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Flowerlike iron oxide nanostructures and their application in microwave absorption

Chenyang Guo, Fangyuan Xia *, Zhen Wang, Li Zhang, Li Xi, Yalu Zuo *

Key Laboratory for Magnetism and Magnetic Materials of Ministry of Education, Lanzhou University, Lanzhou 730000, PR China

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ABSTRACT

Self-assembled flowerlike α-Fe_2O_3, Fe_3O_4 and γ-Fe_2O_3 were fabricated by a simple calcination procedure. The structure characterization shows that the flowerlike morphology and the size of the nanostructures are perfectly maintained in the conversion of precursor to α-Fe_2O_3, Fe_3O_4, and γ-Fe_2O_3. The complex permittivity and permeability results indicate that the dielectric and magnetic loss of Fe_3O_4 flower are both higher than those of γ-Fe_2O_3 flower. In addition, Fe_3O_4 flower shows a good electromagnetic impedance match and its microwave absorption mainly originates from magnetic loss rather than dielectric loss. An optimal reflection loss of −46.0 dB is found at 3.4 GHz for flowerlike Fe_3O_4, which indicates that the sample can be used as a highly efficient microwave absorber.

1. Introduction

Microwave absorbing materials based on the magnetic materials with low reflection and high absorption properties are receiving extensive attention because of their promising application in electronic devices used in commerce, industry, and military affairs [1]. In recent years, carbonyl irons were widely investigated as one of typical magnetic microwave absorbing materials [2–4]. However, the low density and absorption properties of the commercial carbonyl iron restrict its use in the applications. Hollow iron particle with low density is also a new material to improve the microwave absorption properties [5,6]. Besides, iron-based materials such as γ-Fe_2O_3, and Fe_3O_4 are recognized as promising materials for microwave applications because of their relative high magnetization and antioxidation properties in air. Various iron oxides or iron composites with different morphologies such as rods, wires, tubes, flakes, urchins and dendrites have been successfully reported with their application as electromagnetic wave absorber [7–12].

However, the relationship among the structure, morphology and magnetic properties of iron-based nanomaterials has not been fully understood. As we known, large surface areas and high magnetization will improve the microwave absorption properties. Herein, we report the synthesis of novel three-dimensional (3D) flowerlike iron oxide nanostructures with large surface areas by an ethylene glycol (EG)-mediated self-assembly process. The as-synthesized iron oxide precursor was transformed into iron oxide. Moreover, the phase of the final product can be easily controlled to be α-Fe_2O_3, γ-Fe_2O_3, or Fe_3O_4, three of the most common iron oxides, by altering the calcination conditions. The microwave absorption properties of α-Fe_2O_3, γ-Fe_2O_3, and Fe_3O_4 flowerlike nanostructures with almost the same large surface areas are presented in this study.

2. Experimental

The thermal decomposition of metal alkoxide is a simple route to achieving a tailored metal oxide. In a typical procedure, 2.4 g of ferric chloride ($FeCl_3{\cdot}6H_2O$), 5.4 g of urea, and 14.4 g of tetrabutylammonium bromide were dissolved in 360 mL of ethylene glycol. The red solution was refluxed at 195 °C for 30 min. After cooling, the as-synthesized iron oxide precursor was collected as a green precipitate after centrifugation and ethanol-washing cycles. The morphology of the precursor was studied by scanning electron microscopy (SEM, Hitachi S-4800). Fig. 1a shows the SEM image of a typical sample composed of many uniform, flowerlike nanostructures approximately 3 μm in diameter. The detailed morphology of the flowerlike nanostructures is shown in Fig. 1b. The entire structure was found to be built from several dozen nanopetals with smooth surfaces. These nanopetals were 1.5 μm wide and connected to each other through the center to form 3D flowerlike structures. A series of other measurements was also performed to investigate the as-obtained iron oxide precursor. The X-ray diffraction (XRD, Philips X'Pert, with Cu Kα radiation) pattern (Fig. 1c) shows the emergence of diffraction peaks similar to those of other metal oxide precursors reported in the literature [13], especially the strong peak located in the low-angle region ($2\theta = 11°$), although the exact crystal structure of the iron oxide precursor is not yet to be determined.

The effect of calcinations on the crystallization and morphology of the iron oxide precursor was investigated by thermogravimetric analysis–differential thermal analysis (TG–DTA, Perkin Elmer SII) with Ar protection. Fig. 1d shows the TG–DTA curves of the as-synthesized iron oxide precursor. A weight loss was observed at about 250–400 °C in the TG curve. The weight loss can be attributed to the combustion of the resultant organics. One sharp exothermic peak was found at 320 °C, which was accompanied by the aforementioned weight loss. No any other

* Corresponding author. Tel.: +86 0931 8914036; fax: +86 0931 8914160.
E-mail address: zuoyl@lzu.edu.cn (Y. Zuo).

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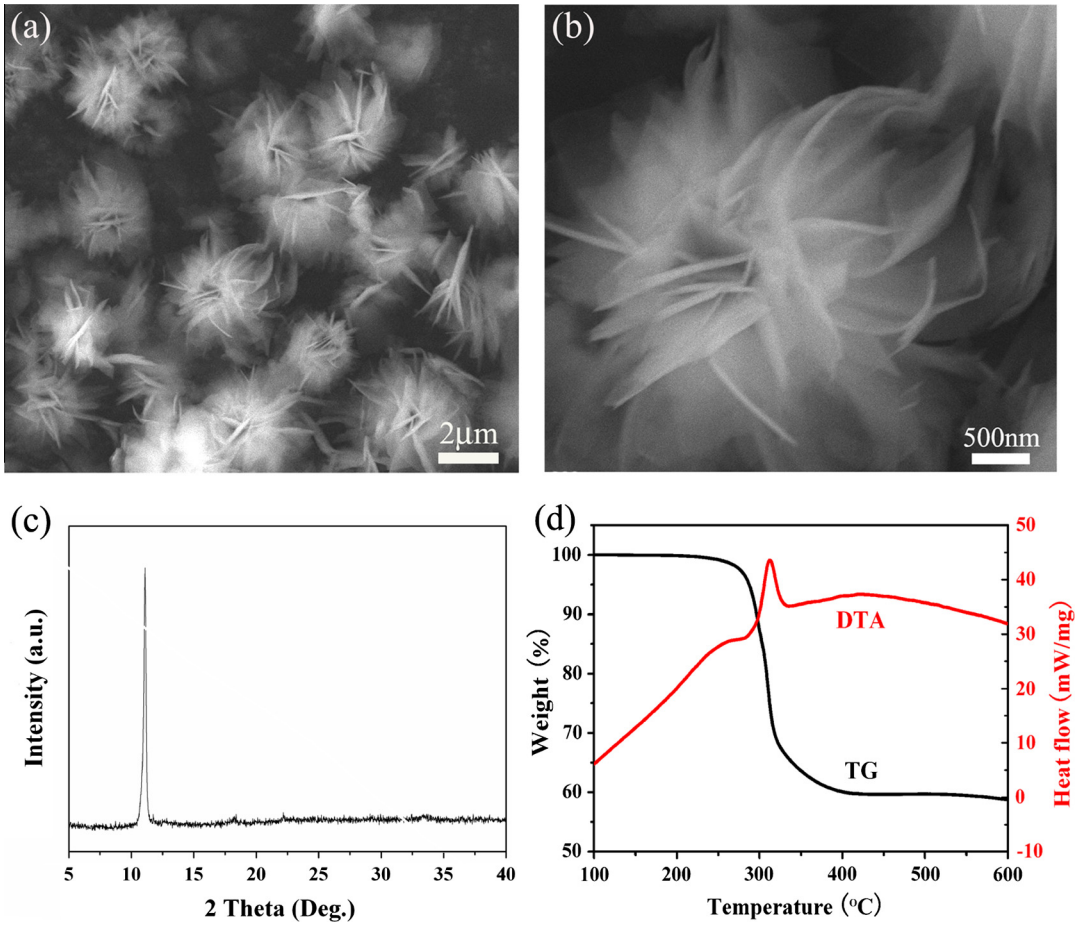

Fig. 1. (a) SEM image of the as-synthesized iron oxide precursor. (b) SEM image of a single flowerlike iron oxide precursor. (c) XRD and (d) TG–DTA curves of the as-synthesized iron oxide precursor.

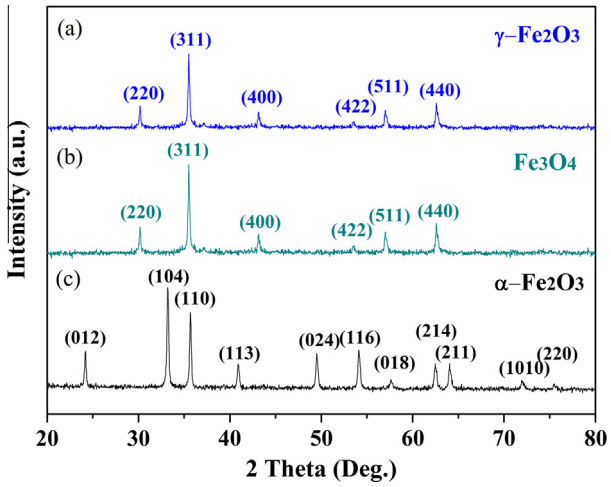

Fig. 2. XRD patterns of the samples: (a) γ-Fe_2O_3, (b) Fe_3O_4, and (c) α-Fe_2O_3 flowers.

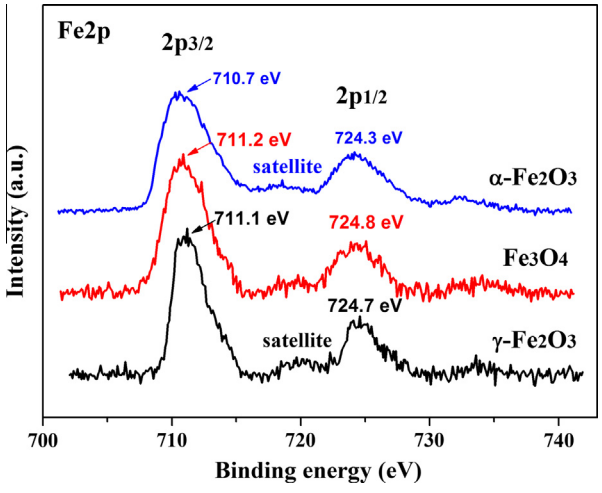

Fig. 3. Fe 2p core-level XPS spectra of α-Fe_2O_3, Fe_3O_4, and γ-Fe_2O_3 flowers.

weight loss in TG or any peak in DTA was observed over 450 °C, confirming that all organic components were burned out at 450 °C. Hence, the as-synthesized iron oxide precursor was transformed into α-Fe_2O_3 (or Fe_3O_4) at 450 °C in air (or under N_2 protection) for 3 h. Then, phase transformation was achieved from Fe_3O_4 to γ-Fe_2O_3 by an oxidation process.

The microstructure of the sample was characterized by high-resolution transmission electron microscopy (HRTEM; JEOL, JEM-2010; at 200 kV) and selected area electron diffraction (SAED) analyses. X-ray photoelectron spectroscopy (XPS; VG ESCALAB MK II) was used to test the chemical valence of Fe ions. The magnetic properties of the samples were measured with a vibrating sample magnetometer (VSM; LakeShore 7304 model). A toroidal sample (inner diameter, 3.04 mm; outer diameter, 7 mm; and thickness, 3 mm) was prepared to fit well the coaxial sample holder for microwave measurements. The complex relative permeability ($\mu_r = \mu' - j\mu''$) and permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) of the composite samples were measured by the coaxial method on an Agilent E8363B vector network analyzer within the range of 0.1–18 GHz.