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Metal-organic framework nanoparticles decorated with graphene: A high-performance electromagnetic wave absorber

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ABSTRACT

A novel metal organic framework (MOF) coated RGO was fabricated by a one-step method. The morphology and microstructure of MOF-53(Fe)/RGO composite were characterized by XRD and TEM. The electromagnetic parameters indicate that MOF-53(Fe)/RGO composite shows enhanced electromagnetic absorption properties compared with MOF-53(Fe). The maximum R_L can reach −25.8 dB at 15.4 GHz and the absorption bandwidth with the reflection loss exceeding −10 dB is 5.9 GHz (from 12.1 to 18 GHz) with the thickness of 2 mm. The possible absorption mechanism was also investigated in detail. Our results indicate the potential application of MOF/RGO composite as a more efficient microwave absorber.

1. Introduction

Electromagnetic waves have become a serious problem in various fields which may not only interrupt electronic devices, but also threatens human life [1]. To solve these problems, many researchers are paying great attention to the development of electromagnetic absorption materials. Recently, graphene has attracted considerable attention for achieving high-performance electromagnetic absorber due to the residual defects, larger interface, high permittivity and low density [2–3]. Nevertheless, the sole graphene suffers from impedance mismatch owing to high conductivity, which results in weak absorption and narrow absorption frequency [4]. Therefore, various magnetic materials such as Fe_3O_4 [5], Ni [6], $NiFe_2O_4$ [7] and $CoFe_2O_4$ [8], etc have been used to decorate reduced graphene oxide (RGO) to enhance electromagnetic attenuation, which contributes to a proper impedance matching between permittivity and permeability. Meanwhile, carbon materials such as MWCNT [9] and PANI [10] also have been added into the surface of RGO to improve the microwave absorption due to the formation of conducting network and unique structural characteristics. Recently, researchers have studied the microwave absorption properties of the multi-element composites due to their multi-functional electrical and magnetic properties, as well as multiple reflections and interfacial polarizations, such as rGO/Carbon Microspheres/rGO Composite [11] and CuS/Magnetically Decorated Graphene [12].

Metal organic frameworks (MOF) are a class of porous materials, which has attracted considerable attention because of high surface area, low density, diverse structural topologies as well as many functionalities [13]. The fascinating properties make MOF used in a variety of application areas, including gas storage, catalysts, sensors and supercapacitors [14–17]. The incorporation of MOF into graphene materials is an effective approach to improve the microwave absorbing properties of graphene. However, to the best of our knowledge, microwave absorption properties of MOF decorated with graphene have never been reported.

In this work, we directly grow MOF-53(Fe) on the surface of graphene by a one-step hydrothermal strategy. Structural and morphological of MOF-53(Fe)/RGO composite have been investigated. The MOF-53(Fe)/RGO composite can obtain good electromagnetic properties compared with MOF-53(Fe).

2. Experimental

The formation mechanism of MOF-53(Fe)/RGO composite can be explained as Fig. 1. Firstly, Graphene oxide (GO) was prepared by Hummer's method [18]. Secondly, GO was dispersed in 64.7 ml DMF (1 mg/ml) by sonication treatment, then 0.81 g $FeCl_3 \cdot 6H_2O$ and 0.5 g terephthalic acid were added and stirred for 30 min. Lastly, the solution was transferred into a 100 ml Teflon-lined stainless steel autoclave and kept in an oven at 150 °C for 12 h. For comparison, MOF-53(Fe) was prepared via a similar hydrothermal

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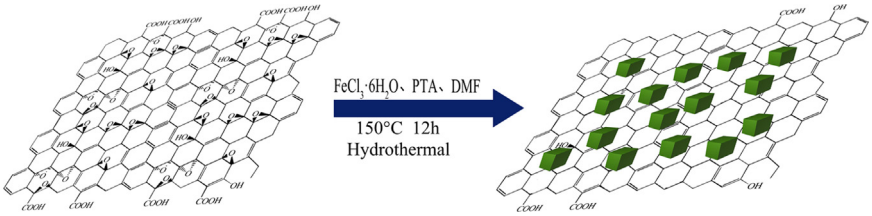

Fig. 1. Schematic illustration of the synthesis procedure of MOF-53(Fe)/RGO composite.

process without GO. After cooling down to room temperature, the products were washed with deionized water and ethanol, then dried at 150 °C under vacuum for 8 h.

The structure was analyzed by X-ray diffraction (XRD) patterns (German Bruker D8 with Cu-Kα radiation). Transmission electron microscopy (TEM, American FEI F30 G^2) was employed to analyze the morphology and the size of the samples. The N_2 adsorption-desorption isotherms were measured on a Quad-rasorb-SI instrument, and the specific surface area was determined by the Brunauer–Emmett–Teller (BET) method. The magnetic properties were measured using a vibrating sample magnetometer (VSM, Lake Shore7307) with a maximum applied field of 13,500 Oe. The electromagnetic parameters were analyzed by using a HP8720ES vector network analyzer in the range of 2–18 GHz.

3. Results and discussion

The morphology of sample was investigated by TEM, as shown in Fig. 2(a–d). The MOF-53(Fe) particles consist entirely of polyhedrons with an average edge length of around 500 nm which indicates the well crystalline nature of MOF-53(Fe). The MOF-53 (Fe) polyhedrons are high dispersible and anchored on graphene surface. The RGO nanosheets are transparent and wrinkled, indicating that RGO is a few atomic layers in thickness and is of good quality. Furthermore, no bare MOF-53(Fe) particles or RGO can be observed, which confirms the strong interfacial bonding between MOF-53(Fe) particles and RGO. Fig. 2e shows the XRD patterns of GO, RGO, MOF-53(Fe) and MOF-53(Fe)/RGO. The XRD patterns of both MOF-53(Fe) particles and MOF-53(Fe)/RGO composite can be perfectly assigned to the phase of MOF-53(Fe) [19]. The diffraction peak of MOF-53(Fe)/RGO composite had remained unchanged after incorporation of the graphene, which indicates that there was no apparent loss of crystallinity and decomposition of the framework structure. Furthermore, the broad peak of RGO at 24.5° can be attributed to the graphite-like structure, and no diffraction peaks resulting from GO (at 10.5°) can be found, which means that oxygen groups have been removed and GO is effectively reduced to RGO [20]. To confirm the microstructure of porous MOF-53(Fe), nitrogen adsorption-desorption measurements were performed to investigate the pore diameter and surface area. Fig. 2(f–g) shows the nitrogen adsorption-desorption isotherm at 77 K and pore diameter distribution of MOF-53(Fe). It can be seen in Fig. 2f that the hysteresis loop of MOF-53(Fe) is formed between $0.8P/P_0$ and $1.0P/P_0$, indicating the existence of meso-pore (2–50 nm) and macro-pore (>50 nm). So, the synthesized MOF-53(Fe) is a kind of the IV-type material [21]. From Fig. 2g, the average pore diameter, volume and BET surface area are 134.22 nm, 0.11 $cm^3\ g^{-1}$, 22.36 $m^2\ g^{-1}$, respectively. Fig. 2h shows the typical magnetization curves of MOF-53(Fe) and MOF-53(Fe)/RGO composite measured at room temperature. The magnetization hysteresis loops of MOF-53(Fe) and MOF-53(Fe)/RGO composite show S-like, indicating the nature of typical superparamagnetic material. The saturation magnetization (M_s) is 13.38 emu/g for MOF-53(Fe), and 6.21 emu/g for the MOF-53(Fe)/RGO composite respectively. The M_s value of MOF-53(Fe)/RGO is lower than that of the MOF-53(Fe), which can be attributed to the existence of non-magnetic RGO.

Fig. 3a shows the real part (ε') and imaginary part (ε'') of MOF-53(Fe) and MOF-53(Fe)/RGO composite. It can be observed that the ε' and ε'' values of MOF-53(Fe)/RGO decrease gradually from 11.3 to 5.1 and 6.2 to 2.6, respectively, with several fluctuations in the frequency range of 2–18 GHz. Moreover, the ε' and ε'' values of MOF-53(Fe) have almost no change. The ε'' values of MOF-53(Fe)/RGO are higher than MOF-53(Fe), implying that the strong dielectric loss is responsible for electromagnetic wave absorption properties of MOF-53(Fe)/RGO. In Fig. 3b, we can see that the μ' values of all samples exhibit several variations at 2–18 GHz. Meanwhile, the imaginary part (μ'') of MOF-53(Fe)/RGO declines gradually at 2–12 GHz, and then exhibits broad resonance peaks at 12–15.5 GHz with a maximum value of 0.41 at 14.8 GHz. The imaginary part (μ'') of MOF-53(Fe) has a similar curve with MOF-53(Fe)/RGO and the broad resonance peak locates at 12.9–15.5 GHz with a maximum value of 0.41 at 14.1 GHz. According to the natural- resonance equation [22]:

$$2\pi f_r = rH_a \tag{1}$$

$$H_a = 4|K_1|/3\mu_0 M_S \tag{2}$$

where r is the gyromagnetic ratio, H_a is the anisotropy energy, and $|K_1|$ is the anisotropy coefficient. The high resonance frequencies of MOF-53(Fe)/RGO and MOF-53(Fe) are attributed to the small size effect and the confinement effect. It is believed that the anisotropy energy of nanometer scale size materials would be remarkably increased due to the surface anisotropic field by the small size effect. The μ'' values of MOF-53(Fe) are slightly larger than MOF-53 (Fe)/RGO, which indicates a higher magnetic loss. From Fig. 3(c–d), we can see that the tan δ_ε values of MOF-53(Fe)/RGO are much higher than MOF-53(Fe) over 2–18 GHz, while the tan δ_m values of MOF-53(Fe) are slightly larger than MOF-53(Fe)/RGO, indicating that the microwave absorption mechanism of MOF-53(Fe)/RGO composite is mainly dependent on the dielectric loss. The phenomenon can be explained in the following factors. In terms of the electromagnetic theory, the dielectric loss of MOF-53(Fe)/RGO composite may be attributed to the layered structure, natural resonance, Debye dipolar relaxation and electron polarization etc [23]. On one hand, according to the free electron theory, $\varepsilon'' = 1/2\varepsilon_0 \pi\rho f$, where ε_0 is the permittivity of a vacuum, ρ is the resistivity, f is the frequency [24]. The conductivity of RGO is high, which enables a reduction of the resistivity, and results in the increase of the dielectric loss. On the other hand, RGO nanosheets form a conducting network, which migrating and hopping electron may enhance eddy current between RGO and MOF-53(Fe). This is why MOF-53(Fe)/RGO composite has a higher dielectric loss. The excellent electromagnetic wave absorption performance is mainly ascribed to two key factors: electromagnetic wave attenuation and impedance matching. The high dielectric and magnetic loss only suggest electromagnetic wave can be absorbed by materials, which means enhanced electromagnetic wave attenuation. The impedance matching indicates that electromagnetic wave can maximum enter material interior without being reflected by