Applied Surface Science 439 (2018) 176–185

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

From nanoscale to macroscale: Engineering biomass derivatives with nitrogen doping for tailoring dielectric properties and electromagnetic absorption

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ARTICLE INFO

Article history:
Received 18 October 2017
Revised 19 December 2017
Accepted 24 December 2017
Available online 6 January 2018

Keywords:
Electromagnetic absorption
Carbon materials
Complex permittivity
Nitrogen doping

ABSTRACT

Since achievement in electromagnetic (EM) technology dramatically promotes the critical requirement in developing advanced EM response materials, which are required to hold various advantageous features in light weight, small thickness, strong reflection loss and broadband absorption, the most important requirements, i.e. strong reflection loss and broadband absorption, are still highly pursued because of the intrinsic shortage in conventional EM absorbers. For addressing such critical problems, a unique three-dimensional nitrogen doped carbon monolith was demonstrated to understand the effects of the nitrogen doping on the dielectric and microwave absorption performance. The chemical components of the nitrogen doped carbon monoliths have been quantitatively determined for fully understanding the effects of nanoscale structures on the macroscopic composites. A modified Cole-Cole plot is plotted for guiding the chemical doping and material process, aiming to realizing the best matching conditions. The results have promised a universal route for achieving advanced materials with strong and broadband EM absorption.

1. Introduction

Since the surge of electronics, telecommunication, detection and aerospace industries has significantly promoted the electromagnetic (EM) technology with a variety of advanced functionalities, EM absorption material [1–4], one of EM response materials [5–9], has attracted great attention in recent years. Exploratory studies have been massively carried out based on the inherent relationship of "components – morphologies – structures – properties", which is established from nano-scale to macro-scale of the materials [10–13]. As shown in Fig. 1, at the molecule and atom level, chemical components are considered as the intrinsic factors that are responsible for generating dipoles and free charges [14,15], directly linked to the polarization and EM energy consumption, respectively (Fig. 1a). Additionally, increasing consideration on the dimensions and morphology of the active materials has been made, with capability of converting EM energy into other forms at the nano-scale level (Fig. 1b). In the bulk composites, complex parameters, including complex permittivity and permeability, coupled with impedance matching conditions are the critical roles in determining the quarter-wavelength resonance and surface reflection (Fig. 1c), thus leading to the EM absorption performance [16–20]. In the macroscopic structures, shapes and sizes of the structures are the key factors for tailoring the interaction between materials and EM waves, responsible for targeting absorption (Fig. 1d) [21,22].

Back to early stage, considerable attempts were done for fabricating numerous composites with different active materials and matrices. Among these composites, polymeric matrices embedded with carbon black or ferrite oxides were known to be the conventional fashions for obtaining effective EM absorption (reflection loss <−10 dB) [23,24]. With growing nanotechnology, nano-sized carbon materials, e.g. one-dimensional (1D) carbon nanotubes [25–27], two-dimensional (2D) graphene [28–30], three-dimension (3D) carbon foams [31,32], are representative electrical substrates for incorporating magnetic nanostructures, with purposing of broadening effective absorption band (bandwidth of reflection loss <−10 dB) [33,34]. For typical examples, Qin and coworkers have utilized atomic layer deposition technology to

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https://doi.org/10.1016/j.apsusc.2017.12.222
0169-4332/

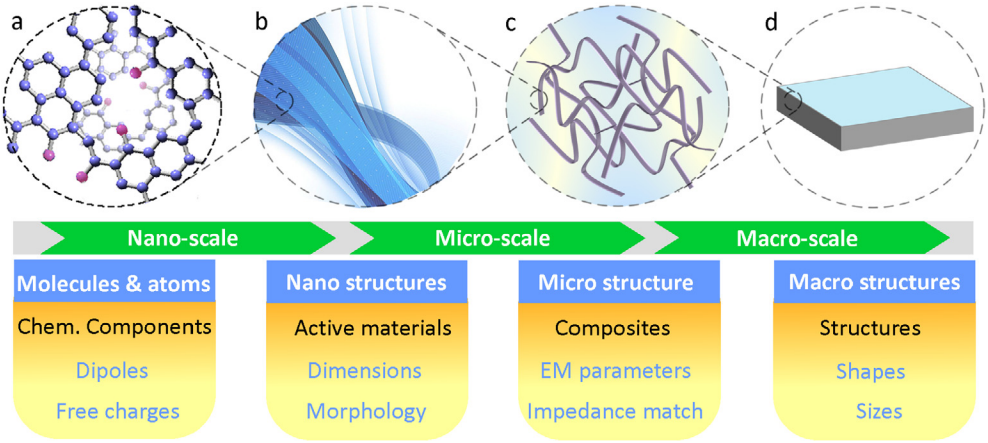

Fig. 1. Schemes of EM absorption materials: perspectives from nano-scale to macro-scale.

prepare hierarchical nanostructure that integrated both dielectric and magnetic loss for enhancing EM energy conversion [35]. Che and workers have reported novel nanoscale structures which are able to tune absorption band in the investigated region, showing unique strategy for improving EM absorption performance [3]. Moreover, Huang and coworkers fabricated tunable 3D graphene foam structures for extending absorption band via manipulating the EM transportation paths and EM energy consumption [31]. Very recently, great progresses have been achieved in characterization technique, which allows for fundamentally understanding the relationship between chemical components and EM absorption performance [36–39].

Generally, the advanced EM absorption materials are required to possess exclusive characteristics of light weight, small thickness, strong reflection loss and broadband absorption. Recently, lightweight materials, particularly carbon-based fillers of small density, have been extensively explored as aforementioned. Thickness in uniform bulk materials determines the quarter-wavelength resonance absorption peak position, and the materials with small thickness are usually prone to generate absorption peak at higher frequency. Apparently, the requirement on strong in reflection loss and broadband in effective absorption is more essential in developing high-performance EM absorption materials. More importantly, these two critical problems have not been well manipulated in the practical design although the general discipline is known, specifically for understanding the internal relationship from microscopic to macroscopic views.

As a continuous study based on understanding the effects of dielectric matrix categories on microwave absorption [40], in this contribution, we utilized nitrogen doping for understanding the effects of nitrogen hetero-atoms on the dielectric and microwave absorption performance in the range of 2–18 GHz. For a convenient demonstration, a controllable method for quantitatively characterizing chemical components has been presented, with an exceptional 3D nitrogen doped carbon monolith achieved as the active absorbers. A modified Cole-Cole plot suggests a simple route to understand the effects of chemical doping and processing parameters on the final EM absorption performance. The results highlight a universal strategy for accelerating designing advanced absorption materials and composites with desirable features.

2. Experimental section

2.1. Materials and composites

In the preparation of carbonized cotton (CC), the commercial cotton was utilized as the carbon source for direct carbonization. A portion of commercial cotton was heated up to 800 °C for 1 h in the N_2 atmosphere, with a heating rate of 5 °C min^{-1} from room temperature to 300 °C and a subsequent heating rate of 7 °C min^{-1} from 300 °C to 800 °C.

Nitrogen-doped carbonized cotton (NCC) was also prepared with the similar procedure, expect for the presence of nitrogen doping source in the carbonization process. In the heating under the N_2 atmosphere, cotton along with urea and melamine mixing powders (with mass ratio of 1:2:2) was positioned in a quartz boat. Likewise, the mixtures were heated up to 800 °C for 1 h for complete decomposition of the nitrogen source.

The carbonized products of CC and NCC were further processed into paraffin for fabricating composites. In the typical preparation, a portion of paraffin matrices was firstly dissolved in an ether solution under vigorous stirring. The as-prepared the active fillers (CC or NCC) with various filler loadings were grinded into powders, followed by adding into the paraffin/ether mixture solution. Until the ether was evaporated completely, the dried mixtures were compacted into a toroidal shape (Φ_{out}, 7.03 mm; Φ_{in}, 3.00 mm) with thickness of 1.7–2 mm. Therefore, six composites samples were obtained, including CC/paraffin composites with loadings of 10, 20 and 30 wt%, short as CC-10, CC-20 and CC-30, and NCC/paraffin composites with loadings of 10, 20 and 30 wt%, short as NCC-10, NCC-20 and NCC-30.

2.2. Material characterizations

Field-emission scanning electron microscopy (SEM) was performed on ZEISS supra 55 system. X-ray powder diffraction (XRD) characterization was carried out on a PANalytical X' Pert PRO MPD diffraction system. Transmission electron microscopy (TEM) images were captured on a JEOL JEM-2010 scanning TEM system. Raman spectra were obtained on a Jobin Yvon T64000 Raman spectrometer equipped with a Melles-Griot 35 mW He-Ne laser source for 633 nm excitation, a triple monochromator, a liquid nitrogen-cooled Symphony detector, and an Olympus BX-41 microscope. X-ray photoelectron spectroscopy (XPS) was acquired on PHI-5300 system. The complex permittivity was measured on an Anritsu 37269D vector network analyzer with the coaxial method from 2 to 18 GHz, with the chamber size of a toroidal shape (Φ_{out}, 7.03 mm; Φ_{in}, 3.00 mm). The EM absorption of the composites at various thicknesses was calculated via Eqs. (1) and (2).

2.3. Establishment of a modified Cole-Cole plot

For establishing a modified Cole-Cole plot, microwave performance was initially obtained by key parameter sweeping (real per-