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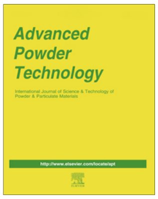

Original Research Paper

The hierarchical three-dimensional cobalt superstructure: Controllable synthesis, electromagnetic properties and microwave absorption

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ABSTRACT

A close-packed hexagonal (HCP)-cobalt superstructure was synthesized on a large scale through a simple, yet low-cost liquid reduction method. The cobalt superstructure was assembled by nanoflakes with strong shape anisotropy. The permittivity $(\varepsilon_r = \varepsilon' - j\varepsilon'')$ and permeability $(\mu_r = \mu' - j\mu'')$ of cobalt superstructure were also studied as a function of frequency in microwave range of 1–18 GHz. It is demonstrated that permittivity displays remarkable multiple dielectric resonance peaks. Multiple magnetic resonances were also exhibited for permeability, which were discussed based on the LLG equation and exchange resonance mode. Multiple dielectric and magnetic resonances were beneficial to widen microwave absorption bandwidth. The calculated reflection loss (RL) indicated that the cobalt superstructure had potential application as a promising candidate for microwave absorption. The reflection loss was attributed to two main reasons, one is the destructive interference, which was related to the thickness of the absorbent layer, and the other one was multiple microwave reflection due to the structure assembled by nanoflakes.

1. Introduction

More and more attentions have been focused on how to obtain excellent electromagnetic shielding materials and high-performance radar-absorbent materials (RAM) [1–6], due to their wide applications in civil and military field with development of scientific technology and modern society, *e.g.* mobile phone, microwave dark-room, and so on [7–9]. The fundamental characteristics, such as strong absorption, wide absorption band, thinner absorbent and light weight are essential to practical application for high-efficiency microwave absorption materials. To meet demands of microwave absorption materials, magnetic metal and their alloy, such as Fe, Co, Ni, and CoNi, have been extensively studied for microwave absorption. These materials have strong microwave attenuation because of their high magnetic loss resulting from high saturation magnetization according to Snoek's limit [10].

The magnetic metallic materials, however, would generate eddy current induced by microwave in GHz range because of their optimal conductivity. The eddy current could result in impedance mismatching between the materials and air space, which would improve microwave reflection and decrease microwave absorption. This problem is still a challenge to many researchers. To our best knowledge, the way to overcome the impedance matching problem is to coat the magnetic particles by inorganic materials and then form into core/shell complex structure, which improve the impedance matching through taking advantage of the dielectric properties of the inorganic materials, such as α-Fe/Y_2O_3 [11], Co/graphite [12], and Fe/SiO_2 [13]. This method was usually two-step complex route, and limited their extensively application to some extent. Recently we try to design the structure of magnetic metallic particles to avoid negative effect produced by eddy current and obtain enhanced microwave absorption materials.

We chose to study cobalt materials because they exhibit many unique magnetic, electronic and chemical properties. Cobalt materials also have high saturation magnetization, and the high magnetic loss could be achieved based on Snoek's limit as mentioned above. Meanwhile, cobalt materials possess high Curie temperature (about 1131 °C) [14], which can makes the materials be used in a wide temperature range. According to reported literatures, the cobalt particles with various morphologies have been synthesized, including dendritic nanocrystals [15], snowflake-like microcrystals [16], dendritic superstructures [17], nanoflowers [18] etc., and these synthesis methods of cobalt materials, to our best knowledge, are relative complex, low-yield and high-cost, which therefore limit their practical application. However, these synthesis

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methods provide inspiration to design and synthesize new structure of cobalt materials for microwave absorption. Thus, there are academic and practical values to synthesize cobalt particles with novel structure through a simple and low-cost method, and further investigate their microwave performances as candidate for microwave absorption.

In this paper, to meet demands of high-efficient microwave absorption materials, hcp-cobalt superstructure was synthesized through liquid reduction method. The effect of process parameters on the morphology and crystal structure of cobalt superstructure were studied in detail. The permittivity and permeability have been investigated as a function of frequency in detail over the frequency range of 2–18 GHz. The calculated microwave absorption demonstrates the cobalt superstructure has potential application as a promising candidate for microwave absorption. Our findings could have the following implications: (1) development of a simple and low-cost synthesis route for self-assembly superstructure composed of cobalt nanoflakes; and (2) opening up a novel way to improve the microwave absorption of cobalt particles.

2. Experiment section

2.1. Material and preparation

All chemicals used in this experiment were analytical grade and used without further purification. A typical synthetic procedure as follows: 0.03 mol $CoSO_4{\cdot}7H_2O$, 0.02 mol $C_{16}H_{33}(CH_3)_3NBr$ (Cetyl Trimethyl Ammonium Bromide, CTAB) and 0.06 mol $C_4O_6H_4KNa$ were added to a beak containing 100 mL deionized water under stirring, then added 50 mL NaOH (7 mol/L) into the above mixed solution, then gradually heated the solution to 90 °C, then 1 mL $N_2H_2{\cdot}H_2O$ were added into the solution, and maintained at this temperature for 30 s. The sample obtained was thoroughly washed with deionized water and absolute ethyl alcohol three times, and then dried at 40 °C for 4 h under vacuum for measurements.

The method to synthesize the cobalt superstructure is reducing complex cobalt ions by hydrazine hydrate. The reaction equation is as follows:

$$Co^{2+} + n(C_4O_6H_4)^{2-} \leftrightarrow [Co(C_4O_6H_4)]_n^{2-2n} \tag{1}$$

$$[Co(C_4O_6H_4)]_n^{2-2n} + 3N_2H_4 \rightarrow [Co(N_2H_4)_3]^{2+} + n(C_4O_6H_4)^{2-} \tag{2}$$

$$[Co(N_2H_4)_3]^{2+} + N_2H_4 + OH^- \rightarrow Co + N_2 + H_2 + NH_3 + H_2O \tag{3}$$

From the Eqs. (1)–(3), we know that the products are gas and water besides cobalt. Thus, the pure cobalt could be achieved through liquid reduction method.

2.2. Characterization

The crystal structure was carried out by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer in Mo Kα radiation ($\lambda = 0.7093$ Å) operated at 50 kV and 30 mA. The SEM images were obtained by a QUANTA600 scanning electron microscopy (SEM) operated at 25 kV. The static magnetic properties were measured by a Lake Shore 7410 vibrating sample magnetometer (VSM). For the microwave performance measurement, the sample was mixed with paraffin into composite (70 wt.%), then compacted into a O-ring (o.d. = 7 mm, i.d. = 3 mm, thickness $d = 2$ mm). The microwave performances were recorded in the frequency range of 2–18 GHz via a HP8722ESS vector network analyzer.

3. Result and discussion

Fig. 1 shows the SEM images of the as-prepared samples. We can see that the particles are three-dimensional superstructure assembled by flakes. The average size of the particles is about 10 μm, and the thickness of the flake is about 500 nm, which demonstrates the micron-sized cobalt superstructure was obtained.

Fig. 2 shows the XRD pattern of the cobalt particles. It is well known that cobalt metal has two crystal structures, i.e. hexagonal close-packed phase (hcp) below 427 °C and face-centered phase (fcc) above 427 °C. The peaks match well with the planes of hcp-cobalt (space group: *P63*/*mmc* (194); JCPDS card: 05-0727, $a = 2.503$ Å, $c = 4.0621$ Å). It demonstrates that the as-prepared cobalt particles are hexagonal close-packed structure. No impure phases, such as $Co(OH)_2$, CoO etc., were observed in the XRD pattern, reflecting the as-prepared samples were pure.

Fig. 3 shows the effect of concentration of $CoSO_4$ on the morphology the cobalt particles. From the figures, we can seen that when the concentration is 0.025 mol/L, the cobalt particles with composed of nanoflakes were obtained with an average size of 8 μm, and the thickness of the nanoflakes are 500 nm (Fig. 3(a)). As increasing the concentration to 0.05 mol/L, the average size of the cobalt particles decreases to around 5 μm. The morphology with flake structure fade away compared to as-prepared cobalt particles under concentration of 0.025 mol/L (Fig. 3(b)). When further increasing the concentration to 0.1 mol/L, the cobalt particles with cavity on the surface were obtained. The particles size is not uniform, and the average diameter is 8 μm (Fig. 3(c)). As shown in Fig. 3(d), we further increased the concentration to 0.2 mol/L, and found the average diameter of the particles decrease to 3 μm. The structure composed of flakes disappears thoroughly. The above result indicates that the cobalt particles evolve from flake-assembled structure to quasi spherical structure with the concentration of the $CoSO_4$ increasing. Interestingly, we found that with the concentration increasing, there were polyhedral particles in as-prepared products, and the higher the concentration was, the more the content was. The effect of Co^{2+} concentration on the morphologies and crystal structures of the cobalt particles has relation to the complex rate ($[C_4O_6H_4]^{2-}/Co^{2+}$). Because there are amounts of $[OH]^-$ ions in the reaction solution, and once the Co^{2+} ions were added into the reaction solution, the precipitating substance, $Co(OH)_2$ would form immediately, which could influence the reaction process. When there are $[C_4O_6H_4]^{2-}$ ions in the reaction solution, the Co^{2+} would combine with the $[C_4O_6H_4]^{2-}$ yet with $[OH]^-$, which avoid the formation of precipitating substance. Meanwhile, it is found that the larger complex rate is, the slower the reaction rate is. When the complex rate is enough large, It is possible to provide enough time for other reaction agent or reaction conditions, such as CTAB and temperature, to modify the morphologies of the cobalt particle. Moreover, the formation of hcp-cobalt needs enough slow reaction velocity. Hence, the complex rate could control the crystal structure through modifying the reaction rate.

Fig. 4 shows the effect of concentration of $CoSO_4$ on the crystal structure of the cobalt particles. The cobalt particles under 0.025 mol/L and 0.05 mol/L are all hcp structure whilst the cobalt particles under 0.1 mol/L and 0.2 mol/L are all a mixture of fcc and hcp structure. The XRD pattern indicated that the crystal structure of the cobalt particles changes from hcp-structure into a mixture of the hcp and fcc-structure with the concentration of $CoSO_4$ increasing. We found the formation of fcc and hcp-cobalt has relation to the reaction velocity. The low reaction velocity confirms the cobalt atoms have enough time to array to satisfy the lowest system energy. The decreased $CoSO_4$ concentration causes the decreased low reaction velocity, thus, the hcp-cobalt particles, a

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