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Original Research Paper

Preparation and electromagnetic wave absorption properties of hollow Co, Fe@air@Co and Fe@Co nanoparticles

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ABSTRACT

In this study, hollow Co, Fe@air@Co and Fe@Co nanoparticles (NPs) have been synthesized respectively by electroless plating Co shell on Fe core and controlling reaction time based on galvanic cell reaction between Co shell and Fe core in hydrochloric acid at room temperature. The electromagnetic (EM) wave absorption properties of these three NPs are also been investigated. The results indicate that the relationship between Fe core and Co shell is critical to the EM wave absorption properties of hollow Co, Fe@air@Co and Fe@Co nanoparticles when blended with 70 wt% in paraffin-based samples. Fe@air@Co nanoparticles shows the best EM wave absorption properties with minimum reflection loss of −42.75 dB and effective bandwidth of 4.1 GHz under −10 dB. The present work has a significant potential for the development of EM wave absorbing materials with core-shell structure.

1. Introduction

In recent years, bimetallic particles with core-shell structure are of widespread interest due to their unique optical [1], thermal [2], adsorption [3], and catalytic [4] properties compared with their monometallic particles and alloys. Bimetallic core-shell particles containing one or two magnetic elements have received extra attention owing to their applications on electromagnetic [5], oxygen evolution [6], biomedical [7], and sensor applications [8]. Thus, researches on the application of bimetallic magnetic core-shell particles have aroused people's great interest because of double advantages of core-shell structure and magnetic properties. An important application of bimetallic magnetic core-shell particles is acting as electromagnetic (EM) wave absorbing materials.

Conventional EM wave absorbing materials, such as magnetic ferrites [9], usually have high density and strict synthetic conditions, which inevitably limit their applications. In addition, some new EM wave absorbing materials, such as graphene [10] and polymers [11], have a complex or high cost fabrication method, which is not in favor of practical applications. A plenty of attentions have been devoted to developing excellent performance EM wave absorbing materials with light weight, low reflection loss, wide band and thin thickness. Core-shell structure material is a new kind of EM wave absorbing materials, which can make the rest of incident EM wave undergo multiple reflections at the interface between core and shell, leading to the improvement of EM wave absorption [12]. Some core-shell structures as EM wave absorbing materials have been reported, for example, Ag@Ni [13], α-Fe_2O_3@$CoFe_2O_4$ [9], Fe@SiO_2 [14], and Fe_3O_4@polypyrrole [15].

However, there is a lack of simple method to synthesize core-shell structure, owing to the difference of intrinsic chemical or physical properties [16]. Therefore, surface modification on cores is necessary before coating shell, which would complicate the synthesis process [17]. Bimetallic magnetic core-shell particles not only have a combination of dielectric loss and magnetic loss, but also have a facile synthetic method due to the similar intrinsic properties, which simultaneously meet the requirements of EM wave absorbing materials. Importantly, many efforts have been devoted to obtaining the desired EM wave absorption properties with thin thickness and broad effective bandwidth. It has been proved that, the structure [18], morphology [19], and shell thickness [20] of materials with core-shell structure are significant in enhancing EM wave absorption properties. But so far, there is still no one pay attention to the effect of relationship between core and shell on EM wave absorption properties of bimetallic magnetic core-shell materials.

In this paper, a facile and expeditious synthesis method of Fe@Co core-shell nanoparticles (NPs) by electroless plating on Fe templates is presented. Hollow Co, Fe@air@Co and Fe@Co NPs

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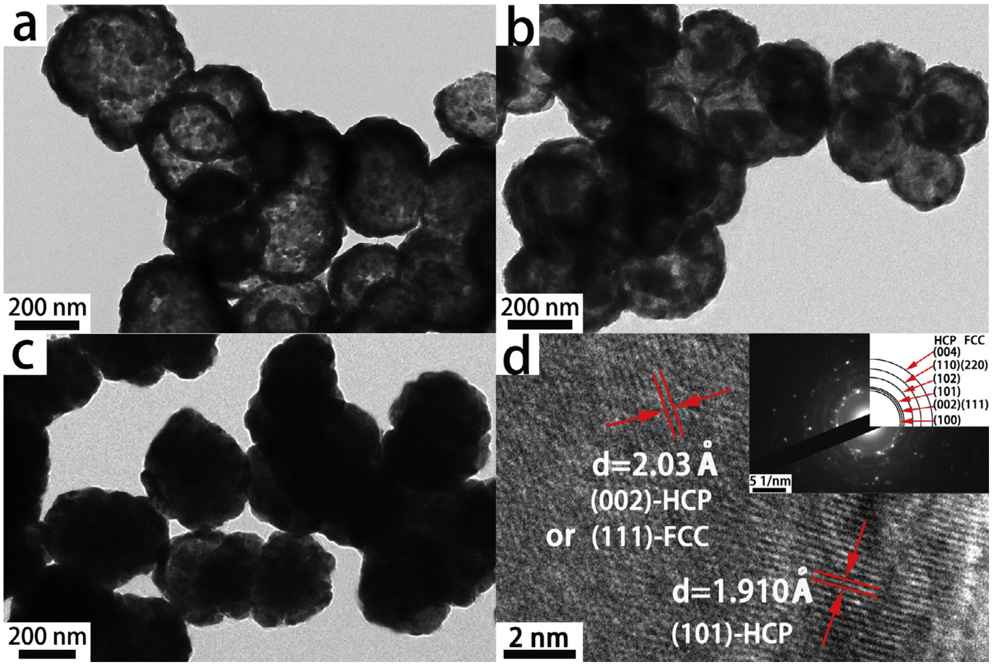

Fig. 1. EM images of (a) hollow Co, (b) Fe@air@Co, (c) Fe@Co NPs and (d) SAED and HRTEM images of Co shell.

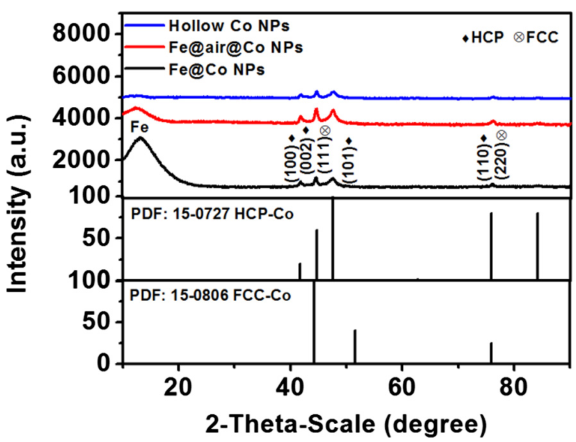

Fig. 2. XRD patterns of hollow Co, Fe@air@Co and Fe@Co NPs.

could be manipulated simply by controlling the corrosion time. The EM wave absorption properties of hollow Co, Fe@air@Co and Fe@Co NPs are investigated.

2. Experimental method

Hollow Co, Fe@air@Co and Fe@Co NPs were prepared by a simple chemical method. First, the mixture solution of $NaBH_4$ and $NH_3{\cdot}H_2O$ was introduced into $FeSO_4$ solution at 40 °C. Then, the synthesized Fe nanoparticles were adding into the mixture solution of $CoSO_4$ and $KNaC_4H_{12}O_{10}$ with pH > 13.5 and T = 50 °C, and the dilute $N_2H_4{\cdot}H_2O$ was injected into the mixture slowly. Fe@Co core-shell NPs were obtained and then collected. Finally, Fe@Co core-shell NPs were placed into 0.323 M HCl solution at room temperature to remove Fe core based on galvanic cell principle. When the reaction time were 0 min, 6 min, and 7 min, the products were collected and then dried in a vacuum chamber.

The samples were characterized by Transmission electron microscopy (TEM; JEOL JEM-2100), Scanning electron microscopy (SEM; FEI Quanta 200F) with energy-dispersive spectrometry (EDS; Oxford, UK), X-ray diffraction (XRD; Rigaku Ultima-III X-ray diffractmeter) and Brunauer-Emmett-Teller (BET; JW-BK112). The relative complex permittivity and permeability″ (ε', ε'', μ', μ'') of hollow Co, Fe@air@Co, Fe@Co NPs were investigated through a vector network analyzer (VNA; Agilent E5071C) from 2 to 18 GHz. Each composite (70 wt%) was homogeneously mixed with paraffin and then was pressed into a ring with 7.0, 3.04, and 2.0 mm in outer diameter, inner diameter, and thickness respectively. The reflection loss (RL) of absorbers can be calculated by the following equations [21]:

$$RL(dB) = -20\log\left|\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right| \tag{1}$$

$$\frac{Z_{in}}{Z_0} = \sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left(j\frac{2\pi fd}{c}\sqrt{\mu_r\varepsilon_r}\right) \tag{2}$$

where Z_{in} is the input impedance, Z_0 is the characteristic impedance of free space, μ_r and ε_r are relative complex permeability and permittivity, c is the speed of light, f is the frequency and d is the thickness of absorber. The EM wave absorption properties are evaluated by the minimum reflection loss (RL_{min}) and the effective bandwidth. When the RL value is less than −10 dB, we believe that 90% of the EM wave are absorbed by the absorbing materials, and the bandwidth is so-called effective bandwidth. Meanwhile, if RL value is under −20 dB, we think that the materials absorb 99% of EM wave. An absorbing material with excellent EM wave absorption properties should contains an increased RL_{min} and broad effective bandwidth.

3. Results and discussion

Fig. 1 shows the morphologies of hollow Co, Fe@air@Co and Fe@Co NPs verified by TEM and it can be seen clearly the average diameter of three samples is about 280 nm. In Fig. 1a, there is a sharp contrast between dark edges and pale center, and the shell thickness is about 38 nm. In Fig. 1b, the shell thickness of Fe@air@Co NPs is about 36 nm and average diameter of Fe core

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