

# Colloidal Processing of Carbon Nanotube/Alumina Composites

Jing Sun, Lian Gao,\* and Wei Li

*The State Key Lab on High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China*

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Preparation of carbon nanotube (CNT)/alumina composites by a simple colloidal processing method has been reported in this paper. The surface modification process of carbon nanotubes was characterized by means of zeta potential measurements and TEM microscopy. The addition of only 0.1 wt % carbon nanotubes in the alumina composite increases the fracture toughness from 3.7 to 4.9 MPa·m<sup>1/2</sup>. Microstructure characterization, performed by SEM, showed that the bridging effect on cracks, the tight bonding between CNTs and alumina matrix, and the pullout of CNTs from matrix are possible mechanisms leading to the improvement of the fracture toughness.

## Introduction

Since the discovery of carbon nanotubes in 1991 by Iijima,<sup>1</sup> many efforts have been devoted to revealing their unique structural, electrical, mechanical, electro-mechanical, and chemical properties.<sup>2–4</sup> At present, carbon nanotubes are available in kilogram quantities with a price that is acceptable compared to that at the initial stage of their discovery. It costs about 2–20 U.S. dollars per gram for multiwall carbon nanotubes (MWNT), depending on the amount purchased. This makes the large-scale production of CNT composites possible and practical. Theoretical and experimental results<sup>5</sup> showed extremely high elastic modulus and tensile strength as high as 1 TPa and 200 GPa, respectively. Therefore, it can be foreseen that CNTs could be used as strong, light, and tough fibers for nanocomposite structures.

A lot of research work on CNT composites has concentrated on polymer-matrix materials for improved electrical conductivity,<sup>6</sup> optical devices,<sup>7</sup> and higher strength.<sup>8</sup> For example, the mechanical properties and the heat deflection temperatures of carbon nanotube/poly (vinyl alcohol) composites<sup>9</sup> and carbon nanotube/poly (methyl methacrylate) composites<sup>10</sup> both prepared by direct mixing were raised with the increase of the

content of CNTs. Kuzumaki et al.<sup>11</sup> characterized the processing and mechanical properties of carbon nanotube-reinforced aluminum composites prepared by hot-pressing, indicating that the mechanical properties of the composites were more thermally stable than that of pure Al. However, there are few studies carried out on CNT-reinforced ceramic matrix composites. Peigney et al.<sup>12–15</sup> developed techniques to synthesize carbon nanotubes in situ to form carbon nanotubes/metal-oxide composite powders. These powders were hot-pressed to obtain composites. The incorporation of the long nanotube bundles grown in situ, however, did not provide the expected improvement in mechanical properties. Chang et al.<sup>16</sup> fabricated the same alumina and alumina matrix composites containing 5–20 volume percent of multiwall carbon nanotubes. An improvement of 24% on fracture toughness compared with that of the single-phase alumina was found. Ma et al.<sup>17</sup> prepared carbon nanotube/SiC composite powder via mixing nanosize SiC particles with 10% carbon nanotubes and then hot pressing it. They reported a 10% enhancement on both the strength and the fracture toughness as compared to the monolithic ceramics.

The effective utilization of nanotubes in composite applications depends strongly on the ability to disperse CNTs homogeneously throughout the matrix. Furthermore, good interfacial bonding is required to achieve load transfer across the CNT–matrix interface, a condition necessary for improving the mechanical properties

\* To whom correspondence should be addressed. Phone: 86-21-5241-2718. Fax: 86-21-5241-3903. E-mail: liangaoc@online.sh.cn.

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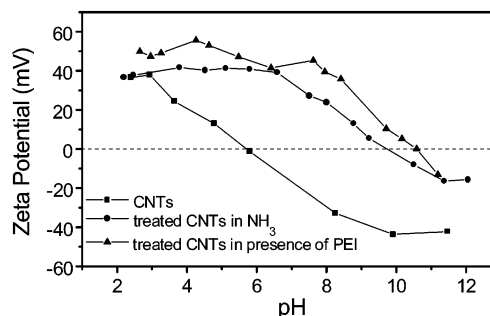
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of ceramic composites. Some references reported recent progress on solving the above problems. Hwang et al.<sup>18</sup> synthesized silicon glass rods by using surfactant–carbon nanotube co-micelles as templates. These glass rods were used as additives to reinforce inorganic ceramics. They showed ~100% enhancement on hardness in the presence of ~6 wt % of CNTs. Gong et al.<sup>19</sup> reported the use of a surfactant as a processing aid to improve the dispersion of single-wall carbon nanotubes (SWNTs) in epoxy resin, leading to a significant improvement of mechanical properties. Jin et al.<sup>20</sup> adopted poly (vinylidene fluoride) to assist the dispersion of MWNT and serve as a glue to increase the interfacial adhesion between MWNT and poly (methyl methacrylate), resulting in an obvious increase of the storage moduli of the composites at low temperatures.

Unlike carbon fibers, the as-prepared CNTs tend to form bundles due to van der Waals forces, and there is still no good way to separate them individually. To obtain high-performance ceramics, it is desirable to find a process that will give green compacts with microstructural homogeneity. Defects found in compacts are usually due to agglomerations or inhomogeneous distribution of components. From the viewpoint of colloidal processing, multicomponents could be distributed evenly when they possess similar surface properties. Successful surface modification of silicon nitride powder with aluminum<sup>21</sup> or other colloidal sintering agent<sup>22</sup> proved more homogeneity in the green compacts compared with that of conventionally prepared samples. In this paper, we attempt to coat the surface of CNTs with alumina, which will not only improve the homogeneous distribution of CNTs in the ceramic matrix, but also make the binding between two phases more tight after sintering. In addition, the mechanical properties, as well as the microstructures, of the composites have been investigated.

### Experimental Procedures

Shenzhen NanoPort Company kindly provided carbon nanotubes, and purity of about 95% was claimed by the producer. We further treated the nanotubes in NH<sub>3</sub> at 600 °C for 3 h to change their surface properties. A certain amount of treated CNTs were put into a solution containing a dispersant of 300 mg/L polyethyleneamine (PEI,  $M_w$  50 000, BDH Laboratory Supplies). Commercially available  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> consisting of particles with a diameter of 30 nm was obtained from Taimei Chemical Co., Ltd., Japan. Alumina (0.04 g) was dispersed into 100 mL of deionized water, and then 300 mg/L poly (acrylic acid) (PAA, from Polymer Sciences, PA) with polymer weight of 50 000 was added into this very dilute alumina suspension. Sodium hydroxide was employed to adjust pH. The prepared dilute alumina suspension with PAA was added dropwise into the vigorously stirred as-prepared carbon nanotube suspension with PEI, and before that both suspensions were ultrasonicated for 30 min. The coated carbon nanotubes collected from the mixed suspension were subsequently added into a concentrated alumina suspension of about 50 wt % in ethanol; finally the content of CNTs was only 0.1 wt % of alumina



**Figure 1.** Zeta potential values changed with pH of pristine CNTs, treated CNTs, and treated CNTs in the presence of PEI.

amount. Further drying and grinding obtained the CNTs–alumina composite powder. The pristine, treated and coated carbon nanotubes were subjected to zeta potential measurement (Zeta Plus, Brookhaven Instruments Corp., Holtsville, NY) to evaluate their surface properties. For the TEM (JEOL, JEM-200CX) study, a drop of the coated CNTs suspension was diluted and ultrasonicated, and then one drop of the diluted suspension was transferred to deposit on a copper grid to observe the coating state.

The single-phase alumina powder and 0.1 wt % CNTs–alumina composite powder were sintered by spark plasma sintering (Dr Sinter 1050, Sumitomo Coal Mining Co., Ltd.) in a graphite die at 1300 °C, with a pressure of 50 MPa for 5 min in an Ar atmosphere, respectively. Densities of the sintered composites were measured using the Archimedes technique. The hardness of the composites was measured using a Vickers hardness tester (AVK-A) with a load of 10 kg applied on the surface for 10 s. The fracture toughness was calculated by the Evans & Charles equation ( $K_{IC} = 0.00824P/C^{3/2}$ ), where  $P$  is the applied load in Newtons and  $C$  is the crack length in meters. Fractured surfaces were examined by scanning electron microscopy (SEM, Instrument JSM 6700F).

### Results and Discussions

Zeta potentials of the pristine CNTs, treated CNTs in NH<sub>3</sub>, and treated CNTs in the presence of PEI were each measured with Zeta Plus in 1 mM NaCl solutions. The results are shown in Figure 1. The isoelectric point ( $pH_{Iep}$ ) of pristine CNTs is located at pH 5.8. It moves to 9.8 after the heat treatment in NH<sub>3</sub> for 3 h at 600 °C. According to the previous research on the surface chemistry of the activated carbon such as carbon blacks,<sup>23</sup> a heat treatment in H<sub>2</sub> or N<sub>2</sub> can lead to so-called L carbons, which have a low isoelectric point. A common observation in the surface charge characterization of many carbon materials is that the absolute value of the positive charge is often much smaller than that of the negative charge. Our trial on the treatment at an optimum temperature in NH<sub>3</sub> results in a so-called H carbon surface, which has a high isoelectric point. The treated CNTs have positive surface charge in wide pH range. Addition of a small amount of PEI not only moves  $pH_{Iep}$  to a little higher pH value, but also promotes a good dispersion after the ultrasonication. Another feature in Figure 1 that should be mentioned is that the zeta potential value of treated CNTs in the presence of PEI is about 20 mV higher than that without dispersant at pH 9, which makes the coating of CNTs have more driving force. Zeta potential measurements of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> without and with PAA are shown in Figure 2. The

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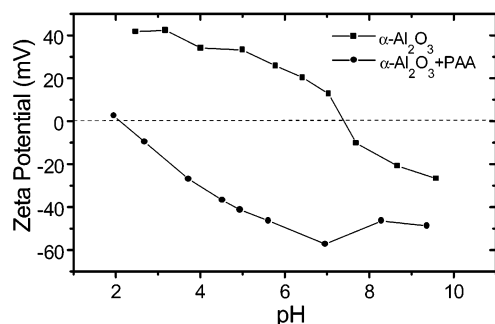
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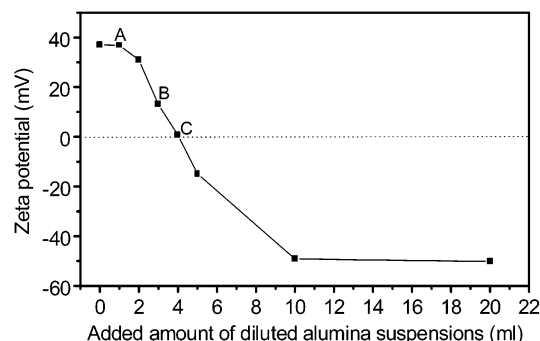
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**Figure 2.** Zeta potential values changed with pH of  $\alpha$ -alumina and alumina in the presence of PAA.

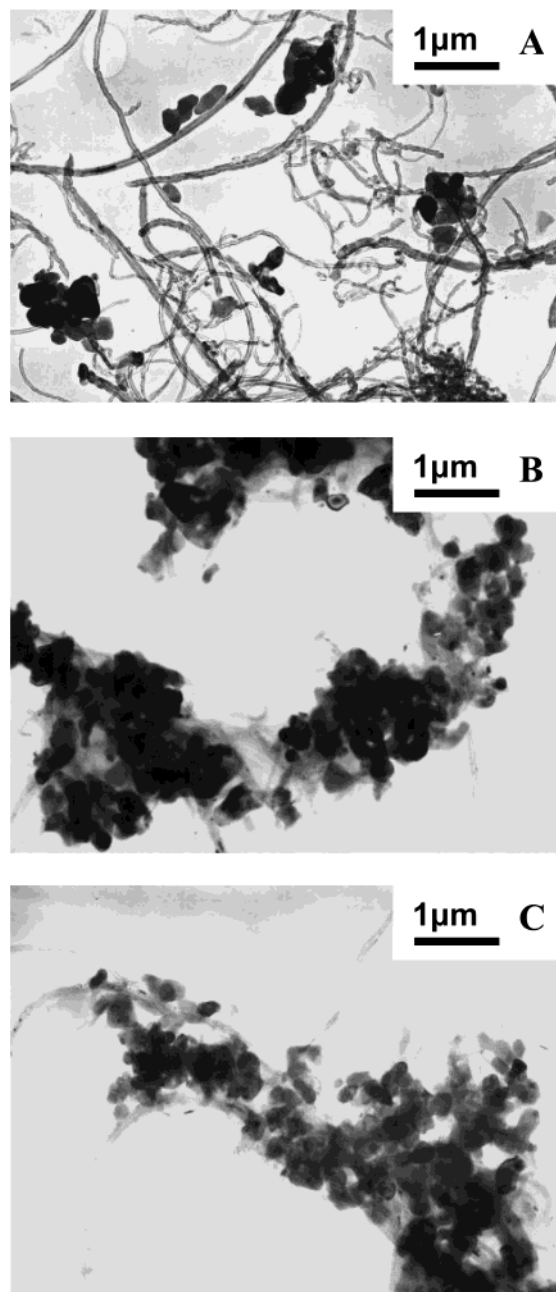


**Figure 3.** Zeta potential values of CNTs as a function of added amount of diluted alumina suspension.

isoelectric point of  $\alpha\text{-Al}_2\text{O}_3$  is located at pH 7.5. After the addition of PAA, it shifts to pH 2.2 due to the specific adsorption of PAA, which correlates well to a previous result.<sup>24</sup> Before performing the coating procedure, the dilute suspension of treated CNTs with PEI is adjusted to pH 8 with zeta potential value about 40 mV, while the diluted suspension of alumina in the presence of PAA is adjusted to pH 9.5 with zeta potential value of about -45 mV. Once these two suspensions are encountered, particles of alumina will bind onto the CNTs because of the strong electrostatic attractive force between each other.

The process of coating alumina particles onto CNTs was characterized by measuring zeta potential values and the results are shown in Figure 3. The initial pH is 8.0 and the zeta potential is 37 mV. It can be noted that the addition of alumina suspensions from 2 mL to 10 mL causes a dramatic decrease of zeta potential values, from 37 mV to -50 mV, while pH value of the CNTs suspension increased from 8.0 to 9.1. Zeta potential values keep constant with the further addition of the diluted alumina suspension. The coated CNTs show a zeta potential value of -50 mV, nearly identical to that of alumina with presence of PAA. Considering that starting CNTs suspensions showed ~40 mV, the sharp decrease in the zeta potential indicated that alumina particles had already adsorbed onto the surface of CNTs. The irreversibility of the adsorption has not been tested. These coated CNTs were added to the concentrated alumina suspension to make the 0.1 wt % CNTs–alumina composite powder.

TEM was employed to observe the coating state. Figure 4(A) corresponded with point A in Figure 3, with



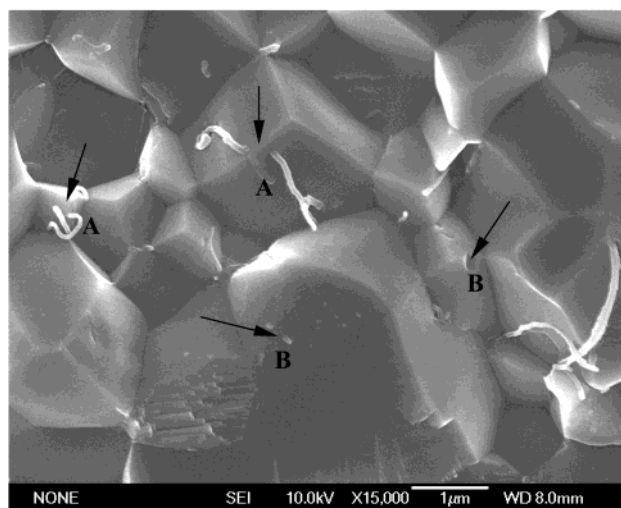
**Figure 4.** TEM micrographs of CNTs in coating states with different amounts of alumina. A, B, and C correspond with points A, B, and C, respectively, in Figure 3.

1 mL addition of the diluted alumina suspension. Only a few alumina particles are observed on nanotubes, so the zeta-potential value remains almost unchanged. With more addition of the alumina suspension, CNTs were observed to be fully coated by alumina particles as shown in Figure 4B and C, which corresponded with point B and C in Figure 3, respectively. No big difference in TEM micrographs could be found between Figure 4B and C, though they showed an obvious difference in their zeta potential values.

The composite powders containing 0.1 wt % CNTs and the single-phase alumina were sintered fully by SPS at 1300 °C for 5 min. The hardness of the alumina was 16.9 GPa, and that of CNTs reinforced composite was 17.6 GPa. Calculations of the fracture toughness were made from measurements of the lengths of cracks created by Vickers indentations. The addition of 0.1 wt

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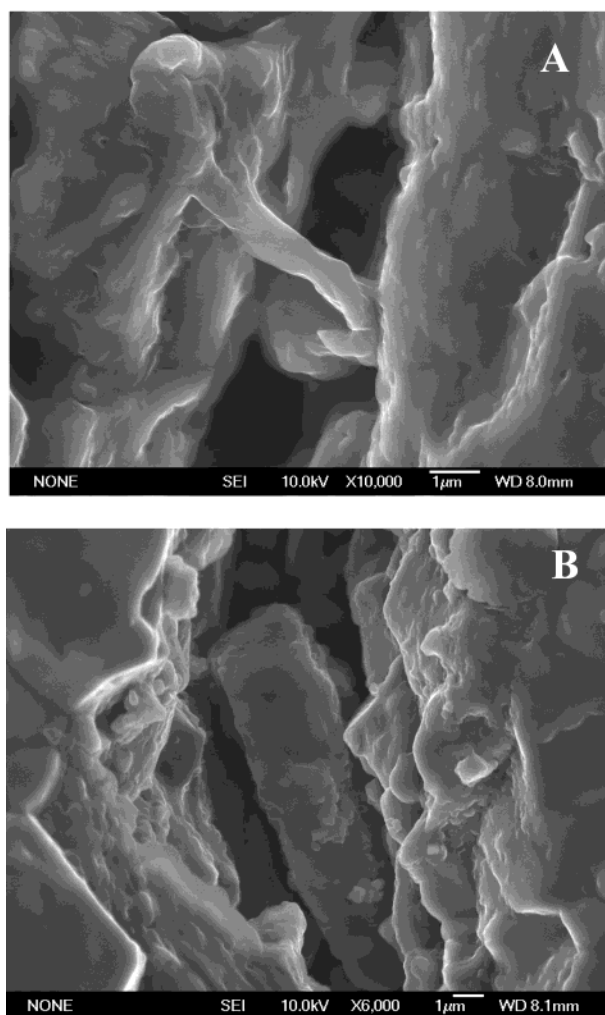
**Figure 5.** SEM micrograph of a fracture surface of the composite with 0.1 wt % CNTs.

% CNTs in the alumina increased the fracture toughness by about 31% from 3.7 to 4.9 MPa·m<sup>1/2</sup>. Compared to the results<sup>16</sup> of 10 vol % MWNT addition to the alumina which increased the fracture toughness by about 24% from 3.4 to 4.2 MPa·m<sup>1/2</sup>, our results showed a more effective and obvious improvement on the mechanical properties by this simple colloidal processing method.

A SEM micrograph used to investigate the fracture surface of the CNTs–alumina composite is shown in Figure 5. The CNTs were dispersed in alumina matrix separately, some located at the boundary of grains, while others located inside the alumina grains. Part of them survived from rupture in the fracture surface (shown by arrows in A areas), and part of them were broken or pulled out (shown by arrows in B areas) indicating that the load transfer from ceramic to nanotubes was sufficient to fracture the nanotubes. Typical examples of interaction between cracks and carbon nanotubes are shown in Figure 6. Some wrapped CNT aligns perpendicular to the crack direction and bridges the crack surface (Figure 6A), while some wrapped CNT traps in the crack (Figure 6B). The tight interfacial bonding ensures a good stress transfer between the nanotube and alumina matrix. Given the above evidence, we can infer that a significant crack-bridging effect, the bonding between CNTs and alumina matrix, and pullout of CNTs at interface are possible mechanisms leading to the improvement of the fracture toughness.

### Conclusion

A colloidal processing route proposed in this work has been proved as an effective way to improve the mechanical properties of carbon nanotube–alumina composites. By adjusting the surface properties of the alumina powder and that of CNTs, it is feasible to make them



**Figure 6.** SEM micrographs of typical interactions between cracks and wrapped CNTs.

bind together with attractive electrostatic forces, which produces strong cohesion between two phases after sintering. During the sintering processing, the growth of alumina particle wrapped carbon nanotubes inside, thus increasing the effectiveness of the reinforcement. The addition of only 0.1 wt % carbon nanotubes in alumina composites increases the fracture toughness from 3.7 to 4.9 MPa·m<sup>1/2</sup>, an improvement of 32% compared with that of the single-phase alumina. Our preliminary results indicate that the coating approach may provide a new way to produce carbon nanotubes/ceramics composites. Future work, including measurements of other important mechanical properties of composites, the optimization of carbon nanotube contents in composites for different applications, the selection of surfactant types for various ceramic matrixes, and detailed investigation on the adhesion between carbon nanotubes and ceramic matrix, is in progress.

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