Journal of Alloys and Compounds 741 (2018) 814–820

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Facile-synthesized carbonaceous photonic crystals/magnetic particle nanohybrids with heterostructure as an excellent microwave absorber

Congpu Mu*, Jiefang Song, Bochong Wang, Fusheng Wen, Can Zhang, Cong Wang, Zhongyuan Liu, Jianyong Xiang**

State Key Laboratory of Metastable Materials Science and Technology and Key Laboratory for Microstructure Material Physics of Hebei Province, School of Science, Yanshan University, Qinhuangdao 066004, People's Republic of China

ARTICLE INFO

Article history:
Received 23 October 2017
Received in revised form
10 January 2018
Accepted 13 January 2018
Available online 17 January 2018

Keywords:
Carbonaceous photonic crystal
Magnetic nanoparticles
Heterostructure
Microwave absorption

ABSTRACT

In this work, carbonaceous photonic crystals (CPCs) were obtained by the carbonization of butterfly wings, and the CPCs/magnetic particle (Fe_3O_4 and Fe) nanohybrids with heterostructure were synthesized by a facile single-mode microwave-assisted hydrothermal method. Scanning electron microscopy and transmission electron microscopy images indicated that CPCs exhibited a distinct structure of a periodic network interconnected by ridges and ribs with a highly smooth surface. The magnetic nanoparticles were also uniformly attached on the ridges and ribs of CPCs. The microwave absorption performances of CPCs/Fe_3O_4 and CPCs/Fe nanohybrids with heterostructure were investigated. The minimum reflection loss (RL) were −49.7 and −31.2 dB for CPCs/Fe_3O_4 and CPCs/Fe nanohybrids, respectively. The effective bandwidths (RL < −10 dB) were 3.6 GHz (14.4–18.0 GHz) for CPCs/Fe_3O_4 and 4.1 GHz (13.6–17.7 GHz) for CPCs/Fe nanohybrids. Compared with the pure Fe_3O_4 and Fe nanoparticles, the microwave absorption performances of CPCs/Fe_3O_4 and CPCs/Fe nanohybrids were markedly improved. These findings illustrated that the CPCs/magnetic particle nanohybrids with heterostructure can be used as an excellent microwave absorber.

1. Introduction

Nanomaterials have been widely investigated because of their potential applications in numerous fields because of their novel properties, which deviate from those of their bulk materials [1–5]. With the extensive usage of wireless communication apparatus and electronic devices, the problems of serious electromagnetic environment pollution have attracted considerable attention in the last decade because of the harmful threats to human health and electronic equipment operation [6–8]. The design and development of highly effective microwave absorption and electromagnetic shielding materials have been focused on addressing such serious issues [9–14]. Nanomaterials and hybrid nanocomposites have garnered interest due to their high microwave absorption performance [15–17]. Based on the microwave loss mechanism, magnetic loss and dielectric loss are two kinds of loss mechanisms in the microwave absorption materials corresponding to magnetic and dielectric materials, respectively [18,19]. Therefore, the relative complex permeability and complex permittivity of microwave absorption materials are vital parameters that can be adjusted to improve microwave absorption performance. In experiments, the electromagnetic parameters of a microwave absorber can be effectively modulated not only by introducing the dielectric and/or magnetic components but also by controlling morphology and structure [7,20–23].

Carbon-based materials, such as graphite, carbon nanotubes, and reduced graphene oxide, have been widely investigated in several fields owing to their excellent physical properties [1,10,12,24–26]. As an important member in the carbon family, carbonaceous photonic crystals (CPCs) present several unique features, such as a periodic optical nanostructure, and have been explored as anodes for lithium and sodium batteries [27]. CPCs can be easily obtained by the carbonization of butterfly wings with a periodic network interconnected by ridges and ribs. A microwave enters CPCs and undergoes scattering and multiple reflections due to the periodic structure of CPCs. This condition is beneficial for the microwave absorption of materials. However, the mechanism of

---

* Corresponding author.
** Corresponding author.
E-mail addresses: congpumu@ysu.edu.cn (C. Mu), jyxiang@ysu.edu.cn (J. Xiang).

https://doi.org/10.1016/j.jallcom.2018.01.180

microwave absorption in CPCs only originates from dielectric loss. Numerous current studies have focused on the heterostructure of carbon-based materials, such as Fe_3O_4/C [28], carbonyl iron/reduced graphene oxide/polyvinyl pyrrolidone ternary [11], multiwalled carbon nanotube (MWCNT)/(Fe, Co, or Ni) [24], MoS_2/CNTs [29], and NiCo/graphene nanosheets [30], for enhancing microwave absorption performance. However, the microwave absorption properties of CPCs/magnetic nanoparticle nanohybrids with heterostructure have rarely been studied. Here, CPC/magnetic nanoparticle nanohybrids with heterostructure were designed as microwave absorbers for the first time. CPCs exhibit a distinct structure of a periodic network interconnected by ridges and ribs with a highly smooth surface, and magnetic nanoparticles is attached on the surface of ridges and ribs in CPCs. The interface is established between magnetic nanoparticles and the surface of CPCs in heterostructure of CPCs/Fe and CPCs/Fe_3O_4. This heterostructure can increase microwave scattering and reflection. In addition, this heterostructure can improve the microwave absorption performance compared with pure CPCs or magnetic nanoparticles. Nanohybrids can also satisfy the lightweight requirements of microwave absorbers due to the low density of CPCs.

In the present work, CPCs were obtained by the carbonization of butterfly wings, and CPCs/Fe_3O_4 and CPCs/Fe nanohybrids with heterostructure were successfully synthesized by a facile single-mode microwave-assisted hydrothermal method. The crystal structure, structural deformation, morphology, and microwave absorption properties of the nanohybrids were systematically investigated.

2. Experimental section

2.1. Fabrication of CPCs

CPCs were obtained through carbonization of butterfly wings. The butterfly wings were calcined in the tubular furnace at 800 °C for 2 h under argon protection. After being naturally cooling to room temperature, the derived CPCs were fabricated successfully and collected for the synthesis of CPCs/Fe_3O_4 and CPCs/Fe nanohybrids. The CPCs structure, which was investigated by scanning electron microscopy (SEM), included a periodic network interconnected by ridges and ribs (Fig. 1).

2.2. Fabrication of CPCs/Fe_3O_4 and CPCs/Fe nanohybrids

The CPCs/Fe_3O_4 and CPCs/Fe nanohybrids with heterostructure were fabricated through a facile synthetic route (Fig. 1). First, $FeCl_3 \cdot 6H_2O$, polyethylene glycol, NaAc, and CPCs were dissolved in 10 mL of ethylene glycol. A transparent brown yellow solution was obtained under magnetic stirring for 30 min. The solution, which was transferred to a microwave-specialized glass tube, was heated at 200 °C for 4 h by a single-mode microwave reactor. The CPCs/Fe_3O_4 product was collected by centrifugation and washed with ethyl alcohol for several times and then dried at 80 °C for 12 h in a vacuum. For obtaining the CPCs/Fe nanohybrids, CPCs/Fe_3O_4 was deoxidized by annealing at 600 °C for 2 h under H_2/Ar atmosphere. The structures of CPCs/Fe_3O_4 and CPCs/Fe nanohybrids are also illustrated in Fig. 1. The mass percentages of Fe and Fe_3O_4 were approximately 63% and 70% in heterostructure, respectively.

In this study, the butterfly wings were purchased from Zhengzhou Zhongkun Agricultural Technology Development Co., Ltd. (China). $FeCl_3 \cdot 6H_2O$ was acquired from Tianjin Kaitong Chemical Reagent Co., Ltd. (China). Ethylene glycol was sourced from Tianjin Juxing Chemical Reagent Co., Ltd. (China). Polyethylene glycol and NaAc were purchased from Sinopharm Chemical Reagent Co., Ltd. (China).

2.3. Characterizations

The crystal structures, structural deformation, and morphologies of the CPCs and CPCs/Fe_3O_4 and CPCs/Fe nanohybrids with heterostructure were investigated using Rigaku SmartLab X-ray diffractometry with Cu-Kα radiation ($\lambda = 1.5406$ Å), Renishaw inVia micro Raman spectroscopy with a laser radiation of 532 nm, SEM (S-4800 Hitachi, Japan), and transmission electron microscopy (TEM, JEM-2010 JEOL, Japan), respectively.

Samples for high-frequency electromagnetic parameter measurement were prepared by mixing the paraffin with 50 wt% CPCs, CPCs/Fe_3O_4, and CPCs/Fe. Then, the mixture was pressed into a toroidal structure with inner and outer diameters of 3.04 and 7.00 mm, respectively. Scattering parameters were measured using transmission/reflection method in the frequency range of 1.0–18.0 GHz by a vector network analyzer (VNA). Relative complex permeability μ_r and relative complex permittivity ε_r can be calculated from scattering parameters. Microwave reflection loss (RL) can be estimated from the relative complex permeability μ_r and relative permittivity ε_r by the following equations based on the transmission line theory [10,31]:

$$Z_{in} = Z_0 \left(\frac{\mu_r}{\varepsilon_r}\right)^{1/2} \tanh\left\{j\left(\frac{2\pi f d}{c}\right)(\mu_r \varepsilon_r)^{1/2}\right\}, \quad (1)$$

$$RL = 20 \log\left|\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right|, \quad (2)$$

where Z_{in} is the input impedance of the absorber, Z_0 is the impedance of air, f is the frequency of the microwave, d is the absorber thickness, and c is the velocity of the light.

3. Results and discussion

The crystal structures of CPCs, CPCs/Fe_3O_4, and CPCs/Fe nanohybrids were characterized by X-ray diffraction (XRD), as displayed in Fig. 2a. Two diffraction peaks assigned to (002) and (100) planes of the graphitic carbon were observed at approximately 23° and 43° in the XRD pattern for pure CPCs. The (002) diffraction peak of CPCs can be also detected in the XRD spectra of CPCs/Fe_3O_4 and CPCs/Fe, indicating that the CPCs exist in the nanohybrids. The heterostructure CPCs/Fe_3O_4 nanohybrids exhibited diffraction peaks located at 30.1°, 35.4°, 43.1°, 53.4°, 56.9°, 62.5°, 73.9°, and 89.6°, which corresponded to the (220), (311), (400), (422), (511), (440), (533), and (731) crystal planes of polycrystal Fe_3O_4 with fcc structure (JCPDS No. 19-0629), respectively [28]. The XRD pattern of CPCs/Fe indicated that all diffraction peaks belonged to pure bcc Fe (JCPDS No. 87-0722). The diffraction peaks of Fe_3O_4 were not detected in the CPCs/Fe nanohybrids, revealing that the Fe_3O_4 nanoparticles were completely reduced to Fe nanoparticles. The average crystallite sizes of Fe and Fe_3O_4 were 22.7 and 85.9 nm obtained by Rietveld method, respectively. Although the peak of CPCs can be found in the XRD patterns of CPCs/Fe_3O_4 and CPCs/Fe, the intensity of CPCs peak was too weak. Therefore, the Raman spectra of CPCs and CPCs/Fe_3O_4 and CPCs/Fe nanohybrids were measured to further show the existence of CPCs in CPCs/Fe_3O_4 and CPCs/Fe (Fig. 2b). We found two typical peaks of graphite, namely, D band at approximately 1345 cm^{-1} and G band at approximately 1588 cm^{-1}, which were associated with the defect-induced mode and E_{2g} mode, respectively [27,32]. The intensity ratio of the D and G bands (I_D/I_G) can be used to illustrate the defects and disorder of graphite [33,34]. All intensity ratios (I_D/I_G) of CPCs, CPCs/Fe_3O_4, and