# Microwave-absorption properties of ZnO-coated iron nanocapsules

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The electromagnetic (EM) characteristics of ZnO-coated Fe nanocapsules synthesized by arc discharging were studied at 2–18 GHz. A reflection loss (RL) exceeding −20 dB was obtained in the frequency range of 6.1–15.7 GHz for an absorber thickness of 1.5–5 mm. An optimal RL of −57.1 dB was found at 7.8 GHz for an absorber thickness of 3.00 mm. The excellent microwave-absorption properties are a consequence of a proper EM match in the nano-microstructure, a strong natural resonance, as well as multipolarization mechanisms. ZnO-coated Fe nanocapsules may be attractive candidates for EM-wave-absorption materials. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2919098]

In recent years, serious electromagnetic (EM) interference pollution arising from the rapidly expanding use of communication devices, such as mobile telephones, local area network systems, and radar systems, have attracted great interest in exploiting a type of microwave-absorption materials with strong absorption in a wide frequency range, low density, and high resistivity. The microwave-absorption properties are determined by the relative permeability ($\mu_\gamma = \mu' - j\mu''$), the permittivity ($\varepsilon_\gamma = \varepsilon' - j\varepsilon''$), the EM impedance match, and the microstructure of the absorber.[1] Metallic magnetic materials have a large saturation magnetization and a high Snoek limit at high frequencies.[1,2] Consequently, the complex permeability can still remain high in the microwave-frequency range, for which it is possible to design thinner absorbers. Nevertheless, the high-frequency permeability of metallic magnetic materials may decrease due to eddy-current losses induced by the EM wave. For this reason, it is better to use metallic particles with a size smaller than the skin depth (1 $\mu$m for iron in the 1–5 GHz range) for suppressing the eddy-current phenomenon to enhance the effective interaction with EM-wave absorbers, which are isolated by insulating materials. Some nanocomposites of this type, including $\alpha$-Fe/SmO,[3] $\alpha$-Fe/$Y_2O_3$,[4] Fe/$Fe_3B$/$Y_2O_3$,[5] Ni/C,[1] etc., have been studied.

Among the candidates for EM-wave absorbers, magnetic particles encapsulated within carbon-nanotube (CNT) composites and magnetic particles coated by carbon have been the focus of extensive study.[6] However, the complex fabrication processes of magnetic-particle-doped CNTs are unfavorable for practical application of such absorbing nanocomposites. Therefore, it is important to search for other kinds of absorbing nanocomposites. Recent interest has been devoted to ZnO-containing nanomaterials, which can be used as high-efficiency microwave-absorbing materials due to the complex permittivity and permeability.[6–9] It is easy to realize large scale synthesis of ZnO-containing nanomaterials for commercial application with very low fabrication costs. Cao *et al.*[6] reported that cagelike ZnO/$SiO_2$ nanocomposites exhibit a relatively strong attenuation of microwaves in the *X* band, which is related to the unique geometrical morphology of the cagelike ZnO nanostructures. Zhou *et al.*[7] showed that composite coatings containing ZnO whiskers have a good efficiency of microwave absorption. Chen *et al.*[8] reported that the ZnO nanowire-polyester composites are strong absorption materials for microwaves in the *X* band, which is attributed to interfacial multipoles at the interface between the polyesters and the ZnO nanowires and to a high surface-to-volume ratio. The purpose of the present letter is to investigate the EM-wave absorption properties of ZnO-coated Fe nanocapsules which match the natural resonance of the Fe cores and the dielectric loss of the ZnO shells.

The ZnO-coated Fe nanocapsules were prepared by the arc-discharge technique with modified strategies.[10] A master $Fe_{97}Zn_3$ alloy was prepared by arc melting Fe and Zn bulk pieces of 99.9 wt % purity under high-purity argon atmosphere. In the arc-discharge process, the $Fe_{97}Zn_3$ alloy served as the anode, while the cathode was a tungsten needle. The anode target was placed into one pit of a water-cooled copper crucible. The distance between the anode and the cathode was about 3 mm. A mixture of Ar(16 000 Pa) and $H_2$(6000 Pa) gas was introduced into an evacuated chamber ($5.0 \times 10^{-3}$ Pa) before a potential was applied between the cathode and the anode. During the experimental process, the current was maintained at 80 A for 5 h, while the potential was maintained at 12 V. After being passivated in 0.01 MPa argon for 24 h, the products were collected in the top of the chamber.

High-resolution transmission-electron microscopy (HRTEM) images show that the nanocapsules are about 10–25 nm in diameter and that the protective ZnO shells are 2–3 nm in thickness, as shown in Figs. 1(a) and 1(b). Com-

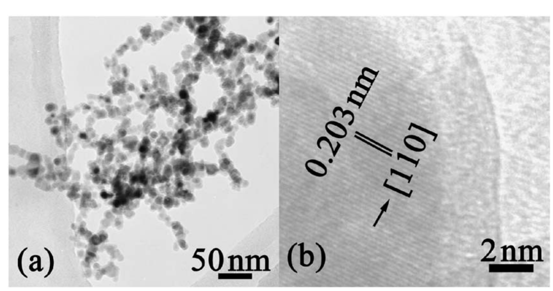


FIG. 1. (a) TEM and (b) HRTEM images of ZnO-coated Fe nanocapsules.

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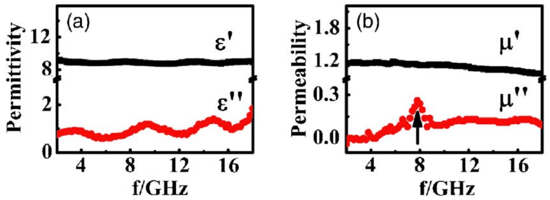


FIG. 2. (Color online) (a) Relative permittivity and (b) relative permeability of a ZnO-coated Fe nanocapsule-paraffin wax sample as a function of frequency.

pared to previous reports on C-coated Ni or Fe nanocapsules,[1,2] the ZnO-coated Fe nanocapsules show a higher dispersion, which implies that the ZnO shell is superior to the C shell in the improvement of the dispersion of the nanocapsules.

A ZnO-coated Fe nanocapsule/paraffin composite was prepared by uniform mixing of powder of ZnO-coated Fe nanocapsules with paraffin, which is transparent for EM waves, and by pressing the mixture into the shape of a cylinder. The cylinder was cut into toroidal-shaped samples of 7.00 mm outer diameter and 3.04 mm inner diameter. The EM parameters of a toroidal-shaped sample of an Fe nanocapsule/paraffin composite with a concentration of the ZnO-coated Fe nanocapsules was 40 wt %, and with a height of 2.00 mm, in which they were measured at 2–18 GHz by using an Agilent 8722ES network analyzer.

Figure 2(a) shows the frequency dependence of the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the relative permittivity of the paraffin-Fe nanocapsule composite sample. $\varepsilon'$ is almost constant in the 2–18 GHz range, while $\varepsilon''$ shows an increase from 0.9 to 1.8 in the whole frequency range. According to free-electron theory,[11] $\varepsilon'' \approx 1/2\pi\varepsilon_0\rho f$, where $\rho$ is the resistivity. The resistivity of the ZnO-coated Fe nanocapsules is around 200 $\Omega$ m, which is higher than that of Ni(C) nanocomposites[1] and Fe(C) nanocapsules.[2] This high resistivity is ascribed to the effective dispersion, as shown in Fig. 1(a), and the protective ZnO shell at the surface of the Fe particles, which plays the role of insulator.[1,4,5] In addition, it has been found that the real and imaginary permittivities of ZnO-coated Fe nanocapsules exhibit significant fluctuations, in the range of 2–18 GHz, which is ascribed to displacement current lag at the "core/shell" interface, which is similar to in Fe(C) nanocapsules.[2]

The characteristic feature of ZnO is that it is dielectric, while the dominant dipolar polarization and the associated relaxation phenomena constitute the loss mechanisms. Composite materials, in which magnetic particles are coated with a dielectric nanolayer, introduce additional interfaces and more polarization charges at the surface of the particles. Since ZnO-coated Fe nanocapsules are a heterogeneous system, the interfacial polarization is an important polarization process and the associated relaxation will also give rise to a loss mechanism. It is reasonable to expect that the dielectric loss may be due to significant contributions to the polarization and the interfacial polarization.[1,9] In general, high electrical resistivity and proper dielectric loss are favorable for improving the microwave-absorption properties.

The real part ($\mu'$) and the imaginary part ($\mu''$) of the relative permeability are plotted in Fig. 2(b) as a function of frequency in the range 2–18 GHz. $\mu'$ decreases from 1.19 to 0.98 in the 2–18 GHz range and $\mu''$ exhibits broad multiresonance peaks at 2–14 GHz, with a maximum value of

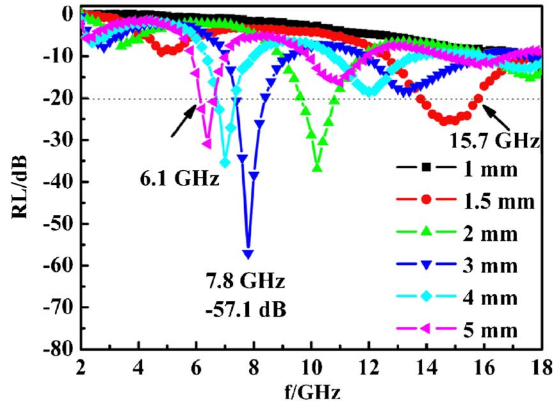


FIG. 3. (Color online) Microwave RL of a ZnO-coated Fe nanocapsule-paraffin wax samples as a function of frequency.

0.26 at 7.2 GHz, which implies that natural resonance occurs in the ZnO-coated Fe nanocapsules. In addition, it can be speculated that the multiresonance peaks, shown in Fig. 2(b), are a consequence of the small size of the particles, the surface effect, and spin-wave excitations, defined as "exchange mode" resonance and where the resonance frequency is dependent on the radii of the particles.[2,12,13] These multiresonance phenomena have been analyzed in detail in recent investigations[12,13] and multiresonance was observed when the size of the metallic magnetic particles was reduced. According to the natural-resonance equation[14] $2\pi f_r = rH_a$, where $r = 2.8$ GHz kOe$^{-1}$ is the gyromagnetic ratio and $H_a = 4|K_1|/3\mu_0 M_s$ is the anisotropy coefficient ($K_1$) for bulk $\alpha$-Fe which is about $4.81 \times 10^4$ J m$^{-3}$ the natural-resonance frequency ($f_r$) should be around several tens of megahertz. The anisotropy energy of small size particles, especially on nanometer scale, may be remarkably increased due to the surface anisotropic field affected by the very-small-size effect.[15] The maximum of the curve for the ZnO-coated Fe nanocapsules has shifted to a higher frequency value (7.2 GHz), which is important for their use as EM-wave-absorption materials in the higher-frequency region.

Generally, excellent EM-wave absorption results from efficient complementarities between the relative permittivity and permeability in materials. Only magnetic loss or only dielectric loss leads to a weak EM matching. In the case of the ZnO-coated Fe nanocapsules, a better EM matching is realized due to the existence of the protective ZnO shells and their particular core/shell microstructure. To further reveal the microwave-absorption properties, the reflection-loss (RL) curves were calculated from the relative permeability and permittivity at a given frequency and absorber thickness by means of the following expressions:[4,5]

$$Z_{\mathrm{in}} = Z_0(\mu_r/\varepsilon_r)^{1/2} \tanh[j(2\pi f d/c)(\mu_r\varepsilon_r)^{1/2}],$$

$$\mathrm{RL} = 20 \log|(Z_{\mathrm{in}} - Z_0)/(Z_{\mathrm{in}} + Z_0)|,$$

where $f$ is the frequency of the EM wave, $d$ is the thickness of the absorber, $c$ is the velocity of light, $Z_0$ is the impedance of air, and $Z_{\mathrm{in}}$ is the input impedance of the absorber.

Figure 3 shows the relationship between the RL and the frequency for the nanocapsules in the 2–18 GHz range. It is seen that an optimal RL of −57.1 dB is reached at 7.8 GHz for a layer of 3.00 mm thickness, while the absorption exceeding −20 dB is obtained in the 6.1–15.7 GHz range for an absorber thickness of 1.5–5 mm. The EM-wave-

TABLE I. EM-wave-absorption properties of some representative nanomaterials.

| Sample | Optimal RL value (dB) | $d_m$ (mm) (RL < −20 dB) | $f_m$ (GHz) (optimal RL) | Frequency range (GHz) (RL < −20 dB) | Reference |
|---|---|---|---|---|---|
| Ni/C | −32 | 2 | 13 | 10.2–18 | 1 |
| Fe/SmO | −52 | 7.9–13.1 | 0.95 | 0.73–1.30 | 3 |
| $Fe/Y_2O_3$ | −36 | 3–5 | 2.6 | 2–3.5 | 4 |
| $Fe/Fe_3B/Y_2O_3$ | −33 | 3–6 | 4.5 | 2.7–6.6 | 5 |
| Fe/C | −34 | 3–5 | 9.6 | 4.4–8.3 | 16 |
| Ni/polyaniline | −22 | 2–6 | 5 | 5–6 | 16 |
| Fe/ZnO | −57.1 | 1.5–5 | 7.8 | 6.1–15.7 | Present work |

absorption properties of Ni/C, Fe/SmO, $Fe/Y_2O_3$, $Fe/Fe_3B/Y_2O_3$, Fe/C, and Ni/polyaniline nanocomposites are summarized in Table I. The RLs for cagelike $ZnO/SiO_2$ nanocomposites,[6] ZnO whiskers,[7] ZnO nanowire polyester,[8] and ZnO-coated barium ferrite composites[9] are relatively poor, with RL > −20 dB in the 2–18 GHz range. It is worth noting that ZnO-coated Fe nanocapsules possess the broader frequencies ranges (RL < −20 dB) and the thinner absorber matching thickness (RL < −20 dB). A RL value of −20 dB corresponds to 99% attenuation of the EM wave and can be considered as effective absorbance in practical applications. In addition, the optimal RL obviously shifts to the lower-frequency range with increasing thickness of the layer. The special core/shell microstructure of the present nanocapsules with ZnO shells and ferromagnetic iron cores is vital for the above phenomenon. It affects the EM properties through homogeneously dispersed nanoparticles coated by ZnO shell, reducing the magnetic-coupling effect between nanoparticles, increasing the effective surface anisotropy of nanoparticles, and realizing EM matching in the nanoscaled geometry.[1]

In conclusion, ZnO-coated Fe nanocapsules exhibit strong EM absorption properties (RL < −20 dB) in the 6.1–15.7 GHz range for an absorber thicknesses of 1.5–5 mm and an optimal RL (−57.1 dB) at 7.8 GHz for a 3.00 mm thick layer. The excellent microwave-absorption properties mainly result from proper EM matching in the microstructure, the strong natural resonance, as well as the multipolarization of the core/shell interface. As a result, nanocapsules with dielectric ZnO shells and ferromagnetic Fe cores are attractive candidates for EM-wave absorption.

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