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Regular Article

Enhancing the microwave absorption properties of amorphous CoO nanosheet-coated Co (hexagonal and cubic phases) through interfacial polarizations

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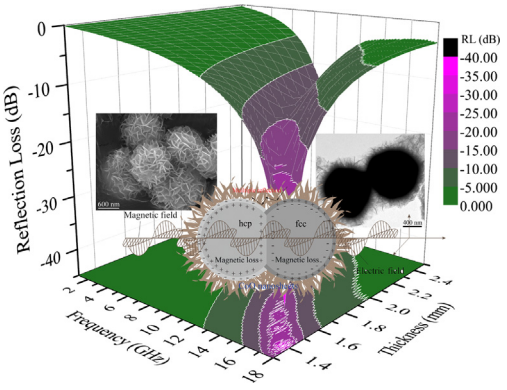
GRAPHICAL ABSTRACT



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ABSTRACT

Core-shell flower-like composites were successfully prepared by a simple polyol method. These composites were formed by coating dual-phased (face-centered cubic [fcc] and hexagonal close-packed [hcp]) Co with amorphous CoO nanosheets. The microwave absorption properties of the flower-like Co@CoO paraffin composites with various Co@CoO amounts were then investigated. Results showed that the paraffin-based composite containing 70 wt% flower-like Co@CoO displayed excellent microwave absorption properties (R_E = 24.74 dB·GHz/mm). The minimum reflection loss of –30.4 dB was obtained at 16.1 GHz with a small thickness of 1.5 mm, and 1.5 mm bandwidth reached 4.6 GHz (13.4–18 GHz) below –10 dB (90% microwave absorption). The excellent microwave absorption properties of flower-like Co@CoO are attributed to the synergetic effect between magnetic loss and dielectric loss, and the magnetic loss makes a main contribution to absorption. The core–shell flower-like structures with dual Co phases also contributed to microwave absorption. The amorphous CoO nanosheets were able to generate

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multiple reflections and exhibit scattering. In addition, the novel absorption mechanism that enhanced interfacial polarization was proposed. This enhancement resulted from the presence of interfaces between the hcp and fcc phases and between the core–shell Co@CoO composites.

1. Introduction

Electromagnetic (EM) pollution promotes the degradation of electronic device performance and has harmful effects on human health, and these negative effects are correlated with the exponential growth of various modern electronics [1,2]. Microwave absorption (MA) materials offset these effects by attenuating unwanted EM energy [3–5]. Microwave absorbers are functional materials that can effectively absorb microwave and convert it into thermal energy or dissipate it by interference [6,7]. Ideal EM absorption materials are lightweight and thin and exhibit broad absorption bands, strong absorptions, and antioxidant ability [8,9].

To achieve these characteristics, many researchers have recently focused on dielectric materials, magnetic materials, or composites formed with magnetic and dielectric materials [10–15]. Among the various absorbing materials, cobalt has the highest permeability because of its high saturation magnetization [16,17]. However, this feature may decrease because of alternated electromagnetic field induced by eddy current. Two main methods are often used to address this problem. First, cobalt particles with special morphologies are synthesized to reduce conductivity. The other method resolves the problem by coating cobalt particles with other materials to form insulated cobalt particles. For example, Tong et al. [18] synthesized flower-like cobalt superstructures, and they were able to obtain a maximum reflection loss of –40 dB, which corresponds to a matching thickness of 2.5 mm, at 6.08 GHz. Meanwhile, Shi et al. [16] prepared hollow cobalt nanochains, which showed two absorption peaks at approximately 12.3 and 14.5 GHz with a thickness of 2.5 mm. Liu et al. [19] fabricated hollow porous Co spheres via a template-free approach, and they were able to prepare epoxy resin composites that contained 30 wt% hollow porous Co spheres, which exhibited wide-band characteristics (RL < −20 dB) in the range of 11.3–18.0 GHz with absorber thicknesses of 1.4–2.0 mm. Ji and coworkers [20] designed a porous three-dimensional flower-like structure of Co@CoO by a simple heated treatment process, and an optimal reflection loss of −50 dB is obtained at 7.2 GHz with a coating thickness of 3.5 mm. Xiang et al. [21] decorated carbon nanofibers with cobalt nanoparticles, and the Co-filled carbon fibers showed a minimum reflection loss value of –63.1 dB at 12.9 GHz with a matching thickness of 1.6 mm. Zhao et al. [22] reported Co-filled carbon nanotubes and the maximum reflection loss was approximately –21.84 dB at 12.2 GHz and with a thickness of 1.0 mm. Sun et al. [23] reported that hexagonal close-packed (hcc) cobalt nanocrystals and face-centered cubic (fcc) cobalt nanospheres with uniform sizes and dispersions were successfully assembled on graphene nanosheets via a facile one-step solution-phase strategy. They also reported that hexagonal close-packed Co/graphene nanocomposites displayed the best EM wave absorption along with a reflection loss value of –47.5 dB at 11.9 GHz. All these results show that the microwave absorption properties of cobalt materials are closely associated with their crystal phases and microstructures. However, no publication has reported the microwave absorption performances of Co with dual crystal phases (fcc and hcp). Thus, the end results of designing core-shell Co-dielectric material composites with dual-phased Co (fcc and hcp) are currently unknown.

In this work, dual-phased Co (fcc and hcp) was coated with amorphous CoO nanosheets. This method facilitated the successful preparation of core-shell flower-like Co@CoO composites by a simple polyol method. The microwave absorption properties of the composites were accurately investigated on the basis of their electromagnetic parameters. The minimum reflection loss reached –38.6 dB at 17.6 GHz, and the 1.4 mm absorption bandwidth (RL below −10 dB) covered 3.5 GHz from 14.5 GHz to 18.0 GHz. A neoteric absorption mechanism involved in the increase of interfacial polarizations was proposed. The polarizations stemmed from the existence of interfaces between the hcp and fcc phases and between the core-shell structures.

2. Experimental section

2.1. Synthesis of flower-like Co@CoO composites

All the chemical reagents were of analytical grade and used without further purification and were supplied by Xilong Chemical Reagent Co. Ltd (Guangdong, China). The flower-like Co@CoO composites were synthesized by a polyol reduction process [24,25]. In brief, cobalt dichloride hexahydrate ($CoCl_2{\cdot}6H_2O$, 1.0 mmol) was dissolved in 60 mL of ethylene glycol and then intensely stirred for 40 min. Sodium hydroxide (NaOH, 40 mmol) was then introduced with vigorous stirring for 90 min. Finally, the precursor solution was transferred into a Teflon-lined stainless-steel autoclave, which was maintained at 200 °C for 6 h and then allowed to cool down to room temperature. After the reaction, the produced black precipitates were collected and washed several times with distilled water and absolute ethanol. The final products were dried in a vacuum oven at 60 °C for 12 h.

2.2. Characterization

The crystalline structures of the synthesized samples were analyzed by X-ray diffraction (XRD, Rigaku Ultima IV) with Cu Ka radiation (λ = 0.15418 nm) in the scattering range (2θ) of 20°–80°. The microstructures of the resultant products were characterized under a field emission scanning electron microscope (JEOL JSM-7001F, Japan) at an accelerating voltage of 15 kV and a transmission electron microscope (JEOL JEM-2100F, Japan) at an accelerating voltage of 200 kV. The compositions of the flower-like core-shell composites were determined by X-ray energy dispersive spectroscopy (EDS, Oxford Instruments) and field emission scanning electron microscopy (FESEM). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet iS10 FTIR spectrometer (USA). Thermogravimetric analysis (TGA) was performed using a Netzsch STA 409/PC analyzer (Germany) from room temperature to 800 °C at a rate of 10 °C/min under air atmosphere. The element chemical state of each flower-like sample was determined through X-ray photoelectron spectroscopy (XPS, XSAM 800, Kratos Co., U. K.). Magnetic hysteresis loop was obtained using a vibrating sample magnetometer (LakeShore 7404). The experimental scattering parameters S_{11} (or S_{22}) and S_{21} (or S_{12}) were tested on an Agilent N5244A vector network analyzer at a frequency range of 1–18 GHz. For coaxial wire analysis, complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability ($\mu_r = \mu' - j\mu''$) were deduced from the scattering parameters on the basis of the standard Nicolson–Ross–Weir algorithm [26,27]. The samples were fabricated by evenly blending with wax, and the mixture was pressed into ring shape with an outer diameter of 7.00 mm and inner diameter of 3.04 mm.