Catalysis Communications 31 (2013) 37–41

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

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

Short Communication

Electrospinning derived hollow SnO_2 microtubes with highly photocatalytic property

Xin Wang, Huiqing Fan *, Pengrong Ren

State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China

ARTICLE INFO

Article history:
Received 27 July 2012
Received in revised form 6 November 2012
Accepted 8 November 2012
Available online 15 November 2012

Keywords:
SnO_2
Microtubes
Electrospinning
Photocatalytic

ABSTRACT

SnO_2 hollow microtubes (MTs) are prepared by electrospinning. A detailed microstructure and mechanism study of the synthesized SnO_2 MTs has been carried out. The SnO_2 hollow MTs provide promising photocatalytic characteristics, with ultra-fast degradation and stable repeatability. These good degradation and repeatability characteristics are dominated by the large surface area and effective separation of photoinduced carriers provided by the MT morphology and fine particle size building the porous shell of SnO_2 MTs.

1. Introduction

During previous decades, photocatalysis, as a "green" technique, has been extensively used in the area of environmental remediation because various kinds of pollutants can be decomposed completely by photocatalytically active semiconductors under light irradiation [1,2]. As an ideal photocatalysis, fast degradation and reusable use are in particular the most important two factors, which are required for real-time purification and cost saving [3,4]. The deposition kinetic is closely related to the effectively contact of pollutants with the photocatalysis surface and the reduction of recombination between photo-induced electrons and holes. And both the aspects can be facilitated by employing large surface area and/or porous nanostructures [5,6]. In addition, the catalysis reaction is strongly influenced by the particle size of photocatalysis [7].

With the steady and fast growing field of nanoscience and nanotechnology, oxide hollow microtubes (MTs) have become a promising nanostructure for photocatalytic applications because the rapid and effective diffusion of pollutants onto the photocatalysis surface via nanoscale shells affords large surface area [8,9]. In addition, if the wall of the MTs is made of fine nanocrystalline particles, the photocatalysis of semiconductor can be greatly improved. Thus far, hollow MTs of SnO_2, In_2O_3, Fe_2O_3, Cu_2O/CuO and WO_3 have been investigated to enhance the photocatalytic performances [10–14]. As one of the most representative photocatalysis material among these options, SnO_2 has been prepared in the form of hollow MT structures via atomic layer deposition (ALD) [15], thermal evaporation [16,17], electrochemical deposition [18,19], hydrothermal [20], sol–gel template [21,22], etc.

In this work, a facile one-step method for the fabrication of SnO_2 hollow MTs by directly annealing electrospun composite microfibers is proposed. The diameter of hollow SnO_2 MTs is around 1 μm, the wall of SnO_2 MTs is polycrystalline and composed of fine nanoscale particles with sizes in the range of 100–150 nm. The formation mechanism of SnO_2 MTs is also proposed. Furthermore, the photocatalysis of Rhodamine B (RhB) is investigated. The prepared SnO_2 MTs are found to show enhanced and fast photocatalytic activity, as well as good repeatability.

2. Experimental

2.1. Preparation of electrospinning solution

Analytical grade tin dichloride dehydrate ($SnCl_2 \cdot 2H_2O$), polyvinyl pyrrolidone (PVP, Mw = 58,000), absolute ethanol were purchased from Shanghai Chemical Co. and used as received. Deionized water was purified using distillation equipment to prepare an aqueous solution. In a typical experiment, 8 g PVP was dissolved into 12 g deionized water. After vigorous magnetic stirring for 30 min, a mixture solution with the mass ratio of $SnCl_2 \cdot 2H_2O$:deionized water:absolute ethanol = 1:1:4 was prepared and added to the PVP solution under continuously stirred for 3 h.

2.2. Preparation of SnO_2 microtubes by electrospinning

A home-made electrospinning setup which contained basically three components: a high-voltage supply (HBGY HB-2603-1AC), a syringe pump and an aluminum (Al) collecting plate. The syringe pump connected to a Teflon tube was used to control the flow rate. The process is that the electrospinning solution was pushed from the syringe at a constant flow rate of 3 ml/h into a 1 mm internal diameter Teflon capillary, whose needle as an anode was 10 cm distant from the grounded cathode Al plate. The Al plate was also used to collect the

* Corresponding author. Tel.: +86 29 88494463; fax: +86 29 88492642.
E-mail address: hqfan3@163.com (H. Fan).

1566-7367/$ – see front matter
http://dx.doi.org/10.1016/j.catcom.2012.11.009

electrospun products under a high voltage of 30 kV. The collected microtubes were then dried at 60 °C and continued to heat at a rate of 2 °C min^{-1} to 600 °C and maintained at the temperature for 2 h. Commercial analytical grade SnO_2 powders produced by Shanghai Chemical Co. were also used to make comparison with as-prepared SnO_2 microtubes.

2.3. Characterization

The phase structure of the as-synthesized samples was examined by X-ray diffraction (XRD; D/Max2550VB+/PC, Rigaku, Tokyo, Japan) with Cu–Kα radiation (λ = 1.5406 Å). The morphologies of the samples were examined using a field emission scanning electron microscopy (FE-SEM; JEOL-6700F, Japan Electron Co., Tokyo, Japan). Transmission electron microscopy (TEM; JEM-3010, Questar, New Hope, USA) equipped with energy-dispersive X-ray spectroscopy (EDS; FeatureMax, Oxford Instruments, Oxfordshire, UK) was performed with an acceleration voltage of 300 kV. The ultraviolet–visible (UV–vis) absorption spectra were recorded by spectrophotometer (UV3150, Shimadzu Corporation, Kyoto, Japan). The porosity and adsorption performance of the products were determined via a nitrogen adsorption apparatus (NOVA 2200e, Quantachrome Instruments, Florida, USA).

2.4. Photocatalytic measurement

The photocatalytic reaction suspension was prepared by adding the sample (40 mg) to 40 ml of Rhodamine B (RhB) solution with a concentration of 10 mg/l. The suspension was sonicated for 30 min and then stirred in the dark for 30 min to ensure an adsorption/desorption equilibrium prior to light irradiation. The suspension was then irradiated using ultraviolet (UV) light (50 W high-pressure mercury lamp with main emission wavelength 313 nm) under continuous stirring. Analytical solution was taken from the reaction suspension after various reaction times and centrifuged at 6500 rpm for 5 min to remove the prepared samples for analysis.

3. Results and discussion

Comparative morphologies of as-prepared and annealed SnO_2 MTs are demonstrated in Fig. 1. Fig. 1a depicts a typical distribution in morphology for the white products collected on the alumina plate. The as-prepared MTs form a network structure and a smooth surface due to the polymeric features before anneal treatment. A higher magnification SEM (Fig. 1b) shows that before anneal, the MTs own a hollow character with smooth outer surfaces. After annealing at 600 °C for 2 h, the MTs retain a macroporous network and exhibit shrinkages for the decomposition of PVP (Fig. 1c). The outer diameters of the MTs are in the range of 650–750 nm, at least several micrometers in length. The inner diameters of the MTs are in the range of 450–550 nm. Meanwhile, a higher magnification of ruptured section in Fig. 1d shows the detailed information of the products and further disclosing their hollow tube structure feature. The 1D nanostructure clearly shows the coarse outer surfaces, the smooth inner surfaces and the rough porous surface of SnO_2 MTs. The wall of the MT is linked by the non-uniform SnO_2 nanoparticles of approximately 100 nm in diameter.

To further understand the internal structure and chemical composition of SnO_2 MTs, TEM accompanied by HRTEM, SAED and EDS are employed. The corresponding TEM and a magnified pattern (Fig. 2a, b) further proves the 1D hollow porous structure, the outer and inner diameter of these microtubes are about 714 nm and 528 nm respectively, in accordance with the SEM observation. It also indicates that these MTs consist of particles in a compact manner and hold uniform sizes with diameter in the range 100–120 nm. The average thickness of the SnO_2 MTs is estimated to be about 110 nm. A typical HRTEM image is shown in Fig. 2c. The spacing between the lattice fringes for the nanoparticles decorated on the microtubes is 0.263 nm, matching the d value for (101) planes of rutile SnO_2. A SAED pattern taken from an individual microtube was shown in the inset of Fig. 2c. All diffraction rings on this pattern can be attributed to tetragonal SnO_2, suggesting a polycrystalline nature. The EDS spectrum (Fig. 2d) from the microtubes shows intense peaks of Sn and O, displaying the composition as Sn and O only. The Cu signals come from the supporting TEM grid. EDS quantitative analysis gives an average Sn/O composition of 1:2 within the accuracy of the technique, matching well with the stoichiometry of SnO_2.

Based on the SEM and TEM observations, the formation process of SnO_2 MT structures can be considered as fabricating from homogeneous polymer-sol-double solvents system and then forming hollow structures due to solvent evaporation and phase segregation, as shown in Fig. 3. During the course of electrospinning, the surface ethanol evaporates rapidly and there is a concentration gradient of ethanol along the diameter of the fiber which is high in the center but low at the edge of the fiber. As a result, tin alkoxide and PVP at the edge

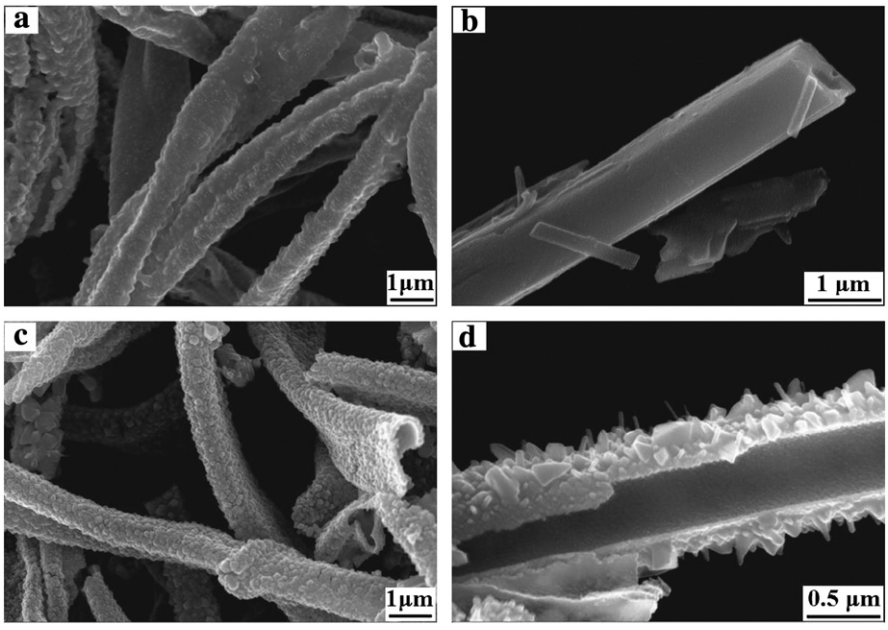

Fig. 1. (a) SEM and (b) high magnification images of the as-prepared SnO_2 microtubes. (c) SEM and (d) high magnification images of the calcined SnO_2 microtubes.