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Facile synthesis, magnetic and microwave absorption properties of Fe_3O_4/polypyrrole core/shell nanocomposite

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ABSTRACT

Fe_3O_4/polypyrrole (PPy) core/shell nanocomposite, with Fe_3O_4 nanoparticle as core and PPy as shell, could be facilely synthesized via *in situ* chemical oxidative polymerization of pyrrole monomers on the surface of Fe_3O_4 nanoparticles. The results indicate that core/shell nanocomposite consists of Fe_3O_4 core with the mean diameter of 100 nm and adjacent PPy shell with a thickness of about 70 nm. The as-prepared Fe_3O_4/PPy core/shell nanocomposite exhibits a saturated magnetization of 20.1 emu/g and coercivity value of 368.3 Oe, respectively. The electromagnetic characteristics of Fe_3O_4/PPy core/shell nanocomposite were also investigated with a vector network analyzer in the 2–18 GHz range. The absorbing peak position moves to lower frequency with increasing the thicknesses of samples. The value of the minimum reflection loss is −22.4 dB at 12.9 GHz for Fe_3O_4/PPy core/shell nanocomposite with a thickness of 2.3 mm, and a broad peak with a bandwidth lower than −10 dB is about 5 GHz. Such strong absorption is attributed to better electromagnetic matching due to the existence of PPy and the special core/shell structure.

1. Introduction

There has been a growing and widespread interest in microwave absorption materials for many years as a result of the serious electromagnetic interference pollution arising from mobile phones, radar systems and various electronic devices [1–3]. Magnetite as a conventional microwave absorption material has drawn considerable attention because of its high specific resistance and excellent microwave absorption property. However, magnetite has some difficulties based on increasing the permeability in GHz region because of Snoek limit induced by the electromagnetic wave. Furthermore, the high density and low resistance from corrosion of magnetite also confine its further application in microwave absorption. Therefore, it is necessary to exploit the new type of microwave absorption materials in a much wider and higher frequency range.

Inorganic nanoparticles coated with conducting polymer to form core/shell structured materials has been demonstrated to be an effective strategy to enhance the stability of composites and widen the applications because of the strong electronic interaction between the inorganic core and polymer shell [4,5]. Polypyrrole (PPy), as a typical conducting polymer, has drawn more attention due to its relatively easy preparation, excellent environmental stability and good electrical conductivity [6,7]. PPy shells containing metal and oxide nanoparticles have been prepared and investigated for different applications. We have successfully fabricated PPy hollow spheres with controllable sizes, which can be applied in as delivery vehicle for the removal of contaminated waste and the controlled release of substances such as drugs, cosmetics and dyes [8]. Xu et al. have synthesized $BaFe_{12}O_{19}$/PPy composite by a conventional *in situ* chemical oxide polymerization and found the composite with enhanced reflection loss properties [9]. Wuang et al. have prepared Fe_3O_4/PPy core/shell composite for application in biomedicine [10]. Therefore, we were motivated to prepare the Fe_3O_4/PPy core/shell nanocomposite with its dielectric loss ability and improve the microwave absorption property of the magnetite.

In this paper, electromagnetic functionalized Fe_3O_4/PPy core/shell nanocomposite was prepared by a conventional *in situ* chemical oxidative polymerization in the presence of Fe_3O_4 nanoparticles. Magnetic studies revealed that Fe_3O_4/PPy core/shell nanocomposite is ferromagnetic with a saturation magnetization of 20.1 emu/g and covercivity value of 368.3 Oe, respectively. The electromagnetic characteristics of Fe_3O_4/PPy core/shell nanocomposite showed that the absorbing peak position moves to lower frequency with increasing thicknesses of samples. The value of the minimum reflection loss is −22.4 dB at 12.9 GHz for Fe_3O_4/PPy core/shell nanocomposite with a thickness of 2.3 mm and a broad

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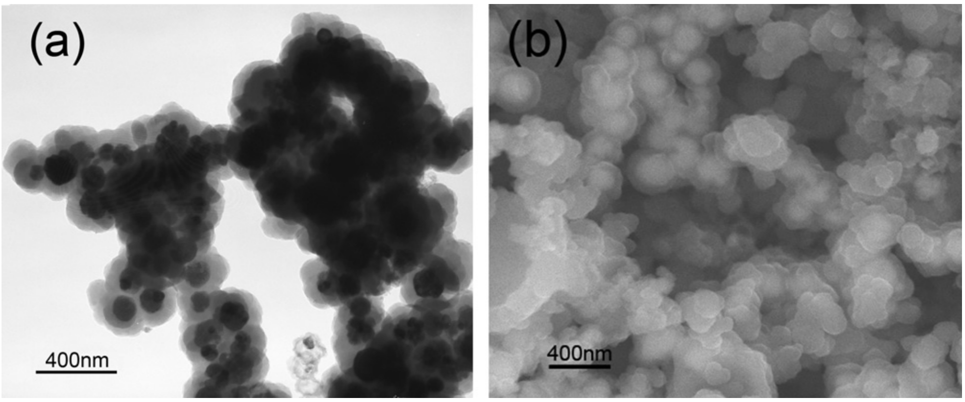

Fig. 1. TEM (a) and SEM (b) images of Fe_3O_4/PPy core/shell nanocomposite.

peak with a bandwidth lower than −10 dB is of about 5 GHz. We believe that the synthetic strategy may afford a practicable route to prepare other core/shell nanocomposites with desirable properties and open up good prospect for large-scale application in microwave absorption materials in the future.

2. Experimental details

2.1. Synthesis of Fe_3O_4/PPy core/shell nanocomposite

All chemicals were analytical grade and used as starting materials without further purification. The preparation of Fe_3O_4/PPy core/shell nanocomposite involved an initial synthesis of Fe_3O_4 nanoparticles as seeds and then a conventional *in situ* chemical oxidative polymerization in the presence of Fe_3O_4 nanoparticles. The Fe_3O_4 nanoparticles were prepared using our previously developed method [11]. Briefly, $FeCl_3{\cdot}6H_2O$ (1 mmol) and $NaAc{\cdot}3H_2O$ (10 mmol) were added into ethylene glycol (8 ml) to form clear solution, which was turned into a Teflon-lined stainless steel autoclave of 50 ml capacity and maintained at 180 °C for 24 h. The synthesis of Fe_3O_4/PPy core/shell nanocomposites was carried out as follows: Fe_3O_4 (0.2 mmol) nanoparticles were dispersed in distilled water (40 ml) by ultrasound treatment for 10 min to form a dark solution, then pyrrole monomers (0.2 ml) were slowly injected in the mixture under ultrasound for 30 min. The ultrasound contributed to pyrrole monomers absorbed on the surface of Fe_3O_4 nanoparticles. Subsequently, $(NH_4)_2S_2O_8$ (10 ml 1 mM) solution was added dropwisely into the mixture. The polymerization was performed at room temperature for 24 h with constant mechanical stirring. The final product was centrifuged and washed with double-distilled water and absolute ethanol several times, and dried in a vacuum at 60 °C for 4 h.

2.2. Characterization

The obtained samples were characterized on a D/max2550 VB+ X-ray powder diffraction (XRD) with Cu Kα radiation (λ = 1.54178 Å). Fourier-transform infrared spectra (FTIR) of the samples were recorded on a Bruker VECTOR22 spectrometer. The size and morphology of the as-synthesized products were characterized by a JEM-200CX transmission electron microscope (TEM) at 160 kV. Scanning electron microscopy (SEM) images were obtained on a XL30 S-FEG microscope operated at 20 kV. Magnetic properties of the samples were measured by a LDJ-9600 vibrating sample magnetometer (VSM). The samples to be measured were prepared from uniformly mixing the powders (50 wt.%) in paraffin matrix with an absorber thickness of 2.7 mm, and then pressing the mixture into a cylindrical shaped compact (Φ_{outer} = 7.00 mm and Φ_{inner} = 3.04 mm). Complex permeability ($\mu_\gamma = \mu' - j\mu''$) and permittivity ($\varepsilon_\gamma = \varepsilon' - j\varepsilon''$) measurements for the samples were measured by an AV3629 vector network analyzer in the 2–18 GHz range.

3. Results and discussion

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were employed to characterize the morphology and size of as-prepared Fe_3O_4/PPy core/shell nanocomposite. Fig. 1a shows a typical TEM image of Fe_3O_4/PPy core/shell nanocomposite, which clearly indicates the spherical Fe_3O_4 core surrounded by PPy shell. SEM image shown in Fig. 1b further demonstrates as-prepared nanocomposite with typical core/shell structure. Several Fe_3O_4 nanoparticles with mean diameter of about 100 nm serve as the core and are coated by PPy shell with mean thickness of about 70 nm. The average size of Fe_3O_4/PPy core/shell nanostructured nanoparticles is about 240 nm.

X-ray diffraction (XRD) was used to characterize the crystal structure and the chemical components of as-synthesized nanocomposite. Fig. 2 shows a typical XRD pattern of as-synthesized Fe_3O_4/PPy core/shell nanocomposite, and the main peaks could be readily identified as the cubic phase [space group: Fd3m (2 2 7)] of Fe_3O_4 with lattice constant a = 8.396 Å (JCPDS 19-0629). Furthermore, a broad peak is clearly observed at $2\theta = 23°$, which is associated with the amorphous PPy [12], indicating that amorphous PPy exists on the surface of Fe_3O_4.

The structural characterization of as-prepared nanocomposite was further characterized through Fourier-transform infrared (FTIR) spectroscopy, as displayed in Fig. 3. In the spectrum, the bands observed at 1568 and 1474 cm^{-1} relate to the fundamental vibrations of the pyrrole rings. The peaks of C–N stretching vibration and =C–H in-plane vibration are found at 1213 cm^{-1} and 1048 cm^{-1}, respectively, while C–C out-of-plane ring deformation vibration corresponds to 927 cm^{-1}. The peak of C–H ring out-of-plane bending mode shows at 793 cm^{-1} [13], while the peak at 680 cm^{-1} refers to the C–C out-of-plane ring deformation vibration or to the C–H rocking vibration [14]. The appearance of peak at 1693 cm^{-1} is attributed to the over oxidization of PPy [15]. Herein, we can find that only infrared peaks related to the PPy shell are observed, which further demonstrate that Fe_3O_4 nanoparticles are encapsulated inside the PPy shell.

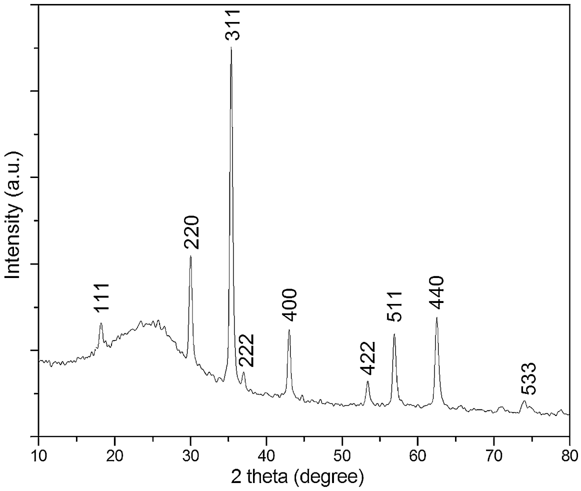

Fig. 2. XRD pattern of Fe_3O_4/PPy core/shell nanocomposite.

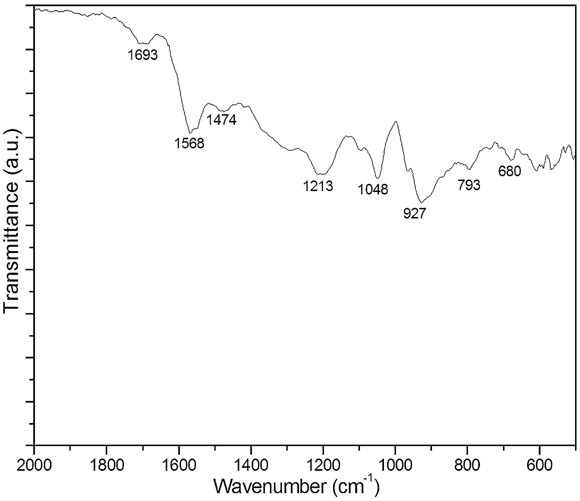

Fig. 3. FTIR spectrum of Fe_3O_4/PPy core/shell nanocomposite.

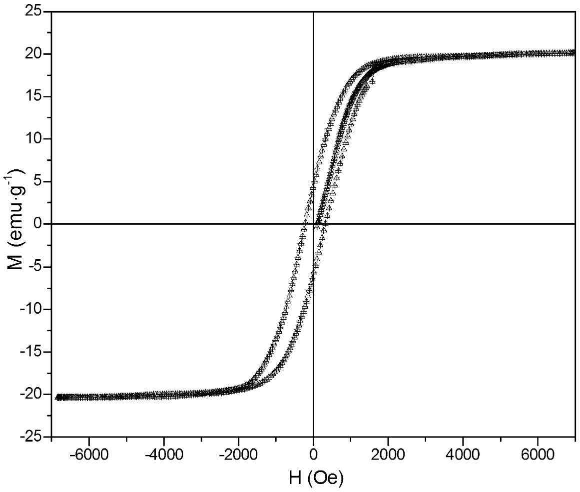

Fig. 4. Magnetic hysteresis loops of Fe_3O_4/PPy core/shell nanocomposite measured at room temperature.

Fig. 4 shows the magnetic property of as-prepared nanocomposite measured at room temperature. The Fe_3O_4/PPy core/shell nanocomposite exhibits a saturated magnetization of 20.1 emu/g and covercivity value of 368.3 Oe, respectively. Compared with the value of pure Fe_3O_4 nanoparticles [11,16], a reduction of saturated magnetization for Fe_3O_4/PPy core/shell nanocomposite can be concluded as a result of the presence of nonmagnetic PPy decreasing the magnetism of magnetic materials.

Complex permeability and permittivity of materials are associated with their microwave absorption properties. As is well known, the real parts of complex permittivity and permeability represent the storage of electric and magnetic energy, respectively. While the imaginary parts of complex permittivity and permeability symbolize the loss of electric and magnetic energy. Fig. 5 shows the real parts and imaginary parts of the relative complex permittivity and permeability of Fe_3O_4/PPy core/shell nanocomposite-paraffin wax sample as a function of frequency. It can be seen that the real part (ε') and imaginary part (ε'') of complex permittivity values of the sample both decline from 11.1 to 3.9 and from 10 to 4.2 in the frequency range, respectively. Compared to other microwave absorption materials [3,17,18], the imaginary permittivity of the sample is higher. This phenomenon may result from the PPy shell due to its dielectric loss at high frequencies. What's more the core/shell microstructure results in additional interface and interfacial polarization at the surface of nanoparticles. The higher imaginary part implies more dielectric loss and makes more electromagnetic energy transfer into heat energy. So it can be inferred that the higher imaginary part could improve the microwave absorption property of the sample. Different from the real and imaginary permittivity, the real permeability (μ') value is nearly constant at about 1.1 with small fluctuation in the range of 2–18 GHz. The imaginary part (μ'') decreases with increasing frequency. It can be seen that it is negative between 7 and 18 GHz, which indicates the magnetic energy is radiated from the nanocomposites with the motion of charges [17].

Generally, the reflection loss (RL) of electromagnetic waves is relative with complex permittivity and permeability as well as thickness of the sample. Excellent RL is originated from efficient complementarities between complex permittivity and permeability in materials. With relative data, the RL (dB) was calculated from the relative permeability and permittivity at the given frequency and absorber thickness using the following equations:

$$Z_{\mathrm{in}} = Z_0\sqrt{\frac{\mu_{\mathrm{r}}}{\varepsilon_{\mathrm{r}}}}\tanh\left[\frac{j2\pi fd\sqrt{\mu_{\mathrm{r}}\varepsilon_{\mathrm{r}}}}{c}\right], \tag{1}$$

$$\mathrm{RL} = 20\log\left|\frac{Z_{\mathrm{in}}-Z_0}{Z_{\mathrm{in}}+Z_0}\right|, \tag{2}$$

where f is the frequency of microwave, c is the velocity of light, d is the thickness of absorber, Z_0 is the impedance of free space

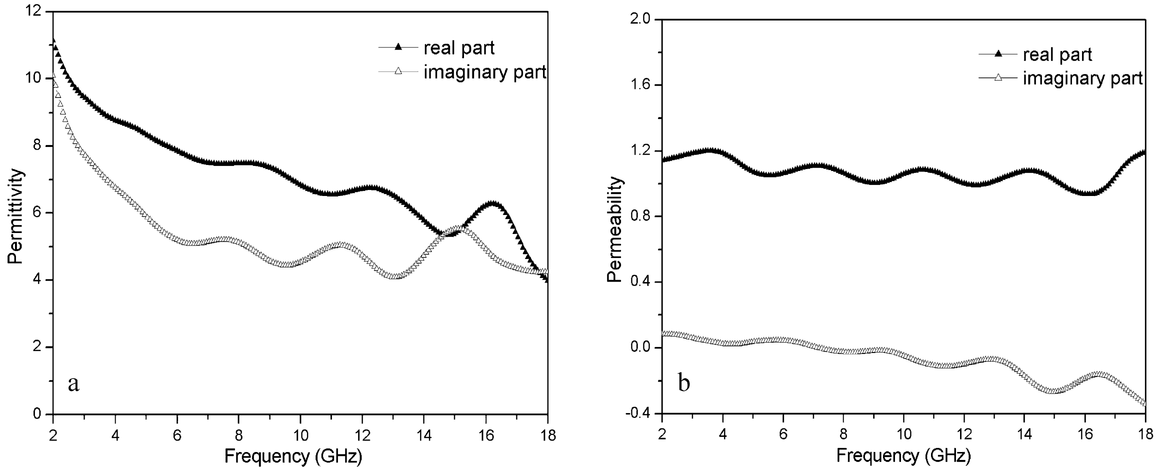

Fig. 5. Complex permittivity and peamibility of Fe_3O_4/PPy core/shell nanocomposite-paraffin wax sample as a function of frequency.

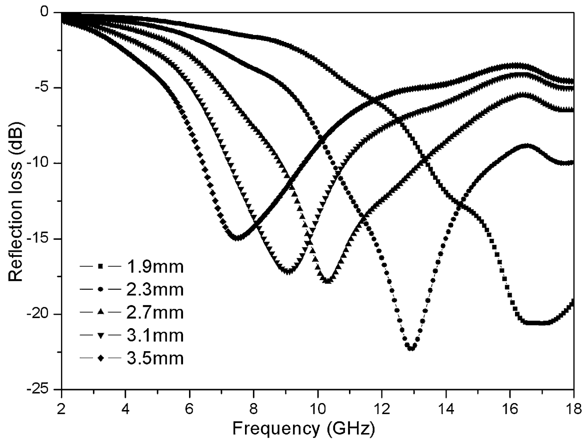

Fig. 6. Reflection loss of Fe_3O_4/PPy core/shell nanocomposite-paraffin wax sample of different matching thicknesses vs frequency.

and Z_{in} is the input impedance of absorber. Based on the equations above, a typical relationship between RL and frequency for the sample in the 2–18 GHz range is acquired and shown in Fig. 6. It is clearly seen that the samples have excellent microwave absorption properties. The structure complexity and frequency impedance of the material become greater with increasing the thickness of samples and thus the greater frequency impedance induces that the position of the strongest peak value shifts from higher frequency region to lower one [3]. The RL model also indicates that there is a best absorbing thickness affiliated with materials of certain electromagnetic parameters. The absorption peak reaches the maximum value of 22.4 dB at 12.9 GHz when the thickness value of sample is 2.3 mm, and the broad peak with a bandwidth lower than −10 dB is about 5 GHz. The excellent microwave absorption properties may result from dielectric loss ability of PPy and special core/shell microstructure of this nanocomposite. The presence of PPy reduces the magnetic-coupling effect between nanoparticles, increases effective surface anisotropy of nanoparticles [19], contributing to better match between the dielectric loss and the magnetic loss. In general, Fe_3O_4/PPy core/shell nanocomposite is promising as new types of microwave absorption materials with usability in a much wider frequency range while maintaining strong absorption.

4. Conclusions

Fe_3O_4/PPy core/shell nanocomposite has been successfully synthesized in large quantities by a simple solution-based *in situ* polymerization approach. The magnetic study reveals that the Fe_3O_4/PPy core/shell nanocomposite is ferromagnetic at room temperature, and the saturation magnetization (Ms) and coercivity (Hc) of as-prepared nanocomposite are 20.1 emu/g and 368.3 Oe, respectively. Due to dielectric loss ability of PPy and special core/shell structure, the imaginary part of permittivity is higher than other composite absorbing materials. The vertex of the every absorbing peak shifts to lower frequency region with increasing the thickness of samples. The value of the minimum RL is −22.4 dB at 12.9 GHz for Fe_3O_4/PPy core/shell nanocomposite with a thickness of 2.3 mm and the broad peak with a bandwidth lower than −10 dB is of about 5 GHz. The core/shell structure forms interface between polypyrrole and Fe_3O_4 nanoparticle and this interface may cause more reflection loss and lead to intenser absorption of microwave than using any of the materials separately. We concluded that the core/shell nanocomposite makes a better electromagnetic matching and increase the comprehensive absorbing properties of the sample.

Acknowledgements

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