



Preparation and photocatalytic activity of N–Ag co-doped TiO₂/C porous ultrafine fibers mat

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Abstract

N–Ag co-doped TiO₂/C porous ultrafine fibers mat was prepared by a sol–gel/electrospinning process using polyacrylonitrile (PAN) as a precursor and Ti(OC₄H₉)₄, AgNO₃, urea as titanium, silver, nitrogen source, respectively. The porous structure was obtained by etching SiO₂ nano-particles. Structure and properties of the fibers mat were characterized by SEM, TEM, XRD, XPS, UV–vis, Raman spectroscopy and N₂ physical adsorption analysis. Silver ion and SiO₂ nano-particles have a great influence on the crystallization of TiO₂. The photocatalytic activity was measured by the degradation of methylene blue (MB) under visible light irradiation. N–Ag co-doped TiO₂/C fibers mat exhibited much higher photocatalytic destruction rate than P25. The photocatalytic efficiency of porous fibers mat increased by 11% after etching.

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1. Introduction

Nano-sized TiO₂ is considered as the most superior photocatalytic material owing to its excellent properties, such as non-toxicity, structural stability, abundance, high oxidation rate and ecological friendliness [1]. It has been used in photocatalytic degradation of organic pollutants, toxic gas and disinfection of polluted water [2]. However, TiO₂ only absorbs UV light for its wide band gap of 3.2 eV and natural sunlight consists of 5% UV light (300–400 nm) [3]. Therefore, the shift of the absorption of TiO₂ from UV light region to the visible light region will have a profound effect on the photocatalytic reaction. Much progress realized the target by importing various dopants into TiO₂ lattice, including Fe, Ag, V, Cr, Co, N, C and F. The dopants of the above elements were applied to amend the electronic capability and light absorption ranges of TiO₂ [3–6]. Recently, the research on kinetics has suggested that the dopants improve the band gap of TiO₂ [7]. Doped TiO₂ exhibited greater

photocatalytic activity under visible light than pure TiO₂ though the UV photocatalytic activity was relatively low in some cases. N–Fe co-doped nano-TiO₂ improved the efficiency of photocatalytic reactions by 75% and 5% under visible and UV irradiations, respectively, compared with the pure TiO₂ [2].

It is known that the photocatalytic activity is relevant to the surface area of the catalyst [8]. In the past decade, porous TiO₂ particles and fibers covered with TiO₂ have been fabricated to increase the photocatalytic efficiency [9,10]. As reported by Ming et al., TiO₂ hollow particles prepared by a hydrothermal method with the BET surface area of 117 m²/g showed higher photocatalytic activity than P25 [11]. Chen et al. deposited TiO₂ on the activated carbon fibers (ACF) by an electrochemical method, possessing much higher photocatalytic efficiency than pristine TiO₂ [10]. Nevertheless, both porous TiO₂ particles and TiO₂/ACF composites cannot reclaim conveniently or take shape as conceived.

In the present work, we fabricated N–Ag co-doped TiO₂/C porous ultrafine fibers mat by a sol–gel/electrospinning method. The photocatalytic activity of fibers mat was evaluated by measurement of the degradation of methylene blue (MB) under visible light irradiation.

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2. Experimental

2.1. Sample preparation

The fibers mat was synthesized by a sol–gel process combined with the electrospinning method. PAN, Ti (OC₄H₉)₄ and acetic acid were used as starting materials. AgNO₃ and urea were used as silver source and nitrogen source, respectively. The spinnable sols were prepared by the following procedures. Firstly, 1.2 g PAN was dissolved in 8.8 g N, N'-dimethylformamide (DMF) under magnetic stirring at 40 °C for 24 h (solution A). 4 g Ti (OC₄H₉)₄ and 0.01 g AgNO₃ were added into 1 ml acetic acid under magnetic stirring for 6 h (solution B). Then golden spinnable sols were obtained by adding solution B and urea into solution A under magnetic stirring for 24 h (The sols for fabricating porous fibers mat were prepared after introducing SiO₂ nano-particles into the golden sols). Finally, the golden sols were brought into the injection and connected with a thin pinhead with an inner diameter of 0.8 mm. The pinhead connecting to a high voltage of 10 KV was served as the positive electrode. The fibers were collected on the aluminum foil which was employed as the negative electrode.

The as-spun fibers mat was stabilized in an oven at 250 °C for 2 h at a heating rate of 3 °C/min. Then, it was pyrolyzed up to 600 °C at a rate of 3 °C/min in a tubular furnace under nitrogen atmosphere. To achieve the porous structure, the fibers mat consisting of SiO₂ was dipped in 10 wt% HF aqueous solution for 24 h to remove SiO₂ nano-particles. The mat was dried at 60 °C for 12 h after washing with ethanol and deionized water. Finally, the fibers mats obtained were denoted as pure TiO₂/C (TC), N-doped TiO₂/C (NTC), N–Ag co-doped TiO₂/C (NATC) and porous N–Ag co-doped TiO₂/C (PNATC).

2.2. Characterization

X-ray diffraction (XRD) patterns, collected in the range 10–70° (2θ) using Siemens D-500 diffractometer (Cu Kα radiation, λ = 1.5406 Å) working at 40 kV and 40 mA, were used to identify phase constitutions and crystallite sizes. The Raman spectra were tested (LabRAM HR, Horiba Jobin Yvon) using a 514.5 nm, air-cooled Ar⁺ laser with 50 × objective and with laser intensity of 1.3 mW. The data acquisition time was kept at 20 s. Scanning electron microscopy (SEM) was used to observe the section and exterior morphology of the electrospun fibers. It was recorded on JEOL JSM-6360LV which operating at 5 kV. The transmission electron microscopy (TEM) observations were obtained on a Tecnai G2 F20. Samples were added on carbon-coated copper grids before observation. The mass ratio of TiO₂ in the fibers mat was measured using a Thermo-gravimetric Analyzer Pyris 1 TGA (Perkin-Elmer); the sample was heated at 10 °C/min under air atmosphere. The X-ray photoelectron spectroscopy (XPS) spectra were obtained by means of a K-Alpha 1063 electron spectrometer using Al Kα radiation. The surface areas of the fibers mat were estimated using the Brunauer–Emmett–Teller (BET) equation

(QuadraSorb Station 3) after preheating the samples at 150 °C for 3 h to eliminate the adsorbed water. Pore size distributions were obtained from the adsorption branches of isotherms by using the Barret–Joyner–Halenda (BJH) model. UV–visible diffuse reflectance spectra were obtained for the fibers mat using a Scan UV–visible spectrophotometer (U-4100, Hitachi).

2.3. Photodegradation of methylene blue

The photocatalytic activity of fibers mat was evaluated by measuring the decomposition of methylene blue with a concentration of 10 mg/L under visible-light irradiation. The visible-light source was a 1000 W halogen lamp. A colored glass filter with cut-off wavelength of 420 nm was used for eliminating UV light. For a typical photocatalytic experiment, 0.1 g of the fibers mat shaped like rectangle was added into 100 ml of the above methylene blue solution in a two neck flask. Then, the flask was installed in a thermostatic waterbath to keep the solution at 20 °C. Before the irradiation, the mixture was magnetically stirred in dark for 30 min to catch the establishment of an adsorption–desorption equilibrium. The air was imitted into the admixture through an air pump to make the rectangle fibers mat rolled in the solution. After a setup exposure time, 3.0 ml mixture solution was sampled and detected by a 722S visible spectrophotometer (INESA, Shanghai) at 661 nm. For comparison, the same experiment was also done in the presence of P25 (purchased from Xiya reagent, Chengdu).

3. Results and discussion

Fig. 1 exhibits the SEM images of NATC (a, b) and PNATC (c). In Fig. 1(a), the nanofibers showed long and straight morphology with uniform diameters ranging from 350 to 450 nm. Fig. 1(b) demonstrates many grooves on the surface of NATC fibers. After etching of SiO₂ by HF, PNATC with a great number of nano-sized holes was obtained (Fig. 1c).

Fig. 2(a) presents a typical magnification TEM image of NATC, suggesting that TiO₂ nano-particles exist in the fibers well-proportioned. A HRTEM image of the sample in Fig. 2(b) showed that Ag nano-particles with the diameters of 5 nm were adhered to the surface of TiO₂. The lattice fringe spacing of 0.35 nm and 0.236 nm corresponded to the anatase-phase TiO₂ (101) plane and Ag with the cubic structure (111) plane, respectively [12].

To determine the composition of the fibers mat and confirm the valence states of various atoms, XPS analysis was carried out (Fig. 3). The binding energy of O 1s in pure TiO₂ is 529.3 eV [13]. While O 1s XPS spectrum of the NATC (Fig. 3a) was divided into two sub-peaks centered at 530.0 eV and 532.1 eV. This was contributed to the formation of O–Ti–N structure and Ti–O–N structure due to the replacement of O in TiO₂ lattice by N atoms [14]. In the Ti 2p XPS spectrum (Fig. 3b), two peaks were observed at 458.8 and 464.5 eV. They were assigned to 2p_{3/2} and 2p_{1/2} respectively, attributing to Ti⁴⁺ in anatase titania [15]. Fig. 3c shows the N 1s spectrum. The feature at around 397 eV was generally

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