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Lightweight and Flexible Graphene Foam Composites for High-Performance Electromagnetic Interference Shielding

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The rapid development of modern electronics packed with highly integrated circuits generates severe electromagnetic radiation, which leads to harmful effects on highly sensitive precision electronic equipment as well as the living environment for human beings. Great effort has been made for the development of high-performance electromagnetic interference (EMI) shielding materials. In addition to high EMI shielding performance, being lightweight and flexible are two other important technical requirements for effective and practical EMI shielding applications especially in areas of aircraft, aerospace, automobiles, and fast-growing next-generation flexible electronics such as portable electronics and wearable devices.[1] Recently, electrically conductive polymer composites have received much attention for EMI shielding applications,[1–12] because of their light weight, resistance to corrosion, flexibility, good processability, and low cost compared to the conventional metal-based materials. The EMI shielding effectiveness of the polymer composites depends critically on the intrinsic electrical conductivity, dielectric constant, magnetic permeability, aspect ratio, and content of conductive fillers.[1–12] It is believed that high electrical conductivity and connectivity of the conductive fillers can improve EMI shielding performance.[1,2,4,7,8]

Many carbon-based materials including carbon filaments, carbon fibers, carbon nanofibers, carbon nanotubes (CNTs), and chemically derived graphene (CDG) have been used as conductive fillers to fabricate composite materials for EMI shielding because of their high electrical conductivity, excellent mechanical properties, light weight, flexibility, and large aspect ratio.[1–12] However, in these polymer composites, individual conductive carbon-based fillers are randomly distributed inside the polymer matrix and are surrounded by the molecular chains of the polymer, and the electrical conductivity of these composites strongly relies on electron percolation between the separated filler particles. As a result, a high content and good dispersion of carbon-based fillers are usually required to form a conductive interconnected network in the insulating polymer matrix to improve the electrical conductivity and EMI shielding effectiveness of the composites. For example, it has been demonstrated that 7 wt% multi-walled CNTs,[1] 15 wt% single-walled

CNTs,[8] or 15 wt% CDGs[9] are required to approach the target value of the EMI shielding effectiveness needed for commercial applications around 20 decibels (dB). However, a high loading of conductive carbon-based fillers may decrease the mechanical properties and processibility of the composites due to severe agglomeration and poor filler-matrix bonding.

To further reduce the weight of carbon-based polymer composites, foam structures[1,4–7] have been made with the aid of expanding agents such as 2,2′-azoisobutyronitrile and supercritical/subcritical CO_2. But the conductive carbon network in the matrix is inevitably impaired in the foaming process,[4] resulting in a poorer EMI shielding effectiveness after foaming compared to solid composites with the same weight percent of conductive filler.[7] And large pores often make the foam composites cracked and brittle.[4] As a result, the specific EMI shielding effectiveness (EMI shielding effectiveness divided by the density) of most foam composites is only a few times larger than that of typical metals.[1,4] For example, the CDG/polymethylmethacrylate (PMMA) composite microcellular foams show a specific EMI shielding effectiveness of 17–25 dB·cm³/g with a CDG loading of 5 wt%.[4] In addition, CDG has been directly used to fabricate various three-dimensional (3D) macroporous foam structures by self-assembly.[13–17] However, these CDG foam structures also suffer from poor electrical conductivity because of the low quality and/or high inter-sheet junction contact resistance of the CDG sheets. Therefore, their EMI shielding performance should be not high. Using a template-directed chemical vapor deposition (CVD) method, very recently, we have fabricated a flexible and highly conductive graphene foams with a 3D interconnected network structure,[18] which opens up the possibility for the use of graphene as a lightweight, flexible, and high-performance EMI shielding material.

Here we demonstrate design and simple fabrication of an ultra-lightweight and highly conductive graphene/polymer foam composite for high-performance EMI shielding application. The composites were fabricated by a one-step process without the use of foaming agents, in which the graphene sheets are prepared by CVD and seamlessly interconnected into a 3D network.[18] A graphene/poly(dimethyl siloxane) (PDMS) foam composite formed by this method shows a density as low as ~0.06 g/cm³, about 20 times smaller than a common solid polymer composite. Its EMI shielding effectiveness is as high as 30 dB for a very low graphene loading of <0.8 wt%, with the specific EMI shielding effectiveness up to 500 dB·cm³/g, which is about one order of magnitude higher than those of typical metals and carbon/polymer composites.[1,4,19] Moreover, the graphene/PDMS foam composites show excellent flexibility, and their shielding effectiveness is almost unchanged after repeatedly bending to a radius of ~2.5 mm for 10,000 times.

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The one-step process for graphene-based foam composite fabrication is illustrated in **Figure 1**a. As an example, we demonstrate here the fabrication of graphene/PDMS foam composites by this method. Graphene was first grown on a nickel foam by CVD of methane at 1000 °C under ambient pressure, which copied the structure of the nickel foam and formed a

Figure 1. a) Schematic of the procedure for fabricating graphene/PDMS foam composites, the scale bars are 500 μm. b, c) photographs of a foam composite, showing its high flexibility. d, e) SEM images of a foam composite, showing its 3D interconnected network structure.

3D network.[18] Then, a thin layer of PDMS was coated on the surface of graphene. After that, the nickel foam substrate was etched away by HCl, and the graphene/PDMS foam composite was obtained. The content of graphene in the composite and the electrical conductivity of the composite were tuned by changing the flow rate of methane used in the CVD growth of graphene.[18] For example, when the CH_4 concentration in the gas flow was increased from 0.3 to 1.4 vol%, the average number of graphene layers changed from ~3 to ~8, and consequently the electrical conductivity increased from ~0.6 to ~2 s/cm (Table S1).[18] This one-step process is different from the previous two-step process reported by our group,[18] where a free-standing graphene foam was first prepared and then the composite was fabricated by fully infiltrating it with PDMS. Compared with the two-step process, the one-step process used in this work is time-saving and easier for large-scale operation. More importantly, the deposition of only a thin layer of PDMS and the subsequent etching of the nickel scaffold leave the composite with a foam-like structure.

The graphene/PDMS foam composite obtained is lightweight, flexible and soft, as shown in Figures 1b, c and Figure S1. The SEM images confirm that the composite is highly porous and perfectly copies the interconnected 3D network structure of the nickel foam (Figures 1d, e). The porosity of the composite is up to ~95%, which is much higher than that of the reported composites expanded by foaming agents.[1,4] This highly porous nature gives the foam composite an ultralow density of <0.06 g/cm³, about 20 times lighter than solid polymer composites. Despite its ultra-light weight, the foam composite is highly conductive due to the seamlessly interconnected 3D graphene network providing a fast electron transport channel inside it. The electrical conductivity of the composite is as high as 2 s/cm with a low graphene loading of ~0.8 wt%, which is more than 3 orders of magnitude higher than the conventional CNT and CDG-based polymer composites.[1,4–10] Therefore, such lightweight and flexible graphene/PDMS foam composites are expected to show a high EMI shielding performance.

The EMI shielding effectiveness of a material is defined as the logarithmic ratio of incoming power (P_i) to transmitted power (P_t) of an electromagnetic wave and is expressed in dB. The higher the dB level of EMI shielding effectiveness, the less electromagnetic wave is transmitted through the shielding material. For example, a material with 20 dB EMI shielding effectiveness (needed for commercial applications) leaves only 1% of electromagnetic waves to be transmitted. The EMI shielding effectiveness of the graphene/PDMS foam composites was measured using samples 150 × 150 mm² and 22.9 × 10.2 mm² in the frequency ranges of 30 MHz–1.5 GHz and 8–12 GHz (X band), respectively, to fit the specific waveguide sample holders. All samples are ~1 mm thick.

Figure 2 shows the EMI shielding effectiveness of graphene/PDMS foam composites with different electrical conductivities measured in the 30 MHz–1.5 GHz and the X-band frequency ranges. A pure PDMS foam without graphene is obviously transparent to electromagnetic waves and exhibits almost no shielding ability (Figure S2). In contrast, the thin graphene/PDMS foam composites show a high EMI shielding effectiveness even at a very low graphene loading, and the shielding effectiveness increases with increasing loading and electrical
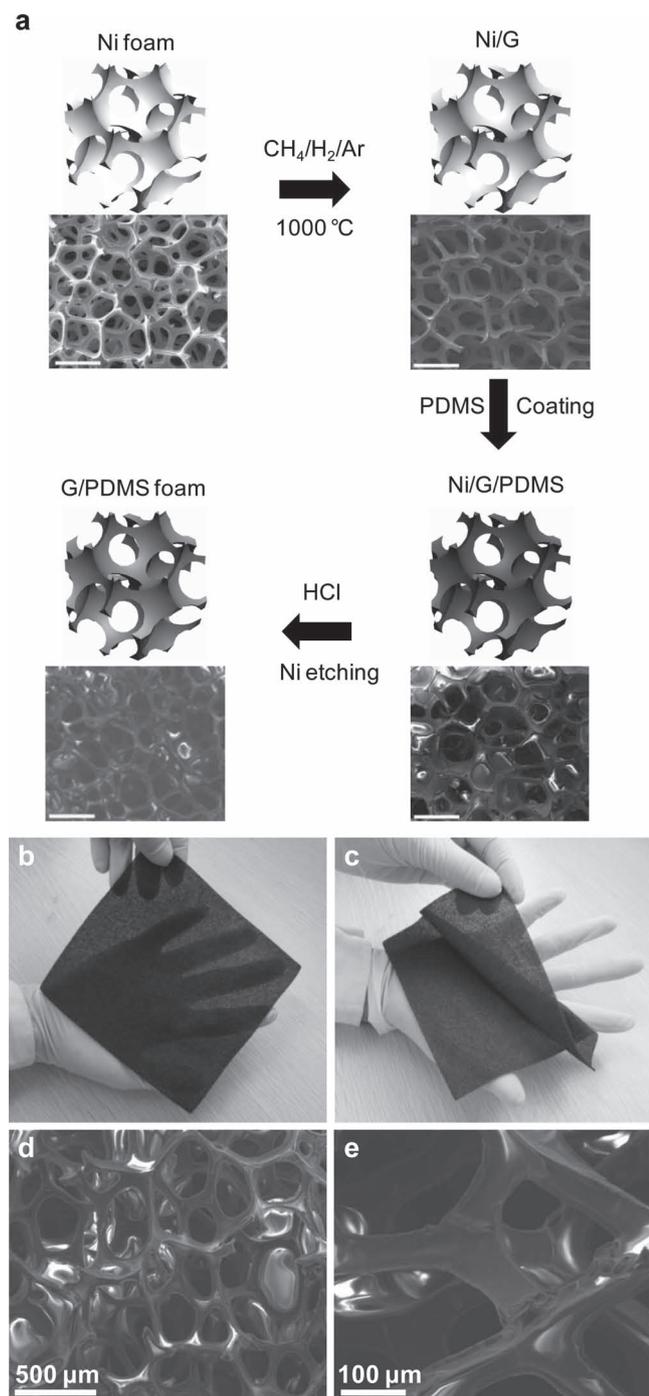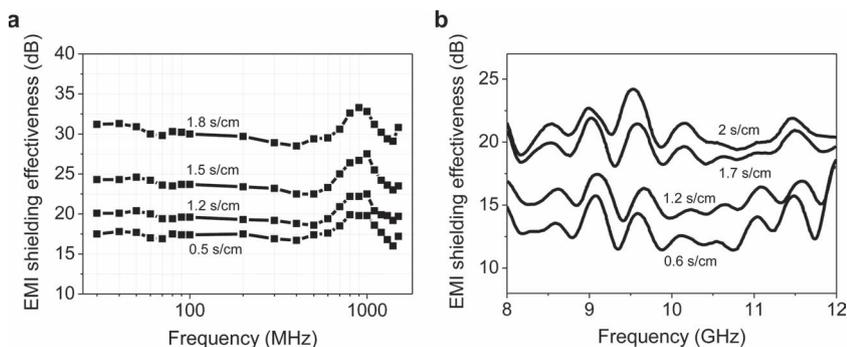
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Figure 2. EMI shielding effectiveness of graphene/PDMS foam composites with different electrical conductivities measured in frequency ranges a) 30 MHz–1.5 GHz, and b) 8–12 GHz (X band).

conductivity in the same frequency range. The EMI shielding effectiveness of the composite with a conductivity of 1.8 s/cm (~0.7 wt% graphene) is measured to be ~30 dB over 30 MHz–1.5 GHz (Figure 2a). The composite with a similar conductivity of 2 s/cm (~0.8 wt% graphene) shows an EMI shielding effectiveness of ~20 dB in the X-band frequency range (Figure 2b). It is worth nothing that the conductive filler loading in the graphene/PDMS foam composites is much lower than that of carbon-based composites reported with similar shielding effectiveness (Table S2). Such a low conductive filler loading is not even large enough to achieve percolation network in these carbon-based composites. For example, it has been demonstrated that 5 wt% CDG,[4] 15 wt% CDG,[9] and 7 wt% CNTs[1] in polymer composites are required to achieve an EMI shielding effectiveness of ~13-19, 21, and 20 dB in the X-band frequency range, respectively.

More importantly, the good effectiveness combined with ultralow density give the graphene/PDMS foam composites a superior specific EMI shielding effectiveness. The specific EMI shielding effectiveness is a more appropriate criterion for use in comparison with the shielding performance between the graphene/PDMS foam composites and other typical materials for applications that need lightweight materials.[1] The specific EMI shielding effectiveness of graphene/PDMS foam composites with ~0.8 wt% graphene loading can reach ~500 dB·cm³/g in the 30 MHz–1.5 GHz frequency range and ~333 dB·cm³/g in the X-band frequency range. These values are much higher than those of typical metals (10 dB·cm³/g for solid copper[19]) and carbon/polymer composites (33.1 dB·cm³/g for foam composites containing 7 wt% CNTs[1] and 17–25 dB·cm³/g for foam composites containing 5 wt% CDGs[4]) (Table S2). The superior specific EMI shielding effectiveness is one of the most outstanding advantages of graphene/ PDMS foam composites as a high-performance EMI shielding material, which allows the use of this material in the areas that need lightweight materials such as aircraft, spacecraft, automobiles and portable electronics.

We also analyzed the EMI shielding mechanism of the graphene/PDMS foam composites. When an electromagnetic wave is incident on a shielding material, the incident power is divided into reflected power, absorbed power and transmitted power. The corresponding power coefficients of absorptivity (A), reflectivity (R), and transmissivity (T) are such that A + R + T = 1. The total EMI shielding effectiveness (SE_{total}) is the sum of the effectiveness of all attenuating mechanisms, including absorption (SE_A), reflection (SE_R), and the multiple reflections (SE_M) in the shielding, and can be expressed in the following equation:[4,20,21] $SE_{total} = -10\log(p_t/p_i) = SE_A + SE_R + SE_M$, where $SE_R = -10\log_{10}(1-R)$, and $SE_A = -10\log_{10}[T/(1-R)]$. The SE_M is generally neglected when SE_{total} >15 dB. Because of the limit of the measurement equipment, we only analyzed the effectiveness contribution of different attenuating mechanisms in the X-band frequency range. **Figure 3**a shows SE_{total}, SE_A, and SE_R of the graphene/PDMS foam composites as a function of electrical conductivity at 9 GHz. It can be seen that, as the electrical conductivity increases, both the SE_{total} and SE_A increase while SE_R remains almost unchanged. Moreover, it is worth noting that the contribution of absorption to the EMI shielding effectiveness is much larger than that of reflection. For the foam composite with a conductivity of 2 s/cm, SE_{total}, SE_A, and SE_R are ~23, 19 and 4 dB, respectively. For the foam composite with a relatively smaller conductivity of 1.2 s/cm, SE_{total}, SE_A, and SE_R are ~17, 15 and 2 dB, respectively. These results suggest that graphene/PDMS foam composites are both reflective and absorptive to electromagnetic radiation in the X-band frequency range, and absorption is the dominant shielding mechanism.

Note that the above EMI shielding mechanism of graphene/ PDMS foam composites is different from those of carbon nanofibers, multi-wall and single-wall CNT/polymer composites,[1,8,12] where reflection is the major contribution to EMI shielding. We suggest that the two-dimensional structure of graphene as well as the large surface area and interface area in graphene/PDMS foam composites are benefit for the multiple reflection of the incident microwaves inside the foam composites and consequently responsible for the absorption-dominant EMI shielding.[4,22] Although reflection can stop the electromagnetic wave propagation beyond the shields, electromagnetic
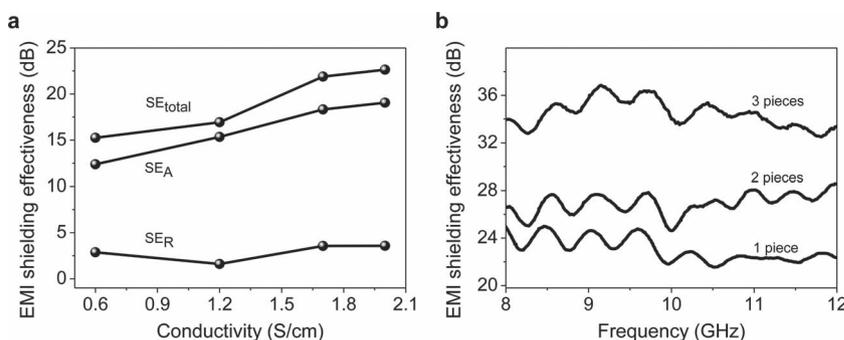

Figure 3. a) Comparison of SE_{total}, SE_A, and SE_R of graphene/PDMS foam composites with different electrical conductivities at a frequency of 9 GHz. b) EMI shielding effectiveness of multiple stacked graphene/PDMS foam composites.

interference prevails in the inner volume as a result of multiple reflections from the walls.[7] These reflections cause damage, e.g., in the case of electronic circuits, because of spurious interferences between the constitutive electronic components: transistors, resistors and chips.[7] This absorption-dominant shielding feature gives graphene/PDMS foam composites great potential as an electromagnetic absorption material in the microwave frequency range, which can be used in areas that need EMI shielding but generate electromagnetic radiation at the same time such as the electronic circuits mentioned above.

It is well established that the EMI shielding effectiveness increases with increasing specimen thickness. It is worth noting that the thickness (~1 mm) of the graphene/PDMS foam composites used in this work is several times smaller than that of the CDG/PMMA composites (2.4–4 mm),[4] but they show a much higher shielding effectiveness, further indicating their advantage for EMI shielding. To further improve the EMI shielding effectiveness of the foam composites, we stacked multiple foam composite sheets together. As expected, the stacked foam composites show a much better EMI shielding effectiveness than one single composite sheet (Figure 3b). More than 33 dB shielding effectiveness in the X-band frequency range is achieved by stacking three graphene/PDMS foam composite sheets together.

In addition, the flexible graphene/PDMS foam composites show excellent stability under mechanical deformation. We tested the electrical conductivity and EMI shielding effectiveness of the foam composite before and after repeated bending. It is interesting to find that the electrical conductivity and shielding effectiveness of the foam composite only show very small decreases after repeatedly bending to a radius of ~2.5 mm 10 000 times (**Figure 4**), which are attributed to the partial structural failure of the graphene network.[18] This excellent

mechanical robustness and flexibility enable potential use of the foam composites as high-performance EMI shielding materials in next-generation flexible electronics,[23,24] such as soft portable electronic products, roll-up displays, wearable devices, and conformable health-monitoring electronic skins. Moreover, flexible foam composites can be mounted on arbitrarily curved surfaces and movable parts, such as the joints of a robot's arm, so as to completely cut off the harmful effect of electromagnetic radiation.

In conclusion, we developed a graphene/PDMS foam composite, which is a lightweight EMI shielding material with outstanding shielding effectiveness and mechanical flexibility. This composite has a density of 0.06 g/cm^3, and its shielding effectiveness is as high as 30 dB in the 30 MHz–1.5 GHz frequency range and 20 dB in the X-band frequency range. More importantly, its specific EMI shielding effectiveness can reach 500 dB·cm^3/g, which far surpasses the best values for metals and carbon-based composite materials. The excellent flexibility of this composite also gives it a stable EMI shielding performance under mechanical deformation. No obvious performance degradation is observed even after repeatedly bending to a radius of ~2.5 mm 10 000 times. The fabrication of this novel material opens up the possibility for the use of graphene as a lightweight, flexible, and high-performance EMI shielding material in areas such as aerospace and next-generation flexible electronics.

Experimental Section

Fabrication of graphene/PDMS foam composites: Graphene was first grown on a nickel foam (Changsha Liyuan New Material Co. Ltd., ~320 g/m^2 in area density, and ~1.6 mm in thickness) by CVD as previously reported.[18]

A diluted PDMS solution was prepared by mixing a PDMS base agent, curing agent (Sylgard 184, Dow Corning) and ethyl acetate in the ratio of 10:1:100. After CVD growth, a thin layer of PDMS was coated on the surface of the graphene grown on the nickel foam by dipping the samples into the dilute PDMS solution for 30 min followed by curing at 100 °C for 1 h. The nickel foam substrate was then etched away by HCl solution (3M) at 80 °C for 12 h to obtain the graphene/PDMS foam composite. The PDMS foam was fabricated by the same process but using a pure nickel foam without graphene as a template.

Characterization: The morphology of the graphene/PDMS foam composites was investigated by SEM (Nova NanoSEM 430, 15 kV). The electrical conductivity of the composites was measured by a two-probe method as previously reported.[18] The EMI shielding effectiveness was measured in the 30 MHz–1.5 GHz frequency range using an Agilent E4440A PSA High-Performance Spectrum Analyzer and in the X-band frequency of 8–12 GHz using a WILTRON 54169A scalar measurement system. The composites were cut into 150 mm × 150 mm and 22.9 mm × 10.2 mm pieces for measurements in the 30 MHz–1.5 GHz and the X-band frequency ranges, respectively. All the samples are ~1 mm in thickness.
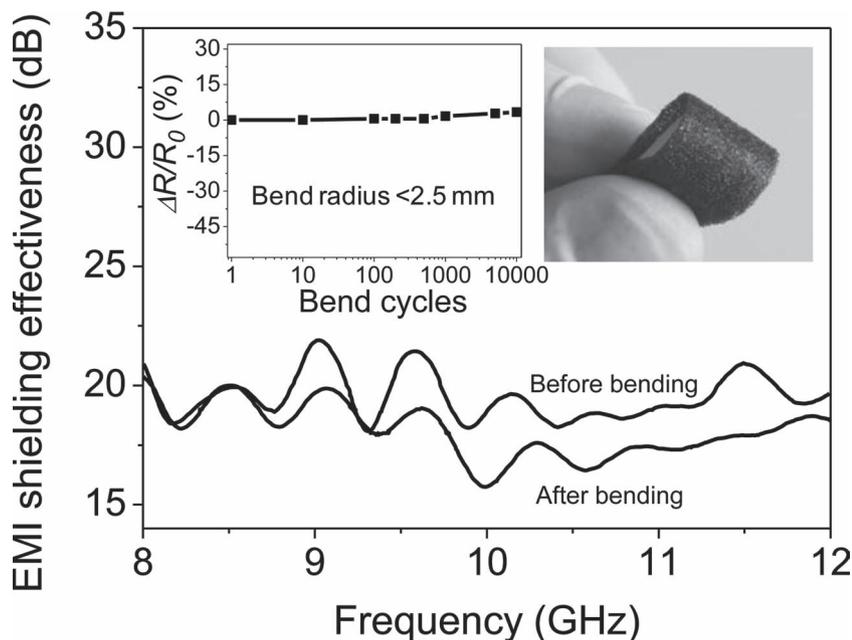

Figure 4. EMI shielding effectiveness of a graphene/PDMS foam composite before and after repeatedly bending to a radius of 2.5 mm 10 000 times. The left inset shows the resistance change of the composite under repeated bending. The right inset shows a photograph of the bent composite.

Supporting Information

Acknowledgements

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