Tuning broadband microwave absorption via highly conductive Fe₃O₄/graphene heterostructural nanofillers

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Abstract

Graphene oxides (GO) have been widely utilized for preparing conductive heterostructures via converting insulating GO back to conductive reduced GO (RGO). Such conversion may substantially impact the results if the introduced heterostructures are sensitive to the conversion processes. To avoid the concerns, herein a novel $\text{Fe}_3\text{O}_4/\text{graphene}$ ($\text{Fe}_3\text{O}_4/\text{GN}$) heterostructure of high electrical conductivity have been prepared by directly using highly conductive GN without any reducing agent or post-treatment. Results of the electrical properties, magnetic properties, complex permittivity and permeability suggest that the $\text{Fe}_3\text{O}_4/\text{GN}$ interfaces are responsible for the influence of the corresponding properties. The intrinsically conductive features coupled with the $\text{Fe}_3\text{O}_4/\text{GN}$ interfaces allow the heterostructures to possess sufficient microwave absorption at relatively low filler loading, with tunable effective absorption bandwidth observed over 4-18 GHz. Fundamental mechanisms indicate the advantages of the simple strategies and resulting heterostructures promise a great arena for advanced graphene heterostructures that are not achievable upon RGO.

Keywords: Composites; interfaces; magnetic materials; dielectric properties; electrical properties.

1. Introduction

Lightweight composites with high-performance microwave absorption and electromagnetic shielding properties have exhibited promising applications, with typical examples from advanced electronics to specific devices in aircrafts and vehicles [1-4]. Among the pursued nanoscale fillers, carbon nanomaterials, one-dimensional (1D) carbon nanotubes (CNTs) and two dimensional (2D) graphene nanosheets (GNs) in particular, have received great attention coupled with extensive development effort due to their exclusive chemical structures and tunable electrical properties [5,6]. In the past decades, CNT- and GN-based nano-fillers with low percolation threshold and appropriated electrical loss have already demonstrated dramatically enhanced microwave absorption performance in the pursued composites [1-4,7-10]. Among various strategies, combination of electrical loss and magnetic loss has shown great potential owing to the excellent flexibility in manipulating complex permittivity and permeability, and thus has been extensively explored [2,11-15]. In the early examples, Che and coworkers have encapsulated iron into the tubular space of the multiwalled CNTs (MWCNTs). The as-prepared Fe@MWCNT heterostructures (filler loading of 20 wt%) were further fabricated into epoxy-based composites and exhibited a broad effective microwave absorption region with the peak absorption up to 25 dB in the span of 2-18 GHz [2]. For the strategy towards interfacial modification on the CNTs, ferromagnetic nanomaterials (nickel, iron and cobalt as examples) and ferrimagnetic nanostructures (ferroferric oxide, related ferrites and etc.) have been widely introduced on the CNT surface to achieve CNT-heterostructures of combined electrical loss/magnetic loss. In the work by Wen et al., MWCNT/Fe, MWCNT/Co and MWCNT/Ni hybrid structures (60 wt% filler loading) have been processed into epoxy matrices to prepare composites, which demonstrate enhanced absorption intensity over 30 dB [11].

On this stage, similar explorative studies have also been attempted in the fabrication of graphene-heterostructure filler with combined electrical loss/magnetic loss. For instance, Chen et al. have recently converted graphene oxide (GO) and Ni precursors into reduced graphene oxide (RGO)/Ni heterostructures. The composites incorporated with such heterostructures at filler loading of 60 wt% possessed a maximum reflection loss ~17 dB [13]. In the report by Sun et al., concentration of Fe_3O_4 was tuned in the process of converting GO into RGO, and the wax-based composites with Fe_3O_4 /RGO heterostructures exhibited a reflection loss up to 27 dB at 40 wt% filler loading [14]. Likewise, Fu et al. synthesized NiFe_2O_4 nanorods on the RGO and fabricated the heterostructures into wax-based composites, showing the best absorption performance up to 29.2 dB at 60 wt% filler loading [16]. Further efforts were also carried out in the preparation of the ternary [17,18] or quaternary [19,20] heterostructures. For example, wax-based composites filled with RGO/CNT/ Fe_3O_4 were fabricated by Wang and coworkers and the maximum absorption peak ~20 dB was observed in the composites with 30 wt% loading [17].

Apparently, implication of the recent report suggests that major efforts have been intensively focused on the strategies of growing magnetic heterostructures, with very few explorations on the chemical structures and electrical properties of the graphene. It is emphasized that two significant factors should be concerned in the microwave absorption fillers in the GHz range. (1) The magnetic nanostructures introduced in the graphene-based heterostructures would mainly contribute to the magnetic loss in the relatively lower frequency regions in GHz. As a consequence, the magnetic loss for microwave absorption at X band (8.2-12.4 GHz) and Ku band (12.4 GHz-18 GHz) is very limited due to the fact that the magnetic moment at higher frequency would not quite follow the changes of external electromagnetic field. (2) The key influence of employing magnetic nanostructures, typically the electrically insulating ones, on the

graphene surface would substantially impact the generation of effective paths for leaking current. For the graphene-based fillers of low electrical properties, their composites are generally required to increase the filler loading to meet the impedance match conditions for achieving sufficient microwave absorption [21]. According to the most work, the preparation of graphene-heterostructure fillers involves the conversion of insulating GO back to conductive RGO using reducing agents or high-temperature thermal annealing [22-24], with unexpected weight losses, morphological changes, phase transitions, and other related concerns observed in the conversion. Consequently, the conductivity recovery in the RGO is generally insufficient with the presence of introduced heterostructures that are sensitive to the treatments.

To avoid the issues arisen by RGO conversion and related concerns in the microwave absorption, in the present work, we demonstrate a facile approach for preparing novel $\text{Fe}_3\text{O}_4/\text{graphene}$ ($\text{Fe}_3\text{O}_4/\text{GN}$) fillers for effective microwave absorption. Direct utilization of the highly electrically conductive GN in the growth of $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures enables them to afford high electrical conductivity with presence of high proportion of insulating Fe_3O_4 . Owing to such unique electrical properties, the wax-based composites embedded with the $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures present broad range in the complex permittivity, by which tunable microwave-absorption performance in the 4-18 GHz could be achieved. The mechanisms based on the interfaces of the $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures coupled with the complex permittivity have been discussed.

2. Experimental Section

Conductive GN: As shown in Figure 1a and 1b, highly electrically conductive GN was prepared via direct chemical exfoliation according to our previous work [25,26]. Briefly, the commercial

graphite powders (grade 3805 from Asbury Carbons, 500 mg) were firstly treated in alcohol aqueous solution under the conditions of stirring and sonication. In the direct chemical exfoliation, the as-treated powders were dried and subsequently dispersed in a mixture solution of nitric acid and sulfuric acid (1:3 in volume ratio) under sonication (2-3 days) for. The resulting mixtures were transferred to 2 L water, followed by washing with abundant water. The samples were further dried in a vacuum oven at 80 °C to obtain conductive GN.

Fe₃O₄/GN heterostructures: In a typical preparation (Figure 1c), a portion of the as-prepared conductive GN (50 mg) was positioned in 10 ml aqueous solution, followed by vigorous needle-sonication for re-dispersing the conductive GN. Until the homogeneous GN suspension was acquired, suspension was further ultra-sonicated for 2 h. On the other hand, ferrous sulfate heptahydrate (FeSO₄·7H₂O, different amounts for each batch) was dissolved in 4 ml aqueous solution by vigorous stirring. Subsequently, the solution was slowly added into the well-dispersed GN aqueous suspension. Until 1 h sonication, NaOH aqueous solution (20 mg NaOH in 4 ml H₂O) was then added to obtain a mixture suspension, followed by transferring to a Teflon-lined stainless steel autoclave for hydrothermal treatment. The process was set at 180 °C for 10 h and the samples were naturally cooled to room temperature. The resultant mixtures were washed with water for several times. The as-prepared sample was dried in a vacuum oven at 80 °C overnight to achieve Fe₃O₄/GN heterostructures.

For the samples of different Fe₃O₄ concentrations, various amounts of FeSO₄·7H₂O powders were used in the hydrothermal treatments. In brief, the resulting Fe₃O₄/GN heterostructures were denoted as Fe₃O₄/GN-1, Fe₃O₄/GN-2 and Fe₃O₄/GN-3 with the presence of FeSO₄·7H₂O in 35 mg, 105 mg and 175 mg, respectively. Therefore, the corresponding Fe₃O₄

concentrations were calculated to be 16%, 28% and 50% for Fe₃O₄/GN-1, Fe₃O₄/GN-2 and Fe₃O₄/GN-3, respectively.

Fe₃O₄/GN wax-based composites: In a preparation of wax-based composite samples (Figure 1d), the paraffin wax (Walgreen) and as-prepared Fe₃O₄/GN heterostructures (as well as neat conductive GN) with different loadings (20, 30 and 40 wt% for each heterostructures) were dispersed in an ether solution under vigorous stirring and sonication. Until the mixed solutions were completely dried at ambient condition, a portion of the mixtures was compacted into a toroidal shape (Φ_{out} , 7.03 mm; Φ_{in} , 3.00 mm) with thickness of 1.5~2 mm. Therefore, the twelve wax-based samples for measurements of complex permittivity and permeability were neat GN/wax composites (with 20, 30 and 40 wt% neat GN loadings), Fe₃O₄/GN-1/wax composites (with 20, 30 and 40 wt% Fe₃O₄/GN-1 loadings), Fe₃O₄/GN-2/wax composites (with 20, 30 and 40 wt% Fe₃O₄/GN-2 loadings) and Fe₃O₄/GN-3/wax composites (with 20, 30 and 40 wt% Fe₃O₄/GN-3 loadings).

Characterizations: The neat GN and Fe₃O₄/GN heterostructures were characterized with various techniques. Field emission scanning electron microscopy (SEM) images were acquired on a ZEISS supra 55 system. Transmission electron microscopy (TEM) images were captured on a JEOL JEM-2010 scanning TEM system. X-ray powder diffraction (XRD) was performed on a PANalytical X' Pert PRO MPD diffraction system. The field dependence of magnetization was measured on a Lake Shore 7410 VSM at room temperature.

In the measurement of surface electrical conductivity (σ), the film-like samples (neat GN and Fe₃O₄/GN heterostructures) were prepared by re-dispersing the hydrothermally treated samples into aqueous water, followed by filtration to fabricate the thin-layer samples. Upon drying, the film-like samples were characterized according to the classical four-probe method by

a multimeter (Keithley 2400, controlled by Lab Tracer 2.0 software, both from Keithley Instruments). The electrical conductivity was calculated by the equation $\sigma = (\ln 2/\pi)(I/V)/d$, where the electrical current (I) and voltage (V) was obtained on a multiheight probe (Jandel) and d is the thickness of the measured film-like samples. In each measurement, three different regions of the thin-layer samples were selected for testing, and the average values were calculated to determine the electrical conductivity.

Complex permittivity and complex permeability: In the typical measurement, the twelve fabricated wax-based composite samples were positioned on an Anritsu 37269D vector network analyzer (VNA) with the coaxial method in the range of 2-18 GHz [21,24] The dimensional of the as-prepared composite samples were slightly larger than the testing chamber, and whereby the unexpected errors induced by the air gap between the samples and coaxial testing probes could be largely diminished. To ensure the accuracy, multiple testing was performed for each sample, and the data errors were generally less than 10%. The corresponding values of complex permittivity and complex permeability were obtained based on the 201 measured points on the VNA.

Microwave absorption: The measured complex permittivity and complex permeability was used to determine microwave absorption. The term reflection loss (R_L) for evaluating the microwave absorbing layers on the metal plane is given as [27]

$$R_L = 20 \log \frac{|Z_{in} - 1|}{|Z_{in} + 1|}. \quad (1)$$

where Z_{in} is the normalized input impedance of microwave absorption layers, and is known as

$$Z_{in} = \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh \left[j \frac{2\pi}{c} \sqrt{\mu_r \epsilon_r} f d \right], \quad (2)$$

where c is the light velocity, d the thickness of the absorber, f the microwave frequency, ϵ_r and μ_r the complex permittivity and complex permeability of the wax-based composite samples, respectively.

3. Results and discussion

In Figure 2, FESEM images of the prepared samples are shown. Figure 2a exhibits a typical view of the direct exfoliated conductive GN, suggesting a 2D planar feature. As displayed in Figure 2b-2d, increasing amount of nanoscale particles related clusters was expected to observe with the increase of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration in the precursor suspension. In the $\text{Fe}_3\text{O}_4/\text{GN}$ -3 sample, it is clear that more particle clusters were found on the surface of the GN due to the enlarged amounts of the nanoparticles.

Figure 3a-3c demonstrates the representative TEM images of the as-prepared $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures. As given in Figure 3a and 3b, the diameter of single nanoparticles in the particle clusters was estimated around 10~40 nm. XRD spectra in Figure 3d indicate the presence of mixed-valence inverse-spinel iron oxide Fe_3O_4 (JCPDS card No. 88-0315) in the $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures. As exhibited in Figure 3b and 3c, the high-resolution TEM image and selected-area electron diffraction (SAED) patterns for the nanoparticle in the $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures are given, respectively. The observation suggests that the lattice space is approximately 0.29 nm, which refers to the d-spacing of (220) crystal plane in the Fe_3O_4 nanoparticles.

The surface electrical conductivity of the film-like samples was calculated based on the measured parameters, as shown in Figure 4a. The results suggest that the average electrical conductivity of the samples was observed to decrease gradually with the increasing deposition of

Fe₃O₄ nanoparticles on the GN surface, due to the enlargement of the interfacial resistivity. Compared to some typical Fe₃O₄/RGO heterostructures in previous report, the Fe₃O₄/GN-3 of 50 wt% Fe₃O₄ nanoparticles (~4900 S/m) here still possesses higher electrical conductance than the Fe₃O₄/RGO samples of less than 8 wt% Fe₃O₄ nanoparticles (<4000 S/m) in the literature [28]. It is noted that the highly conductive feature of the Fe₃O₄/GN heterostructures in this work is owing to the intrinsic high electrical conductive of the neat GN (~31000 S/m), whose chemical structures responsible for electrical conductivity have been well restored in the exfoliation process [24,25]. Magnetic hysteresis loops of the samples were measured in the magnetic field range from -2 to 2 T at room temperature. According to the loops in Figure 4b, corresponding saturation magnetization (M_s), remnant magnetization (M_r) and coercivity of the samples were acquired, implying that both saturation magnetization and remnant magnetization of the Fe₃O₄/GN heterostructures have been largely enhanced compared to those of the neat GN sample. In Figure 4c, the results suggest that saturation magnetization was observed to enhance almost linearly with the presence of increasing magnetic Fe₃O₄ particles, reaching 11, 31, and 47 Am²/kg in the three Fe₃O₄/GN heterostructures separately. Similar tendency has been also seen in the remnant magnetization, showing 1, 4 and 6 Am²/kg in the Fe₃O₄/GN-1, Fe₃O₄/GN-2 and Fe₃O₄/GN-3, respectively. Coercivity of the Fe₃O₄/GN heterostructures has been found to be suppressed around 7241.8-7639.7 A/m (79.58 A/m=1 G) in comparison with that of the neat GN (>79580 A/m).

Toroidal Fe₃O₄/GN wax-based composites were applied to measure in the 2-18 GHz with the coaxial method. The complex permittivity ($\varepsilon=\varepsilon'-j\varepsilon''$), real permittivity (Figure 5) and imaginary permittivity (Figure 6), of the wax-based composites embedded with neat GN, Fe₃O₄/GN-1, Fe₃O₄/GN-2 and Fe₃O₄/GN-3 in various filler loadings are given as marked in the

figures. According to Figure 5, it is shown that real permittivity of the composites is enhanced as the filler loading increases, which is in good agreement with the effective medium theories [29]. Compared to the samples with deposited by Fe₃O₄ particles (Figure 5b-5d), the composites of neat GN (Figure 5a) present a pronounced peak below 5 GHz, which could be associated with the polarization induced by the oxygen-containing functional groups on the GN surface [24,25]. Upon the hydrothermal process, these oxygen-containing functional groups are responsible for nucleation in the growth of Fe₃O₄ particles, and in turn such polarization has been suppressed in the sample embedded with the Fe₃O₄ (Figure 5b-5d). Moreover, increased amount of Fe₃O₄ particles in the heterostructures (Figure 5c and 5d) appears to reduce the real permittivity of the corresponding wax-based composites, compared to the composites of relative lower Fe₃O₄ proportion (Figure 5a and 5b). Such decrease could be mainly attributed to the diminishment of polarization. According to the Debye theory, real permittivity is given as [27]

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + \omega^2 \tau^2}, \quad (3)$$

where ω is the angular frequency, ε_{∞} the relative dielectric permittivity at the high frequency limit and ε_s the static permittivity, τ the polarization relaxation. In general, fast polarization including electronic polarization and atomic polarization predominantly contributes to the real permittivity in the GHz range. Generation of the Fe₃O₄/GN heterostructures could mainly impact the electronic polarization and atomic polarization via the formation of covalent bonding between GN and inorganic particles. Consequently, the diminished polarization could decrease the real permittivity, according to Equation 3.

On the other hand, imaginary permittivity of the wax-based composites is exhibited in Figure 6. Compared to the real permittivity, similar tendency could be also observed in the imaginary permittivity, where the composites of the highest Fe₃O₄ proportion (Fe₃O₄/GN-3) in

the GN tend to possess the lowest values. The Debye theory suggests that imaginary permittivity ε'' is described as [27]

$$\varepsilon'' = \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2} \omega \tau + \frac{\sigma}{\omega \varepsilon_0} , \quad (4)$$

where ε_s is the static permittivity, ω the angular frequency, ε_∞ the relative dielectric permittivity at the high frequency limit, σ the electrical conductivity and τ the polarization relaxation. Apparently, electrical conductivity and polarization primarily contribute the imaginary permittivity. As is shown in Figure 4a, results of electrical conductivity indicate that the generation of $\text{Fe}_3\text{O}_4/\text{GN}$ interface has substantially reduced the interfacial resistivity, which impacts the effective paths for the electron transfer. Therefore, the contribution of leakage current would be suppressed with the presence of Fe_3O_4 . Besides, as discussed above, the diminished polarization would partially influence the imaginary permittivity.

As shown in Figures 7, complex permeability ($\mu = \mu' - j\mu''$) of the wax-based composites embedded with $\text{Fe}_3\text{O}_4/\text{GN}$ -1, $\text{Fe}_3\text{O}_4/\text{GN}$ -2 and $\text{Fe}_3\text{O}_4/\text{GN}$ -3 in various filler loadings is plotted. According to the magnetization results, the complex permeability of the wax-based composites filled with the weakly magnetic neat GN was considered to be approximately 1 and 0 in real and imaginary permeability, respectively. Since the magnetic nanostructures would mainly impact the complex permeability in the relatively lower frequency regions, as is aforementioned, the pronounced peaks associated with magnetic loss induced by the magnetic particles were observed below 4 GHz (Figure 7). In the higher frequency region (>4 GHz), all the wax-based composites exhibit no meaningful difference, with 0.8~1.3 in real permeability and 0~0.2 in imaginary permeability (Figure 7a and 7b). Overall, the presence of $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures would predominantly determine the microwave absorption performance in terms of varying both complex permittivity and permeability.

Figure 8a-8c exhibits the microwave absorption of the twelve composites at layer thickness ~ 1.5 mm. Plotted in Figure 8d is the bandwidth of the effective absorption ($R_L > 10$ dB) for these composites. The results suggest that the sufficient absorption could be achieved in the range of 9-18 GHz via tuning the Fe_3O_4 proportion in the heterostructures and related filler loadings. The composites filled with the neat GN appear to deliver the largest absorption intensity (Figure 8a) in the twelve composites (Figure 8a-8c). However, the other composites of $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures possess much broader effective absorption band (Figure 8d). At the thickness of 1.5 mm, it is obvious that the composites embedded with $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures would effectively broaden the absorption band, particularly in the higher frequency region (>10 GHz) according to Figure 8d.

Likewise, the microwave absorption performance of the twelve composites at layer thickness of 2 mm is displayed in Figure 8e-9g, coupled with the effective absorption region illustrated in Figure 8h. Also, the cases of the layer thicknesses at 2.5 mm and 3 mm are illustrated in Figure 8i-8l and Figure 8m-8p, respectively.

It is interesting to find several crucial points by utilizing $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructural fillers based on the microwave absorption performance. (1) As demonstrated in Figure 8d, 8h, 8l and 8p, it is always to see that the employment of Fe_3O_4 in the hetero-fillers would push the effective absorption band toward higher frequency. The shift could be understood by the factor that the complex permittivity (predominant) and permeability (minor) has been tuned via the $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures. According to the conditions for generating absorption/attenuation (A), the complex permittivity, angular frequency (ω) and thickness (d) should follow the relations as [30]

$$\varepsilon' = \frac{\pi c}{2d\omega} \coth\left(\frac{\pi}{2} \text{tg} \delta\right) \frac{1 - 10^{-A/20}}{1 + 10^{-A/20}}, \quad (5)$$

$$\varepsilon'' = \varepsilon' \times \text{tg} \delta. \quad (6)$$

As a consequence, the frequency for absorption conditions could be changed via tuning the complex permittivity. (2) Although the wax-based composites with neat GN may present greater absorption intensity in some cases, the ones with $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures would offer broader effective absorption band. Such enlargement in the bandwidth could be mainly linked to the presence of the secondary scattering particles. The different electromagnetic features between magnetic/insulating Fe_3O_4 and conductive GN allow them to present dissimilar diffraction index, which leads to scatterings at the $\text{Fe}_3\text{O}_4/\text{GN}$ interfaces. As a result, the interfacial scatterings coupled with varied conditions for generating absorption/attenuation would efficiently tune the absorption band. Therefore, magnetic particles may not greatly contribute to the magnetic loss/complex permeability in the high frequency range; however, they are expected to optimize the microwave absorption performance via varying the interfacial scatterings and corresponding complex permittivity of the bare fillers. This interfacial engineering has been typically reported in the core-shell heterostructures [31,32] and some ternary [17,18] or quaternary [19,20,33] heterostructures. (3) As is generally observed in the literature [18,34,35], the absorption peaks coupled with effective absorption bands were also found to shift toward the lower frequency regions with increasing layer thickness. This phenomenon is mainly associated with the satisfaction of the critical conditions for generating standing waves on the material-air interface, which has been well discussed in our previous work [36]. Due to the $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures of unique electrical properties and complex permittivity, such thickness-dependent shift enable them to achieve a tunable broadband microwave absorption in the range of 4-18 GHz. (4) In our previous work, it is emphasized that there are three different regions observed in the microwave absorption materials, and the explorative efforts should be focused on tuning the impedance conditions to reach the effective absorption region [21]. For the use of such highly conductive

GN for growing $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures, the high electrical conductivity of the heterostructures would effectively decrease the filler loading, compared to some magnetic RGO heterostructures. For typical examples, the wax-based composites filled with $\text{Fe}_3\text{O}_4/\text{RGO}$ heterostructures possessed a reflection loss up to 27 dB at filler loading 40 wt% [14]. Also, the ones with NiFe_2O_4 nanorod/RGO heterostructures offer a maximum absorption ~ 29.2 dB at 60 wt% filler loading [16]. On the contrary, the filler loading could be largely reduced to 20 wt% for any $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructure in this work, owing to the establishment of effective conductive paths for leakage current at lower filler loading.

In a nutshell, the approach here for achieving effective graphene-based microwave absorption fillers is relatively facile and versatile and could be employed to prepare other graphene-based heterostructures, in which the concerns induced by the treatments in RGO could be completely avoided. Moreover, the $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures acquired in this work is considerably higher than some typical RGO-based heterostructures, enabling the $\text{Fe}_3\text{O}_4/\text{GN}$ to afford sufficient microwave absorption with smaller filler loading. Additionally, such high electrical conductivity also allows the heterostructures for serving in broad applications where the multifunctional fillers of electrically conductive are a requirement.

Conclusions

In summary, a novel $\text{Fe}_3\text{O}_4/\text{GN}$ heterostructures of high electrical conductivity have been prepared via a simple strategy, in which highly conductive GN directly serves as the matrix for growing magnetic Fe_3O_4 nanoparticles. Electrical properties, magnetic properties, complex permittivity and permeability based on the heterostructures have been studied. Implication of the microwave absorption performance suggests that the wax-based composites embedded with the

Fe₃O₄/GN heterostructures could present effective microwave absorption at relatively low filler loading in comparison with the other related previous work. The tunable microwave absorption over the range of 4-18 GHz indicates that such highly conductive Fe₃O₄/GN heterostructures hold various advantages, which promise great potential for substituting RGO-based heterostructures in broad fields.

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Figure captions

Figure 1 Schematic of preparing highly conductive GN (b), Fe₃O₄/GN heterostructures (c) and corresponding wax-based composites.

Figure 2 SEM images of the neat GN (a), Fe₃O₄/GN-1 (b), Fe₃O₄/GN-2 (c) and Fe₃O₄/GN-3 (d).

Figure 3 TEM images of the Fe₃O₄/GN heterostructures (a), Fe₃O₄ nanoparticle (b) and SAED pattern of the Fe₃O₄ nanoparticle (c); XRD spectra of the samples as marked.

Figure 4 Electrical conductivity of the samples as marked (a); magnetic hysteresis loops (b), saturation magnetization (c) and remnant magnetization (d) of the samples as marked.

Figure 5 Real permittivity of the wax-based composites embedded with the samples as marked.

Figure 6 Imaginary permittivity of the wax-based composites embedded with the samples as marked.

Figure 7 Complex permeability of the wax-based composites embedded with the samples as marked.

Figure 8 Microwave absorption of the wax-based composites embedded with the samples as marked (layer thickness=1.5 mm (a-c), 2 mm (e-g), 2.5 mm (i-k) and 3 mm (m-o); effective absorption regions (RL>10 dB) of the samples at thicknesses of 1.5 mm (d), 2 mm (h), 2.5 mm (l) and 3 mm (p).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8