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Regular Article

Reduced graphene oxide decorated with carbon nanopolyhedrons as an efficient and lightweight microwave absorber

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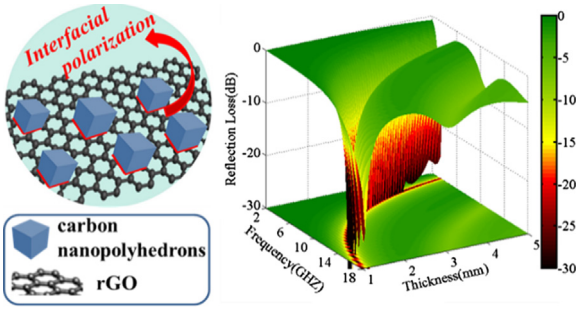
GRAPHICAL ABSTRACT



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ABSTRACT

Graphene-based composites are becoming a new kind of microwave absorbers that can overcome the challenges related to the performance and light weight in electromagnetic pollution precaution. Herein, a series of reduced graphene oxide decorated with carbon nanopolyhedrons (CNPs/rGO) composites have been successfully fabricated through *in situ* pyrolysis of ZIF-8/GO hybrids. It is found that GO can restrain the growth of ZIF-8 crystals and produce small-size CNPs after high-temperature pyrolysis, and CNPs will suppress the re-stacking of rGO nanosheets. More importantly, the coupling of CNPs and rGO not only generates the desirable synergistic effects, but also accounts for the profitable interfacial polarization. Therefore, the electromagnetic parameters and microwave absorption properties of these composites can be rationally modulated in terms of the amount of GO. The optimized CNPs/rGO composite exhibits strong reflection loss [−66.2 dB (6.2 GHz, 2.89 mm)] and broad qualified bandwidth (over −10 dB in 3.2–18.0 GHz with integrated absorber thickness of 1.0–5.0 mm), which are superior to many graphene-based composites with high-density magnetic components. Electromagnetic analysis reveals that good attenuation ability and impedance matching are responsible for its excellent performance. It is believed that these results may inspire the design of lightweight microwave absorbers in the future.

1. Introduction

With rapid development of electronic devices and communication facilities working at the gigahertz range, the radiation of excessive electromagnetic (EM) waves has become a serious

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pollution issue, which not only disturbs the operation of electronic instruments, but also threatens physical health of human beings [1,2]. Microwave absorbers can attenuate EM waves effectively by converting EM energy into thermal energy or dissipating the EM waves through destructive interference [3], and thus the exploration of high-efficiency microwave absorbers has attracted considerable attention in recent years. Among various kinds of microwave absorbers, carbon nanomaterials, including carbon nanosheets (CNSs) [4], carbon nanotubes (CNTs) [5], carbon nanocoils (CNCs) [6], and carbon nanofibers (CNFs) [7], have been widely studied due to their relative low density, tunable properties, abundant resource, easy preparation, and diverse forms. Graphene, being an excellent representative in carbon family, has also been reported to exhibit excellent dielectric properties because of its high charge carrier mobility, extraordinary electrical and thermal conductivity [8–10]. However, sole graphene still suffers from impedance mismatching caused by large difference between complex permittivity and complex permeability, which hinders its practical application in the field of microwave absorption [11]. Constructing graphene-based composites by incorporating secondary components, such as magnetic metals (Fe, Co, Ni) [12–14], metal oxides (Co_3O_4, ZnO) [15–17], and ferrites ($NiFe_2O_4$, $CoFe_2O_4$) [18,19], has been investigated as an imperative way to improve its matching of characteristic impedance and enhance the microwave absorption performance. Although these microwave absorbers show much better performance, it has to mention that this enhancement on microwave absorption is at the expense of low density and anti-corrosion of graphene owing to the embedment of these metal-based secondary components. These unexpected disadvantages cannot guarantee the durable performance of graphene-based composites. As a result, some groups attempted to replace these metal-based secondary components with lightweight polyaniline (PANI) [20], poly(ethylene oxide) [21], CNTs [22], and carbon microspheres [23,24]. However, naturally faded conductivity of PANI and poor dielectric loss ability of poly(ethylene oxide) still make their composites as unpopular candidates for novel microwave absorbers. In contrast, CNTs and carbon microspheres are stable incorporators with tunable dielectric property, and thus they can make prominent contribution to amending the dielectric property, reinforcing the microwave absorption performance, and endow those composites with desirable durability [22–24]. It is unfortunate that CNTs and carbon microspheres have large size and usually agglomerate together in graphene oxide (GO) suspension, leading to inadequate interfaces between graphene and secondary components. Therefore, it remains a challenge to couple graphene with small size carbon incorporators, which can provide an upgraded synergistic effect and enhance microwave absorption performance substantially.

Recently, *in situ* pyrolysis of metal-organic frameworks (MOFs)/GO hybrids appears as a very attractive strategy for the synthesis of carbon/graphene composites [25,26]. As metal ions and oxygen groups of GO have strong coordination effects, there will be abundant nucleation sites on the surface of GO and the size of MOFs crystals will be remarkably reduced [27], and the interaction between reduced GO (rGO) and MOFs-derived carbon in final composites can be consequently strengthened. The obtained MOFs-derived carbon/rGO composites have indeed exhibited their exciting performances in the fields of oxygen reduction reaction [27], Li-ion batteries [28], and super capacitors [29]. In addition to sufficient heterogeneous interfaces, MOFs-derived carbon/rGO composites also possess porous microstructure and rich defects (heteroatoms substitution), which can also create auxiliary consumption of EM energy through multiple reflection/scattering behaviors and dipole orientation polarization [1,30]. All these features suggest that this kind of graphene-based composites may be taken as promising microwave absorbers, however, there are quite few related reports accessible. In this study, we demonstrate the synthesis of rGO decorated with carbon nanopolyhedrons (CNPs/rGO) by employing ZIF-8/GO as the self-sacrificing precursor, and investigate its EM property and microwave absorption in detail. It is found that CNPs on the surface of rGO have very small size (10–20 nm), and they can effectively modulate the dielectric loss of rGO through reducing high carrier mobility and inducing considerable interfacial polarization [31]. As a result, CNPs/rGO composites can display improved impedance matching and enhanced microwave absorption. When the relative content of CNPs/rGO is optimized, an excellent performance, including strong reflection loss of −66.2 dB (6.2 GHz) and broad qualified bandwidth of 14.8 GHz (3.2–18.0 GHz), can be realized. Compared with graphene-based composites ever reported, the desirable advantages of CNPs/rGO composites, e.g. lightweight, high efficiency, and good chemical stability, will render them as eligible candidates for the oncoming generation of microwave absorbers.

2. Experimental section

2.1. Synthesis

GO was firstly prepared by the modified Hummers method according to a previous study [32]. For ZIF-8/GO hybrids, 0.366 g of $Zn(NO_3)_2{\cdot}6H_2O$ was firstly dissolved in 12 mL of methanol, and then a required amount of GO suspension solution [1 mg/mL in water/methanol (V_{water}:$V_{methanol}$ = 1:4)] was introduced. The mixed solution was stirred for 5 min before adding 20 mL of 2-methyimidazole (2-MI) methanol solution for the crystallization of ZIF-8 for another 3 h. The grey precipitate was collected by centrifugation (8000 rpm for 5 min), washed with methanol for several times, and dried at 60 °C for 12 h. The obtained hybrid was denoted as ZIF-8/GO-X, where X referred to the volume of GO suspension solution. ZIF-8/GO-X hybrid was further pyrolyzed in a horizontally tubular furnace under Ar atmosphere at 800 °C for 3 h, and the heating rate from room temperature to 800 °C was precisely controlled at 2 °C/min. Finally, the pyrolyzed products were treated with 3 M HCl solution to remove the remaining metal species, and then washed with deionized water. The as-obtained carbon/rGO composites were named as CNPs/rGO-X according to their precursors. For comparison, GO and pure ZIF-8 were also pyrolyzed under the same conditions.

2.2. Characterization

Powder X-ray diffraction (XRD) data were measured on a Rigaku D/MAXRC X-ray diffractometer with Cu Ka radiation source (45.0 kV, 50.0 mA). Scanning electron microscope (SEM) images were achieved on a Quanta 200S (FEI), and transmission electron microscope (TEM) images were obtained on a Tecnai F20 operating at an accelerating voltage of 200 kV. Raman spectra were performed on a confocal Raman spectroscopic system (Renishaw, InVia) using a 532 nm laser. The thermogravimetric analysis was conducted on a SDT Q600 TGA (TA Instruments) in the temperature range of room temperature to 800 °C at a heating rate of 10 °C/min. Nitrogen adsorption isotherms were obtained at 196 °C on a QUADRASORB SI-KR/MP (Quantachrome, USA). Samples were normally prepared for measurement by degassing at 120 °C. An Agilent N5230A vector network analyzer (Agilent, USA) was utilized to obtain the relative permeability and permittivity in the frequency range of 2.0–18.0 GHz for the calculation of reflection loss. A sample containing 40 wt% of prepared composites was pressed into a ring with a thickness of 2 mm, an outer diameter of 7 mm, and an inner diameter of 3 mm for microwave measurement in which paraffin wax was applied as the binder.