Large-scale solvent-thermal synthesis of graphene/magnetite/conductive oligomer ternary composites for microwave absorption

Dong-Xu He, Yao Qiu, Lin-Ling Li, Rui Zhao* and Wei-Dong Xue*

Nanocomposites exhibiting high electric conductivity and high saturation magnetization were synthesized in bulk using a solvent-thermal route, which combined the hybridization growth of Fe_3O_4 nanoparticles, graphene oxide, and a conductive oligomer in one step. The hybrid spheres with diameters of 100–300 nm (mostly approximately 200 nm) consisted of a homogenous phase without obvious interfaces between the ternary components. The electric conductivity of the hybrid material was greatly improved after heat treatment at high temperature. Because of the interfacial polarization and good separation property due to its magnetism properties, the interpenetrating nature of the materials yielded good synergistic effects on the electromagnetic wave absorbing properties. The multi-frequency reflection band covering the C band and Ku band with a maximum reflection loss of -45 dB for a thickness of 5 mm is promising for lightweight and strong electromagnetic attenuation applications.

INTRODUCTION

With the growing demand for controlling electromagnetic pollution and developing electromagnetic wave absorption materials, excellent electromagnetic shielding materials that are lightweight, exhibit strong absorptivity and high thermal stability, and have a broad absorption frequency bandwidth are needed.

Dense inorganic-organic hybrid materials offer opportunities to attain unusual properties or combinations of properties of their component [1]. The magnetic property based on the inorganic molecules and electronic conductivity originating from the delocalized electrons in organic materials can be combined through the formation of an organic-inorganic assembly, a common approach for developing multifunctional hybrids with numerous fascinating applications.

Magnetite (Fe_3O_4) nanoparticles (NPs) have received interest recently because of their unique electric and mag-

netic properties resulting from the transfer of electrons between Fe^{2+} and Fe^{3+} in the octahedral sites [2–4]. To achieve high performance in function-specific applications, magnetic particles must be spherical and have narrow size distributions, a high magnetic saturation (σ_s) to provide maximum signal strength, and good dispersion in liquid media [5–7]. However, the physical properties of magnetic materials exhibit a strong dependence on particle size, lattice defects, and chemical stoichiometry [8–10]. In our previous work [11], we synthesized mono-dispersed Fe_3O_4 microspheres with diameters of 300 nm, which exhibited good electromagnetic interference shielding properties. Two microwave magnetic loss peaks appeared, one at 4.0–5.0 GHz and the other at approximately 16.0–17.0 GHz. The magnetic loss peak at high frequency was attributed to the effect of the morphology of the hierarchical structure.

Graphene, the so-called “thinnest material in the universe”, is a single layer of sp^2 -bonded carbon atoms [12] and has drawn tremendous scientific interest because of its extremely high mobility and ballistic transport of electrons [13,14]. Many types of graphene-based materials have been fabricated to further extend their physicochemical properties and applications, which include chemical sensors [15], Li-ion batteries [16], and field-effect transistors [17]. To date, electromagnetic (EM) wave absorbing materials have attracted much attention because of the expanded EM interference (EMI) problem. Carbon and its composites are very promising EM absorbing materials [18,19]. As a new class of two-dimensional carbon nanostructures, graphene with a very high surface area has exhibited excellent EMI properties [20,21]; however, the carrier mobilities of high-quality graphene at room temperature are as high as $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is harmful to its EM absorption properties in terms of the impedance match mechanism [22]. In addition, the EMI properties of materials exhib-

Institute of Applied Electrochemistry, State Key Laboratory of Electronic Thin Films and Integrated Devices, Institute of Microelectronics and Solid-State Electronics, University of Electronic Science and Technology of China, Chengdu 610054, China

* Corresponding authors (emails: ruizhao@uestc.edu.cn (Zhao R); xuewd@uestc.edu.cn (Xue W))

it a strong dependence on particle size, morphology, and chemical stoichiometry, which depend heavily on the various synthesis methods.

To achieve the hybridization of magnetic materials with conductive materials, which could potentially yield outstanding properties that could not be attained by either component alone, we synthesized graphene-Fe₃O₄ micro- and nano-scale hybrid spheres with diameters of ~100 nm [23]. The hybrid materials consisted of a homogenous phase without obvious interfaces between graphene and Fe₃O₄ and yielded good synergistic effects in terms of the electromagnetic wave absorbing properties. A multi-frequency reflection band covered the C band and Ku band with a maximum reflection loss of -20 dB for the matching thickness of 5 mm. However, the high carrier mobility of graphene at room temperature (1000 cm² V⁻¹ s⁻¹) is harmful to its EM absorption properties; experimentally, the ratio of iron ion and graphene oxide in the precursors is very critical. According to the EM energy conversion principle, the relative complex permittivity, relative complex permeability, and proper matching between the complex permittivity and permeability determine the reflection and attenuation characteristics of EM absorbers. Thus, determining how to design and prepare good EM absorbing materials based on graphene still remains a challenge.

Therefore, using the high performance of each component, the graphene/magnetite/conductive oligomer ternary composites were synthesized using a one-step method for the first time. The unique permittivity and permeability properties of the organic conductive oligomer improve the impedance matching and enhance the interfacial effects by providing an interpenetrating network structure with other components.

EXPERIMENTAL DETAILS

Preparation of graphene oxide

The following procedure based on reference [24] was used with minor modifications: a 9:1 mixture of concentrated H₂SO₄/H₃PO₄ (360 mL:40 mL) was added to a mixture of graphite flakes (3.0 g, 1 wt. equiv.) and KMnO₄ (18.0 g, 6 wt. equiv.), producing a slight exotherm process to 30°C. The reaction mixture was cooled to room temperature and vigorously stirred for 72 h. The reaction mixture turned from dark green-black to maroon. The mixture was then carefully poured into 600 mL of deionized water, producing another drastic exothermic reaction. Next, 30% H₂O₂ (10 mL) was added to neutralize the overdosed KMnO₄. The color of the solution turned from dark purple to light yellow, yielding a stable graphene oxide water colloid. The

graphene oxide was isolated by centrifugation, purified by washing repeatedly with deionized water, and vacuum dried at 60°C for 24 h.

Preparation of graphene/Fe₃O₄/phthalocyanine oligomer ternary composites

Ultrasonic dispersed graphene oxide (0.0103 g) was added to an ethylene glycol (EG) (100 mL) and polyethylene glycol 2000 (PEG 2000) (2.5 g) mixture at 80°C to yield a light yellow solution followed by the addition of FeCl₃·6H₂O (9.70 g) to form a brown mixture. After the addition of 4,4'-bis(3,4-dicyanophenoxy)biphenyl (0.48 g), the solution became turbid. Then, urea (3.63 g) was slowly added, and the solution was vigorously stirred for 2 h. The entire process was carried out in ultrasonic condition to prevent the graphene oxide from being aggregated again. Next, the brown mixture was sealed in a Teflon-lined stainless-steel autoclave, heated to 200°C and maintained at this temperature for 24 h, and then allowed to cool to room temperature. The black products were obtained by magnetic separation, washed several times with ethanol and deionized water, and dried at 80°C overnight.

Heat treatments of the graphene/Fe₃O₄/phthalocyanine oligomer ternary composites were performed separately by heating in an oven under a nitro atmosphere to 300°C at 1°C min⁻¹ and maintained for 3 h or to 400°C at 1°C min⁻¹ and maintained for 3 h.

Characterization techniques

The synthesized products were characterized by X-ray diffraction (XRD) (Rigaku RINT 2400 using Cu K α radiation), scanning electron microscopy (SEM) (JSM, 6490LV), and transmission electron microscopy (TEM) (Hitachi, H600). A magnetic study was performed using a vibrating sample magnetometer (VSM, Riken Denshi, BHV-525). The electromagnetic measurement samples were prepared by homogeneously mixing the products with wax in a mass ratio of 4:1. The complex permeability μ ($\mu = \mu' - j\mu''$) and permittivity ϵ ($\epsilon = \epsilon' - j\epsilon''$) were measured using a vector network analyzer (Agilent 8720ET) at 1.0–18 GHz.

RESULTS AND DISCUSSION

The structure and morphology of the as-prepared graphene/Fe₃O₄/phthalocyanine oligomer ternary composites were investigated using SEM, TEM, and XRD. The crystalline structures of the composites are shown in Fig. 1. Magnetite is believed to be the major crystalline phase for the synthesized microspheres, as identified by the diffraction peaks at 30.1°, 35.5°, 43.1°, 53.4°, 56.9°, and 62.4°. These peaks correspond to the six indexed planes (220),

Figure 1 XRD images of graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites.

(311), (400), (422), (511), and (440), respectively. The positions and relative intensity ratios of the diffraction peaks match those of Fe_3O_4 (JCPDS 75-1609), which suggests that the FeCl_3 precursor was completely reduced into magnetite

oxide. Remarkably, no apparent diffraction peak could be identified at $10\text{--}20^\circ$, where the typical peak of graphene oxide appears, indicating that graphene oxide could efficiently interpenetrate into the spherical Fe_3O_4 network.

The morphology and structure of the graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites were investigated by SEM and TEM. Fig. 2a present a representative SEM image of the products. The composites have a rough appearance and are composed of many small Fe_3O_4 NPs with no obvious interfaces between the graphene oxide, phthalocyanine oligomer, and Fe_3O_4 . The composites were spherical, and the average size of the spherical particles is ~ 200 nm; no other product morphology is observed.

We also investigated the effects of the crystallization time on the final sizes of the products. When the crystallization time was 12 h at 200°C , the average size of the graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites was uniform, and the size of the products ranged from 100 to 300 nm (Fig. 2b). Therefore, the crystallization time could affect the final size of the composites; however, the composites still had a very sharp size distribution and a

Figure 2 SEM images of graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites: (a) 24-h crystallization time, (b) 12-h crystallization time, and (c) after high-temperature treatment. (d) TEM images of graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites after a 24-h crystallization time.

uniform magnetite fraction in each nanosphere. After the high-temperature heat treatments at 400°C, the sizes of the composites were stable; no obvious crashing or swelling morphology was observed (Fig. 2c).

For the TEM images, although it was difficult for the electron beam to transmit through the microspheres, the contrast of the TEM images also confirmed the hierarchical spherical structure of the products. TEM characterization further validated the well-crystalline texture that was entirely Fe_3O_4 in interpenetrating contact with graphene oxide (Fig. 2d). Although currently, the detailed mechanism of growth of the graphene/ Fe_3O_4 /phthalocyanine oligomer hybrid spheres was not very clear, it is certain that the Fe_3O_4 NPs could nucleate and aggregate to a spherical morphology with simultaneous incorporation of graphene oxide to yield an interpenetrating network structure. Similar to earlier reports [23], we demonstrated that the graphene/ Fe_3O_4 /phthalocyanine scaled hybrid spheres could be fully recovered to open graphene sheets by the removal of iron oxide particles through acid washing. The TEM images revealed the paper-like nanosheet morphology of graphene with randomly folded edges created after the graphene/ Fe_3O_4 /phthalocyanine scaled hybrid spheres were dissolved in HCl solution for several minutes (Fig. 3).

The relationship between the microwave frequency and reflection loss was measured at the 1–18 GHz range for the graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites, and the results are presented in Fig. 4. According to the measured permittivity and permeability data, the reflection loss (RL) can usually be evaluated using the following equation:

$$\text{RL} = 20 \log \left| \frac{Z_{\text{in}} - Z_0}{Z_{\text{in}} + Z_0} \right|, \quad (1)$$

Figure 3 TEM image of graphene sheets with the removal of Fe_3O_4 particles through acid washing.

where Z_0 is the impedance of free space and Z_{in} is the input characteristic impedance, which can be expressed as

$$Z_{\text{in}} = Z_0 \sqrt{(\mu_r / \epsilon_r)} \tanh \left\{ j(2\pi f d / c) \sqrt{\mu_r \epsilon_r} \right\}. \quad (2)$$

Here, c is the velocity of light, f is the frequency and d is the thickness of an absorber. In this manuscript, the d values were in millimeters. μ_r and ϵ_r are the measured relative complex permeability and permittivity, respectively. For microwave absorbing applications [25], when RL is less than -20 dB, Z_{in} and Z_0 were matched. When the impedances were matched, the frequency and absorber thickness were termed the “matching frequency” (f_m) and “matching

Figure 4 (a) Microwave reflections of graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites at different matching thickness in the frequency range of 1–18 GHz. (b) Comparison of microwave reflections of graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites (1) and graphene/ Fe_3O_4 composite (2) at the matching thickness of 5 mm in the frequency range of 1–18 GHz.

thickness" (d_m), respectively. As observed from the electromagnetic data (Fig. 4a), the ferromagnetic graphene/ Fe_3O_4 /phthalocyanine oligomer ternary nanocomposites exhibited good microwave absorption ability. With the matching thickness d_m of 5 mm, the bands corresponding to RL below -10 dB (i.e., over 90% microwave absorption) were covered by two bands: the C band and Ku band with maximum reflection loss $R_{\max}$ -45 dB. The bandwidth corresponding to reflection loss below -10 dB was approximately 4 GHz, which indicated that the ferromagnetic graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites exhibited good broadband microwave absorption behaviors. The EM wave absorption properties of the ternary composites are better than most of those previous reports for the single components or composites, such as graphene foam [26], Fe_3O_4 NPs [11], graphene- Fe_3O_4 hybrid spheres [23], and Fe-CNTs (carbon nanotubes) [18]. Compared with the microwave absorption properties of graphene- Fe_3O_4 hybrid spheres that we reported before [23], these graphene- Fe_3O_4 hybrid spheres exhibited $R_{\max} = -20$ dB at the same thick-

ness (Fig. 4b). The good microwave absorption properties of the ternary composites were assumed to result from the synergistic effects generated by graphene oxide and phthalocyanine oligomer.

Considering that the graphene oxide and phthalocyanine oligomer both have a two-dimensional plane structure, several factors may influence the ternary components: the van der Waals forces were energetically favorable, which caused the graphene oxide and phthalocyanine oligomer sheets to aggregate simultaneously, and the π - π interaction in the overlap region of the graphene oxide decreased the total free energy, which helped the Fe_3O_4 NPs incorporate into the network of graphene oxide and phthalocyanine oligomer to yield an interpenetrating structure. We also observed that after high thermal treatment, the electric conductivity of the ternary composite increased from 10^7 to $10^6 \Omega \text{ cm}$, and the improved electric properties were beneficial to the microwave reflection loss. Detailed discussions will be reported later.

Fig. 5a shows that the real part (ϵ') and imaginary part

Figure 5 Electromagnetic properties of graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites in the frequency range of 1–18 GHz: (a) permittivity spectra, (b) permeability spectra, (c) microwave permittivity loss $\tan \delta_e$ ($\tan \delta_e = \epsilon''/\epsilon'$) and microwave permeability loss $\tan \delta_m$ ($\tan \delta_m = \mu''/\mu'$); and (d) typical Cole-Cole semicircles (ϵ'' vs. ϵ').

(ϵ'') of the relative complex permittivity of the graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites, where the ϵ' values of the composites remained at a constant of approximately 7.0 from 1 to 8 GHz and exhibited an abrupt decrease at 11–12 GHz. Notably, the ϵ'' values of the sample also achieved maximum values at the frequency of 11–12 GHz. As the real and imaginary part of the relative complex permittivity represent the energy storage ability and loss ability, respectively, ϵ' and ϵ'' of the graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites exhibited sharp fluctuations throughout the entire frequency range, indicating that the material possessed good dielectric loss. As for the permeability properties of the graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites (Fig. 5b), the real part of μ' values of the sample exhibited an abrupt decrease from 2.0 to 0.5 at the frequencies of 1–11 GHz and then increased at the frequencies of 11–13 GHz. At the same time, the imaginary part μ'' values reached a maximum value of approximately 1.0. The resonance peak due to the multi-domain wall dominant in the magnetic NPs occurred at lower frequency. However, compared with conventional magnetite, at high frequency of approximately 15–16 GHz, another magnetic loss was clearly observed. We hypothesize that the magnetic loss peak at high frequency can be attributed to the effect of the morphology of the loose structure. Surprisingly, within the frequency range of 11–12 GHz, the microwave permeability with imaginary parts was larger than that with real parts in this composite, indicating that this graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composite could have unique magnetic loss properties.

Conventionally, the permittivity can be represented by the Debye dipolar relation expression,

$$\epsilon_r = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + 2\pi f \tau} = \epsilon'(f) + i\epsilon''(f), \quad (3)$$

where f , τ , ϵ_s , and ϵ_∞ are the frequency, relaxation time, stationary dielectric constant, and optical dielectric constant, respectively. From Equation (3), it can be deduced that

$$\epsilon'(f) = \epsilon_\infty + \frac{2\pi f \tau (\epsilon_s - \epsilon_\infty)}{1 + (2\pi f)^2 \tau^2}, \quad (4)$$

$$\epsilon''(f) = \frac{2\pi f \tau (\epsilon_s - \epsilon_\infty)}{1 + (2\pi f)^2 \tau^2}. \quad (5)$$

According to Equations (4) and (5), $(\epsilon' - \epsilon_\infty)^2 + (\epsilon'')^2 = (\epsilon_s - \epsilon_\infty)^2$ and the plot of ϵ' vs. ϵ'' would be a single semicircle,

which is usually defined as a Cole-Cole semicircle. Fig. 5c shows the curve characteristics of ϵ' vs. ϵ'' for the graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites. It is noteworthy that the samples exhibited at least one segment of semicircles; the presence of semicircles suggested that there was at least one dielectric relaxation process, and the semicircle corresponded to a Debye dipolar relaxation.

Fig. 5d also revealed that the dielectric loss and magnetic loss of the graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites resulted in the frequency dispersion effect. One peak originated from the dielectric loss and magnetic loss centered at 11–12 GHz; according to the EM energy conversion principle, the relative complex permittivity, relative complex permeability, and proper matching between the complex permittivity and permeability determine the reflection and attenuation characteristics of EM absorbers. Therefore, the dielectric loss and magnetic loss of the graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites with a proper match under a relatively narrow frequency could enhance the electromagnetic reflection of the composites, which was attributed to synergistic effects generated by the graphene oxide and the magnetite.

The magnetization curves measured at 300 K for the graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites reveal that the magnetic saturation values of the composites are $\sim 70 \text{ emu g}^{-1}$, and the magnetic properties allow them to be easily manipulated by an external magnetic field, which is important for their applications in the biological field.

CONCLUSION

We synthesized graphene/ Fe_3O_4 /phthalocyanine oligomer ternary composites with diameters of 100–300 nm via a solvent-thermal route, which combined the hybridization growth of graphene, Fe_3O_4 NPs, and a conductive oligomer in one step. The hybrid spheres consisted of a homogeneous phase without obvious interfaces between graphene and Fe_3O_4 . Because of the interfacial polarization and good separation of the magnetic properties, the interpenetrating constitution of the materials yielded good synergistic effects on the electromagnetic wave absorbing properties. A multi-frequency reflection band covered the C band and Ku band with a maximum reflection loss of $\sim 45 \text{ dB}$ at a matching thickness of 5 mm showed promise for lightweight and strong electromagnetic attenuation applications.

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Conflict of interest The authors declare that they have no conflict of interest.

Dong-Xu He received his BSc degree in physics from Jiamusi University in 2013. Now he is a PhD candidate under the supervision of Prof. Wei-Dong Xue at the University of Electronic Science and Technology of China (UESTC). His research interest focuses on materials science and engineering.

Rui Zhao received her BSc degree from Northwest University in 1999 and PhD degree from Lanzhou Institute of chemical Physics, Chinese Academy of Sciences in 2004. Then, she had her post-doc experience from Namur college, University of Leuven. Currently, she is a professor at the UESTC. Her research interests include inorganic functional material, graphene and its composite material.

Wei-Dong Xue received his BSc degree from Sichuan Normal University and PhD degree from Sichuan University. Currently, he is a professor at the School of Microelectronics and Solid-State Electronics, UESTC. His main research interests focus on the new energy materials, chemical engineering and technology.

中文摘要 石墨烯材料优异的性能使其在各个领域得到广泛的应用. 本文利用水热法合成出了具有高电导率和磁饱和磁化强度的石墨烯/四氧化三铁/高分子化合物三元复合纳米材料, 经高温处理进一步提升了该材料的电导率. 该材料所形成的直径在100–300 nm之间的三元微球与石墨烯交联形成的互穿网络结构, 使其不同组分在电磁波吸收方面表现出了良好的协同效应. 通过测试表明吸波层厚度为5 mm时最大反射损耗达到了−45 dB, 且具有较大的吸收带宽. 这些优异的性能展现了该材料在电磁屏蔽领域的广阔的应用前景.