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Three dimensional hexagonal boron nitride nanosheet/carbon nanotube composites with light weight and enhanced microwave absorption performance

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ABSTRACT

Three dimensional hexagonal boron nitride nanosheet decorated carbon nanotube composites (3D *h*-BNNS/CNTs) have been fabricated through a facile thermal treatment process. *h*-BNNSs randomly distribute among CNTs to form 3D network structure. The microwave absorption properties of these 3D *h*-BNNS/CNTs are obviously improved comparing with those of CNTs. And the minimum reflection loss (RL) can reach up to −36.5 dB when the absorber thickness is 2.5 mm for 3D *h*-BNNS/CNTs1 derived from the precursor with boric acid, urea and CNTs molar ratio of 2:4:1. Besides, the maximum absorption bandwidth (RL ≤ −10 dB) is as large as 4.0 GHz when the absorber thickness drops to 2.0 mm. More important, *h*-BNNS/CNTs1 has a low density of 112.6 ± 3.6 mg/cm^3, which is beneficial for practical applications. The significant enhancement in MA performance of *h*-BNNS/CNTs is mainly attributed to the improvement of impedance matching, interfacial polarization and multiple scattering after introduction of *h*-BNNSs.

1. Introduction

Recently, the popularity of electronic devices as well as the rapid development of radar detection technology has generated a large quantity of electromagnetic waves, resulting in serious electromagnetic pollution. This pollution can not only interfere in the normal functions of highly sensitive electrical equipment, but also are harmful for human beings and wild life [1–4]. Particularly, it can promote the growth of tumors which are seriously threatening human health [1]. In addition, under the condition of modern informatization, the outcome of war is closely related to the discovery speed and detection accuracy of enemies [5]. Generally, weapons and equipment utilized in battlefield, such as stealth aircraft, armor and warships show strong viability, so it is very important to apply different stealth technology to enhance their survivability [6,7]. Currently, radar is the most important system to detect battlefield targets [8], and present research spot for stealth technology against radar detection is mainly focused on the utilization of radar wave absorbing materials. Therefore, the stealth technology has high and emergent requirements on highly efficient microwave absorption (MA) materials.

The research on high-performance MA materials have attracted more and more interests, since their designing and preparation are effective approaches to prevent electromagnetic wave interference and improve defense capabilities [9–12]. Generally, the high efficiency and light weight of MA materials are two main factors to promote their practical applications in commercial, military, aerospace and healthcare fields [13]. Recently, carbon-based composites have attracted considerable attention as electromagnetic shielding and MA materials due to their high efficiency and light weight features. For example, graphene foam/carbon nanotube/poly (dimethyl siloxane) and PMMA/Fe3O4@MWCNTs composites with lightweight and excellent MA properties have been fabricated for exceptional microwave shielding [14,15]. Besides, graphite/SiC hybrid nanowires have also been prepared for MA applications, which present a minimum reflection loss (RL) value of −22 dB at 16.8 GHz with a thin thickness of 1.7 mm [16]. Among the carbon based materials, carbon nanotubes (CNTs) have attracted considerable attention as high-efficient microwave absorbers because of their special electromagnetic properties, light weight, high

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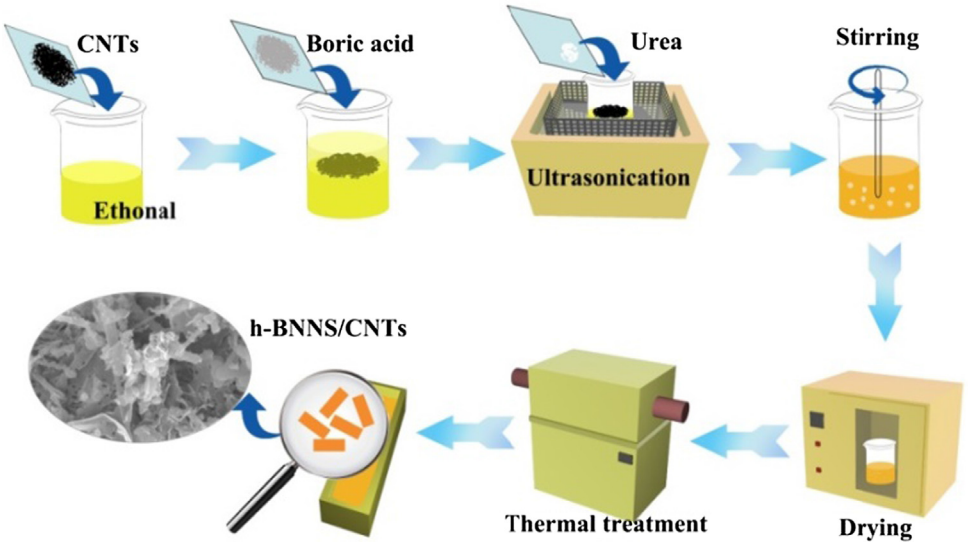

Fig. 1. Schematic illustration for the fabrication of *h*-BNNS/CNT composites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

conductivity, high aspect ratio, good resistance against corrosion and excellent mechanical properties [11,13,17,18]. However, pure CNTs based absorbers show relatively low absorption capacity as well as narrow bandwidth [19–22]. Therefore, to improve the absorption capacity of CNTs to satisfy various practical applications is still highly required. Currently, hybridization of dielectric/magnetic nanomaterials with CNTs is regarded as an effective strategy to improve their MA performance [23]. For example, Wen et al. have fabricated a series of multi-walled carbon nanotubes (MWCNTs)/Fe, MWCNTs/Co, and MWCNTs/Ni nanocomposites by simple chemical method, which exhibit excellent MA properties due to the proper combination of the complex permeability and permittivity caused by magnetic nanoparticles and lightweight MWCNTs [24]. Chen et al. have developed a novel three-dimensional Fe_3O_4 nanocrystal-MWCNTs (3D Fe_3O_4-MWCNTs) composites, which show enhanced double-band MA at various thicknesses in the investigated frequency range of 2–18 GHz [13].

Currently, the hybridization materials with CNTs are mainly focused on the magnetic ones, including metals, metal oxides or metal alloys. Although the hybridization of such magnetic materials with CNTs can effectively improve their MA performance, the poor resistance to corrosion and high density restrict their practical applications since they cannot be used in highly corrosive environment and in large quantity as fillers in absorbers [25–28]. Comparing with magnetic nanomaterials, dielectric materials become more attractive because of their low density as well as high resistance to corrosion. In our previous work, we have demonstrated that the decoration of hexagonal boron nitride nanocrystals (*h*-BNNCs) onto graphite nanoflake surface can effectively improve the MA performance of graphite nanoflakes [9]. A minimum reflection loss (RL) value of −32.38 dB (> 99.99% attenuation) was achieved when the thickness of *h*-BNNC/graphite nanoflake based absorbers was 2.0 mm, and this MA performance is superior to the other graphite based MA materials recently reported [9]. This result indicates that the introduction of *h*-BN can effectively improve the MA performance of carbon based materials through adjusting the multiple scattering, interface polarization as well as the improvement of electromagnetic impedance matching [9].

h-BN, as a structurally analogue to carbon materials with almost the same crystal lattice parameters, possesses larger electrical resistivity and cannot influence the attenuating electromagnetic wave energy of CNTs [9,29]. Additionally, *h*-BN exhibits low density, remarkable mechanical properties, high chemical inertness and thermal stability, excellent resistance to oxidation, making it very attractive for producing ideal electromagnetic MA composites with CNTs. Therefore, in this report, *h*-BN nanosheets (*h*-BNNSs) were selected to hybridize with CNTs to adjust their electromagnetic parameters. These special *h*-BNNS/CNT composites were fabricated through a facile thermal treatment process with boric acid, urea and CNTs as precursors. The density of the as-obtained h-BNNS/CNT composites was calculated in term of weighing method. The composition and structure of the as-obtained *h*-BNNS/CNT composites were confirmed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), transmission electron microscope (TEM), and energy dispersive X-ray spectroscopy (EDX). The relevant MA performance of these *h*-BNNS/CNT based absorbers with different thicknesses was systemically investigated in the frequency range of 2–18 GHz. Finally, the mechanism for the enhanced MA properties of these as-obtained *h*-BNNS/CNT composites was also studied in detail.

2. Experimental

2.1. Material

CNTs were supplied by XF NANO Technology Co., Ltd. Boric acid (99.5%) and sodium dodecyl sulfate (SDS, 99.5%) were supplied by Tianjin Hengxing chemical Preparation Co., Ltd. (Tianjin, China). Urea (99%) was purchased from Tianjin Beichen Founder Reagent Factory (Tianjin, China).

2.2. Fabrication of h-BNNS/CNT composites

As illustrated in Fig. 1, dried urea, boric acid and CNTs were firstly mixed with ethanol solvent in a certain ratio to prepare a suspension, and a small amount of SDS was added as a dispersant to prevent agglomeration. Subsequently, the mixture was ultrasonicated at room temperature for 30 min followed by heated at 75 °C under stirring. When the ethanol was completely evaporated, the powder was transferred into a drying oven and dried at 60 °C for 2 h. Finally, the powder was shifted to a tube furnace for thermal treatment at 1400 °C under the protection of N_2. The precursors with the molar ratios of boric acid, urea, and CNTs were 2:4:1, 2:4:2, 2:4:3, 2:4:4, and 2:4:5, and the resultant samples were named as *h*-BNNS/CNTs1 to *h*-BNNS/CNTs5 according to the ratios of CNTs in the precursors. In addition, the sample derived from the precursor with boric acid and urea molar ratio of 2:4 was also prepared for comparison,