PREPARATION OF GRAPHENE WITH CONTROLLED REDUCTION DEGREE AND STUDY OF ELECTROMAGNETIC PROPERTIES OF THEIR NANOCOMPOSITES

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1 Introduction
Nanoscale materials based on single-layered 2-D graphene sheets have attracted much attention recently because of their excellent properties: It has a large theoretical specific surface area (2630 m²g⁻¹), high intrinsic mobility (200 000 cm²v⁻¹s⁻¹) [1, 2], high Young’s modulus (~1.0 TPa) [3], high thermal conductivity (~5000Wm⁻¹K⁻¹) [4], optimal optical transmittance (~97.7%) and good electrical conductivity, merit attention for many potential areas [5, 6]. Graphene based materials have various promising applications [7], one of which is in polymer nanocomposite area [8] to behave high electromagnetic performance. At present, though composite materials employing carbon-based materials are dominated by carbon nanotubes, the intrinsic bundling of carbon nanotubes, the impurities from the catalysts and high costs have been hampering their applications [9]. It has been studied that these issues could be solved by incorporating graphene based nanosheets into polymer matrix as the effective filler to replace carbon nanotubes. Both graphene oxide (GO) and reduced graphene oxide (RGO, normally accepted as chemically generated graphene) are functional fillers for nanocomposites due to their special structure, dispersion quality and electromagnetic properties [7]. It is vital to note that the electrical conductivity of graphene nanosheets and its aromatic network can be partially restored through removal of functional groups by chemical reduction from graphene oxide. Recently we reported preparing GO with modified Hummers method to achieve a better oxidation degree and synthesis of large scale of several microns of the nanosheets [10]. There are several ways to achieve reduced graphene oxide [11] and among those the method using hydrazine monohydrate was found to be highly effective and most widely used. Since graphene can be further synthesized by reduction from GO with hydrazine monohydrate in aqueous solution, it also can be modified by cations during the reduction process in order to achieve a better dispersion quality [12] thus can be well dispersed into solvents and polymer matrix. Herein, we report a facile synthesis method to prepare reduced graphene oxide nanosheets with hydrazine monohydrate, by adjusting various reaction times to reach different reduction degrees of RGO nanosheets without sacrificing their dispersion quality. The as-prepared nanosheets can serve as functional fillers in epoxy matrix by fast pre-dissolving them into acetone as organic solvent and diluter, then we prepared their nanocomposite samples by vaporizing the diluter, and characterized the electromagnetic properties of them with various reduction degrees of graphene fillers.

2 Experimental Section
2.1 Preparation of RGO with Controlled Reduction Degree
Modified Hummers method was employed to prepare graphite oxide from natural graphite powder which was oxidized by potassium nitrate and potassium permanganate, in the presence of sulfuric acid as our previous work indicated [10]. After oxidation, the as-prepared graphite oxide aqueous solution was cooled down to room temperature, concentrated and washed with deionized water several times. Before the next step, we adjust 2 hours’ sonication to the graphite oxide aqueous solution to achieve single layer GO nanosheets. RGO was achieved from as-synthesized GO with the help of hydrazine monohydrate (purchased from Beijing Chemical Co.,Ltd.) under a mild condition:
at 40°C in aqueous solution (GO:2mg/ml; hydrazine monohydrate:3mg/ml) after the adjustment of pH value by NaOH to 9~10 [12]. Various reaction times (4 h, 8 h and 12 h) were employed for reduction to achieve RGO-1, RGO-2 and RGO-3 respectively, thus to reach different reduction degrees. After the reduction process, the product was immediately washed with deionized water and ethanol several times, then dried under 70°C in a vacuum oven. Before the preparation of the nanocomposites, the RGO products were grinded to powders.

### 2.2 Preparation of RGO/epoxy Nanocomposites

Same loading amount, 1% weight percent, of fillers (GO and various RGO powder samples) were weighed out respectively and well dispersed in acetone as the diluter firstly and then added in E51 epoxy resin (purchased from Beijing Chemical Co.,Ltd.) to form a mixed solution. The RGO/epoxy suspension was well sonicated for 1 h at 60°C, then the solution was transferred from the sonicator to a rotary evaporator, by keeping the same temperature and with the help of a vacuum pump, the diluter was removed easily while the resin kept a low viscosity. Then the curing agent was added in the suspension. The well stirred mixture was poured into moulds as shown in Fig. 1 and the resin was cured at room temperature for 24 h to fabricate specimens for electromagnetic parameters testing [13]. Pure epoxy resin sample was prepared as the control group.

### 2.3. Instruments and measurements

X-ray diffraction (XRD) analysis was conducted with a Rigaku D/max-rB diffractometer using Cu Kα radiation. Atomic force microscopy (AFM) images were obtained by a Multimode Nano4 in tapping mode. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nexus 670 spectrometer, in the range of 500-4000 cm⁻¹. The Raman spectra was measured on LabRam Aramis HORIBA Jobin Yvon S.A.S (lex=632.8 nm). X-ray photoelectron spectroscopy (XPS) measurements were performed using an AXIS ULTRA DLD spectrometer with a monochromated Al K radiation (1486.6 eV). Calibration of all XPS spectra was performed using the C1s line at 284.8 eV and curve fitting and background subtraction were conducted by XPS PEAK Version 4.0 software. Thermogravimetric analysis (TGA, NETZSCH STA409) was performed under nitrogen flow from 30 to 700 °C at a heating rate of 10 °C/min for nanopowders. Scanning electron microscope (SEM, FEI Quanta 200F) was used to observe the section surface morphology of various RGO/epoxy nanocomposites. The surfaces were sputtered with gold before SEM observation. An 8722ES vector network analyzer was applied to determine the complex relative permeability $\mu_r = \mu'_r - j\mu''_r$, ($\mu'_r$: the real part of permeability, $\mu''_r$: the imaginary part of permeability) and relative permittivity $\varepsilon_r = \varepsilon'_r - j\varepsilon''_r$ ($\varepsilon'_r$: the real part of permittivity, $\varepsilon''_r$: the imaginary part of permittivity) in the frequency range of 8.2~12.4 GHz and 12.4~17.8 GHz.

### 3 Results and Discussion

Atomic Force Microscope is a direct method to characterize two dimensional nanomaterials by depositing the nanosheets onto a mica substrate and measuring their heights. The AFM images show that graphite oxide was successfully exfoliated and via sonication process, the GO nanosheets were well dispersed in aqueous solution (Fig. 2a). The thickness of the nanosheets is around 1 nm indicating that the nanosheets were dispersed as single-layer. It is widely accepted that after reduction, the RGO will reduce some of its oxygen functional groups which can lead to various extent of agglomeration and thus diminish the dispersion quality in aqueous solution. However, by modifying nanosheets with cations such as K⁺ and Na⁺ and reduce GO under a mild reduction condition, the single-layer status will be remained [12]. We adjusted pH value from 9~10 of the solution by adding a few drops of NaOH solution in order to modify the nanosheets with a charge repulsion effect, and then reduced the nanosheets at a relatively low temperature, 40 °C, in order to prevent the nanosheets from agglomerating heavily. Fig. 2b, Fig. 2c and Fig. 2d show that these RGO-1, RGO-2 and RGO-3 nanosheets can be retained as single-layer (about 1 nm thick) during the reduction process, indicating a good dispersion quality without serious graphitic layer restacking in the dissolved state. However, the side effect of reduction of removing oxygen functional groups still exists: during the reduction, the nanosheets were irregularly broken.
into small pieces. The original piece scale was around 5 microns appeared as a full square-like or circle-like shape while with the longest reduction time of 12 h, the nanosheets were tore into ribbon-like shape (Fig. 2d) and the pieces were much smaller from the observation under AFM.

The crystal structure of solid state RGO-1, RGO-2 and RGO-3 in each corresponding reduction stage are illustrated by XRD, and the results are shown in Fig. 3. In our previous work, a diffraction peak occurs at 26.6° in the XRD pattern of graphite corresponding to the (002) reflection, while the sharp peak shifts to 10.8° in graphite oxide, indicating that the interlayer distance of pristine graphite is widened from 0.334 nm to 0.818 nm, due to the intercalation of oxygen functional groups and H2O [10]. Here, the XRD result shows the change of interlayer structure during the mild reduction process. After reduction for 4 h, the diffraction peak around 11° is still significant, revealing the powder state reduction product has some remained oxygen functional groups linked on the surface, because the expanded layer structure still existed in the solid state. However, in contrast with solid GO XRD pattern, the solid RGO-1 XRD pattern appears to have a small wide peak around 24°, showing a slight extent of reconstruction of graphite stacking. During the reaction time from 4 h to 8 h, the peak intensity around 11° diminishes considerably while the wide peak around 24° becomes stronger, indicating more graphite structures were reconstructed thus the monolayer nanosheets tended to restack with each other in the solid state. After reduction for 12 h, the peak caused by expanded layer structure almost disappears in the solid RGO-3 XRD pattern. XRD results of RGO-1, RGO-2 and RGO-3 can show that there is a gradually changed interlayer structure during reduction process, and the graphite structure are slightly reconstructed in each reduction stage.

In order to confirm the reduction process and verify that the reduction degrees are under control, we conducted FT-IR. In our previous work, the GO spectrum has an intensive broadened peak at about 3500 cm⁻¹, which is corresponding to the O-H stretching vibrations of the C-OH groups and the water molecules intercalated into GO [10]. The RGO-1, RGO-2 and RGO-3 also share this peak (Fig. 4), indicating the controlled reduction degree and the remained oxygen functional groups which were attached with water molecules. Along with other peaks at 1045 cm⁻¹ (alkoxy C-O groups), and 1725 cm⁻¹ (carboxyl and carbonyl C-O groups), this broadened peak simultaneously confirms the presence of hydroxyl, carboxyl and carbonyl groups in RGO-1, RGO-2 and RGO-3. Besides, more peaks around 1223 cm⁻¹ indicate that epoxy groups also remained linked to RGO-1, RGO-2 and RGO-3. Those strong absorptions around 1223 cm⁻¹ and 1045 cm⁻¹ gradually disappear in the spectrum of RGO-1. RGO-2 and RGO-3 nanosheets, revealing that some alkoxy and epoxy groups were removed during the reduction process. Meanwhile, the peak around 1630 cm⁻¹ becomes sharp, which represents the stretching of C-C in aromatic rings of graphene and reveals that the aromatic structure was gradually reconstructed. Hence, it can be concluded that GO was partially reduced to RGO-1, RGO-2 and RGO-3 by hydrazine monohydrate according to these variations of IR absorptions, and these results show a gradually decreased intensity of oxygen functional groups with a longer reaction time, also a higher level of reduction degree. Moreover, from RGO-1 to RGO-2, a more obvious disappearance of the peak around 1223 cm⁻¹ firstly shows up, while from RGO-2 to RGO-3, the peak intensity around 1045 cm⁻¹ strongly diminishes. This phenomenon may be due to the mechanism of the reduction process by firstly reducing the epoxy group or may be due to the relatively larger amount of epoxy group which were reduced at the first 4 hours’ reaction.

The XPS is employed to better illustrate the precise reduction degree, the results are shown in Fig. 5. The reduction of gradually reduced GO during reduction process is well confirmed: by taking the ratio of C1s to O1s peak area in XPS spectra of RGO-1, RGO-2 and RGO-3, we obtained the atomic ratio of C/O. The gradual increase of atomic C/O ratio (GO: 2.06 [10], RGO-1: 3.58, RGO-2: 4.03, RGO-3: 5.19) and peak shifts in Fig. 6 indicate that RGO-1, RGO-2 and RGO-3 were of different reduction degrees under the mild reduction condition, it not only verifies the reduction degree can be controlled to a differential level, but also shows the subtle change of the oxygen functional group during the process. With the help of the software, we adjust peaks centered at 284.5, 285.6, 286.7, 287.8, and 288.8 eV, which are associated with sp²C, sp³C, C-O, -C=O, and –COO- groups, respectively [17, 18]. Compared with XPS results of GO in our previous
work, RGO-1 has significantly increased percentage of sp$^2$C and sp$^3$C while the percentage of C-O and C=O decrease extensively. The results indicate that from GO to RGO-1, the oxygen functional group became less and reduction degree varied from 2.06 to 3.58. RGO-2 and RGO-3 have much less oxygen functional groups than that of RGO-1 since the peak around 288 eV becomes considerably weak, revealing that the reduction degree increased according to longer reaction times. We can also find out that from RGO-2 to RGO-3, the intensity of peak centered at 287.8 eV which represents the C=O group is weakened, showing that during reaction time from 8 h to 12 h, the carbonyl group was mainly reduced. Besides, from three samples we observe a high percentage of sp$^3$C and it represents that there existed some defects on the RGO-1, RGO-2 and RGO-3 nanosheets because of reduction.

TGA is employed to determine the thermal stability of the product RGO-1, RGO-2 and RGO-3. GO is thermally unstable and starts to lose mass upon heating even at a very low temperature, but the major mass loss occurs around 200°C, presumably due to pyrolysis of the labile oxygen functional groups, yielding CO, CO$_2$ and steam [14, 15]. Hence, the thermal decomposition of GO can result in a rapid thermal expansion of the material and a large mass loss during a more rapid heating regime [16]. Meanwhile, the removal of the thermally labile oxygen functional groups by reduction will increase the thermal stability of the RGO (Fig. 6). Below 100°C, the loss of mass can be attributed to the removal of the adsorbed water molecule, a slight mass loss was detected when the material was heated around to 200 °C, which indicates that like original GO nanosheets, there were still some oxygen functional groups linked onto the nanosheets of RGO samples. While it might be expected that the nanosheets will be more and more thermally stable when they are reduced to a higher level because less thermally labile oxygen functional groups exist after reduction, the thermal stability actually turns out to be not only correlate with the reduction degree. Interestingly RGO-1 is the most stable product among the three since it lost least weight during heating. The thermal stability of RGO-3 is slightly higher than that of RGO-2 (see Fig. 6) as the product lost less weight when heating even to 700°C. We can deduce that another factor which affects the thermal stability is the resulted defect density on the nanosheets. With a longer reaction time, more defects will be employed onto the nanosheets thus decrease the thermal stability. Being another factor, it will compete with the reduction degree and they together control the thermal stability of the product. As a matter of fact, although RGO-1 has the lowest reduction degree, its low defect density contributes to its highest stability among the three products.

Raman spectra results show the subtle change of graphitic domain structure through the reduction process such as the added defects and area of the graphitic parts. Raman spectrum of the pristine graphite displays a prominent G peak as the only feature corresponding to the first-order scattering of the E2g mode [19]. In the Raman spectrum of GO, the G band is broadened and shifted. In addition, the D band becomes prominent with the reduction in size of the in-plane sp$^2$ domains, possibly due to the extensive oxidation [19]. The Raman spectrum of the RGO also displays both G and D bands (see Fig. 7) at around 1580 cm$^{-1}$ and 1350 cm$^{-1}$ respectively. And D/G intensity ratio will increase after reduction compared to that in GO. This ratio suggests an increase of defect density of the nanosheets at different levels of reduction, and can be explained if new graphitic domains are created that are smaller in size to the ones present in GO before reduction, but more numerous in number [16]. Deducing from previous experiments of RGO, the defects should have increased with a higher reduction degree to cause the thermal stability to decrease, thus we choose to characterize the intensity ratio of D and G band to reveal the slight change of micro structure of the nanosheets. Table 1 is the Raman spectra results of I(D)/I(G). From the reduction time of 4 h to 8 h and then 12 h, the intensity ratio gradually grows from 1.22 to 1.27 and finally to 1.28, indicating the increasing amount of defects and turning of smaller graphitic domains rebuilt by reduction. Admittedly the thermal stability of graphitic area is higher than that of the oxidized parts, however with more defects of boundaries and holes as vulnerable area, the thermal stability decrease considerably. As a consequence, although reduction helps to rebuild the graphitic domain, it also brings more defects onto the nanosheets which lead to the decline of the thermal resistance capability.

GO and as-prepared various RGO samples with different reduction degrees are carefully filled into
Epoxy resin (E-51) to fabricate nanocomposites separately. Before curing, a well dispersed mixture of fillers and resin must be attained with the help of sonication and diluter in order to make the samples only vary in the content of oxygen in fillers. Since the fillers are of different reduction stages, SEM images of section surfaces are carried out to illustrate what effects the fillers have on the morphology of nanocomposites after mixing and curing. Fig. 8 shows the SEM images of section surfaces of GO/Epoxy, RGO-1/Epoxy, RGO-2/Epoxy and RGO-3/Epoxy nanocomposite samples. Although by employing diluter used for better mixing, the resin cannot be cured with a very high density, however with section surface morphology in these images, the variance of roughness can be observed which is mainly ascribed to the changing dispersion quality and compatibility of filler with resin: the more difficult filler disperse and is compatible with resin, the higher roughness and more flake-like structure could be observed. Hence it can explain the gradually varied section surface morphology of the four samples. From the result, it can be concluded that GO has the best compatibility with E51 resin while with the reduction degree increases, the compatibility decreases which cause more flake-like structure in RGO-2/Epoxy and RGO-3/Epoxy nanocomposite samples.

The electromagnetic parameters of the nanocomposites are measured to calculate the electromagnetic properties. Herein, the RGO nanocomposite samples were characterized by a vector network analyzer which represents the typical dielectric and magnetic properties of the samples in this work. The electromagnetic results are illustrated in Fig. 9 and Fig. 10. The results in Fig. 9a show an increased complex relative permittivity parameter of RGO nanocomposites compared to the pure epoxy sample and GO/Epoxy nanocomposite sample. As widely accepted, with better conductivity, the material will have a higher relative permittivity due to a better network formed by fillers [13]. However the formation of a conductive network of fillers is determined not only by the conductivity of the filler, it is also determined by the ability of the fillers to form a uniform mixture with resin. As the reduction degree increases, the real part of relative permittivity of RGO-1/Epoxy nanocomposite grows, so does RGO-2/Epoxy nanocomposite sample. Interestingly, RGO-3/Epoxy nanocomposite has a lower parameter value compared with RGO-2/Epoxy nanocomposite which performed the highest real part of complex relative permittivity among all the samples. It probably can be explained by the competition between two main factors: a) the graphitic domain reconstruction degree which leads to a higher conductivity, and b) the dispersion quality of fillers, since they are both strongly related to the formation of a conductive network in matrix thus they both affect the parameters. Meanwhile, all the samples have relatively low imaginary parts of relative permittivity without significant regular patterns (see Fig. 9b), indicating that adding fillers as GO and various RGO with different reduction degrees do not significantly change the imaginary part value which represents for electrical loss of the sample.

Some kinds of magnetic materials or magnetically functionalized materials who serve as fillers could enhance the magnetic properties of composites [20], but in this work the increase was not obvious as GO and RGO samples are of low magnetic property themselves. Fig. 10 show the complex permeability of GO and various RGO nanocomposites with different reduction degrees. As shown in the figure, both the real part of permeability and the imaginary part of permeability in all nanocomposite samples are of very low values and are almost the same as the pure resin, indicating no trend of increasing or decreasing magnetic properties.

4 Conclusions

Reduced graphene oxide (graphene) can be successfully prepared with controlled reduction degree by changing reaction time under a mild aqueous condition. RGO/Epoxy nanocomposite samples were carefully fabricated from a well dispersed mixture of fillers with E51 resin to characterize section surface morphology and their electromagnetic properties. The retained single layer structure after reduction and the increase of the real part of complex relative permittivity indicates a potential application of graphene with adjustably reduction degrees: it can serve as both functional fillers and supporting materials in matrix. The discussion about co-functioned factors a) graphitic domain reconstruction degree and b) dispersion quality and compatibility of fillers with resin, can help to design and employ a proper reduction level of RGO for electromagnetic composite fields.
Table 1. Raman spectra results of intensity ratio

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<td>1.22</td>
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Fig. 1. The schematic of specimen for electromagnetic testing (a: specimen for testing in the frequency range of 8.2 – 12.4 GHz, and b: specimen for testing in the frequency range of 12.4 – 17.8 GHz).

Fig. 2. AFM images and the measurements of the thickness of the nanosheets: GO (a), RGO-1 (b), RGO-2 (c) and RGO-3 (d).

Fig. 3. XRD patterns of RGO-1, RGO-2 and RGO-3.

Fig. 4. FT-IR spectra of RGO-1, RGO-2 and RGO-3.
Fig. 5. C1s Curve-fitting results of XPS spectra: RGO-1 (a), RGO-2 (b) and RGO-3 (c).

Fig. 6. TG analysis results of RGO-1, RGO-2 and RGO-3.

Fig. 7. Raman spectra of RGO-1, RGO-2 and RGO-3.

Fig. 8. SEM images: GO/Epoxy nanocomposites (a); RGO-1/Epoxy nanocomposites (b); RGO-2/Epoxy nanocomposites (c); RGO-3/Epoxy nanocomposites (d).
Fig. 9. The complex relative permittivity, real part (a) and imaginary part (b), of RGO/Epoxy nanocomposites, GO/Epoxy nanocomposite and pure epoxy resin sample. The frequency range is 8.20-18.00 GHz.

Fig. 10. The complex relative permeability, real part (a) and imaginary part (b), of RGO/Epoxy nanocomposites, GO/Epoxy nanocomposite and pure epoxy resin sample. The frequency range is 8.20-18.00 GHz.
References


