Fabrication and Investigation on Double-Hollow Shell CoFe Oxide@TiO₂ Nanocube with Superior Electromagnetic Properties

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Abstract: Electromagnetic wave absorbing materials are urgently required in the fields of medicine, communication, and military. However, the thickness, weight, narrow effective bandwidth, and weak absorbing ability of the materials restrict their further application. In this work, a double-layer hollow nanocube with a dielectric titanium dioxide (TiO_2) shell and a magnetic CoFe oxide inner shell is prepared. Prussian blue (PB) is prepared by the hydrothermal method, and used as the template to prepare PB@CoFe PB analogue (PBA). After selective etching and further calcination, hollow CoFe oxide particles are obtained. The obtained particles are then coated with SiO₂ and TiO₂, respectively, and the intermediate layer is dislodged to obtain the final CoFe oxide@TiO₂ with the hollow double shell structure. The obtained double-layer hollow structure can effectively capture the incident electromagnetic waves, and increase the propagation path. Moreover, the obvious enhancement of interface polarization and the improvement of impedance matching enhance the wave absorbing ability of the material. The analysis results show that, the structure is stable and the dispersion is good. The maximum reflection loss (RL) at 10 GHz is as high as - 46.1 dB with the sample thickness of 1.6 mm. The light-weight and high-efficiency CoFe oxide@TiO₂ absorber is promised to be used in commercial and military aerospace fields.

Key words: microwave absorption; CoFe oxide; titanium dioxide (TiO_2) ; dual-shelled dual-cavity structure; nanocube

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0 Introduction

The electromagnetic radiation pollution brought by the progress of electromagnetic wave technology and the evergrowing demand for stealth materials in the military call for broadband, efficient, and lightweight electromagnetic wave absorbing materials^[1-3]. Recently, tremendous efforts have been devoted to constructing high-efficiency absorbing materials, e. g., physically mixing magnetic materials with dielectric materials and depositing magnetic materials on a two-dimensional conductive network^[4-8]. However, there are still many unresolved problems for traditional absorbing materials^[9-10]. For example, the nanosystem prepared by the sol-gel method is prone to spontaneous agglomeration, and thus ordinary physical mixing can hardly distribute the dielectric and magnetic components uniformly^[11-12]. Therefore, the preparation of uniform and dispersed high-performance

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absorbing materials still faces many challenges^[13-14].

In order to solve the above problems, researchers turn to design the microscopic morphology of absorbing materials and control the size of nanoparticles, e.g., one-dimensional structures like nanotubes and nanorods^[15-18], two-dimensional structures like nanofilms and nanosheets, and three-dimensional structures like sea urchin structures and core-shell structures^[19-20]. Among three-dimensional absorbing materials, the core-shell structured absorbing materials with strong ferromagnetic resonance properties and domain wall displacement, e.g., Fe₃O₄, become popular candidates, which would nevertheless lead to greater density and unavoidable narrow absorption bandwidths^[21-26]. LIU et al.^[27] prepared a series of CoNi, i.e., CoNi@SiO2 core-shell, CoNi@SiO2@TiO2 coreshell, and CoNi@Air@TiO2 egg yolk shell microspheres, and concluded that the reflection loss (RL) value of the CoNi@SiO2@TiO2 absorber was the greatest. It is proved that the rich interface polarization of the multi-layer hierarchical shell structure contributes to scattering microwaves repeatedly, which in turn leads to the absorption and depletion of the microwaves^[28]. Researchers have also found that the microscopic shape of nanoparticles has a huge impact on the absorbing performance of the nanoparticles^[29-31]. The performance of nanoabsorbing materials with irregular shapes, e.g., cubes and flowers, are better than that with a regular spherical shape in most cases^[32-34]. For example, LIANG et al.^[35] prepared a metal-organic framework cube from Prussian blue analogue (PBA) after heating treatment. They obtained that the CoFe/C nanoabsorbent material had a minimum reflection loss value of -44.6 dB with the material thickness of 2.15 mm, and the effective bandwidth could reach 5.5 GHz. The precise cube structure may bring exchange resonance at high frequencies, and most of the polyhedral materials are anisotropic, contributing to the higher coercivity and hysteresis loss.

Inspired by this, we take the advantages of CoFe oxide and titanium dioxide (TiO_2) to construct a novel double-hollow shell cubic structure. The air layer is expected to ensure that most of the incident

microwave penetrates the small impedance gap magnetic core. The CoFe oxide covers the inner template Prussian blue (PB), which is selectively etched after cladding. Then, silicon dioxide (SiO_2) and TiO_2 are, respectively, coated on the surface of the prepared hollow CoFe oxide core, and the middle SiO₂ layer is selectively etched to obtain the double-layer hollow CoFe oxide@TiO₂. CoFe oxide is a hard magnetic material with high saturation magnetization and coercivity, which are tens of times of those of ordinary magnetic alloys^[36-37], and has excellent magnetic loss performance and strong chemical stability. TiO₂ has high dielectric constant and good dielectric loss performance^[38-40]. The combination of CoFe oxide and TiO₂ can effectively improve the absorbing efficiency. On the one hand, through the impedance matching with the air medium, not only the wave absorbing can be ensured but also the loss of microwaves inside the material can be increased and the density of the final material can be reduced^[41-42]. On the other hand, the cubic microscopic shape can increase not only the transmission of the incident waves inside the material but also the contact area between the incident wave and the two layers of the absorbing materials. The minimum reflection loss of the final double-layer hollow CoFe oxide@TiO2 reaches - 46.1 dB at 10.0 GHz with stable structure and good dispersion (6.32 GHz effective bandwidth). In summary, it is a new type of "thin, wide, light, and strong" absorbing material, and is expected to be used in commercial and aerospace fields.

1 Materials and methods

1.1 Chemicals and materials

Potassium ferricyanide, cobalt chloride hexahydrate, sodium citrate, polypropylene pyrrolidone (PVP), tetraethyl orthosilicate (TEOS), tetrabutyl titanate (TBOT), ethanol, acetone, concentrated hydrochloric acid, and concentrated ammonia solutions (28%) are of analytical grade. They are purchased from Shanghai Chemical Company, and used as received.

1.2 Synthesis of PB

Polyvinylpyrrolidone (PVP) (1 g), sodium citrate (0.3 g), and potassium ferricyanide (K₃ [Fe (CN)₆]) (0.11 g) are mixed in the 30 mL ethanol aqueous solution where the volume ratio of ethanol to water is 1:2. Then, 0.4 mL concentrated hydrochloric acid is added to the above solution and stirred for 10 min. The mixture is removed into a hydrothermal kettle and reacts at 80 °C for 12 h. After the reaction, the blue product (PB) is centrifuged and washed three times with deionized water and ethanol, and then dried in vacuum oven.

1.3 Synthesis of PB@CoFe PBA

20 mg PB is firstly dispersed and sonicated in 30 mL deionized water, and then 143 mg cobalt chloride hexahydrate, 0.3 g PVP, and 0.25 g sodium citrate are added. The obtained liquid is recorded as Solution A. Then, 66 mg potassium ferricyanide is added to 20 mL deionized water, and the solution is marked as Solution B. Solution B is added to Solution A with a dropper at a slow rapid and stirred for 10 min. The mixture ages for 24 h at room temperature, and after that the final PB@CoFe PBA is obtained through centrifugation and three times wash with deionized water and ethanol.

1.4 Synthesis of hollow CoFe oxide

Take 0.075 g product obtained in the previous step, and disperse it into 15 mL ethanol by sonication. Then, add 15 mL 0.04 mol/L NaOH solution to the dispersion, and stir for several minutes to etch PB. The resulting product is obtained by centrifugation and washed three times with water. After that, the washed product is ultrasonically dispersed in 30 mL eionized water, and 0.25 mL concentrated HCL is added. After centrifugation and three times water wash, the hollow CoFe PBA is obtained. To prepare the final hollow CoFe oxide, the hollow CoFe PBA should be removed to a calciner and be calcinated at 300 °C for 2 h (air atmosphere) at the heating rate of 0.5 °C/min to avoid structural collapse.

1.5 Synthesis of hollow CoFe oxide@SiO₂

Take 0.016 g product from the above step, and ultrasonically disperse it in 30 mL deionized water. Then, add 0.5 g PVP to the dispersion, and stir for 12 h. After reaction, the reaction solution is centrifuged and washed three times with water. Ultrasonically disperse the product in 71 mL ethanol aqueous ammonia solution (the volume ratio of ethanol, deionized water, and ammonia water is 56: 14: 1), and add 0.06 mL tetraethyl silicate in the solution at a uniform speed. After 12 h stir and reaction, the hollow CoFe oxide@SiO₂ is obtained. Wash the obtained product three times with deionized water and ethanol, and dry it for later use.

1.6 Synthesis of hollow CoFe Oxide@SiO₂@TiO₂

Prepare 90.3 mL mixed solution of ethanol, acetone, and ammonia (the volume ratio of ethanol, acetone, and ammonia is 40: 50: 0.30), add the product obtained in the previous step to the prepared mixed solution, and disperse by ultrasound. Take 0.24 mL tetrabutyl titanate, dissolve it in 10 mL ethanol, then add the obtained mixture to the above mixed solution. Stir and react at room temperature for 2 h. The product is separated by centrifugation, washed with deionized water and ethanol for three times, and dried. Finally, the dried product is calcined at 500 °C for 2 h (air atmosphere) under the heating rate of 1 °C/min to obtain hollow CoFe oxide@SiO₂@TiO₂.

1.7 Synthesis of double-layer hollow CoFe oxide@TiO₂

The product of the above steps is ultrasonic dispersed to 40 mL deionized water with the addition of 0.2 g NaOH and stirred for 6 h at 60 °C to etch the SiO₂. The obtained new product is centrifugated, separated, and washed three times with deionized water and ethanol. After dry, the final product, i.e., double-layer hollow CoFe oxide@TiO₂, is obtained. The preparation procedure is shown in Fig. 1.



Fig. 1 Schematic diagram of the preparation of double-layer hollow CoFe oxide@TiO2

2 Characterization

The morphology and crystalline structure of the as-prepared samples are characterized by field-emission scanning electron microscopy (FESEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL-2100F). An X-ray diffraction (XRD) analysis is carried out on a D/MAX 2550 VB/PC rotating anode X-ray multicrystal diffraction spectrometer equipped with Ni-filtered Cu K α radiation. The magnetic properties are determined with a superconducting quantum interference device (SQUID). The electromagnetic properties (i. e., relative complex permittivity and permeability) are measured on a vector network analyzer (VNA), Agilent E8363B, with the coaxial transmission line method over the frequency range from 2 GHz to 18 GHz. The samples are prepared by mixing 60% of hollow CoFe oxide, hollow CoFe oxide@SiO2@TiO2, and double-layer hollow CoFe oxide@TiO₂, respectively, with 40% paraffin wax, as the paraffin wax barely contributes to permittivity and permeability. The obtained samples are then molded into toroids with an outer diameter of 7 mm, an inner diameter of 3 mm, and a thickness of 3 mm. Thermogravimetric analysis (TGA) is conducted at the heating rate of 10 °C•min⁻¹ under the nitrogen gas flow.

3 Morphology and structural characterization

The PB is prepared by the polymer-assisted hydrothermal method, which can effectively avoid excessive crystallization speed due to high temperature to obtain uniform cubic form, as shown in Fig. 2 (a) ^[43-44]. Hollow CoFe oxide is obtained after etching the PB core and calcining. The surface of the CoFe oxide nanocube is coated with SiO₂ through the hydrolysis of tetraethyl silicate under the pH condition of the ammonia water. Moreover, the external layer is covered by TiO₂, and SiO₂ is selectively etched to form another hollow layer. From Fig. 2(a), it can be seen that the synthesized PB nanocubes are offspherical and have a uniform particle size distribution with a side length of about 220 nm.

The outer layers are not obvious after coated with CoFe under TEM, while the side length increases to 240 nm and the edge becomes sharper, as shown in Fig. 2(b). The PB inside the nanoparticle is further etched by the NaOH solution to form a spherical cavity, leaving a shell with a thickness of 20 nm, as shown in Fig. 2(c). It can be clearly observed in Fig. 2(d) that the CoFe oxide formed after calcination is still cubic, but the outer layer structure is more loose. After the subsequent coating of SiO₂, the nanoparticle is still cubic and there is a clear gap between the uniform 20 nm thick SiO₂ layer and the CoFe oxide (see Fig. 2(e)).

From Fig. 2 (f), it can be seen that the nanoparticle is a cube with soft corners after further coating with 40 nm thick TiO_2 . After the second etching, the double-layer hollow nanocube is finally obtained. The Fe, Ti element mapping is shown in Fig. 2 (g). The thickness of the cavity is about 20 nm, and the interface between the layers is smooth, which proves that SiO_2 has been completely etched and the obtained double-layer hollow CoFe ox-ide@TiO₂ has good structural stability, which is further confirmed in the XRD.



Fig. 2 SEM, TEM, and mapping images of microspheres obtained from the synthesis of CoFe oxide@TiO₂

The XRD patterns of hollow CoFe oxide, hollow CoFe oxide@SiO₂, hollow CoFe oxide@SiO₂@TiO₂ and double-layer hollow CoFe oxide@TiO2, are shown in Fig. 3. It can be seen that with the diffraction peaks of the hollow CoFe oxide structure at $2\theta =$ 35.4° , 57° and 62.6° correspond to the peak data of PDF#22-1086, indicating that the sample formed is CoFe₂O₄ with the inverse spinel face center cubic (FCC) structure. Owing to the existence of the broad carbon peak around 25° and the amorphous structure of silica, the peak shape of hollow CoFe oxide@SiO₂ does not change significantly after coating SiO₂. Furthermore, the obvious characteristic peaks appear at 25.3° and 48° prove the success of TiO2 coating and the subsequent etching does not affect the structure of TiO₂.



Fig. 3 XRD of hollow CoFe oxide, hollow CoFe oxide@SiO₂, hollow CoFe oxide@SiO₂@TiO₂ and double-layer hollow CoFe de@TiO₂

4 Magnetic and microwave absorbing properties

In order to explain the microwave absorbing mechanism by double-layer hollow CoFe oxide@TiO₂, the microwave absorption model is depicted in Fig. 4. On the one hand, CoFe oxide@TiO2 consisting of dielectric shell TiO₂ and magnetic core CoFe oxide contributes to the excellent absorbing performance. Due to the effective void space between the magnetic and dielectric components, impedance matching can be promoted according to the complex permittivity and permeability. According to the Maxwell-Wagner effect, the inevitably discontinuous areas or defects in the interfaces brought by the doublelayer structure inside the particles will lead to corresponding charge accumulation, which will bring interface polarization. On the other hand, the microwaves incident on the CoFe oxide@TiO2 microspheres can pass through the outer TiO_2 shell, and may be further reflected on the CoFe oxide core, causing multiple reflections of electromagnetic waves between the core and the shell. The dielectric TiO₂ shell and the magnetic CoFe oxide core will produce adjustable reflection loss. The incident wave energy can quickly convert into heat and dissipated because of the block of the two layers of cavity. On the whole, the density is greatly reduced due to the presence of air in the cavity, which is very important for the design of lightweight absorbers.



Fig. 4 Microwave absorbing mechanism experienced by double-layer hollow CoFe oxide@TiO₂

Theoretically, the magnetic field radiated by the CoFe oxide core can penetrate the oxide shell, and magnetically couple and interact with adjacent microspheres to form a magnetic absorption network. As shown in Fig. 5, the magnetic field properties of hollow CoFe oxide, hollow CoFe oxide@SiO₂@TiO₂, and double-layer hollow CoFe oxide@TiO₂ from -2 387 kA/m to 2 387 kA/m are studied on the SQUID magnetometer (temperature: 300 K). None of the three hysteresis loops shows remanence or coercivity, indicating that all the three samples exhibit quasi-superparamagnetism at room temperature. The saturation magnetization (M_s) of hollow CoFe oxide is about 10.8 emu•g⁻¹.



Fig. 5 Hysteresis loops of hollow CoFe oxide, hollow CoFe oxide@SiO₂@TiO₂, and double-layer hollow CoFe oxide@TiO₂

After the hollow CoFe oxide is coated with SiO₂ and TiO₂ in sequence, the M_s values of Fe₃O₄@SiO₂ core-shell microspheres and Fe₃O₄@SiO₂@TiO₂ double-layer core-shell microspheres are reduced to around 0.5 emu·g⁻¹. This is because the cladding layers SiO₂ and TiO₂ are non-magnetic. In order to reveal the microwave absorbing properties of the asprepared samples, we measure the complex permittivity (ϵ', ϵ'') and complex permeability (μ', μ'') of the three-step product in the frequency range from 2 GHz to 18 GHz to study the microwave absorption performance of the final product (see Fig. 6). Owing to the dielectric property promotion brought by the outermost TiO_2 , ϵ' and ϵ'' of double-layer hollow CoFe oxide@TiO₂ are relatively high and stable compared with those of hollow CoFe oxide and hollow CoFe oxide@SiO₂@TiO₂. This may also be ascribed to the introduction of the cavity which increases the polarization area and generates more polarization charges. This further explains the reason why ϵ'' increases slightly as the frequency increases. The final product, i. e., double-layer hollow CoFe oxide@TiO₂ microspheres, has a larger dielectric loss tangent value than other samples, and the magnetic loss tangent value is relatively high, between 0.20 and 0.28. It is anticipated that electromagnetic waves will experience a large degree of attenuatio, resulting in strong microwave absorption.

The reflection loss $(E_{\rm RL})$ is another crucial parameter to assess the microwave absorption performance. $E_{\rm RL}$ can be deduced from the transmission line theory based on the measured relative permittivity and permeability as follows^[5]:

$$Z_{\rm in} = \sqrt{\frac{\mu_{\rm r}}{\epsilon_{\rm r}}} \tanh\left(j\frac{2\pi fd}{c}\sqrt{\mu_{\rm r}\epsilon_{\rm r}}\right) \tag{1}$$

$$E_{\rm RL}(\rm dB) = 20 \lg \left| \frac{Z_{\rm in} - 1}{Z_{\rm in} + 1} \right|$$
(2)

where *f* is the microwave frequency, *d* is the thickness of the absorber, *c* is the speed of light, and ε_r and μ_r are the complex relative permittivity and the complex relative permeability, respectively. The microwave absorption capacity is stronger when the value of E_{RL} is lower. The reflection loss values of hollow CoFe oxide, hollow CoFe oxide@SiO₂@TiO₂, and double-layer hollow CoFe oxide@TiO₂ are obtained from the above formulae.

As shown in Figs. 7(a), 7(b) and 7(c), the E_{RL} peaks of all three samples shift from low frequency to high frequency with the decrease in the thickness.



Fig.6 Complex permittivity, complex permeability, and loss tangent values of hollow CoFe oxide, hollow CoFe oxide@SiO₂@TiO₂, and double-layer hollow CoFe oxide@TiO₂







(b) Reflection loss plots of hollow CoFe oxide @SiO2@TiO2-2 mm



Fig. 7 Reflection loss plots of hollow CoFe oxide, hollow CoFe oxide@SiO₂@TiO₂, and double-layer hollow CoFe oxide@TiO₂

It is worth noting from Fig.8(d) that the minimum E_{RL} of the hollow CoFe oxide is -12.8 dB and decreases to -24.6 dB after coating with SiO₂ and TiO₂, while the minimum E_{RL} of double-layer hollow CoFe oxide@TiO₂ is -46.1 dB with a thickness of 2 mm. This indicates that the existence of TiO₂ not only balances the original impedance but also increases the dielectric loss. More importantly, after the

selective removal of SiO₂, the resulting CoFe oxide@TiO₂ exhibits the best microwave absorbing performance among hollow CoFe oxide, hollow CoFe oxide@SiO₂@TiO₂, and double-layer hollow CoFe oxide@TiO₂. In addition, the absorption bandwidth with $E_{\rm RL}$ lower than $-10~{\rm dB}$ (the reflection loss is more than 90%) reaches up to 6.32 GHz, which is also an increase over 5.44 GHz CoFe oxide@SiO2@TiO2 and 3.76 GHz CoFe oxide. It also reveals the superiority of the double cavity structure. It is supposed that the incorporation of dielectric TiO₂ as well as the magnetic CoFe alloy into the microwave absorption system has generated massive magnetic and dielectric dipole interactions at the material interfaces, and has a positive effect on the matching of permittivity and permeability.



In order to preliminarily estimate the use conditions of the material, we conduct a TGA test on the final product. The results show that the mass loss does not exceed 1% at a high temperature of 500 °C (see Fig. 8), indicating that the material has good thermal stability with the potential for high temperature and other harsh environments.

5 Conclusions

In summary, hollow CoFe oxide, hollow CoFe oxide@SiO₂@TiO₂, and double-layer hollow CoFe oxide@TiO₂ are successfully synthesized. The architecture and compositions of properly designed dual shells and dual cavities (i.e., magnetic CoFe oxide and dielectric TiO₂ for achieving optimal magnetic and dielectric loss) collectively render efficient

trapping of the incident wave via multiple internal reflections and sufficient interfacial polarization, and markedly improve the impedance matching, which in turn contribute to the outstanding microwave absorption performance of double-layer hollow CoFe oxide@TiO2. The double-layer hollow CoFe oxide@TiO₂ absorbers significantly enhance the microwave absorption ability with the minimum $E_{\rm RL}$ up to -46.1 dB at 10 GHz with a thin thickness of only 2 mm and the absorption bandwidth up to 6.32 GHz (<10 dB). All these results have highlighted the superiority of dual shells and dual cavities, which may shed some light on the crafting of high-performance yet thin and lightweight microwave absorbers promising for use in electromagnetic radiation protection, including mobile communication devices and amplitude modulation (AM) radio.

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