Composites Part B 132 (2018) 141–150

Contents lists available at ScienceDirect

Composites Part B

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

Facile fabrication of boron and nitrogen co-doped carbon@Fe_2O_3/Fe_3C/Fe nanoparticle decorated carbon nanotubes three-dimensional structure with excellent microwave absorption properties

Bo Zhong [a], Chaojun Wang [a], Guangwu Wen [a, c], Yuanlie Yu [b, *], Long Xia [a, **]

[a] School of Materials Science and Engineering, Harbin Institute of Technology at Weihai, Weihai 264209, People's Republic of China
[b] R&D Center of Lubricating and Protecting Materials, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China
[c] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, People's Republic of China

A R T I C L E I N F O

Article history:
Received 23 March 2017
Received in revised form
28 August 2017
Accepted 1 September 2017
Available online 5 September 2017

Keywords:
3-Dimensional reinforcement
Microstructures
Surface analysis
Heat treatment
Carbon@Fe_2O_3/Fe_3C/Fe nanoparticles
Enhanced microwave absorption

A B S T R A C T

Herein, we report a facile process to massively synthesize three-dimensional (3D) boron and nitrogen co-doped carbon@Fe_2O_3/Fe_3C/Fe nanoparticle decorated carbon nanotubes (B/N co-doped C@Fe_2O_3/Fe_3C/Fe-CNTs). The fabrication involved a simple one-step chemical vapor deposition process. These as-synthesized 3D B/N co-doped C@Fe_2O_3/Fe_3C/Fe-CNTs based absorbers exhibited excellent microwave absorption properties with tunable strong absorption wavebands in the frequency range of 2–18 GHz. A minimum reflection loss (RL) value of −42.6 dB was observed at 6.88 GHz with absorber thickness of 3.5 mm. Moreover, the absorption bandwidth for RL less than −10 dB was as large as 4.14 GHz when the absorber thickness dropped to 2.0 mm. A possible absorption mechanism was proposed in detail, which can be attributed to the synergy of the impedance matching and enhancement of multiple reflection among 3D B/N co-doped C@Fe_2O_3/Fe_3C/Fe nanoparticles.

1. Introduction

The contemporary rapid development of electronic information technologies generates massive electromagnetic (EM) radiations due to the increasingly usage of electrical and electronic devices, such as wireless data communication, local area networks, personal digital assistants, satellite television and self-concealing [1,2]. Such EM radiations not only adversely disturb the operation of electronic devices but also are harmful to human health and wild life [2–4]. Therefore, great efforts have been made to develop high performance microwave absorption (MA) materials [5–27]. Generally, high efficiency and light weight of MA materials are the two key factors promoting their practical in a wide range of commercial, military, aerospace and healthcare applications [6]. Recently, carbon based materials such as carbon fibers [2], graphite [28], carbon nanotubes (CNTs) [16], graphene [29], carbon nanocoils [30] and carbon foam [31] have been regarded as good microwave absorbers due to their excellent chemical and physical properties. Among them, CNTs have attracted considerable attention for high-efficient microwave absorption because of their light weight, high conductivity, high aspect ratio, good resistance against corrosion and excellent mechanical properties [6]. However, the pure CNT based absorbers display low reflection losses (RL) typically lower than −23 dB and narrow bandwidth [21,32–34]. Therefore, the MA performance of CNTs must be improved for various demands, such as high capacity and broad bandwidth.

Integrating dielectric and/or magnetic nanostructures with CNTs is an effective way to improve the MA performance of CNTs, because the microwave absorption properties of MA materials are closely associated with their dielectric and magnetic properties [35]. For example, Hao Sun et al. have fabricated a novel lightweight and frequency-tunable aligned CNT films [16]. The maximal absorption frequency of this aligned CNT films can be controlled by varying their intersectional angles [16]. Moreover, the maximum microwave RL can be further increased by increasing the stacked number of aligned CNT films or incorporation of other moieties such as inorganic Fe and organic polymer [16]. Fusheng

* Corresponding author.
** Corresponding author.
E-mail addresses: yuanliehll@163.com (Y. Yu), xialong@hit.edu.cn (L. Xia).

http://dx.doi.org/10.1016/j.compositesb.2017.09.001
1359-8368/

Wen et al. have prepared a series of multi-walled carbon nanotubes (MWCNTs)/Fe, MWCNTs/Co, and MWCNTs/Ni nanocomposites by simple chemical method [36]. These MWCNT/metal based composites exhibit excellent microwave absorption properties in S-band due to the proper combination of the complex permeability and permittivity resulting from the magnetic nanoparticles and lightweight MWCNTs [36]. It was found that the RL exceeded −20 dB from 2.04 to 3.47 GHz for the absorber thickness between 3.36 and 5.57 mm [36]. And a minimum RL value of −39 dB was observed at 2.68 GHz for MWCNTs/Fe composite with a matching thickness of 4.27 mm [36]. Recently, Yihua Chen et al. developed a novel approach to tune the electromagnetic properties of CNTs by hybridizing three-dimensional Fe_3O_4 nanocrystals and MWCNTs (3D Fe_3O_4-MWCNTs) through a simple co-precipitation route [6]. Enhanced double-band microwave absorption has been observed in the investigated frequency range of 2–18 GHz and at various thicknesses for these novel 3D Fe_3O_4-MWCNTs composites [6]. The minimum RL loss values of −23.0 dB and −52.8 dB are obtained at 4.1 GHz and 12.8 GHz [6], respectively. Yihua Chen et al. attribute this enhanced MA properties to the combination of dielectric loss, magnetic loss, as well as the enhancement of multiple reflection among 3D Fe_3O_4 nanocrystals [6].

Herein, novel 3D boron and nitrogen co-doped carbon@Fe_2O_3/Fe_3C/Fe nanoparticle decorated carbon nanotubes (3D B/N co-doped C@Fe_2O_3/Fe_3C/Fe-CNTs) have been fabricated *via* a simple one-step chemical vapor deposition (CVD) process. Usually, metals are used to improve the properties of carbon based materials [37–40]. In addition, previous researches have demonstrated that the decoration of Fe-Fe_3C or iron oxide nanoparticles onto the surfaces of carbon nanomaterials and the incorporation of B and N into graphene can effectively improve the MA performance of carbon materials [6,8,9,14,25,41–43]. Wanxi Li et al. find that the Fe-Fe_3C nanoparticle decorated carbon microspheres exhibit excellent MA performance with the effective bandwidth (RL less than −10 dB) reaching up to 4 GHz when the thickness of the sample was as thin as 1.5 mm [42]. Yue Kang et al. reported that B and N incorporated graphene showed a minimum RL value of −33.6 dB at 15.28 GHz with a thickness of 1.6 mm [41]. The reflection values below −20 dB were in the frequency range of 7.76–17.84 GHz with the thickness of 1.6–3 mm [41]. Therefore, we selected carbon@Fe_2O_3/Fe_3C/Fe nanoparticles and B and N to couple with CNTs to improve their MA properties. The morphology, crystalline structure and composition of these novel 3D B/N co-doped C@Fe_2O_3/Fe_3C/Fe-CNTs were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), transmission electron microscope (TEM), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The MA properties of these novel 3D B/N co-doped C@Fe_2O_3/Fe_3C/Fe-CNTs based absorbers with different thickness were systemically investigated in the frequency range of 2–18 GHz. Furthermore, the absorption mechanism for the enhanced MA performance of these novel 3D B/N co-doped C@Fe_2O_3/Fe_3C/Fe-CNTs was also discussed in detail in terms of the characterization on their morphology, structure, and electromagnetic parameters. The high MA capacity and wide absorption bandwidth combining with the outstanding properties of CNTs make these 3D B/N co-doped C@Fe_2O_3/Fe_3C/Fe-CNTs very attractive for practical applications.

2. Experimental details

2.1. Sample preparation

The 3D B/N co-doped C@Fe_2O_3/Fe_3C/Fe-CNTs were synthesized through a facile one-step CVD process under argon atmosphere. The schematic of the setup for the synthesis is shown in Fig. 1. Ammonia borane synthesized according to the method described in the literature [44] was used as B/N precursor. In a typical growth, the first heating zone was ramped up to 90 °C with a heating belt to produce B and N precursor (Fig. 1I). The on-off valve between the first and second heating zone was closed most of the time, except during the fabrication of 3D B/N co-doped C@Fe_2O_3/Fe_3C/Fe-CNTs, to prevent undesired growth. The second heating zone (Fig. 1II) was heated up to 1300 °C with a heating rate of 5 °C min^{-1} and held for 60 min under argon atmosphere. After the reaction, the sample was cooled down to room temperature naturally. Additionally, the undoped CNTs without B/N precursor introducing were also prepared for the MA performance comparison.

2.2. Sample characterization

The crystalline structure of the as-synthesized samples was characterized by XRD (Rigaku D/max-γB X-ray diffractometer with Cu K radiation, $\lambda = 0.154178$ nm). The morphology of the as-synthesized samples was examined by SEM (TESCAN VEGA II) equipped with an EDS detector. The interior structure of the as-synthesized samples was probed by FEI Tecnai G2 F30 TEM. The composition and bonding information of the as-synthesized samples were investigated by XPS performed on PHI 5700 spectrometer with Al Kα excitation radiation (1486.6 eV).

2.3. Electromagnetic parameter measurements

The microwave absorption performance of 3D B/N co-doped C@Fe_2O_3/Fe_3C/Fe-CNTs and undoped CNTs was evaluated by a vector network analyzer (VNA; Agilent N5245A) in the frequency range of 2–18 GHz. The electromagnetic parameters of the 3D B/N co-doped C@Fe_2O_3/Fe_3C/Fe-CNTs and undoped CNTs were calculated by HP85071 software. The 3D B/N co-doped C@Fe_2O_3/Fe_3C/Fe-CNTs and undoped CNT based absorbers were prepared by

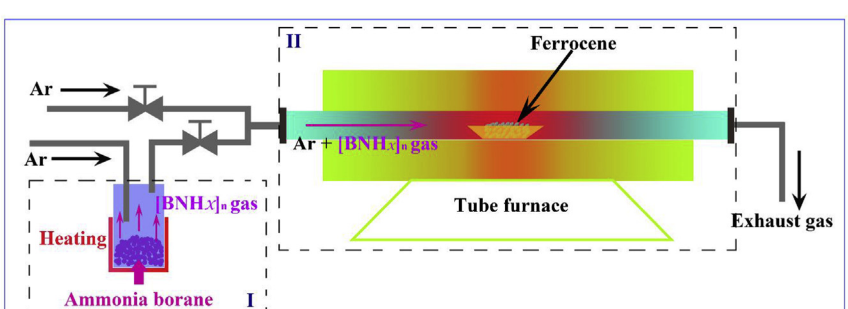

Fig. 1. Setup for the preparation of 3D B/N co-doped C@Fe_2O_3/Fe_3C/Fe-CNTs.