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Original Research Paper

Silicon carbide/carbon nanotube heterostructures: Controllable synthesis, dielectric properties and microwave absorption

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ABSTRACT

Carbon nanotube (CNTs) based heterostructures, such as CNT/metal, CNT/polymer, CNT/semiconductor, are attractive for the combined properties and unique applications in cutting-edge electronics and devices. Here in this work, nanostructured beta-silicon carbide (β-SiC)/CNTs heterostructures were synthesized by carbothermal reduction of silica (SiO_2) and CNTs with diverse mixing ratios of n_C:n_{Si}. Different techniques were carried out for the characterization of the structures and morphologies of the achieved heterostructures, demonstrating dramatic different morphologies which were associated with the different starting ratios of the n_C:n_{Si}. The dielectric properties and microwave absorption of wax-based composites were investigated. The parameters for morphologically controllable synthesis and related mechanism for dielectric properties and electromagnetic attenuation were discussed.

1. Introduction

Carbon nanotubes (CNTs) with attractive properties such as high strength, excellent flexibility, low density, outstanding electromagnetic (EM) characteristics and high thermal transport [1–4], have been investigated for possible applications in mechanical reinforcement, nanoelectronic devices, EM wave absorbers, field emitter, etc. [5–8]. However, the defective oxidation of CNTs limits their applications at high temperatures. CNTs are thus always incorporated into a second phase such as metals, polymers and ceramics to fabricate CNT-based composites [9–11]. The appropriate matrices and their compatibility with CNTs are important to CNT-based composites. Silicon carbide (SiC) ceramics are well-known high-temperature applied materials, which possess remarkable mechanical and electrical properties [12]. The CNT/SiC ceramic composites are promising for potentials in structural materials coupled with both excellent mechanical and EM attenuation properties. However, there are great challenges in the nanotube dispersion and nanotube/matrix interaction [13]. Recent literature have suggested effective approaches by modifying CNTs surface with nano-sized SiC, thus resulting in CNTs miscible in ceramic matrices. Morisada et al. [14,15] suggested that the SiC-coated CNTs synthesized by chemical vapor deposition (CVD) via SiO (g) and CO (g) in SiC matrices could increase microhardness by 20% and toughness by 12.5%. Lupo et al. [16] reported that the nanometric zirconia particles grown on CNTs were observed to form a ceramic layer by a hydrothermal process. Our previous work has also demonstrated the ceramic coatings could improve the weak adhesion between CNTs and various ceramics matrixes, showing good dispersion of CNTs [11,17].

In this work, we reported a novel carbothermal reduction route to produce SiC-coated CNTs heterostructures, aiming at increasing defects to enhance the dielectric loss and improve interfacial connections of CNTs in matrices. Silica (SiO_2) and multi-walled carbon nanotubes (MWCNTs) were selected in the carbothermal reduction, and different resulting morphologies were found mainly due to the different ratios of n_C to n_{Si}. The resulting samples were fabricated into wax-based composites for further dielectric and microwave attenuation investigation. The corresponding dielectric and microwave absorption properties of the MWCNT-based heterostructures were discussed.

2. Experimental

The MWCNTs, purchased from Sun Nanotech Co. Ltd., China, used in this work were fabricated by CVD (20–40 nm diameter, 5–20 μm length, 1.8 g/cm^3 density). In the typical pre-treatment,

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the commercial MWCNTs were soaked in an acid blend (98% sulfuric and 68% nitric acids, 3:1 in volume) for about 72 h after ultrasonic stirring for 2 h, followed by washing the samples until neutral pH value in the washing solution. The pretreated MWCNTs were re-dispersed in ethanol by ultrasonic stirring, followed by adding to the silica sol prepared with tetraethoxysilane (TEOS), ethanol and distilled water by a sol–gel process [18]. The pH value of the mixed suspension was adjusted to 9 by adding ammonia water, and the resulting mixture was transferred to the vacuum oven for drying at 50 °C. The mol ratios of MWCNTs to SiO_2 were 3:1, 5:1 and 8:1 in each individual process, respectively. Subsequently, the resulting dried powders were transferred to a tube furnace. After evacuation of the furnace chamber to about 20 Pa, a high-purity (99.99%) argon gas was introduced at a constant pressure of 0.1 MPa and a flowing rate range of 0.5–2 L/min during the calefactive process. When the temperature reached to 1400 °C by the rate of 15 °C/min, stop to provide argon gas and occlude the reaction system. Heat treatment was carried out at 1400 °C for 60 min to make the carbothermal reduction adequately and then cooling was permissible at the fastest rate by water chiller equipment.

Morphologies and compositions of the resulting materials were described by means of X-ray powder diffraction (XRD) and other techniques. XRD was carried out on a D/MAX 2250 V X-ray powder diffraction system with Cu Kα radiation in the range of $20° < 2\theta < 80°$. X-ray photoelectron spectroscopy (XPS) was applied on an Axis Ultra, Kratos (UK) system using monochromatic Al Kα radiation (150 W, 15 kV, 1486.6 eV). The vacuum in the spectrometer was 10^{-9} Torr. Binding energies were calibrated relative to the C1s peak (284.8 eV) from hydrocarbons adsorbed on the surface of the samples. Scanning electron microscopy (SEM) was achieved on a JEOL-JSM6700F system operated at low energies between 2 and 5 kV. The selected-area electron diffraction (SAED) and transmission electron microscopy (TEM) were carried out on a JEOL-JEM 3010 system with an energy-dispersive X-ray spectrometer and employing an accelerating voltage of 300 kV.

The dielectric properties were applied on an Agilent E8362B vector network analyzer by the wave guide method at X band and Ku band. For dielectric measurement, all the resulting samples (10 wt%) were dispersed into wax to fabricate wax-based composites for complex permittivity measurement. In a typical experiment, the wax was heated to melt, followed by adding the resulting samples under vigorous stirring. Until cooling down to room temperature, the mixture powders were grinded and reheated to melt again. By repeating this cycle process for several times, ethanol was added into the resulting powders, followed by cutting into powders with emulsifying machine. Subsequently, the as-prepared powders were pressed into dimensions of 22.86 mm × 10.16 mm × 2 mm and 7.90 mm × 15.80 mm × 2 mm, respectively. The as-pressed samples were tested in X band and Ku band, respectively.

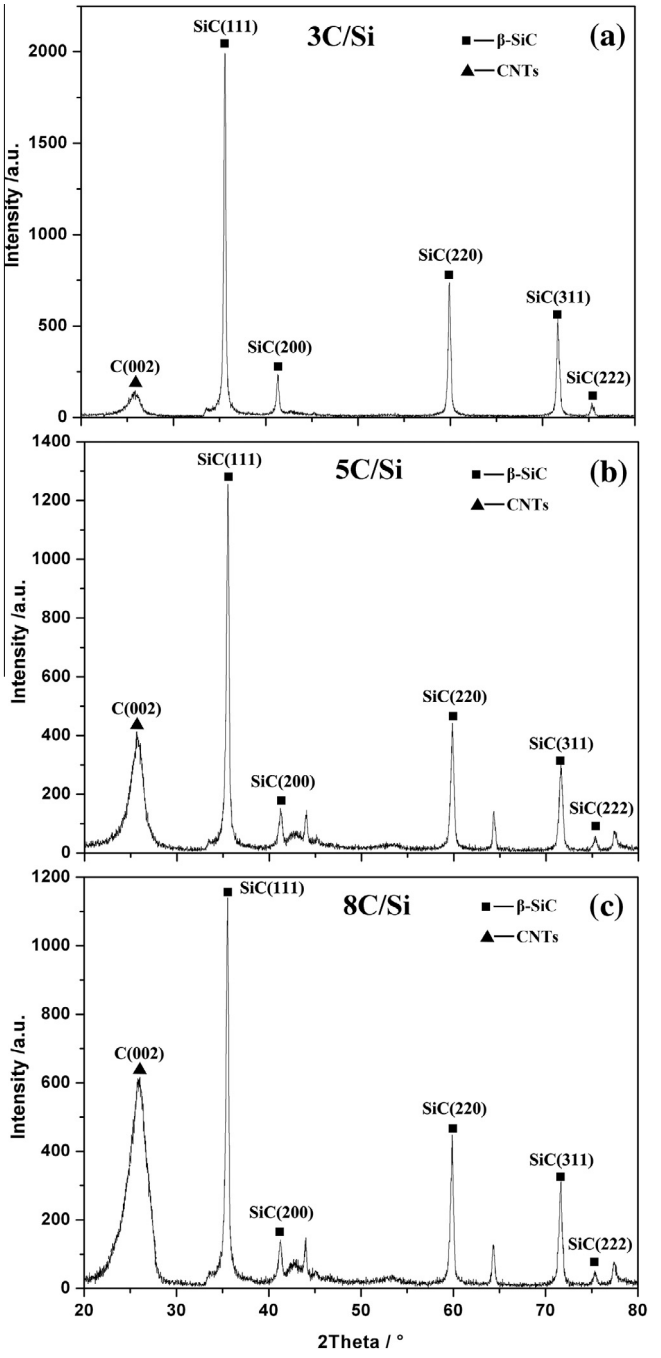

Fig. 1. XRD patterns of the heterostructure powders synthesized by carbothermal reduction with diverse reactant ratios. (a) $n_C:n_{Si} = 3:1$, (b) $n_C:n_{Si} = 5:1$, (c) $n_C:n_{Si} = 8:1$.

3. Results and discussion

The XRD patterns of the resulting powders with different mol ratios of $n_C:n_{Si}$ are shown in Fig. 1, which all exhibit characteristic peaks of β-SiC centered at $2\theta = 35.6°$, 41.4°, 60.0°, 71.8° and 76.5°, associated with (111), (200), (220), (311) and (222) planes of β-SiC, respectively. The noticeable carbon peak C (002) was observed in all three samples. Apparently, the intensity ratios of C to β-SiC peaks increase with increasing mol ratios of C–Si, showing more MWCNTs residues in the resulting heterostructures. As supplement, the unclear XRD patterns of Fig. 1(b) and (c) were analyzed. These should signify the presence of graphite-2H (JCPDS Card No.: 41-1487), which exhibit characteristic peaks at $2\theta = 26.38°$, 44.39°, 63.68°, 77.24°, associated with (002), (101), (015), and (110) planes. This phenomenon should be caused by the hole or the defects at the wall of MWCNTs which came from the carbothermal reduction.

The SEM and TEM images of the samples with mol ratios of 3:1 (3C/Si) are shown in Fig. 2. Orbicular powders with dimensions of 200–600 nm were observed in Fig 2(a). The images in Fig. 2(b) also demonstrate small quantities of residual MWCNTs in the resulting samples, meanwhile, several particles were integrated with the existent style of linear array as shown in Fig. 2(c). It should be relative to the flocculent structure of MWCNTs as starting materials of carbothermal reduction. According to previous literature [19], the

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