

# Coin-like $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@CoFe<sub>2</sub>O<sub>4</sub> Core–Shell Composites with Excellent Electromagnetic Absorption Performance

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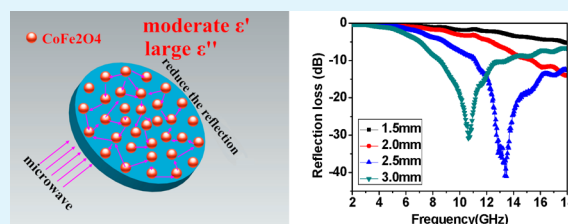
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**ABSTRACT:** In this paper, we designed a novel core–shell composite for microwave absorption application in which the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and the porous CoFe<sub>2</sub>O<sub>4</sub> nanospheres served as the core and shell, respectively. Interestingly, during the solvothermal process, the solvent ratio (*V*) of PEG-200 to distilled water played a key role in the morphology of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> for which irregular flake, coin-like, and thinner coin-like forms of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can be produced with the ratios of 1:7, 1:3, and 1:1, respectively. The porous 70 nm diameter CoFe<sub>2</sub>O<sub>4</sub> nanospheres were generated as the shell of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. It should be noted that the CoFe<sub>2</sub>O<sub>4</sub> coating layer did not damage the original shape of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. As compared with the uncoated  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, the Fe<sub>2</sub>O<sub>3</sub>@CoFe<sub>2</sub>O<sub>4</sub> composites exhibited improved microwave absorption performance over the tested frequency range (2–18 GHz). In particular, the optimal reflection loss value of the flake-like composite can reach –60 dB at 16.5 GHz with a thin coating thickness of 2 mm. Furthermore, the frequency bandwidth corresponding to the RL<sub>min</sub> value below –10 dB was up to 5 GHz (13–18 GHz). The enhanced microwave absorption properties of these composites may originate from the strong electron polarization effect (i.e., the electron polarization between Fe and Co) and the electromagnetic wave scattering on this special porous core–shell structure. In addition, the synergy effect between  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and CoFe<sub>2</sub>O<sub>4</sub> also favored balancing the electromagnetic parameters. Our results provided a promising approach for preparing an absorbent with good absorption intensity and a broad frequency that was lightweight.

**KEYWORDS:**  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@CoFe<sub>2</sub>O<sub>4</sub>, core–shell structure, microwave absorption properties, lightweight absorber



## 1. INTRODUCTION

Microwave absorption materials have attracted a great deal of attention because of the growth in the utilization of wireless equipment, mobile phones, and radar systems.<sup>1–3</sup> It is well-known that the microwave absorbent is a type of functional material that can effectively absorb an electromagnetic wave and attenuate it in the form of thermal energy by magnetic or dielectric loss.<sup>4</sup> Thus, microwave absorption materials are mainly divided into two types depending on how they attenuate the electromagnetic wave.<sup>5,6</sup> Sometimes, a single magnetic loss or dielectric loss material cannot simultaneously meet the requirements of having a thin coating thickness and a broad absorption bandwidth and being lightweight.<sup>7</sup> Therefore, to achieve novel absorption properties, much effort has been devoted to combining two or more kinds of functional materials to adjust the electromagnetic parameters for achieving a desired reflection loss (RL) value. For example, magnetic loss-based composites, including Ag@Ni,<sup>8</sup> Co@MnO<sub>2</sub>,<sup>9</sup> Fe/SiO<sub>2</sub>,<sup>10,11</sup> Fe<sub>3</sub>O<sub>4</sub>@ZnO,<sup>12</sup> Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub>,<sup>13–15</sup> and Fe<sub>3</sub>O<sub>4</sub>@poly(3,4-ethylenedioxythiophene),<sup>16</sup> carbon-based composites like FeCo/C<sup>17,18</sup> reduced graphene oxide (RGO)–MnFe<sub>2</sub>O<sub>4</sub> nanocomposites,<sup>19</sup> graphene/NiFe<sub>2</sub>O<sub>4</sub>,<sup>20</sup> and RGO/CoFe<sub>2</sub>O<sub>4</sub><sup>21</sup> have been reported in recent years. It is worth noting that the

interesting three-dimensional (3D) SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> core–shell nanorod array–graphene architecture had been synthesized as a representative magnetically based absorbent, and the optimal reflection loss value can reach –31.9 dB at a thickness of 2.5 mm.<sup>22</sup> As a result, we may conclude that the enhanced microwave absorption performance of these composites may originate from the improved impedance matching properties caused by the balancing of the complex permittivity and permeability perfectly.<sup>23,24</sup> More importantly, the interface between different materials may form a new type of bond that is also attributed to the electron polarization and results in an increase in the level of electromagnetic attenuation.

Currently, Fe<sub>2</sub>O<sub>3</sub>-based microwave absorbents have been attractive because of their high chemical stability, environmentally friendly nature, and low cost.<sup>25,26</sup> In fact, pure Fe<sub>2</sub>O<sub>3</sub> has a lower real part permittivity value (3–5) that is apt to yield high impedance matching. However, the poor attenuation ability has been the major shortcoming of the EMA materials because of the lower  $\epsilon''$  value. Therefore, a solution is to mix

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$\text{Fe}_2\text{O}_3$  with another material that exhibits strong attenuation ability but poor impedance matching. For instance, Chen et al. successfully loaded the  $\text{Fe}_2\text{O}_3$  nanoparticles into the multi-walled carbon nanotubes and found that the composite exhibited an excellent microwave absorption properties with a minimal reflection loss value of  $-32.7$  dB under a coating thickness of  $2.7$  mm.<sup>27</sup> Numerous  $\text{Fe}_2\text{O}_3$  nanosheets with a thin thickness of  $5$  nm arrayed on the graphene also exhibited improved microwave absorption performance with an optimal RL value of  $-64.1$  dB at a thickness of  $4.92$  mm.<sup>28</sup> Similarly, the leaf-like  $\text{Fe}_2\text{O}_3$ /polyaniline composite provided an RL value of  $-50$  dB with a thickness of  $5.3$  mm.<sup>29</sup> Although the strong reflection loss value was exhibited by these  $\text{Fe}_2\text{O}_3$  composites, the coating thickness is too large. In this paper, we report a new  $\text{Fe}_2\text{O}_3$ -based composite, namely the  $\text{Fe}_2\text{O}_3$ @ $\text{CoFe}_2\text{O}_4$  core-shell composite, which effectively solves this problem. These special core-shell structures have significantly improved the microwave absorption compared with that of the single composition of  $\text{Fe}_2\text{O}_3$  or  $\text{CoFe}_2\text{O}_4$ , especially with a coating thickness of  $<2$  mm.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Iron nitrate [ $\text{Fe}(\text{NO}_3)_3$ ], barium nitrate [ $\text{Ba}(\text{NO}_3)_2$ ], ferric trichloride ( $\text{FeCl}_3$ ), ammonium acetate ( $\text{NH}_4\text{Ac}$ ), cobalt acetate [ $\text{Co}(\text{Ac})_2$ ], and sodium hydroxide ( $\text{NaOH}$ ) were purchased from Nanjing Chemical Reagent Co. Ethylene glycol (EG) and polyethylene (PEG-200) were purchased from the Sinopharm Chemical Reagent Co. All of the chemical reagents used in this work were analytically pure and used without further purification.

**2.2. Synthesis of  $\alpha\text{-Fe}_2\text{O}_3$ .** The  $\alpha\text{-Fe}_2\text{O}_3$  used in this study was prepared by a simple hydrothermal process. Briefly,  $8$  mmol of  $\text{Fe}(\text{NO}_3)_3$  and  $1$  mmol of  $\text{Ba}(\text{NO}_3)_2$  were first dissolved in  $40$  mL of a PEG-200/distilled water mixing solution via mechanical stirring for  $15$  min until the solution became clear. Then,  $2.0$  g of  $\text{NaOH}$  was added to the mixing solution and the mixture stirred for an additional  $15$  min. After that, the mixed solution was transferred into a Teflon-lined stainless steel autoclave and subsequently sealed and heated at  $220$  °C for  $24$  h. Finally, the resulting sample was collected by centrifuge, washed with absolute ethanol and distilled water several times, and dried in a vacuum drying oven at  $60$  °C for  $6$  h.

**2.3. Synthesis of the  $\alpha\text{-Fe}_2\text{O}_3$ @ $\text{CoFe}_2\text{O}_4$  Core-Shell Structure.** The  $\alpha\text{-Fe}_2\text{O}_3$ @ $\text{CoFe}_2\text{O}_4$  composites were prepared by a simple hydrothermal approach. Briefly,  $0.2$  g of the as-prepared  $\text{Fe}_2\text{O}_3$  was first dispersed in  $60$  mL of EG by being stirred for  $10$  min, followed by addition of  $\text{Co}(\text{Ac})_2$  ( $0.25$  g),  $\text{FeCl}_3$  ( $0.6$  g), and  $\text{NH}_4\text{Ac}$  ( $0.5$  g). After being stirred for an additional  $10$  min, the mixed solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of  $100$  mL. The autoclave was heated at  $200$  °C for  $24$  h and then allowed to cool to room temperature. The final products were washed with ethanol by magnetic decantation four times and dried at  $100$  °C for  $4$  h in a vacuum.

**2.4. Characterizations.** The powder X-ray diffraction (XRD) pattern measurements were taken on a Bruker D8 ADVANCE X-ray diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154178$  nm) with a scanning voltage of  $40$  kV, a scanning current of  $40$  mA, and a scanning range from  $20^\circ$  to  $60^\circ$ . A Hitachi S4800 type scanning electron microscope (operating at an acceleration voltage of  $3.0$  kV and equipped with an energy dispersive X-ray spectroscope) was used to observe the morphology features and sizes of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ @ $\text{CoFe}_2\text{O}_4$ . The morphology of the coin-like composite was further characterized by transmission electron microscopy (TEM) (JEM JEOL 2100). The atomic ratio was tested by inductively coupled plasma (ICP) (Optima 5300 DV). The focused ion beam (FIB) system was utilized to test the shell thickness of the coin-like  $\text{Fe}_2\text{O}_3$ @ $\text{CoFe}_2\text{O}_4$  (FEI versa 3D). The magnetic properties, including coercive force and saturation magnetization, were determined by a vibrating sample magnetometer (VSM, Lakeshore, model 7400 series) at room

temperature. The XPS spectrum was measured in a PHI 5000 VersaProbe system with an  $\text{Al K}\alpha$  X-ray source operating at  $150$  W. The  $S$  parameter, including  $S_{11}$ ,  $S_{12}$ ,  $S_{21}$ , and  $S_{22}$ , was tested with an Agilent PNA N5224A vector network analyzer using the coaxial-line method by preparing the sample by homogeneous mixing of the paraffin wax and sample (mass ratio of  $1:1$ ) and then pressing it into toroidal-shaped samples ( $\Phi_{\text{out}} = 7.0$  mm, and  $\Phi_{\text{in}} = 3.04$  mm). Afterward, software that has been installed in Agilent PNA can calculate the  $\epsilon'$ ,  $\epsilon''$ ,  $\mu'$ , and  $\mu''$  values. Finally, the RL values with different thicknesses can be calculated by using the following formulas.<sup>30–32</sup>

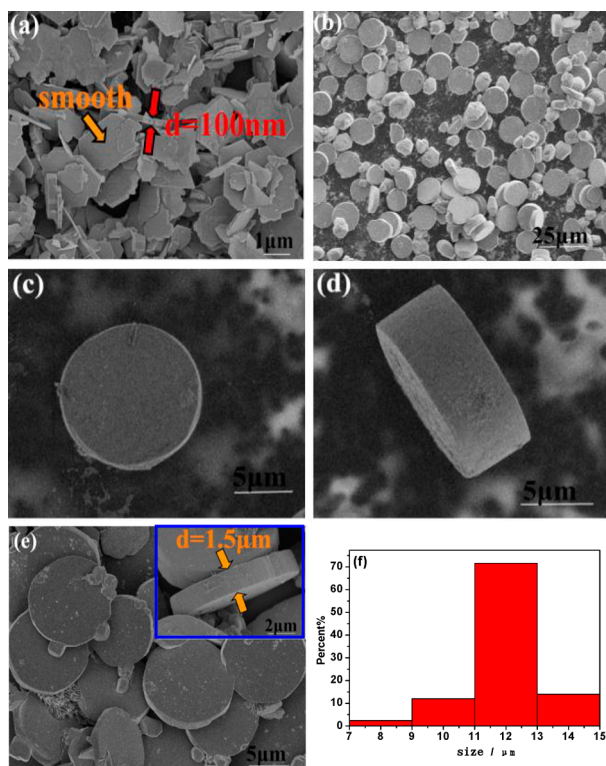
$$Z_{\text{in}} = Z_0 \sqrt{\mu_r/\epsilon_r} \tanh[j(2\pi f d/c)] \sqrt{\mu_r \epsilon_r} \quad (1)$$

$$\text{RL (dB)} = 20 \times \log|(Z_{\text{in}} - Z_0)/(Z_{\text{in}} + Z_0)| \quad (2)$$

where  $Z_0$  represents the impedance of free space,  $Z_{\text{in}}$  is the input impedance of the absorber,  $f$  is the frequency of the electromagnetic wave,  $d$  is the coating thickness of the absorber,  $c$  is the velocity of the electromagnetic wave in free space, and RL is the minimal reflection loss value.  $\epsilon_r$  ( $\epsilon_r = \epsilon' - j\epsilon''$ ) and  $\mu_r$  ( $\mu_r = \mu' - j\mu''$ ) are the complex permittivity and permeability of the absorber, respectively.

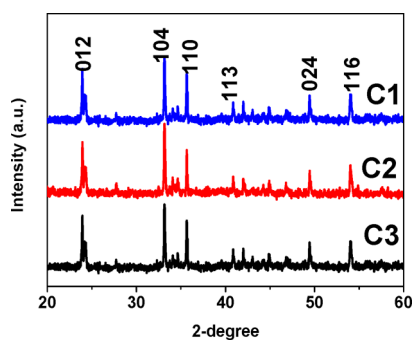
## 3. RESULTS AND DISCUSSION

Among all the chemical synthesis methods, the solvothermal method has attracted the most attention because of its easy modification of the morphology.<sup>33</sup> During the solvothermal process, many factors, such as the surfactant:molar ratio of the precursor salt can determine and affect the morphology of final products. In this study, the shape and thickness of flake- or coin-like  $\alpha\text{-Fe}_2\text{O}_3$  can be easily tuned by adjusting the volume ratio ( $V$ ) between PEG-200 and distilled water. When a volume ratio of  $1:7$  is maintained in the solvent, the flake-like  $\alpha\text{-Fe}_2\text{O}_3$  particles (marked in C1) with a thickness of  $100$  nm are gained while they are not in a regular shape as shown in Figure 1a. Clearly, monodisperse coin-like  $\alpha\text{-Fe}_2\text{O}_3$  particles (C2) with a uniform shape and size can be obtained (seen Figure 1b) when  $V$  is increased to  $1:3$ . From the high-resolution SEM images (Figure 1c,d), one can see that the coin-like particles have a very smooth surface and a narrow thickness range from  $4$  to  $5$   $\mu\text{m}$ . The average diameter of these coin-like particles can be confirmed to be  $11\text{--}13$   $\mu\text{m}$  from the histogram of the particle size distribution (Figure 1f). It is expected that the large and smooth surface of these coin-like particles could be a good platform for growing  $\text{CoFe}_2\text{O}_4$  nanospheres. Furthermore, if  $V$  is further increased to  $1:1$ , the thickness of these coin-like particles decreases to  $1.5\text{--}2.5$   $\mu\text{m}$  (named thinner coin-like, C3) while the diameter is unchanged (Figure 1e). It is noteworthy that the particle size distribution becomes wider and some irregular particles appear. The morphology transition between the flake- and coin-like particles can be well explained according to the Hansen solubility parameter (HSP) theory.<sup>34,35</sup> On the basis of previous similar research results, the solutions with different alcohol:water ratios will result in different Ra values, and these Ra values will decrease at first to a local minimum and finally increase again with a continuous increase in alcohol content. Meanwhile, the results also reveal that a smaller Ra value will be responsible for the regular morphology. In that way, it can easily explain the fact that the initial high Ra value leads to the formation of the irregular flake-like particle and the decreased Ra value makes the particle shape more uniform and coin-like particles are formed, further increasing the Ra value that will change the particle shape back to inhomogeneous.



**Figure 1.** (a) SEM image of flake-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. (b–d) SEM images of coin-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. (e) SEM image of thinner coin-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. (f) Size distribution of coin-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

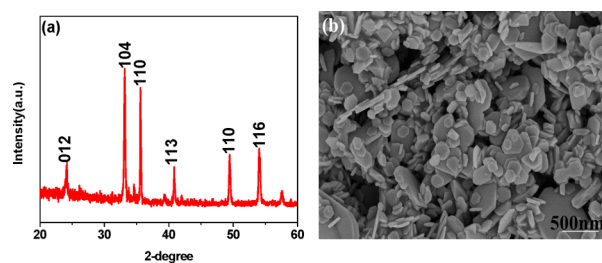
Figure 2 reveals the XRD patterns of the starting material  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Obviously, all the diffraction peaks at 23.78°, 33.05°,



**Figure 2.** XRD diffraction patterns of flake-, coin-, and thinner coin-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

35.61°, 40.75°, 49.45°, and 54.02° can be easily indexed to the (012), (104), (110), (113), (024), and (110) peaks of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDS Card No. 33-0664), respectively. However, the high temperature and the pressure during the solvothermal process may generate the Ba ferrite, as shown in the presence of a diffraction peak [beside the (012) peak of Fe<sub>2</sub>O<sub>3</sub>]. To prove the probable presence of Ba, the coin-like Fe<sub>2</sub>O<sub>3</sub> has been tested by ICP. The result shows that the concentrations of Ba and Fe are 11.2 and 74.5 mg/L, respectively, corresponding to an atomic ratio of 0.061. However, the diffraction peak of Ba ferrite is so weak that it can be neglected.

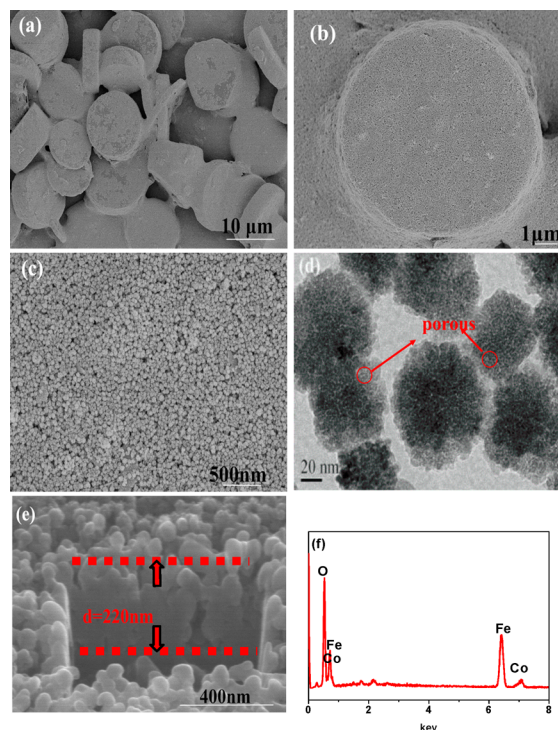
To explore the role of Ba(NO<sub>3</sub>)<sub>2</sub> in the reaction procedure, we conducted an additional experiment ( $V_{\text{PEG-200}}/\text{distilled} = 1:3$ ) without adding Ba(NO<sub>3</sub>)<sub>2</sub>. From Figure 3a, we easily find that



**Figure 3.** (a) XRD patterns and (b) FE-SEM of the sample prepared without adding Ba(NO<sub>3</sub>)<sub>2</sub>.

the diffraction peaks still belonged to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDS Card No. 33-0664). Meanwhile, the impurity peak beside (012) disappeared, which indirectly proved that such an impurity may result from Ba ferrite. Subsequently, the SEM image shows that the as-prepared Fe<sub>2</sub>O<sub>3</sub> presents a flake-like structure with a size that ranged from 100 to 500 nm, which is much smaller than that of coin-like Fe<sub>2</sub>O<sub>3</sub>. At the same time, most of the flake-like Fe<sub>2</sub>O<sub>3</sub> exhibits a tendency toward hexagonal structure. Thus, we may deduce that during the solvothermal process, Ba(NO<sub>3</sub>)<sub>2</sub> may contribute to the enlargement of flake Fe<sub>2</sub>O<sub>3</sub>. At the same time, with the assistance of Ba(NO<sub>3</sub>)<sub>2</sub>, the hexagonal-like structure is turned to a coin-like structure.

To prepare the Fe<sub>2</sub>O<sub>3</sub>@CoFe<sub>2</sub>O<sub>4</sub> composite, 0.2 g of the as-prepared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was added to the EG solvent for the solvothermal process, with Co(Ac)<sub>2</sub> and FeCl<sub>3</sub> as the precursors. Interestingly, the coin-like structure is completely covered by CoFe<sub>2</sub>O<sub>4</sub> as shown in Figure 4a. Via the close-up views in panels b and c of Figure 4, we find that the coating layer consists of numerous nanospheres with an average diameter of ~70 nm. Figure 4d displays the TEM image of



**Figure 4.** (a–c) SEM images of the coin-like Fe<sub>2</sub>O<sub>3</sub>@CoFe<sub>2</sub>O<sub>4</sub> composite. (d) TEM image of CoFe<sub>2</sub>O<sub>4</sub>. (e) FIB image of the Fe<sub>2</sub>O<sub>3</sub>@CoFe<sub>2</sub>O<sub>4</sub> composite. (f) EDX pattern of the coin-like composite.

the composites; it is consistent with Figure 4b that the  $\text{CoFe}_2\text{O}_4$  has a sphere-like structure. However, the white region marked in each  $\text{CoFe}_2\text{O}_4$  nanosphere demonstrates that  $\text{CoFe}_2\text{O}_4$  exhibits a porous structure. The thickness of the shell is  $\sim 220$  nm as displayed in Figure 4e. The EDX spectrum is proof of the presence of Co and Fe together with elemental O in the composite (Figure 4f).

The XRD pattern of the representative coin-like  $\text{Fe}_2\text{O}_3@$  $\text{CoFe}_2\text{O}_4$  composite is shown in Figure 5. After the sample had

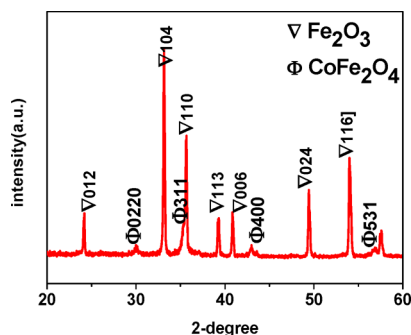


Figure 5. XRD patterns of the coin-like composite.

been coated with a  $\text{CoFe}_2\text{O}_4$  layer, new diffraction peaks appeared at  $29.91^\circ$ ,  $35.31^\circ$ ,  $43.01^\circ$ , and  $65.61^\circ$ ; they can be indexed into the cubic phase of  $\text{CoFe}_2\text{O}_4$  (JCPDS Card No. 22-1086), while the intrinsic peaks of  $\alpha\text{-Fe}_2\text{O}_3$  are almost unchanged, indicating that  $\text{CoFe}_2\text{O}_4$  successfully coats the surface of the coin-like form without altering the phase structure of  $\alpha\text{-Fe}_2\text{O}_3$ .

The X-ray photoelectron spectrum was also recorded to compare the oxidation states of the coin-like  $\alpha\text{-Fe}_2\text{O}_3$  and its composite. From Figure 6a, the binding energy values of Fe

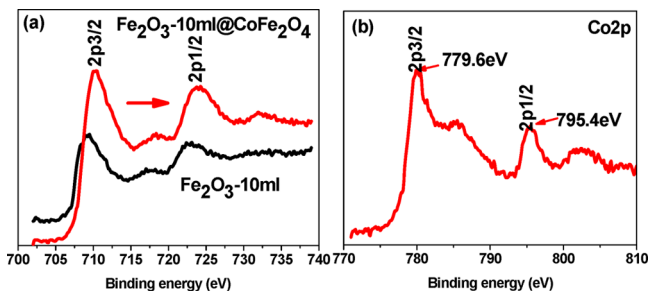


Figure 6. XPS spectra of (a) Fe 2p for coin-like  $\alpha\text{-Fe}_2\text{O}_3$  and its composite and (b) Co 2p for the coin-like composite.

$2p_{3/2}$  and  $2p_{1/2}$  are located at 709.1 and 723.1 eV, respectively, which agree with the XPS results published by Sun et al. for  $\alpha\text{-Fe}_2\text{O}_3$ .<sup>36</sup> For Fe 2p in the  $\text{Fe}_2\text{O}_3@$  $\text{CoFe}_2\text{O}_4$  composite, the values were 710.4 and 724.1 eV, respectively, slightly higher than those of pure  $\alpha\text{-Fe}_2\text{O}_3$ . Furthermore, the opposite tendency is exhibited by Co 2p, for which binding energy values are observed at 779.6 and 795.4 eV, respectively, in the composite, slightly lower than those of pure  $\text{CoFe}_2\text{O}_4$  [780.3 and 795.8 eV, respectively (see Figure 6b)].<sup>37</sup> Such a chemical shift for Fe 2p and Co 2p may originate from the interaction between  $\text{Fe}_2\text{O}_3$  and  $\text{CoFe}_2\text{O}_4$ .<sup>38,39</sup> Specifically, the electronegativity value of elemental Fe is 1.83, slightly smaller than that of elemental Co (1.88). After  $\text{CoFe}_2\text{O}_4$  had been coated on the surface of  $\text{Fe}_2\text{O}_3$ , the electron density of Fe is weakly

affected by the attraction of Co, which resulted in the increase in the level of electron polarization of Fe–Co. Thus, the corresponding values of Fe 2p shift to a higher-energy region while those of Co 2p to a lower-energy region.<sup>40</sup>

The magnetic hysteresis loops of  $\text{Fe}_2\text{O}_3@$  $\text{CoFe}_2\text{O}_4$  composites were tested by a vibrating sample magnetometer as shown in Figure 7. It is clearly seen that the composites show novel

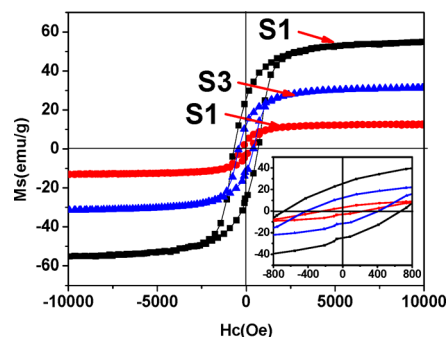


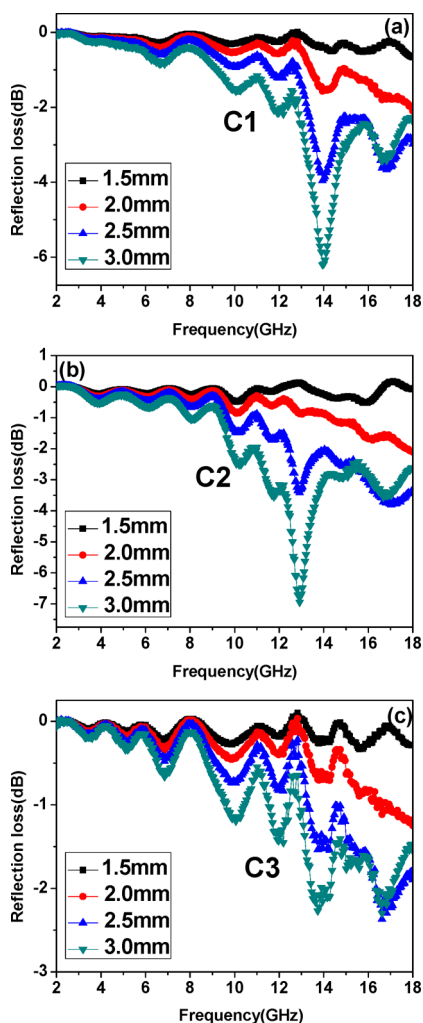
Figure 7. Hysteresis loops of the flake-, coin-, and thinner coin-like composites.

ferromagnetism due to the entry of  $\text{CoFe}_2\text{O}_4$  into the composite. The magnetization of flake-like composite S1 (54 emu/g) is much higher than the values for the coin-like (19 emu/g) and thinner coin-like (33 emu/g) forms. The difference in magnetization values is related to the specific surface area of  $\alpha\text{-Fe}_2\text{O}_3$ . Compared with the large size of coin-like  $\text{Fe}_2\text{O}_3$ , the flake-like  $\text{Fe}_2\text{O}_3$  composite has a larger specific area. Under identical conditions, this composite can introduce more and more  $\text{CoFe}_2\text{O}_4$  nanospheres. As far as the coercivity force (Hc) is concerned, it is well known that Hc is a vital parameter for assessing the magnetic properties, and the absorbent with a high Hc value may cause a high-frequency resonance.<sup>41</sup> Moreover, the Hc value is strongly related to grain size, and a small grain size may lead to a high coercivity.<sup>42</sup> Herein, the flake-like composite with the smallest size has the largest coercive force of 673 Oe, compared with those of the coin-like (S2) and thinner coin-like (S3)  $\alpha\text{-Fe}_2\text{O}_3$ .

Figure 8 shows the calculated reflection loss values of the  $\alpha\text{-Fe}_2\text{O}_3$ . The pure  $\alpha\text{-Fe}_2\text{O}_3$  with different morphologies exhibits poor microwave properties at coating thicknesses of 1.5–3 mm. It can be found from Figure 8a that the minimal reflection values of C1 (flake-like  $\alpha\text{-Fe}_2\text{O}_3$ ) increase with increasing thickness. The  $\text{RL}_{\min}$  value of  $-6.3$  dB is obtained at 14 GHz with a thickness of 3.0 mm. Such poor absorption properties also occur for other two kinds of  $\alpha\text{-Fe}_2\text{O}_3$  as seen in panels b and c of Figure 8, with an  $\text{RL}_{\min}$  value of  $-7.2$  dB for the coin-like form (C2) and  $-2.5$  dB for the thinner coin-like form (C3) with the same thickness of 3 mm. In fact, the pure  $\text{CoFe}_2\text{O}_4$  still performed badly in microwave absorption according to the recent literature; the pure  $\text{RL}_{\min}$  value of the  $\text{CoFe}_2\text{O}_4$  was less than  $-5$  dB with a coating thickness of 2–5 mm.<sup>37</sup>

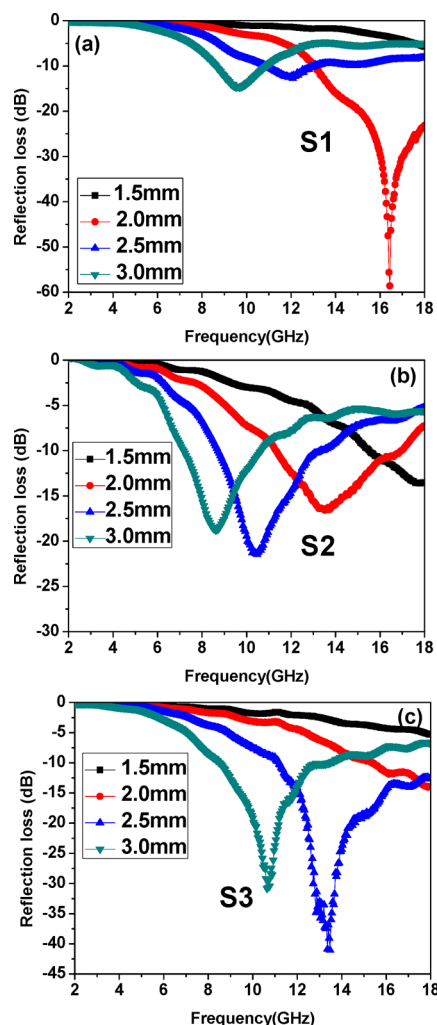
After samples had been coated with  $\text{CoFe}_2\text{O}_4$  nanospheres, the microwave absorption properties of three kinds of composites are significantly improved in terms of the minimal value and frequency width, as described in Figure 9. Meanwhile, all of the composites present the same tendency in that the optimal RL peaks are shifted to the lower-frequency region with an increase in thickness, according to the equation<sup>43</sup>

$$t_m = nc/4f_m (\epsilon_r \mu_r)^{1/2}$$



**Figure 8.** Reflection loss curves for the (a) the flake-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, (b) the coin-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and (c) the thinner coin-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

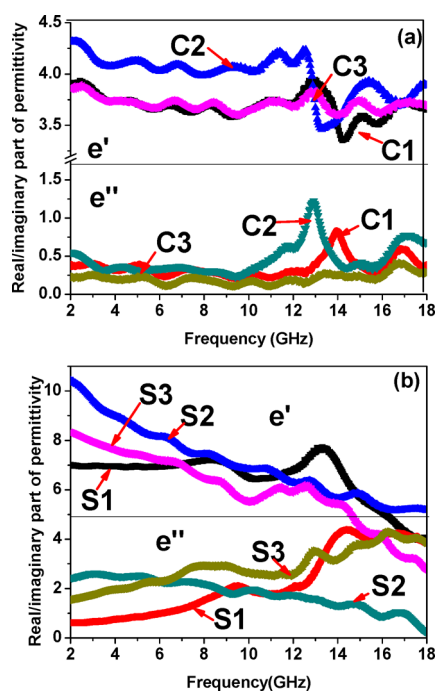
where  $t_m$  and  $f_m$  represent the matching thickness and frequency of a RL peak, respectively,  $\mu_r$  and  $\epsilon_r$  are the complex permeability and permittivity at a matching frequency, respectively, and  $C$  is the velocity of light. It is worth mentioning that S1 with a thickness of 2 mm presents an optimal  $RL_{\min}$  of  $-60$  dB at 16.3 GHz, which is much higher than the values of other types of Fe<sub>2</sub>O<sub>3</sub>- or CoFe<sub>2</sub>O<sub>4</sub>-based composites. Furthermore, the frequency bandwidth of less than  $-10$  dB (comparable to 90% attenuation of incidence EM; thus, the value of less than  $-10$  dB is considered to be an ideal value) reaches 5 GHz (13–18 GHz), which will easily meet the requirements of being lightweight and having an absorption intensity and a broad frequency. The RL data of coin- and thinner coin-like composite are displayed in panels b and c of Figure 9. Also, the enhanced absorption properties can be found in these two types of composites; S2 shows the optimal value of  $-23$  dB with a thickness of 2.5 mm, while the minimal reflection loss value of S3 is up to  $-41$  dB with a thickness of 2.5 mm. Furthermore, with a coating thickness of just 2 mm (in practical application, the coating thickness should be  $<2$  mm), both coin- and thinner coin-like forms exhibit better absorption. For example, the coin-like form has an  $RL_{\min}$  value of  $-17$  dB with a bandwidth of 5.5 GHz (11.3–16.8 GHz), but S3 has an  $RL_{\min}$  value that reaches  $-14$  dB with a frequency bandwidth of 2.6 GHz (15.4–18 GHz).



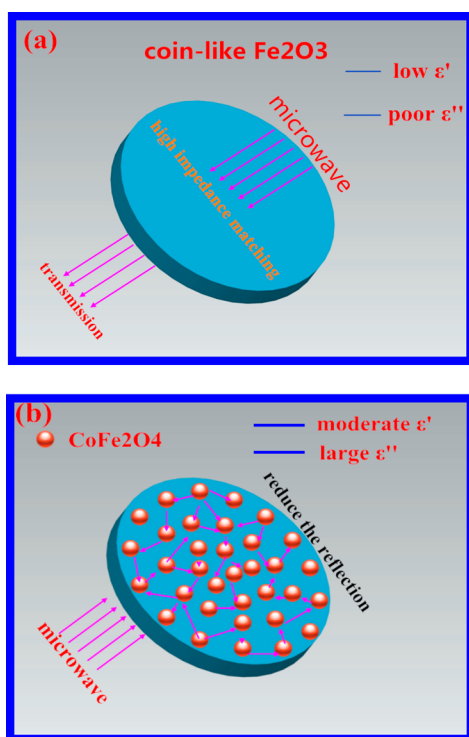
**Figure 9.** Reflection loss curves of (a) the flake-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite, (b) the coin-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite, and (c) the thinner coin-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite.

We investigated the electromagnetic parameters of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and its composites to reveal the enhanced microwave absorption mechanism. It is clearly seen in Figure 10a that all forms of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> have lower  $\epsilon'$  values (approximately 4.3–3.8). Such a low value may lead to high impedance matching behavior. However, the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with a lower  $\epsilon''$  value has almost no ability to attenuate the incidence electromagnetic wave. When the CoFe<sub>2</sub>O<sub>4</sub> was coated on the surface of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Figure 10b), apparent improved  $\epsilon'$  values among the composites were found compared with those of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. At the same time, the novel increase in  $\epsilon''$  values not only maintains the good impedance matching behavior but also makes contributions to EM attenuation.

These special core-shell structures also make an important contribution to the microwave absorption properties. In Figure 11, we find that the high impedance matching of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can arouse more and more incidences of the electromagnetic wave passing into the absorber, but it is difficult to attenuate the electromagnetic wave by the lower  $\epsilon''$  value of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>; thus, most of the electromagnetic wave is reflected via transmission from the internal  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. As for the composites, this composite has a good impedance matching condition (despite the fact that a slightly increased  $\epsilon'$  value may decrease the impedance properties, while the increase in the  $\mu'$  and  $\epsilon''$  values



**Figure 10.** Electromagnetic characteristics (real/imaginary part of permittivity) of (a) three types of  $\alpha\text{-Fe}_2\text{O}_3$  and (b) three types of composites.



**Figure 11.** Schematic illustration of the absorption mechanism of (a)  $\alpha\text{-Fe}_2\text{O}_3$  and (b)  $\text{Fe}_2\text{O}_3@/\text{CoFe}_2\text{O}_4$  composites.

also can increase the impedance matching), which can let most of the incident EM wave go into the materials and be absorbed by the material itself. Meanwhile, because of the coating layer of the spherical  $\text{CoFe}_2\text{O}_4$  ferrite particles, the rest of the incident EM wave will undergo a multireflection at the surface and can be further absorbed, as well.

## 4. CONCLUSION

In summary, three kinds of  $\text{Fe}_2\text{O}_3@/\text{CoFe}_2\text{O}_4$  composites, including flake-, coin-, and thinner coin-like structures, have been prepared by an efficient two-step solvothermal process. The Ra value of the mixed solvent (PEG-200/distilled water) has played a crucial role in the original  $\alpha\text{-Fe}_2\text{O}_3$  morphology. We compared the microwave absorption properties of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3@/\text{CoFe}_2\text{O}_4$  composites and found that all of the  $\alpha\text{-Fe}_2\text{O}_3$ -based composites exhibit remarkable enhancements in both the RL value and frequency bandwidth. In particular, the flake-like composite has an optimal RL value of  $-60$  dB, the bandwidth is up to 5 GHz, and the thickness was just 2 mm. The enhanced microwave absorption properties of the composites have been discussed in this paper. On one hand, the synergy effect between the core and shell may increase the extent of electron polarization. On the other, the high impedance matching of the composites can lead to strong absorption. Then, the incidence of the electromagnetic wave is apt to scatter among the porous  $\text{CoFe}_2\text{O}_4$  nanospheres. These kinds of composites have potential applications in intensity absorption, lightweight, and broad frequency absorbents.

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### Notes

The authors declare no competing financial interest.

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