

Conducting polymer coated metal-organic framework nanoparticles: Facile synthesis and enhanced electromagnetic absorption properties



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ABSTRACT

A hybrid polyaniline coated metal organic framework (MOF/PANI) was designed and fabricated via hydrothermal and in situ chemical polymerization methods. The microstructure and morphology were examined by XRD, FTIR, FESEM and TEM. The results showed that MOF (Fe) particles were completely coated by PANI and formed a core-shell composite. The hybrid MOF (Fe)/PANI composite exhibited enhanced EM wave absorption capability compared with MOF (Fe), including the higher absorption intensity (-41.4 dB at 11.6 GHz) and excellent absorption bandwidth (5.5 GHz exceeding -10 dB with an only thickness of 2 mm), which was due to enhanced interfacial effects, attenuation constant and the synergic effect between MOF (Fe) and PANI. Therefore, such a core-shell MOF (Fe)/PANI composite is a promising absorber for application in microwave absorption field.

1. Introduction

In recent years, electromagnetic (EM) wave absorption materials have attracted increasing attention because of the rapid development of electromagnetic wave devices [1,2]. The EM wave absorbing materials can convert the incident EM wave into thermal energy to dissipate EM wave. According to the loss mechanism of EM wave, the microwave absorption materials are comprised of dielectric loss and magnetic loss, such as ferrite [3,4], nickel [5], cobalt [6,7], carbon nanotubes [8–10], conducting polymers [11,12] and graphene [13–16]. However, these traditional microwave absorbers can not satisfy the requirements (thin, light, wide and strong) of ideal absorbers at the same time due to a mismatch impedance. In terms of the EM energy principle, a proper impedance matching between permittivity and permeability determines the absorption intensity and wide frequency range characteristics of EM absorbers. Hence, it should be promising and meaningful to study the novel composite materials, which can accord with the demand of high performance EM wave absorbers for improving impedance matching feature.

Metal organic framework (MOF) is a kind of hybrid porous materials, which has drawn much attention and shown various potential applications such as gas storage [17], catalysts [18,19], microwave absorption [20], sensors [21] and supercapacitors [22]. Owing to low permittivity and mismatch impedance, pure MOF displays poor microwave absorption properties. In recent years, organic-inorganic nanocomposites have turned into a hot issue of research due

to their synergetic or complementary effects [23]. Among kinds of conducting polymers, polyaniline (PANI) has attracted significant attention for EM wave absorbers because of its controllable conductivity, easy production, low price and good chemical stability [24]. Hosseini et al. [25], prepared MnFe_2O_4 /PANI composites with a core-shell structure with dodecyl benzene sulfonic acid (DBSA) as the surfactant and dopant. The studies showed that there was an interaction between PANI and MnFe_2O_4 , and the maximum reflection loss was -15.3 dB at 10.4 GHz for the 1.4 mm absorption thickness. Zhang et al. [26], synthesized Fe_3O_4 /PANI hybrid microspheres via chemical oxide polymerization process and the composites displayed enhanced microwave absorption, which a maximum absorption of -37.4 dB at 15.4 GHz can be achieved with a PANI thickness of 100 nm. The introduction of PANI can not only decrease the weight of absorbers, but also lead to a proper impedance matching, which can provide an idea for ideal EM wave absorbers. Except for impedance matching characteristic, the microwave absorption properties of materials are closely associated with the special nanostructures. MOF materials possess the special porous structure and result in multiple scattering to increase microwave absorption, which is interesting for improving EM wave absorbing property due to the complicated geometrical morphologies.

Herein, we reported the synthesis of novel MOF (Fe)/PANI composite. In the first step, MOF (Fe) particles were prepared by hydrothermal route. Then, PANI was coated on the surface of MOF (Fe) by chemical polymerization method. The microwave absorption results indicate that the core-shell structure exhibits improved microwave absorption capa-

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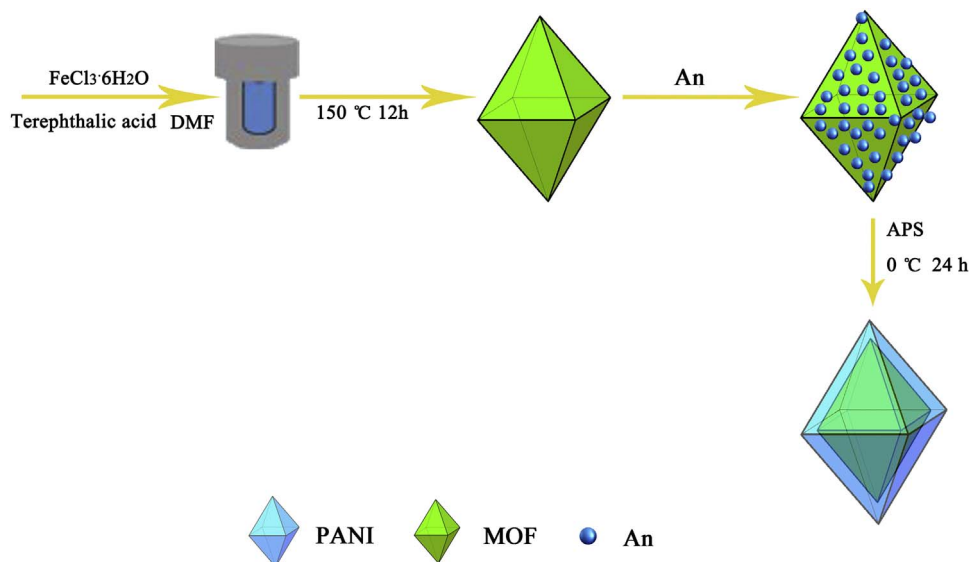


Fig. 1. Schematic illustration of the fabrication process of MOF (Fe)/PANI composite.

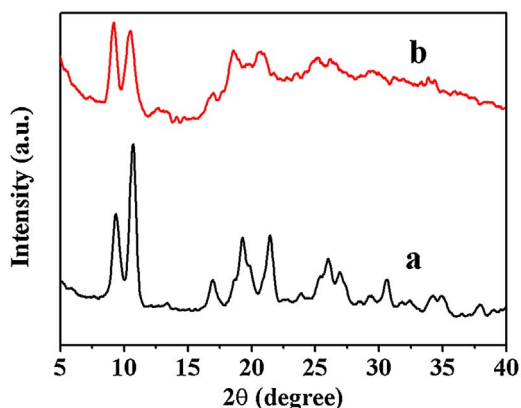


Fig. 2. XRD patterns of samples (a. MOF (Fe), b. MOF (Fe)/PANI).

cities in terms of the maximum microwave absorption and effective bandwidth, which is attributed to multi-interfaces, geometric effect and impedance match of MOF (Fe) cores and PANI shells. The maximum reflection loss can achieve -41.4 dB at 11.6 GHz and the absorption bandwidth below -10 dB is 5.5 GHz with a thickness of 2 mm. The microstructure and morphology of the as-prepared composites were examined by XRD, FESEM, TEM, BET and FTIR.

2. Experimental

2.1. Preparation

The core-shell MOF (Fe)/PANI composite were prepared as illustrated in Fig. 1. The MOF (Fe) particles were prepared by hydrothermal route. 0.81 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.5 g terephthalic acid were dissolved in 64.7 ml DMF and stirred for 30 min. The obtained solution was transferred into a 100 ml Teflon-lined autoclave and maintained at 150 °C for 12 h. After letting it cool down to room temperature naturally, the products were washed three times with ethanol and water, then dried at 150 °C for 8 h. 0.4 g of the resulting MOF (Fe) was dispersed in 150 ml acidic aqueous solution and the solution was cooled

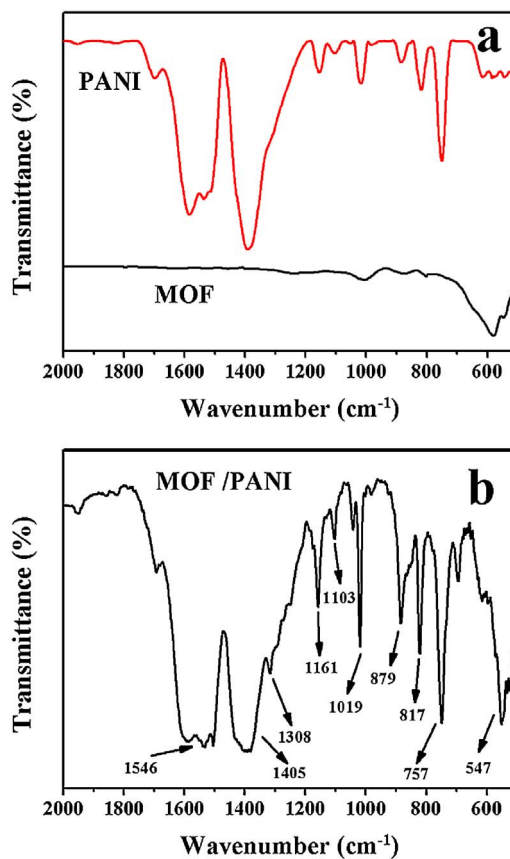


Fig. 3. FTIR spectra of MOF (Fe), PANI and MOF (Fe)/PANI composite.

down to 0 °C under stirring, then 0.2 ml aniline was added and stirred for 20 min. The $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.5 g) dissolved in 20 ml distilled water was added slowly to the mixture with constant stirring for 24 h at 0 °C. Lastly, the reactants were washed and dried to get MOF (Fe)/PANI composite.

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