Materials Chemistry and Physics 170 (2016) 303–311

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

A powerful approach to graphene/stainless steel web hybrids for large scale electromagnetic shielding applications

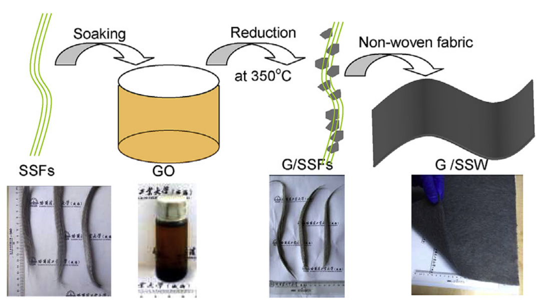
T. Zhang [a], B. Zhong [a], L. Xia [a, *], G. Wen [a, b, **]

[a] School of Materials Science and Engineering, Harbin Institute of Technology (Weihai), Weihai, 264209, PR China
[b] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin, 150001, PR China

HIGHLIGHTS

- Large-scale graphene/stainless steel web hybrids were successfully fabricated.
- The architectures exhibit excellent microwave absorption property.
- The described method has high probability to develop in industrial application.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 April 2015
Received in revised form
1 October 2015
Accepted 20 December 2015
Available online 28 December 2015

Keywords:
Composite materials
Electron microscopy
Raman spectroscopy and scattering
Dielectric properties

ABSTRACT

Graphene/Stainless Steel web hybrids were fabricated using soaking-annealing method. The microstructure was characterized by field emission scanning electron microscope an X-ray diffraction. The results showed that Graphene uniformly dispersed on the surface of stainless steel fibers which were further prepared to large scale graphene/Stainless steel web. For the as-prepared products a minimum reflection loss (RL) of −42.6 dB was achieved at 8.5 GHz. Moreover, the frequency range with RL peak value below −10 dB was achieved in a broad frequency bandwidth of 9.8 GHz, suggesting the excellent microwave absorption properties.

1. Introduction

Recently, the widespread applications of information technology, communication devices and military stealth equipments have intrigued serious problems of electromagnetic (EM) wave radiation. Most of the daily EM waves have the effect of high-frequency radiation, namely at the frequency of 2–18 GHz. Therefore, many efforts have been devoted to high-frequency EM wave absorption materials in the frequency range of 2–18 GHz. Traditional microwave absorption materials, especially magnetic metals, have been extensively studied and commercially used for EM wave absorption. However, some disadvantages, such as high densities, sophisticated processing and environmental-unfriendly fabrication restrict their universal applications. Therefore microwave absorption materials with low densities, easy processing and wide EM wave absorption are becoming desirable.

* Corresponding author.
** Corresponding author. School of Materials Science and Engineering, Harbin Institute of Technology at Weihai, Weihai, 264209, PR China.
E-mail addresses: swliza@hit.edu.cn (L. Xia), g.w.wen@gmail.com (G. Wen).

http://dx.doi.org/10.1016/j.matchemphys.2015.12.055

Carbon-based materials, such as carbon nanotubes and porous carbon filled with metal magnetic nanoparticles have been extensively studied as EM wave absorbents [1–5]. F1-37metal nanoparticles enveloped carbon composites. In the previous works, some methods have been proposed on the synthesis of one-dimensional (1D) absorbents, including nanobelts, nanotubes and may kinds of nanofibers by chemical vapor deposition (CVD) and pyrolysis and electrospinning et al. [6–11]. However, the microwave absorption properties of these 1D nanomaterials significantly depend on the homogeneous distribution of the absorbents in matrix, which is difficult to obtain excellent absorbents in large-scale dimension with flexible character. The exploration of new absorbents together with flexible appearance for large-scale applications is highly desired. Graphene, a monolayer of sp^2-bonded structure, shows good conductivity and light weight which suggests a new EM wave absorbent [12]. Recently, large-scale and high-quality graphene with controlled number of layers can be successfully fabricated by CVD method [13]. However, the application of graphene in EM wave absorption materials are few reported. For example, the dielectric properties of graphene-based epoxy resin were reported by I. Kranauskaite team [14]. They found that 2 wt% of exfoliated graphite-based composite has an intensive absorption at 30 GHz. P. Kuzhir et al. reported that exfoliated graphite could replace expensive CNTs in epoxy for producing effective electromagnetic materials in microwave and low-frequency ranges [15]. M. Han et al. reported graphene-wrapped ZnO exhibiting a maximum absorption of −45.05 dB at 9.7 GHz with a sample thickness of only 2.2 mm [16]. Nanoparticle modified graphene composites also exhibit the capability of microwave absorption properties [17,18].

Meanwhile, metallic soft magnetic materials are a potential candidate for EM wave absorption (especially in high frequency range) comparing to ferrite materials [19]. Soft metallic magnetic materials can absorb high frequency (GHz) EM wave due to its' excellent dielectric and magnetic loss [20]. The 316L stainless steel fibers (SSFs) produced by bundle drawing process [21] are low carbon austenitic stainless steel. The austenitic SSFs are known to have martensitic transformation from a paramagnetic austenite (γ-fcc) to a ferromagnetic martensite (α-bcc) by strain-induced deformation [22,23]. The ferromagnetic steel-based composites exhibit high dielectric constant due to the existence of space charge polarization between adjacent metallic components [24].

When graphene is combined with SSFs to fabricate a graphene/stainless steel web (G/SSW), the EM wave absorption properties of the G/SSW can be anticipated. In this study, G/SSW hybrid architectures were successfully fabricated using soaking-annealing method from graphene oxide and SSFs. For the hybrid architectures, a minimum reflection loss (RL) of −42.6 dB was obtained at 8.5 GHz and a broad absorption bandwidth of (RL value below −10 dB) is achieved suggesting the excellent microwave absorption properties.

2. Experimental

2.1. Synthesis of graphene oxide (GO)

GO was successfully obtained by a modified Hummers method [25,26]. Purified graphite (5 g), H_2SO_4 (150 ml) and KNO_3 (3.5 g) were blended together at the temperature of 45 °C and cooled down to room temperature. $KMnO_4$ (18 g) was added to the mixture slowly and reacted for 3 h at the assistance of ultrasonic dispersion. After that, the solution was diluted with deionized water (800 ml) follow by addition of H_2O_2 (20%, 50 ml). The resulting GO was washed for several times. Then, GO solution was prepared by high-energy ultrasonic exfoliation and centrifuged for 40 min at a speed of 5500 rpm. Finally, stable GO solution was obtained by dialysis purification (the pH value is about 6) and its concentration was adjusted to 0.4 mg/l.

2.2. GO/SSFs preparation

Austenitic SSFs (316L, 2200 filaments) produced by Huitong Hunan Co. Ltd with a diameter of 22 μm were used in this work. The SSFs were introduced into GO solution (0.4 mg/l) and soaking for 30, 60 and 100 min, respectively at room temperature. Then, the SSFs were dried and annealed at 350 °C for 30 min in ambient atmosphere.

2.3. G/stainless steel web (SSW) preparation

The SSFs decorated by graphene were further cut to sort fibers (about 5 cm, 12.5 g in total) and then prepared to stainless steel web by a custom random air laid non-woven apparatus at room temperature. The dimension of the as-prepared sample is 400 × 400 × 5 mm with a surface density about 70 g/m^2. All the SSFs have a 3 dimension (3D) distribution in the SSW forming the flexible G/SSW hybrid architectures. The whole fabrication process is illustrated in Fig. 1.

2.4. EM wave absorption sample preparation

EM wave absorption properties of the G/SSW samples were measured on a vector network analyzer (Agilent, N5224A) with transmission reflection mode in the range of 2–18 GHz at room temperature. The G/SSW samples for EM wave absorption measurements were prepared by mixing the product with a paraffin wax in mass ratio of 1:3 (this ratio is an empirical value, at which the G/SSW can be uniformly dispersed in paraffin and the sample has a good formability), and then being pressed into a steel mold with an inner diameter of 3.0 mm and outer diameter of 7.0 mm (the membrane products were introduced into the mold layer by layer and mixed with paraffin wax). After that, the composite samples were measured by coaxial line from 2 to 18 GHz.

3. Results and discussions

As shown in Fig. 2A, the 3D graphene architectures were first established on a SSFs substrate by simply soaking it in a GO solution and another annealing step as we demonstrated in experimental parts. In aqueous solutions, GO nano-sheets are homogeneously suspended due to the electrostatic repulsion effect [27]. These GO nano-sheets could break the stabilization and anchor on the SSFs substrate due to the reductive surface of stainless steel. As shown in Fig. 2A, the decoration of graphene on SSFs substrate is achieved by the reduction of GO at the soaking and annealing steps. The SSFs substrate could act as an anode where metal atoms (Fe°) are partially oxidized into Fe^{2+}, while GO could serve as a cathode for the reduction of desired graphene (removing epoxy and carboxyl groups).

Fig. 2B(a) shows the typical XRD pattern of the as-prepared GO (2θ = 11°, 43.2°). Fig. 2B(b) shows XRD pattern of the GO/SSFs prepared at the soaking time of 30 min. The diffraction peaks at 2θ = 43.6, 50.7 and 74.6° are corresponding to (111), (200) and (220) planes respectively suggesting the face-centered Austenitic stainless steel (PDF No.310619). A small representative peak at 11° can still be observed revealing the successful GO decoration. The typical peak of GO (2θ = 11°) has completely disappeared in the G/SSW sample (Fig. 2B(c)), accompanied with a new broad peak at about 23.1 ° for anchored graphene revealing that the desired graphene coating has been obtained.