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Hierarchical graphene/SiC nanowire networks in polymer-derived ceramics with enhanced electromagnetic wave absorbing capability

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ABSTRACT

A high-performance electromagnetic wave absorbing composite based on graphene and polysiloxane-derived SiOC ceramic is realized via the polymer pyrolysis process. Hierarchical architecture consisting of two-dimensional graphene and one-dimensional SiC nanowire in ceramic matrix is achieved owing to the heterogeneous nucleation of SiC nanowires promoted by graphene at lower temperature. The dielectric and microwave absorption properties of the composites were studied at 293–673 K. When graphene oxide loading is 3 wt%, the composite attains a minimum reflection loss value of −69.3 dB at 10.55 GHz with a thickness of 2.35 mm. With the increase of temperature, the composite exhibits better absorbing performance that the effective absorption bandwidth reaches 3.9 GHz at 673 K. The hierarchical networks with graphene/SiC nanowires achieved in SiOC matrix provide a feasible process for the realization of efficient electromagnetic wave absorption in ceramic-based composites at high temperature.

1. Introduction

With the explosive growth of electronic apparatuses, such as high-power radar, communication antenna and microwave heating devices, electromagnetic (EM) wave absorbing and shielding materials have drawn extensive attentions to reduce EM pollution [1–6]. Reduced graphene oxide (rGO), which has abundant residual oxygen functional groups and large surface area coupled with high mechanical flexibility, moderate conductivity and unique two-dimensional (2D) structure, provides a great platform to achieve good EM wave attenuation and tunable frequency, while pristine graphene is an excellent candidate for EM shielding materials [7–15].

Up to now, the studies on multiple-phase hybrids based on rGO aiming to obtain more polarizations along with relaxation behaviors have made significant progress [16–20]. The hybrid materials with hierarchical architectures have demonstrated a new stage to enhance EM absorbing capability [21,22]. More recently, rGO-based composites with three-dimensional (3D) hierarchical structures, which possess bridged conductive network and multiple interfaces with large surface area, have presented great potential [10,23,24]. In a typical example, graphene aerogels with in-situ grown carbon nanotubes (CNTs) were prepared using chemical vapor deposition, and the 3D architecture was demonstrated to achieve high electronic transportation and strong polarizations [23].

As one kind of important semiconductor materials, one-dimensional (1D) SiC nanowire is a good candidate for EM wave absorbing materials at high temperature, owing to its high thermal stability, chemistry resistivity and adjustable electronic conductivity, besides its high surface-to-volume ratio which has the advantages similar to CNTs for microwave absorption [25,26]. Therefore, the absorber with hierarchical structure combining rGO with SiC nanowires could achieve efficient EM wave attenuation. Recently, Dai et al. has succeeded in preparing the three-dimensional structure composed of SiC nanowire and graphene sheets by a high frequency heating process [27]. Unfortunately, this structure only can be the filler in a polymer matrix which cannot be applied in high temperature. The hierarchical structure based on graphene in ceramic-based EM absorbing materials which play important roles in harsh environments still cannot be achieved [28–31]. The major challenge associated with graphene/ceramic composites is that the conventional molding and sintering processes hinder the formation of multiple dimensional architectures.

In this study, a feasible and simple strategy based on polymer-derived ceramics (PDCs) for the achievement of hierarchical rGO/SiC nanowire network in ceramic matrix is reported. Graphene oxides (GO) were mixed stably and uniformly with the liquid polymer precursor via tetrahydrofuran (THF) and low temperature curing. Significantly, during the pyrolysis and sintering process, the in-situ growth of SiC nanowires was achieved, owing to that

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rGO lowered the nucleation temperature of SiC nanowires in SiOC ceramic as nucleating agent. The hierarchical architecture combining rGO and SiC nanowires is demonstrated to enhance EM wave attenuation through the subsequent dielectric measurement. To the best of our knowledge, the G/SiOC ceramics exhibit an optimum EM absorption performance for PDC-based absorbing materials at room and high temperatures. Moreover, the fundamental reflection loss mechanisms based on effective complex permittivity and conductivity are also discussed.

2. Experimental

2.1. Preparation of rGO/SiOC ceramics

Graphene oxide (XF Nano Materials Tech Co., Nanjing) was prepared using the modified Hummers' method [32]. Polysiloxane (PSO) and curing agent were supplied by University of Chinese Academy of Science (Beijing, China). All the chemicals in the experiments were used without further purification.

In a typical preparation procedure (Fig. S1), 0.13 g of GO was dispersed in 250 mL of THF under sonication for 4 h. The obtained suspension was added into the mixed solution consisting of 3.5 g of PSO and 100 mL of THF under stirring. The curing agent containing 1.5 wt% Pt (5 ppm of PSO) was dropped into the solution under stirring at 50 °C until THF volatilized absolutely. The uniformly mixed GO/PSO precursor was obtained with the curing process at 175 °C for 2 h. The as-obtained precursor was cold pressed into green body under a pressure of 70 MPa after being ball milled for 10 h. The green body was pyrolyzed at 900 °C and then sintered at 1400 °C for 2 h in a flowing argon atmosphere. In order to measure the dielectric properties, rGO/SiOC ceramics with different proportion of GO (1, 2, 3 and 5 wt%) were prepared. In addition, the pure SiOC ceramic prepared with the same sintering process was supplied for comparison.

2.2. Characterization

The morphology of the as-prepared samples was examined by scanning electron microscopy (SEM; S-4700, Hitachi, 15 kV, Tokyo, Japan) and transmission electron microscopy (TEM; F-30, FEI-Tecnai, 300 kV, Hillsboro, USA). X-ray diffraction (XRD) measurements were carried out on an X′ Pert Pro system (Philips, Almelo, The Netherlands), using Cu Ka (λ = 1.54 Å) radiation. Raman spectra were obtained on a Renishaw Ramoscope (Confocal Raman Microscope, inVia, Renishaw, Gloucester-shire, U.K.) equipped with a He-Ne laser (λ = 514 nm). X-ray photoelectron spectra (XPS) were recorded using a Thermo Scientific X-ray photoelectron spectrometer (K-Alpha, Thermo Scientific, Waltham, MA, USA).

The effective complex permittivity of the as-received samples with dimensions of $22.86 \times 10.16 \times 2.0\,mm^3$ was measured at temperature ranging from 293 K to 673 K, using a vector network analyzer (VNA, MS4644A; Anritsu, Japan) in X-band (8.2–12.4 GHz). The high-temperature waveguide measurement system was shown as Fig. 1. During the measured process, the as-prepared samples were placed vertically in the centre of testing chamber. The set-point temperatures were held 10 min to ensure the accuracy of data. In order to avoid the testing error, the waveguide system was calibrated at room temperature. The direct-current electrical conductivities of the samples were measured using a high resistance meter (4339B, Agilent, USA) equipped with a temperature controller (TP94, Linkam, Surrey, U.K.) over a temperature range of 293–673 K at a heating rate of 20 °C/min. Silver electrodes were coated on both surfaces of the samples to form a metal–insulator–metal (MIM) capacitor for the electrical test. In order to avoid testing error as much as possible, the conductivity was confirmed by the testing data at the same set-point during the cooling process.

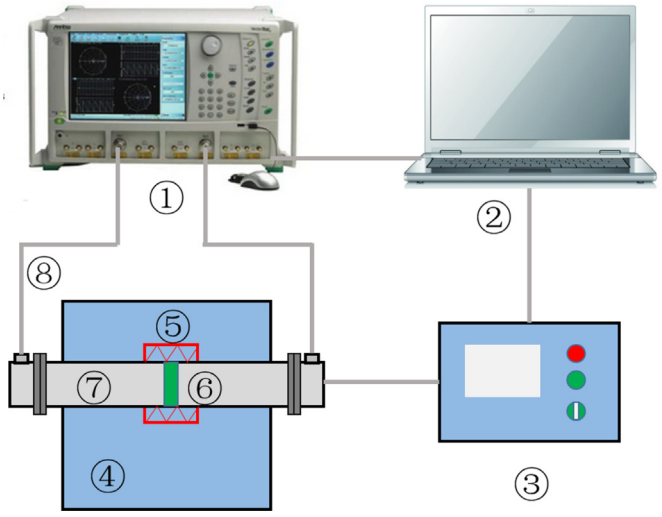

Fig. 1. Illustration of the high-temperature waveguide measurement system: (1) VNA, (2) computer, (3) the temperature controller, (4) the cooling system, (5) the heater, (6) the sample, (7) the waveguide chamber and (8) coaxial cable.

3. Results and discussion

3.1. Characterizations of G/SiOC ceramics

The morphologies of as-prepared SiOC and G/SiOC ceramics with 3 wt% GO loading were examined by SEM. Fig. 2a shows the typical SiOC structure with plenty of macropores which provide sufficient space for the in-situ growth of SiC nanowires. When the precursor homogeneously mixed with GO was sintered, it is observed that graphene sheets tightly wrapped on the surface of SiOC matrix, as presented in Fig. 2b. The local magnified image is shown in the upper right inset, in which the separated graphene edge is flexible and thin. The surface of SiOC ceramic is smooth, yet the G/SiOC ceramic exhibits rough textures, which are associated with the presence of the graphene sheets (Fig. S2). Fig. 2c presents a view of G/SiOC with 3 wt% GO composites. Owing to the addition of GO, SiC nanowires were in situ grown in the pores of SiOC matrix. As shown in Fig. 2d, linear SiC nanowires with a sharp tip are observed, and the length reaches several micrometres. 1D nanowire and 2D graphene formed unique 3D hierarchical absorbing architecture. In order to further investigate the microstructure, the TEM images were performed. As shown in Fig. 2e, SiC nanowire with a diameter about 50 nm can be observed clearly, associating with SiOC matrix and flexible few-layer graphene (FLG; Fig. S3). The high-resolution transmission electron microscopy (HRTEM) image presents the interface spacing of 0.25 nm belonging to (1 1 1) plane of β-SiC. The corresponding selected area electric diffraction (SAED) pattern indicates the existence of dense stacking faults, which originates from the environmental disturbances [33].

Fig. 3shows the details of connected SiC nanowires in G/SiOC with 3 wt% GO composites. As shown in Fig. 3a, SiC nanowires are connected with others. The TEM analysis provides clearer images of the joint (Fig. 3b and c). The HRTEM image indicates the point of contact was packed by the amorphous phase which is the typical medium to connect the SiC nanowires. This structure facilitates the building-up of conductive network which is of benefit to the conductive loss. In addition, the defects at the point of join can contribute to the orientation polarization.

The as-prepared G/SiOC ceramics were further characterized by XRD and Raman to identify the crystallographic structure and