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Cleaning Preparation of Ni/C Nanocomposites and Enhanced Electromagnetic Properties

Nan Zhang¹, Jinfeng Li¹, Zhigang Li¹, Qiang Wang¹, Hongtao Zhao^{1*}

¹Institute of Technical Physics, Heilongjiang Academy of Science, Harbin, Heilongjiang, 150009, China

*Corresponding author's e-mail: zhaohongtao1976@163.com

Abstract. Carbon/magnetic-metal composites with excellent properties have become an important development trend and research hot-spot in the field of microwave absorbing materials. By using polypyrrole as carbon source, the electromagnetic functionalized Ni/C nanocomposites were prepared by carbonization treatment assisted with in-situ oxidation polymerization and γ -irradiation induced reduction technique. The structure and morphology of the composites were characterized by XRD, SEM and TEM analysis, respectively. The electromagnetic properties of the composites in the frequency range of 2-18 GHz were studied by mixing the composites with paraffin by the mass ratio of 1:4. The maximum R_L of the composite was up to -44 dB at 14.4 GHz with the thickness of 2.5 mm and the absorption bandwidth under -10 dB was 6.5 GHz. The excellent EM absorption performance was attributed to an appropriate impedance matching and interfacial polarization.

1. Introduction

Nowadays, great efforts have been made to obtain high performance electromagnetic (EM) absorbing materials with the rapid development of electromagnetic wave devices [1-3]. At present, the microwave absorbing materials with a single loss mechanism cannot meet the design requirement of ideal absorbing materials with "thin, light, wide and strong" because of the poor impedance matching. Scholars devote to the research of composite microwave absorbing materials with both electric loss and magnetic loss. Carbon materials have excellent dielectric property, light weight, controllable structure and other properties, which are suitable as the electrical loss component of composite materials [4-5]; Magnetic metals have higher saturation magnetization and permeability than ferrite, as well as stronger magnetic loss ability, so they are more suitable as magnetic loss components of composite materials [6-7]. Carbon/magnetic-metal composites have become the most important development trend and research hotspot in the field of microwave absorbing materials for their excellent properties. Using Ni particles as precursors, Liu *et al.* [8] prepared porous Ni/C composites by high-temperature carbonization process. It was proved that temperature has a great influence on the morphology and structure of the composites, thus the complex permittivity and permeability of the composites were affected. Liu *et al.* [9] reported Fe/C composite materials by in-situ carbonization of Fe precursor-encapsulated Zn-based metal organic framework (ZIF8). When the filler loading of Fe/C composite was as low as 15 wt% in paraffin matrix, the absorber exhibited a minimum reflection loss of -29.5 dB at a thickness of 2.5 mm. Wu *et al.* [10] provided a facile method to prepare carbon sphere/Fe₃O₄-Fe composite. Phenolic resin sphere (RS)/Fe-glycolate was firstly prepared through thermal-decomposition method, and then converted into amorphous sphere and Fe₃O₄ or Fe quantum dots by another high-temperature carbonization process. The composite showed excellent



electromagnetic absorption properties whose effective electromagnetic absorption region covered 5.8 GHz with the thickness of 1.5 mm. At present, great progress has been made in the research of carbon/magnetic-metal composites. However, most preparation processes are complicated and the technological conditions are harsh, which are not conducive to large-scale production.

In this paper, the polypyrrole derived Ni/C microwave absorbing materials were prepared by carbonization treatment assisted with in-situ oxidation polymerization and γ -irradiation induced reduction technique. γ -irradiation technique is a unique, green preparation method which is simple, the reaction condition is not harsh, only at room temperature and atmospheric pressure, without additional reductants, and the materials obtained are very pure [11-14], which will be benefit for the EM absorption properties of the materials. The as-fabricated Ni/C nanocomposite, combining the synergetic EM absorption effect from carbon (dielectric loss) and Ni (magnetic loss), showed enhanced EM absorption properties.

2. Experimental

2.1. Materials

Pyrrole (Py) and nickel acetate were obtained from Aladdin. Isopropanol (IPA) and absolute ethanol were supplied by Tianjin Guangfu Fine Chemical Research Institute. Ammonium persulphate (APS) was provided from Nanjing Fanke Chemical Reagent Co., Ltd. All of the reagents were used as received.

2.2. Preparation of Ni/C composite

5 mmol nickel acetate hexahydrate was added to deionized water and 10 ml isopropanol was added as the radical scavenger. The solution was purged with nitrogen gas for 0.5 h to remove oxygen dissolved in the solution, and then placed in the field of a ^{60}Co γ -ray source at a dose rate of 80 Gy/min. The solution obtained was filtered, washed and dried at the temperature of 80°C to get Ni particles. The obtained Ni particles and the pyrrole monomer (molar ratio of 4:1) were dispersed into 100ml deionized water and stirred at 900 rpm for 0.5 h, then a solution of sodium persulfate (APS) in 10 ml deionized water was added dropwise under the condition of ice-water bath. The molar ratio of Py and APS was 1:1. The solution was washed with deionized water and absolute ethanol until the filtrate became colorless and then dried in a vacuum oven at 60°C for 12h to obtain the Ni/PPy composite. The obtained Ni/PPy sample was carbonized at 600°C for 2h in a tube furnace, under the nitrogen atmosphere with a heating rate of 5°C/min. Then, the as-prepared Ni/C composite was obtained by simply cooling down to room temperature. For comparison, the pure carbon sample was treated with the same procedure except for the addition of Ni particles induced by γ -irradiation reduction technique.

2.3. Characterization

The structures of the samples were characterized using Powder X-ray diffraction (XRD) (RigakuD/MAXRC, Rigaku, Japan) with a Cu Ka radiation source (45.0 kV, 50.0 mA). The microstructure of the sample was observed using a Quanta 200S scanning electron microscopy (SEM) (FEI, Holland) and a TECNAI2-12 transmission electron microscope (TEM) (FEI, Holland). An Agilent N5234A vector network analyzer (Agilent, USA) was applied to determine the relative permeability and permittivity in the frequency range of 2-18 GHz for the calculation of reflection loss. A sample containing 20 wt% of the obtained composite was pressed into a ring with an outer diameter of 7 mm, an inner diameter of 3 mm, and a thickness of 2 mm for microwave measurement in which paraffin wax was used as the binder.

3. Results and discussion

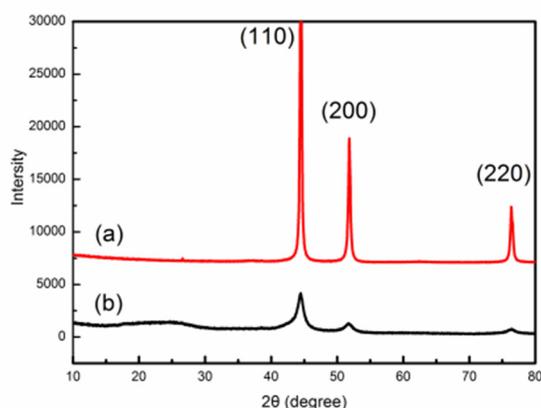


Figure 1. XRD patterns of Ni(a) and Ni/C(b).

XRD analysis was carried out to characterize the crystal structure and phase purity of Ni and Ni/C, as seen in figure 1. Figure 1(a) showed the XRD pattern of Ni particles obtained by γ -irradiation induced reduction technique. All peaks at $2\theta=44.6^\circ$, 51.9° and 76.4° can be well indexed to the (111), (200) and (220) planes of face-centered cubic Ni crystals (JCPDs 70-0989) [15]. Furthermore, no impurity peaks were found, indicating that the irradiated Ni particles were pure without oxidation. The XRD pattern of the Ni/C composite was shown in figure 1(b). As seen from figure 1(b), compared with the diffraction peaks of Ni particles, there existed another broad amorphous diffraction peak at $2\theta=24.8^\circ$, which was corresponding to the characteristic of carbon. There were also no detected peaks of impurities in the composite, which suggested the purity of the sample.

The SEM images of Ni, C and Ni/C with different magnification were shown in figure 2. In figure 2(a), the Ni particles reduced by γ -irradiation were monodispersed without conglomerates, and the particles were in nano-scale. In figure 2(b), the pure carbon material grew into the spheroidal aggregating structure, due to the polymerization and carbonization of pyrrole, the diameter of the pure carbon material was about $0.2\ \mu\text{m}$. It was interesting to find in figure 2(c) and figure 2(d) that the Ni/C composite was also with overlapped irregular-sphere structure, with no Ni particles found on the surface of the composite. The result indicated that the Ni particles might be wrapped in the carbon matrix.

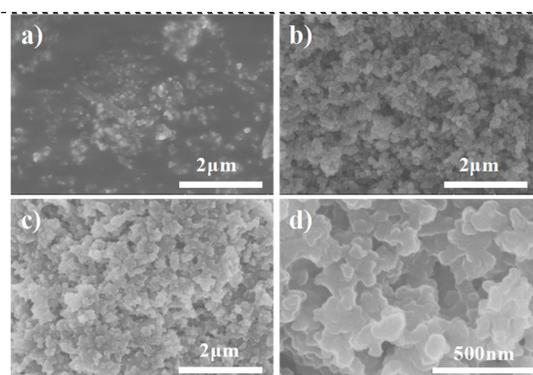


Figure 2. SEM images of Ni(a), C(b) and Ni/C(c,d).

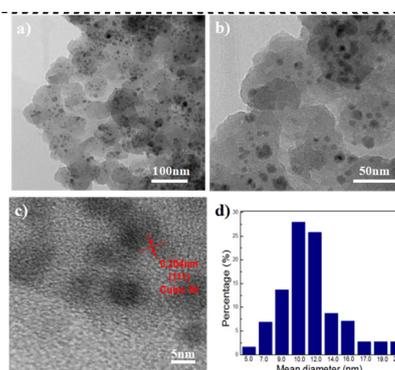


Figure 3. TEM images of Ni/C(a,b), HRTEM image of Ni/C(c), and size distribution of the Ni nanoparticles wrapped in carbon matrix (d).

The morphologies and size of Ni/C composite was revealed by TEM images, as shown in figure 3. In figure 3(a-b), it can be seen that the Ni nanoparticles were wrapped in the carbon matrix and

monodispersed with diameter of about 12 nm, the particle size of the Ni particles were evaluated from TEM micrograph, as seen in figure 3(d). The HRTEM image in figure 3(e) clearly showed the lattice fringes, indicating highly crystallization of the Ni nanoparticles. The TEM results agreed with the SEM and XRD analysis.

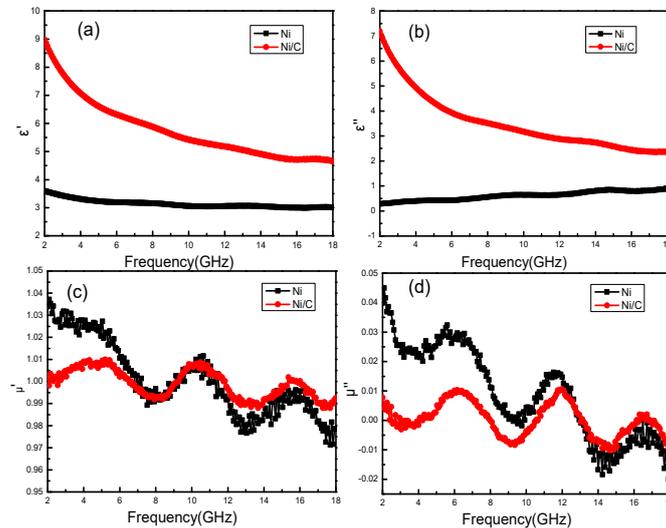


Figure 4. ϵ' (a), ϵ'' (b), μ' (c) and μ'' (d) of the Ni and Ni/C samples.

The electromagnetic parameters of Ni and Ni/C composite are shown in figure 4, in which ϵ' and ϵ'' represent the real part and imaginary part of complex dielectric permittivity respectively, μ' and μ'' represent the real part and imaginary part of complex dielectric permeability respectively [16]. In the frequency range of 2-18 GHz, ϵ' and ϵ'' of Ni nanoparticles had almost no change ($\epsilon' \approx 5$, $\epsilon'' \approx 0.75$), while ϵ' and ϵ'' of Ni/C were higher than that of Ni nanoparticles and decreased gradually throughout the whole frequency range, showing the dielectric response of the frequency. For complex permeability, both μ' and μ'' fluctuated high in the whole frequency range of 2-18 GHz, μ' had three peaks at 5.12 GHz, 10.57 GHz and 15.89 GHz, similar to μ'' at 6.57 GHz, 12.25 GHz and 16.89 GHz. This was mainly due to eddy current loss and natural resonance of Ni nanoparticles. In the whole frequency range of 2-18 GHz, the dielectric loss was higher than the magnetic loss, indicating that the EM absorption performance of the composite mainly came from the dielectric loss, which may be due to the synergistic effect between the Ni nanoparticles and the carbon material, so as to enhance the EM absorption property of the composite.

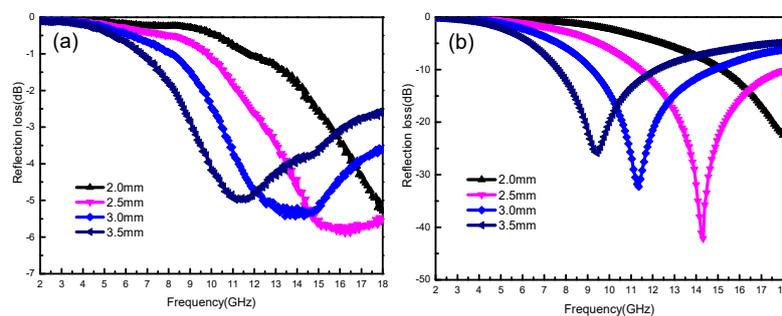


Figure 5. The EM absorption performance of Ni (a) and Ni/C (b) samples.

The EM absorption performance was portrayed by reflection loss (R_L) values, according to the transmission line theory [17]. The R_L values of samples with different thickness were calculated, and the results were shown in figure 5. The Ni sample exhibited poor EM wave absorption abilities, the R_L values were all upon -10 dB with the thickness of 2-3.5 mm. However, with the introduction of carbon matrix, the maximum R_L value run up to -44 dB at 14.4 GHz, for the thickness of 2.5 mm, and the bandwidth under -10 dB was 6.5 GHz. On one hand, the introduction of carbon matrix improved the

impedance matching. On the other hand, as the Ni nanoparticles were wrapped in the carbon matrix, there existed more interfaces so as to induce more interfacial polarization. The synergistic effect mentioned above improved the EM absorption performance of the composite. Moreover, the purity of the material was enhanced with the method of γ -irradiation in the preparation of Ni particles, which might be benefit for the microwave absorption property.

4. Conclusion

In summary, the electromagnetic functionalized Ni/C nanocomposites were prepared by carbonization treatment assisted with in-situ oxidation polymerization and γ -irradiation induced reduction technique. The Ni nanoparticles were uniformly dispersed and wrapped in the carbon matrix. The composite was purer with the introduction of γ -irradiation induced reduction technique. The introduction of carbon matrix improved the EM absorption performance of the composite. The maximum R_L of the composite was up to -44 dB at 14.4 GHz with the thickness of 2.5 mm and the absorption bandwidth below -10dB was 6.5 GHz. The Ni/C composite had good properties such as low density, strong absorption, and wide adsorbing frequency. The excellent EM absorption performance was attributed to an appropriate impedance matching and interfacial polarization.

Acknowledgments

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