrolysis of tetrabutyl-titanate within samples, then sent into a furnace and annealed at 450 °C in air for 3 h with the heating rate of 5 °C per min, after naturally cooling down to room temperature (RT), the porous SnO_2/TiO_2 nanofibers were obtained, which was marked as PST-0.5%. For further comparison, the solid pure TiO_2 nanofibers (marked as SPT-0%), solid SnO_2/TiO_2 nanofibers with Sn–Ti mass ratio of 0.5% (marked as SST-0.5%), and porous pure TiO_2 nanofibers (marked as PPT-0%) were also prepared by the similar procedures. All of the chemical reagents used in the experiments were analytical reagent (provided by Lanzhou Zhongke Kate Equipment Distribution Co. Ltd., Lanzhou, China) and without further purification, the plant oil (Model number: 0085927522) was purchased from Tongda Oil Processing Co. Ltd. (Lanzhou, China), and all of the experiments were employed at RT under the ambient environment.

2.2. Characterization

The morphologies of the samples were characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4800) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai F30), the crystal structures were measured by grazing-angle X-ray diffraction (XRD, Philips, X'Pert Pro, Cu-Kα1, 1.54056 A) and HRTEM. And the chemical compositions were analyzed by X-ray photoelectron spectroscopy (XPS, PHI-5702 X-ray photoelectron spectrometer, 250 W, 14 kV). Moreover, N_2 absorption–desorption measurements were conducted on a Tristar II 3020 Specific Surface Area and Pore Size Analyzer at 77K for analysis of the surface structure and pores distribution of nanofibers, and photoluminescence spectra were measured by JY-HR800 micro-Raman spectroscope using a YAG laser of 532 nm wavelength for analyzing the defects and recombination rate of photo-generated charge carriers of samples.

2.3. Photocatalytic test

Before the measurements, 50 mg solid photocatalyst was put into 50 ml of RhB solution with an initial concentration of 10 mg/L, and then the mixture solution was filled in a photoreactor, designed with an internal UV–visible light source (170 W), was surrounded by a water-cool system. The distance between light and surface of solution was 8 cm. The solution was stirred in the dark for 30 min to obtain a good dispersion and establish adsorption − desorption equilibrium between the organic molecules and the photocatalysts surface. In the certain illumination time (10 min), 4 ml of samples was taken out and centrifuged instantly by a centrifugal machine for followed analysis. Decrease in the concentration of RhB