Enhanced microwave absorbing performance of CoNi alloy nanoparticles anchored on a spherical carbon monolith

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CoNi alloy nanoparticles anchored on a spherical carbon monolith (CoNi–C) were prepared by a solvothermal route and subsequent heat treatment without any templates. Their permittivity and permeability behaviors were studied in the frequency range of 2–18 GHz. The CoNi–C composites showed the best microwave absorbing performances compared to those of Co–C and Ni–C. The maximum reflection loss of the CoNi–C nanocomposites can reach −50.2 dB at 7.7 GHz with samples of 4 mm in thickness, better than that of the Ni–C composites, while the Co–C composites showed almost no absorption at all. The absorption mechanism of the three absorbents was also discussed.

1. Introduction

With high demand for solving the expanded electromagnetic interference (EMI) problems in recent years, considerable theoretical and experimental investigations have been focused on designing and fabricating effective electromagnetic wave absorption materials with promising applications in electronic devices for commercial, industrial and military affairs. The crucial factors that influence the performance of the absorbing materials are their complex permittivity ($\varepsilon_r = \varepsilon' + i\varepsilon''$) and permeability ($\mu_r = \mu' + i\mu''$). Therefore magnetic and conductive materials continue to play a leading role in the investigation and application of microwave absorbers. Cobalt and nickel both are metallic soft magnetic materials that are potential candidates for microwave absorption at high frequency. However, their relative complex permeability may decrease due to eddy current phenomena induced by electromagnetic waves. Therefore it is better to use isolated metallic particles with a size less than the skin depth. Besides, nanosized metallic powders are usually unstable since they are easily agglomerated and oxidized. Carbon has an electrical resistivity of $10^{-8}$ Ω cm and is a strong reflector of microwaves. Being stable in most situations and light-weight, it has become an ideal choice as a substrate for magnetic nanoparticles to achieve a perfect match of the two parameters (permittivity and permeability), enhancing their absorbing properties. Various carbon materials like nanotubes, graphene or spheres and magnetic nanoparticles such as Ni, Co, CoNi, FeNi and CoFe$_2$O$_4$ have been combined together by different approaches to form composites with high strength, moduli and carrying capacity, and a low microwave cross-section. These composites have recently received increasing recognition due to their advantages of excellent uniformity, good resistance to corrosion, oxidation and low labor costs. Fan et al. reported that the magnetic nanoparticle–carbon fiber composites exhibited improved microwave absorption properties, which is attributed to the better match between the magnetic loss and the dielectric loss. Deng and Han also reported multi-wall carbon nanotubes with impurities of magnetic Ni nanoparticles, with greater microwave absorption properties affected by the “geometrical effect”. However, it should be noted that the metal nanoparticles decorated on the surface of carbon substrates (e.g. graphene, carbon nanotubes) may easily fall off under high pressure or after extended usage and usually are not resistant to acid or strong alkali. Therefore, it is urgent to design magnetic nanocomposites with small sizes that are tightly wrapped by carbon as stable, effective, lightweight and environmentally friendly microwave absorbers.

In this paper, we report superfine magnetic alloy nanoparticles (CoNi) with the average size of ~12 nm evenly and tightly anchored in a spherical carbon monolith matrix that showed excellent microwave absorbing performance. It is worth mentioning that these uniformly dispersed alloy nanoparticles are hard to remove even by aqua regia, thus ensuring the chemical and physical stability of the composites.

2. Experimental

Preparation of CoNi–C

Ni(NO$_3$)$_2$, Co(NO$_3$)$_2$ and ascorbic acid were first dissolved in 50 mL ethanol with stirring to form a transparent solution.
2 mL of hydrazine hydrate was then slowly added to the solution which was later transferred to and sealed in an 80 mL Teflon-lined stainless steel autoclave, and heated at 120 °C in an electric oven for 24 h. The naturally formed spherical monolith with diameter ~1.5 cm floating on the liquid surface was directly transferred to a furnace without washing for annealing at 400 °C for 2 h in a nitrogen atmosphere. The ball shrank to ~1 cm in diameter with a shiny black color and was then ground in a mortar by pestle for 10 min until no obvious lumps were observed (Fig. 1).

Preparation of Ni–C
Ni(NO$_3$)$_2$ and ascorbic acid were first dissolved in 50 mL ethanol with stirring to form a transparent solution. 2 mL of hydrazine hydrate was then slowly added to the solution which was later transferred to and sealed in an 80 mL Teflon-lined stainless steel autoclave, and heated at 120 °C in an electric oven for 24 h. The naturally formed spherical monolith was then directly transferred to a furnace without washing for annealing at 400 °C for 2 h in a nitrogen atmosphere. The product was ground in a mortar by pestle for 10 min until no obvious lumps were observed.

Preparation of Co–C
The preparation of Co–C was basically identical to the Ni–C preparation except the Ni(NO$_3$)$_2$ was replaced with Co(NO$_3$)$_2$.

Characterization
The composition and phase purity of the as-synthesized samples were analyzed by X-ray powder diffraction (XRD) with monochromatized Cu K$_\alpha$ (\(\lambda = 1.54178 \text{ Å}\)) incident radiation by a Shimadzu XRD-6000 operated at a voltage of 40 kV and current of 50 mA. XRD patterns were recorded from 2° to 80° (2\(\theta\)) with a scanning step of 0.02°. The size distribution and morphologies of the samples were characterized by FE-SEM (JEOL S-4800). A H-8100 TEM operating at an accelerating voltage of 200 kV was used for TEM. X-ray photoelectron spectroscopy (XPS) was recorded on an ESCALAB 250 spectrometer (Perkin-Elmer) to characterize the surface composition. The magnetic hysteresis loop was obtained by a Quantum Design MPMSXL-7 quantum interference device magnetometer.

Microwave absorbing measurement
The composite specimens for reflection loss measurements were prepared by uniformly mixing the powders in a paraffin matrix, which is transparent to electromagnetic waves, in the mass ratio of 1 : 1. Variations of the reflection loss (in dB) versus frequency in the range of 2–18 GHz at room temperature for the composite samples was investigated using a HP 8722ET vector network analyzer. All of the measurements were performed at room temperature.

3. Results and discussion
The XRD patterns of the three samples Co–C, Ni–C and CoNi–C are shown in Fig. 2. For the Co–C sample, the three broad peaks observed at 44.6°, 50.2°, and 76.4° well match the JCPDS Card No. 89-4307, which could be indexed to face-centered cubic (fcc) cobalt. For Ni–C, three peaks centered at 44.5°, 51.5°, and 76.4° were found, which can be assigned to face-centered cubic (fcc) nickel (JCPDS Card No. 04-0850). No signals of nickel hydroxide or nickel oxide were observed.

The peaks at 44.4°, 51.8°, and 76.2° for the CoNi–C sample correspond to the (111), (200) and (220) planes of the face-centered cubic (fcc) phase of the CoNi alloy. The broad peak at 23.1° for all three samples is attributed to amorphous carbon after annealing at 400 °C. This XRD result preliminarily indicates the complexation of the magnetic nanoparticles and carbon materials.

Here it should be pointed out that the three samples have almost the same morphology and therefore we use the CoNi–C sample as an example in the following section to describe its morphology and microstructure in details. Representative transmission electron microscopy (TEM) images (Fig. 3a and b) of the as-synthesized CoNi–C sample at increasing magnification reveal a uniform anchoring of CoNi nanoparticles on the matrix of carbon. The CoNi nanoparticles have an average diameter of ~12 nm. Almost no agglomeration was observed, and each piece of the sample shows the same structure. The scanning electron microscopy (SEM) image (inset in Fig. 3b) reveals the porous structure of the sample. The pores may be formed in the solvothermal process when hydrazine decomposes into hydrogen, nitrogen and ammonia under high temperature thus producing gas bubbles in the ball, resulting in the light weight and porous structure of the materials. Fig. 3c shows the high-resolution TEM image of the CoNi–C sample, from which it can be seen that the CoNi particles are tightly encapsulated within the carbon even after extensive grinding. The interlayer spacing of the lattice fringes of the presented CoNi particle is 0.22 nm, which is consistent with the CoNi crystal structure. The considerably sharp ring-like features of the corresponding selected electron diffraction pattern (Fig. 3d) indicate the polycrystalline nature of the CoNi particles.
the as obtained sample with clear (220), (111) and (200) diffractions. To illuminate the distribution of Co and Ni elements in the as prepared sample, the elemental maps of a single piece are shown in Fig. 3e–h. The results demonstrate a very homogeneous element distribution in the CoNi–C sample, which implies that the sample is an alloy rather than a random mixture of Co and Ni nanoparticles. For the same sample, the deconvoluted XPS spectrum of Co2p3/2 in Fig. 4a shows the main peak at 777.8 eV, which can be attributed to metallic Co. The peak at 781.4 eV (the satellite peak) can be indexed to the Co2+ oxidation state. This result implies the possible coexistence of metallic Co and Co2+ in the carbon matrix.

The binding energy of 854.7 eV in Fig. 4b can be assigned to metallic Ni in the sample while the binding energy of 861.4 eV can be assigned to Ni2+ in the composite as well.

To test and compare their microwave absorbing ability, CoNi–C, Ni–C and Co–C were uniformly mixed in a paraffin matrix (50 wt%), which is transparent to electromagnetic waves, and pressed into a compact cylindrical shape. Then they were cut into rings (7.00 mm outer diameter and 3.00 mm inner diameter) and measured in the range of 2–18 GHz by a HP 8722ET vector network analyzer.

As is shown in Fig. 5, Co–C showed almost no absorption in the range of 2–18 GHz while for Ni–C and CoNi–C, the maximum absorption peaks all reached below −10 dB at different thickness, which ensures the practical application of these research results. For Ni–C, at the sample thicknesses of 2, 2.5 and 3 mm, the absorption peaks are wide and centered at around −22 dB, comparable to similar samples reported. As the sample thickness increases, the maximum reflection loss obviously shifts to a lower frequency range with an average of −33 dB.

The results from the CoNi–C sample are slightly better with an average reflection loss of −25 GHz, an exceptional absorption peak at 7.7 GHz and a maximum reflection loss of −50.2 dB, which is far better than most of the reported results. Fig. 5d gives the comparison of the three samples at the thickness of 4 mm. Here we need to point out that the effect of microstructure of the...
samples on the reflection loss could be ruled out since the three samples have the same morphology. Compared to CoNi–C and Ni–C, the Co–C sample exhibits significantly weaker adsorption performance, which is probably due to its poor conductivity caused by its low degree of crystallinity at 400 °C.

To test and better understand the mechanism of the microwave absorption, we independently measured the complex relative permittivity and permeability of these three samples. It is obvious in Fig. 6 that for Co–C, the values of the real and imaginary parts of the permittivity are very small with no obvious resonance effect compared to the other two samples. This result indicates the poor conductivity of the Co–C sample, which may be the cause of its unsatisfying performance for microwave absorption.

For Ni–C and CoNi–C, the permittivity decreases as the frequency increases, exhibiting an obvious frequency-dependent dielectric response. This may arise from the lag of the induced charges to follow the reversing external field at high frequencies and finally causes a reduction in the electronic oscillations. The permittivity peaks of CoNi–C between 7–16 GHz indicate a resonance behavior, which usually emerges when the material is highly conductive. The peak appearing at 7.7 GHz for CoNi–C in both the real and imaginary parts of the permittivity are very small with no obvious resonance effect compared to the other two samples. This result indicates the poor conductivity of the Co–C sample, which may be the cause of its unsatisfying performance for microwave absorption.

The magnetic hysteresis loops for the different samples are shown in Fig. 7a. The saturation magnetization values $M_s$ for Co–C, Ni–C and CoNi–C are 11.3, 5.5 and 16.9 emu g$^{-1}$, respectively.

As is well known for the application of microwave absorption, the initial permeability ($\mu_i$) of the absorber should be as high as possible. The permeability of ferromagnetic materials can be expressed as follows:

$$\mu_i = \frac{M_s^2}{akH_sM_s + b\xi^2}$$  \hspace{1cm} (1)

where $M_s$ is the saturation magnetization, $a$ and $b$ are two constants determined by the material composition, $\lambda$ is the magnetostriction constant, $\xi$ is an elastic strain parameter of the crystal, $k$ is a proportion coefficient, and $H_c$ is the coercive field.

It can be seen from eqn (1) that both higher $M_s$ and lower $H_c$ are favorable to the improvement of the $\mu_i$ value, which will in
turn enhance the microwave absorption. In our case, the average diameter \(D_p\) of the nanoparticles is small enough that superparamagnetism occurs \((H_c = 0)\) and therefore the higher \(M_s\) is, the better the microwave absorption that can be achieved. The CoNi-C sample enjoys the highest \(M_s\) value of 16.9 emu \(g^{-1}\) and proper electrical parameters, which are responsible for its improved microwave absorbing performance.

Annealing temperature is another crucial factor that affects the microwave absorbing performance of the materials as well. After increasing the temperature to 500 °C in the same nitrogen atmosphere and annealing for two hours, the level of crystallinity and conductivity of the three samples increased obviously while their absorption ability decreased drastically (Fig. 7b). None of the materials reached the reflection loss of \(-10\) dB in the testing range of 2–18 GHz, which means they are of no practical use in industry or real life. This result proves again that mere strong dielectric loss may induce weak electromagnetic wave absorption properties due to the imbalance of the electromagnetic match.\(^8\)

4. Conclusions

In conclusion, well dispersed CoNi alloy nanoparticles anchored in a spherical carbon monolith were synthesized by a simple approach, which exhibit excellent electromagnetic properties. The electromagnetic match in microstructure, the strong natural resonance, as well as the lags of polarization contribute to the outstanding performance. The band width with a reflection loss less than \(-10\) dB covers a wide frequency range from 5 to 18 GHz and the maximum reflection loss is \(-50.2\) dB at 7.7 GHz with a 4 mm thick sample layer. This easily reproducible solvothermal approach for carbon-coated nanoparticles with dielectric shells and ferromagnetic cores may lead to various novel materials being used as microwave absorbers.

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