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Microwave absorption properties of holey graphene/silicone rubber composites

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ABSTRACT

The complex permittivity and return loss (RL) for the composites of silicone rubber filled with holey graphene nanosheets (HGNS, prepared by ultra-rapid heating during the step of thermal reduction/exfoliation of graphite oxide) were measured in the 3–18 GHz range. HGNS-based composites were found to have significantly higher microwave absorption than composites incorporating other types of graphene reduced at lower heating rates. Even with only 1 wt.% loading, its experimentally measured RL reached −32.1 dB at 13.2 GHz with a thickness of 2 mm, and simulation suggested that at a thickness of 3 mm its RL can be as low as −45.3 dB at 7.8 GHz. Material characterization indicated that the density of the holes increased with the temperature ramp rate, and the hole sizes ranged from 5 to 300 nm. Compared to other graphene samples, HGNS possessed significantly larger specific surface area and higher density of defects, suggesting that defect-induced losses, interfacial polarization, and multiple reflection/scattering at the interfaces are the major loss mechanisms. Our simple and low-cost process as well as the very low loading ratio of HGNS are advantageous for cost reduction in future applications.

1. Introduction

Due to their wide applications in consumer electronics, communication devices, and stealth technology, extensive studies have been carried out on the development of microwave absorbers and shields [1–13]. There have also been wide studies on polymer-based composites containing microwave-absorbing carbon ingredients, such as carbon black, graphite, expanded graphite, carbon fiber, CNTs, and graphene (or reduced graphene oxide, RGO) [14–34]. These efforts have been motivated by their advantages of high absorption ability, wide band, light weight, thinness, flexibility, low cost, and stable thermal and chemical properties. In particular, carbon nanotubes (CNTs) [18–20,24] and graphene [12,13,21–25,30–34] have the greatest potential as high-performance absorbing materials owing to their many desirable properties, including unique geometry effects, high specific surface area, and high conductivity. In 2008, Liang et al. [31] first reported a microwave shielding effectiveness of 21 dB at 8.2 GHz in epoxy composites filled with 15 wt.% of graphene. In 2011, Bai et al. [21] and Wang et al. [22] separately discovered that graphene could also provide remarkable microwave absorption. Subsequently, Bhattacharya et al. [24] found that graphene can offer higher microwave absorption than CNT, and Wen et al. [32] reported that RGO outperforms graphite nanoplatelets in microwave shielding. To explain why graphene is superior to other nano-carbon microwave absorbers, some researchers proposed that graphene has a unique loss mechanism: multiple reflections from the dihedral angle formed between neighboring graphene sheets [21,23] and multiple scattering from the corrugated graphene surfaces [32]. Recently we have reported that well-dispersed, highly exfoliated graphene is capable of providing excellent microwave absorption

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(−37.8 dB at 12.3 GHz) at very low loading of 1 wt.% [30]. Additional studies on the temperature-dependent microwave shielding [33] and absorption [34] performances of graphene have confirmed its usefulness at elevated temperatures. Combinations of graphene with other dielectric or magnetic nano-fillers, such as CNTs [25], Fe_3O_4 [35], hematite [36], α-Fe [37], CuS [38], Ni [39], and $NiFe_2O_4$ [40], have also been demonstrated. These hybrid fillers have exhibited improved microwave absorption compared to pure graphene. Here we present a study on the extraordinary microwave absorption performances of *holey* graphene—a new type of graphene full of holes, which can considerably affect its electromagnetic properties.

Due to its two-dimensional (2-D) geometry, graphene easily restacks during the fabrication process in many applications and thus loses its exceptional physical properties to a great extent. For example, restacking of graphene leads to lower capacity and rate capability in applications of Li ion batteries (LIBs) [41–43] and supercapacitors (SCs) [44]. Therefore, creating anti-restacking 3-dimensional (3-D) structures [45–54] is important for realizing the full advantage of graphene. Researchers have reported excellent microwave absorption properties of many well-designed 3-D porous materials, which have complicated structures and anti-restacking capability. For example, hierarchical porous ZnO flowers [55], hollow porous Ni/SnO_2 hybrids [56], hierarchical hollow CuS microspheres [57], ordered honeycomb SnO_2 foams [58], flower-like CuS hollow microspheres composed of nanoflakes [59], yolk–shell structured composites [60,61], 3-D free-standing graphene foam [62], and graphene/polymer foam [63] have been successfully synthesized and their superior microwave absorption/shielding properties have been demonstrated.

Alternatively, we have found that creating a holey structure on graphene nanosheets with outward-opening hole edges and a significantly roughened surface morphology resulted in good resistance to restacking [44]. Using such kind of holey graphene, improvements in the performances of LIBs [64–67] and SCs [44,68,69] have been achieved because the holes offer shortcuts for the ions to diffuse rapidly into the interlayer space. Several methods have been proposed to produce holey graphene by different research groups [64–71], and studies on its applications to LIBs and SCs have been reported recently. Another unique feature of holey graphene is the high density of defects around the hole edges, which can serve as active sites for capturing extra Li ions and thus improve the electrochemical properties of LIBs [72,73]. These defects can equally play an important role in microwave absorption according to many previous studies [22,33,35,36,74–76]. The attractive properties of holey graphene—the anti-restacking ability and high defect density—suggest that it should be very suitable for the application in microwave absorption as well. We demonstrate here the excellent microwave absorbing performance of holey graphene produced by an ultra-rapid heating method.

2. Experimental details

2.1. Materials

The starting material for the production of graphene nanosheets (GNS) and holey graphene nanosheets (HGNS) was natural graphite powder (200 mesh, or particle sizes $\leq$ 74 μm, acquired from Alfa Aesar), which has 99.9995% purity and 2.25 g/cm^3 density.

The silicone rubber (Momentive, RTV-615A and B) was a two-component (base A and curative B) liquid product, which cures by mixing the base and the curative in a 10:1 wt ratio. The curing takes 24 h at 25 °C to permit handling, but the time can be shortened considerably by heating.

2.2. Preparation of GNSs with various heating rates

Natural graphite was oxidized by the Staudenmaier method to form graphite oxide (GO). The GO powder was then thermally reduced/exfoliated into various kinds of GNSs (or RGO) by heating to 300 °C in an air-filled quartz tube at different temperature ramp rates. The GNS samples prepared at temperature ramp rates of 1, 10, and 30 °C/min were named GNS300-1, GNS300-10, and GNS300-30, respectively.

2.3. Preparation of HGNS

The HGNS sample was obtained using an ultra-rapid heating method [44]. To achieve an extremely high temperature ramp rate, GO powder was dumped onto the central zone of the quartz tube surface preheated to 300 °C using a long metal tool, and instantaneously reduced/exfoliated into HGNS. An ultra-high temperature ramp rate of about 100 °C/s (6000 °C/min) was achieved by this means, and the GO was rapidly reduced while CO_2 gas was generated between neighboring layers much faster than it could escape. The huge pressure not only exfoliated the layers but also created numerous holes at weak spots in the graphene sheets.

2.4. Material analysis

Observation of the morphology of the GNS and HGNS samples was carried out using a scanning electron microscope (SEM, Hitachi, S-3000N) and a transmission electron microscope (TEM, FEI, Tecnai G2 F30). X-ray diffractometry (XRD, Rigaku D/Max 2200) was utilized to examine the crystal structure of graphene. Furthermore, a Renishaw inVia Raman Microscope was used to characterize the D and G bands of GNS and HGNS samples. Nitrogen adsorption isotherms were measured at 77 K with a Micromeritics ASAP 2010 Surface Area and Porosity Analyzer to determine the Brunauer-Emmett-Teller (BET) specific surface area (SSA) for GNS and HGNS samples. We also employed elemental analysis (EA, Thermo Scientific, Flash EA2000 CHNS/O Analyzer) for analyzing the O and C atomic contents of the GNSs and HGNS.

2.5. Preparation of the microwave absorbing composite sheets

Uniform dispersion of graphene in the matrix is of utmost importance for maximizing the performance of the composite. Premixing using a planetary mixer in combination with repetitive calendering (three roll milling) was employed to ensure a high degree of graphene dispersion. A planetary centrifugal mixer (Thinky, AR-250) was employed in premixing graphene (GNS300-1, GNS300-10, GNS300-30, or HGNS) powder with silicone rubber base (RTV-615A) for 10 min before degassing for 5 min. Once premixing was complete, the viscous solution was further mixed by a three roll mill (Exakt, 80E). This was repeated 9 times so that uniform dispersion of GNS or HGNS could be attained. The angular speed ratio of the three rollers was 1:3:9, with adjacent rollers rotating in the opposite directions. Agglomerates were effectively ripped apart by the large shear forces created by the speed differences of rollers. To ensure uniform distribution of graphene fillers throughout the matrix, the gaps at the front (between the 1st and 2nd roller) and at the rear (between the 2nd and 3rd rollers) were gradually reduced to 35 μm and 25 μm, respectively, down from original 90 μm and 80 μm. Finally, the curative (RTV-615B) was added and the mixture was further mixed by the planetary mixer for an additional 5 min and then degassed for 2.5 min.

With the curative and graphene fully dispersed in the base, the liquid mixture was ready to be shaped. This was accomplished by pouring the viscous mixture into a 16 cm × 16 cm panel mold 2 mm