Facile synthesis of iron oxides/reduced graphene oxide composites: application for electromagnetic wave absorption at high temperature

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Iron oxides/reduced graphene oxide composites were synthesized by facile thermochemical reactions of graphite oxide and FeSO₄·7H₂O. By adjusting reaction temperature, α-Fe₂O₃/reduced graphene oxide and Fe₃O₄/reduced graphene oxide composites can be obtained conveniently. Graphene oxide and reduced graphene oxide sheets were demonstrated to regulate the phase transition from α-Fe₂O₃ to Fe₃O₄ via γ-Fe₂O₃, which was reported for the first time. The hydroxyl groups attached on the graphene oxide sheets and H₂ gas generated during the annealing of graphene oxide are believed to play an important role during these phase transformations. These samples showed good electromagnetic wave absorption performance due to their electromagnetic complementary effect. These samples possess much better electromagnetic wave absorption properties than the mixture of separately prepared Fe₃O₄ with rGO, suggesting the crucial role of synthetic method in determining the product properties. Also, these samples perform much better than commercial absorbers. Most importantly, the great stability of these composites is highly advantageous for applications as electromagnetic wave absorption materials at high temperatures.

Iron oxides/reduced graphene oxide composites were synthesized by facile thermochemical reactions of graphite oxide and FeSO₄·7H₂O. By adjusting reaction temperature, α-Fe₂O₃/reduced graphene oxide and Fe₃O₄/reduced graphene oxide composites can be obtained conveniently. Graphene oxide and reduced graphene oxide sheets were demonstrated to regulate the phase transition from α-Fe₂O₃ to Fe₃O₄ via γ-Fe₂O₃, which was reported for the first time. The hydroxyl groups attached on the graphene oxide sheets and H₂ gas generated during the annealing of graphene oxide are believed to play an important role during these phase transformations. These samples showed good electromagnetic wave absorption performance due to their electromagnetic complementary effect. These samples possess much better electromagnetic wave absorption properties than the mixture of separately prepared Fe₃O₄ with rGO, suggesting the crucial role of synthetic method in determining the product properties. Also, these samples perform much better than commercial absorbers. Most importantly, the great stability of these composites is highly advantageous for applications as electromagnetic wave absorption materials at high temperatures.

Nowadays, severe electromagnetic (EM) radiation is being generated everywhere due to the increasing use of wireless communication tools, local area network, personal digital devices, and so on. EM radiation has become a serious pollution issue, not only influencing the operation of electronic devices, but also affecting human health and raising problems concerning their military applications¹,². In this regard, high performance EM wave absorption materials have attracted more and more attention as an effective strategy to solve these problems. The desired properties for ideal EM wave absorption materials include strong absorption capability, wide absorption range, lightweight, good thermal and oxidation stability, etc. Most conventional EM wave absorption materials are magnetic or metallic particles with electromagnetic parameters not functioning well in the GHz range. Combining with the high density and phase instability, their practical applications have been greatly limited. In contrast, carbon-based materials (carbon black, graphite flakes, carbon fiber, carbon nanotubes, reduced graphene oxide, etc) could potentially solve these issues due to their unique properties such as low density, high complex permittivity and superior thermal stability. Unfortunately, their EM wave absorption property mainly originates from dielectric loss because of their non-magnetic feature. The preparation of carbon-based composite materials with magnetic particles could efficiently solve this problem via controllable modifications of their dielectric and magnetic properties³,⁴.

Recently, rGO was reported to demonstrate enhanced EM wave absorption, comparing with graphite, carbon nanotubes and high quality graphene⁵. This was attributed to their defects and functional groups. However, the value of EM wave absorption is only −7 dB⁶, −3 dB away from the minimum requirement for practical applications (−10 dB). Various iron oxides/rGO composites have been explored to address this issue. Recently, Zhang et al. reported a maximum absorption of −33.5 dB from a rGO/α-Fe₂O₃ composite hydrogel prepared via a two-step process⁷. He et al. reported a facile solvothermal route to prepare laminated rGO/Fe₂O₃ composites, with reflection loss (RL) below −10 dB at 2 GHz and a maximum absorption of −26.4 dB⁸. Yin et al. fabricated rGO/γ-Fe₂O₃ composite with RL of −59.65 dB at 10.09 GHz⁹. Among these fabrication methods including hydrothermal, solvothermal, sol-gel process and chemical route⁶–⁹, most of them suffer from...
complicated and time-consuming procedures, which greatly limit their potential large scale application. The development of a facile, cost-effective and scalable method to synthesize iron oxides/rGO composite with high EM wave absorbing performance is highly desired.

A huge disadvantage of the conventional magnetic absorbing materials is the loss magnetic properties and consequently EM wave absorbing properties under high temperatures\(^{3,4}\). In fact, the temperature increment due to the conversion of electromagnetic energy into heat may cause serious damage to magnetic absorbing materials and related\(^{11}\). This is especially true for military stealth materials for radar cross section (RCS) reduction. The heat generated on the surface of hyper-velocity missiles, bombers, rockets, aircrafts and spacecrafts due to friction can result in high temperatures (600–800 °C), leading to composition changes and even destruction the EM wave absorbing materials.

Herein, we report a simple, efficient and scalable procedure for the synthesis of iron oxides/rGO composite from thermochemical oxidation of FeSO\(_4\cdot7\)H\(_2\)O and reduction of graphite oxide. Interestingly, the initially formed \(\alpha\)-Fe\(_2\)O\(_3\)/rGO composite was converted to Fe\(_3\)O\(_4\)/rGO composite via \(\gamma\)-Fe\(_2\)O\(_3\)/rGO intermediate when the temperature was increased from 500 °C to 800 °C. In contrast, treating FeSO\(_4\cdot7\)H\(_2\)O powders without the aid of rGO under the same conditions generated \(\alpha\)-Fe\(_2\)O\(_3\) at every temperature point. This is the first example of phase transition between \(\alpha\)-Fe\(_2\)O\(_3\), \(\gamma\)-Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\) regulated by rGO. All three composites showed great EM wave absorption abilities. More importantly, the thermal stability of the Fe\(_3\)O\(_4\)/rGO composite at up to 800 °C may open up a whole new field for high temperature application of carbon-based composite materials as EM wave absorption materials.

**Results**

**Experimental Procedure and Samples Labeling.** Experimental details can be found in **Methods** section. The starting material S90 was obtained by drying FeSO\(_4\cdot7\)H\(_2\)O and GO at 90 °C in air for 24 h. After heating, the products were grounded in an agate mortar, annealed at a certain temperature and labeled as SX, where X denotes the treating temperature. The control samples were prepared by treating FeSO\(_4\cdot7\)H\(_2\)O powders (without GO) under the same conditions, and labeled as S\(_X\)X, where X denotes the treating temperature.

**X-ray Diffraction (XRD) and Raman Analysis.** XRD patterns of GO and S90 are shown in Figure 1a. The characteristic peak at 2\(\theta\) = 10.2° is indexed to the (001) plane of GO, indicating the oxidation of graphite to graphite oxide. The disappearance of the peak at 2\(\theta\) = 10.2° in the XRD patterns of S90 (inset in Figure 1a) is due to the interruption of the GO layered structures with the intercalation of Fe\(^{2+}\) and SO\(_4^{2-}\) ions. All the peaks for S90 are well indexed to szomolnokite (FeSO\(_4\cdot7\)H\(_2\)O, JCPDS 45-1365) and butlerite (Fe(OH)SO\(_4\cdot7\)H\(_2\)O, JCPDS 25-0409), resulting from the loss of water molecules and the partial oxidation of FeSO\(_4\) during the drying process at 90 °C\(^{12,13}\). XRD patterns of control samples are shown in Supplementary Figure S1 in Supplementary Information.

Figure 1b shows the XRD patterns of samples S500, S600, S700 and S800. For S500, the appearance of iron sulfate (FeSO\(_4\), JCPDS 17-0783 and JCPDS 33-0682) can be attributed to the loss of water from FeSO\(_4\cdot7\)H\(_2\)O at high temperature\(^{12,13}\), and the thermal decomposition of FeSO\(_4\) led to the formation of hematite (\(\alpha\)-Fe\(_2\)O\(_3\), JCPDS 33-0664)\(^{13}\). At 600 °C, parts of hematite are transformed into maghemite (\(\gamma\)-Fe\(_2\)O\(_3\), JCPDS 39-1346). Based on TG/DTG analysis and the XRD pattern of sample S540 (\(\alpha\)-Fe\(_2\)O\(_3\), Supplementary Figure S1), a mixture of \(\alpha\)-Fe\(_2\)O\(_3\) and \(\gamma\)-Fe\(_2\)O\(_3\) was observed at the temperatures between 540 °C and 700 °C. At 700 °C, the product was dominated by magnetite (Fe\(_3\)O\(_4\), JCPDS 19-0629) with a little bit of hematite. At 800 °C, only magnetite phase was observed. Based on the above results, a clear phase transition sequence between the three iron oxides can be summarized:

\[
\text{FeSO}_4 \xrightarrow{<540°C} \alpha\text{-Fe}_2\text{O}_3 \xrightarrow{>540°C} \gamma\text{-Fe}_2\text{O}_3 + \alpha\text{-Fe}_2\text{O}_3 \xrightarrow{>700°C} \text{Fe}_3\text{O}_4
\]

It is usually difficult to distinguish \(\gamma\)-Fe\(_2\)O\(_3\) from Fe\(_3\)O\(_4\) based on XRD analysis due to their analogous inverse spinel structures. Therefore, Raman analysis was carried out, which showed that sample S500 is mainly \(\alpha\)-Fe\(_2\)O\(_3\), S600 is the mixture of \(\alpha\)-Fe\(_2\)O\(_3\) and \(\gamma\)-Fe\(_2\)O\(_3\), S700 and S800 are Fe\(_3\)O\(_4\) (Supplementary Figure S2). These results are fully consistent with the XRD analysis.

**Transmission Electron Microscopy (TEM) Analysis.** Figure 2 shows the TEM images, HR-TEM images and SAED patterns of S600, S700 and S800. Many thin sheets of rGO decorated with iron oxides particles were detected, suggesting that they are easily exfoliated by sonication during the TEM test, since aggregation of rGO layers was observed in SEM images (Supplementary Figure S3). Iron oxide particles in the size of ~230 nm or smaller are well distributed on the surface of rGO sheets. HR-TEM images of d and e correspond to the (202) plane of \(\gamma\)-Fe\(_2\)O\(_3\) and (221) plane of \(\gamma\)-Fe\(_2\)O\(_3\), and SAED patterns of h and i correspond to electron diffraction patterns of \(\alpha\)-Fe\(_2\)O\(_3\) and \(\gamma\)-Fe\(_2\)O\(_3\). These results indicate that S600 is a mixture...
of $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$. The TEM, HR-TEM and SAED analysis of S700 and S800 (Figure 2 b, c, f, g, j and k) suggests the existence of only Fe 3O 4 phase. All of these results are consistent with XRD and Raman analysis. In addition, no significant morphological difference was observed among these three oxides.

Fourier Transformed Infrared (FT-IR) and Thermogravimetric/Differential Thermogravimetry (TG/DTG) Analysis. In order to understand the mechanism of phase transitions of iron oxides, FT-IR and TG/DTG measurements were carried out and the results are shown in Supplementary Figure S4 and S5. The characteristic peaks of various carbon-oxygen functional groups from GO disappeared for S700 and S800, indicating the complete removal of epoxide and hydroxyl groups. For S800, only peaks of Fe 3O 4 are detected (Supplementary Figure S4). Compared with pure FeSO$_4$·7H$_2$O, the introduction of graphite oxide into S90 greatly reduces the starting decomposition temperature and the maximum weight loss temperature (510°C vs 430°C, 578°C vs 538°C). In addition, the endothermic peak at 538°C was identified as the decomposition temperature of FeSO$_4$ to $\alpha$-Fe$_2$O$_3$ (Supplementary Figure S5).

Discussion

Generally, $\gamma$-Fe$_2$O$_3$ tends to convert to $\alpha$-Fe$_2$O$_3$ under high temperatures$^{15}$ or other extreme conditions$^{16}$. Kachi pointed out that an orientation relationship (OR) exists when both phases coexist: (0001)$_{\alpha}$//(111)$_{\gamma}$, and [1−100]$_{\alpha}$// [−110]$_{\gamma}$, which implies that a common plane with the hexagonal closed packing of oxygen ions remains undistorted after phase transformation. After decades of investigations, the conversion of $\alpha$-Fe$_2$O$_3$ to $\gamma$-Fe$_2$O$_3$ can only be realized by mechanical grinding in ethanol$^{16}$, high energy ball milling in ethanol$^{19}$ and high temperature annealing of $\alpha$-Fe$_2$O$_3$ in H$_2$ atmosphere$^{20,21}$. In the process of mechanical grinding and ball milling, ethanol is believed to play a key role in preventing the reduction of $\alpha$-Fe$_2$O$_3$ and avoiding the formation of aggregates and favoring the rearrangement of O$^{2−}$ from hexagonal closed packing to cubic closed packing. The exact mechanism behind the transformation of $\alpha$-Fe$_2$O$_3$ to $\gamma$-Fe$_2$O$_3$ is still unclear.

Four main types of functional groups are believed to exist at the edges and on the surface of graphene oxide sheets: epoxide, carbonyl, carboxyl and hydroxyl$^{22}$. Epoxide and hydroxyl groups are more stable than the other two kinds of functional groups$^{23,24}$. This was confirmed in our FT-IR study, which showed that only epoxide and hydroxyl groups remained after annealing at 600°C. Based on the above analysis, a possible mechanism for the transformation from $\alpha$-Fe$_2$O$_3$ to $\gamma$-Fe$_2$O$_3$ in our system is proposed. From 540°C to 700°C, the temperature field provides energy for the rearrangement of O$^{2−}$ from hexagonal closed-packing to cubic closed-packing. The hydroxyl groups and H$_2$ gas generated from the thermal reduction of graphite oxide are believed to play an important role in the transformation considering the similarities in conditions of our system with previously reported reaction systems. For example, the adsorbed hydroxyl groups have been reported to be crucial to the structural transformation from $\alpha$-Fe$_2$O$_3$ into $\gamma$-Fe$_2$O$_3$, and the formation of $\gamma$-Fe$_2$O$_3$ phase started after the hydroxyl groups were exhausted$^{25}$. Recently, ab initio calculations showed that the adsorption of H$_2$ on the Fe-terminate $\alpha$-Fe$_2$O$_3$ surface gained adsorption energy of −0.7 eV per H$_2$ molecule and the angles and bond lengths of Fe-O bond were changed$^{26}$. The chemical bonds in $\alpha$-Fe$_2$O$_3$ have a tendency to those of $\gamma$-Fe$_2$O$_3$, implying that hydrogen plays a key factor to the phase transformation. Considering the complexity of our sample, the exact transformation mechanism is to be explored.

The transition from $\gamma$-Fe$_2$O$_3$ to Fe$_3$O$_4$ was believed to be facilitated by the porosity of the sample, which efficiently traps the reducing
gases from the thermal reduction of graphite oxide. Nitrogen adsorption-desorption isotherm analysis was carried out for sample S800 (Supplementary Figure S6). The calculated specific surface area and the most probable pore diameter are 20.1 m²/g and 4 nm. It was shown before that the thermal reduction of graphite oxide could generate reducing gases including CO, CH₄ and H₂²⁸.²⁸ Due to its porous structure, sample S800 could adsorb and confine these reducing gases especially when the sample is dense solid, thus providing reducing atmosphere for the reduction of γ-Fe₂O₃ to Fe₃O₄.

In addition, this mechanism was supported by the fact that phase transition initially takes place in the inner part of samples with unchanged γ-Fe₂O₃ shells covering the sample surface (Supplementary Figure S7 and Supplementary Figure S8). The reducing agents CH₄, CO and H₂ first reacted with the particles inner surface (Supplementary Figure S9a), removing the oxygen ions at the surface layers and transforming Fe³⁺ ions into Fe²⁺ ions. The diffusion of the initially formed Fe²⁺ ions from the surface into the lattice generates the corresponding positive charges. Therefore, electron hopping process took place from the ferrous ions at the surface to the ferric ions inside the lattice. Consequently, Fe²⁺ ions are regathered at the surface and the reduction process continues. The concentration gradient difference of iron/oxygen ratio between the surface and the inner part of the particles is responsible for the diffusion process. Considering the dimensions of the particles, smaller grain size could facilitate the diffusion process. With the aid of rGO sheets, electron hopping between Fe²⁺ and Fe³⁺ ions in Fe₃O₄ may also take place between neighboring Fe₃O₄ particles²⁹.

In support of the proposed mechanism, the grinding of S90 into powders is harmful to the γ-Fe₂O₃ to Fe₃O₄ transition. As mentioned above, S800 contains only Fe₂O₃ phase. In contrast, annealing of S90 powders at 800 °C afforded ground sample containing mainly α-Fe₂O₃ (nonmagnetic) phase as indicated by XRD analysis (Supplementary Figure S9b, S9c). M-H hysteresis measure at 300 K indicates that the saturated magnetization of the ground sample and the most probable pore diameter are 20.1 m²/g and 4 nm. It was shown before that the thermal reduction of graphite oxide could generate reducing gases including CO, CH₄ and H₂²⁸.

The small magnetization of the ground sample suggests the importance since the absorption frequency ranges can be tuned easily by changing the thickness of the absorbers, and broadband absorption can be achieved by multilayered absorbing structure⁴⁰.

When the GO dosage in the starting materials is increased from 5% to 10%, the microwave absorption performance of the sample annealed at 700 °C is further improved, with RL value of −20.8 dB at 6 GHz (Figure 3d).

The microwave absorption properties of materials are related with the impedance matching between dielectric loss and magnetic loss. The imaginary parts of complex permittivity and complex permeability symbolize the loss of electrical and magnetic energy, respectively. Loss tangents (tanδε and tanδμ) represent the loss properties of incident electromagnetic wave in the microwave absorbent. Higher values of ε′′, μ′′, tanδε and tanδμ imply better performance of microwave absorption. To investigate the possible mechanism of microwave absorption of the above three samples, the complex permittivity, complex permeability and corresponding dielectric and magnetic tangent loss of the samples with the thickness of 3 mm were measured at room temperature and the results are shown in Figure 4 and Table 1.

Figure 4a and 4b display the frequency dependence of the real part (ε′) and imaginary part (ε′′) of the complex permittivity, which represent the energy storage and inner dissipation abilities, respectively. It can be seen that the ε′ of S600 first decreases from 24 to 17 in the range of 2–12 GHz, then increases and fluctuates and finally approaches a constant. On the other hand, the ε′ of S700 and S800 are about 8 and 11 at 2 GHz, respectively and stay constant up to 8 GHz and show a small fluctuation between 8 and 18 GHz, indicating a resonance behavior. The ε′ of S600 decrease first and then increase to 4.8 with a minor fluctuation in the 11.7–18 GHz range. For S700 and S800, the ε′ are about 0.5 and 1.5 at 2 GHz, respectively and stay constant up to 8 GHz and show a small fluctuation between 8 and 18 GHz. It is well known that the resonance behavior of the permittivity originates from the electron polarization, ion polarization, space charge polarization, dipole polarization, and interfacial polarization. The ion polarization and electron polarization often take place in the range of THz and PHz, the resonance of permittivity are believed to be from the space charge polarization, dipole polarization, and interfacial polarization. For Sample S700, a layer of covered dielectric α-Fe₂O₃ effectively decreases the electric conductivity and enhances the space charge polarization. Meanwhile, the dielectric α-Fe₂O₃ layer also introduces additional interfacial polarization charges. In addition, with the increase of frequency, the dipole polarization was reported to be the dominant factor, resulting in the fluctuation of complex permittivity, which is consistent with our experimental results (Figure 4b).

Where η, μ, and ε are the wavelength in the materials, complex permeability at ε′′, and complex permittivity at μ′′, εμ and nμ are the peak frequency and the matching thickness of maximum microwave absorptions, and c is the velocity of light. According to the eq. 3, the improved μ and ε of the materials are necessary to obtain small matching thickness tμ in lower frequency. These results are of importance since the absorption frequency ranges can be tuned easily by changing the thickness of the absorbers, and broadband absorption can be achieved by multilayered absorbing structure.⁴⁰
Figure 4c and 4d show the real part ($\mu'$) and imaginary part ($\mu''$) of the complex permeability of sample S600, S700 and S800. Except the range of 8–12 GHz, all of them show a similar frequency dependence of the $\mu'$. The imaginary part $\mu''$ is often used to indicate the magnetic loss. The $\mu'$ of S600 decrease with the increasing frequency from 2 to 9 GHz and exhibit broad peak in the 9–14.4 GHz range due to the $\gamma$-$\text{Fe}_2\text{O}_3$ phase with high permeability, then keep almost unchanged in the 14.4–18 GHz with a minor fluctuation. The real peak in the 9–14.4 GHz range can be attributed to the existence of $\gamma$-$\text{Fe}_2\text{O}_3$ phase. The slightly lower $\mu'$ value of S700 than S800 in the range of 2–16 GHz means a smaller magnetic loss. In general, magnetic loss is reported to be dependent of magnetic hysteresis, domain-wall resonance, eddy current effect, exchange resonance and natural resonance. Considering the weakly applied magnetization field during the electromagnetic measurement, magnetic hysteresis could be neglected. The domain-wall resonance is reported to takes place in the MHz range, and can also be excluded. For S700, the eddy current effect is effectively suppressed and can also be excluded due to the existence of the insulative $\alpha$-$\text{Fe}_2\text{O}_3$ layer. Therefore, the magnetic loss of S700 is mainly from the exchange resonance and natural resonance. Based on the reported exchange resonance frequency at about 12 GHz for cobalt, the peak of $\mu''$ around 17 GHz can be attributed to the exchange resonance based on the Aharoni theory.

Figure 4e and 4f show the dielectric and magnetic tangent loss for the three samples, respectively. For S600, in the range of 10–15 GHz, the $\tan\delta_e$ is low; while in other frequency range, it is high. On the other hand, the $\tan\delta_M$ shows an opposite trend to that of $\tan\delta_e$. These results suggest that in the low frequency range, the microwave absorption mainly results from the dielectric loss of $\alpha$-$\text{Fe}_2\text{O}_3$, while in the high frequency range, magnetic loss of $\gamma$-$\text{Fe}_2\text{O}_3$ dominates. For both S700 and S800, $\tan\delta_e$ values are relatively low in the low frequency range (2–10 GHz) and then increase in the range of 10–18 GHz with a fluctuation, while the $\tan\delta_M$ of both samples are high in the low frequency (2–10 GHz) range and then decrease with the increasing frequency. Noteworthily, in the range of 16–18 GHz, S700 shows an abrupt increase, similar to the $\mu''$. Although the magnetic loss of S700 is lower than that of S800, the effective complementarity of the complex permittivity and permeability is more important to improve the microwave absorption property than merely a high magnetic loss, which can explain the microwave absorption of S700 is superior to S800. The slightly lower $\mu'$ value of S700 than S800 in the range of 2–16 GHz means a smaller magnetic loss. In general, magnetic loss is reported to be dependent of magnetic hysteresis, domain-wall resonance, eddy current effect, exchange resonance and natural resonance. Considering the weakly applied magnetization field during the electromagnetic measurement, magnetic hysteresis could be neglected. The domain-wall resonance is reported to takes place in the MHz range, and can also be excluded. For S700, the eddy current effect is effectively suppressed and can also be excluded due to the existence of the insulative $\alpha$-$\text{Fe}_2\text{O}_3$ layer. Therefore, the magnetic loss of S700 is mainly from the exchange resonance and natural resonance. Based on the reported exchange resonance frequency at about 12 GHz for cobalt, the peak of $\mu''$ around 17 GHz can be attributed to the exchange resonance based on the Aharoni theory.

Moreover, the EM wave absorption performance of the mixture of separately prepared $\text{Fe}_3\text{O}_4$ powders and rGO sheets were studied. The $\text{Fe}_3\text{O}_4$ powders was fabricated by one-pot co-precipitation method based on ref 41. The XRD pattern, Raman spectrum and SEM images of $\text{Fe}_3\text{O}_4$ powders and $\text{Fe}_3\text{O}_4$ powders/rGO can be found in Supplementary Figure S10 and S11. Figure 5a shows the RL of $\text{Fe}_3\text{O}_4$/rGO mixture. Compared with our samples, the RL loss is only $-6$ dB at 3 mm thickness. This clearly demonstrates the importance of synthetic procedure in the control of the EM wave absorption properties.
Moreover, commercial absorber: [Fe,Ni] (Beijing Reintech Electronics Technologies Co. Ltd, China) was selected for the comparative study in the same frequency range. Figure 5b and c shows the RL of [Fe,Ni] before and after heating. The RL of the as-obtained [Fe,Ni] is only $-7$ dB at 3.5 mm thickness. After being heated at 800°C for 1 hour in Ar, the RL was decreased to $-5$ dB, both of which are much inferior to our samples. In contrast, the RL for sample S700 under the same conditions is $-17$ dB at 3.5 mm thickness. These results clearly demonstrate the advantages of the synthetic strategy, the great EM wave absorption properties of the as-prepared samples, and the excellent thermal stability of these samples.
In summary, we reported the synthesis of iron oxides/rGO composites via a facile thermochemical process using graphite oxide and FeSO$_4 \cdot 7$H$_2$O. Through the regulation of the preparation temperature, we can obtain $\alpha$-Fe$_2$O$_3$/rGO, $\gamma$-Fe$_2$O$_3$/rGO, and Fe$_3$O$_4$/rGO composites conveniently. Interestingly, graphite oxide and rGO sheets were shown to regulate the phase transition from $\alpha$-Fe$_2$O$_3$ to Fe$_3$O$_4$ via $\gamma$-Fe$_2$O$_3$. The hydroxyl groups in graphene oxide sheets and the H$_2$ gas generated from the thermal reduction of graphene oxide were believed to be responsible for the transformation from $\alpha$-Fe$_2$O$_3$ to $\gamma$-Fe$_2$O$_3$ in the 540°C–700°C. The reducing gases (CO, CH$_4$ and H$_2$) may facilitate the transformation from $\gamma$-Fe$_2$O$_3$ to Fe$_3$O$_4$. Electromagnetic wave absorption studies indicated that these samples showed great EM wave absorption performances. With the increase of GO dosage, the absorption performances can be greatly improved. These samples perform much better than the mixture of rGO with Fe$_3$O$_4$, as well as commercial absorbers. Most importantly, our samples possess advantages for high temperature applications due to its excellent stability in high temperature (up to 800°C).

**Methods**

**Synthesis of iron oxides/graphene composites.** In a typical synthesis, 5.04 g (0.018 mol) FeSO$_4 \cdot 7$H$_2$O was dissolved into 20 mL distilled water with stirring for 30 min. Graphene oxide was synthesized by a modified Hummers method. The resulted concentration of GO aqueous solution was 4.0 mg mL$^{-1}$.

The preparation of the iron oxides/rGO composites was based on ref 43. GO aqueous solution was mixed with 20 mL FeSO$_4 \cdot 7$H$_2$O aqueous solution with ultrasonication for 30 min and vigorous stirring for 1 h. Then, the mixed suspension was dried at 90°C for 24 h, and the resulted black solid bulk was put in a quartz boat and placed in the middle part of a quartz tube, which was mounted horizontally inside a furnace. A protective gas of high purity argon (99.999%) was passed through the quartz tube at a rate of 500 standard cubic centimeters per minute (sccm) for 10 min to purge the air in the tube. The system was then heated to expected temperatures at a heating rate of 3°C per minute and held at that temperature for 1 hour before it cooled down to room temperature in the protective gas. The exhaust was imported into high concentration of NaOH solution in order to absorb SO$_2$ and SO$_3$ gases produced from

| Samples | $\varepsilon'$ | $\varepsilon''$ | $\mu'$ | $\mu''$ | $\tan\delta_E$ | $\tan\delta_M$ |
|---------|---------------|---------------|--------|--------|---------------|---------------|
| S600    | 16.88–24.44   | 1.21–7.61     | 0.89–1.32 | 0.05–0.35 | 0.28–0.43 | 0.05–0.31 |
| S700    | 7.74–11.16    | 1.44–4.08     | 0.93–1.26 | −0.22–0.23 | 0.13–0.50 | −0.21–0.20 |
| S800    | 6.92–8.18     | 0.44–2.35     | 0.86–1.36 | −0.17–0.36 | 0.06–0.33 | −0.19–0.30 |

Table 1 | The values of $\varepsilon'$, $\varepsilon''$, $\mu'$, $\mu''$, $\tan\delta_E$ and $\tan\delta_M$ of S600, S700 and S800

Figure 5 | Electromagnetic wave RL of (a) mixture of Fe$_3$O$_4$ and rGO, (b) commercial [Fe, Ni], (c) [Fe, Ni] after annealling at 800°C for 1 hour in Ar.
the reaction process. The control samples were prepared by directly heating FeSO₄·7H₂O powders in furnace with the same procedure without GO.

Figure 6 shows the schematic diagram of sample preparation process. Graphene oxide is negatively charged due to the rich electronegative oxygen species (epoxy, carboxyl, carbonyl and hydroxyl) on the surface and edges. FeSO₄·7H₂O is easily dissolved in water and ionized into Fe²⁺ and SO₄²⁻ ions. After mixing, the positively charged Fe²⁺ will be adsorbed on the GO sheets due to the electrostatic interaction, leading to the intercalation of Fe²⁺ and SO₄²⁻ ions into GO layers.

Electromagnetic wave absorption tests. The samples used for microwave absorption test were prepared by homogeneously mixing the composites with paraffin and pressed into a toroid with an outer diameter of 7.0 mm and inner diameter of 3.04 mm. The relative complex permittivity and permeability of the paraffin test were prepared by homogeneously mixing the composites with paraffin and pressed into a toroid with an outer diameter of 7.0 mm and inner diameter of 3.04 mm. The relative complex permittivity and permeability of the paraffin composites containing 50 wt% of the samples were determined by using a coaxial method with the vector network analyzer (Agilent E5071C, Agilent, USA) in the frequency range of 2–18 GHz. Finally, the microwave absorption properties were evaluated by the transmission line theory.

Characterization. The structures, microstructures, and morphologies of the as-obtained samples were characterized by X-ray powder diffraction (XRD Bruker D8-ADVANCE) using an 18 kV advanced X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å), Raman spectroscopy (inVia Reflex, Renishaw, UK), Field–emission scanning electron microscopy (FE-SEM, S4800, Hitachi, Japan), Transmission electron microscopy (TEM, JEM-2100, JEOL, Japan), Fourier transform infrared microscopy (VERTEX 80+HYPERION2000, Bruker Optics, Germany), Simultaneous thermal analyzer (DSC/DTA-T) STA 449 F3 Jupiter®, Netzsch, Germany). Magnetic properties were measured by Physical Property Measurement System (PPMS-9T (EC-II), Quantum Design, USA), Barrett-Emmett-Teller (BET) method in the relative pressure P/P₀ range of 0.01–0.20 was applied for the calculation of the pore volume, which was determined from the adsorption branch of the N₂ isotherm curve at the P/P₀ = 0.97 signal point. The pore diameter was derived from the maximum of the pore size distribution curve obtained using Barrett-Joyner-Halenda (BJH) method based on the adsorption branch of the N₂ isotherm curve.

1. Zhu, W. et al. Electromagnetic and microwave-absorbing properties of magnetic nickel ferrite nanocrystals. Nanoscale 3, 2862–2864 (2011).
2. Sun, G., Dong, B., Cao, M., Wei, B. & Hu, C. Hierarchical dendrite-like magnetic materials of Fe₃O₄, γ-Fe₂O₃, and Fe with high performance of microwave absorption. Chem. Mater. 23, 1587–1593 (2011).
3. Zhang, H. et al. Novel rGO/Fe₂O₃ composite hydrogel: synthesis, characterization and high performance of electromagnetic wave absorption. J. Mater. Chem. A 1, 8547–8552 (2013).
4. Ren, Y.-L. et al. Quaternary nanocomposites consisting of graphene, Fe₃O₄@Fe core@shell, and ZnO nanoparticles: synthesis and excellent electromagnetic absorption properties. ACS Appl. Mater. Interfaces 4, 6436–6442 (2012).
5. Wang, C. et al. The electromagnetic property of chemically reduced graphene oxide and its application as microwave absorbing material. Appl. Phys. Lett. 98, 072906 (2011).
6. Sun, X. et al. Laminated magnetic graphene with enhanced electromagnetic wave absorption properties. J. Mater. Chem. C 1, 765–777 (2013).
7. Kong, L. et al. Electromagnetic wave absorption properties of reduced graphene oxide modified by maghemite colloidal nanoparticle clusters. J. Phys. Chem. C 117, 19701–19711 (2013).
8. Wang, T. et al. Graphene–Fe₃O₄ nanohybrids: synthesis and excellent electromagnetic absorption properties. J. Appl. Phys. 113, 024314 (2013).
9. Zhao, X. et al. Excellent microwave absorption property of graphene-coated Fe nanocomposites. Sci. Rep. 3, 3421 (2013).
10. Peng, C.-H., Shiu, Chen, P. & Chang, C.-C. High-temperature microwave bilayer absorber based on lithium aluminum silicate/lithium silicate-SiC composite. Ceram. Int. 40, 47–55 (2014).
11. Song, N. et al. Integrating giant microwave absorption with magnetic refrigeration in one multifunctional intermetallic compound of LaFe₁₁.₆Si₁.₄Co₀.₂H₁.₇. Sci. Rep. 3, 2291 (2013).
12. Swami, M., Prasad, T. & Sant, B. Thermal analysis of ferrous sulphate heptahydrate in air. II. The oxidation-decomposition path. J. Therm. Anal. 16, 471–478 (1979).
13. Masset, P., Poinso, J.-Y. & Poinso, J.-C. TG/DTA/MS study of the thermal decomposition of FeSO₄·6H₂O. J. Therm. Anal. Cal. 83, 457–462 (2006).
14. Petkova, V. & Pelovsky, Y. Comparative DSC study on thermal decomposition of iron sulphates. J. Therm. Anal. Cal. 93, 847–852 (2008).
15. Liu, S., Zhou, J. & Zhang, J. Effects of crystalline phase and particle size on the properties of plate-like Fe₃O₄ nanoparticles during γ-to-α phase transformation. J. Phys. Chem. C 115, 3602–3611 (2011).
16. Zhu, H. et al. Pressure induced phase transition of nanocrystalline and bulk magnesium (γ-Fe₂O₃) to hematite (α-Fe₂O₃). J. Phys. Chem. Solids 71, 1183–1186 (2010).
17. Kachi, S., Momiyama, K. & Shimizu, S. An electron diffraction study and a theory of the transformation from α-Fe₂O₃ to γ-Fe₂O₃. J. Phys. Soc. Jpn. 18, 106–116 (1963).
18. Meillon, S., Dammak, H., Flavin, E. & Pascard, H. Existence of a direct phase transformation from haematite to maghemite. Philos. Mag. Lett. 72, 105–110 (2000).
19. Randrianantoandro, N., Mercier, A., Hervieu, M. & Grenèche, J. Direct phase transformation from hematite to maghemite during high energy ball milling. Mater. Lett. 47, 150–158 (2001).
20. Aharoni, A., Frei, E. H. & Schieber, M. Some properties of γ-Fe₂O₃ obtained by hydrogen reduction of α-Fe₂O₃. J. Phys. Chem. Solids 23, 545–554 (1962).
21. Han, Q. et al. Growth and properties of single-crystalline γ-Fe₂O₃ nanowires. J. Phys. Chem. C 111, 5034–5038 (2007).
22. Schimpf, H. C. et al. Functionalized single graphene sheets derived from splitting graphite oxide. J. Phys. Chem. B 110, 8535–8539 (2006).
23. Paredes, J., Villar-Rodríguez, S., Martínez-Alonso, A. & Tascón, J. Graphene oxide dispersions in organic solvents. Langmuir 24, 10560–10564 (2008).
24. Huh, S. H. [Thermal reduction of graphite oxide] Physics and Applications of Graphene-Experiments [Mikhalin, S. (ed.)] [73–90] (InTech, Shanghai, 2011).
25. Chernyshova, I. V., Hochella, M. F. Jr. & Madden, A. S. Size-dependent structural transformations of hematite nanoparticles. 1. Phase transition. Phys. Chem. Chem. Phys. 9, 1736–1750 (2007).
26. Shulga, Y. et al. Gaseous products of thermo- and photo-reduction of graphite oxide. Chem. Phys. Lett. 498, 287–291 (2010).
27. Acik, M. et al. The role of intercalated water in multilayered graphene oxide. ACS Nano 4, 5861–5868 (2010).
28. Balandin, A. A. et al. Superior thermal conductivity of single-layer graphene. Nano Lett. 8, 902–907 (2008).
29. Matsumoto, M. & Miyata, Y. Thin electromagnetic wave absorber for quasi-microwave band containing aligned thin magnetic metal particles. IEEE T. Magn. 33, 4459–4464 (1997).
30. Imui, T. & Konishi, K. Fabrications of broad-band RF-absorber composed of planar hexagonal ferrites. IEEE T. Magn. 35, 3148–3150 (1999).
31. Park, K.-Y., Lee, S.-E., Kim, C.-G. & Han, J. Fabrication and electromagnetic characteristics of electromagnetic wave absorbing sandwich structures. Compos. Sci. Technol. 66, 576–584 (2006).
32. Li, W., Lv, B. & Xu, Y. Sub-30 nm Fe₃O₄ and γ-Fe₂O₃ octahedral particles: preparation and microwave absorption properties. J. Nanopart. Res. 15, 1–9 (2013).
33. Zhang, H., Xie, A., Wang, C., Shen, Y. & Tian, X.-Y. Room temperature fabrication of RGO/Fe3O4 composite hydrogel and their excellent wave absorption properties. RSC Adv. 4, 14441–14446 (2014).
34. Watts, P. C. P., Hsu, W.-K., Barnes, A. & Chambers, B. High permittivity from defective multiwalled carbon nanotubes in the X-band. Adv. Mater. 15, 600–603 (2003).
35. Chen, Y. J. et al. Synthesis, magnetic and electromagnetic wave absorption properties of porous Fe3O4/Fe/SiO2 core/shell nanorods. J. Appl. Phys. 106, 054303 (2009).
36. Liu, T., Pang, Y., Zhu, M. & Kobayashi, S. Microporous Co@CoO nanoparticles with superior microwave absorption properties. Nanoscale 6, 2447–2454 (2014).
37. Ma, F., Qin, Y. & Li, Y.-Z. Enhanced microwave performance of cobalt nanoflakes with strong shape anisotropy. Appl. Phys. Lett. 96, 202507 (2010).
38. Ma, Z. et al. Analyses on multiple resonance behaviors and microwave reflection loss in magnetic Co microflowers. Phys. Status Solidi B. 249, 575–580 (2012).
39. Gangopadhyay, S. et al. Magnetic properties of ultrafine iron particles. Phys. Rev. B: Condens. Matter 45, 9778–9787 (1992).
40. Aharoni, A. Exchange resonance modes in a ferromagnetic sphere. J. Appl. Phys. 69, 7762 (1991).
41. Zong, M. et al. One-pot simplified co-precipitation synthesis of reduced graphene oxide/Fe3O4 composite and its microwave electromagnetic properties. Mater. Lett. 106, 22–25 (2013).
42. Marcano, D. C. et al. Improved synthesis of graphene oxide. ACS Nano 4, 4806–4814 (2010).
43. Singh, V. K. et al. In situ synthesis of graphene oxide and its composites with iron oxide. New Carbon Mater. 24, 147–152 (2009).
44. Li, D., Müller, M. B., Gilje, S., Kaner, R. B. & Wallace, G. G. Processable aqueous dispersions of graphene nanosheets. Nat. Nanotech. 3, 101–105 (2008).
45. Ramesha, G., Vijaya Kumara, A., Muralidhara, H. & Sampath, S. Graphene and graphene oxide as effective adsorbents toward anionic and cationic dyes. J. Colloid Interface Sci. 361, 270–277 (2011).
46. Gallagher, P., Johnson, D. & Schrey, F. Thermal decomposition of iron (II) sulfates. J. Am. Ceram. Soc. 53, 666–670 (1970).

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Author contributions
L.Z., X.Y. and H.H. designed and carried out the project. Z.L., Y.L., M.W. and C.C. wrote the manuscript. Z.W. and G.L. measured the electromagnetic wave absorption. Z.S. characterized the samples. All authors contributed to discussions of the results. All authors reviewed the manuscript.

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