Composites Communications 9 (2018) 70–75

Contents lists available at ScienceDirect

Composites Communications

journal homepage: www.elsevier.com/locate/coco

Waste cotton-derived magnetic porous carbon for high-efficiency microwave absorption

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ARTICLE INFO

Keywords:
Cotton
Magnetic porous carbon
Interfacial polarization
Microwave absorption

ABSTRACT

In this study, using nickel nitrate and waste cotton as precursors, porous carbon combined with well-dispersed Ni nanoparticles were formed via an in-situ growth strategy. Due to the distinction of complex permittivity among different components, the expanded interface in the Ni/C heterostructure could improve the interfacial polarization relaxation, which lead to the enhanced dielectric loss and EM absorbing capability. The results show that excellent microwave absorption properties could be exhibited over a wide frequency range with a filler loading of only 10 wt.%, which compete well with what has been observed in the carbon-based composites with much higher filler loadings. This work provides a low-cost and effective approach for lightweight and high-efficiency microwave absorption, which also greatly facilitates the recycling of waste cotton.

1. Introduction

With the recent rapid expansion of microelectronic devices into the GHz range, worldwide concern about electromagneticinterference (EMI) and microwave pollution is increasing [1,2]. At present, the main ways to solve electromagnetic pollution are EMI shielding and microwave absorbing materials. A variety of conductive filler/polymer composites with high EMI shielding performances have been developed by dispersing conductive fillers into polymer matrices. It is believed that the uniform dispersion and the formation of an interconnecting network of conductive fillers are crucial for endowing polymers with high electrical conductivity and EMI shielding effectiveness (SE) [3]. Differently, microwave absorption materials are required to absorb the emitted electromagnetic wave (EMW) energy and to minimize the reflection of EMW in the direction of the enemy radar receiver, which can absorb the incident EM energy effectively and attenuate it in the form of thermal energy via dielectric or/and magnetic losses. Generally, high-efficiency microwave absorption materials require good EM wave dissipation capability and impedance matching [4,5]. Thus, it may be an efficient way of improving the wave-absorbing performance through reducing the surface reflection by the introduction of wave-transparent components and enhancing the wave-transmitting capacity by the interface scattering loss. The heterogeneous components could usually contribute to a proper complementarity between the complex permeability ($\mu_r = \mu_r' + i\mu_r''$) and the complex permittivity ($\varepsilon_r = \varepsilon_r' + i\varepsilon_r''$) via adjustment of the dielectric and magnetic components [6,7]. Therefore, many efforts have been devoted to various efficiency microwave absorbents via optimization of the magnetic/dielectric composition, the specific microstructures and heterogeneous interfaces [8–11].

Among the candidates, magnetic porous carbon (MPC) materials are considered to be attractive candidates for high-performance microwave absorption materials [12–14]. On the one hand, the density of the MPC is much lower than that of conventional high-density ferrites [15]. On the other hand, the heterogeneous components could contribute to a proper complementarity between the complex permeability and the complex permittivity, thus optimizing the match in EM impedance. More importantly, the porous structure could endow composite absorbents with an additional pathway for the transmission of EM waves, thus leading to multiple reflections and improvement in EM absorption [16]. However, although some developments have been made, a high functional filler loading is still required due to their limited dispersity and/or limited EM resonance performance, which greatly restricts their practical applications [17,18].

To exhibit an ideal absorbing performance with a low filler content and thin matching thickness, the enhanced complex permeability and permittivity are usually required [19,20]. Because further improvement of the permeability of carbon-based absorbers by variation of their magnetic components is quite limited, much attention has been directed towards the search for unique EM loss capabilities [21]. As a commonly dielectric loss form, the interface polarization behaviour of

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https://doi.org/10.1016/j.coco.2018.06.007
Received 6 June 2018; Received in revised form 21 June 2018; Accepted 22 June 2018
Available online 27 June 2018

the composite absorbers has been emphasised in recent years with systemic research [22]. Based on those investigations, to enhance the interface polarization relaxation, the various components in the absorber must be uniform and well-dispersed [23,24].

In recent years, using waste cellulose as precursor to prepare carbon materials began to arouse the attention of scholars in environment and material fields [25–28]; Here, we develop a simple method for the synthesis of MPC with nickel nitrate and waste cotton as the starting materials. During the carbothermal reduction process, nickel ion is reduced to nickel nanoparticles, and cotton is converted to carbon. Simultaneously, a porous structure could be expected with the thermal decomposition of nickel nitrate. The experimental results show that the MPC composites display prominent EM absorption behaviour when the filler content is as low as 10 wt.%. With its simple and inexpensive synthesis approach and significant EM characteristics, the cotton derived MPC composites could be an attractive candidate as a lightweight and high-efficiency microwave absorber.

2. Experimental

2.1. Materials and preparation of MPC

In a practical procedure, 20.0 g cotton were boiled in 17 wt. % NaOH solution for 2 h, followed by washing with distilled water until pH = 7. Then, after been dried in vacuum at 60 °C for 12 h, the resultant cotton was dipped into 0.5 M nickel nitrate solution ($Ni(NO_3)_2{\cdot}6H_2O$, Tianjin Kermel Chemical Co, Ltd, China) for 24 h to obtain the precursors and dried overnight in a vacuum at 80 °C. Finally, in the annealing process, the precursors were calcined at 800 °C in flowing H_2/Ar for 4 h to produce MPC.

2.2. Characterisation method

The morphologies of the prepared hybrids were characterised by field-emission scanning electron microscopy (JEOL JSM-5600LV; accelerating voltage, 20 kV) and transmission electron microscopy (JEOL JEM-2010; accelerating voltage, 200 kV). The phase structures were characterised with X-ray diffraction (Philips Corp, Germany) operating with Cu Kα radiation (λ = 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. The relative complex permittivity and permeability were determined with an Agilent N5244A vector network analyser at EM wave frequencies of 2 to 18 GHz. To optimise the EM wave dissipation capability and impedance matching performance, the measured samples were prepared by uniformly mixing 5 wt.%, 10 wt.% and 15 wt.% MPC with paraffin. For convenience, the corresponding products were coded as S-5, S-10 and S-15, respectively.

3. Results and discussion

The X-ray diffraction and Raman patterns of the as-prepared MPC were measured to investigate the phase composition. As shown in Fig. 1(a), the sample exhibits diffraction peaks at 2θ = 44.4°, 51.7° and 76.3°, ascribed to the typical (111), (200) and (220) diffraction of face-centred cubic nickel (JCPDS 04–0805) [13], which confirms the complete reduction of Ni^{2+}. The small peak centred at 25.8° could be assigned to (002) of graphitic carbon, which confirms the complete carbothermal reduction and decomposition of cellulose [29]. Raman spectroscopy usually exhibits two broad peaks about 1333 cm^{-1} (labeled as the D peak for 'disordered carbon') and 1590 cm^{-1} (labeled as the G peak for 'graphite carbon'; Fig. 1(b)). The ratio of D and G bands (I_D/I_G) was 1.7 (as calculated by the software Origin 9.1/Peak Fitting Module), which indicated the existence of a considerable number of defect carbons in the MPC.

Fig. 2 shows the typical scanning electron microscopic and transmission electron microscopic microstructures of the MPC at various magnifications. The fibrous morphology of the precursor was maintained after the carbothermal reduction and decomposition process. Under further magnification, a large amount of Ni nanoparticles with diameters from 50 to 100 nm can be seen uniformly dispersed and embedded in the carbon matrix. Here, both the high specific surface area of the porous structure and the isolated nickel nanoparticles could provide more opportunities to interact with the EM wave, thus leading to significant interfacial polarization effects. Moreover, the very high porosities might improve the impedance matching behaviour of the MPC, and the incident EM microwaves can easily enter the inside of the composite with less reflectivity. Thus, the multiple reflection and sufficient microwave attenuation properties of the EM wave and the desired EM absorption properties could be expected with a low filler content.

To ascertain the porous structure formation mechanism of the MPC, the effect of the nickel nitrate concentration on the morphology of the Ni/carbon hybrids was investigated. As shown in Fig. S1, thermal annealing may induce the carbothermal reduction of the cotton but no porous structures were formed in the absence of nickel nitrate, which indicates that the porous structure originates mainly from the decomposition of nickel nitrate. Thus, by increasing the concentration of nickel nitrate in the precursor from 0.3 M to 1.0 M, a large amount of gas (NO_x) is released from the thermal decomposition of nickel nitrate and numerous pores were constructed in the product.

According to the transmission line theory, the relative complex permittivity and permeability of absorbents determine their reflection and attenuation characteristics. To investigate the influence of the filler content on the EM properties of MPC composites, we examined the complex permittivity and permeability of S-5, S-10 and S-15 between 2.0 and 18.0 GHz.

Fig. 3 shows that significant enhancement was achieved in both real (ε_r') and imaginary (ε_r'') parts of the complex permittivity as the MPC loading in paraffin increased. It is known that ε_r' and ε_r'' represent energy storage (polarization) and dissipation capability (dielectric loss), respectively. In general, the permittivity mainly originates from electronic polarization, ion polarization and intrinsic electric dipole polarization. At the microwave frequencies, the electron and ion polarizations are extremely weak, which occur at frequencies higher than the infrared frequency [30]. Usually, the electric dipolar polarization that can be induced by microstructural defects, interfaces or both is considered to be a main contributor to the polarization process. In this case, with the increasing loading of MPC in the samples, enhanced interfacial polarisability could be expected, which could be adopted to explain the increased permittivity and dielectric loss. Moreover, from the free-electron theory, $\varepsilon_r'' = 1/2\varepsilon_0\pi\rho f$, where ε_0 is the permittivity of a vacuum, ρ is the resistivity and f is the microwave frequency, it could be speculated that a higher ε_r'' value at 2 to 18 GHz corresponds to lower electric resistivity. Here, the increased carbon-based filler loading caused the conductive interconnections and the enhanced conductivity, which led to pronounced enhancement in the imaginary permittivity.

It is widely believed that dielectric loss behaviour results from polarization and conductive loss. In general, the high-frequency (> GHz) polarization form results primarily from interface polarization [31,32]. According to the Debye theory, the dielectric behaviour of composites can be explained based on the Cole-Cole model because the relationship between ε_r' and ε_r'' can be attributed to

$$\left(\varepsilon_r' - \frac{\varepsilon_s + \varepsilon_\infty}{2}\right)^2 + \varepsilon_r''^2 = \left(\frac{\varepsilon_s - \varepsilon_\infty}{2}\right)^2 \quad (1)$$

The plot of ε_r' versus ε_r'' would be a single semicircle (denoted as the Cole-Cole semicircle), and each semicircle refers to one Debye relaxation process [33]. Fig. S2 (a) shows the Cole-Cole plots to indicate the response behaviour of the composites with different filler contents from 2 to 18 GHz. For sample S-5, owing to the weakly conductive loss and