Preparation of Carbon Encapsulated Magnetic FeCo Alloy Nanoparticles Supported on Carbon Nanotubes for Enhanced Microwave Absorption

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Abstract. A mixture of multi-walled carbon nanotubes in an ethanol solution of Fe(NO₃)₃·9H₂O and Co(NO₃)₂·6H₂O, were used to prepare an Fe₂O₃-CoO catalyst supported on carbon nanotubes by a supercritical fluid drying method. The carbon encapsulated FeCo nanoparticles were prepared by the catalytic decomposition of methane over the catalyst at 850°C for 30 mins. The morphology and microstructure of the catalyst and carbon encapsulated nanoparticles (CEP) were characterized by XRD, FESEM, EDS and TEM analyses. The electromagnetic characteristics and microwave absorption properties of the CEP product were also studied. Results show that the CEP product possesses high complex permittivity and good permeability in the microwave frequency range from 2 to 18 GHz. The maximum absorption peak was observed at 9.44 GHz for a large reflection loss (R) of 13.3 dB, with a band width of 7.4 GHz and 2.56 GHz, at R< -5 dB and R< -10 dB, respectively.

1. Introduction

Since S. Gangopadhyay [1] discovered a typical core-shell type of structure with an α-Fe core and an oxide coating, widespread attention has been given to researching metal nanoparticles, which have been encapsulated in protective carbon shells (carbon nanocapsules) [2-8]. These novel structures can induce unique electronic [9,10], optical [11], and magnetic [6,8,12] properties, which are undoubtedly important for the evolution of nanotechnology. Further to this, they can lead to a variety of potential applications, such as magnetic nanoparticles in recording media. This is due to their environmental stability and low magnetic coupling between individual particles, which facilitate the handling of such nanoscale air-sensitive materials [13,14].

With the fast advancement of wireless communication, microwave absorbing materials are becoming increasingly important for specialized outdoor purposes, such as silent rooms, radar systems and military applications. Current electromagnetic wave absorption materials do not display the properties of “strong absorption, low density, wide absorption frequency, thin thickness and compatibility characteristics” [15]. Carbon and carbon nanotubes which have been used to encapsulate magnetic metal particles (i.e., carbon encapsulated nanoparticles, CEP) are one of the new microwave absorbents recently reported [16-20] in an attempt to solve this problem. This is due to their improved...
electromagnetic characteristics and the protection provided to the encapsulated magnetic nanoparticles against environmental oxidation and chemical erosion.

In this work, the carbon encapsulated iron and cobalt nanoparticles were synthesized by catalytic decomposition of methane over an Fe$_2$O$_3$-CoO catalyst supported on carbon nanotubes (Fe$_2$O$_3$-CoO/CNTs). The morphologies and microstructure of the catalyst and the CEP product were characterized using XRD, EDS, FESEM and TEM. The dynamic electromagnetic parameters and absorption properties of the CEP product used as microwave absorbing materials were investigated.

2. Experimental

2.1. Preparation of multi-walled carbon nanotubes

The multi-walled carbon nanotubes were synthesized by catalytic decomposition of methane over a NiO/SiO$_2$ aerogel catalyst [21]. The carbon product was then treated by magnetic stirring in hydrofluoric acid for 48 hours to remove the silica support and the nickel particles. Finally, the sample was thoroughly washed in distilled water to remove the hydrofluoric acid.

2.2. Preparation of the catalyst and the CEP

Fe(NO$_3$)$_3$.9H$_2$O and Co(NO$_3$)$_2$.6H$_2$O were mixed at a molar ratio of 66∶34 in ethanol using magnetic stirring for 12 hours at room temperature to get an alcosol. Then, certain quantities of purified carbon nanotubes used as carrier were added into the alcosol to form a homogeneous mixture by using strong magnetic agitation and ultrasonic vibration. The mixture was then placed in an autoclave and dried under the supercritical conditions of 240°C and 7.0 MPa pressure for 15 mins. The alcohol was then slowly discharged and the autoclave was cooled to room temperature with a flowing nitrogen to obtain an Fe$_2$O$_3$-CoO/CNTs catalyst.

About 1 g of the catalyst was placed into a quartz boat and then inserted into a tubular furnace, then heated at a rate of 5 °C/min under nitrogen to 850°C. The nitrogen gas was replaced by hydrogen gas and then held for 30 mins in order to reduce the catalyst. Thereafter, a mixture of methane and hydrogen with a flowing ratio 200/100 in mL/min was introduced to promote the decomposition reaction for 30 mins. After the reaction, the product was cooled to room temperature under a nitrogen atmosphere to obtain the CEP product.

2.3. Characterization

X-ray diffraction (XRD) analysis of the catalyst and the carbon product were performed by a D/MAXIIIC X-ray diffractometer using filtered Cu radiation. The morphologies and microstructure of the carbon nanotubes, the catalyst and the CEP product were characterized by a Carl Zeiss LEO 60 mm 1530 field emission gun scanning electron microscope (FESEM) equipped with an energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM) was conducted on a JEOL JEM-2000FX II.

3. Results and discussion

3.1. Morphology and structure of the carbon nanotubes, the catalyst and the CEP

FESEM and TEM images of purified multi-walled carbon nanotubes used as metal catalyst carrier are shown in Figure 1. It shows that the carbon nanotubes are curved and possess a diameter of 20~40 nm and a length typically 3~8 μm. Figure 2(a-b) shows the FESEM and TEM images of the typical catalyst, which mainly consists of nanosized particles supported on carbon nanotubes. The interfacial adhesion strength between the nanoparticles and the carbon nanotubes is strong, despite a few particles peeling off from the walls of carbon nanotubes. It can be seen from Figure 2(c-d) that the CEP product mainly consists of particles with a diameter in the range 50~100 nm and the carbon nanotubes are covered up by the particles.
Figure 1. Typical (a) FESEM and (b) TEM images of purified multi-walled carbon nanotubes.

Figure 2. Typical (a) FESEM, (b) TEM images of the catalyst and (c-d) FESEM of the CEP product.

Figure 3 shows the XRD patterns of the catalyst and the CEP product obtained at 850°C for 30 mins, which illustrates that the catalyst mainly consists of carbon, CoFe₂O₄, and Fe₂O₃. The CEP product mainly consists of carbon and a Co₃Fe₇ alloy, with a small presence of an Fe₆₄Ni₃₆ alloy as a by-product. This by-product can be attributed to the carbon nanotubes that have encapsulated a few Ni particles [21] and are not completely eliminated in this purification process.
EDS spectrum of the catalyst and the CEP product are shown in Figure 4, which indicates that the catalyst and the CEP product are both mainly composed of three elements, i.e., carbon, iron and cobalt. The elemental content of iron in the catalyst was higher than that found in the CEP product, in contrast, the carbon content for the catalyst was lower than that of the CEP product. The elemental weight ratio of the CEP product listed in Table 1 further confirms the above result. The EDS analysis also discovered a small amount of nickel, which is in agreement with the XRD pattern analysis.

Table 1: The elemental weight ratio of the catalyst and CEP product.

| Sample          | Elemental weight ratio/ % |
|-----------------|---------------------------|
|                 | C  | Fe   | Co   | Ni   | X  |
| catalyst        | 50.18 | 37.23 | 7.12  | 5.00 | 0.47|
| carbon product  | 69.88 | 16.21 | 12.17 | 1.30 | 0.44|

Note: “X” indicates a small mass impurity in the sample.

In order to clearly observe the morphology and microstructure of the CEP product, TEM measurements of these samples are conducted. It can be seen from Figure 5 that the CEP product is linked together and mainly consists of particles with a diameter of 50–100 nm. Figure 5(b) looks like a pearl necklace and the ellipsoidal shaped metal nanoparticles look like the necklace’s beads which are completely encapsulated by carbon layers. The thickness of the coating layers observed is about 15–30 nm as shown in Figure 5(c).
The secondary electron image and EDS spectrum distribution of the CEP’s are shown in Figure 6. When the electron beam was scanned across two carbon encapsulated particles, it can be observed that the nanoparticles consist of carbon, cobalt and iron. The carbon element was distributed outside the nanoparticles and the metals appear inside, which indicates that the FeCo alloy was completely encapsulated by the carbon, despite potential influence of the thickness of encapsulating layers. The element weight content of nanoparticles by EDS analysis shown in Figure 6(c) is in good agreement with that of CEP product shown in Figure 4(b).

3.2. Dynamic electromagnetic parameters and absorption property of the CEP

Figure 7 shows the dynamic electromagnetic parameters (complex permittivity $\varepsilon_r = \varepsilon' - j\varepsilon''$ and complex permeability $\mu_r = \mu' - j\mu''$) of the CEP product’s obtained by coaxial measurement, from 2 to 18 GHz, using an S parameter vector network analyzing instrument. Over the range of microwave frequencies 2 to 18 GHz, the change of the real part ($\varepsilon'_r$, $\mu'_r$) and imaginary part ($\varepsilon''_r$, $\mu''_r$) of complex permittivity are obvious. By increasing the microwave frequency from 2 to 18 GHz, $\varepsilon'_r$ decreases from 106.4 to 2.7, and $\varepsilon''_r$ decreases from 240.9 to 16.2. In addition, $\mu'_r$ decreases from 1.2 to 0.5 and $\mu''_r$ increases from 0.34 to 1.15, then decreases to 0.2, which indicates that the CEP product possesses good frequency-responding characteristics [22,23].
Figure 7. Complex permittivity (a) and complex permeability (b) spectra of CEP product at the microwave frequency range from 2 to 18 GHz.

Figure 8 displays the reflection loss (R) and the frequency curves of olefin composites incorporated with the CEP product at a weight ratio of 1:2, the thickness of the composites is 2 mm. In the microwave frequency range from 2 to 18 GHz, the maximum absorption peak of the composites was 13.3 dB at 9.44 GHz. The composites showed band widths of 7.4 GHz (R < -5 dB) and 2.56 GHz (R < -10 dB) which indicates that the CEP product possess good microwave absorption properties [20,23,24].

Figure 8. Reflection loss and frequency curves of olefin composites incorporated with (FeCo)@C/CNTs magnetic nanoparticles.

4. Conclusions
Synthesis of carbon encapsulated FeCo magnetic nanoparticles can be controlled by a catalytic chemical vapor deposition method, using an FeO_2-CoO/CNTs catalyst. The dynamic electromagnetic parameters of the prepared encapsulated product show a high complex permittivity and good permeability in the microwave frequency range from 2 to 18 GHz. The prepared carbon encapsulated nanoparticles are good candidates for microwave absorption materials with widely applications as they possess high dielectric loss and ideal microwave absorption properties.

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