Ag nanoshell-induced dual-frequency electromagnetic wave absorption of Ni nanoparticles

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The electromagnetic wave absorption properties of the epoxy resin composites containing Ni, Ag, and Ni–Ag core-shell nanoparticles were studied. Interestingly, Ni–Ag core-shell nanoparticles showed a dual-frequency absorption property in 2–18 and 18–40 GHz, although Ni nanoparticles exhibited absorption only in 18–40 GHz and no absorption was observed for Ag nanoparticles in the whole frequency range. The additional absorption of Ni–Ag core-shell nanoparticles in 2–18 GHz might be due to the lags of polarization between the core/shell interfaces, which contributed to the dielectric loss. The frequency dependences of permittivity and permeability and the absorber thickness effect were also investigated. © 2007 American Institute of Physics. [DOI: 10.1063/1.2731706]

Recently, various electronic and communication devices using the electromagnetic (EM) wave of 1–40 GHz range are being developed rapidly because of the advantage of large data transmission.1 For the normal operation of devices, the human health, and the applications in microwave darkrooms and national defense industry, the corresponding EM wave absorbers received increasingly considerable attention.2,3 The reflection and attenuation properties of EM wave absorbers depend on the matching frequency, layer thickness of absorbers, and the relative complex permeability and permittivity, which are determined by their nature, shape, size, and microstructure.4,5 Compared to the conventional ferrites, metallic soft magnetic materials may be more suitable as the microwave absorbers in the frequency range over gigahertz because of the high Snoek’s limit.1,5 However, their relative complex permeability may decrease due to the eddy current loss. To avoid this problem, it is better to use the isolated metallic particles with size less than the skin depth.4,5 So, many submicrometer-sized metallic magnetic particles and nanocomposites embedded in the nonconductive matrices have been developed.1,2,4,5 Now the EM wave absorbers are further requested to possess more advantages such as light and thin, wide absorption frequency, multifrequency absorption, high thermal stability, and antioxidation. Metal magnetic nanoparticles may be quite suitable as EM wave absorbers because of small size, large specific surface area, high surface atom percentage, and more dangling chemical bonds, which might lead to the interface polarization and the activation of nanoparticles. However, each kind of nanoparticles has its intrinsic properties and usually can be used only in a specified frequency range. To meet the above requirements, the development of composite nanoparticles may be an efficient strategy.

Recently we prepared monodisperse Ni–Ag core-shell nanoparticles.6 They not only possessed the optical property of Ag nanoshells and the magnetic property of Ni cores but also exhibited better antioxidation property than Ni nanoparticles. Such a product may be used as an EM wave absorber. So, the EM wave absorption property was studied in this work.

Ni–Ag core-shell nanoparticles were prepared by the successive hydrazine reduction of nickel chloride and silver nitrate in ethylene glycol using polyethyleneimine (PEI) as a protective agent.6 Firstly, Ni nanoparticles were prepared by adding nickel chloride (50 mM), hydrazine (1.0M), and 0.1M NaOH (40 μl/ml) into ethylene glycol and then heating the solution to 60 °C. When the solution became gray black which indicated the formation of Ni nanoparticles, the solution was immediately cooled in an ice bath at 0 °C to avoid the agglomeration of Ni nanoparticles. Secondly, for the coating of Ag nanoshells, PEI (5 wt %) was added and the solution was thermostated in an ultrasonic bath at 25 °C and mixed with an equal volume of ethylene glycol solution containing silver nitrate (56 mM). The solution became brown immediately, revealing the formation of Ni–Ag core-shell nanoparticles. For comparison, pure Ag nanoparticles were prepared following the above Ag-coating process in the absence of Ni nanoparticles. The products were characterized by x-ray diffraction (XRD), transmission electron microscope (TEM), and superconducting quantum interference device magnetometer to determine their structures, sizes, and magnetic properties.

Epoxi resin composites were prepared by homogeneously mixing the Ni, Ag, or Ni–Ag core-shell nanoparticles with the ethanol solution of epoxy resin and casting on the transparency film. The ratio of metal nanoparticles to the epoxy resin was fixed at 4:5 by weight. The composites were cured and then cut into sheet samples of 15×15×1 cm³ with thicknesses of 1.45, 2.0, and 1.8 mm for the cases of Ni, Ag, and Ni–Ag core-shell nanoparticles, respectively. The reflection loss (RL) of each sheet sample backed by the same-sized reference metal plate in 2–18 and 18–40 GHz was measured using free space method developed by Damaskos Inc., known as free-space antenna-based inverted arch system, and a HP8722ES network analyzer. The RL values were obtained using the reflection level of reference metal plate. The relative permittivity (εr) and permeability (μr) values were calculated from the scattering parameters measured by the HP8722ES network analyzer. The RL curves at various fre-
had face-centered cubic structure and were nearly superparamagnetic. More detailed information could be found elsewhere.6

The RL curves for the epoxy resin composites containing Ni, Ag, and Ni–Ag core-shell nanoparticles 2–40 GHz were obtained as indicated in Fig. 2. Obviously, Ni nanoparticles showed a significant absorption in 18–40 GHz with a maximum RL of 23.3 dB at 31.8 GHz, revealing magnetic metal nanoparticles indeed could be used as EM wave absorbers. For Ag nanoparticles, no significant absorption was observed in the whole frequency range examined, probably due to the fact that Ag was not magnetic metal and no interconnected network was formed within the matrix. It is interesting and notable that Ni–Ag core-shell nanoparticles not only remained a significant absorption in 18–40 GHz with a maximum RL of 25.7 dB at 31.5 GHz, but also showed an additional absorption in 2–18 GHz with a maximum RL of 23.6 dB at 10.8 GHz. Recently, Zhang et al. reported the EM wave absorption of the carbon-coated Ni nanocapsules in 2–18 GHz.5 Unfortunately, the absorption behavior in 18–40 GHz was not studied. Such a dual-frequency EM wave absorption property of the magnetic metal nanoparticles coated with nonmagnetic metal nanoshells has not been reported. Since Ag nanoparticles had no absorption in 2–18 GHz, the additional absorption of Ni–Ag core-shell nanoparticles in this frequency range might be due to the lags of polarization between the core/shell interfaces as the frequency was varied, which contributed to the dielectric loss.3 The true mechanism needs more studies. Because the multiresonance absorption peaks in the RL curves might be arisen from the differences in the complex permittivity and permeability or the thickness of absorbers,7,8 further investigations about these effects were given below.

Figure 3 shows the frequency dependences of the real parts ($\varepsilon'_r$ and $\mu'_r$) and imaginary parts ($\varepsilon''_r$ and $\mu''_r$) of the relative complex permittivity and permeability for the epoxy resin composites containing Ni–Ag core-shell nanoparticles. The frequency dependences of the $\varepsilon'_r$, $\varepsilon''_r$, $\mu'_r$, and $\mu''_r$ values of the epoxy resin composites containing Ni–Ag core-shell nanoparticles in 2–40 GHz were indicated in Fig. 4. In 18–40 GHz, the frequency dependences of $\varepsilon'_r$, $\varepsilon''_r$, $\mu'_r$, and $\mu''_r$ values were similar to those for Ni nanoparticles, revealing they were contributed by the Ni cores. In 2–18 GHz, with increasing frequency, the $\varepsilon'_r$ value decreased from 27 to 5 while the $\varepsilon''_r$ value roughly remained constant (within 9–14). Also, both values were large, revealing the dielectric loss was significant. This could be attributed to the lags of polarization between the core/shell interfaces and accounted for the appearance of an additional absorption in 2–18 GHz. In addition, the $\mu'_r$ value remained almost constant while the $\mu''_r$ value decreased slightly with increasing frequency in 2–18 GHz. Accordingly, it could be deduced that the dual-frequency absorption phenomenon of Ni–Ag core-shell nanoparticles should belong to the changes in the complex permittivity and permeability, particularly the increase of $\varepsilon'_r$. 

The frequency dependences of the $\varepsilon'_r$, $\varepsilon''_r$, $\mu'_r$, and $\mu''_r$ values of the epoxy resin composites containing Ni–Ag core-shell nanoparticles in 18–40 GHz were indicated in Fig. 4. In 18–40 GHz, the frequency dependences of $\varepsilon'_r$, $\varepsilon''_r$, $\mu'_r$, and $\mu''_r$ values were similar to those for Ni nanoparticles, revealing they were contributed by the Ni cores. In 2–18 GHz, with increasing frequency, the $\varepsilon'_r$ value decreased from 27 to 5 while the $\varepsilon''_r$ value roughly remained constant (within 9–14). Also, both values were large, revealing the dielectric loss was significant. This could be attributed to the lags of polarization between the core/shell interfaces and accounted for the appearance of an additional absorption in 2–18 GHz. In addition, the $\mu'_r$ value remained almost constant while the $\mu''_r$ value decreased slightly with increasing frequency in 2–18 GHz. Accordingly, it could be deduced that the dual-frequency absorption phenomenon of Ni–Ag core-shell nanoparticles should belong to the changes in the complex permittivity and permeability, particularly the increase of $\varepsilon'_r$. 

The frequency dependences of the $\varepsilon'_r$, $\varepsilon''_r$, $\mu'_r$, and $\mu''_r$ values of the epoxy resin composites containing Ni–Ag core-shell nanoparticles in 18–40 GHz were indicated in Fig. 4. In 18–40 GHz, the frequency dependences of $\varepsilon'_r$, $\varepsilon''_r$, $\mu'_r$, and $\mu''_r$ values were similar to those for Ni nanoparticles, revealing they were contributed by the Ni cores. In 2–18 GHz, with increasing frequency, the $\varepsilon'_r$ value decreased from 27 to 5 while the $\varepsilon''_r$ value roughly remained constant (within 9–14). Also, both values were large, revealing the dielectric loss was significant. This could be attributed to the lags of polarization between the core/shell interfaces and accounted for the appearance of an additional absorption in 2–18 GHz. In addition, the $\mu'_r$ value remained almost constant while the $\mu''_r$ value decreased slightly with increasing frequency in 2–18 GHz. Accordingly, it could be deduced that the dual-frequency absorption phenomenon of Ni–Ag core-shell nanoparticles should belong to the changes in the complex permittivity and permeability, particularly the increase of $\varepsilon'_r$. 

FIG. 1. Typical TEM images of Ni (a), Ag (b), and Ni–Ag core-shell (c) nanoparticles.

FIG. 2. Reflection loss curves for the epoxy resin composites containing Ni, Ag, or Ni–Ag core-shell nanoparticles in 2–18 (a) and 18–40 GHz (b).

FIG. 3. Frequency dependences of the real part ($\varepsilon'_r$ and $\mu'_r$) and imaginary part ($\varepsilon''_r$ and $\mu''_r$) of the relative complex permittivity and permeability for the epoxy resin composites containing Ni–Ag core-shell nanoparticles.
and \(\varepsilon''_r\) values in 2–18 GHz owing to the lags of polarization between the core/shell interfaces.

Moreover, it is noticeable that the \(\varepsilon'_r\), \(\varepsilon''_r\), \(\mu'_r\), and \(\mu''_r\) values were negative in some frequency ranges. This might be meaningless in physics because these values were obtained by simulation based on the scattering parameters and the negative values might be just arisen from noise or experimental artefacts. However, theoretically, the metallic magnetic nanoparticles might be used as the material with negative permeability and permittivity (so-called left-handed materials) whose permittivity and permeability were negative.\(^9\)-\(^11\) So, the negative \(\varepsilon'_r\), \(\varepsilon''_r\), \(\mu'_r\), or \(\mu''_r\) values also might imply that Ni or Ni–Ag core-shell nanoparticles had the potential as the left-handed materials. More studies and precise measurement were necessary.

According to Eqs. (1) and (2), the RL curves for the epoxy resin composites containing Ni or Ni–Ag core-shell nanoparticles at various thicknesses could be calculated as shown in Fig. 5. For Ni nanoparticles, a maximum RL of 26.0 dB at 32.5 GHz appeared at an absorber thickness of 1.4 mm in 18–40 GHz. For Ni–Ag core-shell nanoparticles, a maximum RL of 37.0 dB at 13.3 GHz appeared at an absorber thickness of 1.4 mm in 2–18 GHz and a maximum RL of 26.0 dB at 32.0 GHz at an absorber thickness of 1.8 mm in 18–40 GHz. In addition, in the thickness range examined, the change in the thickness just resulted in the shift of absorption frequency in 2–18 or 18–40 GHz. No multiresonance absorption peaks appeared due to the change in the thickness of absorber. So, the dual-frequency absorption phenomenon of Ni–Ag core-shell nanoparticles could not be referred to the difference in the thickness of absorber. Thus, it could be concluded that the dual-frequency absorption phenomenon of Ni–Ag core-shell nanoparticles was mainly arisen from the changes in the complex permittivity and permeability.

In summary, the EM wave absorption behaviors of the epoxy resin composites containing Ni, Ag, and Ni–Ag core-shell nanoparticles were investigated. It was found that Ag nanoparticles had no significant absorption in 2–40 GHz and Ni nanoparticles showed a significant absorption in 18–40 GHz, but Ni–Ag core-shell nanoparticles exhibited dual-frequency absorption behavior in 2–18 and 18–40 GHz. Such a finding was interesting and important.

The permittivity, permeability, and the RL curves at various absorber thicknesses were also studied. This work will be helpful for the development of multifrequency EM wave absorbers.

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