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Preparation and microwave characterization of submicrometer-sized hollow nickel spheres

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Abstract

The hollow structural submicrometer-sized nickel spheres were successfully fabricated by the autocatalytic reduction method. Because of the metallic and ferromagnetic behaviour of the nickel spheres, the low-density microspheres could obtain high dielectric constant and magnetic loss in microwave frequencies. The abrupt variation of the real part and the sharp peaks of the imaginary part of permittivity and permeability were observed for the micrometer-sized and nanometer-sized nickel hollow spheres. Reflection loss less than −25 dB were predicted over 11 GHz with a thickness of 1.5–2.0 mm.

Keywords: Submicrometer-sized particles; Hollow spheres; Autocatalytic reduction; Microwave absorption

1. Introduction

There is intensive interest in the preparation of electromagnetic (EM) materials with low reflectivity recently. Because EM interference has been a serious problem due to explosive growth in the utilization of electronic devices in industrial, commercial, and military applications [1]. One way to make EM absorbers is to disperse magnetic powders including ferrites and iron, cobalt, and nickel metal or alloy powders in an insulating matrix [2,3]. Previous studies [4,5] showed that the microwave properties of EM materials largely depend on particle shape, granulometry, and structure. And increasing interest has been given to the synthesis of micrometer- and nanometer-sized EM materials with specific morphologies in recent years.

There were also reports [6–10] on submicrometer-sized particles with hollow structure often exhibiting novel properties dramatically different from their solid counterparts in the fields of chemistry, physics, biotechnology, and materials science, and thus making them attractive from both scientific and technological viewpoints. However, studies of hollow particles for the application in microwave absorbers were very limited. In the present study, the microwave absorption behaviours of the submicrometer-sized hollow nickel particles by an autocatalytic reduction method are reported.

2. Experimental methods

2.1. Preparation of hollow nickel spheres

By means of an autocatalytic reduction method [11], hollow nickel spheres were prepared with analytically pure $NiSO_4 \cdot 6H_2O$, $NaH_2PO_2 \cdot H_2O$, NaOH, acetic acid and citric acid as starting materials. During the preparation process, 20 g nickel sulfate was dissolved in 200 ml solution containing 0.1 g acetic acid and 0.15 g citric acid to prepare a mixed nickel solution. About 25 g sodium hydroxide and 3 g sodium hypophosphite were dissolved in 200 ml de-ionized water in beakers, respectively. And the solutions were preheated at 80 °C for 5 min. Then the nickel solution and alkali solution were mixed by violent stirring, and a viridescent colloid was produced. And then the sodium hypophosphite solution was added to the as-prepared colloid by evenly stirring. Finally, a dark-gray powder was obtained after the reaction had taken place for 2–5 min, and the powder was repeatedly washed with

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ammonia and de-ionized water. The final products were dried in vacuum furnace at 100 °C for 2 h.

2.2. Characterization techniques

Field-emission scanning electron microscopy (FESEM) measurements were performed with a Philips XL30FEG operated at an accelerating voltage of 10 kV. FESEM samples (on silicon surface) were coated with about 5 nm Au. Transmission electron microscopy (TEM) images were recorded on a Philips CM200FEG microscope operating at 50 kV. Samples for TEM were sonicated in acetone for 10 min (to redisperse the hollow spheres) and subsequently deposited onto a carbon grid. Structural characterization was performed by means of X-ray diffraction using a D/Max-γB diffractometer with Cu-Kα radiation at an accelerating voltage of 40 kV.

The composite samples were prepared by homogeneously mixing the nickel powders with polypropylene in a volume ratio (volume of nickel powder/volume of polypropylene) of 1:1. The mixture was made into toroidal-shaped samples with an outer diameter of 7.0 mm and inner diameter of 3.0 mm. The complex permeability and permittivity of composite were measured using an Agilent E8362B PNA network analyzer in the frequency range of 2–18 GHz.

3. Results and discussion

In our studies, the submicrometer-sized hollow nickel spheres were fabricated by the autocatalytic reduction method [11]. The redox reaction used in electroless nickel (EN) deposition process was catalyzed around the nickel hydroxide ($Ni(OH)_2$) colloidal particles and the metal nickel assembled around the particle surfaces and the colloidal particles sacrificed during the process. Typical examples of nickel particles obtained by autocatalytic reduction method are provided by the FESEM micrography in Fig. 1. The particles are perfect spherical with the mean diameter $d_m = 1\,\mu m$ (Fig. 1(a)) and $d_m = 60\,nm$ (Fig. 1(b)), and show the narrow size distribution and the low degree of agglomeration. The colloid nuclear give particles in the submicrometer-size range and allow their mean diameter to be controlled by varying the concentration of NaOH used to form the colloid particles [11]. A broken sphere (Fig. 1(a) inset) was obtained by slightly grinding the samples shown in Fig. 1(a), demonstrating the samples with the hollow inner and the shell outside. A hollow nanometer-sized nickel spheres was shown in Fig. 1(b) inset by the TEM.

From X-ray diffraction (XRD) patterns (Fig. 2) it can be inferred that both the diffraction peaks of the micrometer-sized and nanometer-sized spheres were broadened and the nanometer-sized spheres show a broader peak. The XRD

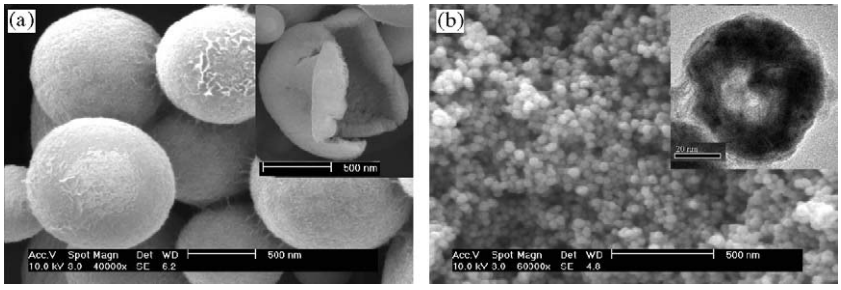

Fig. 1. FESEM micrographs of micrometer-sized (a) and nanometer-sized (b) nickel spheres were obtained by autocatalytic reduction. A broken sphere can be seen in (a) inset, and a hollow structural nanometer-sized sphere by TEM is shown in (b) inset.

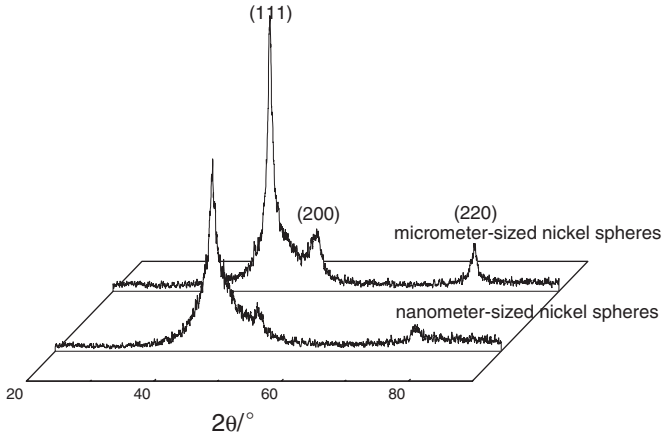

Fig. 2. XRD pattern indicated the Ni spheres were the face-centered cubic (FCC) structure.

patterns of the samples indexed both the micrometer-size and nanometer-size nickel spheres as the face-centered cubic (FCC) lattice. It is well known that nickel crystallize with a FCC lattice and $\alpha = 0.3528$ nm [12]. However, the as-synthesized spheres show their lattice parameters are 0.35147 nm (micrometer-sized particles) and 0.35102 nm (nanometer-sized particles). These phenomena indicate that the spheres are composed of nanocrystallites and the crystallites have distinct shrinkage.

Fig. 3 shows the real and imaginary of permittivity ε'_r,ε''_r of nickel hollow spheres–polypropylene composites. It is interesting that the curves of the real part of permeability exhibit the abrupt decrease, while the imaginary part of permeability shows the sharp peak at the corresponding frequency. This suggests a resonance behavior, which is expected when the composite is highly conductive and skin effect becomes significant [13]. In our studies, the resonant frequency of the nickel spheres composite is related to the hollow structure and the high conductivity of nickel. However, the exact mechanism yet is not ascertained. The decreasing amplitude of ε'_r is higher for the micrometer-sized nickel spheres composites than the nanometer-sized ones, and the abrupt decrease shifts to higher frequency. The higher value of dielectric constant is attributed to better metallic behavior of micrometer-sized nickel spheres compared with nanometer spheres.

The real and imaginary part of permeability μ'_r,μ''_r of nickel hollow spheres–polypropylene composites is shown in Fig. 4. As shown in the figures, the real part and imaginary part of the complex permeability also exhibit a sharp curve at the resonance frequency regions. The value of μ'_r decreases at frequency $\leqslant 9$ GHz for composites of micrometer-sized nickel hollow spheres and at frequency $\leqslant 12$ GHz for composites of nanometer spheres, and the abrupt increase occurs subsequently. The sharp peaks of μ''_r are observed at frequency 10.6 GHz for composites of micrometer-sized nickel hollow spheres and at 13.8 GHz for composites of nanometer spheres. Such behavior may be related to the resonance frequency of the nickel hollow spheres, and the shift of the resonance frequency can be interpreted by a variation of particle size [14].

The normalized input impedance Z_{in} of a single metal-backed microwave absorbing layer is given by [15]

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \frac{2\pi f d \sqrt{\mu_r \varepsilon_r}}{c}, \quad (1)$$

where μ_r and ε_r are the relative complex permeability and permittivity, respectively, of the composite medium, c the velocity of electromagnetic waves in free space, f the

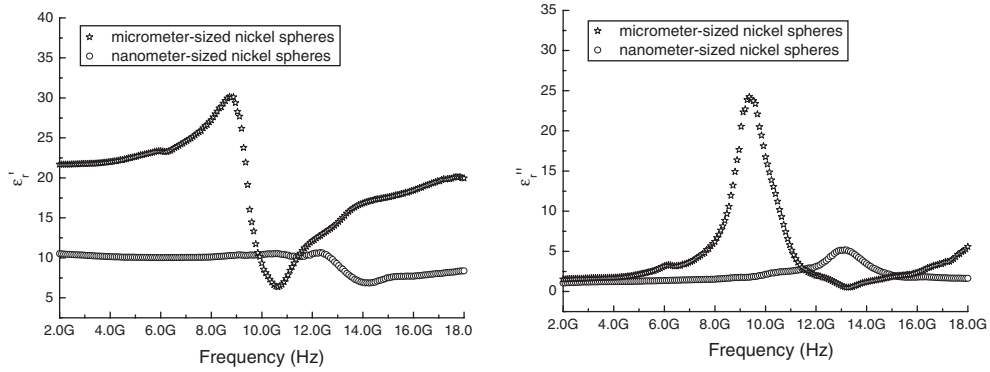

Fig. 3. Frequency dependence of the real part and imaginary part of the complex permittivity of micrometer-sized and nanometer-sized nickel hollow sphere composites.

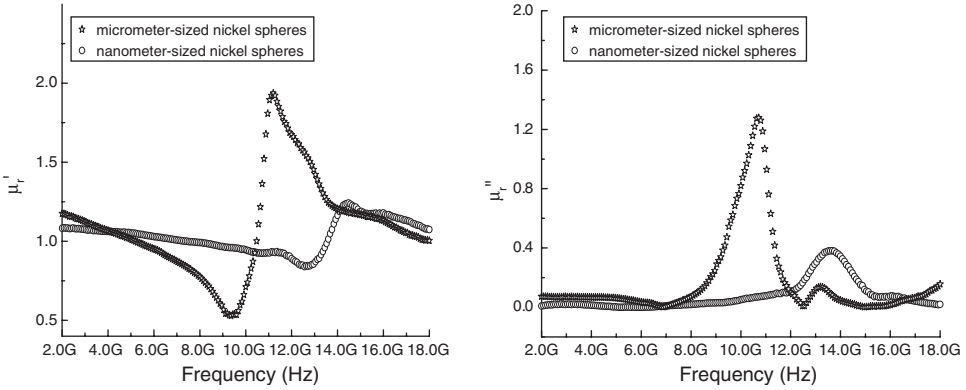

Fig. 4. Frequency dependence of the real part and imaginary part of the complex permeability of micrometer-sized and nanometer-sized nickel hollow spheres composites.

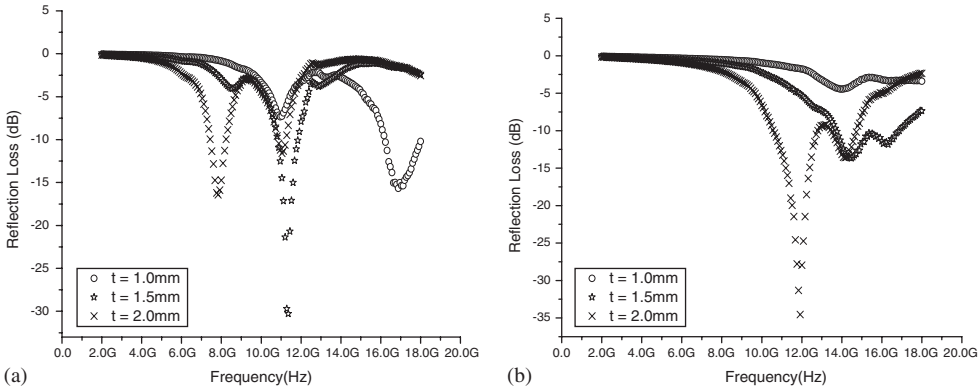

Fig. 5. Frequency dependence of the reflection loss of the nickel hollow spheres: (a) micrometer-sized and (b) nanometer-sized composites at various sample thickness.

frequency of microwaves, and d the thickness of the absorber. The reflection loss is related to Z_{in} by [15]

$$R_L = 20lg\left|\frac{Z_{in}-1}{Z_{in}+1}\right|. \quad (2)$$

Thus, the surface reflectance of an absorber is a function of six characteristic parameters, viz., μ'_r,μ''_r,ε'_r,ε''_r, f, and d. Fig. 5 shows the calculated reflection loss as a function of frequency for micrometer-sized and nanometer-sized nickel hollow spheres composites of different thicknesses. The calculations use the actual values of ε_r and μ_r as shown in Figs. 3 and 4. The reflection loss is found to depend sensitively on the thickness of the absorber. The maximum attenuation of the incident wave is predicted for a thickness of 1.5 mm for micrometer-sized nickel hollow spheres composites, and 2.0 mm for nanometer spheres. The minimal reflection of the nanometer hollow spheres composites is decreased with an increase in the thickness of the absorber ($d = 2.0$ mm, $R_L = -34.5$ dB); however, the micrometer spheres composites have the minimal reflection loss (−30 dB) in the thickness at 1.5 mm. It is suggested that the reflection loss is related to a matching thickness.

4. Conclusion

The hollow structural submicrometer-sized nickel spheres were successfully fabricated by the autocatalytic reduction method. Due to the hollow structural, the low-density (3.0359 g/cm^3) microspheres could be prepared, and high dielectric constant and magnetic loss could be obtained in microwave frequencies because of the metallic and ferromagnetic behavior of the nickel spheres. The abrupt variation of the real part and the sharp peaks of the imaginary part of permittivity and permeability were observed for the micrometer-sized and nanometer-sized nickel hollow spheres. Reflection loss less than −25 dB were predicted over 11 GHz with a thickness of 1.5–2.0 mm. This absorber is well advanced in both mass and thickness in comparison with the conventional ferrite absorber.

Acknowledgments

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