Materials Science and Engineering B 194 (2015) 9–13

Contents lists available at ScienceDirect

Materials Science and Engineering B

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

Preparation and photocatalytic activity of ZnO/Fe_2O_3 nanotube composites

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ARTICLE INFO

Article history:
Received 5 October 2014
Received in revised form
25 November 2014
Accepted 11 December 2014
Available online 23 December 2014

Keywords:
ZnO/Fe_2O_3
Nanotube
Photocatalytic
Synergistic

ABSTRACT

Fe_2O_3 nanoparticles were grown on ZnO nanorods (NRs) to form ZnO/Fe_2O_3 nanotube (NT) composites via photochemical deposition under ultraviolet light irradiation at a room temperature. Fe^{3+} ions in the solution preferentially adhere to the metastable Zn-rich (0 0 0 1) polar surfaces in ZnO NRs, which leading to the formation of ZnO/Fe_2O_3 NTs. ZnO/Fe_2O_3 NT nanocomposites show a great improvement in photocatalytic characteristics compared with the bare ZnO NRs. It can be inferred that the enhanced photocatalytic performance of ZnO/Fe_2O_3 is benefit from the synergistic effect of ZnO and Fe_2O_3 semiconductors.

1. Introduction

As the population growth and economic development, the environment deteriorates seriously, and people have a growing demand for clean water. However, water pollution is an increasingly serious problem with hazardous heavy ions and organic dyes as common pollutants. The using of green water chemical techniques has become a necessary requirement for the sustainable development. The purification treatment of domestic and industrial sewage can reduce the pollution of the global environment and allow recycling of water resources. Photocatalysis, as a new environmental technique, has been widely used due to its convenience and efficiency [1,2].

In recent years, due to the easy availability, nontoxic nature, biological and chemical stability, nanostructured semiconductor metal oxides have become promising photocatalysts in environmental remediation [3,4]. Thus, numerous semiconductor metal oxide photocatalysts, such as TiO_2, ZnO, SnO_2, and ZrO_2 have been developed for creating a safer environment for society [5,6].

ZnO nanomaterials are natural n-type semiconductors with a wide band gap ($E_g = 3.37$ eV). As a versatile material, ZnO is one of the most important semiconductor photocatalysts and has been widely used in photocatalysis [7–12]. However, it is still a challenge to enhance the photocatalytic efficiency of ZnO nanocatalysts to meet their practical applications, because the rapid recombination of photo-generated electrons and holes reduce quantum yield consumedly. Therefore, if the separation efficiency of photo-generated electron–hole pairs can increase, the photocatalytic activity of ZnO will be enhanced. Nowadays, great efforts have been made to synthesize ZnO-based nanocomposites to increase the photocatalytic ability of ZnO. Many new nanocomposites have been successfully synthesized such as ZnO–CuO, ZnO–Fe_2O_3, ZnO–NiO and so on [13–15]. These efforts could improve the photocatalytic activity by extending the photo response range and increasing the electron–hole pair separation efficiency.

Among these materials, ZnO–Fe_2O_3 nanocomposite is a promising candidate. Fe_2O_3 has a narrow band gap ($E_g = 2.2$ eV), outstanding photoconductivity, field emission, and photovoltaic properties [15–21]. ZnO–Fe_2O_3 nanocomposite may have better photocatalytic efficiency because of its larger specific surface area and higher light absorbing ability. The hetero-nanostructure of these two oxides (ZnO–Fe_2O_3) is also expected to display enhanced abilities, such as a broader light absorption range and high efficiency electron–hole separation [22].

In this paper, the synthesis of ZnO/Fe_2O_3 NT composites using a low-temperature hydrothermal and photochemical deposition process was studied. The photocatalytic characteristics between ZnO/Fe_2O_3 NT composites and bare ZnO NRs were also compared. Under UV radiation, the ZnO/Fe_2O_3 NT composites had a much better photo degradation of methylene blue, which indicates

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http://dx.doi.org/10.1016/j.mseb.2014.12.021
0921-5107/

the potential of ZnO/Fe_2O_3 composites in sewage purification applications. The effects of the structure and interfacial electronic interaction between ZnO and Fe_2O_3 on the photocatalytic activity were also systematically investigated.

2. Materials and methods

ZnO NRs were grown on glass using a simple low-temperature hydrothermal method. Glass flakes (20 mm × 15 mm) were immersed in 0.1 mol/l $ZnCl_2$ (98%, Aldrich) aqueous solution with the right amount of ammonia (25 wt% in water, Aldrich), and then the solution was heated at 95 °C for 3 h. After the ZnO NRs grown up, the ZnO sample sheets were removed from the solution, rinsed with deionized water (DI) and then dried in air at 60 °C for 1 h, which was marked as sample S0.

ZnO/Fe_2O_3 NTs were prepared by photochemical deposition [21]. ZnO NRs-coated substrate was immersed in a 6 mmol/l $FeCl_3 \cdot 6H_2O$ (98%, Aldrich) and $NaNO_3 \cdot 6H_2O$ (98%, Aldrich) aqueous solution, and then irradiated with UV light (365 nm, 300 W) respectively at room temperature for 60 min, 90 min, 120 min and 150 min, and then marked as samples S1, S2, S3 and S4. The sample without UV light at room temperature for 120 min marked as S5. The prepared samples were annealed in ambient air at 400 °C for 2 h.

3. Results and discussion

The scanning electron microscopy (SEM, S4800) was employed to investigate the morphology of ZnO and ZnO/Fe_2O_3 composites. Fig. 1 shows the SEM images of samples S1, S2, S3, S4 and S5. The inset in Fig. 1(a) shows the ZnO prepared by hydrothermal method (S0). The length and diameter of ZnO NRs are about 4 μm and 500 nm, respectively. As shown in Fig. 1, with the UV irradiation time extension, more and more Fe_2O_3 nanoparticles were coated on the surfaces of ZnO NRs, finally the nanocomposites formed tubular structure gradually and clearly. In Fig. 1(c), it can be observed that the sample S3 has the best tubular morphology. In Fig. 1(e) and (f), there is no NT. Ultraviolet irradiation is conducive to the formation of tubular structures.

The energy dispersive X-ray spectroscopy (EDX, EX-250) and X-ray diffraction (XRD, Siemens D5005) patterns were used to reveal the precise material composition and elemental distribution of nanocomposites (Fig. 2). A SEM image of sample S3 is shown in Fig. 2(a), it can be observed that the Fe_2O_3 nanoparticles nucleate and grow on the surface of ZnO. Fig. 2(b) shows EDX elemental mapping of sample S3 which reveals the element distribution of Zn and Fe in ZnO/Fe_2O_3 nanocomposites clearly (green for iron and red for zinc). Fig. 2(c) is the EDX analyses of sample S3, which identify the composition of Fe, Zn and O in the composite. The XRD diffraction peaks in Fig. 2(d) are in good agreement with the standard patterns of hexagonal wurtzite ZnO. There are two diffraction peaks of Fe_2O_3 in Fig. 2(d). The XRD patterns reveal the highly crystalline character of ZnO/Fe_2O_3 composites.

Fig. 3 shows the UV–vis absorption spectra (UV-2401PC spectrometer) of samples (S0, S1, S2, S3 and S4). The bare ZnO NRs shows a strong absorption peak in the ultraviolet region with a spectral wavelength between 300 and 400 nm. However, ZnO/Fe_2O_3 NTs can absorb wavelengths up to 700 nm which is much wider than bare ZnO NRs.

The growth mechanism of ZnO/Fe_2O_3 NT composites is schematically shown in Fig. 4. Under the UV irradiation, the

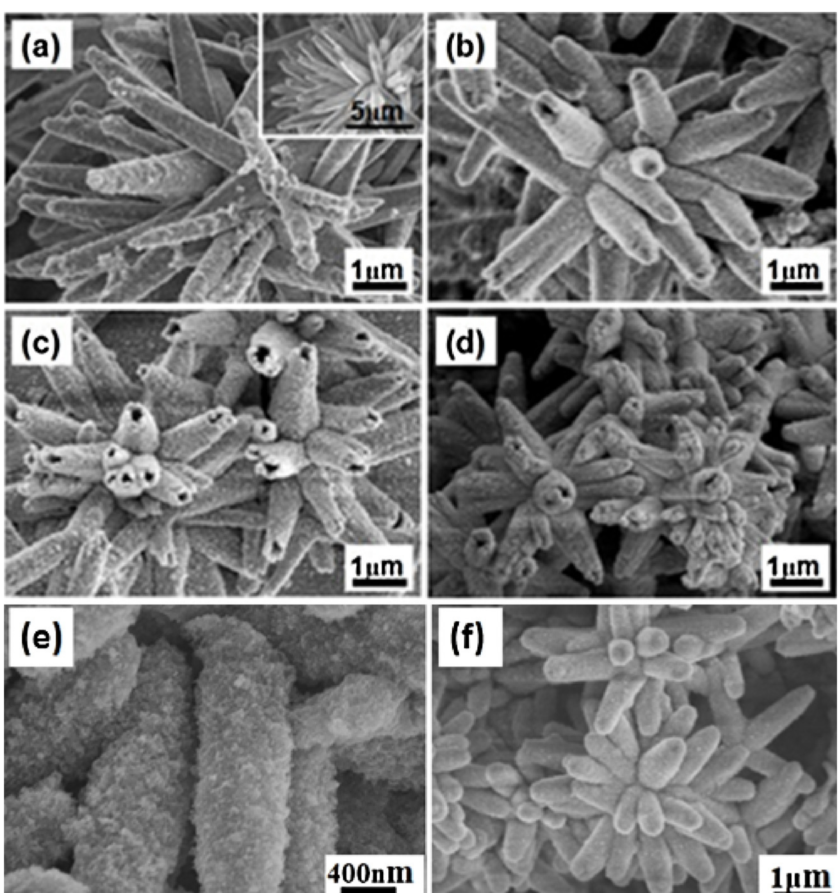

Fig. 1. SEM images of sample (a) S1, (b) S2, (c) S3, (d) S4 and (e, f) S5. The inset in (a) shows the sample S0.