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Microcellular graphene foam for improved broadband electromagnetic interference shielding

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ABSTRACT

As reported, the foaming of layered graphene films into porous graphene foams could improve their performance for absorbents, catalysis and supercapacitors. Herein, to emphasize the impact of porous structure on electromagnetic interference (EMI) shielding, the direct comparison between graphene film (G-film) and corresponding microcellular graphene foam (G-foam) in terms of EMI shielding efficiency has been investigated in a broadband frequency range of 8.2–59.6 GHz, including X-band, Ku-band, K-band, Ka-band, and U-band. Consequently, despite the lower electrical conductivity of the as-prepared G-foam, it exhibited an improved average shielding effectiveness (SE) of ~26.3 dB over the entire frequency range in comparison with that of G-film (~20.1 dB). Implication of the results suggested that the foaming of layered graphene films into porous graphene foams could lead to an improvement in EMI shielding, which should be ascribed to the formation of improved internal multiple reflections at the large cell–matrix interfaces owing to the existence of microcellular structure in G-foam. We believe that this research would open up new opportunity for the development of graphene foams in the field of EMI shielding.

1. Introduction

With the rapid development of communication technology along with electronic devices, the electromagnetic interference (EMI) problem has been increasing at a noticeable rate [1–3]. Therefore, designing new high-performance EMI shielding materials with a broadband shielding frequency range is becoming an urgent challenge to be addressed. To date, varieties of nanostructures, especially carbon-based composites, have been widely investigated in order to meet the ideal targets for EMI shielding [2–10].

Graphene, a new class of two-dimensional carbon nanostructure, possesses not only a stable structure but also a high specific surface area and excellent electronic property [11–13], which make it very promising as lightweight EMI shielding materials [14–19]. Early studies focused on dispersing graphene into the insulating polymer matrices to form effective conductive network in composites, thereby improving the EMI shielding performance [16–23]. Despite good EMI shielding effectiveness (SE) of ~20 dB with graphene loading of ~5–15 wt%, their drawbacks, such as brittleness and large effective thickness of several millimeters, have severely hindered their application in some ultrathin flexible electronic devices. In order to take full advantage of graphene's superior electrical property, macroscopic layered graphene films with an electrical conductivity of ~180–1450 S/cm were fabricated through different process, and high EMI SE of ~20–60 dB has been achieved with effective thickness only from a few microns to dozens of micron range [24–28]. Moreover, such graphene films were also characterized by excellent flexibility [24]. Obviously, graphene films represent a more advantageous configuration in comparison with polymer/graphene composites for effective EMI shielding.

More recently, the foaming of layered graphene films into porous graphene foams is attracting more and more attention since graphene foams have already exhibited greater potential in many fields including absorbents, catalysis and supercapacitors [29–32]. For instance, the introduction of porous structure in graphene film

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could increase its accessible surface area and enhance solution diffusion in electrochemistry, thereby improving the adsorption capacity of an absorbent and the specific capacitance of a supercapacitor based on graphene foams [29–31]. Because the prior work on flexible graphite (made by compressing exfoliated graphite flakes without a binder) has mentioned that a large surface area of the conductor was preferred for better EMI shielding [33], we suppose that the porous structure in graphene foam should be beneficial to improve its shielding efficiency. However, the direct comparison between graphene film and corresponding graphene foam in terms of EMI shielding efficiency, with the purpose of understanding how the porous structure of material could affect the final shielding performance, has been rarely investigated. Furthermore, although the broadband shielding frequency is important for the practical application of EMI shielding materials, most of the studies focused on the research of graphene-based materials for EMI shielding in X-band (8.2–12.5 GHz) [16–28], and much less effort has been devoted to the exploration of their performance in much broader frequency range. Overall speaking, investigating the impact of porous structure on the EMI shielding efficiency of graphene foam in a broad frequency range and further clarifying the underlying mechanism are necessary.

Herein, layered graphene film (G-film) and microcellular graphene foam (G-foam) with quite similar microstructure were fabricated, and the direct comparison of their shielding performance was investigated in a broadband frequency range of 8.2–59.6 GHz, including X-band, Ku-band, K-band, Ka-band, and U-band. Despite the lower electrical conductivity of the as-prepared G-foam, it exhibited an improved average SE total of ~26.3 dB over the entire frequency range in comparison with that of G-film (~20.1 dB), indicating the fact that the foaming of layered graphene films into porous graphene foams could lead to an improvement in EMI shielding. The underlying mechanism for such improvement should be mainly attributed to the formation of improved internal multiple reflections owing to the existence of microcellular structure. Besides, the comparison between G-foam and other reported all-carbon porous materials was also conducted for the sake of highlighting the more advantageous all-carbon configuration of G-foam.

2. Experimental

2.1. Materials preparation

Graphene oxide (GO) film was prepared by direct evaporation of GO suspension under mild heating according to our previous work [24]. The G-foam was fabricated by using a hydrazine-foaming method from GO film. In a typical experiment, 3 ml hydrazine monohydrate (50%) was added into a Teflon vessel (100 ml), and then a piece of GO film was suspended above the hydrazine level in order to avoid direct wetting. After that, the vessel was sealed in a stainless steel autoclave and treated at 90 °C for 3 h to obtain the G-foam. The G-film was prepared by gentle thermal-reducing of the same GO film. In a typical experiment, the GO film was firstly heated to 90 °C in order to remove the absorbed water. Then it was further heated to 180 °C with a low heating rate (<5 °C/min) and maintained at this temperature for some time to obtain the G-film. To ensure that the microstructure of G-film, such as structural integrity and chemical composition, is quite similar with that of G-foam, the annealing time at 180 °C should be controlled at about 2 h.

2.2. Characterizations

Scanning electron microscopy (SEM) observation was performed with a Hitachi S-4800 field emission SEM at an accelerating voltage of 4 kV. The diffraction behavior of the samples was studied using a Bruker AXS X-ray diffractometer with CuKa radiation at a generator voltage of 40 kV and a generator current of 40 mA. Raman spectra were excited with a laser of 532 nm and record with Labram spectrometer (Super LabRam II system). XPS analysis was carried out a Kratos AXIS ULTRA Multifunctional X-ray Photoelectron Spectroscope using Al (mono) Kα radiation (1488.6 eV) under 1.2×10^{-9} Torron. The electrical conductivity of the samples was measured using a standard four-probe method on a Napson Cresbox Measurement System. The average electrical conductivity and corresponding errors of each sample were determined by the three measured values.

2.3. EMI shielding

The S parameters (S_{11} and S_{21}) of the samples were measured with a Rohde & Schwarz ZVA67 vector network analyzer (VNA) using the wave-guide method in X-band, Ku-band, K-band, Ka-band, and U-band. The dimension of the sample holder is 22.8 × 10.0 mm for X-band, 15.7 × 7.8 mm for Ku-band, 10.6 × 4.3 mm for K-band, 7.1 × 3.5 mm for Ka-band, and 4.7 × 2.3 mm for U-band, respectively. During the measurement, the film-like samples were sandwiched between the waveguide sample holders. The total SE as well as SE absorption and SE reflection were determined based on the measured S parameters as follows:

$$R = |S_{11}|^2, T = |S_{21}|^2$$

$$A = 1 - R - T$$

$$SE_{ref}(dB) = -10\log(1-R) \quad SE_{abs}(dB) = -10\log(T/(1-R))$$

$$SE_{total}(dB) = 10\log\left(\frac{P_I}{P_T}\right) = SE_{ref} + SE_{abs}$$

where R is reflection coefficient, T is transmission coefficient, and A is absorption coefficient. P_I is the incident power, and P_T is the transmitted power. To ensure the accuracy of the measurements, three specimens of each sample were selected for testing, and the average SE total together with corresponding errors were determined from the three measured values.

3. Results and discussion

Since it is difficult to fabricate graphene foam directly from graphene film, G-foam and G-film here were fabricated by using the same GO film as a precursor. It should be noted that, to strip out other variables that could influence the final EMI shielding performance, the microstructure of G-film, such as structural integrity and chemical composition, was adjusted to the same as that of G-foam by controlling the fabrication process. In other words, G-foam could be considered as the product fabricated by the direct foaming of G-film, and they would have quite similar microstructure and solid thickness, except for with or without microcellular structure.

The overall fabrication process is shown schematically in Fig. 1a. Firstly, GO film was prepared according to the method described in our previous work [24]. SEM observation showed that such GO film exhibited a compacted layer-by-layer nanostructure with a thickness of ~20 μm, as shown in Fig. 1b. XRD analysis of GO film presented a diffraction peak at ~10.3° (Fig. 2a), indicating an interlayer spacing of 0.86 nm. In order to achieve the foaming of GO film simultaneously with the reduction of GO sheets, a hydrazine-