General Synthesis of Homogeneous Hollow Core−Shell Ferrite Microspheres

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A general method has been developed for the synthesis of homogeneous hollow core−shell microspheres of spinel ferrites (MFe_2O_4, M = Zn, Co, Ni, Cd) by using carbonaceous saccharide microspheres as template. The products were characterized by X-ray powder diffraction, inductively coupled plasma-atomic emission spectroscopy, scanning electronic microscopy, transmission electron microscopy, and nitrogen sorption measurement. The effects of the concentration of metal salts have been studied using $ZnFe_2O_4$ as an example. Increasing the concentration of metal salts could avoid the generation of impurity phase. The core size and shell thickness of hollow spheres obtained can be manipulated by changing the concentration of metal salts. Gas-sensor investigations revealed the $ZnFe_2O_4$ hollow spheres used as gas-sensor materials possess high sensitivity and quick responses to organic gases such as ethanol.

1. Introduction

Spinel ferrites (MFe_2O_4, M = Zn, Co, Ni, Cd, etc) are among the most important magnetic materials and have been widely used in electronic devices, information storage, magnetic resonance imaging (MRI), and drug-delivery technology.[1−4] In addition to the magnetic-related applications, transition-metal ferrites can also be used as catalysts in several processes,[5−8] as adsorbents for the removal of toxic gases,[9,10]or as sensor materials in gas-sensing systems.[11−16] Hollow spheres with nanometer or micrometer size often exhibit special physical and chemical properties different from solid particles, owing to their low density, larger specific surface area, hollow structure, and nanostructured wall. According to these properties, ferrite spheres with hollow structure are expected to have advantages over their solid counterparts in some areas, including catalysis, adsorbents, and gas sensors, and attract much attention from researchers. $CoFe_2O_4$ hollow spheres have been prepared through hydrothermal treatment of an aqueous solution containing glucose, ammonium iron(II) sulfate hexahydrate [$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$], and cobalt(II) sulfate heptahydrate [$CoSO_4 \cdot 7H_2O$], followed by calcination.[17] However, this method could hardly be extended to synthesize hollow spheres of other ferrites, due to the chemical reactivity difference among different metal ions. Finding general methods that are simple, direct, controllable, low-cost, and suitable for large-scale production remains a challenge for the synthesis of ferrite hollow nanostructures.

Template-assisted synthesis is one of the most facile and most applied methods for the synthesis of hollow micro- or nanospheres. The templates can be of different compositions, normally silica spherical particles[18−22] or polystyrene (PS) spherical particles.[23−27] Very recently, an interesting sacrificial core of monodisperse carbonaceous saccharide microspheres, which are generated by the hydrothermal treatment of aqueous solutions of glucose and sugar, was presented.[28,29]These sacrificial cores inherit functional groups and have reactive surfaces, which facilitate the absorption of cationic metal ions and the precipitation of metal precursors.[29−31] Hollow spheres of various single-metal oxides, including Ga_2O_3,[30] Co_3O_4,[31] TiO_2,[32] and WO_3[33] have been synthesized by using carbonaceous saccharide spheres as templates. Eu^{3+}-doped Y_2O_3, YOF, La_2O_3, and LaOF hollow spheres also have been synthesized by using this template.[34] However, this method could not be extended from single-metal oxides to binary-metal oxides, for example ferrites, by rote, since the difference of adsorption ability of functional groups to different metal ions makes it difficult to precisely control the molar ratio of both metal elements in the resultant product and often result in an impurity phase besides the desired binary-metal oxides.

Herein, we report a general method applicable to synthesizing hollow spheres of spinel ferrites (MFe_2O_4, M = Zn, Co, Ni, Cd), by using carbonaceous saccharide microspheres as template. We found that increasing the concentration of metal salts could avoid the generation of impurity phases. More interestingly, homogeneous hollow core−shell microspheres of pure ferrites could be obtained under higher concentration of metal salt, and the core size and shell thickness increase with increasing concentration of metal salt. This homogeneous hollow core−shell structure possesses a total surface area including both core and inner shell surface, which is more than that of the common hollow structure. Furthermore, the core is removable if it is entirely detached from the shell. Such materials have advantages as catalysts owing to their higher reaction activities.[35]

2. Experimental Section

2.1. Synthesis. All reagents (purchase from Beijing Chemical Co., Ltd.) were analytical grade and were used as raw materials without further purification. Metal nitrates were used as metal precursors. Taking $ZnFe_2O_4$ hollow spheres as an example, the typical synthesis process was as follows. Carbonaceous saccharide microspheres were synthesized through the emulsion polymerization reaction of sugar under hydrothermal conditions as described elsewhere.[28] The obtained microspheres (about 0.4 g) were then dispersed in 10 mL of water by ultrasound to form uniform template suspension. Zinc and iron nitrates with

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