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Letter to the Editor

Electromagnetic interference shielding of graphene/epoxy composites

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ABSTRACT

Composites based on graphene-based sheets have been fabricated by incorporating solution-processable functionalized graphene into an epoxy matrix, and their electromagnetic interference (EMI) shielding studies were studied. The composites show a low percolation threshold of 0.52 vol.%. EMI shielding effectiveness was tested over a frequency range of 8.2–12.4 GHz (X-band), and 21 dB shielding efficiency was obtained for 15 wt% (8.8 vol.%) loading, indicating that they may be used as lightweight, effective EMI shielding materials.

Nanoscale materials based on single-layered 2-D graphene sheets have attracted much attention recently due to many unusual properties predicted [1]. Perfect graphene itself does not occur naturally, but bulk and solution-processable functionalized graphene (SPFG) can now be prepared through extensive chemical attack of graphite crystals to introduce oxygen-containing defects in the graphite stack, followed by complete exfoliation into sheets of atomic-thickness through either thermal or mechanical treatments [2,3]. It is important to note that the electrical conductivity of SPFG and its aromatic network can be partially restored through the removal of the functional groups by chemical reduction. 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 application. It has been proposed that these issues could be mitigated by incorporating single-layered graphene sheets into composite materials [3,4]. These novel graphene materials may offer another intriguing nanoscale filler material with low density for various composite applications. Because of the wide use of commercial, military and scientific electronic devices and communication instruments, electromagnetic interference (EMI) shielding of radio frequency radiation continues to be a serious concern for modern society. Compared with conventional metal-based EMI shielding materials, conducting polymer composites are lightweight, resistant to corrosion, and flexible and offer processing advantages [5]. The EMI shielding effectiveness (SE) of a composite material mainly depends on the filler's intrinsic conductivity, dielectric constant and aspect ratio [5]. Thus, it is expected that the use of atomic-thick graphene, with large aspect ratio and high conductivity, would provide a high EMI SE. Herein, we report the first result of EMI SE (in the X-band) of graphene/epoxy composites based on graphene-based sheets. An EMI SE up to 21 dB at 8.2 GHz was obtained for these composites with 15 wt% (8.8 vol.%) loading of SPFG.

The graphene/epoxy composites were prepared using an *in situ* process. Graphite oxide (GO), prepared by the modified Hummers method [6] from graphite, was first completely

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exfoliated to SPFG sheets in H_2O via sonication to form a dispersion of SPFG/H_2O solution. Hydrazine hydrate (80%) was then added, and the solution was heated at 100 °C [5] to make partially reduced graphene-based sheets. The partially reduced graphene-based sheets was collected by filtration, washed with water and then dried. An epoxy/hardener (4:1, in acetone) solution was added to the partially reduced graphene-based sheets suspension and then, sonicated and stirred for hours. After that, the mixture was poured into suitable molds to let the solvent evaporate completely at 60 °C. All the samples were cut to slabs of the desired sizes, and were then annealed at 250 °C for 2 h under N_2 to fully reduce the partially reduced graphene-based sheets and increase its conductivity [7]. Fully reduced graphene-based sheets were prepared from partially reduced graphene-based sheets by annealing at 250 °C for 2 h under N_2.

Fig. 1 displays atomic force microscopy (AFM) images of SPFG sheets from H_2O solution. The thickness of the sheets can be estimated from the cross-sectional profile depicted in Fig. 1b and d. Analysis of a large number of AFM images revealed that most of the SPFG sheets had thicknesses in the range of 0.8–1.1 nm, which is characteristic of an individual SPFG sheet. [2,6,7]. The thermogravimetry analysis (TGA) curves for GO, partially reduced graphene-based sheets and fully reduced graphene-based sheets are given in Fig. 2. The major mass loss of more than 30% occurs at ~200 °C for the GO. This is likely due to the pyrolysis of the labile oxygen-containing groups [2]. Furthermore, there is still approximately 12% mass loss for the partially reduced graphene-based sheets at ~200 °C, indicating that some oxygen-containing groups still remain on the graphene sheets after only reduction by hydrazine hydrate [2]. However, the fully reduced graphene-based sheets shows only a very slow mass loss up to 800 °C, indicating almost complete removal of the functional groups. These results show that annealing at 250 °C during our preparation of composites for EMI shielding studies should restore most of the original graphene structure and enhance the electrical conductivity of the composites.

Fig. 3 shows the direct current conductivity (σ) of these composites as a function of SPFG volume fraction (p), which

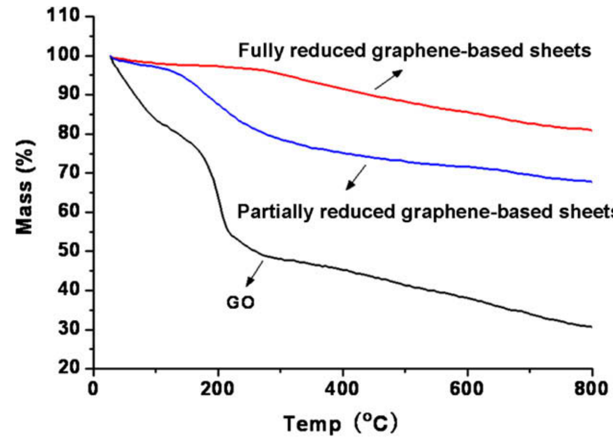

Fig. 2 – The TGA curves with heating rate of 5 °C/min from room temperature to 800 °C under N_2 for GO, partially reduced graphene-based sheets and fully reduced graphene-based sheets.

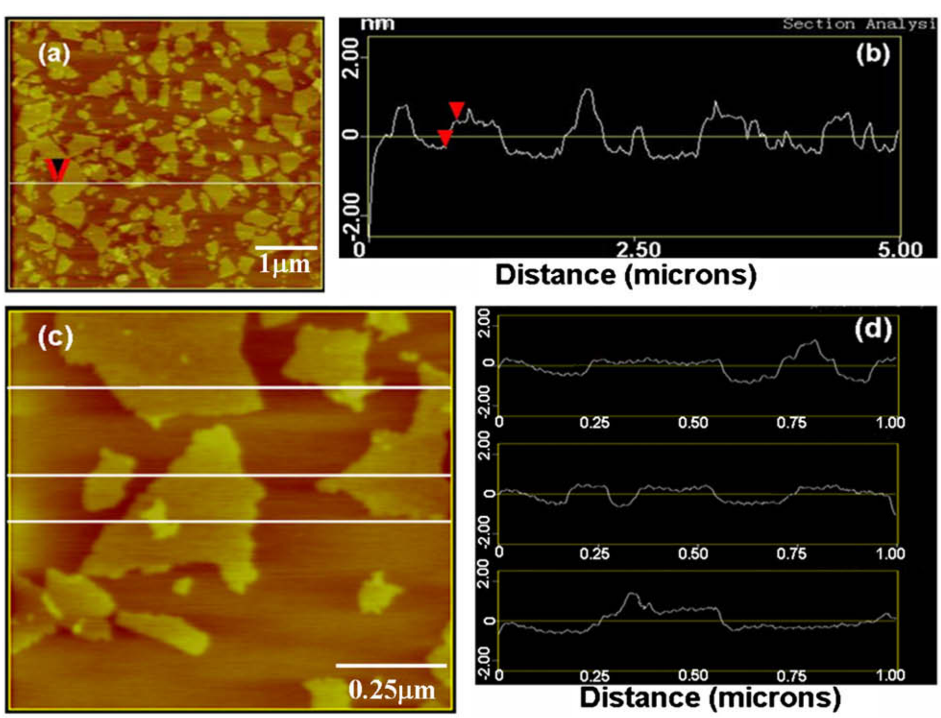

Fig. 1 – (a) A typical tapping mode AFM image of many individual single-layered SPFG sheets deposited on a mica substrate. (b) The corresponding height cross-section along the line in panel (a); the height difference between red arrows is ~0.8 nm. (c) A typical enlarged AFM image of several SPFG sheets deposited on a mica surface. (d) The corresponding height cross-section along the three lines in panel (c).

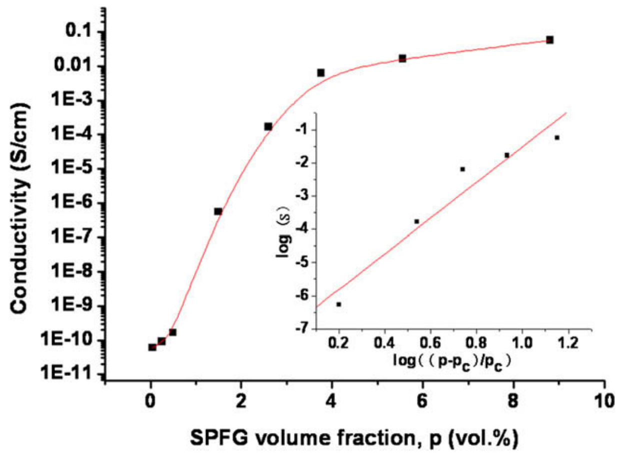

Fig. 3 – log10 DC conductivity (σ) vs. volume fraction (p) of graphene/epoxy composites measured at room temperature. Inset: log–log plot for σ vs. $((p-p_c)/p_c)$ for the same composites. The straight line in the inset is a least-squares fit to the data using Eq. (1). The best fit gave values p_c = 0.52 vol.% and β = 5.37 with a correlation factor of 0.97.

was determined using the standard four-point contact method. It is well known that the conductivity of a conductor-insulator composite follows the critical phenomena around the percolation threshold (Eq. (1)) [8]:

$$\sigma \propto (p - p_c)^{\beta} \tag{1}$$

where σ is the composite conductivity, p is the SPFG volume fraction, p_c is the percolation threshold and β is the critical exponent. The conductivity of graphene/polymer composites agrees very well with the percolation behavior predicted by Eq. (1). The straight line in the inset figure, with p_c = 0.52 vol.% and β = 5.37, gives a good fit to the data. The low percolation threshold is comparable to that obtained using isocyanate-derivated GO [3] and other two-dimensional fillers [9]. This could be attributed to the high aspect ratio of the graphene-based sheets and its homogeneous dispersion in the epoxy matrix [8]. The well dispersion state of graphene-based sheets in the polymer matrices can be found from the scanning electron microscopy (SEM) images (Fig. 4) of cross-section of the graphene/epoxy composite with 7 wt% loading. Fig. 5 shows the variation of EMI SE over the frequency range of 8.2–12.4 GHz for graphene/epoxy composites with various SPFG loadings. It is observed that over the entire frequency range, SE increases with increased loading of SPFG, which is mainly attributed to the formation of conducting interconnected graphene-based sheets networks in the insulating epoxy matrix. The target value of the EMI SE needed for commercial applications is around 20 dB. As presented in Fig. 5, our graphene/epoxy composites exhibited SE ~21 dB in the X-band for 15 wt% (8.8 vol.%) loadings, indicating the composites can meet the commercial application demands.

In conclusion, the EMI SE of graphene/epoxy composites based on graphene-based sheets has been studied. These composites show a low percolation threshold of 0.52 vol.%. The highest EMI SE of the composites containing 15 wt% (8.8 vol.%) SPFG was measured at 21 dB in the X-band. These EMI shielding results, combined with the advantages of a cheap and abundant supply of graphite and the solution processability of the functionalized graphene sheets at high purity, indicate that graphene/polymer composites can be used commercially as effective and lightweight shielding materials for electromagnetic radiation.

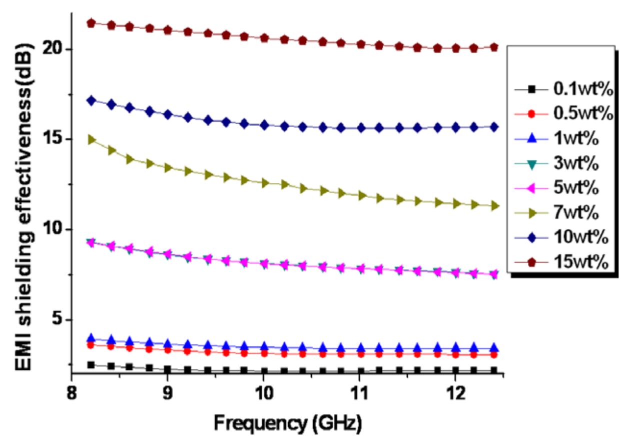

Fig. 5 – EMI SE of graphene/epoxy composites with various SPFG loadings as a function of frequency in the X-band. The graphene/epoxy composites exhibited SE ~21 dB in the X-band for a 15 wt% loading.

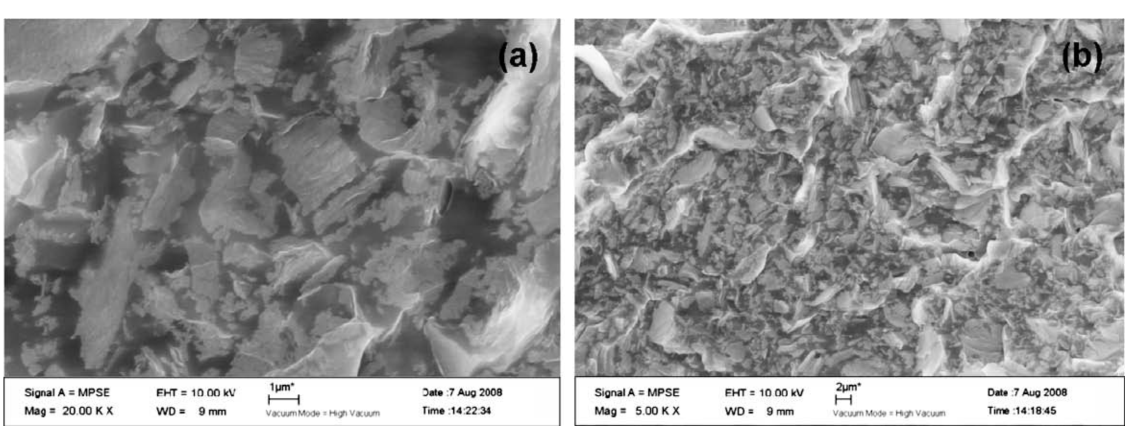

Fig. 4 – Representative SEM images with two different resolution magnitudes for the cross-section of graphene/epoxy composites with 7 wt% loading of SPFG.

Acknowledgments

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REFERENCES

[1] Geim AK, Novoselov KS. The rise of graphene. Nat Mater 2007;6(3):183–91.

[2] Stankovich S, Dikin DA, Piner RD, Kohlhaas KM, Kleinhammes A, Jia Y, et al. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. Carbon 2007;45(7):1558–65.

[3] Stankovich S, Dikin DA, Dommett GHB, Kohlhaas KM, Zimney EJ, Stach EA, et al. Graphene-based composite materials. Nature 2006;442(7100):282–6.

[4] Ramanathan T, Abdala AA, Stankovich S, Dikin DA, Herrera-Alonso M, Piner RD, et al. Funtionalized graphene sheets for polymer nanocomposites. Nat Nanotechnol 2008;3:327–31.

[5] Bryning MB, Islam MF, Kikkawa JM, Yodh AG. Very low conductivity threshold in bulk isotropic single-walled carbon nanotube-epoxy composites. Adv Mater 2005;17(9):1186–91.

[6] Hirata M, Gotou T, Horiuchi S, Fujiwara M, Ohba M. Thin-film particles of graphite oxide 1: high-yield synthesis and flexibility of the particles. Carbon 2004;42(14):2929–37.

[7] Becerril HA, Mao J, Liu ZF, Stoltenberg RM, Bao ZN, Chen Y. Evaluation of solution-processed reduced graphene oxide films as transparent conductors. ACS Nano 2008;2(3):463–70.

[8] Garboczi EJ, Snyder KA, Douglas JF, Thorpe MF. Geometrical percolation-threshold of overlapping ellipsoids. Phys Rev E 1995;52(1):819–28.

[9] Li J, Vaisman L, Marom G, Kim JK. Br treated graphite nanoplatelets for improved electrical conductivity of polymer composites. Carbon 2007;45(4):744–50.