Applied Surface Science 420 (2017) 858–867

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Enhanced microwave absorption properties of graphite nanoflakes by coating hexagonal boron nitride nanocrystals

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ARTICLE INFO

Article history:
Received 10 February 2017
Received in revised form 24 May 2017
Accepted 25 May 2017
Available online 29 May 2017

Keywords:
Hexagonal boron nitride nanocrystals
Graphite nanoflakes
Composite
Electromagnetic microwave
Absorption property

ABSTRACT

We report herein the synthesis of a novel hexagonal boron nitride nanocrystal/graphite nanoflake (*h*-BNNC/GNF) composite through a wet-chemistry coating of graphite nanoflakes and subsequent *in-situ* thermal treatment process. The characterization results of X-ray diffraction, scanning electron microscope, transmission electron microscope, energy dispersive X-ray spectrum, and X-ray photoelectron spectroscopy demonstrate that *h*-BNNCs with diameter of tens of nanometers are highly crystallized and anchored on the surfaces of graphite nanoflakes without obvious aggregation. The minimum reflection loss (RL) value of the *h*-BNNC/GNF based absorbers could reach −32.38 dB (>99.99% attenuation) with the absorber thickness of 2.0 mm. This result is superior to the other graphite based and some dielectric loss microwave absorption materials recently reported. Moreover, the frequency range where the RL is less than −10 dB is 3.49–17.28 GHz with the corresponding thickness of 5.0–1.5 mm. This reveals a better electromagnetic microwave absorption performance of *h*-BNNC/GNFs from the X-band to the K_u-band. The remarkable enhancement of the electromagnetic microwave absorption properties of *h*-BNNC/GNFs can be assigned to the increase of multiple scattering, interface polarization as well as the improvement of the electromagnetic impedance matching of graphite nanoflakes after being coated with *h*-BNNCs.

1. Introduction

Electromagnetic microwave absorption materials have gained increasing attention due to the high demand for effective reduction of the electromagnetic radiation and improvement of anti-electromagnetic interference from industrial to military fields [1–5]. In the past decades, an overwhelming research on the novel electromagnetic microwave absorption (MA) materials has been made [1–28]. Dielectric and magnetic materials are currently two main types of materials that are used as electromagnetic MA materials [29]. The electromagnetic microwave absorbing properties of such materials are determined by their dielectric properties (the complex permittivity; $\varepsilon_r = \varepsilon' - j\varepsilon''$), magnetic properties (the complex permeability; $\mu_r = \mu' - j\mu''$), electromagnetic impedance matching as well as the thickness of the absorbers [1,5,29–32]. However, there are some other shortcomings restricting their practical applications. For example, the dielectric absorption materials exhibit narrow absorbing frequency bandwidth while the magnetic absorption materials possess high density that cannot be used in large quantity as fillers of absorbers [33]. As a result, for many civil and military applications, research is still focused on developing novel electromagnetic MA materials with thin thickness, low density, high thermal stability, and absorption over broad electromagnetic frequency bandwidth [5,30,34].

Comparing with magnetic loss absorption materials, the electrical loss absorption material have become one kind of the most preferred absorption materials due to their relatively low density [29]. Among them, carbonaceous materials are the typical electrical loss absorption materials, because these materials possess relatively low density, tunable properties, abundant resources, simple preparation process, and low cost [29], *etc.* Graphite flakes, a kind of typical carbonaceous materials, have attracted considerable attention owing to their unique properties, such as low density, good chemical inertness, excellent mechanical performance, high oxidation resistance, outstanding electrical conductivity as well as the sufficient dielectric loss property [25]. Moreover, the graphite flakes are present in abundance naturally. Therefore, graphite flakes are considered as ideal electromagnetic MA materials. However,

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http://dx.doi.org/10.1016/j.apsusc.2017.05.232
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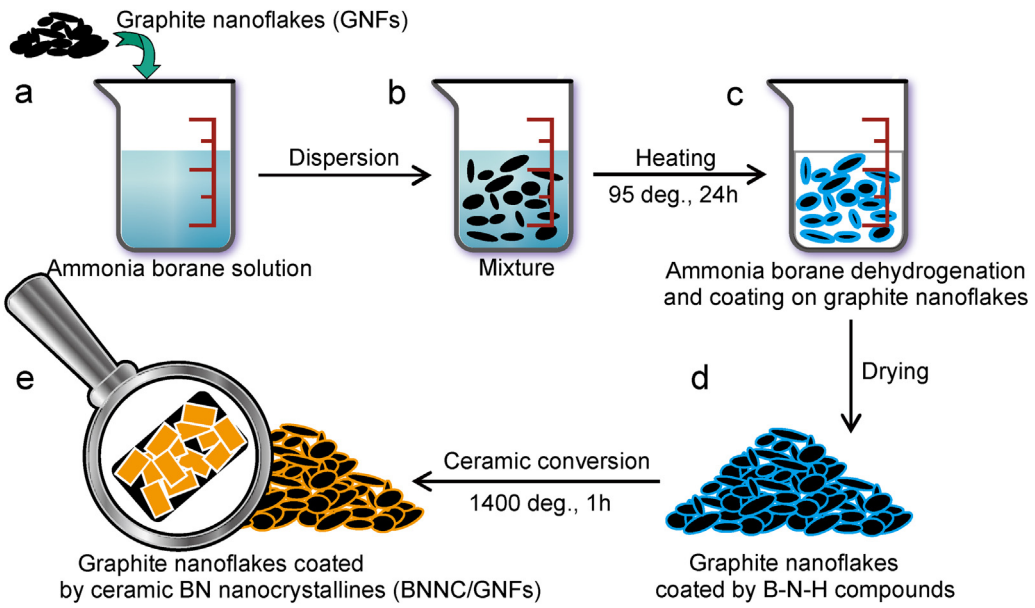

Fig. 1. Schematic illustration of the fabrication process of *h*-BNNC/GNFs.

large dielectric loss of graphite flakes often results in the unexpected reflection of microwaves. Hence, it is of great necessity for graphite flakes to combine with other materials to improve their electromagnetic microwave absorbing properties. Currently, the main research focuses on the modification or decoration of graphite flakes, which produces graphite oxide or nano-graphite and thus form high performance graphite based absorbing materials [29,35–40].

Hexagonal boron nitride (*h*-BN) composed of sp^2 bonded boron and nitride atoms, is structurally analogous to carbon materials with almost the same crystal lattice parameters [41]. Moreover, *h*-BN possesses larger electrical resistivity and cannot influence the attenuating electromagnetic wave energy of graphite. These unique properties combining with the remarkable mechanical properties, high chemical inertness and thermal stability, excellent resistance to oxidation make *h*-BN an excellent alternative candidate for producing ideal electromagnetic MA composites with graphite flakes. Therefore, in current report, we have selected nonmagnetic *h*-BN nanocrystals which differ from the conventional magnetic and dielectric phases to adjust the electromagnetic parameters of graphite flakes. These special *h*-BN nanocrystal/graphite nanoflake (*h*-BNNC/GNF) composite is fabricated through a facile wet-chemistry coating and subsequent *in-situ* thermal treatment process. The composition and structure of this novel *h*-BNNC/GNF composite are confirmed by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). The microwave absorbing properties of *h*-BNNC/GNF based absorbers with different thicknesses are systemically investigated in the frequency range of 2–18 GHz. Noticeable enhancement of MA property is achieved after coating *h*-BNNCs on the surfaces of graphite nanoflakes. Finally, the mechanism for the enhanced MA properties of these *h*-BNNC/GNFs has also been studied in detail.

2. Experimental

2.1. Materials

Ammonia borane used in this work was synthesized according to the literature [42] using sodium borohydride and ammonium formate as starting materials. Graphite nanoflakes with average diameter of 500 nm were purchased from Dongguan Jiecheng graphite Co., Ltd. All other reagents were of analytical grade, and provided from Tianjin Kermel Chemical Reagent Co. Ltd. (Tianjin, China), and used without further purification.

2.2. Preparation of h-BNNC/GNFs

The synthesis of *h*-BNNC/GNFs has been carried out *via* a wet-chemistry coating and subsequent thermal treatment process as shown in Fig. 1. In a typical procedure, ammonia borane was first dissolved in 1, 4-dioxane to form a clear solution with a concentration of 0.1 mol/L. Secondly, 0.1 g natural graphite nanoflakes were dispersed into the solution by ultrasonication. Then, the as-obtained slurry was maintained at a temperature of 95 °C for 24 h under mechanical stirring followed by the evaporation of 1, 4-dioxane at the same temperature. Finally, the powder collected by filtration and following vacuum drying process were further calcined in a tubular furnace at 1400 °C for 60 min under the protection of high purity argon (100 sccm) to achieve the crystal conversion.

2.3. Structure characterization

XRD spectrum of the as-obtained sample was recorded using Rigaku X-ray diffractometer with Cu Kα radiation, and the diffraction points were recorded from 10° to 80°. The structure of the as-obtained sample was characterized by SEM (TESCAN VEGA II) and TEM (JEM-2100, equipped with EDX system). XPS (Kratos Axis Ultra DLD) operating at 10 mA and 15 kV was utilized to investigate the elemental composition and surface chemical bonds of the as-obtained sample.

2.4. Electromagnetic parameter measurements

To evaluate the MA performance of the samples (natural graphite nanoflakes and *h*-BNNC/GNFs), composite samples were prepared by firstly mixing the sample powders and paraffin wax with mass ratios of 2:3. Then the mixtures were pressed into toroidal shaped rings with inner diameter of 3 mm, outer diameter of 7 mm, and thickness of 3 mm. The electromagnetic parameters of the composites were measured on a vector network analyzer