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CNFs@carbonaceous Co/CoO composite derived from CNFs penetrated through ZIF-67 for high-efficient electromagnetic wave absorption material

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ABSTRACT

In this work, Metal Organic Frameworks (MOF)-derived the necklace-like carbon nanofibers (CNFs) @carbonaceous Co/CoO composite is synthesized by wet chemical and pyrolysis method. The CNFs are penetrated through the derived carbonaceous Co/CoO frameworks which retain the ZIF-67's sizes. Due to their unique structure and the well controlling of experimental parameters, the optimum reflection loss value of −53.1 dB at 6.56 GHz is obtained, and the corresponding bandwidth below −10 dB (90% absorption) is up to 13.52 GHz with the thickness range of 2.0–5.0 mm. Due to the low density of CNFs and MOF-derived carbon in the composite, the as prepared CNFs@carbonaceous Co/CoO composite can act as a new member of lightweight and high-efficient EM wave absorbents.

1. Introduction

With the development of modern science and technology, more and more electronic devices are used in people's daily life and brought us great convenience. At the same time, these products make the users under a long time of hazard electromagnetic radiation which resulted in great health problems. In order to solve these problems, many researchers pay great attention to develop high efficient electromagnetic (EM) wave absorption materials to absorb the unwanted EM waves [1–3]. In addition, today's modern warfare is a high-tech electronic battle. The technology of radar detection is become more and more advanced. Therefore, there is a quite demand to exploit corresponding radar stealth technology [4]. So, developing high performance EM wave absorbents is one of the effective means to satisfied the demand of modern warfare [5].

The wave absorption material is a kind of functional material that can absorb, attenuate incoming EM waves and convert the EM energy into heat or other forms of energy dissipation [6]. The new requirements for efficient EM wave absorbents are thin, light, wide and strong [7–10]. Carbon nanomaterials have the remarkable advantage of lightweight, and they become one of the most important branches in nanotechnology research. Many carbon-based materials such as graphene [11–14], carbon nanotubes [7,15,16], carbon nanocoils [17,18] and carbon nanofibers [19,20] have demonstrated a potential application prospect in microwave absorbing field. Among them, carbon nanofibers (CNFs) with low density, high strength, high electrical conductivity, good thermal conductivity and stability properties, have been widely used in electrode materials, adsorption materials, catalyst carriers and so on [21,22]. However, the pure CNFs are a kind of typical dielectric loss material. The permittivity is high, but the permeability is very low, which makes the poor electromagnetic impedance matching. When they used alone as EM absorbents, the general shortcomings are narrow absorption band and low intensity of absorption value. Therefore, the effective way to improve the EM wave absorption properties is to combine some semiconductors or magnetic materials into the CNFs. As the previous studies, Xiang et al. synthesized carbon nanofibers with ferromagnetic metal nanoparticles (CNF–M, M = Fe, Co, and Ni) by electrospinning and thermal reduction method [23]. The minimum reflection loss value

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of −67.5, −63.1, and −61.0 dB is achieved for CNF—Fe, CNF—Co, and CNF—Ni, respectively. But the high voltage is required for the electrospinning and the high temperature for thermal reduction process. Ki-Yeon Park et al. used CNFs as dielectric loss materials and NiFe particles as magnetic loss materials, and then mix them together to obtain wave absorbents [24]. Although the wave absorption properties are improved, but they are not very satisfied. Besides these, magnetite-decorated CNFs [25], CI/CNF/LSMO [26], CNF—Fe_3O_4 nanocomposites [27] are also used as effective wave absorbents, but the wave absorption properties are needed to be further improved.

Metal-Organic Frameworks (MOFs), new materials consisting of metal ions and organic units, have been widely used in the fields of electrode materials, electrocatalysis and adsorbents in recent years [28–30]. They have been proven to be a promising precursor to construct the corresponding porous metal oxides with preferably morphologies [31]. Due to the designable frameworks with a modular assembly process, metal oxide derived from MOFs can integrate various applications [32,33]. For instance, Zhang et al. designed iron-based MOF exhibiting good recharge ability in solid oxide batteries [34]. Dou et al. obtained Co nanoparticle-embedded N-doped carbon nanotube/porous carbon by pyrolyzing MOF encapsulated Co_3O_4, which exhibited highly efficient activities for the ORR and OER [29]. Yin et al. prepared rGO/Co_3O_4 composites derived from GO-MOFs exhibiting outstanding performances for LIBs and SCs [28]. In previous reports, MOF-derived metal oxide can also be used as a kind of microwave absorbents. Especially for Co based MOF, lv et al. [30] obtained porous Co/C composite nanomaterials derived from ZIF-67 (a kind of Co-based MOF) show excellent electromagnetic wave absorption properties, the minimum reflection loss can reach to −35.3 dB. Liang et al. [35] prepared the composite of ZnO/NPC@Co/NPC from the heat treatment of core—shell structured ZIF-8@ZIF-67 crystal, the composite has the minimum reflection loss of −28.8 dB and a broad absorption bandwidth of 4.2 GHz (RL values exceeding −10 dB). Our group designed carbonaceous Co_3O_4/Co/RGO composite derived from GO/ZIF-67 and the minimum RL can reach up to −52.8 dB [36]. Therefore, it is an effective way to obtain good wave absorption properties from MOF derived metal oxide combining with other absorption materials.

In this paper, owing to the effective properties of CNFs and MOFs-derived composite, the necklace-like CNFs@carbonaceous Co/CoO composite derived from CNFs combined with ZIF-67 is designed and synthesized to improve the EM wave absorption properties. Necklace-like CNFs@ZIF-67 is firstly fabricated by chemical coordination of activated CNFs with ZIF-67. After a simple pyrolysis process, the ZIF-67 is derived to carbonaceous Co/CoO hybrid and penetrated throughout the CNFs to form the target product. Attributed to the unique structure in conductive network and synergistic effect of electric loss, magnetic loss and impedance matching, the EM waves will suffer multiple reflection and scattering and then be sufficient absorbed. Therefore, the CNFs@carbonaceous Co/CoO composite display high absorbing abilities and broad absorbing bands, it is a lightweight and high performance wave absorbents candidate.

2. Experimental

2.1. Preparation of acid-treated CNFs

In order to make the CNFs easily interacted with the Co^{2+}, we use concentrated HNO_3 to treat them. 0.5 g commercial CNFs were added to 100 mL concentrated HNO_3 (65 wt%) at the temperature of 90 °C. After stirring for 30 min, the acid-treated CNFs were washed with deionized water several times, and dried at 60 °C overnight for further using.

2.2. Preparation of CNFs@ZIF-67

Different amount of acid-treated CNFs such as 0.15 g, 0.1 g and 0.075 g were dissolved in 100 mL methanol, respectively. After ultrasonication for 30 min, triplicate of 1.494 g $Co(NO_3)_2 \cdot 6H_2O$ with methanol solution were added to the above solutions. Keep stirring about 6 h, when the acid-treated CNFs were sufficiently interacted with Co^{2+}, triplicate of 1.968 g 2-methylimidazole with methanol solutions were rapidly poured into the above mixtures and stirred for 24 h at room temperature. The products were collected and washed with methanol more than three times, dried at 60 °C overnight. The obtained products were CNFs@ZIF-67 with different mass ratio of CNFs and ZIF-67. We named them as Sample 1, Sample 2 and Sample 3, respectively.

2.3. Preparation of CNFs@carbonaceous Co/CoO

The obtained Sample 1, Sample 2 and Sample 3 were calcined at 600 °C. In all the calcination processes, argon is acted as protected atmosphere, the calcination time is keeping for 4 h, the heating rate is 2 °C min^{-1}. The final products were named as 600°C-1, 600°C-2 and 600°C-3, respectively. To investigate the calcination temperature how to affect the wave absorption performance, the Sample 2 is also calcined in 500 °C and 700 °C. And we named them as 500°C-2 and 700°C-2.

The characterization instruments and related parameters were stated in Supporting Information 1 (SI1).

3. Results and discussions

The CNFs@carbonaceous Co/CoO composite is firstly synthesized by wet chemical method and carbonization process, as illustrated in Scheme 1. In essence, the fabrication process is mainly divided into four steps. Firstly, we use concentrated HNO_3 treated with CNFs to make them have many negative groups which can be better combined with positive cobalt ions. Secondly, the positive cobalt ion was successfully recognized with the negative groups such as hydroxyl and carboxyl groups on the acid-treated CNFs. Thirdly, the 2-Methylimidazole is added to the solution and coordinate with the Co^{2+} to form the ZIF-67, which are penetrated throughout the CNFs. At last, the necklace-like CNFs@ZIF-67 are calcined at different temperatures (500 °C, 600 °C and 700 °C) under Ar atmosphere for 4 h. After the pyrolysis process, the ZIF-67 was derived to carbonaceous Co/CoO and the target product CNFs@carbonaceous Co/CoO composite is obtained. For the Co and CoO nanoparticles, they are very small (about a few nanometers) and homogeneous dispersed into the carbonaceous Co/CoO frameworks. So, we don't clearly label them in these frameworks.

The XRD patterns of pure CNFs, ZIF-67 and CNFs@ZIF-67 are displayed in Fig. 1a. For pure CNFs, there is a dispersive peak locating at around 26°, suggesting amorphous carbon existing in the sample. For pure ZIF-67, it is corresponding to the simulated pattern of ZIF-67's single crystal data [30]. For CNFs@ZIF-67, it is not only reserved all the feature peaks from ZIF-67, but also retained the little diffraction peak placed at about 26°, suggesting ZIF-67 and CNFs are composited in the samples. The Sample 2 of CNFs@ZIF-67 is calcined in different temperatures such as 500 °C, 600 °C and 700 °C, respectively. Fig. 1b shows the XRD patterns of the calcined samples, three samples are composed of the typical diffraction peaks of CNFs, Co and CoO. Especially for 600°C-2, the peak located at 26° (labeled as "♣") can be assigned to carbon in CNFs and there is a little hunch between 20 and 30° can be due to the carbon in carbonized MOFs. The three obvious diffraction peaks appearing at