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Nano-Bi_2WO_6 functionalized flexible SiO_2 fibrous film for water purification

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ABSTRACT

Electrospinning-derived nanofibrous films functionalized by photocatalysts have been extensively studied in the applications of environmental remediation. In this investigation, we propose a simple strategy for preparation of flexible and chemically stable nanofibrous films with high photocatalytic efficiency. Specifically, SiO_2 nanofibrous film modified with Bi_2WO_6 nanoparticles was studied as a representative. Flexible SiO_2 nanofibers were derived through sol–gel and electrospinning techniques. By simple soaking in precursor solution of Bi_2WO_6 and calcination, the SiO_2 nanofibrous film was functionalized by Bi_2WO_6 nanoparticles, forming hierarchically porous composite film. Micro morphology, mechanical property and photocatalytic performance were tuned via changing the concentration of the soaking solution. Photocatalytic removal of organic pollutant from water was performed using RhB (Rhodamine B) as a model. The strategy proposed here is also widely applicable for preparation of composite films modified with other kinds of photocatalysts. SiO_2–Bi_2MoO_6, SiO_2–TiO_2 and SiO_2–CuO composite films were prepared in a similar way to demonstrate the versatility of the proposed preparation strategy.

1. Introduction

With the unique characters of extremely high aspect ratio, huge specific surface area, two-dimensional quantum confinement, enhanced mechanical strength, etc., micro/nanofibers have been extensively investigated in the application fields of environmental remediation [1], new energy developing [2], tissue engineering [3], etc. Electrospinning is currently acknowledged as one of the most promising techniques for fabrication of continuously long micro/nanofibers, due to its high efficiency, scalability, versatility, and most importantly the ability to assemble fibers to macroscopic materials with predesigned functionalities [4–7]. Nonwoven film is one of the most representative materials assembled by electrospun nanofibers. The electrospun nanofibrous films are highly porous, possess huge specific surface area and tunable porous structure, which are very beneficial for environmental remediation [1]. On the other hand, considering the environmental and energy crisis, photocatalytic decomposition is one of the most efficient approaches for eliminating air or water pollutants [8–10]. A great deal of researches have been devoted to developing photocatalytic nanofibrous films with optimized synthetic performance based on the electrospinning technique [11–15].

Photocatalytic electrospun nanofibrous films mainly can be categorized by three types. The first type include semiconductor (photocatalyst) electrospun nanofibers and ceramic electrospun nanofibers functionalized by photocatalyst nanostructures [16–18]. This type of nanofibrous films possess relatively high photocatalytic efficiency, but usually lack enough mechanical strength required in practical use. The second type refers to electrospun polymer or carbon nanofibers functionalized with photocatalysts via post treating or in situ doping in the spinning solution [14,19,20]. For this type, the post functionalization with photocatalysts are usually limited by the relatively poor chemical nature of the polymer nanofibers. Although carbon nanofibers are inert at low temperature, they are prone to oxidizing in air at high temperature, which constrains the functionalization approaches that need thermal treating. The in situ doping of photocatalysts in spinning solution can readily circumvent the above problem, however, the incorporation of photocatalysts by the polymer matrix will inevitably decrease the photocatalytic efficiency. In the third type, glassy nanofibers derived by sol–gel and electrospinning are employed as the scaffold for supporting photocatalysts, which have been reported in our previous researches [21,22]. This type of

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photocatalytic nanofibrous films are flexible, possess acceptable mechanical strength and active surface property, and meanwhile are chemically and thermally stable. Various kinds of approaches, including hydrothermal/solvothermal reaction, chemical/physical deposition, sol–gel coating, etc., can be applied in functionalization with photocatalysts. Moreover, due to the stubborn nature of the glass-photocatalyst composite films, regeneration of their functionality can be realized conveniently.

Bismuth-based oxides represent the most interesting and promising candidates for various photocatalytic applications under visible-light irradiation, due to the high-efficient visible-light activity, photostability, and nontoxicity [23–25]. Bismuth tungstate (Bi_2WO_6) has been a subject of intense research for its outstanding photocatalytic performance in water splitting and organic contaminants decomposition under visible-light irradiation [26–28]. Many works have been devoted to this versatile material in the applications of pollutant decomposition. Though flexible and efficient Bi_2WO_6 nanostructures decorated glass nanofibers have been successfully prepared via electrospinning and post hydrothermal treating [22], the low preparation efficiency and poor scalability limits the practical use of this approach.

Herein, we report the preparation of Bi_2WO_6 nanoparticles modified SiO_2 glassy nanofibrous films based on electrospinning and simple post soaking and calcination. Different from our previous works [22], the fabrication strategy proposed here can be realized at atmospheric pressure (autoclave free), and it is suitable for preparation of large-area films, which usually is difficult to hydrothermal/solvothermal approaches. Meanwhile, the strategy proposed here is also widely applicable for preparation of other composite films based on glassy nanofibers, which was also demonstrated here by taking SiO_2–TiO_2, SiO_2–Bi_2MoO_6 and SiO_2–CuO films as examples. The SiO_2–Bi_2WO_6 composite films were characterized with SEM, TEM, XRD, XPS and N_2 adsorption–desorption isotherms. Mechanical strength and water purification performance were also evaluated. Compared with other approaches, the strategy for preparation of photocatalytic nanofibrous films proposed here is much simpler, more scalable, and universally applicable to wide range of materials. In the following introduction, the SiO_2–Bi_2WO_6 composite films are nominated as S-BWO for convenience.

2. Experimental

2.1. Preparation of SiO_2 glassy nanofibrous film

30 mL TEOS was mixed homogeneously with EtOH, then 4.5 mL deionized water and 0.2 mL concentrated HCl were added into the TEOS–EtOH solution accompanied by magnetic stirring. The mixed solution was shifted into an oil bath pot and reacted at 75 °C for 4 h to form spinnable SiO_2 sol. The electrospinning was performed with an integrated electrospinning system with a motor controlled aluminum drum as the fiber collector. The solution feeding rate, applied voltage and capillary-to-collector distance were set to be 2 mL/h, 12 kV and 10 cm, respectively, while the rotating speed of the collector was maintained to be 500 rpm. The whole electrospinning process was carried out in ambient atmosphere at room temperature. After 3 h of collection, the white nonwoven film of SiO_2 nanofibers was peeled off the aluminum drum cautiously and dried in an oven at 100 °C for 12 h.

2.2. Preparation of S-BWO films

The S-BWO films were prepared with a simple soaking-and-calcination approach. Briefly, the solution for soaking the films was prepared by dissolving 0.83 g $Na_2WO_4{\cdot}2H_2O$, 2.42 g $Bi(NO_3)_3{\cdot}5H_2O$, 6.3 g citric acid into the mixed solution of 40 mL ethylene glycol and 1 mL fuming nitric acid. In order to investigate the influence of the solution concentration to the morphology and composition of the S-BWO film, the pristine solution was diluted for 2 and 3 times (the corresponding samples were nominated as S-BWO3, S-BWO2 and S-BWO1, respectively). Disk-shaped SiO_2 nonwoven films with the size of ~16 mm × 0.2 mm (radius × thickness) and mass of ~0.06 g were soaked in the above solution for 1 h, then picked out and held above the solution until dripping stopped, followed by drying in an oven at 120 °C for 2 h. The dried films were transferred to a muffle furnace and annealed at 500 °C for 3 h to get the final S-BWO films. The mass of S-BWO1, S-BWO2 and S-BWO3 was about 0.1 g, 0.14 g and 0.25 g, respectively. The whole procedure for preparation of S-BWO films is schematically illustrated in Fig. 1.

2.3. Characterization

Micro morphologies of the samples were observed with SEM (scanning electron microscopy, Nova NanoSEM 430, FEI, Eindhoven, Netherlands) and TEM (Transmission Electron microscopy, JEM-2100F microscope, JEOL, Tokyo, Japan); chemical composition of the samples were determined by EDS (Energy Dispersive Spectrometer, Model Inca350, Oxford, London, UK); structure of the samples was investigated via XRD (X-ray Diffraction, AXS D8 Advance, Bruker, Zurich, Switzerland); chemical state of the elements in the sample was investigated by XPS (X-ray photoelectron spectroscopy, AMICUS, Shimadzu, Japan); porosity of the samples was tested through N_2 adsorption–desorption isotherms (Quantachrome, Delray Beach, FL); mechanical property of the films was studied with a universal materials tester (INSTRON, Boston, MA). For the test of mechanical property, the films were cut into rectangular pieces sized length × width = 30 mm × 10 mm (their thickness was about 0.3 mm).

2.4. Photocatalytic performance

Two sets of experiments were designed to evaluate the photocatalytic performance of the S-BWO films using Rhodamine B (RhB) as a model pollutant. In the first set of experiments, the photocatalysts were dispersed in RhB solution to form suspensions, as performed in references [29–32]. Briefly, 0.135 g S-BWO1 (containing 0.05 g BWO) or 0.05 g BWO powder (peeled off from S-BWO1 by fierce untrasonication) or 0.13 g of SiO_2 nanofibers were dispersed into 50 mL of RhB solution with the initial concentration of 20 mg/L contained in a cylindrical glass vessel with a water-cooling jacket. During the solution feeding, an Xenon light with a 420 nm cut-off wave filter was employed to provide visible light to trigger the photocatalytic reaction. The distance from the bottom of the lamp bulb to the solution surface was set to be 8 cm, and the irradiation power at the solution surface was tuned to be 580 mW. Before light irradiation, the suspension was agitated in dark for 1 h to ensure saturated adsorption of RhB on the photocatalysts. 2 mL of suspension was sucked and pressure-filtrated with a syringe filter. The photolysis of RhB was also investigated through similar experiment except without addition of photocatalyst. In the second set of experiments, RhB aqueous solution with a concentration of 20 mg/L was constantly fed into a glass funnel with the S-BWO film at the bottom acting as a filter. The feeding rate was maintained to be 30 mL/h. The same light source as in the first set of experiments was used to irradiate the reaction solution. The radiation power at the surface of the RhB solution in the funnel was set to be ~500 mW. Concentration of the pristine and filtered RhB solution was measured with a UV–vis/IR spectrophotometer (Perkin Elmer Lambda 900, Waltham, MA). The transparent filtrated solution free of photocatalyst was kept for measuring the concentration of remaining RhB.