Carbon 140 (2018) 494–503

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Tunable and high performance electromagnetic absorber based on ultralight 3D graphene foams with aligned structure

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A R T I C L E I N F O

Article history:
Received 17 July 2018
Received in revised form
18 August 2018
Accepted 1 September 2018
Available online 4 September 2018

A B S T R A C T

To meet the demand for accurate shielding of stealth aerospace, a tunable and high performance electromagnetic (EM) absorber based on unidirectional graphene foams (UGFs) is demonstrated in this work. Taking advantage of anisotropic design, a highly porous structure with long-range alignment has been pertinently constructed and the EM absorption performance was investigated in 2–18 GHz as a function of the intersection angle ϕ between the aligned direction and polarized direction of incident EM wave. By in-plane rotating the samples, it was suggested that both the reflection loss (R_L) and peak frequency of UGFs were readily tunable. The specific regularities were closely related to the thermal reduction degree determined by annealing temperature. A dual-absorption mechanism arising from dielectric loss and induced current was also proposed, through which the tunable absorption was attributed to variation of coupling alignment between aligned structure and their directionalities upon the fields of EM wave. Particularly at the optimal alignment, a maximum R_L up to −65 dB has been obtained, which is the highest value for all the graphene based EM absorption materials. Besides, owing to the dual absorption feature, a qualified bandwidth of 10.9 GHz was also achieved.

1. Introduction

With the explosive development of the electronic industry and information technology, electromagnetic (EM) absorption is highly demanded for both civilian and military applications [1–5]. Whereat, abundant of researches have been directed towards designing various EM absorption materials since they were firstly proposed. Separated solid particle absorbents like ferrites [6,7], ceramics [8], magnetic metals [9] and their hybrids have been widely explored by simply dispersing them in EM transparent matrixes. However, owing to the high density and high filler loading required, applications of these traditional EM absorption materials are limited, especially in the front fields like aerospace that are extremely weight-sensitive [10,11]. Therefore, the ultra-light weight EM absorber with excellent efficiency in a broadband will be advantageous.

Considerable effort has been firstly made on developing new generations of materials, including polymers, chiral materials, Schiff base salt, carbon based materials and so on [12–14]. Particularly, being a special member of carbon materials with unique two-dimensional feature, graphene or reduced graphene oxide (rGO) has also grabbed significant attention due to the versatile properties, such as the light weight, ultra-high specific surface, intense dielectric loss and excellent electrical conductivity, etc. that bestow a higher efficiency [15–18]. The work conducted by Zhang et al. [19] suggested that a maximum reflection loss (R_L) up to −25 dB could be obtained for polyvinyl diene fluoride (PVDF)/rGO composites at the loading of only 3 wt %. It could be one of the most promising candidates for preparation of light weight and high performance EM absorber. Anyhow, the high permittivity and conductivity of rGO is a double-edged sword, which may also result in impedance mismatching. Thus the qualified band width with reflection loss more than −10 dB was only 4.3 GHz and the absorption efficiency was decreased with further increase of rGO content. To solve this problem, incorporation of graphene with other lossy materials involving various hierarchical structures was also widely studied [20–25].

Towards realizing the lightweight optimization of EM absorber, structural design of the traditional or newly developed materials has been also attempted simultaneously, and among the most promising is porous structure. Besides the sharply reduced density,

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https://doi.org/10.1016/j.carbon.2018.09.014
0008-6223/

it is also favored regarding to the enhanced interaction with incident EM wave [13,26]. Firstly, the much smaller permittivity (originated from the ultrahigh porosity) makes it less resistive to the incident EM wave, which enables a more effective absorption in a wide frequency range. Furthermore, the multiple-absorption of incident EM wave via intra-re-reflection and scattering in the interconnected network is sure to result in a higher absorption efficiency. So far, considerable attention has been paid to porous particles, like conductive polymers [27], silicon carbide [28], carbon [13] and carbon nanotube [3] etc. which can be only applied as ultralight fillers in composites and reduce the weight to some extent. Recently, exploration of macroscopically porous carbon monolith has opened up a significant progress towards substantially ultralight materials for EM absorption and shielding [29,30]. The tentative investigation conducted by Huang et al. [31,32] with graphene foams (GFs) suggests that the long-range interconnected network has brought about much superior performance. Being a dielectric and electrical lossy material with bulk density lower than 3 mg/cm^3, the maximum R_L in 2–18 GHz could be over −30 dB and the qualified bandwidth was over 10 GHz. It is ideal for application on stealth aerospace and aviation.

However, important as it is for the development of ultralight EM absorption materials, less effort has been devoted to the is-situ regulation of an existing EM absorption material, which is demanded for accurate shielding of stealth aerospace against the gradual maturation of novel advanced anti-stealth radars such as phase array radar, multi-static radar and passive radar. Hence in present work, tunable and high performance EM absorption materials based on ultralight graphene foams will be developed. In previous studies, it has been unambiguously revealed that most of the energy loss mechanisms are directionally oriented. Take the graphene for instance, the energy loss through dielectric polarization can be severely enhanced when the sheets are perpendicular to the external field [33]. While for a conductive porous material, the EM absorption through induced current decay is possible only when the reticulated structure could couple with the incident EM wave as a solenoid does [34]. In this consideration, anisotropic GF monolith with unidirectional aligned porous structure was proposed and studied in this work. Instead of unhandily changing either the composition, thickness, network density or compress strains, it is supposed to realize in-situ tuning of the EM absorption performance by conveniently regulating the coupling alignment of the unidirectional graphene foams (UGFs) with fields of incident EM wave through in-plane rotation. Besides, an ultra-high absorption could be also expected when the coupling alignment is properly optimized.

2. Experimental

2.1. Preparation of graphene oxide dispersion

To obtain fully oxidized graphene Nano-sheet and preserve the lateral size, the GO precursor was synthesized based on the modified chemical method using expanded graphite (EG). Typically, 2 g dried EG and 300 ml H_2SO_4 were mixed and stirred in a three-neck flask. 20 g $KMnO_4$ was then introduced to the mixture followed by stirring for 24 h. The solution was transferred to an ice bath, 300 ml DI water and 100 ml H_2O_2 were poured slowly into the mixture where the color of the suspension changed from dark green to light brown. Having stirred for another 30 min, the graphene oxide was obtained, which was washed with HCl solution and DI water until the pH of the solution became about 5–6. The GO dispersion was diluted with DI water to a concentration of 2 mg/ml.

2.2. Preparation of unidirectional graphene foams (UGFs)

The UGF boards were fabricated through unidirectional freeze casting of GO dispersion using the designed apparatus as illustrated in Fig. 1. Briefly, the GO dispersion were poured into a customized Acrylic mold, which was plugged with a well-match aluminum stand at bottom so as to realize effective thermal conduction between the GO dispersion and the cooling source. The fixed mold was tightly wrapped with heat insulating materials and rested in a Styrofoam container, while the aluminum stand was adiabatically sealed in the underneath compartment and liquid nitrogen was pooled as the cooling source to initiate unidirectional freezing of GO dispersion from bottom to top. Then, the frozen GO dispersion was freeze-dried for 48 h after which a GO aerogel with a highly aligned porous structure was obtained. Finally, the unidirectional aerogels (UGAs) were reduced through thermal treatment and the products were denoted as UGF-T in which T indicated the annealing temperature. It was normally conducted in a dry N_2 environment for 1 h at a constant heating rate of 5 °C/min.

2.3. Characterizations

A scanning electron microscopy (SEM) using the secondary electron at the voltage of 20 kV and a field emission transmission electron microscopy (TEM) were applied to examine the structure and morphology of UGA. Knowing that the structural integrity of UGA has been well maintained after freeze drying, the bulk density was obtained by weighting the mass of UGA and dividing it by the volume of GO dispersion precursor. By comparing it with the one of neat graphene, the porosity was also approximately estimated. The reduction degree of UGFs were characterized through Raman spectroscopy with He–Ne laser at the wavelength of 632.8 nm. The XPS was used to study the elemental compositions and the assignments of the carbon peaks of UGFs. The DC electrical conductivity $\boldsymbol{\sigma}$ of UGFs were measured using the linear four-point probe method. The EM absorption in the frequency range of 2–18 GHz was evaluated through direct measurement of reflection loss based on the arch method. As shown in Fig. S2, four UGFs (90mm × 90mm × 10mm) arranged on a rectangular aluminum plate (180mm × 180mm) with the same aligned direction were applied as the sample as whole. The arch frame with a radium of 150 cm was equipped with standard gain horn antennas which were connected to an AV3618 scalar quantity network analyzer. As the angle between the transmitting and receiving horns are only 10°, the incident EM wave (TEM mode) can be approximately regarded perpendicular to the UGFs boards. By in-plane rotating the sample, the measurement was normally carried out as a function of the coupling angle $\boldsymbol{\phi}$ denoting the intersection of aligned direction with polarized direction (electric field $\overline{\boldsymbol{E}}$) of EM wave as shown in Fig. 2 (a). The relative permittivity ($\boldsymbol{\varepsilon}^* = \boldsymbol{\varepsilon}' - j\boldsymbol{\varepsilon}''$) and permeability ($\boldsymbol{\mu}^* = \boldsymbol{\mu}'\text{-}j\boldsymbol{\mu}''$) of UGFs in the frequency range were measured using a KEYSIGHT N5225 network analyzer. The toroidal samples (7 mm in outer diameter and 3.04 mm in inner diameter) with alignment vertical to the transmission line as depicted in Fig. 2 (b) were fabricated by vacuum impregnating the UGFs with paraffin.

3. Results and discussion

3.1. Preparation and structure of UGAs

The unidirectional freeze casting technique has been applied in preparation of UGAs with a long-rang aligned graphene network. Comparing to other techniques taking advantage of GO sheets self-alignment [33] or alignment induced by external fields [35], it is preferred regarding to the simple process and facile control to build