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Short Communication

Controlled synthesis of Sn doped ZnO microspheres stringed on carbon fibers with enhanced visible-light photocatalytic activities

Jianchao Sun, Hai Fan *, Nan Wang, Shiyun Ai *

College of Chemistry and Material Science, Shandong Agricultural University, Taian 271018, Shandong, PR China

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ABSTRACT

Sn doped ZnO microspheres stringed on carbon fibers composites like sugar-coated haws on a stick were successfully prepared by a precursor method. Firstly, Sn doped $Zn_5(CO_3)_2(OH)_6$ microspheres were successfully formed on carbon fibers. Then, after calcination, Sn doped ZnO microspheres stringed on the carbon fibers composites were successfully obtained. X-ray diffraction (XRD), field emission scanning electronic microscope (FESEM), and transmission electron microscope (TEM) were used to characterize the products. The studies of photocatalytic degradation on Methylene blue (MB) indicate that the composites show enhanced visible-light-driven photocatalytic activities for degradation of organic pollutants. Furthermore, the free-standing Sn doped ZnO/carbon fibers composites can be easily thrown into and recovered from a wastewater solution with stable recycling performance. This work provides a facile method for the preparation of carbon fibers based composite materials, which may have potential applications in the environment field.

1. Introduction

Water pollution has become one of the most serious environmental problems over the world. Organic pollutants in wastewater such as organic dyes are harmful to human health and living creatures. Traditionally, many strategies have been developed for the removal of organic pollutants from wastewater. Adsorption [1] and flocculation [2] have highly efficient removal of organic wastes, but cannot eliminate them from the environment. Chemical oxidation [3] needs consume much oxidizing agents. Compared with the above methods, photocatalytic degradation technique shows great advantage. It makes full use of the solar light energy to adopt semiconductors as reusable photocatalysts, which is a green energy saving and promising methods [4,5]. Therefore, much attention has been focused on the development of high efficiency, low-cost and visible-light-driven photocatalyst [6].

Semiconductors have been widely studied owing to its wide applications in utilization of solar energy, photochemical water splitting, organic pollutants degradation Tong et al. [7]. Among various oxide semiconductor photocatalysts, ZnO has been intensively studied due to its high photosensitivity, nontoxic nature, high luminescence properties and low cost [8]. Some of the recently experimental results showed that, ZnO, due to its large initial rates of activities and absorption efficiency of solar radiations, shows a higher photocatalytic activity than TiO_2 [9–11]. However, ZnO has almost the same band gap (3.2 eV) as TiO_2, mainly absorbs the ultraviolet light, which limits its sufficient use of solar light for wide applications.

Doping the semiconductors with foreign species has been received as the most popular approach to narrow the band gap of semiconductors [12]. For example, N, S and C have been successfully doped in TiO_2 for enhancing the visible light absorption [13–17]. Several metals and nonmetals elements such as Sb, Cu, N, C and S have been doped into ZnO semiconductors for attempting to narrow the band gap of ZnO [18–22].

The other challenge is how to enhance the photocatalytic efficiency of ZnO because of the bottleneck of poor quantum yield caused by the rapid recombination of photogenerated electrons and holes. Several strategies have been proposed to reduce the recombination of photo-induced electron–hole pairs. Among them, carbon based materials have aroused great attention due to their excellent electron conduction [23,24]. For example, carbon nanotubes and graphene or graphene oxide nanosheets have been widely used in the photocatalytic nanocomposites for the enhancement of photocatalytic activity [25–28].

Carbon fibers as one of important carbon materials also show efficient electron capture and transport ability, thus, can be applied as based materials for the improvement of the photocatalytic activity [29,30]. Some reports have demonstrated that photogenerated

* Corresponding authors.
E-mail addresses: fanhai@sdau.edu.cn (H. Fan), chemashy@163.com (S. Ai).

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electrons could be efficiently captured and further transported through highly conductive carbon fibers [31,32]. Furthermore, carbon fibers with long flexible length can be more easily separated from solution. The excellent photocatalytic activity of Sn doped ZnO driven by visible light, the efficient electron transfer property and the easy separation property of carbon fibers, inspired us to combine Sn doped ZnO and carbon fibers together. The prepared composites would not only have efficient solar light absorption ability, but also hinder the recombination of electrons and holes, and thus could obviously improve the photocatalytic efficiency and recyclable property.

Herein, we successfully synthesize Sn doped ZnO microspheres stringed on carbon fibers by a precursor method. Firstly, Sn doped $Zn_5(CO_3)_2(OH)_6$ spheres were successfully formed on carbon fibers, then, after calcination, Sn doped ZnO spheres stringed on the carbon fibers composites were successfully obtained. The photocatalytic degradation studies show that the prepared photocatalyst composites not only displayed efficient visible-light-driven photocatalytic activities, but showed stable recycling property for degradation of organic dyes.

2. Experimental

2.1. Materials

Chemical reagents including $SnCl_4$, $Zn(CH_3COO)_2{\cdot}2H_2O$ and hexamethylenetetramine (HMT) were obtained from Tianjin BASF chemical Co., Ltd. Carbon fibers were purchased from Yixing Hengtong Carbon Fiber Weaving Co., Ltd. ZnO with analytical reagent was purchased from Tianjin Kaitong chemical Co., Ltd. Methylene blue (MB) was obtained from Shanghai Jingchun Reagent Company (China). All these chemicals were used as delivered without further purification.

2.2. Synthesis of Sn doped ZnO microspheres stringed on the carbon fibers

Sn doped $Zn_5(CO_3)_2(OH)_6$ microspheres stringed on carbon fibers were prepared before the synthesis of Sn doped ZnO microspheres stringed on the carbon fibers. Firstly, the surface of carbon fibers was treated with HNO_3 solution. Then 50 mL $Zn(CH_3COO)_2$ solution (0.5 mol L^{-1}) and suitable volume of $SnCl_4$ solution were added into the suspension of carbon fibers. After that, 20 mL HMT (1 mol L^{-1}) was added into the above solution. The mixed solution was transferred into a 120 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 120 °C for 6 h, and then allowed to cool to room temperature naturally. The obtained products were washed with absolute ethanol and distilled water several times respectively and finally air dried at room temperature.

To obtain Sn doped ZnO microspheres stringed on the carbon fibers composites, the above prepared Sn doped $Zn_5(CO_3)_2(OH)_6$ microspheres stringed on carbon fibers were calcinated at 300 °C for 2 h, then, Sn doped ZnO microspheres stringed on the carbon fibers composites were successfully prepared.

2.3. Characterization

Field emission scanning electron microscopy (FESEM) images were obtained by FESEM (JEOL, JSM-6700F). The powder X-ray diffraction (XRD) patterns were analyzed by XRD (Bruker, D8-Advance X-ray diffractometer, CuKa, $\lambda = 1.5406$ Å). High-resolution transmission electron microscopy (HRTEM) images associated with energy dispersive X-ray spectroscopy (EDS) analyses were performed by using an H-7650 TEM with an acceleration voltage of 200 kV.

2.4. Photocatalytic tests

To evaluate the photocatalytic activities of the products, Methylene blue (MB) was selected as one of the typical organic pollutants. The photocatalytic degradation of MB aqueous solution was performed at room temperature under visible light irradiation using a 300 W Xe lamp (>420 nm). 0.1 g of the prepared Sn doped ZnO/carbon fibers composites were dispersed in a MB aqueous solution (10 mg L^{-1}, and 50 mL). Then the solution was placed in the dark to reach an adsorption–desorption equilibrium. After visible light irradiation, 1 mL of the solution was taken out from the reaction solution at certain time intervals and centrifuged to get the upper clear solution. The concentration change of MB solution was monitored by a UV–vis absorption spectroscopy (Shimadzu UV 2550).

3. Results and discussion

3.1. The formation process of the Sn doped ZnO microspheres on carbon fibers

The formation process of Sn doped ZnO microspheres on carbon fibers was schematically illustrated in Scheme 1. Firstly, carbon fibers were treated with HNO_3 solution in order to obtain carboxyl on the surface. When HMT was added into the carbon fiber suspension, HMT could be adsorbed on the surface of carbon fibers by the electrostatic attraction between NH_2 group on the HMT and carboxyl group on the surface of carbon fibers. Furthermore, Zn^{2+} and little Sn^{4+} could be fixed on the surface of carbon fibers due to the complexing action between NH_2 and metal ions. Then, Sn doped $Zn_5(CO_3)_2(OH)_6$ microspheres stringed on carbon fibers were obtained by hydrothermal method at 120 °C for 6 h. After that, the above prepared Sn doped $Zn_5(CO_3)_2(OH)_6$ microspheres stringed on carbon fibers were calcinated at 300 °C for 2 h. Thus, Sn doped ZnO nanostructure spheres stringed on carbon fibers composites were successfully prepared in the end.

3.2. Characterization of the products

The XRD patterns of the as-prepared samples and pure carbon fibers were shown in Fig. 1. From Fig. 1a–c, the broad peak centering at around 25.60° was attributed to the (002) plane of the carbon phase in carbon fibers. Compared with the pure carbon fibers, the other diffraction peaks in Fig. 1b are attributed to the $Zn_5(CO_3)_2(OH)_6$ phase (JCPDS No. 72-1100), which is similar to the literature's reports [33]. In Fig. 1c, apart from the peak of carbon fibers, the other diffraction peaks are in good agreement with the ZnO phase (JCPDS No. 80-0075). No peaks corresponding to SnO_2 crystals or other Sn phase were detected in Sn-doped ZnO sample. Moreover, the XRD patterns show narrow and sharp diffraction peaks, indicating the good crystallinity of the as-synthesized samples. The EDS spectrum further confirmed the composition of the product. It was clearly seen that Sn element was observed in the product with the weight ratio of 2.3%, besides Zn and O.

The morphologies of the products were characterized by FESEM, as shown in Fig. 2. Fig. 2a clearly showed that Sn doped $Zn_5(CO_3)_2(OH)_6$ microspheres were stringed on the carbon fibers like a string of sugar-coated haws on a stick. From the magnified image in Fig. 2b and c, it can be seen that each Sn doped $Zn_5(CO_3)_2(OH)_6$ microspheres were composed of crosslinking nanosheets. As shown in Fig. 2c, the thickness of these nanosheets was about 20 nm. The prepared Sn doped $Zn_5(CO_3)_2(OH)_6$/carbon