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Short communication

Synthesis of hollow Fe_3O_4 at ZnO at anatase TiO_2 core–shell structured spheres

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Abstract

Hollow Fe_3O_4 at ZnO at anatase TiO_2 core–shell structured spheres have been successfully synthesized through a simple two-step sol–gel method and the synthesis process is illustrated as an explicit schematic diagram. Surfactant cetyltrimethylammonium bromide was employed to realize the mesoporous anatase TiO_2 shell on the surface of Fe_3O_4 at ZnO composite spheres. Electron microscopy examinations indicate that the composite core–shell structured hollow spheres have a homogeneous ZnO interlayer and an anatase TiO_2 shell outside the ZnO layer, both of which have a thickness of about 20 nm. The magnetization hysteresis curves of the samples show that the core–shell structured composites have a magnetic saturation value of 41.5 emu/g, suggesting that the obtained product can be separated easily from reaction system and put into recyclable applications.

Keywords: B. Electron microscopy; B. Nanocomposites; Hollow Fe_3O_4 at ZnO at anatase TiO_2 spheres

1. Introduction

Hollow composite spheres (HCS) in nano/micro-scale with well-defined structure are promising materials with a wide range of potential applications owing to their lightweight, high specific surface area and other unique properties [1–7]. As semiconductor materials, ZnO and TiO_2, have been attracting intensive research interests due to their applications in photocatalysis, photoluminescence, gas sensing and the like [8–12].

In recent years, the preparation of ZnO and TiO_2 hollow spheres and the investigation of their photodegradation activity to organic pollutants have been widely conducted because of their lightweight, low cost, excellent chemical stability and the non-toxic feature to environment [8–11,13]. Deng et al. fabricated nano-sized ZnO hollow spheres through a template approach, and the hollow spheres exhibited good photocatalytic activity [8]. Sub-micrometer titania hollow spheres were also synthesized by employing functionalized polystyrene spheres as templates, and the obtained hollow spheres had very high efficient photodegradation ability [9]. Agrawal et al. also prepared the hollow ZnO/TiO_2 composite spheres and the composite hollow spheres could decompose the organic dyes much faster than both pure ZnO and TiO_2 hollow spheres due to the synergetic effect of ZnO/TiO_2 composite structures [14].

The above researches provide efficient routes to the degradation of organic pollutants, but the separation and recycling of the photocatalysts are still a serious problem. Fortunately, magnetic separation offers a convenient way to remove and recycle the magnetic composite materials by applying an external magnetic field. Previous studies have indicated that the combination of a magnetic core with a photocatalyst shell can facilitate the separation of the nano-sized photocatalyst particles from the liquid-phase system [15]. Xuan et al. synthesized hollow Fe_3O_4/TiO_2 magnetic spheres, and they found that the recyclable photocatalysts have better decomposition activity to the dyes than the commercially available P25 as well as solid TiO_2 spheres [16]. In addition, Ye at al. reported the synthesis of Fe_3O_4 core/SiO_2–TiO_2 double-shell composites spheres, in which SiO_2 interlayer played a key role in protecting the Fe_3O_4 core and enhancing the photocatalytic performance of TiO_2 shell, and the composite spheres

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can be easily separated and reused [13]. Herein, we propose a simple route to the synthesis of hollow Fe_3O_4 at ZnO at anatase TiO_2 core–shell composite spheres, in which a uniform coating of ZnO interlayer was firstly formed on the hollow magnetite spheres, and then a porous shell of titania grew on the hollow Fe_3O_4 at ZnO composite spheres with the assistance of surfactant cetyltrimethylammonium bromide (CTAB). In literatures, CTAB have been used to fabricate the Fe_3O_4 at SiO_2 at $mSiO_2$ spheres with mesopore diameter of 3 nm on the outer silica shell [17,18]. In the composite materials, ZnO interlayer plays double roles of protecting the hollow Fe_3O_4 spheres and improving the photocatalytic activity of the outer anatase TiO_2 shell as reported previously [14]. To the best of our knowledge, there has no report on the fabrication of such magnetically separable photocatalysts with hierarchical shells. It is believed that the hollow Fe_3O_4 at ZnO at anatase TiO_2 core–shell composite spheres would exhibit enhanced photo-degradation performance to organic pollutants due to their lightweight and synergetic effect of ZnO/anatase TiO_2 composite structures, and facilitated the separation and recycling of the photocatalysts [19].

2. Experimental

The synthesis of hollow magnetite spheres was conducted according to the approach reported by us previously [20]. The hollow Fe_3O_4 at ZnO composite spheres were synthesized by a facile sol–gel method. Typically, 0.2 g magnetite hollow spheres were placed in a three-neck round bottom flask followed by the addition of 100 ml ethanol solution containing 1 g Zinc Acetate. The mixture was exposed to ultrasonic treatment for 10min, and then 25 ml 0.25 M NaOH ethanol solution was dropped into the mixed solution under mechanical stirring. The reaction was maintained at 333 K for 4 h. The black precipitate was collected, and then dried at 323 K for 12 h. In the following step, 0.1 g Fe_3O_4 at ZnO particles and 0.05 g CTAB were dispersed in 250 ml ethanol in a three neck round-bottom flask, and then the suspension was stirred for 30 min. 1.5 ml TBOT was dropped into the suspension under stirring for 24 h at ambient temperature. After the coating process, the product was re-dispersed in acetone for refluxing at 353 K to remove the absorbed CTAB. The obtained sample was dried in a vacuum oven at 323 K for 6 h. In order to obtain the hollow Fe_3O_4 at ZnO at anatase TiO_2 core–shell spheres, the prepared Fe_3O_4 at ZnO at $Ti(OH)_4$ particles were heated at 723 K for 3 h under the protection of argon atmosphere. The microstructures of product were examined by a SU-70 field emission scanning electron microscope (FE-SEM) and a Hitachi H-800 transmission electron microscope (TEM). The magnetization hysteresis curves of the samples were recorded by a vibration sample magnetometer (Tamakawa, TM-VSM2014-MHR-Type).

3. Results and discussion

The synthesis process of the hollow Fe_3O_4 at ZnO at anatase TiO_2 core–shell composite spheres is illustrated in Fig. 1. Firstly, hollow magnetite spheres with the diameter of ca. 525 nm were fabricated [20]. A layer of ZnO with the thickness of about 20 nm was formed on the magnetite spheres through a sol–gel route. Following the formation of hollow Fe_3O_4 at ZnO composite spheres, CTAB was employed to functionalize Fe_3O_4 at ZnO spheres. The rod-shaped CTAB assembling in a orderly fashion onto the surface of Fe_3O_4 at ZnO spheres can be a structure-directing agent for the growth of $Ti(OH)_4$ film in the interspace among CTAB rods due to the Coulomb force between the CTAB template and the newly formed $Ti(OH)_4$ particles [17]. After the extraction of CTAB template, the hollow Fe_3O_4 at ZnO at $Ti(OH)_4$ spheres were obtained. Finally, the sample was annealed to produce the hollow Fe_3O_4 at ZnO at anatase TiO_2 composites. The purity, composition and successful synthesis of the product were conformed by X-ray powder diffraction (XRD) and Energy dispersion spectrum (EDS) (See Fig. S1 in Supplementary material).

Fig. 2 shows the FE-SEM and TEM images of products obtained in the synthesis process. The SEM and TEM images demonstrate that the hollow Fe_3O_4 spheres with the diameter of around 500 nm and empty interior of 200 nm have rough surface (Fig. 2(a) and (b)). After the coating of ZnO layer, the surface of the spheres became rather smooth and the diameter of the spheres increased by around 40 nm (Fig. 2(c)). In the TEM image of Fe_3O_4 at ZnO spheres, it is clear that a gray ZnO shell coated the Fe_3O_4 spheres judging from the apparent color contrast between the edge and the core. In comparison of Fe_3O_4 hollow spheres, the black core of Fe_3O_4 at ZnO spheres without a pale center suggested that the electron beam cannot penetrate through the spheres, also confirming the coating of ZnO shell (Fig. 2(b) and (d)). From the SEM and TEM images of Fe_3O_4 at ZnO at $Ti(OH)_4$ spheres we can see that the diameter of spheres increased by around

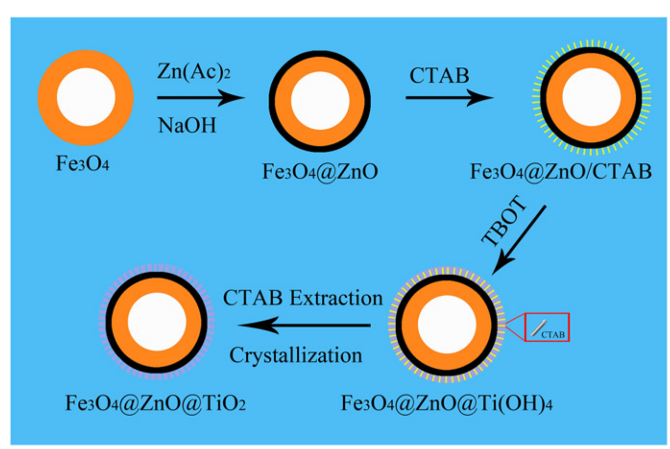

Fig. 1. The schematic diagram for the formation of hollow Fe_3O_4 at ZnO at anatase TiO_2 core–shell spheres.

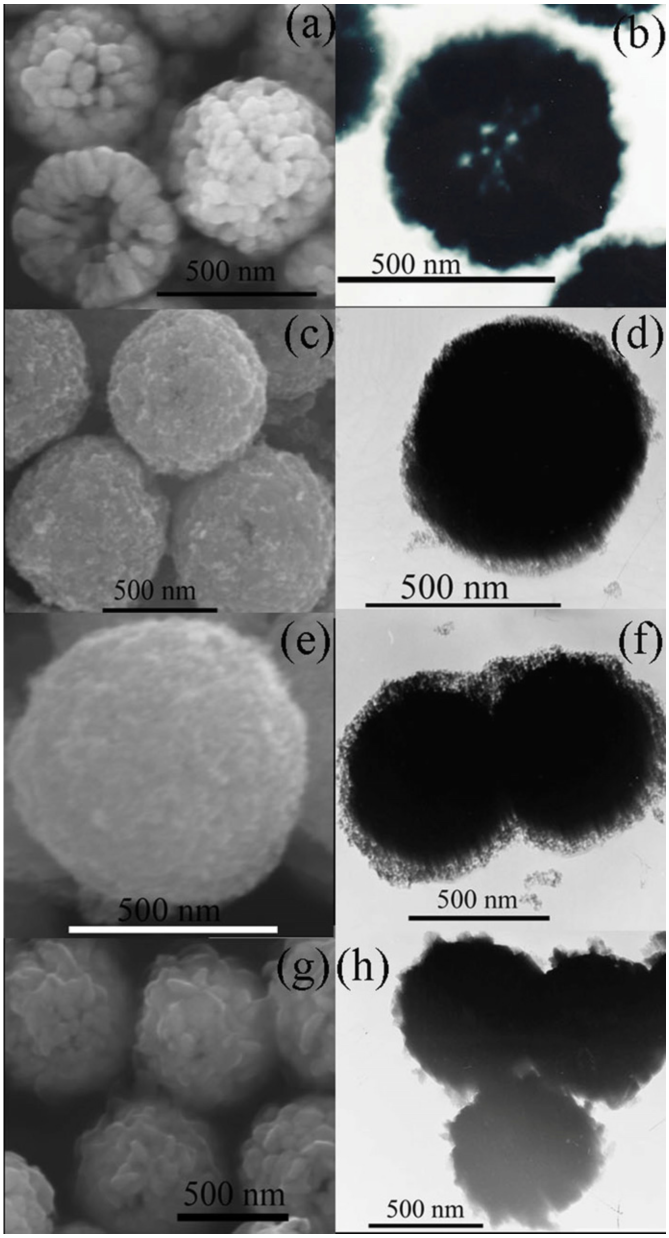

Fig. 2. SEM, TEM images of Fe_3O_4 spheres (a) and (b), Fe_3O_4 at ZnO spheres (c) and (d) Fe_3O_4 at ZnO at $Ti(OH)_4$ spheres (e) and (f) and Fe_3O_4 at ZnO at anatase TiO_2 spheres (g) and (h).

40 nm indicating the successful formation of the $Ti(OH)_4$ shell (Fig. 2(e) and (f)). It is noteworthy, from the TEM image, that $Ti(OH)_4$ formed a outer shell with nanoporous characteristic after the removal of CTAB. After the annealing process, it can be seen clearly from the SEM image that the surface of the spheres become rougher, and some flakes appear on the surface of the spheres (Fig. 2(g)), which have good agreement with the needles on the surface observed from the TEM picture (Fig. 2(h)).

Fig. 3 shows the typical magnetization hysteresis curves of the products measured at room temperature. The measured M_s values of the Fe_3O_4 spheres, Fe_3O_4 at ZnO spheres and Fe_3O_4 at ZnO at anatase TiO_2 spheres are

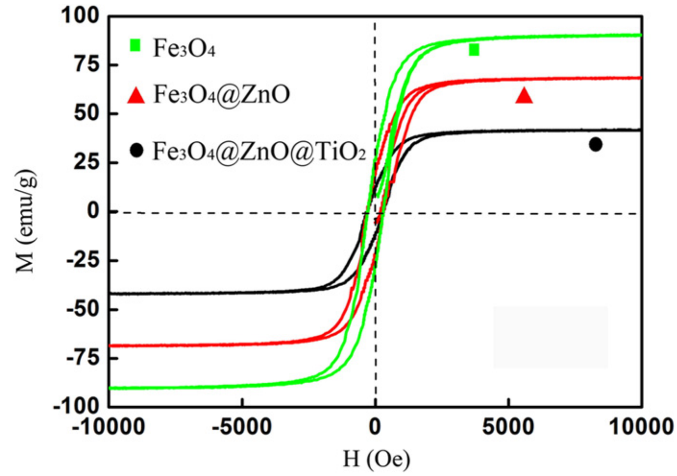

Fig. 3. Hysteresis loops of Fe_3O_4 spheres, Fe_3O_4 at ZnO spheres and Fe_3O_4 at ZnO at anatase TiO_2 spheres measured at room temperature.

90.6 emu/g, 68 emu/g and 41.5 emu/g, respectively. The M_s value of the composite spheres decreased because of the addition of non-magnetic components. The relatively high M_s value of the composites indicates that the Fe_3O_4 at ZnO at anatase TiO_2 spheres can be efficiently removed and recycled from the liquid reaction system, suggesting their promising applications as renewable photocatalyst.

4. Conclusions

In this study, hollow Fe_3O_4 at ZnO at anatase TiO_2 composite spheres were synthesized. The SEM and TEM images demonstrated that the uniform magnetic composite spheres with a 20 nm ZnO interlayer and a 20 nm anatase TiO_2 outer shell were obtained by a simple two-step sol–gel process. The relatively high M_s value of the composites indicates that the product would have potential applications as recyclable photocatalyst.

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Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ceramint.2012.04.080

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