



# Ultralight graphene aerogel enhanced with transformed micro-structure led by polypyrrole nano-rods and its improved microwave absorption properties



Bin Liu<sup>1</sup>, Jinhuan Li<sup>\*,1</sup>, Lufang Wang, Jiahui Ren, Yanfang Xu

College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

## ARTICLE INFO

### Article history:

Received 18 December 2016

Received in revised form 12 February 2017

Accepted 2 March 2017

Available online 6 March 2017

### Keywords:

A. Graphene

A. Hybrid

B. Electrical properties

B. Magnetic properties

## ABSTRACT

By a simple one-step reduction self-assembly process, a three-dimensional composite material graphene/polypyrrole aerogel (GPA) has been fabricated. The polypyrrole nanorods (PNRs) not only act as a spacer to avoid the graphene sheets aggregation and enhance mechanical strength but also effectively adjust the permittivity of GPAs to gain expected microwave absorption (MA) performance. Compared with pure graphene aerogel (GA), these aerogels with the ultralow density of around 0.020 g/cm<sup>3</sup> show improved MA performance that the maximum reflection loss (RL) can reach −51.12 dB at the frequency of 6.4 GHz, and the effective absorption bandwidth (RL < −10 dB) was 5.88 GHz (10.48–16.36 GHz) corresponding to an absorber thickness of 3.0 mm. Such outstanding MA performances are attributed to the polarization and relaxation process that is correlated with the transformed microstructure of GPAs.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

With the ever-accelerating speed of technological development and technological innovation, electromagnetic (EM) wave pollution become a serious threat to both human health and ecological environment [1–4]. To face this problem, researchers have made great efforts in the research of microwave absorbing (MA) materials [5–14]. However, developing MA materials with intense absorption ability, broad absorption bandwidth, ultralight weight and thin thickness is still a challenge. Recently, taking graphene as MA materials [15–21] for EM wave suppression has grabbed considerable attention due to their excellent properties, including low density, high specific surface area, large aspect ratios and versatile processing [22,23]. However, EM wave absorption of sole graphene materials is not impressive due to the mis-matching of interfacial impedance derived from their improper electrical conductivity and limited loss mechanism [24–27]. Therefore, composites of graphene with other lossy materials have been widely explored as an approach to enhance MA performance. For example, the composites of graphene with ferrite [28], nickel [29], cobalt [30], ceramics [31,32] have been reported. These works mainly focus on introducing magnetic nano-materials to provide magnetic

loss. However, these metals bring several drawbacks, such as high density, poor stability and large loading content which partly detracted their practical applicability.

The other problem for graphene applications is its poor dispersion in matrix because of the strong  $\pi$ - $\pi$  interaction between graphene sheets. The aggregation will reduce the surface area and decrease the conductivity of graphene, and thus, lead to inferior MA properties. Construction of three-dimension (3D) graphene network from individual graphene sheets paves a new way to address the aggregation problems [18,33–35]. Furthermore, 3D graphene still maintains super properties of graphene sheets which will guarantee the promising applications including EM wave absorption. For instance, Zhang [33] reported that graphene foam expressed the effective bandwidth of 14.3 GHz for X bands and further its MA performance can be tuned through mechanical compression. Huang [35] prepared the graphene foams with different internal microstructure and compositions and summarized that the highly intricate interconnected long-range conductive network is significant to the excellent MA property. The above investigations also indicate that graphene aerogel, a form of 3D graphene facially prepared from graphene oxide through sol-gel reaction, has a potential good EM wave absorbing properties which deserved to be explored.

As known, sole 3D graphenes, including graphene foams and graphene aerogels are all hard to meet the requirements of engineering applications because of their low strength as monolithic

\* Corresponding author.

E-mail address: [jinhuan\\_nj@nuaa.edu.cn](mailto:jinhuan_nj@nuaa.edu.cn) (J. Li).

<sup>1</sup> These authors contributed equally to this work.

materials. Introduction of polymer components is an effective approach to increase the strength of graphene aerogels, which calls for a careful design of the composition because the extra components usually suppress the superior property of graphene for target applications. Till now many excellent performance of graphene aerogels such as high compressibility and superhydrophobicity [36], high strength and stimuli-response [37] and super conductivity [38] have been realized through cooperating polymers.

Polypyrrole (Ppy), one of the most extensively studied conducting polymers, has attracted great interest in microwave absorber construction for its light weight, high electrical conductivity and favorable physicochemical properties [39,40]. It can be anticipated that introduction of Ppy can adjust the dielectric properties of graphene aerogel. And also, inspired by fiber reinforcement, we prepared Ppy nanorods as the lossy material to construct the nanocomposites of graphene and PNRs. Hopefully PNRs can avoid the stacking of graphene sheets, adjust the permittivity and enhance the strength of graphene aerogel as well. What's more, in view of high energy consumption of hydrothermal method we fabricated this strong graphene/PNRs aerogel (GPA) through a simple one-step reduction self-assembly process at a much lower temperature. It showed promising MA performance with an ultralow density of  $0.020 \text{ g/cm}^3$  and the mechanism of MA is detailed discussed.

## 2. Experimental section

### 2.1. Materials

Pyrrole monomer was purchased from Aladdin Chemical Reagent, China. Natural graphite powder (325 mesh) was purchased from Sinopharm Chemical Reagent, China. All the chemicals and reagents were of analytical grade and were used as received without any purification. Deionized water was produced in our laboratory and was used for all experiments.

### 2.2. Preparation of PNRs

The synthesis of PNRs is through the soft-template method [41]. Briefly, methyl orange (0.392 g) was dissolved in deionized water (250 mL) with  $\text{FeCl}_3$  (1.944 g), firstly, a flocculent precipitate appeared. Then a certain amount of pyrrole monomer (0.84 mL) was dropped in with softly stirring for 24 h, and the suspension turned black color. The as prepared precipitate was obtained by filtering and washing with ethanol and water alternately several times followed by freeze-drying for 48 h and vacuum drying at  $60^\circ\text{C}$  for another 12 h.

### 2.3. Preparation of GPAs

The GPAs were prepared by a simple one-step reduction self-assembly process. Firstly, a uniform 10 mL graphene oxide (GO, 4 mg/mL) was synthesized according to the modified Hummers method [42]. Then, a certain amount of PNRs were mixed with GO suspension under rigorous stirring for 5 h, followed by ultrasonication for another 2 h. After dropping ethylenediamine (30  $\mu\text{L}$ ) into the above suspension, the mixtures were immediately sealed into a  $60 \times 30 \text{ mm}$  glass vials before reaction at  $95^\circ\text{C}$  for 6 h. The as prepared hydrogels were soaked with deionized water for seven days before the GPAs were obtained by freeze-drying. According to the weight (mg) ratio of GO and PNRs, the samples were marked as GPA2:1, GPA1:1, GPA2:3. For comparison, the GA was prepared without PNRs at the same condition.

### 2.4. Characterization

The morphology of PNRs and GPAs were characterized by a Hitachi S-4800 field-emission scanning electron microscopy (SEM). Fourier-transform infrared (FTIR) spectra were obtained with a Nicolet Nexus 670 infrared spectrometer. Raman spectra were measured with HoloLab series 5000 Raman spectroscopy system (514 nm excitation of the laser). Transmission electron microscopy (TEM) images were obtained on a Philips Tecnai 12 microscopy at 120 kV. The real and imaginary parts of the complex permittivity  $\epsilon$  ( $\epsilon = \epsilon' - j\epsilon''$ ) and permeability  $\mu$  ( $\mu = \mu' - j\mu''$ ) were measured using a vector network analyzer (PAN-X N5244A) at the range of 2–18 GHz. For measurement the prepared GA and GPAs were broke into pieces and dipped in paraffin at ratio of 1:1. The as prepared mixtures were pressed into a toroidal shape with an outer diameter of 7.0 mm, an inner diameter of 3.0 mm and a thickness of about 2.0 mm.

## 3. Results and discussion

### 3.1. Formation and morphological structure

SEM was performed to explore the microstructure and morphology of the PNRs, GA and GPA1:1. Fig. 1a shows that the as-prepared PNRs have well-defined nanorod morphology with the diameter of 20–40 nm and the length of 2–4  $\mu\text{m}$ , which would behave much like nano-fibers in GPAs. As shown in Fig. 1b and c, graphene sheets derived by  $\pi$ - $\pi$  and hydrogen bond interaction form a platelike unidirectional porous structure layer-by-layer during the assembly preparing process. This unique morphology is typical structure derived from the liquid crystalline phase of the graphene oxide dispersion. [43,44]. And the larger size image (Fig. 1b) confirms that the GA still shows porous structure. It is interesting to find that the GPA1:1 exhibits a 3D interconnected network transformed from platelike unidirectional porous structure as shown in Fig. 1d and e, in which PNRs do not embed into the pores formed by graphene sheets of GA, but attach on graphene sheets. To further identify the morphology of PNRs and the GPAs, the TEM of PNRs and GPA1:1 were carried out. Fig. 2a further shows that PNRs is a 1D nanorod structure with the diameter of 20–30 nm and the length of 2–3  $\mu\text{m}$ , and some bundles staking can be observed. For GPA1:1 in Fig. 2b, most PNRs are decerned to be attached on the surface of graphene sheets and the distribution of the PNRs is more homogeneously compared with that of pure PNRs. This implies that the interaction between PNR and GA is stronger than that among PNRs.

Fig. 3 depicts the formation process of GA and GPA. At first, GO plane sheets are dispersed randomly in the solution with ultrasonic power helping. During the self-assembly process for GA, graphene sheets are assembled via a facial-pattern, the large size GO sheets tended to self-align and the ice crystals grew preferentially along the horizontal direction during the freeze drying process, which also is the reason for the morphology of GA. For previous studies [43,44], the aligned larger sheets may lower the ice front velocity, resulting in an anisotropic growth of ice crystals in other directions. Therefore, the pores were much longer in the horizontal direction than others. For GPAs, Because of the interaction of graphene sheets and PNRs, the plane sheets of GO are transformed to twist due to the unbalanced attachment of PNRs. During its assembly process, the twisted graphene sheets with PNRs on them get close to each other and the PNRs prevent the restacking of graphene sheets to a certain extent. The final result is that the GPA is obtained with a 3D interconnected network and the GA with a platelike unidirectional porous microstructure. In the meantime, the surfaces of graphene sheets of GA are smooth and flat, and

Download English Version:

<https://daneshyari.com/en/article/5439644>

Download Persian Version:

<https://daneshyari.com/article/5439644>

[Daneshyari.com](https://daneshyari.com)