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Ultralight lamellar amorphous carbon foam nanostructured by SiC nanowires for tunable electromagnetic wave absorption

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ABSTRACT

Three-dimensional hybrid foams of SiC nanowires (SiC NWs) coated and bonded with nanostructured lamellar carbon films are, herein synthesized for the first time, by combination of unidirectional freeze drying and carbonization techniques. The crystallinity of the carbon films was tunable from amorphous carbon to graphene-like carbon by heat treatment of the as-received hybrid foams to different temperatures within the range of 600–1500 °C. The SiC NWs-nanostructured lamellar carbon (SiC NWs/C) hybrid foams exhibited electromagnetic (EM) wave absorbing properties highly superior to current state-of-the-art counterparts, at filler loadings as low as 9.2 mg/cm^3. Effective absorption bandwidth of the SiC NWs/C foam was observed to cover the whole X-band frequency range of 8.2–12.4 GHz, with reflection loss values reaching −31 dB for an optimum thickness of 3.3 mm. The absorption efficiency of the SiC NW/C hybrid foams is discussed in the text in view of the highly absorbing layered morphology of the developed material, of interfacial polarization and multiple reflections effects and of polarization relaxation effects.

1. Introduction

Electromagnetic (EM) wave pollution is responsible for significant interference to wireless communications and electronic instruments which harms the operational safety of corresponding equipment. In military operations specifically, the target acquisition capability is greatly improved with the rapid development of modern electronic technology and detection systems [1–4]. A great part of EM pollution resides in high frequency bands such as the X-band occupying the range of 8.2–12.4 GHz [5]. Key to preventing such undesirable interference is the development of thin electromagnetically absorbing materials with wide absorbing ranges and strong absorbing efficiencies which meet the requirements of modern electromagnetic absorption applications and aid the electromagnetic purification of the environment [6,7].

Carbon-based materials, such as reduced graphene oxide (rGO), carbon nanotubes (CNTs), carbon fibers and colloidal elemental carbon, have attracted extensive attention as high-performance EM wave attenuation candidates owing to their low weight, high dielectric loss and high electronic conductivity [8–13]. Recent advances show that 3D reduced graphene oxide foams exhibit significant EM absorption features due to their ultralow density and interconnected conductive network [14–17]. Zhang et al. reported that the absorption bandwidth of macroscopic rGO foams can reach 50.5 GHz [8]. However, the thickness of pure rGO foams required for efficient absorbance of such radiation can be as high as 10 mm. It is currently suggested that combining rGO and dielectric materials could be an efficient route for improving the absorption efficiency and broadening the effective absorption bandwidth (EAB) of EM absorbers [18,19].

Silicon carbide (SiC) is an important dielectric material combining a broad frequency absorption band with excellent thermal and chemical stability at room and high temperatures [20]. Previous works indicate that silicon carbide's EM properties are optimum when the material is of nanoscale dimensions, as for example is the case with β-SiC nanowires (NWs) which, compared to bulk SiC, deliver higher EM loss contribution [21,22]. Such NWs are considered excellent candidates for EM absorbing applications due to their high specific surface areas, abundant stacking faults, twinning interfaces and adjustable electrical conductivity [23–25]. Foams of rGO and in situ-grown SiC NWs were very recently synthesized for the first time by freeze-drying and carbothermal reduction processes [26,27]. Therein, SiC NWs grew on the surface

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of rGO, hence limiting the extent of the interface region between the two phases whereas the EM absorption capacity of the material could be adjusted by controlling the quantity of SiC NWs under a fixed rGO phase [27].

Recent findings by Kang et al. indicate that absorption is greater in layered structures where the possibilities of electron migrating and hopping for microwave consumption are increased compared to plain structures [18]. We have recently shown that similar layered morphologies can be accomplished as a result of the forced phase separation due to macroscopic growth of columnar ice during freeze-drying-based synthesis of porous SiC NWs/SiC ceramics [28,29]. In such layered 3D-structured materials, the vast amount of interfaces is anticipated to multiply EM transmission path and consume significant amount of EM energy. We believe that by coating the specific morphology with a controlled thin carbon film, even more efficient EM wave attenuation could be achieved.

The aforementioned ideas constitute the motivation behind the research presented here, wherein, interconnected SiC NWs skeletons coated by nano-structured lamellar carbonaceous thin films were prepared for the first time using ice templating method. The films which offered the necessary bonding to the SiC NWs structure, were fabricated by carbonizing CMC (carboxymethyl cellulose) films. The resultant hybrid material exhibited foam morphology comprised of unidirectional SiC NWs/carbon lamellae and is, thereafter, termed SiC NWs/C 3D hybrid foam. The study demonstrates that by heat treatment of the nanostructured films at varying temperatures, different film morphologies ranging from amorphous carbon to graphene-like structure with different graphitization degrees can be achieved hence enabling tuning and optimization of the EM absorption properties of the hybrid foams.

2. Experimental

2.1. Preparation of SiC NWs/C hybrid foam

Initially, 0.8 g of β-SiC NWs (Sinet Advanced Materials Co. Ltd., Changsha, China) of diameters in the range of 0.1–0.6 μm, lengths in the range of 50–100 μm and of purity greater than 96%, were added in 100 ml of 0.8 wt% aqueous carboxymethyl cellulose solution (CMC; viscosity 600–1000mpa.s, UPS, Aladdin, Shanghai). SiC nanowire dispersion was achieved by ultrasonication of the suspension for 1800 s in a BILON-1500 ultrasonic homogenizer (Xian Bilon Biological Technology Co. Ltd., Xi'an, China). The purpose of CMC presence was the formation of carbonaceous films which would bond the SiC NWs during the freeze-drying process. The resultant slurry was poured into a mold composed of two parts: a metallic one, with high thermal conductivity, attached to the mold bottom, and the mold side made of polytetrafluoroethylene (PTFE), of lower thermal conductivity than the primer part. The mold was subsequently placed on the stainless-steel circular tray of a freeze-dryer (LGJ-18S, Song Yuan Hua Xing Science and Technology Develop Co. Ltd., Beijing, China) which was precooled at Ts = −80 °C. A schematic of ice templating method is shown in Fig. 1 [28]. During the freezing process, the slurry in the special mold froze unidirectionally because of the higher thermal conductivity of the bottom metal part of the mold compared to that of PTFE side. Columnar ice growth was forced to occur macroscopically in the vertical direction, causing the phase separation of ice and the mixture layer of nanowires and CMC. After the slurry froze completely, vacuum conditions were imposed by a vacuum pump and the stainless steel circular tray was heated and the frozen specimens lyophilized. At the end of the sublimation step, the 3D hybrid foam of interconnected SiC NWs skeletons supported by unidirectional CMC thin film (SiC NWs/CMC) was formed. Freeze-drying allowed for achievement of monoliths which preserved the size and shape of the parent container submitted to freezing.

The SiC NWs/CMC hybrid foams were heated to 600 °C under inert (Ar) atmosphere for 2 h, for carbonization of CMC and obtainment of the SiC NWs/C 3D hybrid foams. Different foams were subsequently heated to 600, 900, 1200 and 1500 °C under inert (Ar) atmosphere for 2 h, respectively, for inducing crystallization of varying degrees to the carbon films. Ultimately, the SiC NWs/C foams were purified for removal of unwanted substances, such as free Na, in deionized water solution of HCl [30]. Foams were designated as F-600, F-900, F-1200 and F-1500 respective to the different heat treatment temperature (600, 900, 1200 and 1500 °C).

2.2. Characterization

The morphology of foams was observed under scanning electron microscopy (SEM; S-4700, 15 kV, Hitachi, Japan) and transmission electron microscopy (TEM; JEM-2100F, 200 kV, JEOL, Japan). The phase composition of the foams was examined by X-ray diffraction (XRD; X' Pert Pro, PANalytical B.V., The Netherlands) using Cu Kα radiation. Raman spectra were recorded on an inVia confocal Raman Microscope system (Renishaw, U.K.) equipped with a laser source of wavelength of 532 nm. Thermogravimetric-differential scanning calorimetry (TG-DSC) analysis was carried out in a TGA/DSC 1 analyzer (Mettler Toledo, Switzerland) in the temperature range of 25–1500 °C with a heating rate of 10 °C min^{-1}.

Next, standard-shaped samples for electrical conductivity and dielectric measurements were prepared by encapsulating SiC NWs/C hybrid foams in epoxy resin. As an insulator, epoxy resin has an imaginary permittivity in X-band (8.2–12.4 GHz) which is zero while is also features negligible electrical conductivity and dielectric loss contribution [31]. As-prepared SiC NWs/C hybrid foams (F-600, F-900, F-1200 and F-1500) were impregnated with the epoxy resin/curing agent mixture under the assistance of vacuum conditions. The samples were thermally cured at 140 °C with a post-curing/hardening step at 160 °C for 12 h. Room temperature electrical conductivity of the hybrid foam/epoxy samples was measured using a Keithley 6220 Low Noise Precision DC Current Source (Tektronix, Oregon, USA). The effective complex permittivity of the foam/epoxy with dimensions of 22.86 × 10.16 × 2.00 mm^3 was measured by a waveguide method using a vector network analyzer (VNA; MS4644A, Anritsu, Japan) in the X-band frequency range (8.2–12.4 GHz). Foam/epoxy samples were designated as S-600, S-900, S-1200 and S-1500 respective to different heat treatment temperatures (600, 900, 1200 and 1500 °C).

3. Results and discussion

3.1. Characterization of SiC NWs/C hybrid foam

The macro- and micro-scopic morphologies of fabricated SiC NWs/CMC and SiC NWs/C hybrid foams observed under optical microscope are shown in Fig. 2. In Fig. 2a, depicting freestanding SiC NWs/CMC and SiC NWs/C foams, the primer foams are seen to demonstrate the same chartreuse color of as-received SiC NWs. After carbonization, the macroscopic appearance of SiC NWs/C foams heat-treated up to 1200 °C was similar to the originating SiC NWs/CMC, albeit a darkening in color caused by CMC-prone carbon. At a heat treatment temperature of 1500 °C, foam color turns grey and slight volumetric contraction appears.

Fig. 2b–c presents SEM micrographs of the as-fabricated SiC NWs/CMC hybrid foams. Fig. 2b is a top view of the foam, from a plane perpendicular to that of ice formation. The lamellar structure of SiC NWs bonded by CMC film is observed; the inter-lamella distance ranges between 100 μm and 200 μm. Fig. 2c