Full Length Article

Electromagnetic interference shielding properties and mechanisms of chemically reduced graphene aerogels

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ABSTRACT

Graphene was recently demonstrated to exhibit excellent electromagnetic interference (EMI) shielding performance. In this work, ultralight ($\sim$5.5 mg/cm^3) graphene aerogels (GAs) were fabricated through assembling graphene oxide (GO) using freeze-drying followed by a chemical reduction method. The EMI shielding properties and mechanisms of GAs were systematically studied with respect to the intrinsic properties of the reduced graphene oxide (rGO) sheets and the unique porous network. The EMI shielding effectiveness (SE) of GAs was increased from 20.4 to 27.6 dB when the GO was reduced by high concentration of hydrazine vapor. The presence of more sp^2 graphitic lattice and free electrons from nitrogen atoms resulted in the enhanced EMI SE. Absorption was the dominant shielding mechanism of GAs. Compressing the highly porous GAs into compact thin films did not change the EMI SE, but shifted the dominant shielding mechanism from absorption to reflection.

1. Introduction

All electrical and electronic devices emit electromagnetic (EM) fields at various frequencies. Electromagnetic interference (EMI) occurs when electronic devices are subject to EM radiation from unexpected sources at the same frequency ranges at which these devices operate [1,2]. This may cause the degradation of the electronic devices and posed serious threat to the work place's safety [3]. The rapid advancement in modern electrical and electronic devices drives the development of advanced EMI shielding materials to minimize the harmful effects arising from the unwanted interferences. In addition to high EMI shielding performance, light weight is an additional important technical requirement for potential applications especially in the areas of automobile and aerospace. Searching for the library of EMI shielding materials, conductive polymer composites foams [4,5], carbon foams [6] and conductive aerogels [7] emerged as potential EMI shielding materials due to their advantages in effective weight reduction, chemical stability and design flexibility. Electrical conductive fillers, such as carbon nanofibers (CNFs) [8,9], carbon nanotubes (CNTs) [10,11] and graphene sheets [12–14], were commonly used to form a conducting network with desirable electrical conductivity within the

intrinsically insulating polymer foam matrix, a crucial requirement for effective EMI shielding properties. However, to overcome the processing issues associated with fillers and to achieve well interconnected filler networks are not trivial tasks. Thus, non-filler containing conducting foams, such as carbon foams [3,15] were used as alternatives. Nevertheless, the EMI SE of carbon foams was highly dependent upon the char yield of polymer precursors and the demanding carbonization conditions. Therefore, a new filler-free light weight EMI shielding material which can be prepared without the stringent processing conditions are in demand.

Graphene aerogels (GAs), firstly fabricated by Worsley [16], exhibited great performance in various applications, such as energy storage [17,18], supercapacitor electrode [19,20], gas sensor [21], etc. The applications greatly benefitted from the assembly of two-dimensional (2D) graphene sheets into three-dimensional (3D) porous structures and the intrinsic advantages shown by graphene itself, such as high electrical conductivity, large aspect ratio, and excellent mechanical properties [22–26]. Recently, the great potential of employing GAs for electromagnetic interference (EMI) shielding applications has been demonstrated. Song et al. [27] reported EMI shielding effectiveness (SE) of 27 dB using a GA-carbon textile hybrid of thickness 2 mm. The achieved EMI SE was contributed by both the carbon textile and the GA. The 3D scaffold GA greatly enhanced the electrically conducting network while maintaining the benefit of the light weight carbon textile. Wan et al. [28] prepared an epoxy nanocomposite containing 1 wt.% GA. The

obtained EMI SE of around 20 dB (sample thickness of 2 mm) was solely contributed by the 3D electrically conducting GA network, since epoxy is intrinsically transparent to EM wave. Singh et al. [29] studied the EMI SE of pure GA. 20 dB was achieved by GA with a thickness of 2 mm and a density of ~75 mg/cm^3. They discussed the EMI shielding mechanisms by correlating the EM wave interaction with respect to the overall 3D porous structure. However, there is no study on the influence of intrinsic properties of graphene, such as the degree of reduction, or extrinsic properties such as different porosity on EMI SE.

In this work, for the first time, we carried out a comprehensive study of EMI shielding properties and mechanisms of an aerogel solely consisted of graphene sheets. The GA was realized through assembling different amounts of graphene oxide (GO) by a freeze-drying method followed by the chemical reduction of GO aerogel. The extent of chemical reduction of GO was tailored in order to investigate the EMI shielding properties of the resulting GAs. The EMI shielding mechanisms behind the exceptional performance were systematically discussed with respect to the intrinsic properties of reduced graphene oxide (rGO) sheets of various extent, such as the degree of nitrogen-doping, the amount of residual functional groups and carbon main structures, and extrinsic properties i.e., the unique highly porous macrostructure of GA. Different extent of chemical reduction changed the degree of nitrogen-doping and the amount of residual functional groups on the rGO surface, which is believed to contribute differently to EMI shielding behaviors. The EMI shielding properties and mechanisms of the highly porous GA and the respective compressed dense film were investigated as well. The observation was contradictory to the previous outcomes that higher electrical conductivity or the better connection of the network tended to obtain higher EMI SE. Instead, the EMI SE is highly dependent on the amounts of the effective materials response to the EM waves.

2. Experimental

2.1. Materials

Graphite powder (<20 μm), sulfuric acid (H_2SO_4, 95–98%), potassium permanganate ($KMnO_4$) and hydrazine monohydrate (NH_2NH_2, 64–65%, 98%) were purchased from Sigma-Aldrich. Hydrogen peroxide (H_2O_2, 30 wt.% in water) was supplied by VWR Company. Distilled water was used during sample treatment. All chemicals were used without further purification.

2.2. Preparation of GAs

GO was obtained by oxidation of natural graphite powder according to the modified Hummers' method [30]. GO aqueous dispersions with different GO concentrations (3, 5, 7, and 9 mg/mL) were poured into the desired mould and frozen in the refrigerator of −20 °C followed by freeze-drying for 2 days. The as-prepared GO aerogels were chemically reduced by hydrazine vapor with the concentration of 32 g/L at 90 °C for 24 h. GA3, GA5, GA7 and GA9 were labelled with the number corresponding to the GO concentration. 64 g/L of hydrazine vapor was used to chemically reduce GO aerogel with 9 mg/mL as well, labelled as GA9H. The average thickness of all samples was 2.5 mm. GA9 with the thickness of 4 mm was also prepared using the same approach. Graphene film (GA9F) was fabricated by compression of GA9 using hydraulic press. The physical properties of different GAs were listed in Table 1.

2.3. Characterization

Fourier transform infrared spectroscopy (FTIR) was performed on a Perkin Elmer in transmission mode over the wavenum-

ber range of 650–4000 cm^{-1}. The chemical state of the surface was characterized by X-ray photoelectron spectroscopy (XPS) on a Thermo VG Scientific ESCALab 220i2XL, using a monochromatized Al Ka source (1486.6 eV) operating at 15 kV and 15 mA. X-ray diffraction (XRD) was performed on a Bruker D8 Advanced XRD using Cu Kα radiation (λ = 1.5406 Å) in the scattering range (2θ) of 8–35° with a scan rate of 0.02° s^{-1} and slit width of 0.1 mm. For the electrical measurement, two-point measurement was done by Hewlett Packard 4140 B pA Meter/DC Voltage source [31]. The samples were fabricated into plates with the dimensions of $10 \times 10 \times 2.5$ mm^3 (GAs) and $10 \times 10 \times 0.1$ mm^3 (GA9F). The I–V curve was measured, at ambient condition, over a range of 0.2 to −0.2 V with a step of 0.01 V. In order to reduce the deformation of aerogels and eliminate the effect of contact resistance, needle electrodes were used to touch the edges of GAs or GA9F placed on a glass slide (see **Fig. S1**). The electrical conductivity was obtained from l/RA, where l is the length of the sample, A is the cross-sectional area of the sample, and R is the electrical resistance obtained from the slope of I–V curve. The results are reported as an average value based on data collected from five specimens. The densities of GAs (ρ_{GA}) were determined from the mass divided by the volume. The density of rGO sheets (ρ_{rGO}) was measured by Automatic Density Analyzer of ULTRAPYC 1200e (Quantachrome Instruments). Field Emission Scanning Electron Microscope (FE-SEM) analysis was carried out on the Jeol JSM 7600F microscope with an acceleration voltage of 5 kV. Thermogravimetric Analysis (TGA) was obtained using Q500 (TA instrument) under nitrogen atmosphere. The heating rate was 10 °C min^{-1} from 50 to 700 °C. Raman spectra were recorded using a Renishaw inVia Raman microscope by the excitation wavelength of 514.5 nm. The S-parameters (S_{11}, S_{22}, S_{12}, and S_{21}) were measured using N9917A FieldFox Microwave Analyzer (Agilent Technologies) measurement system in the frequency range of X-Band at room temperature. The samples were fabricated into rectangular plates with a dimension of $25.4 \times 12.7 \times 2.5$ mm^3 to fit the waveguide WR90. The total EMI SE can be calculated using equations [3,9,32], $R = |S_{11}|^2 = |S_{22}|^2$, $T = |S_{21}|^2 = |S_{12}|^2$, $A = 1 - R - T$, $A_{eff} = A/(1 - R)$, $SE_{total} = -10\log P_t/P_i = -10\log T$, where R is reflection coefficient, T is transmission coefficient, A is absorption coefficient, A_{eff} refers to effective absorption and the EMI SE_{total} of a material is defined as the ratio of transmitted power (P_t) to incident power (P_i) of an EM wave. SE is generally expressed in decibels (dB). The complex permittivity ε' and εẅere retrieved using the Keysight 85071E Materials Measurement Software.

3. Results and discussion

Fig. 1 gives a schematic illustration for the preparation process of GAs and GA9F. The GO aerogel was reduced to GAs by hydrazine vapor with different concentrations and graphene film (GA9F) was fabricated by compression of GA9 using hydraulic press. FTIR spectroscopy (**Fig. S2A**, Supporting Information) shows the typical peaks of GO at wave number of 1730, 1630, 1400, 1060 cm^{-1}, corresponding to C=O, C=C, C−OH and epoxide C−O−C, respectively. The disappearance of the peaks of GA at 1730 cm^{-1} indicated the occurrence of reduction, however, the broad peak at 1100 cm^{-1} proved the reduction process was incomplete. The residual polar functional groups not only performed as a bridge to maintain the structural integrity of aerogel, but also acted as polarization centers to absorb EM wave. XRD spectra of GO and GA (**Fig. S2B**, Supporting Information) were performed to understand the structural transformation during chemical reduction. A typical graphitic peak (002) at 2θ = 23.9° in GA implied the presence of reduced GO. The reduced interlayer spacing of GA (0.374 nm) from that of GO (0.839 nm)