

Synthesis and characterization of bifunctional magnetic-optical Fe₃O₄@Hollow@ZnS core-shell microspheres

Xuegang Yu^{*}, Yan Shan, Kezheng Chen^{**}

Lab of Functional and Biomedical Nanomaterials, College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

HIGHLIGHTS

- Fe₃O₄@Hollow@ZnS microspheres were fabricated with a simple hard-template method.
- Fe₃O₄ cores and ZnS layers endow good magnetic and fluorescent properties.
- The hollow structures contribute to the improvement of photocatalytic efficiency.

ARTICLE INFO

Article history:

Received 9 August 2017

Received in revised form

11 February 2018

Accepted 15 March 2018

Available online 16 March 2018

Keywords:

Core/shell

Magnetic-optical

Photocatalytic properties

ABSTRACT

Bifunctional Fe₃O₄@ZnS microspheres with hollow heterostructures have been successfully fabricated by a simple hard-templating method. XRD, TEM, MPMS, and fluorescence spectrophotometer had been to investigate the as-prepared materials. The results showed that there is controllable hollow structure between Fe₃O₄ cores and ZnS layer. The Ms values of Fe₃O₄ and Fe₃O₄@Hollow@ZnS microspheres are 86.2 emu/g and 53.1 emu/g at 300 K, respectively. When excited by 353 nm low-power UV lamps, the composites have a broad blue light emission band between 440 and 500 nm. As the hard template, the amorphous SiO₂ plays a key role in the forming process of the hollow structure. The presence of the hollow structures blocks the energy transfer between ZnS and Fe₃O₄ particles, which reduces the probability of fluorescence quenching. Furthermore, the hollow cavity size of the microspheres can be easily controlled by adjusting the thickness of SiO₂ layer, which can affect the photocatalytic properties.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

In the past decade, the preparation and characterization of core-shell materials with hollow heterostructures have attracted considerable attention [1–4]. The integrated functionalities and the special hollow interiors endow the composites with a potential application in the fields of catalysis, drug delivery, photonic crystals, and medical sciences [5–8].

Compared with the solid material, hollow structural materials have low density and the more catalytic activity sites, which provide unique catalytic, lithium ion storage, drug delivery, energy conversion and plasmonic nanosensing features [9–13]. Wang et al. used a simple corrosion-aided Ostwald ripening method to synthesize superparamagnetic fluorescent Fe₃O₄/ZnS hollow

nanospheres (HNSs) with diameters of <100 nm [14]. The synthetic procedure is very easy and straightforward. The as-synthesized sample has good drug loading and drug controlled release performance because of the hollow structures. Qi et al. prepared Fe₃O₄/ZnS HNSs by using the same method [15]. The as-prepared material is an effective magnetic heterogeneous catalyst for the synthesis of 5-substituted 1H-tetrazole via nitriles and sodium azide. The authors thought the high catalytic activity may be attributed to the high BET surface area resulted by the hollow structures. Weng et al. prepared gold solid (AuNS) and hollow (AuHS) nanosphere nanoparticles to catalyze Eosin Y (EY) [16]. The corresponding experiment results exhibited that the catalytic ratio of hollow nanospheres was 3 times higher than that of the solid nanospheres. Mahmoud et al. catalyzed the reduction of 4-nitrophenol with sodium borohydride with five different hollow cubic nanoparticles, which reveal the existence of the cavity provide more catalytic active site [17]. Compared with commercial solid TiO₂, the hollow core-shell mesoporous TiO₂ spheres prepared by Yoon et al.

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: yuxuegang@qust.edu.cn (X. Yu), kchen@qust.edu.cn (K. Chen).

exhibited a higher capacity of >200 mAh/g with good cyclability and high rate capability in lithium ion storage field [10]. Dong et al. demonstrated controllable synthesis of several structures of multishelled ZnO hollow microspheres by using carbonaceous microspheres as templates via a simple programmable heating process. The prepared ZnO hollow microspheres with higher surface area exhibited better energy conversion efficiency when used in the dye-sensitized solar cells [18].

The fabrication route of core-shell materials with hollow structure are usually prepared by hard-, soft-, self- and non-templating method [19–21]. Among the above method, hard-templating method has great advantages as follows: (1) simple synthesis procedure, (2) high repeatability, (3) relative lower cost, (4) easier to control hollow cavity size. Chen et al. successfully fabricated $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CdS}@\text{SiO}_2$ core/shell heterostructures through a simple chemical bath deposition method assisted by the bridging of SiO_2 transition layer [22]. The corresponding results show that SiO_2 is a good hard template. Chu et al. successfully used Co acetate as the cobalt source to prepare highly uniform and monodispersed $\text{Co}_2\text{V}_2\text{O}_7$ hollow nanoprisms via a simple hard-templating method [23]. The hollow $\text{Co}_2\text{V}_2\text{O}_7$ particles coated by carbon layer exhibit apparently enhanced lithium-ion-battery performances. Therefore, the hard-templating method is particularly interesting and frequently used to fabricate hollow structural materials with homogeneous and dense layers [24–28].

Compared with other magnetic materials, Fe_3O_4 have great advantage in practical applications due to the controllable magnetic properties and good biocompatibility. Up to date, Fe_3O_4 have been used in many fields including drug delivery, cell separation, stem cell labeling, and magnetic resonance imaging [29–32]. Compared with other II–VI compound semiconductors, ZnS has the largest energy band gap ($E_g \sim 3.6$ eV) and strong fluorescent property, which can be prepared with simple synthesis method. ZnS materials had been commercially used as a phosphor, light-emitting diodes, and also in thin-film electroluminescent devices [33–36]. Furthermore, ZnS is a good photocatalytic material. Under UV light irradiation, the photocatalytic reaction occurs on the surface of ZnS, which can degrade dehalogenation of halogenated benzene derivatives, toxic organic pollutants and photoreduction of CO_2 with strong oxidizing capability [37–40].

In this paper, we designed a facile approach to the synthesis of magnetic-optical $\text{Fe}_3\text{O}_4@\text{Hollow}@\text{ZnS}$ core-shell microspheres by using amorphous silica as a transition layer. The procedure is illustrated in Fig. 1. First, by using a simple hydrothermal method, Fe_3O_4 microspheres were prepared as the cores. Second, by using a modified Stöber method, an amorphous silica layer was coated on the surface of magnetic cores. The silica layer plays the following essential roles: (1) because crystal structures of Fe_3O_4 and ZnS are different, it's difficult for crystalline ZnS to grow directly on the surface of Fe_3O_4 . Therefore, by using silica layer as a bridge, the combination of Fe_3O_4 and ZnS can be achieved successfully. (2) Because of the existence of amorphous silica, zinc sulfide particles can not contact magnetite cores directly, which can reduce the probability of fluorescence quenching by way of preventing energy transfer of the metal ions. (3) The thickness of silica layer can be easily controlled through controlling the amounts of silicon source,

which can easily adjust the surface area of the outer shell. Third, by using a simple chemical deposition method, a uniform ZnS layer was generated on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres. Fourth, bifunctional magnetic-optical $\text{Fe}_3\text{O}_4@\text{Hollow}@\text{ZnS}$ core-shell microspheres had been successfully fabricated after the etching with NaOH aqueous solution. The resulting microspheres with hollow structures have good magnetic, fluorescent and photocatalytic properties, which endow the composites with great potential applications in drug controlled releasing, targeting, bioseparation, diagnostic analysis and photocatalyst.

2. Experimental section

2.1. Materials

All reagents, including Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium acetate (NaAc), ethylene glycol (EG), polyethylene glycol (PEG-2000), ethanol, tetraethylorthosilicate (TEOS), ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$), zinc acetate ($\text{Zn}(\text{Ac})_2$), thioacetamide (TAA), isopropanol (IPA), sodium hydroxide (NaOH) and rhodamine B (RhB), were all purchased from Shanghai Chemical Reagents company and used directly without further purification. High purity water (18.2 M Ω cm) was obtained from a Milli-Q system (Millipore).

2.2. Synthesis of Fe_3O_4 microspheres

Briefly, a typical synthesis process for the preparation of Fe_3O_4 microspheres is as follows [41]: Typically, 8.88 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was first dissolved in 60 mL of EG, then 5.88 mmol of NaAc and 0.05 mmol of PEG-2000 were added into the above solution under constant stirring for 30 min. The resulting solution was transferred into a Teflon-lined stainless-steel autoclave. The autoclave was heated to 200 °C for 8 h, and then cools to room temperature naturally. Finally, the black precipitate was centrifuged and further washed with water and ethanol for several times, and then dried in a vacuum at 60 °C for 12 h.

2.3. Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell microspheres

In a typical experiment, Fe_3O_4 microspheres (1.29 mmol) were subjected to ultrasonic treatment with HCl aqueous solution (0.05 M). After 30 min, the Fe_3O_4 microspheres were washed with water for three times. Then, the treated Fe_3O_4 microspheres were redispersed in 1 mL of ammonia, 20 mL of high purity water and 60 mL of isopropanol solution. The above mixture was then transferred into a three-neck round-bottom reaction flask. Finally, the mixed solution of 0.3 mL TEOS and 20 mL isopropanol was added dropwise. The obtained solution was vigorously stirred for 6 h at the room temperature. The products were collected by magnetic separation and washed with water and ethanol for several times to remove the excess SiO_2 , and then dried in a vacuum at 60 °C for 12 h.

2.4. Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{ZnS}$ core-shell microspheres

0.1 g of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres were dispersed in 30 mL of $\text{Zn}(\text{Ac})_2$ (0.6 mmol) isopropanol solution. After vigorous stirring for 30 min, the above solution was transferred into a three-neck round-bottom reaction flask in a water bath, and then 30 mL of TAA (0.05 g, 0.67 mmol) aqueous solution was added dropwise. The resulting reaction solution was heated to 65 °C and kept for 3 h. The obtained products were magnetically collected and washed with water and ethanol for several times to remove the excess ZnS, and then dried in vacuum at 60 °C for 12 h.

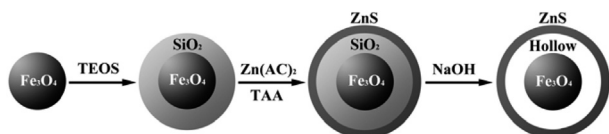


Fig. 1. Schematic illustration of the formation of $\text{Fe}_3\text{O}_4@\text{Hollow}@\text{ZnS}$ microsphere.

Download English Version:

<https://daneshyari.com/en/article/7921682>

Download Persian Version:

<https://daneshyari.com/article/7921682>

[Daneshyari.com](https://daneshyari.com)