



## Regular Article

# High electrical conductivity and anisotropy of aligned carbon nanotube nanocomposites reinforced by silicon carbonitride



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## ABSTRACT

Aligned carbon nanotube (CNT) sheets reinforced with silicon carbonitride were prepared by the infiltration and pyrolysis of liquid polysilazane into mechanically stretched CNTs. The resultant nanocomposites contained a high volume fraction of CNTs (60 vol%), and due to alignment, reached an electrical conductivity of up to  $2.2 \times 10^5 \text{ S m}^{-1}$ . The electrical conductivity was anisotropic based upon the CNT alignment and changed from 3.3 to 9.2 after the pyrolysis process. The high electrical conductivity of the nanocomposites contributes to their potential application in electromagnetic interference shielding.

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In recent years, electromagnetic interference (EMI) shielding materials have been mostly studied on metal-based and polymer-based materials [1,2]. For high temperature environments, advanced ceramics are one suitable candidate for EMI shielding due to their oxidation resistance and thermophysical stability. However, the crystallinity and electron consumption in ionic/covalent bonds typically makes conventional ceramic materials display poor electrical conductivity and therefore they are not suitable for EMI shielding applications [3,4].

Recently, it has become highly desirable to achieve high electrical conductivity for multifunctional properties in ceramic materials [5,6]. As carbon nanotubes (CNTs) have remarkable electrical properties, they are considered as one important promising additive to improve the electrical properties of ceramic materials. In some research CNTs can be mixed in ceramic powders or directly with ceramic polymeric precursor to prepare CNT-reinforced ceramic matrix composites [7–9]. However, due to challenges in fully dispersing individual nanotubes into the matrices, the properties of CNT-reinforced nanocomposites are far below theoretical predictions. The electrical conductivity of CNT-reinforced composites has been investigated using the percolation theory (Eq. (1)) [10–13]:

$$\sigma \propto (p - p_c)^t \quad (1)$$

where  $\sigma$  is the electrical conductivity,  $p$  is the fraction of CNTs,  $p_c$  is the percolation threshold, and  $t$  is the critical exponent. It is found that the electrical conductivity is well fitted by the scaling law of the percolation theory when the volume fraction of CNTs in ceramic nanocomposites is up to 11 vol% [10]. Various values have been reported from 0.002 to 4 wt.% for the percolation threshold [13,14]. It has been found that the electrical conductivity of composites reinforced by CNTs increases with the volume fraction of CNTs. Concurrently, an increase in EMI shielding effectiveness is ascribed to the increase in the composites' electrical conductivity [3]. Therefore, factors such as the volume fraction, alignment state and aspect ratio of CNTs, are important in determining the electrical properties of CNT-reinforced composites [12]. In the past decades, different methods have been invented to produce assemblies of aligned CNTs, such as using field force (e.g., magnetic field and electrical field), or drawing aligned CNTs sheets/fibers directly from CNTs forests synthesized by chemical vapor deposition (CVD) [15–20].

In our research, aligned CNTs sheets were obtained from mechanically stretched random CNT sheets (Nanocomp Technologies, Inc., USA). The microstructure of random and aligned CNT sheets was observed using scanning electron microscope (SEM, JEOL JSM-7401F, Japan), as shown in Fig. 1. The diameter and length of multi-walled CNTs in the random CNT sheets are 6–8 nm and 1 mm respectively. The high volume fraction of CNTs allows their properties to dominate the overall composite properties and the volume fraction of CNTs in our research can be carried out up to 60 vol% [21]. The extremely high aspect ratio (>100,000) of CNTs ensures high ductility and super

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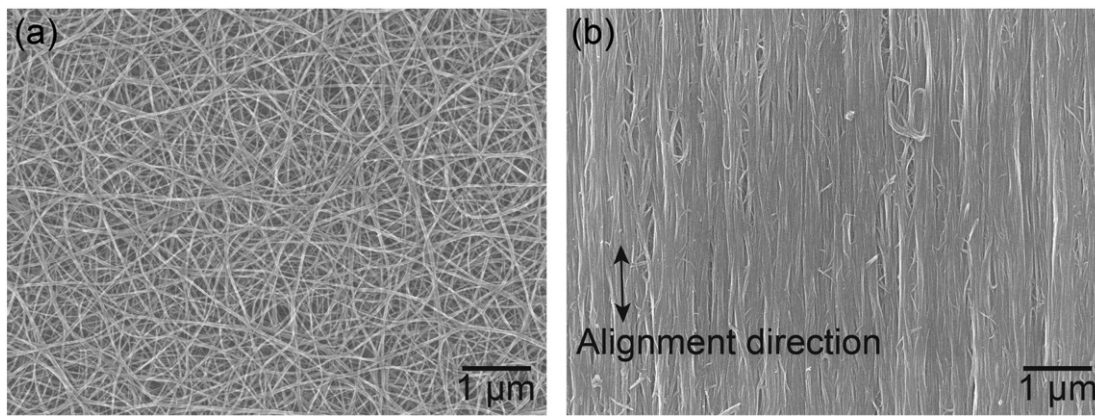


Fig. 1. SEM images of random and aligned CNTs sheet. (a) Random, (b) aligned.

elasticity of the CNTs networks, which allows them to be highly aligned by a mechanical stretching process [22]. The random CNT sheets were mechanically stretched by a specified strain. The elongation percentage or strain was monitored and the machine was stopped at a specific amount of strain. In this research, the elongation percentage was controlled at 35%.

Aligned CNT-reinforced silicon carbonitride nanocomposites were prepared by infiltrating and pyrolyzing liquid polysilazane (PSZ, KION Defense Technologies, Inc., USA) into the aligned CNT sheets. Polysilazane, a low viscosity liquid thermosetting resin with repeat units in which silicon and nitrogen atoms are bonded in an alternating sequence, was used as the liquid preceramic precursor of silicon carbonitride (SiCN) and 4 wt.% dicumyl peroxide (Sigma-Aldrich Corporation, USA) was used as the thermal initiator. Because silicon carbonitride ceramics show high thermal stability in air (up to 1400 °C), CNT-reinforced silicon carbonitride nanocomposites have high temperature stability in flowing air up to 1000 °C [23]. Several reports have been explored to prepare CNTs reinforced with silicon carbonitride based on directly mixing CNTs in the polymeric precursor, however, only a limited volume fraction of CNTs can be infused into the ceramic matrix [24,25]. Our process is based on the wet infiltration of liquid ceramic polymeric precursors, which is commonly called the polymer impregnation and pyrolysis (PIP) process, and is a versatile method to fabricate carbon fiber or carbon nanofiber reinforced ceramic nanocomposites [26,27]. In the first step, the liquid precursor is forced into aligned CNT sheets by a vacuum-assisted process. Next, it is cured into a solid preceramic state by thermal crosslinking at 140 °C in an air atmosphere for 24 h to obtain solid CNT/PSZ. During the pyrolysis process at elevated temperature (1000 °C) for 1 h in a nitrogen atmosphere, the cured solid precursor in the CNT sheets decomposes into an amorphous silicon carbonitride ceramic to form the resultant ceramic nanocomposites. Additional iterations of the PIP process are needed to obtain near fully-densed nanocomposites. According to the above description, four stages can be listed in the process: (a) aligning the CNT sheets, (b) infiltrating the CNT sheets with polysilazane (CNT/PSZ), (c) exposure to high temperature pyrolysis to generate CNT-reinforced silicon carbonitride nanocomposites (CNT/SiCN1), and (d) additional infiltration and pyrolysis to generate more dense CNTs reinforced with silicon carbonitride (CNT/SiCN2).

The nanocomposites were characterized with Raman spectroscopy on a inVia micro-Raman system (Renishaw plc, USA) using a 785 nm excitation wavelength (1.58 eV) diode laser. Typical laser power was 0.5 mW with a 50× magnification objective lens, and the laser beam size was around 1 mm in diameter. As shown in Fig. 2, the peaks at the D band and G band are the main features of sp<sup>2</sup> crystalline graphitic structures [28]. Compared with the aligned CNT sheet and CNT/PSZ, the intensity of the D band became much higher in the CNT/SiCN1 and CNT/SiCN2 composites, which means that the intensity ratio ( $R = I_G/I_D$ ) is

becoming smaller after the pyrolysis process. For the four stages from aligned CNT sheet to CNT/SiCN2, the intensity ratio is 3.11, 2.68, 1.03, and 1.01, respectively. The intensity ratio can be used to evaluate the defect concentration of CNTs with a higher value denoting fewer defects [29]. During the pyrolysis of polysilazane, some reactions have been proven by mass spectrometry to account for the departure of some volatile products, such as NH<sub>3</sub> and H<sub>2</sub> [30]. The chemical reactivity in CNTs is primarily due to the π orbital misalignment that exists between the adjacent carbon atoms oriented at an angle to the tube circumference [31]. Therefore, a strong van der Waals interaction between the aromatic group and the π-π stacking of the CNT sidewalls is very likely to occur [31]. Some defects of the CNTs may be brought into the composites in this process, which may ascribe to the large changes of the intensity ratio in Raman analysis [28]. The peak at G' band reveals that the CNTs have few layers in the as-received state and in the resultant nanocomposites and the relatively lower G' band suggests that even after the pyrolysis process that CNTs in the resultant nanocomposites still possess overlapping and multi-walled CNTs.

The electrical conductivity of the nanocomposites was measured using the four-probe method (Jandel universal probe system with Keithley 2002 MEM multimeters, USA). It was tested five times for each sample and calculated as an average value. The influence of the pyrolysis process on the anisotropy of the electrical properties was investigated. In our research, high volume fraction, high aspect ratio (>100,000) and well-aligned CNTs result in ceramic nanocomposites that demonstrate ultra-high electrical conductivity. The electrical conductivity both parallel along ( $\sigma_{\parallel}$ ) and vertical to ( $\sigma_{\perp}$ ) the length direction is summarized in Fig. 3. As the electron charge runs along the length of the CNTs much more readily than it jumps through the

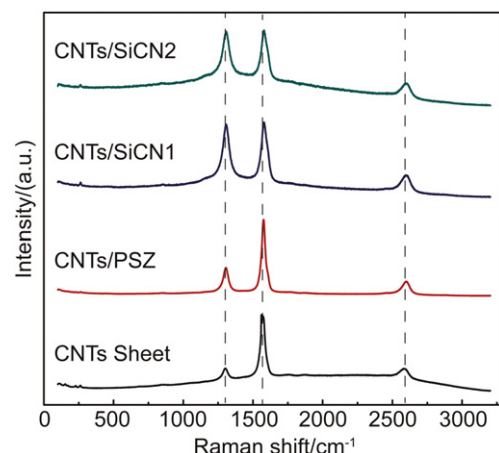


Fig. 2. Raman analysis of the samples from CNT sheet to CNTs/SiCN2.

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