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Island-like nickel/carbon nanocomposites as potential microwave absorbers—Synthesis via in situ solid phase route and investigation of electromagnetic properties

Hongjie Meng [a,b], Xiaowei Zhao [a,b], Laigui Yu [b], Yongshuai Jia [b], Haojie Liu [a,b], Xiaoyan Lv [b], Chunhong Gong [a,c,*], Jingfang Zhou [c,*]

[a] College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China
[b] Key Laboratory for Special Functional Materials of the Ministry of Education, Henan University, Kaifeng 475004, China
[c] Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia

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ABSTRACT

In this work, nickel–carbon (Ni/C) nanocomposites were prepared facilely as potential light-weight microwave absorbers *via* the calcination of nickel nitrate–polyacrylamide mixture in flowing ammonia. The electromagnetic properties of as-prepared Ni/C nanocomposites were investigated in relation to their composition and microstructure. Findings indicate that as-prepared Ni/C nanocomposites are of island-like morphology and consist of uniformly dispersed Ni nanoparticles and porous carbon medium. The electromagnetic properties of Ni/C nanocomposites are highly dependent on calcination temperature; and the Ni/C nanocomposite obtained at 600 °C exhibits excellent electromagnetic properties. This is attributed to the special porous structure and desired electromagnetic impedance matching of the carbon medium as well as the uniform dispersion of Ni nanoparticles in the carbon medium. Namely, the carbon medium is accessible to induced multi-dielectric polarization thereby improving the microwave absorbing properties of the Ni/C nanocomposites, and it also contributes to improving the thermal stability, chemical stability, and dielectric performance of the nanocomposites while the intrinsic magnetic properties of metallic Ni are retained.

1. Introduction

The rapid development of electromagnetic wave communications in many civil and military fields often refers to intensified pollution caused by electromagnetic radiation. To fight against the electromagnetic pollution, researchers have made considerable efforts to pursue advanced electromagnetic absorbers which exhibit excellent absorbing properties over a broad band of microwave frequency [1–4] and many conventional magnetic metal absorbers have been extensively studied [5]. The practical application of conventional magnetic metal absorbers, unfortunately, is highly limited by their liability to corrosion, high specific gravity [6] and high conductivity [7].

To deal with those drawbacks and acquire satisfactory absorption at a targeted frequency, one may consider substituting micro-sized metallic particles with nano-sized ones. In this sense, magnetic nanoparticles as electromagnetic absorbers could be of special significance, because they exhibit small size and large specific surface area, which is beneficial to enhancing interfacial polarization and to suppressing eddy current. In fact, when the size of metallic particles is less than the skin depth, eddy current in high frequency region is suppressed even in the case of low resistivity [8,9]. Meanwhile, the combination of magnetic materials with dielectric materials also favors efficient electromagnetic absorption in a broad frequency range [10,11].

It should be noted that magnetic nanoparticles, due to their intrinsic magnetic nature and large surface area, are vulnerable to serious aggregation and oxidation. The incorporation of carbon is beneficial to effectively preventing magnetic nanoparticles from agglomeration and constructing desired interface between magnetic nanoparticles and C, thereby contributing to the dielectric loss and improving the attenuation of electromagnetic waves in association with the interfacial polarization relaxation loss and the intrinsically dipolar polarization relaxation of amorphous carbon. Moreover, carbon with good thermal stability and low density might improve the environmental adaptability of magnetic

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* Corresponding authors at: College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China. Tel./fax: +86 371 23881589 (C. Gong).
E-mail address: gongch0378@foxmail.com (C. Gong).

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nanoparticles and broaden their application scope under harsh environment. In recent studies, carbon-coated ferromagnetic metal (Fe, Co, Ni) nanoparticles have attracted some attention in electromagnetic absorption materials (RAMs) [7,12–14]. However, it still remains a challenge to develop facile and efficient technique for inhibiting nanoparticles aggregation and increasing the compatibility between different components [15].

In the present work, we apply a simple in situ solid phase synthesis technique to fabricate island-like nickel–carbon (denoted as Ni/C) nanocomposites as potential advanced microwave absorbers. Through the reduction of nickel nitrate in flowing ammonia in the presence of polyacrylamide (denoted as PAM) as the carbon source (i.e., the solid-phase isolator), Ni/C nanocomposites consist of uniformly dispersed size-controllable Ni nanoparticles and porous carbon medium are obtained. This article reports the electromagnetic properties of as-prepared Ni/C nanocomposites in relation to the function of carbon medium in preventing magnetic Ni nanoparticles from agglomeration, oxidation and corrosion as well as in providing the hybrid nanocomposites with extra interfacial polarization mechanism favorable for electromagnetic wave absorbing [16–19].

2. Experimental

2.1. Materials and preparation of island-like Ni/C nanocomposites

Island-like Ni/C nanocomposites were prepared with nickel nitrate as the nickel source and PAM (Tianjin Kermel Chemical Co., Ltd., China) as the carbon source. All the reagents are analytical grade, commercially available and used without further purification. Firstly, 4 g of nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$, Tianjin Kermel Chemical Co., Ltd., China) was dissolved in 100 mL of distilled water and mechanically stirred at room temperature to allow the generation of a transparent green solution after homogeneous dispersion of Ni^{2+}. Then 2 g of PAM was added into the solution, followed by heating at 60 °C under vigorous stirring until a uniform green viscous liquid was obtained. Finally, the viscous liquid was transferred into a porcelain boat and dried at 80 °C in an oven to yield the sponge mixture which was used as the precursor. The precursor was calcinated in flowing ammonia for 4 h to afford target Ni/C nanocomposites. To determine the suitable calcination condition for preparing Ni/C nanocomposites, the precursor was calcinated in ammonia at 500 °C, 600 °C, and 700 °C. Corresponding target products are denoted as S1, S2 and S3, respectively.

2.2. Characterization method

The morphologies of as-prepared Ni/C nanocomposites were examined with a field emission scanning electron microscope (FESEM, JEOL JSM-5600LV, accelerating voltage 20 kV). A Philips X'Pert Pro X-ray diffractometer (XRD, Philips Corporation, the Germany) was performed to analyze the phase structure of as-synthesized Ni/C nanocomposites (Cu Kα radiation, $\lambda = 1.5406$ Å). Raman scattering spectra were measured with a confocal microscopic Raman spectrometer (RM-1000, Renishaw, England) using a 632.8 nm laser as the excitation source. Magnetic measurements were conducted with a vibrating sample magnetometer (VSM, Lake Shore 7400, America). Moreover, a proper amount of as-synthesized Ni/C nanocomposite was homogeneously dispersed in paraffin at a mass ratio of 1:1 and then pressed into a toroidally-shaped sample (inner diameter 3.04 mm, outer diameter 7.00 mm) for measurements of electromagnetic properties [20]. The electromagnetic properties of resultant Ni/C-paraffin composites were measured in a frequency range of 2.0–18.0 GHz with an Agilent N5230A vector network analyzer (Agilent, America).

3. Results and discussion

3.1. Structure and morphology analyses of Ni/C composites

Fig. 1 shows the X-ray diffraction (XRD) patterns and Raman spectra of Ni/C nanocomposites obtained at calcination temperatures of 500 °C, 600 °C and 700 °C (corresponding products are denoted as S1, S2 and S3). It is seen that products S1, S2 and S3 all exhibit the diffraction peaks of face-centered cubic Ni at 45.1°, 52.4° and 76.5°, while S1 alone exhibits a minor peak of hexagonal Ni_3N impurity [21]. This indicates that a small amount of Ni_3N is generated during the calcination of nickel nitrate–PAM mixture in flowing ammonia at 500 °C. As indicated in our former work, this is possibly attributed to the nitriding of nascent Ni particles thereat [22]. Then, at a higher temperature, Ni_3N, as a thermally labile compound, would decompose to metallic nickel and nitrogen gas. Thus, no Ni_3N phase in the composite could be detected at a higher temperature (600 °C and 700 °C) [23]. Besides, the relative intensity of the diffraction peaks of Ni nanoparticles increases with increasing calcination temperature, which implies that the carbon content of as-prepared Ni/C nanocomposites decreases therewith. As to Raman spectrum, peak D is assigned to impurities and defects, and its intensity is related to the degree of disorder of carbon. Peak G refers to the regularity and orderliness of carbon, and it tends to be narrowed with increasing carbon orderliness. As shown in Fig. 1b, all the three Ni/C nanocomposites exhibit D and G peaks of carbon at about 1333 cm^{-1} and 1590 cm^{-1}, which directly proves that they all contain carbon. Moreover, the ratio of peak G to peak D tends to rise with the increase of calcination temperature, which means that the Ni/C nanocomposites obtained under higher calcination temperatures exhibit increased degree of graphitization.

Fig. 2 shows the scanning electron microscopic (SEM) images of the three Ni/C nanocomposites. It is seen that Ni/C nanocomposites S1, S2 and S3 are all of island-like microstructure and consist of nanoscale Ni particulates well dispersed in porous carbon medium. During the prepare process of the precursor, the Ni^{2+} and PAM were mixed uniform in a liquid, thus the homogeneous dispersion of Ni^{2+} in PAM at a molecular level could be achieved. Along with the increase of the calcination temperature, PAM would decompose to carbon and Ni^{2+} ions were reduced to zero valence Ni, simultaneously, it would grow up and agglomerate to form Ni cluster and/or nanoparticles. Along with the further increase of the temperature, the cluster and/or the nanoparticles would coalesce to bigger particles. Though the dispersion is not the molecular level, Ni particles could be distributed uniformly in carbon matrix. Moreover, such an island-like microstructure should be favorable for acquiring desired electromagnetic properties. This is because, on the one hand, the porous carbon medium can help prevent nickel nanoparticles from aggregation, oxidation and corrosion. On the other hand, the nickel nanoparticles isolated by carbon medium can more effectively interact with electromagnetic wave than the aggregated counterparts. The uniform dispersion of carbon and nickel is confirmed by element mapping in energy dispersive X-ray spectroscopy measurements installed in the FE-SEM system, as shown in Fig. S1. What is of special attention is that the nickel particles in products S1 and S2 have a similar size of 100–200 nm, but in product S3 there is a large amount of nickel particles with a size of above 200 nm. Thus it can be inferred that too high calcination temperature (700 °C) is unsuitable for acquiring desired electromagnetic properties of Ni/C nanocomposites, since larger size Ni nanoparticles exhibit decreased specific surface area as well as reduced dispersion uniformity in the carbon medium.

3.2. Measurement and calculation of specific surface area

The N_2 adsorption–desorption isotherms of products S1, S2 and S3 are presented in Fig. S2, where the Brunauer–Emmett–Teller (BET in short) specific surface areas are calculated from N_2 adsorption–desorption isotherms at 200 °C. Ni/C nanocomposites S1, S2 and S3 exhibit a specific surface area of 26.5 $m^2\,g^{-1}$, 40.5 $m^2\,g^{-1}$ and 32.8 $m^2\,g^{-1}$, respectively, which indicates that a moderate calcination temperature (600 °C) is suitable for fabricating desired Ni/C nanocomposites.

The porous construction is the main contribution of the big BET surface area of the Ni/C nanocomposites. There are two possible reasons for the formation of the porous construction. Firstly, along