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

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A B S T R A C T

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 $2.2 \times 10^5$ 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]:

$$\sigma = (p-p_c)^s$$  \hspace{1cm} (1)$$

where $\sigma$ is the electrical conductivity, $p$ is the fraction of CNTs, $p_c$ is the percolation threshold, and $r$ 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 CNT 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...
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 precursor of silicon carbonitride (SiCN) and 4 wt.% dicumyl peroxide (Sigma-Aldrich Corporation, USA) was used as the thermal initiator. Because silicon carbonitride (SiCN) and 4 wt.% dicumyl peroxide (Sigma-Aldrich Corporation, USA) was used as the liquid preceramic precursor of silicon carbonitride ceramic to form the resultant ceramic nanocomposites have 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 infiltration and pyrolysis (PIP) process, and is a versatile method to fabricate ceramic 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 sp2 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_D/I_G) 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 NH3 and H2 [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 (σ∥) and vertical to (σ⊥) 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. 1. SEM images of random and aligned CNTs sheet. (a) Random, (b) aligned.](image)

![Fig. 2. Raman analysis of the samples from CNT sheet to CNTs/SiCN2.](image)
CNTs, the CNT alignment leads to the anisotropy of $\sigma_\parallel$ and $\sigma_\perp$ [32]. In all cases, the values of $\sigma_\parallel$ are much higher than that of $\sigma_\perp$, which is also demonstrated by the value of $\sigma_\parallel/\sigma_\perp$ in Fig. 3c.

For the CNT sheet, the values of $\sigma_\parallel$ and $\sigma_\perp$ are 5.3 $\times$ 10$^4$ and 1.6 $\times$ 10$^4$ S m$^{-1}$ respectively, meaning $\sigma_\parallel/\sigma_\perp$ is equal to 3.3. The high electrical conductivity is attributed to the percolation network of CNTs. The high concentration and alignment realize a high degree of CNTs contact. There are two sources of electrical resistance in the CNT sheets: the intrinsic resistance along CNTs and the contact resistance at the CNT junction points. It has been demonstrated that the electrical resistance strongly depends upon the contact length at the CNT junctions, CNT diameter and atomic structures in the contact region [33]. The high concentration and alignment promise a high degree of contact between rigid neighboring CNTs. After the polymeric precursor is infiltrated into CNT sheets to fabricate CNT/PSZ, the pores in the aligned CNT sheets are filled with polymeric precursor. Since the polymer is insulating, both $\sigma_\parallel$ and $\sigma_\perp$ become slightly reduced compared to the value of the CNT sheets, as shown in Fig. 3a and b.

The pyrolysis process from CNT/PSZ to CNT/SiCN1 leads to a dramatic change of the electrical conductivity. The value of $\sigma_\parallel$ for CNT/SiCN1 reaches up to 2.3 $\times$ 10$^5$ S m$^{-1}$ in Fig. 3a. The value of $\sigma_\parallel$ almost doubles from CNT/PSZ to CNT/SiCN1 in Fig. 3b. However, $\sigma_\parallel$ is significantly higher than $\sigma_\perp$ and $\sigma_\parallel/\sigma_\perp$ increases to 9.2 after the pyrolysis process, demonstrating more significant anisotropy for CNT/SiCN1 (Fig. 3c). After one additional polymer infiltration and pyrolysis process, CNT/SiCN2’s electrical conductivity becomes 2.2 $\times$ 10$^5$ S m$^{-1}$, and the $\sigma_\parallel/\sigma_\perp$ remains at 9.2. Fig. 3d shows the comparison of our aligned CNT-reinforced with silicon carbonitride with other representative CNT-reinforced ceramic nanocomposites [10,34,35]. Unprecedentedly high electrical conductivity is achieved in our ceramic nanocomposites. It is found in Fig. 3d that the electrical conductivity of our ceramic nanocomposites is much better than most current nanocomposites due to the high volume fraction and alignment of the CNTs in sheets.

The intrinsic conductivity and contact resistance of the CNTs are the most important factors that influence the electrical properties of the resultant composites [36]. Since the intrinsic conductivity of CNTs is highly anisotropic, the importance of alignment can be further studied by evaluating the resistance ($R$) of aligned CNT sheets and the resultant nanocomposites (θ) as a function of the alignment angle (θ), as follows [37]:

$$R(\theta) = R(\theta = 0^\circ) \cos^2(\theta) + R(\theta = 90^\circ) \sin^2(\theta)$$  (2)

In our research, it can be assumed that the alignment angle (θ) is zero as the composites demonstrate well-aligned CNT morphology, which contributes to significant electron transport. It has been found in our previous paper that electron transport in aligned CNT/SiCN1 almost doubles from CNT/PSZ to CNT/SiCN1 in Fig. 3b. However, $\sigma_\parallel$ is significantly higher than $\sigma_\perp$ and $\sigma_\parallel/\sigma_\perp$ increases to 9.2 after the pyrolysis process, demonstrating more significant anisotropy for CNT/SiCN1 (Fig. 3c). After one additional polymer infiltration and pyrolysis process, CNT/SiCN2’s electrical conductivity becomes 2.2 $\times$ 10$^5$ S m$^{-1}$, and the $\sigma_\parallel/\sigma_\perp$ remains at 9.2. Fig. 3d shows the comparison of our aligned CNT-reinforced with silicon carbonitride with other representative CNT-reinforced ceramic nanocomposites [10,34,35]. Unprecedentedly high electrical conductivity is achieved in our ceramic nanocomposites. It is found in Fig. 3d that the electrical conductivity of our ceramic nanocomposites is much better than most current nanocomposites due to the high volume fraction and alignment of the CNTs in sheets.

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In our research, it can be assumed that the alignment angle (θ) is zero as the composites demonstrate well-aligned CNT morphology, which contributes to significant electron transport. It has been found in our previous paper that the pyrolysis process results in a great volume shrinkage for the resultant composites [38]. Raman results also show that CNTs maintain the multi-wall feature so that the intrinsic conductivity of CNTs is not damaged during the pyrolysis process. Therefore, shrinkage may improve the electrical conductivity of ceramic nanocomposites from two aspects.

First, shrinkage improves electrical conductivity because CNTs exhibit highly anisotropic mechanical and functional properties whereby shrinkage occurs at different rates along the thickness, width and length directions of the CNTs, as shown in Table 1. There is noticeable shrinkage along the thickness and width directions, making the cross sectional area (perpendicular to the alignment direction) decrease by 42.42% and CNTs stack closer. However, the shrinkage doesn’t affect the alignment of CNTs. Instead, closer contact between each CNT and larger contact length are obtained. The CNTs contact length is important for electron transport and larger contact lengths improve the conductivity of the resultant composites [37]. It is shown that the contact resistance ($R_{contact}$) is the summation of CNT direct contact resistance ($R_{direct\ contact}$) and the interfacial resistance ($R_{interfacial}$), as shown in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Shrinkage percentage</th>
<th>Length</th>
<th>Width</th>
<th>Thickness</th>
<th>Cross-sectional area</th>
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<tr>
<td>0.08%</td>
<td>13.37%</td>
<td>31.71%</td>
<td>42.42%</td>
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</tr>
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tunneling resistance \( R_{\text{tunnel}} \) due to an insulating thin film, as shown in Eq. (3) [36]:

\[
R_{\text{contact}} = R_{\text{direct contact}} + R_{\text{tunnel}}
\]  

(3)

The tunneling resistance depends on the thickness and material composition of the insulating layer. Eq. (3) ensures that the contact resistance is properly represented when there is no insulating layer between each CNT and the tunneling resistance can be assumed to zero based upon the closer contact obtained by the pyrolysis process in our research [36]. Therefore, closer contact between each CNT leads to lower contact resistances for aligned CNTs.

Second, shrinkage improves electrical conductivity because the thin polymer layer formed on the surface of the CNT sheet, which hampers the electron charge for CNT/PSZ, is degraded upon pyrolysis leading to exposed CNTs on the surface for CNT/SiCN1. These explanations can be verified by the microstructure characterization of our nanocomposites from CNT/PSZ to CNT/SiCN1 in Fig. 4. Fig. 4 shows the AFM and SEM analysis of CNT/PSZ and CNT/SiCN1. The microstructure of our ceramic composites was observed using a scanning electron microscope (SEM, JEOL JSM-7401F, Japan) and atomic force microscope (AFM, Veeco Instruments Inc., USA). The thin polymer layer is coated on the surface of the CNT sheets for CNT/PSZ, as shown in Fig. 4a and c. After the pyrolysis process, CNTs are found exposed on the surface for CNT/SiCN1, as shown in Fig. 4b and d. The closer contact between each CNT due to the shrinkage is verified by the SEM images. The surface SEM images in our previous results show that the size of CNTs assembled in CNT sheets is about 30 nm and it is approximately 150 nm in CNT/SiCN1 after the pyrolysis process [38]. The cross-sectional SEM images in Fig. 4e and f show that some CNTs are bunched together with diameters of 145–180 nm.

In summary, we have developed a unique method to prepare ceramic matrix nanocomposites with high electrical conductivity using aligned CNT sheets. As CNTs are characterized by highly anisotropic properties, different shrinkage rates occur along the length, width and thickness directions during the pyrolysis process. The well-aligned CNT morphology contributes to significant electron transport. The electrical conductivity of our ceramic composites along the alignment direction is 2.2 × 10^5 S m⁻¹, which is at the same level as the electrical conductivity of graphite in the basal plane. The anisotropy of electrical conductivity increases from 3.3 to 9.2 after the pyrolysis process. Therefore, the highly electrically conductive nature of the unique ceramic composites makes them attractive candidates for electromagnetic interference shielding applications.

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References


