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One-pot Synthesis of Novel Energy Materials: Sub-micron Fe₂O₃ Encapsulated Carbon Spheres Core-shell Composite

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Abstract

Sub-micron Fe₂O₃ encapsulated carbon spheres core-shell composite (Fe₂O₃/C) has been successfully prepared through one-pot solvothermal reaction of acetylacetone and FeCl₃ at 500 °C. The phase and morphology of the sample were examined by XRD, TEM, SEM, HRTEM, XPS and TGA. Meanwhile, magnetic property of the sample was measured. Experimental results showed that the as-obtained Fe₂O₃/C composite with ferromagnetic property possesses excellent corrosion resistance against acid and alkali as well as high tolerable temperature (≤400 °C). Potential applications are envisioned in many fields such as biotechnology, sensors, catalysis and especially, electrode materials for Fe-air battery, proton exchange membrane fuel cells (PEMFC), supercapacitor or Li-ion battery.

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Keywords: Fe₂O₃ encapsulated carbon spheres; core-shell composite; corrosion resistance against acid and alkali; magnetic properties; energy materials.

1. Introduction

Nanoscale iron oxide is an important magnetic material which can be used in biotechnology, sensors, catalysis, etc. Owing to its easy deactivation, a supporting matrix is needed for protection. Carbon materials possessing excellent stability and large specific surface area are suitable candidate and a series of iron oxide/carbon composites have been successfully fabricated for diverse applications [1]. For example, iron oxide/carbon composites have been utilized for degradation of phenol [2], adsorption of dyes [3], treatment of textile wastewater [4], removal of atrazine from aqueous medium [5], removal of heavy metal ions and radionuclides (Ni and Sr) from waste solutions [6], catalytic dehydrogenation of ethylbenzene [7], sensors for electrochemical detection of H₂O₂ [8], and so forth.

More interesting and significant is that iron oxide/carbon composites can be excellent energy materials for Fe-air battery, proton exchange membrane fuel cells (PEMFC), supercapacitor or Li-ion battery. With energy crisis being more and more urgent, the hunting for novel energy materials has aroused unprecedented attentions. Therefore, iron oxide loaded carbon composites have been examined and evaluated for energy applications. Hang BT et al. studied systematically the electrochemical properties of Fe₂O₃-loaded carbon electrodes for iron-air battery anodes which showed small redox current but large capacity due to the highly uniform distribution of iron oxide on the carbon surface [9, 10]. Recently, a carbon-supported iron oxide nanoparticle catalyst for PEMFC was fabricated with a larger normalized

current density and normalized power density than commercial Pt/C catalysts [11]. Iron oxide/carbon nanotube composite can also be anode material for novel hybrid supercapacitor with improved high specific energy density of 50 Wh kg^{-1} thanks to the incorporation of carbon nanotubes into the iron oxide anodes [12]. More recently, iron oxide nanorods on carbon nanofiber scaffolds and high-surface-area $\alpha\text{-Fe}_2\text{O}_3$ /carbon nanocomposite were developed for novel anode material for Li-ion battery which exhibited high capacity, enhanced rate capability and excellent cycle stability due to the extensive contact between active materials and the electrolyte, enhancement of lithium and electron transport, and accommodation of the volume change [13, 14]. All above-mentioned stirring explorations have attracted more interests and stimulate further research involving both preparation and performance.

For the realization of above-mentioned conceits, the first thing to solve is to develop a facile and efficient route to prepare iron oxide/carbon composite with good dispersion. Previously the general procedure adopted a two-step method: firstly synthesize iron oxide nanoparticles or carbon supports and subsequently form carbon-coated iron oxide composite materials using various methods. In this report, a convenient one-pot route is developed to prepare sub-micron Fe_2O_3 encapsulated carbon spheres core-shell composite. The experiment results showed that Fe_2O_3 nanoparticles were protected by carbon layers which can supply an active space and facilitate the reactions of active Fe_2O_3 nanoparticles.

2. Experimental

2.1 Materials

FeCl_3 , acetylacetone, hydrochloric acid and anhydrous alcohol were of analytical-grade purity (Shanghai Chem. Co.) and used without further purification.

2.2 Preparation of sub-micron Fe_2O_3 encapsulated carbon spheres core-shell composite

In a typical experimental procedure, FeCl_3 (1.6 g) and acetylacetone (30 ml) were mixed into a 60 ml stainless steel autoclave. The autoclave was then sealed and put into an electric furnace. The temperature of the furnace was increased from room temperature to 500°C and maintained at 500°C for 10 h. After the autoclave was cooled to room temperature naturally, the crude products were collected and agitated in concentric hydrochloric acid for 10 h and then washed with ethanol and distilled water several times to eliminate the byproducts. Finally, the product was filtered and dried in a vacuum at 60°C for 6 h. A black powder sample was obtained.

2.3 Characterization

X-ray powder diffraction (XRD) measurement was carried out using a Bruker D8 Advanced X-ray diffractometer equipped with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Transmission electron microscopy (TEM) images were obtained with a Hitachi H-600 (accelerating voltage of 100 KV). Scanning electron microscope (SEM) images were taken with a JEOL JSM-6300F field emission electron microscope. Microstructure analysis was performed by high resolution TEM (HRTEM) (accelerating voltage of 200 KV). Thermal gravimetric analysis (TGA) was taken on a EXSTAR 6000 thermal analyzer apparatus (Seiko Instruments Inc.) in following air with an increasing rate of $10^\circ\text{C}/\text{min}$. X-ray photoelectron spectroscopy (XPS) was measured with ESCALAB 250 XPS apparatus (ThermoFisher SCIENTIFIC). Magnetic properties were evaluated with VSM-7300 vibrating sample magnetometer (Lake Shore Cryotronics Inc.).

3. Results and Discussion

3.1 XRD analysis

The XRD pattern of as-obtained product was shown in Fig. 1. It can be observed that the product was composed of two phases: graphite and Fe_2O_3 . The wide diffraction peak with low intensity at 2θ values of 26.2° can be attributed to the diffraction of (002) crystallographic plane of graphite which implicated low crystallinity. All other relatively sharp diffraction peaks can be indexed as $\gamma\text{-Fe}_2\text{O}_3$. The peaks located at

18.32°, 30.22°, 35.51°, 43.27°, 53.72°, 57.04°, and 62.72° correspond to (111), (220), (311), (400), (422), (511) and (440) crystallographic planes of γ -Fe₂O₃ (JCPDS card no. 39-1346), respectively. No other discernable peaks from impurities were detected which implicated high purity.

3.2 XPS characterization

The magnetic phase in the composite was further confirmed by XPS (Fig. 2). The positions of the Fe (2p_{3/2}) and Fe (2p_{1/2}) peaks are marked at 710.74 and 723.40 eV, respectively, which are in good agreement with the values reported for γ -Fe₂O₃ in the literature [15]. This strongly suggests the formation of γ -Fe₂O₃ in the composites.

3.3 Morphology observations

It can be found from the SEM images (Fig. 3a) that the product is constituted by large amount of carbon spheres and a few irregular graphite platelets. The diameters of carbon spheres range from 7 to 15 μ m. Based on the distinct TEM image backing contrast in Fig. 3b, it is obvious that Fe₂O₃ nanoparticles are encapsulated in carbon spheres. HRTEM images of nuclear particles in Fig. 3c showed its crystal lattice distance is 0.293 nm, which accords with (220) crystallographic plane of γ -Fe₂O₃ and further confirms the presence of γ -Fe₂O₃ nanoparticles in carbon spheres. Moreover, the reservation of magnetic nanoparticles after treatment in concentrated hydrochloric acid showed that the inner magnetic nanoparticles received extra protection by carbon coating and can withstand the corrosion of concentrated acid and alkali. From high resolution SEM image of a single carbon sphere it can also be found that the carbon spheres possessed nearly perfect spherical morphology with no evident defects and thereby encapsulated tightly the magnetic nanoparticles. This feature facilitated the utilization of as-obtained composite in complicated and rigorous environment.

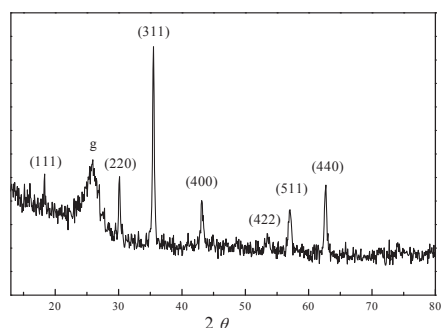


Fig. 1 XRD patterns of the sample.

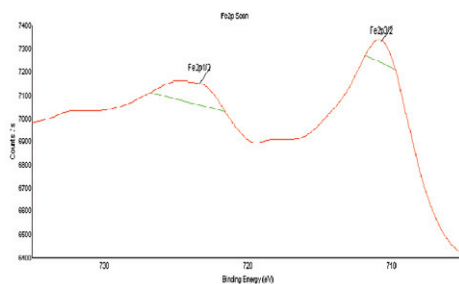


Fig. 2 XPS patterns of the sample.

3.4 TGA results

TG analysis was carried out to evaluate the thermal stability of the composite (Fig. 4). The initial weight loss of the sample from 420 °C to 710 °C reached 96% which can be attributed mainly to the evaporation and subsequent decomposition of the amorphous carbon coating or irregular graphite platelets. As we know, the Fe_3O_4 will transfer into Fe_2O_3 with a weight increase when the temperature is higher than 500 °C [16]. However, there was no obvious inflexion point in the interval of our TG curves, which confirmed the absence of Fe_3O_4 in the as-obtained product. Above 710 °C the residue weight became constant which showed that the final residue was stable Fe_2O_3 . From the TG analysis, the mass ratio of the Fe_2O_3 in the magnetic composite is about 4%. Overall, the as-obtained composite can be used above 400 °C.

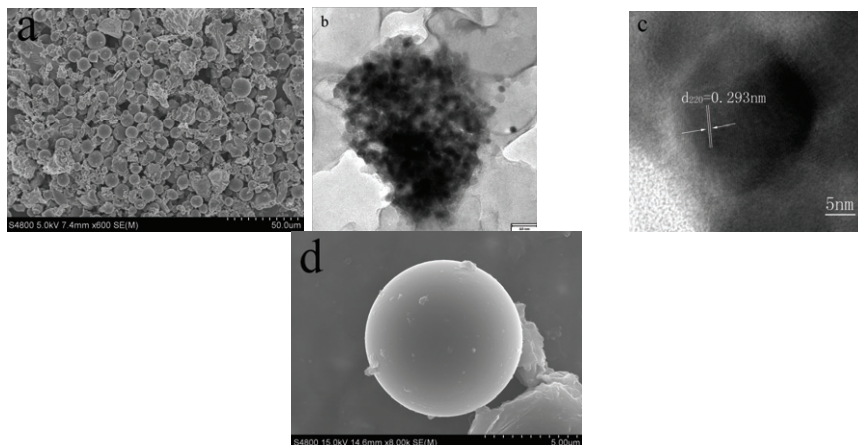


Fig. 3 SEM (a) and TEM (b) images of the sample; c: HRTEM image of the encapsulated particle; d: high resolution SEM image of a single carbon sphere.

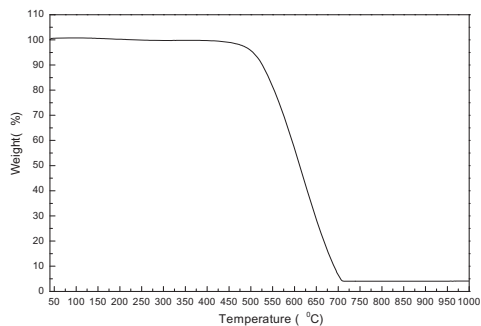


Fig. 4 TG curves of the sample.

3.5 Magnetic properties

For nanoparticles, the particle size, structure, morphology and the bonding state with other magnetic or non-magnetic materials are key factors affecting the magnetism of nanoparticles. Therefore, in order to further study the magnetic properties of combination of Fe_2O_3 nanoparticles and carbon shell, magnetic test for such composite was performed under ambient conditions. The magnetization curve (Fig. 5) suggested the ferromagnetic feature of the product. The saturation magnetization (M_s), remanent magnetization (M_r)

and coercivity (H_c) was 0.873 emu/g, 0.095 emu/g and 129.50 Oe, respectively. The saturation magnetization was much lower than that of bulk Fe_2O_3 , which may be caused by carbon coating at the surface of Fe_2O_3 , the nanoscale size and low content of Fe_2O_3 particles [17]. The product exhibited relatively high coercivity maybe attributed to high anisotropy feature of the composite structure [18]. Owing to that high coercivity is prerequisite to applications of ferromagnetic materials in high-density optoelectronic storage, the novel composite structure suggested promising applications in high-performance magnetic recording device.

4. Conclusions

Core-shell Fe_2O_3/C composite materials were successfully prepared through a facile one-pot route. The as-obtained composite exhibits extra stability even in concentrated acid and alkali plus high oxidation resistance below 400 °C, which implicates potential applications under rigorous conditions. Meanwhile, Fe_2O_3 nanoparticles encapsulated in carbon spheres still retain good magnetic performance and high coercivity suggesting promising materials for high-performance magnetic recording device. Moreover, the as-prepared Fe_2O_3/C composite may act as useful materials for energy storage system such as Fe-air battery, proton exchange membrane fuel cells (PEMFC), supercapacitor or Li-ion battery. The exploration of such Fe_2O_3/C composite for energy applications is under way.

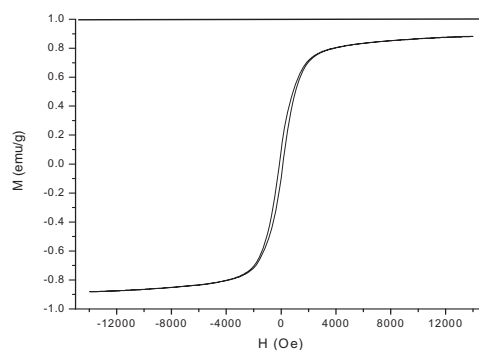


Fig. 5 Magnetization curve of the product.

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