Applied Surface Science 258 (2012) 3789–3794

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Fabrication and characterization of electrospun orthorhombic $InVO_4$ nanofibers

Lingjun Song, Suwen Liu*, Qifang Lu, Gang Zhao

Shandong Provincial Key Laboratory of Processing and Testing Technology of Glass & Functional Ceramics, Shandong Polytechnic University, Jinan 250353, PR China

ARTICLE INFO

Article history:
Received 10 September 2011
Received in revised form
20 November 2011
Accepted 6 December 2011
Available online 13 December 2011

Keywords:
Orthorhombic $InVO_4$
Electrospinning technique
Sintering
Nanofibers

ABSTRACT

The novel orthorhombic $InVO_4$ nanofibers have been successfully synthesized by annealing electrospun precursor fibers. Citric acid was used as a ligand for it could react with metal salts to get a transparent homogeneous precursor solution and homogeneous precursor sol for electrospining. Polyvinyl pyrrolidone (PVP, K-30) was used as a binder and a structure guide reagent because it was one kind of water-soluble polymers. It is easy to gain one-dimensional materials while the viscosity of the citrate/PVP sol was suitable. The structure, morphology and photocatalytic properties of the nanofibers were characterized by X-ray diffraction (XRD), thermogravimetry analysis (TGA), scanning electron microscopy (SEM) analysis, UV–vis spectrophotometer and fluorescence spectrophotometer. The nanofibers calcined at 700 °C were orthorhombic $InVO_4$ with a width in the range of 30–100 nm and length in micron-grade. This one-dimensional pure orthorhombic $InVO_4$ had the higher photocatalytic activity under visible light irradiation. The photo-degradation rate of nitrobenzene aqueous solution under visible light reached 69% after 6 h. It is obvious that the orthorhombic $InVO_4$ nanofibers have a potential application in wastewater-treatment.

1. Introduction

Nowadays, $InVO_4$ has become a promising photo-catalyst with a narrow band gap (Eg = 2.0 eV), which is able to induce hydrolysis of water molecules under visible-light irradiation [1–3]. $InVO_4$ belongs to a large family of orthovanadate compounds with a general formula $M^{3+}VO_4$ (M^{3+} = In, Fe, Cr, Al, rare earths) [4,5] which has two phases: the stable high-temperature orthorhombic $InVO_4$-III (Cmcm) phase and low-temperature metastable monoclinic $InVO_4$-I phase [6,7]. The structure of $InVO_4$ is composed of chains of the InO_6 octahedral linked together by the VO_4 tetrahedral [8], and the only difference is that the structure of monoclinic $InVO_4$-I phase consists of compact In_4O_{16} which groups of four edge-shared InO_6 octahedra linked to each other by VO_4 tetrahedra and the orthorhombic $InVO_4$ is composed of chains of InO_6 octahedra which are linked together by VO_4 tetrahedra [9]. As a new type of semiconductor, orthorhombic $InVO_4$ has also attracted considerable interests for its special photocatalytic properties [4,10].

One-dimensional nanostructures, such as nanowires, nanofibers, and nanobelts are expected to play an important role due to their potential applications in nanodevices. Various one-dimensional nanostructured materials have been fabricated by a variety of methods, including templating direction [11], solid-state reaction method [12], hydrothermal treatment [13], etc. Besides, electrospinning is a unique fiber spinning process because it can make fibers with a diameter of 50–500 nm [14]. Single-crystalline $InVO_4$ nanotubes produced by annealing electrospun precursor fibers have been first reported by Yi and Li [15]. To the best of our knowledge, other morphological $InVO_4$ nano-products synthesized by electrospinning technology have not been reported. So, it is very interesting and essential to prepare the $InVO_4$ nanoscale one-dimensional materials via the electrospinning route.

In the present work, the electrospinning technique was used to prepare citrate/PVP composite fibers. Orthorhombic $InVO_4$ nanofibers were obtained by calcining the precursor nanofibers above 700 °C.

2. Experiment

2.1. Synthesis procedure

NH_4VO_3 (99.0%) was bought from Shanghai Chemical Reagent Co. Ltd., ethanol of analytical grade was bought from Tianjin Guangcheng Chemical Reagent Co. Ltd. $In(NO_3)_3{\cdot}4.5H_2O$ with a purity of 99.5% and Polyvinyl pyrrolidone (PVP (K-30), $Mw = 4.0 \times 10^4$) were purchased from Sinopharm Chemical Reagent Co. Ltd.

A schematic of the electrospinning process is shown in Fig. 1. In a typical experiment for the preparation of the electrospinning solution, 2 mmol $In(NO_3)_3{\cdot}4.5H_2O$ was dissolved into 10 mL distilled water under magnetic stirring to form a colorless transparent

---

* Corresponding author. Tel.: +86 0531 89631632; fax: +86 0531 89631227.
E-mail address: liusw@spu.edu.cn (S. Liu).

0169-4332/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2011.12.029

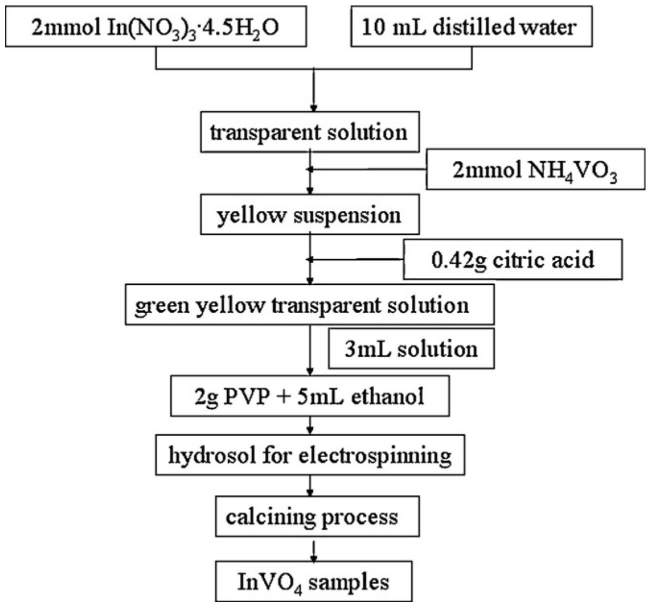

Fig. 1. The preparation process of $InVO_4$ samples.

solution. Then 2 mmol NH_4VO_3 was added into the above solution to form an orange suspension. 2 mmol citric acid used as a chelating agent was gradually added into the beaker under continuous stirring until the suspension turned into a yellow green transparent precursor solution (recorded as precursor A). 2 g PVP (K-30) was dissolved in 5 mL ethanol (recorded as precursor B). Then 3 mL precursor solution A was transferred to precursor B and the mixture was further stirred for 10 min to form a viscous hydrosol for electrospinning. Here, PVP (K-30), one kind of water-soluble polymers, was used as a binder and a structure guiding reagent.

Besides, another precursor A′ without citric acid was prepared by adding $In(NO_3)_3$ solution into hot NH_4VO_3 solution directly while all other things being equal.

The precursor sol was drawn into a syringe connected with a stainless steel capillary with inner diameter of 0.40 mm and outer diameter of 0.60 mm. The positive terminal of a variable high-voltage power supply (BGG-200 kV/20 mA) was connected to the needle tip of the capillary while the other was connected to the collector plate. During the electrospinning, the applied voltage was kept at 25 kV and the distance between spinneret and collector was optimized and around 28 cm. The feeding rate of the solution was kept at 0.5 mL/h at room temperature. When the spinning was completed, the as-prepared precursor composite fibers were collected by a forcep, dried at 80 °C for 12 h. And then all gel fibers were put into an air-atmosphere programmable tube furnace for heat treatment according to the TG result. The fibers were fired from room temperature to desired temperatures at a rate of 1 °C/min with a hold time of 1 h. The products were naturally cooled to room temperature in the furnace to obtain the resulting $InVO_4$ nanofibers. Then the calcined nanofibers were given characterization.

2.2. Characterization

The phase and crystallinity of the $InVO_4$ products were examined by X-ray diffraction (XRD, Rigaku D/Max 2200PC, Germany) with Cu K_α radiation ($\lambda = 1.5148$ Å) at a scanning rate of 0.02°/s in the range of 20–60°, and the accelerating voltage and the applied current were 28 kV and 20 mA, respectively. The morphology and microstructure of the orthorhombic $InVO_4$ samples were characterized with a field emission scanning electron microscopy (Hitachi FESEM-4800, Japan, working voltage of 10 kV and operating distance of 7.7 mm). TG analysis of composite fibers was measured with a thermal analyzer (TGA/SDTA 851, Mettler) at an O_2 flow rate of 20 mL/min, using a heating rate of 20 °C/min in air. The purity of O_2 was 99.5%. UV–vis diffuse reflectance spectra and the photodegradation decoloring rate of the samples were measured using a Shimadzu UV-2550PC spectrophotometer. The photocatalytic activities of the as-synthesized samples were determined through the degradation of nitrobenzene (NB). The formation of hydroxyl radicals ($^{\bullet}$OH) was detected by the photoluminescence (PL) spectra which were measured on a Hitachi F-4500 fluorescence spectrophotometer.

0.12 g photocatalysts were added in 30 mL NB solution with a concentration of 20 mg/L under stirring, using a 500 W Xenon lamp with a UV-cutoff filter ($\lambda \leq 400$ nm) as the light source. Took 4 mL solution out once every one hour, centrifuged and measured the absorbance at the maximum absorption wavelength ($\lambda = 268$ nm) of the NB. The decoloring ratio of the NB was estimated according to the equation: $\eta = [(A_0 - A_t)/A_0] \times 100\%$, where η is the degradation ratio of NB, A_0 is the initial absorbency, and A is the absorbency at a certain time. Additionally, the photodegradation ratio of NB solution without photocatalyst was also measured under the same condition to estimate the influence of the photodegradation over the organic compounds.

The detection experiment process of the $^{\bullet}$OH is similar to the photodegradation experiment, with the exception of a basic terephthalic acid solution instead of NB solution. Terephthalic acid (5×10^{-4} M) was dissolved in NaOH solution (2×10^{-3} M). The sampling was carried out every 10 min, and the withdrawn solution was measured after centrifugation. The product of terephthalic acid hydroxylation can give a characteristic fluorescence peak at about 425 nm by excitation with the wavelength of 315 nm.

3. Results and discussion

3.1. TG analysis

Fig. 2 shows the typical thermal behavior of the precursor composite nanofibers. The TG curve indicates four different weight loss steps with the increase of temperature in the whole combustion process. The first weight loss (∼16.48%) occurred before 190 °C was mostly attributed to the gradual evaporation of free

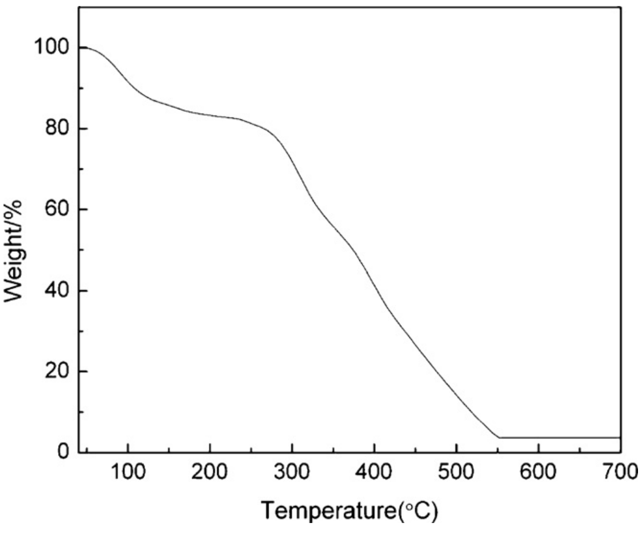

Fig. 2. The TG curve of the precursor composite fibers.