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Magnetic graphene for microwave absorbing application: Towards the lightest graphene-based absorber

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ABSTRACT

Application of graphene derived nanomaterial in microwave absorption has been limited by the issue of excessively high dielectric loss. To address this issue, instead of resorting to burdensome compositing with metal and ceramic particles, we put forward the idea of approaching impedance match by transforming graphene from diamagnetic to ferromagnetic and meanwhile suppress the conductivity. In this study, we synthesized the Nitrogen-doped graphene (NG) by a facile hydrothermal method with graphene oxide (GO) and urea as precursors. In comparison with GO and reduced GO (rGO), the nitrogen doping along with reduction process boosted the magnetism via a Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism. Pyrrolic-N has been found to dominate the magnetic property induced, which cooperates with the suppression of conductivity to benefit the absorption performance. The reflection loss of nitrogen doped graphene can achieve −11.3 dB absorption maximum at 12.7 GHz and an absorption bandwidth of 12.2−14.3 GHz (reflection loss < −10 dB) at a thickness of 3 mm, which proves to be favourable with respective to the density as compared to existing graphene-based absorbers.

1. Introduction

With the rapid development of communication technology and increasing use of electronic device, electromagnetic radiation has become a new kind of pollution which results in serious concerns to human life [1–4]. It has become the fourth pollution after noise pollution, air pollution and water pollution [5–7]. To alleviate this problem, two methods have been proposed, one is distance protection, the other is using electromagnetic interference and microwave absorbing materials to attenuate or absorb this energy [5]. The former is based on the principle that the intensity of electromagnetic wave in the environment is inversely proportional to the square of distance between the radiation source and human body. By means of expanding the distance between radiation source and the body appropriately, the electromagnetic radiation intensity is likely to be substantially weakened, but this method is limited by the space [5,7]. That is why much effort has been concentrated on the design and exploration of high efficient microwave absorption materials. Ideal microwave absorber should meet the features of light weight, fine thickness and strong absorption over a broad frequency [6]. According to the absorption mechanism, absorbing materials can be largely divided into two categories: (1) dielectric loss materials, such as nonconductive ZnO [8,9] and conductive polymers [10–12]; (2) magnetic loss material, such as Fe [13], Co [14], Ni [15] magnetic particles and their oxides [16,17]. In the first category, ceramics like ZnO typically boast good thermal stability, weather-stability, selectable mechanical properties for structural absorber and excellent dielectric property. But the permittivity decreases at high frequency and heavy loading or high thickness are necessary to realize practical microwave absorbing (MA) performance. Microwave absorption of conductive polymer mainly arises from polarization relaxation process, e.g. electron polarization, molecular polarization and interfacial polarization, but its good conductivity will lead to significant impedance mismatch; this issue is shared by majority of such conductive absorbents. For the second category, magnetic absorbents have the advantages of large permeability and encourage the absorber to be as thin as possible. But their high density and poor chemical stability, especially the processing difficulties caused by the aggregation tendency during the synthesis process, will compromise their performance in one way or another. Overall, the conventional absorbing materials relying on single constituent face common issues including high density, poor stability, large loading content, mismatched magnetic

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or dielectric loss, weak microwave absorption characteristic and narrow effective frequency bandwidth. The current development of MA material therefore has a tendency of making MA composites, adaptive and intelligent [6,18].

Graphene, a two dimensional carbon nanomaterial consisting of sp2 hybrid carbon atoms, has attracted tremendous attention since its discovery. It has excellent thermal conductivity, electrical conductivity, mechanical properties and high specific surface area with ultrathin thickness, all these properties make graphene a potentially ideal MA material [19,20]. But its high electrical conductivity will lead to significant impedance mismatch when used alone. Hence, many kinds of graphene-based composites and structures have been fabricated to further extending their electromagnetic properties and microwave absorption performance. To name but a few, advantages of structure design were approached by Zhang et al., who developed an ultra light and highly compressible graphene foam absorber with a broadband and tunable high-performance microwave absorption property [21]. Compositing strategy was widely practiced from two-component system such as ZnO/graphene [8], graphene−Ni [22,23], ferroferric oxide/graphene [2,24,25], conductive polymer/rGO [10−12], graphene/rubber composites [26] to three-component such as ternary rGO/Fe3O4 incorporated with CNT or conductive polymer composites [27,28] and to four-component such as graphene@Fe3O4@SiO2@NiO nanosheet hierarchical structures [29]. It is worth mentioning that by configuring the multiple component absorber, multiple absorbing mechanism will be invoked accordingly, in particular the interface introduced and impedance matching achieved by the constituents. Admittedly, compositing can elevate the microwave performance significantly, and delicate structure design is surely a lucrative way to maximize the performance of absorbents, but only on the condition that the absorbent itself proves to be a good one.

Therefore, researchers spend a lot of efforts studying the magnetic properties of graphene, both from the theoretical calculation and experimental aspects. As pure graphene is diamagnetic due to the lack of localized magnetic moments, a plausible strategy to improve its microwave absorption capability is to combine and balance both the dielectric and magnetic loss, i.e., to lower the conductivity of graphene and make it magnetic simultaneously. To this end, one can fashion on purpose zigzag edges [30−32] or vacancies [33,34], and introduce some adatoms [35−37] or heteratoms [38−42]. Wu et al. computed the effect of adatoms such as N, O, F atoms and found that N adatom has an unsaturated electron, inducing 0.84 μB magnetic moment per N atom for graphene; while both F and O adatoms results in no net magnetic moment [36]. It has been demonstrated that too many vacancies can make graphene fragile and reduce its structural stability; adatoms are inclined to be lost due to the low adsorption energy. By contrast, chemical doping can keep the structural stability and introduce more point defects into graphene [33], hence intrinsically modify and improve graphene's physical and chemical properties. Notably, among the potential dopants, N atom is considered as an ideal candidate in that it has equivalent atomic size with carbon atom. Nowadays, nitrogen-doped graphene (NG) has attracted much attention because of its excellent performance in electro-catalyst for fuel cells, lithium ion batteries, energy conversion and storage, sensors and electronics, etc. [43]. N-doping can make graphene electron-rich, deviating the Fermi level from zero value [44]. First principle calculations have also demonstrated that N-5 atom can introduce a net magnetic moment of 0.95 μB at either the edge or defect thanks to the contribution of the π bonds [38,39].

In this context, we propose the idea of using only light graphene material to reach impedance match for microwave absorption [45], We propose herein adopting nitrogen doping to make graphene magnetic and lower its electrical conductivity simultaneously. A thorough discussion of the mechanism for generating magnetism in graphene and its interactions with electromagnetic wave is performed. With so many inconsistent results reported, we have also experimentally studied here the relationship between the magnetic properties and amount and position of doped N so as to provide an optimization guide of the doping process and further improve the magnetic properties of graphene for practical microwave absorption purposes. In short, following this carbon-only idea, it would be possible to realize a superb absorber to meet all-round requirements of an ideal absorber, namely, thin, light, broad and strong.

2. Experimental details

2.1. Synthesis of GO

As the first step of materials preparation illustrated in Fig. 1, graphene oxide was prepared according to the modified Hummers' method [46,47]. Experimentally, graphite powder (2 g) and $NaNO_3$ (1 g) were added into the concentrated H_2SO_4 (46 ml 98%), the mixture was kept at ice bath (0 °C) for 0.5 h. After that, KMnO4 (6 g) powder was added into the mixture very slowly and stirred continuously for another 3 h. Subsequently, the mixture was heated to 35 °C for 0.5 h, and then deionized water (46 ml) was gently added into the above mixture. The temperature of the mixture was increased to 98 °C and maintained for 0.5 h; 36 ml H_2O_2 and 200 ml H_2O were subsequently introduced. When the whole reaction was completed, the final solution was washed with HCl (5 wt.%) and deionized water until pH near 7, and the GO aqueous solution was finally obtained.

2.2. Synthesis of rGO

Reduced graphene oxide was synthesized by annealing graphene oxide in a tube furnace at Ar atmosphere with programmable temperature (cf Fig. 1). Firstly, GO was kept at 300 °C for 1 h to eliminate the oxygen-containing groups that are easily removed such as hydroxyl. However, knowing that when the temperature is no higher than 500 °C, the C/O ratio is less than 7, and when temperature reaches 750 °C, the C/O ratio could be higher than 13 [48,49], we increased the annealing temperature to 900 °C for 0.5 h to remove the oxygen-containing groups and hence increase the C/O ratio. In this way, the rGO sample was obtained.

2.3. Synthesis of NG

To synthesize the nitrogen-doped graphene (NG), a one-step facile hydrothermal method was adopted as shown in Fig. 1. In the first place, GO (0.05 g) was dissolved in 50 ml deionized water through ultrasonic for 10 mins to disperse GO into single layer, urea (0.5 g) was added subsequently and the mixture was treated by ultrasound for another 5 mins. Different Urea/GO weight ratios (10:1, 20:1, 30:1, 40:1, 50:1) were set to prepare the series of NG samples [50]. GO and urea were used as the precursors, the reduction of GO and nitrogen doping process were accomplished at the same time.

2.4. Structural and magnetic characterization

The morphology and microstructure of the synthesized samples were examined using a Hitachi S-4800 cold field emission scanning electron microscopy (FE-SEM). FETEM was performed on FEI TECNAI G^2 F20 S-TWIN field emission transmission electron microscopy (FE-TEM). Raman spectrum was registered on a DXR Smart Raman spectrometer (irradiation wavelength: 532 nm). Quantum