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Synthesis of SiC nanofibers with superior electromagnetic wave absorption performance by electrospinning

Peng Wang [a, b], Laifei Cheng [a, b, *], Yani Zhang [a, b], Litong Zhang [a, b]

[a] Science and Technology on Thermostructural Composite Materials Laboratory, Northwestern Polytechnical University, 710072, Xi'an, China
[b] State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, 710072, Xi'an, China

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ABSTRACT

A method combined electrospinning and preceramic polymer pyrolysis, annealing has been developed to fabricate SiC nanofibers. In this work, the effects of polycarbosilane (PCS) mass ratio (8.7 wt% ~ 11.8 wt%) in precursor solution on microstructure and electromagnetic (EM) absorption properties of SiC nanofibers are systematically studied. The phase composition of SiC nanofibers are mainly inclusive of abundant SiC nanocrystallines, a small quantity of graphitic-like carbon coated on fibers surface and randomly distributed amorphous SiO_xC_y phase. When PCS mass ratio is 10 wt%, the SiC nanofibers present a minimum reflection loss (RL) value of −57.8 dB at 14.6 GHz with a absorber coating thickness of 1.9 mm and the effective absorption bandwidth (RL < −10 dB, 90% EM wave absorbed) covers from 6 to 18 GHz. As PCS mass ratio increasing, the EM absorption performance of SiC nanofibers gradually becomes poor. Multi-reflection among SiC nanofibers gradually weaken the incident EM wave. Moreover the interfacial polarization originated from heterogeneous interfaces which exist among SiC nanocrystallines, graphite carbon, amorphous SiO_xC_y dissipates EM wave energy contributed to high EM performance of SiC nanofibers. This work demonstrates a new kind of nano SiC EM absorption materials that has potential to be applicated in harsh environments.

1. Introduction

Now with the rapid development of electronic information technology, the electromagnetic (EM) wave pollution generated by the increasing employment of advanced electronic devices has become a thorny problem [1–5]. The EM pollution not only have a harmful effect on human health which weaken immune system and cause cancers but also affect the operation of highly sensitive precision electronic equipments which are applicated in civil, commercial and military fields [6,7]. In order to deal with EM pollution problems, considerable efforts have been made to explore high performance EM wave absorption materials in the gigahertz (GHz) band which have low density, stronger absorption capability, broad effective absorption bandwidth (EAB), thinner thickness, high temperature stability, superior anti-oxidation properties *etc* [8–13].

Owing to their high mechanical strength, high temperature stability, corrosion resistant properties in alkali and acid environment, unique EM wave absorption characteristics, one dimension SiC nanomaterials and their composites have been considered as suitable candidates for EM wave absorbers [14–17]. According to the reported literature, conventional one dimensional SiC nanomaterials are mainly inclusive of SiC nanowires (SiCNWs), SiC nanobelts, SiC nanotubes, SiC whiskers and so on [14,16,18–22]. Generally SiCNWs can be able to used as reinforcements to toughening ceramic matrix composites also enhancing their EM wave loss ability [23–25]. Many researchers have put lots of efforts for investigating dielectric and microwave absorption characteristics of SiCNWs. Wu et al. synthesized SiCNWs through molten-salt-mediated method and paraffin composites loaded with 30 wt% SiCNWs demonstrated a minimum refection loss (RL of −17.4 dB at a coating thickness of 3 mm with a 2.5 GHz effective absorption bandwidth [26]. Zhang and coworkers investigated the effects of stacking faults and unoccupied densities of state on EM properties of SiCNWs and the nanowires obtained from 1400 °C represented a minimum RL value of −30 dB at a thickness of 4.6 mm and its EAB covered a frequency range of 3.7 GHz [27]. Chiu et al. studied the

* Corresponding author. Science and Technology on Thermostructural Composite Materials Laboratory, Northwestern Polytechnical University, 710072, Xi'an, China.
E-mail addresses: wangpengnwpu@126.com (P. Wang), chenglf@nwpu.edu.cn (L. Cheng).

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EM absorption properties of SiCNWs/epoxy composites and found that the composites loaded with 35 wt% SiCNWs present a minimum reflection loss of −31.7 dB at 8.3 GHz with a thickness of 2 mm and its EAB only covers 2.5 GHz from 7.1 to 9.6 GHz [16]. However single polarization mechanism, lower impedance matching and poor dielectric loss for pure SiCNWs can't fulfill higher requirements for high EM performance of absorbers i.e. lower reflection loss (RL < −20 dB), wider absorption bandwidth (>4 GHz), smaller absorber coating thickness (<2 mm) *etc* [28].

Therefore recently doping or hybridizing with magnetic metal or metal oxides for SiCNWs have become a hot point for improving their EM performance. Liang et al. have fabricated SiC-Fe_3O_4 dielectric-magnetic hybrid nanowires, the reflection loss of paraffin composites contained 50 wt% hybrid nanowires can be as low as −51 dB also by changing the loading of Fe_3O_4 the best microwave absorption performance can be achieved in 2–18 GHz [29]. Wang and coworkers reported the EM properties of Co/SiC hybrid nanowires and found that its EAB covers a frequency range of 10–16.6 GHz when the Co content is 25.1 wt% in the hybrids [30]. Sun et al. have synthesized 3D ZnO nano-crystals grown on 1D SiCNWs and wax composites loaded with 30 wt% as-prepared samples showed enhanced attenuation peaks beyond −40 dB at a thickness of 3.5 mm with an effective absorption bandwidth of 6.6 GHz [31]. It is very clear that EM wave loss capability of SiCNWs can be improved a lot by hybridizing with metal or metal oxides. However these additives generally have their large density and are susceptible to corrosion which can not fulfill fast growing demands for high performance EM absorbers. Additionally for magnetic additives their magnetic loss characteristics will disappear when working temperature is higher than their curie temperature.

Owing to their highly flexible designability in precursor, the preceramic polymer-derived ceramics is an interesting and attractive method towards fabricating ceramic fibers, whiskers, and composites [32,33]. Through doping or modification of precursor, ceramics such as SiC, Si_3N_4, SiOC with improved dielectric and electromagnetic shielding or absorbing properties can be achieved [34]. The microstructure and chemical composition of the resulted ceramics can be tailored by changing the polymer/filler ratio. Polycarbosilane (PCS) have always been used as precursor to synthesize SiC nanocrystallines, SiC fibers, SiCNWs *etc*. After high temperature pyrolysis, PCS would be decomposed into main phase of SiC, free carbon, bits of amorphous SiO_xC_y. Large quantities of heterogeneous interfaces formed among SiC, free carbon, amorphous SiO_xC_y. Interfacial polarization caused by heterogeneous interfaces have always played an important role in detemining EM performance of absorbers [35,36]. With the fast development of advanced manufacturing technology, owing to their cost effective, facile, versatile, electrospinning (ESN) has been widely used to fabricate various nanofibers, nanowires, nanotubes *etc* on a large scale [37,38]. A high voltage was applied between the spinneret and collecting substrate, the solution ejected form spinneret exposed with a charge and then was transformed into thin nanofibers of tens to hundreds nanometers in diameter by strong electric field. Up to now, various kinds of supercapacitors, lithium-ion batteries, photocatalysis, gas sensors, EM wave absorbers i.e. can be produced by electrospinning [39]. By electrospinning, self-assembly SiC nanofibers mainly contained SiC nanocrystallines, free carbon, amorphous SiO_xC_y were prepared. As far as we know up to now very few works on fabrication of SiC nanofibers have been reported. Furthermore the potential of SiC nanofibers as EM wave absorbers has not been discovered yet.

Combined the ESN technique with polymer-derived ceramics method, we successfully fabricated SiC nanofibers with excellent dielectric and EM wave absorption properties over the frequency range of 2–18 GHz. Polycarbosilane was used as precursor of SiC, the mixture of chloroform and dimethyformamide (DMF) as the solvent. Polyvinylpyrrolidone (PVP) was added into solution to increase the spinnability then was removed through subsequent high temperature pyrolysis. By adjusting the mass ratio of PCS in precursor solution, it is found that both reflection loss values and effective absorption bandwidth of SiC nanofibers can be tuned. Moreover the fundamental mechanism for their improved EM performance are also discussed.

2. Experimental section

2.1. Materials

Polycarbosilane (PCS, 1400–1680 g/mol) was obtained from the Xiamen university, China. Polyvinylpyrrolidone (PVP, 1300000 g/mol) was purchased from Shanghai Maclin Biochemical Co. Ltd., China. All organic solvents were purchased from Changsha Huihong Co. Ltd., China, and used without further purification. High purity argon was purchased from Changsha Jingxiang Co. Ltd., China.

2.2. Fabrication of SiC nanofibers

Initially 4.3 wt% PVP were added into the mixture solvent of N'N-dimethylformamide, chloroform with weight ratio of 1:4, followed by vigorously stirring for 2 h. Then the PCS were added into homogenous solution, a series of products were prepared, to give different PCS mass ratio: 8.7 wt%, 10 wt%, 10.7 wt%, 11.5 wt%, 11.8 wt % respectively followed by dramatically stirred for 24 h. The homogeneous solution was then transferred into a 10 ml plastic syringe with a 21 G spinneret and the collector is a stainless steel plate coated with a graphite paper. During electrospinning, the distance between spinneret and collecting substrate is 16 cm, the electrospinning voltage (V) is 20 kV, and the fed rate of precursor (Q) is 2.388 ml/h. The electrospun PCS/PVP nanofibers were collected on graphite paper substrates. The details about SiC nanofibers preparation are shown in Fig. 1a.

The electrospun PCS/PVP nanofibers were maintained in vacuum at 70 °C for 24 h to vapor the solvent out completely. To maintain the fibers shape in the procedure of heat treatment, the fibers must be cured. The PCS/PVP nanofibers were cured in a muffle furnace from room temperature to 180 °C with a heating rate of 2 °C/min, then to 210 °C with a heating rate of 1 °C/min and holding for 2 h in air.

Finally a series of cured nanofibers were put in a tubular furnace for annealing, from room temperature to 250 °C with a heating rate of 2 °C/min, then to 850 °C with a heating rate of 1 °C/min (the details are shown in Supporting information) then the temperature of the furnace ramped to 1300 °C at a rate of 2 °C/min and maintained at that temperature for 2 h. The final products were marked as PCS-8.7, PCS-10.0, PCS-10.7, PCS-11.5, PCS-11.8.

2.3. Characterization

A Hitachi S-4700 Field-Emission Scanning Electron Microscope (FE-SEM) was used to explore the morphology of nanofibers with an acceleration voltage of 15.0 kV. Gold (5 nm) was sputtered on all nanofibers using a scanning electron microscope coating unit (E−1010) from Polaron Equipment Limited. X-ray diffraction (XRD) data were collected from 10 to 90° (2θ) by Bruker AXS D8 Advance device using Cu-Ka radiation (λ = 1.54 Å) with a scanning rate of 2θ = 0.05° per second. Raman spectra were obtained on a Renishaw Confocal Raman Microscope (in Via, Renishaw, Gloucestershire, U.K.) equipped with a He–Ne laser (λ= 532 nm). Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM,