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Abstract

A successful fabrication of novel hierarchical graphene@Fe₃O₄ nanocluster@carbon@MnO₂ nanosheet arrays composites has been developed for the first time. The fabrication process involves the deposition of Fe₃O₄ nanocluster on graphene's surface using a simple in situ hydrothermal method, subsequent introduction of carbon on the surface of graphene@Fe₃O₄ nanocluster by combining the hydrothermal reaction and thermal treatment process, and final formation of the hierarchical composites via a simple in situ redox replacement reaction between potassium permanganate (KMnO₄) and carbon on the surface of graphene@Fe₃O₄ nanocluster. Moreover, the microwave absorption properties of both graphene@Fe₃O₄ nanocluster and hierarchical graphene@Fe₃O₄ nanocluster@carbon@MnO₂ nanosheet arrays composites were investigated between 2-18 GHz microwave frequency bands. The electromagnetic data demonstrates that graphene@Fe₃O₄ nanocluster@carbon@MnO₂ nanosheet arrays hierarchical composites exhibit significantly enhanced microwave absorption properties compared with graphene@Fe₃O₄ nanocluster, which probably originate from the unique hierarchical structure and larger surface area.

Keywords: graphene; microwave absorption; MnO₂ nanosheet arrays

1. Introduction

Graphene, a new class of carbon nanostructure consisting of a two-dimensional sp² bonded sheets, exhibits high mechanical strength (Yong's modulus E=1000 GPa) [1], thermal conductivity (5000 W m⁻¹ K⁻¹) [2], electrical conductivity (6000 S cm⁻¹) [3], specific surfaces area (1000 m² g⁻¹) [4] and aspect ratio (~1500) [5]. These properties make graphene or graphene-based materials

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very promising in electromagnetic interference shielding, which is designed to absorb and dissipate incident electromagnetic waves by converting them to thermal energy [6]. In addition, low cost graphene can be produced in bulk through a chemical oxidation and reduction process using graphite as raw materials [7]. Generally, the graphene product obtained by the above method is also known as reduced graphene oxide (RGO). The residual defects and groups in RGO cannot only improve the impedance match characteristic and prompt energy transition from contiguous states to Fermi level, but also introduce defect polarization relaxation and groups' electronic dipole relaxation, which are all in favor of electromagnetic wave absorption [8]. Thus, RGO sheets show enhanced microwave absorption compared with graphite and carbon nanotubes, and can be expected to display better microwave absorber. However, the microwave absorption property of pure graphene is very poor due to its high electronic conductivity. Therefore, how to design and prepare good electromagnetic absorbing materials based on graphene still remains a challenge.

Recently, considerable efforts have been made towards the development of graphene-based composites for microwave absorption materials, and all of them showed strong microwave absorption properties. Qi and colleagues prepared graphene- Fe_3O_4 composites, and the maximum reflection loss reached -40.36 dB at 7.04 GHz with a thickness of 5.0 mm, while the absorption bandwidth with reflection loss lower than -10 dB was about 2 GHz [9]. He et.al prepared laminated magnetic graphene, and the maximum reflection loss was -26.4 dB with a thickness of 4.0 mm at 5.3 GHz, and the absorption bandwidth with reflection loss less than -10 dB was 2 GHz [10]. Yang et.al synthesized bowl-like Fe_3O_4 hollow spheres/reduced graphene oxide composites, the as-synthesized composites with a coating layer thickness of 2.0 mm exhibited a maximum absorption of -24 dB at 12.9 GHz as well as a bandwidth of 4.9 GHz (from frequency of 10.8-15.7 GHz) corresponding to reflection loss at -10 dB [11]. Ouyang et.al investigated the electromagnetic absorption properties of graphene/Fe₃O₄@Fe core@shell/ZnO quaternary composites [12], the results showed that the maximum reflection loss values were lower than -30 dB for the quaternary composites with a thickness of 2.5-5 mm and the absorption bandwidth was up to 7.3 GHz (in the frequency range of 5.9-15.2 GHz) with reflection loss values lower than -20 dB. Yang et.al fabricated three-dimensional $SiO_2(a)Fe_3O_4$ core/shell nanorod array/graphene

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architecture, which exhibited a maximum absorption of -31.9 dB as the thickness was 2.5 mm [13]. Cao et.al designed three-dimensional graphene/polyaniline nanorod arrays composites, and the results showed that the poor electromagnetic absorption property of graphene could be significantly improved by perpendicularly growing polyaniline nanorod arrays on the surfaces of graphene sheets. The maximum reflection loss reached -45.1 dB with the thickness of only 2.5 mm, and o[4]. It can be concluded from the above-mentioned research literatures that good EM absorption properties combining lightweight and wide absorption frequency band can be achieved by designing and constructing Fe_3O_4 -based core@shell heteronanostructures or three-dimension composites on surface of graphene.

Manganese oxides (MnO_2) has been found wide applications in many fields such as energy storage [14], molecular sieves [15] and catalysts [16] because of its low cost, environmentally friendly nature and high theoretical specific capacitance. However, only few studies showed that manganese oxides could be used as microwave absorbing materials [17-19]. Herein, the hierarchical structures of graphene@Fe₃O₄ nanocluster@carbon@MnO₂ nanosheet arrays were successfully assembled via a multi-step route, and the microwave absorption properties were investigated. The results show that the hierarchical structure exhibits enhanced electromagnetic absorption in terms of both the maximum reflection loss value and the absorption bandwidth compared with graphene@Fe₃O₄ nanocluster. The maximum reflection loss value can reach -38.8 dB at 15 GHz with a thickness of only 1.8 mm and the bandwidth corresponding to the reflection loss below -10 dB is 5.4 GHz (from 12.3 to 17.7 GHz).

2. Experimental

All of the chemicals and reagents were purchased from Sinopharm Chmical Reagent Co., Ltd, China and used as received. Deionized water was used for all experiments.

2.1 Preparation of graphene@Fe₃O₄ nanocluster@carbon composites

Graphene Oxide (GO) was synthesized using natural graphite flakes according to Hummer method [20]. Graphene@Fe₃O₄ nanocluster (Graphene@Fe₃O₄ NC) composites were synthesized using a simple in situ hydrothermal method [21]. Graphene@Fe₃O₄ NC@carbon composites were prepared according to the literature method [22]. Briefly, graphene@Fe₃O₄ NC composites were dispersed in 60 mL deionized water and sonicated for 30 min. Then, 0.378 g glucose was added to the solution and stirred for 30 min at room temperature. The solution was transferred to an autoclave and heated to 180 °C for 10 h. After letting it cool down, the product was harvested via several rinse-centrifugation cycles and fully dried at 60 °C, then the black precipitate was sintered at 500 °C for 2 h under argon atmosphere to obtain the final composites of graphene@Fe₃O₄ NC@carbon composites. In addition, RGO (reduced graphene oxide) was prepared following the same procedure as for graphene@Fe₃O₄ NC, without addition of Fe(acac)₃.

2.2 Preparation of graphene@Fe₃O₄ nanocluster@carbon@MnO₂ nanosheet arrays hierarchical composites

Hierarchical graphene@Fe₃O₄ nanocluster@carbon@MnO₂ nanosheet arrays composites were fabricated by a facile hydrothermal route [14]. In a typical experiment, 100 mg graphene@Fe₃O₄ NC@carbon composites were dispersed in deionized water (200 ml) under ultrasonication for 1 h. Then, 0.185 g KMnO₄ was added and the mixture was stirring for 30 min. After that, the mixture was then sealed in a Teflon-line stainless autoclave and maintained at 150 °C for 6 h and then naturally cooled to room temperature. The dark brown products (graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites) were washed with deionized water by magnetic decantation for several times and dried at 60 °C for 12 h in a vacuum oven.

2.3 Characterization

The obtained products were characterized by X-ray diffraction (XRD, PANalytical, Holland), Fourier transform infrared (FTIR) spectroscopy (Nicolet 6700, thermoscientific USA), transmission electron microscopy (TEM, Philips Tecnai-12 transmission electron microscopy), X-Ray photoelectron spectroscopy (ESCALAB 250, Thermofisher Co), vibrating sample magnetometer (VSM) and thermogravimetric analysis (TGA) (TGA/DTA92 Setaram II testing system). The N₂ adsorption–desorption isotherms were measured at 77 K using an adsorption instrument (TriStarII, Micromeritics Company, USA) to evaluate their pore structures and N₂-BET surface area. The electormagnetic parameters were analyzed using a HP8753D vector network analyzer. The measured samples were prepared by uniformly mixing 25 wt % of the sample with a

paraffin matrix.





Fig.1 Schematic illustration of the three-step preparation of graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays hierarchical composites

As illustrated in Fig.1, the preparation of graphene@Fe₃O₄ nanocluster@carbon@MnO₂ nanosheet arrays hierarchical composites consists of three main steps. First, Fe₃O₄ nanocluster-attached graphene sheets were prepared by simultaneously forming Fe₃O₄ nanocluster and reducing GO in ethylene glycol. Second, carbon-coated graphene@Fe₃O₄ nanocluster was synthesized *via* a hydrothermal route by using glucose as the carbon source. Third, MnO₂ nanosheet arrays were fabricated on graphene@Fe₃O₄ NC@carbon surface via a facile green hydrothermal reaction between carbon and KMnO₄. The redox reaction is described in the following equation:

 $4KMnO_4 + 3C + H_2O = 4MnO_2 + K_2CO_3 + 2KHCO_3$ (1)

Here, the carbon on surfaces of graphene@ Fe_3O_4 nanocluster serves as not only a reductant that converts aqueous permanganate (MnO₄-) to MnO₂, but also a substrate material that guarantees MnO₂ deposition on the surface.



Fig.2 XRD patterns (A) and FTIR spectra (B) of GO, RGO, graphene@Fe₃O₄NC, graphene@Fe₃O₄NC@carbon and graphene@Fe₃O₄NC@carbon@MnO₂ nanosheet arrays; TG curves (C) of graphene@Fe₃O₄NC and graphene@Fe₃O₄ NC@carbon; typical N₂ adsorption–desorption isotherms (D) of graphene@Fe₃O₄ NC (curve a) and graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays (curve b).

Typical XRD patterns of GO, RGO, graphene@Fe₃O₄ NC, graphene@Fe₃O₄ NC@MnO₂ nanosheet arrays are present in Fig.2 (A). As displayed in Fig.1 (A), GO shows the characteristic diffraction peak at $2\theta = 9.8^{\circ}$ corresponding to a d-spacing of 0.90 nm, which is due to the formation of the oxygen functionalities groups between the layers of GO. In the XRD pattern of RGO, the intense peak at 9.8° disappears and a broad band appears at 25.3° and its interlayer spacing is 0.34 nm. This shift in the d-spacing can be attributed to the successful reduction of GO and formation of graphitic structures. For graphene@Fe₃O₄ NC, the detected diffraction peaks can be indexed in the cubic inverse spinel structure of Fe₃O₄ (JCPDS card, File No.19-0629). After coating with a carbon shell, no characteristic peaks related to other materials can be detected in graphene@Fe₃O₄ NC@carbon, indicating the carbon coating is amorphous. To obtain the carbon coating content, TGA was performed on graphene@Fe₃O₄ NC and graphene@Fe₃O₄ NC@carbon composites under air atmosphere at a heating rate of 10 °C min⁻¹, as shown in Fig.2 (C). For graphene@Fe₃O₄ NC, 3% mass loss around 120 °C and 24% mass loss around 450 °C are attributed to evaporation of absorbed solvent and decomposition of graphene, respectively. By subtracting the absorbed water, a weight ratio of graphene:Fe₃O₄ = 1:3 is determined. The losses due to the absorbed water, decomposition of graphene and carbon for the graphene@Fe₃O₄ NC@carbon composite are 5 and 49 wt%, respectively. By taking into account for both the absorbed water weight and the graphene to Fe₃O₄ weight ratio (1:3), a net carbon coating content is determined to be 33.7 wt%. As for the graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays, the XRD pattern shows new characteristic diffraction peaks, which can be assigned to the α -MnO₂ (JCPDS No.44–0141).

FT-IR was also carried out to detect the functional groups of the samples, as shown in Fig.2 (b). Briefly, GO shows four peaks at around 3424, 1727, 1402, 1224 and 1065 cm⁻¹, which can be attributed to the O-H stretching, C=O, O-H deformation, C-O epoxy and alkoxy, respectively [23]. After hydrothermal reaction for 24 h, the peak at 1727 cm⁻¹ almost disappears and the intensities of the oxygen functional groups are reduced to great extent, indicating removal of the oxygenated groups and restoration of the carbon basal plane in RGO. Compared with RGO, a new peak at 585 cm⁻¹ attributed to Fe₃O₄ [24] for graphene@Fe₃O₄ NC composites is observed, indicating the formation of graphene@Fe₃O₄ in one step. For graphene@Fe₃O₄ NC@carbon, the intensities of peak at 585 cm⁻¹ are reduced to great extent, illustrating that surfaces of the graphene@Fe₃O₄ NC are coated by carbon and formed sandwich-structured graphene@Fe₃O₄ NC@carbon composite. In the spectra of graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites, the existence of MnO₂ is evidenced by two peaks located at 567 and 615 cm⁻¹, which can be ascribed to the Mn-O and Mn-O-Mn vibrations [25].

The N₂ adsorption-desorption isotherms were measured to gain information about the specific surface area of the graphene@Fe₃O₄ NC and graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet

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arrays composites (Fig. 2(D)). This isotherm profile can be categorized as type IV with a small hysteresis loop observed at a relative pressure of 0.02-1.0. As calculated by Brunauer-Emmett-Teller (BET) method, graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites attain a BET area of 220.8 m²g⁻¹, compared with 126.6 m²g⁻¹ for graphene@Fe₃O₄ NC.



 $\label{eq:Fig.3} Fig. \ 3 \ Room-temperature \ magnetization \ curves \ of \ graphene \\ @Fe_3O_4 \ NC \ (a), \ graphene \\ @Fe_3O_4 \ NC \\ @carbon \\ @MnO_2 \ nanosheet \ arrays \ (c).$

The field-dependent magnetizations for graphene@Fe₃O₄ NC, graphene@Fe₃O₄ NC@carbon and graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays were measured by a vibrating sample magnetometer at room temperature, as shown in Fig.3. All the magnetic hysteresis loops are S-like curves, indicating that these samples exhibit superaramagnetic behavior at room temperature with neither coercivity nor remanence. The specific saturation magnetization (Ms) is 59.8 emu g⁻¹ for graphene@Fe₃O₄ NC, 32.8 emu g⁻¹ for graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays. This decrease in magnetism is mainly attributed to the decrease in weight ratio of Fe₃O₄ in the composites.

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Fig.4 XPS spectra of survey scan (A) for GO, graphene@Fe₃O₄ NC, graphene@Fe₃O₄ NC@carbon and graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays; XPS spectra of Cls for GO (B) and graphene@Fe₃O₄ NC (C); XPS spectra of Fe 2p for graphene@Fe₃O₄ NC (D); XPS spectra of Mn 2p (E) and O1s (F) for graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays.

The surface composition of the synthesized samples was further confirmed by XPS measurements. The XPS spectra of GO, graphene@Fe₃O₄ NC, graphene@Fe₃O₄ NC@carbon and graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays over a wide range of binding energy (0-1000 eV) are shown in Fig.4 (A) , and the corresponding atomic ratios of elements are shown in table 1. For GO, only the peaks corresponded to C1s and O1s are detected, and the atomic ratios of C and O is 64.46% and 31.54%, respectively. After the hydrothermal reduction, the XPS survey scan of graphene@Fe₃O₄ NC composites indicates the presence of N and Fe elements, besides C and O. The relative low atomic ratios of O (14.78%) and the presence of Fe elements confirm the successful synthesis of graphene@Fe₃O₄ NC in one step, while the observation of nitrogen with

the atom percentage of 3.82% indicates the successful nitrogen doping with the hydrothermal method with NH₄AC. Furthermore, the above results are also supported by the corresponding Cls and Fe 2p XPS spectra. Deconvolution of the C1s peak of GO (Fig.4 (B)) contains four components that correspond to carbon atoms in different functional groups: C-C/C=C (284.6 eV) in the aromatic rings, C-O (286.5 eV) of epoxy, C=O (288.3 eV) and O-C=O (289.1 eV) groups. Compared with GO, the oxygen content of graphene $@Fe_3O_4$ NC (Fig. 4(C)) decreases rapidly and a new peak at 285.5 eV corresponded to $N-sp^2 C$ is observed, suggesting a reduction of GO and doping N into the graphitic layer of graphene. In the XPS spectra of Fe 2p for graphene@Fe₃O₄ NC, the binding energy peaks at 710.6 and 723.9 eV are corresponding to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, suggesting the existence of Fe₃O₄ [26]. As for graphene@Fe₃O₄ NC@carbon, the atomic ratio of carbon increases to 88.27%, revealing that a carbon layer is formed on the surfaces of graphene@ Fe_3O_4 NC (see table 1). After reaction with KMnO₄, the survey spectrum shows that the as prepared composites contain C, O, N, Fe and Mn. The high-resolution spectrum of Mn 2p in Figure 4(E) obviously shows that the peaks centered at 642 and 653.6 eV can be assigned to Mn 2p3/2 and Mn 2p1/2 peaks, respectively, confirming the presence of MnO₂ in the composites [27]. In addition, the spectrum of O1s also indicates the existence of MnO_2 in the composites. The deconvolution peaks of O 1s spectrum can be divided into two peaks centered at 529.6 and 531.3 eV, which corresponds to O–Mn bonding configuration and C–O bonding configuration [27], respectively.

Table 1. Atomic ratios of elements measured by XPS

Element (Atomic %)	С	0	Ν	Fe	Mn
GO	64.46	31.54			
graphene@Fe ₃ O ₄	78.01	14.78	3.82	3.39	
graphene@Fe ₃ O ₄ NC@carbon	88.27	7.92	2.72	1.09	
$graphene @Fe_{3}O_{4}\ NC @carbon @MnO_{2}\ nanosheet\ arrays$	75.28	18.41	1.89	0.72	3.69



Fig.5 TEM images of graphene@Fe₃O₄ NC (A), graphene@Fe₃O₄ NC@carbon (B) and graphene@Fe₃O₄ NC@carbon@MNO₂ nanosheet arrays composites (C), SEM images and corresponding EDX element C, O, Fe and Mn maps of graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays (D).

Fig.5 shows TEM image of graphene@Fe₃O₄ NC (A), graphene@Fe₃O₄ NC@carbon (B), graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites (C), SEM and EDS images of graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites and EDX element maps of C,

O, Fe and Mn. As shown in Fig.5 (A), Fe_3O_4 nanoclusters with an irregular shape of 50-90 nm are dispersed on the surfaces of graphene, and the nanoclusters are composed of small size 10-25 nm nanoparticles. The lattice fringe spacing (0.253 nm) displayed in HRTEM image is consistent with the lattice spacing of (311) planes of cubic magnetite and the electron dispersive spectroscopy result also indicates the presence of Fe element in the composites. Fig.5 (B) shows the TEM image of graphene@ Fe_3O_4 NC@carbon, it is clear that the graphene sheet in the composites shows a distinctly more crumpled structure around Fe₃O₄ NC compared with that of graphene@Fe₃O₄ NC, which could be induced by shrinking of a carbon layer on surface of graphene@ Fe_3O_4 NC and the further reduction of graphene during sintering under argon atmosphere. In addition, the HRTEM image (the right in Fig.5 (B)) shows that Fe₃O₄ NC@carbon core-shell microstructures are formed on the surfaces of graphene, and the thickness of the carbon layer is about 3 nm. Fig.5 (C) displays a typical TEM image of graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites. It is obvious that large two-dimensional structures can be observed under TEM microscope, and the corresponding energy-dispersive X-ray (EDX) image confirms the presence of Mn element in the composites. The dark line in magnified TEM image (left in Fig.5 (C)) demarcates the edge of MnO_2 nanosheet approximately oriented perpendicular to surface of graphene@Fe₃O₄ NC@carbon, and the corresponding HRTEM image reveals lattice fringes with a distance of 0.71nm corresponding to (110) plane of the tetragonal MnO₂ structure. As shown in Fig.5 (D), SEM image of graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites is consistent with the above TEM analysis and the MnO₂ nanosheet arrays are mostly grown upright on top of the graphene@Fe₃O₄ NC@carbon support. Moreover, EDX (energy dispersive X-ray) mapping results (elements distribution of C, O, Fe and Mn) further confirm that MnO₂ nanosheet are grown on the surface of graphene@Fe₃O₄ NC@carbon and the atom ratio of C, O, Fe and Mn are 77.04%, 21.39%, 0.17% and 1.40%, respectively.



Fig.6 Complex permittivity (A), permeability (B), dielectric loss tangent and magnetic loss tangent (C) from 2 to 18 GHz for graphene@Fe₃O₄ NC (a) and graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays (b)

composites with 25 wt.%.

The microwave absorption property of materials is generally determined by the complex relative permittivity and permeability as well as both of their tangent loss (dielectric tangent loss: $\tan \delta_{\epsilon} = \epsilon''/\epsilon'$; magnetic tangent loss: $\tan \delta_{\mu} = \mu''/\mu'$). Fig. 6 (A) shows the real part (ϵ') and imaginary part (ϵ'') of the complex permittivity of graphene@Fe₃O₄ NC and graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites. For the graphene@Fe₃O₄ composites, the ϵ' value is in the range of 3.5-5.4 and ϵ'' is in the range of 0.4-1.7. When the graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays hierarchical structures are assembled, the ϵ' value increases to a range of 6.7-15.1 and ϵ'' value floats in the range of 2.7-8.6. It can be seen that both ϵ' and ϵ'' values of graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composite arrays composite are higher than those of graphene@Fe₃O₄. The higher ϵ' for graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites is due to the fact that the further reduction of graphene during sintering (500°C for 2 h under argon atmosphere) may increase the electric polarization and electric conductivity, since ϵ'

is an expression of the polarizability of a material, which consists of dipolar polarization and electric polarization at microwave frequency [28]. Furthermore, the higher ε " graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites may be ascribe to the enhanced polarization induced by the multi-interfaces and triple junctions (graphene@Fe₃O₄, Fe₃O₄ NC@carbon, carbon@MnO₂ nanosheet) as well as associated loss mechanism. In addition, it is also found that the values of complex permittivity of graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites are lower than carbon nanotubes composites [29], which are induced by the lower conductivity of graphene.

Fig. 4 (B) shows the real part (μ ') and imaginary part (μ ") of the complex permeability of graphene@Fe₃O₄ NC and graphene@Fe₃O₄ NC@carbon@NiO nanosheet arrays composites. It can be seen that the values of both μ ' and μ " for graphene@Fe₃O₄ NC@carbon@NiO nanosheet arrays composites are higher than those of graphene@Fe₃O₄ NC, which can be attributed to the magnetic losses in MnO₂ nanosheets.

Fig. 4(C) shows the dielectric tangents $\tan \delta_{\epsilon}$ loss and magnetic tangent loss of $\tan \delta_{\mu}$ of graphene@Fe₃O₄ NC and graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites. It is clear that graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites possess a far higher dielectric tangent loss than graphene@Fe₃O₄ NC. The enhanced dielectric loss could stem from the enhanced interfacial polarization relaxation in graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites. For the magnetic tangent loss, the value of graphene@Fe₃O₄ NC is slightly greater than that of graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites. In addition, it is worth noting that the dielectric tangent loss of the two composites is greater than the magnetic tangent loss.



Fig.7 The calculated reflection losses for graphene@Fe₃O₄ NC (A), and graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays (B) paraffin wax composites with different thicknesses in the frequency range of 2-18 GHz

To further study the microwave absorption properties, the reflection losses (RL) of the graphene@Fe₃O₄ NC (a) and graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays (b) composites can be evaluated by

$$RL (dB) = 20 \log \left| \frac{Z_{in} - 1}{Z_{in} + 1} \right|$$
 (2)

While the normalized input impedance (Z_{in}) was calculated by

$$Z_{\rm in} = \sqrt{\mu_r / \varepsilon_r} \tanh \left[j (2\pi f d / c) \sqrt{\varepsilon_r \mu_r} \right]$$
(3)

where *f* is the microwave frequency, *d* is the thickness of the absorb layer, *c* is the velocity of electromagnetic wave in vacuum, and ε_r and μ_r are the complex relative permittivity and permeability, respectively. The calculated reflection loss (RL) curves of the graphene@Fe₃O₄ NC and graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites with different thickness are shown in Figure 7. In the investigated region, graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites exhibit significantly enhanced microwave absorption compared with graphene@Fe₃O₄. As shown in Fig.7 (A), graphene@Fe₃O₄ NC composites exhibit the maximum RL of -10.5 dB at the optimal sample thickness of 5.0 mm. When graphene@Fe₃O₄ NC@carbon hierarchical structures are formed, the maximum RL value increases to -38.8 dB at 15 GHz with a thickness of only 1.8 mm and a bandwidth corresponding to the reflection loss below -10 dB is 5.4 GHz (from 12.3 to 17.7 GHz) (Fig.7(B)). It is clear that graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays composites display enhanced microwave absorption properties in terms of both the maximum RL values and the absorption bandwidths.

The enhanced microwave absorption properties of graphene@Fe₃O₄ NC@carbon@MnO₂ nanosheet arrays hierarchical structures can be explained by the following facts. First, the multi-interfaces and triple junctions of raphene@Fe₃O₄ NC, Fe₃O₄ NC@carbon and C@MnO₂ are advantageous for electromagnetic attenuation due to the existing interfacial polarization [30]. Then, the void space among MnO₂ nanosheet arrays results in relatively large specific surfaces areas and high porosities, providing more active sites for reflection and scattering of electromagnetic wave [31]. Finally, the void space between Fe₃O₄ and MnO₂ nanosheet arrays can effectively interrupt the spread of electromagnetic wave and generate dissipation due to the existing impendence difference and enhanced the microwave absorption properties [32].

4. Conclusion

Hierarchical structures of graphene@Fe₃O₄ nanocluster@carbon@MnO₂ nanosheet arrays were prepared by multi-step route. When evaluated as microwave absorbers, the hierarchical structures exhibit enhanced microwave absorption properties in terms of both the maximum reflection loss value and the absorption bandwidth. The maximum reflection loss of graphene@Fe₃O₄ nanocluster@carbon@MnO₂ nanosheet arrays is -38.8 dB at 15 GHz and the absorption bandwidth with a reflection loss below -10 dB ranges from 12.3 to 17.7 GHz with a thickness of only 1.8 mm. Thus, it is believed that such hierarchical structures will be developed toward a wide spectrum of applications in the area of microwave absorption.

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