Composites Part B 152 (2018) 316–323

Contents lists available at ScienceDirect

Composites Part B

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

Ultra-small Co/CNTs nanohybrid from metal organic framework with highly efficient microwave absorption

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ARTICLE INFO

Keywords:
Metal organic framework
Carbon nanotube
Cobalt
Nanohybrid
Microwave absorption

ABSTRACT

The application of composites of carbon matrix and ferromagnetic nanoparticles as electromagnetic wave absorption materials has received extensive attention. In this study, we successful synthesized metal organic framework (MOF) with dodecahedron shape by the decomposition of Co-based precursor of zeolitic imidazolate framework (ZIF -67). And to further improve the absorbing performance, acetylene was introduced to obtain ultra-small Co/CNTs nanohybrids. During CVD process, Co nanoparticles of MOF cracked into Co nanocrystals catalyzing the growth of carbon nanotubes (CNTs). Among three composites of ZIF-67, MOF and Co/CNTs, the Co/CNTs presented the better performance for electromagnetic wave absorption. Particularly, the maximum reflection loss (RL) of Co/CNTs reached −49.16 dB in case of the absorber thickness of 2.5 mm. The excellent absorbing performance is more likely attributed to the novel structure and the double losses of magnetic Co and dielectric CNTs.

1. Introduction

Electromagnetic (EM) pollution has aroused extensive attention including environmental and health problem, which seriously affects the survival of mankind and the normal production and other activities [1–4]. To deal with EM pollution, more and more efforts have been taken in the past decade aiming to design high-performance microwave absorbers with the purpose of lightweight, strong absorption and wide absorption bandwidth [3,5]. Several kinds of novel materials [6–10] such as magnetic loss materials, including ferrites [11,12], ferromagnetic metal oxides [13,14], and ferromagnetic metals [15] and alloys [16,17] and dielectric loss materials such as carbons [18–21] and conducting polymers [22–24] have been investigated because of their microwave absorption property. However, single absorbers can't achieve high-performance microwave absorption (MA) property due to the poor impedance matching. According to the impedance matching mechanism $Z_{in} = Z_0\sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left(j\frac{2\pi f}{c}d\sqrt{\mu_r\cdot\varepsilon_r}\right)$, it is easy to know that the combination of magnetic loss materials and dielectric loss materials is an effective approach for absorbers to achieve good impedance matching to decrease the reflection of microwave and make sure electromagnetic wave as much as possible enter into the interior of absorbers [25–27]. Accordingly, many efforts have been applied to study MA property of the combination for dielectric loss materials with magnetic loss materials [28,29], such as Fe−Fe_3O_4@C [30], Ni@TiO_2 [31], Fe_3O_4@C [32–34], graphene/$CoFe_2O_4$ [35], and Co/TiO_2 [36], *etc*. By designing the constituent and structure of nanohybrid absorbers, excellent MA property in 2–18 GHz is expected to be obtained through adjusting the permittivity and permeability of nanohybrid absorbers.

Recently, metal−organic framework (MOF) derived carbon absorbers possess dual characteristics with dielectric loss and magnetic loss, which is considered as an ideal potential MA absorber. For instance, Lu and his group [37] reported a porous Co/C composite derived from a pyrolyzed Co-based zeolitic imidazolate framework (ZIF-67) which had excellent MA property with an optimized reflection loss (RL) of −35.3 dB at a Co/C and paraffin loading of 60 wt%. Similarly, Qiang et al. [38] synthetized Fe/C composite to address strong MA property

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https://doi.org/10.1016/j.compositesb.2018.08.109
Received 12 August 2018; Accepted 23 August 2018
Available online 27 August 2018
1359-8368/

with a maximum RL value of −20.3 dB at the filler loading of 40 wt%. Additionally, Shui's group [39] achieved high-performance MA property in Co−C/MWCNTs composite with a minimum RL value of −48.9 dB at a filler loading of 15 wt%, which is due to the conductive network, the orientation-enhanced dielectric loss, and the synergistic effect between magnetic and dielectric components. Unfortunately, most MOF-derived carbon-based absorbers have poor conductivity attributed to poor graphitization degree, which is bad for electron transport and thus weakens the attenuation of microwave. Therefore, it is necessary to increase the conductivity of absorbers to obtain excellent microwave absorption property. Previously, our group prepared Fe_3O_4/GCs composite *via* the combination of catalytic chemical vapour deposition (CCVD) and hydrothermal methods [40]. The 3D GCs with relatively high conductivity due to the accumulation of charges at the interfaces, which is beneficial to achieve high-performance MA property for composite with minimum RL value of −32 dB at 8.76 GHz, meanwhile possess wide absorption width of 12.4 GHz for RL value lower than −10 dB. This work and Shui' finding gave us inspiration to improve the microwave absorption performance of MOF-derived absorbers by designing magnetic nanoparticles-decorated carbon nanotubes (CNTs) composites. The high conductivity and one-dimensional structure provideadditional dielectric loss due to an interconnected network.

Herein, we prepared ultra-small Co/CNTs nanohybrid *via* the pyrolysis of ZIF-67 and CCVD method. This synthetic method is facile, controllable, and low-cost. Interestingly, the optimized Co/CNTs nanohybrid exhibited strong MA property with RL value up to −49.2 dB for a 2.5 mm absorber thickness with 30 wt% Co/CNTs nanohybrid loading. The ultra-small Co/CNTs nanohybrid with strong MA property can be applied as lightweight, strong absorption and ultra-small MA absorbers for practical applications.

2. Experimental section

2.1. Synthesis of the ZIF-67

Zeolitic imidazolate framework of ZIF-67 was synthesized by the solvothermal procedure. In detail, 1.436 g of $Co(NO_3)_2{\cdot}6H_2O$ and 3.244 g of 2-methylimidazole were dissolved in 100 mL methanol at 25 °C, respectively. The solution of $Co(NO_3)_2{\cdot}6H_2O$ was poured into the solution of 2-methylimidazole under vigorous stirring for 12 min and then kept statically for 20 h at 25 °C. The blue porous product was separated by centrifugation and washed with methanol for three times, followed by vacuum drying at 150 °C for 8 h.

2.2. Preparation of MOF and Co/CNTs nanohybrid

ZIF-67 was decomposed into MOF at 650 °C for 3 h under argon with a flow rate of ∼30 mL/min. In a typical reaction, Afterwards, the silicon boat filled with ZIF-67 was transported into a horizontal CVD furnace. The decomposition of ZIF-67 was carried out at 650 °C for 3 h under Ar at the heating rate of 0.5 °C/min. After the completion of the reaction, the furnace was cooled down at the rate of 0.5 °C/min and the final black color product of MOF was collected, which was used for further analysis and the synthesis of Co/CNTs nanohybrid. The hybrid was prepared from the catalytic reaction of acetylene at 350 °C for 30 min with the gas flow rate of C_2H_2 (40 mL/min) and Ar (60 mL/min). After the reaction was completed, it was naturally cooled to room temperature to obtain the Co/CNTs nanohybrid in black.

2.3. Characterizations

The morphology and microstructure of ZIF-67, MOF and Co/CNTs nanohybrid were studied using scanning electron microscopy (SEM), X-ray diffraction (XRD), and high transmission electron microscopy (HRTEM). And Raman spectra were performed on a confocal Raman spectroscopic system (Renishaw, In Via) using a 532 nm laser. The relative complex permeability ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permittivity ($\mu_r = \mu' - j\mu''$) of the sample-wax composites were determined by the coaxial line method through an Agilent N5234A vector network analyzer system. The sample-paraffin are mixed evenly according to different proportions, and the mixture is pressed into a coaxial ring with an inner diameter of 3 mm and an outer diameter of 7 mm, and the thickness is about 3.5 mm. According to the transmission line theory, the reflection losses RL (dB) of the composites can be calculated, using the measured data of relative complex permeability and permittivity.

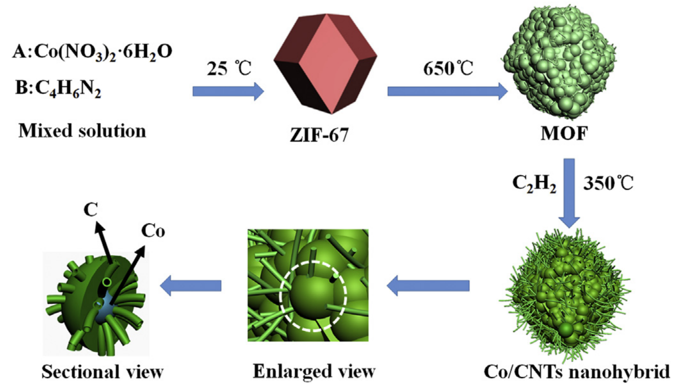

Fig. 1. Synthetic progress of ZIF-67, MOF and Co/CNT nanohybrid.

3. Results and discussion

Fig. 1 shows the preparation process of complex Co/CNTs. $Co(NO_3)_2{\cdot}6H_2O$ (A) and 2-methylimidazole (B) are dissolved in methanol at 25 °C, and the reaction mixture in a water bath at 25 °C, then the ZIF-67 of the rhombic dodecahedral morphology can be collected. Through the carbonization process (650 °C), ZIF-67 converts into MOF. During the carbonization, ZIF-67 is decomposed into tiny particles with cobalt atoms as the core, and these tiny particles gather together and basically maintain the structure of the rhombic dodecahedral morphology, and there are a little carbon nanotubes exist on the outside of the tiny particles. Then Co/CNTs was obtained by carbon coating experiment at 350 °C, there are a large number of carbon nanotubes appeared on the outside of the rhombic dodecahedral morphology, so the specific surface area of Co/CNTs was increased.

Fig. 2 shows the XRD patterns of ZIF-67, MOF and Co/CNT nanohybrid. These three samples present different XRD characteristic peak. For the precursor of MOF, the XRD peaks correspond to ZIF-67 which is agreement with previous literature reports [41]. After the change from ZIF-67 to MOF, only two peaks for as-prepared MOF was found in the XRD pattern positioned at 44° and 51.5° corresponding to the (111) and (200) crystal faces of the cobalt, respectively, which confirms that Co nanocrystals exist after the carbonization process. Furthermore, Co/CNT nanohybrid was obtained from the catalytic reaction of acetylene by MOF. Compared with pure MOF containing Co(111) and Co(200) peaks, two more weak peaks were found that: one peak was located at the position of 36.2°, and another peak positioned at 41.49°. After checking the standard PDF card, the peak at 41.49° is assigned to Co_2C (002) plane. The formation reason is related to the reaction action of acetylene by Co catalyst. Besides, the peak at 36.2° is attributed to CoO (110) plane, which is from the catalytic oxidation of oxygen impurity during the CCVD reaction system.

SEM testing and particle size distribution analysis were performed for ZIF-67, MOF, and Co/CNTs shown in Fig. 3. The SEM images of the precursor of ZIF-67 are shown in Fig. 3 (a, b). It can be seen that ZIF-67 presents a standard rhombohedra dodecahedron with uniform shape. Fig. 3 (c) shows the particle size distribution of ZIF-67 in the range of 230 nm–380 nm, and the average particle size is about 280 nm. More