High-yield growth and morphology control of aligned carbon nanotubes on ceramic fibers for multifunctional enhancement of structural composites

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ABSTRACT

We present an in-depth study of CNT growth on commercially-available woven alumina fibers, and achieve uniform growth of dense aligned CNTs on commercially-available cloths up to 5×10 cm in area. By systematically varying the catalyst concentration, catalyst pre-treatment time, and sample position within the tube furnace, we isolate key factors governing CNT morphology on fiber surfaces and classify these morphologies as related to the processing conditions. Synthesis employs a low-cost salt-based catalyst solution and atmospheric pressure thermal CVD, which are highly attractive approaches for commercial-scale processing. The catalyst solution concentration determines the uniformity and density of catalyst on the fibers, H_2 exposure mediates formation of catalyst clusters, and thermal decomposition of the reactant mixture activates the catalyst particles to achieve uniform aligned growth. Under conditions for aligned CNT growth, uniform radially-aligned coatings are achieved with shorter CNT length, and these split into "mohawks" as the CNT length increases. Radially-aligned growth for 5 min adds a typical CNT mass fraction of 3.8% to the initial sample mass, and a uniform morphology exists throughout the weave. Composites prepared by standard layup techniques using these CNT "fuzzy" alumina fibers are attractive as integral armor layers having enhanced ballistic and impact performance, and serve as a model system for later implementation of this technology using carbon fibers.

1. Introduction

While there are numerous methods for controlling carbon nanotube (CNT) growth on planar substrates such as silicon wafers, applications of CNTs in structural composites necessitate integration of CNTs with three-dimensional arrangements of advanced fibers. In comparison to dispersion of CNTs in epoxies [1] followed by impregnation of fibers, direct growth of CNTs on fiber substrates [2–4] is an alternative and more promising approach to achieve uniform CNT distribution throughout a composite. In such "fuzzy-fiber" reinforced plastics (FFRP), CNTs form nanoscale mechanical connections among adjacent fibers, which also serve as electrically and thermally conductive pathways throughout the composite.

Improvements are observed in the interfacial shear strength of the individual fibers in matrix [5,6] and in the multifunctional properties of the final CNT-fiber-matrix composites [3,4].

To this end, previous work has grown CNTs on the surfaces of various fibers by thermal chemical vapor deposition (CVD); these include carbon fibers [4–9], ceramic fibers [3,10,11], and glass fibers [12]. Due to unfavorable catalyst-carbon interactions, CNTs grown on carbon fibers are often tangled, and catalyst dissolution into the fibers during the growth process can degrade the fiber tensile strength [6]. Growth on ceramic or glass fibers, which typically do not react with the catalyst, has previously been limited to non-woven fibers or has been achieved only on the outer surfaces of woven cloths rather than through the weave. To most effectively use these new composite architectures, it is critical to understand and control the high-yield growth of aligned and uniformly distributed CNTs of appropriate length on the fiber surfaces, and to achieve these results throughout three-dimensional fiber architectures which are used in composite structures. Scalable manufacturing of composite materials which integrate surface-bound CNTs requires a process which can uniformly coat large areas of fibers with CNT growth catalyst, as well as a precise understanding of the catalyst pre-treatment and CVD reaction conditions.

In this work, we identify the key factors governing the morphology of CNTs grown directly on commercially-obtained alumina fiber cloths, and create the catalyst using a scalable low-cost method by dip-coating of a Fe-salt solution [13]. By controlling the catalyst concentration, H_2 pre-treatment time, and sample position within the tube furnace, we observe transitions in the CNT morphology from a tangled layers, to locally-aligned groupings, to short radial coatings, to bifurcated "mohawks" at longer lengths. Further, by establishing an equivalent gas composition and residence time in a larger tube furnace, we demonstrate the scalability of our process to achieve highly uniform growth throughout woven cloth samples up to 5×10 cm in area. The applications of these CNT-fiber-matrix composites include next-generation armors and ballistic protection materials, wherein ceramic and glass fibers are chosen over carbon fibers due to their higher energy absorption per weight [14,15].

2. Materials and methods

The CNT growth process developed in this study is based on our previous approach for growing millimeter-high vertically-aligned CNT "forests" on silicon wafer substrates [16]. In this current work, we coat surfaces of Al_2O_3 fibers with an Fe salt-based catalyst precursor, to enable uniformly aligned CNT forest growth on the fiber surfaces, as illustrated in Fig. 1. The fibers are used as manufactured as a woven cloth (McMaster-Carr, 1687T21) with a 0°/90° satin pattern where each fiber is ≈11 μm diameter. The cloth has a dry volume fraction of 65% and an areal density of 1.0 mg/mm².

First, the as-obtained cloth is cut into $2\,cm \times 4\,cm$ swatches and soaked in a solution of iron nitrate $(Fe(NO_3)_3 \cdot 9H_2O)$ dissolved in 2-propanol. The cloth is subsequently dried by hanging vertically in ambient air for 5–6 h.
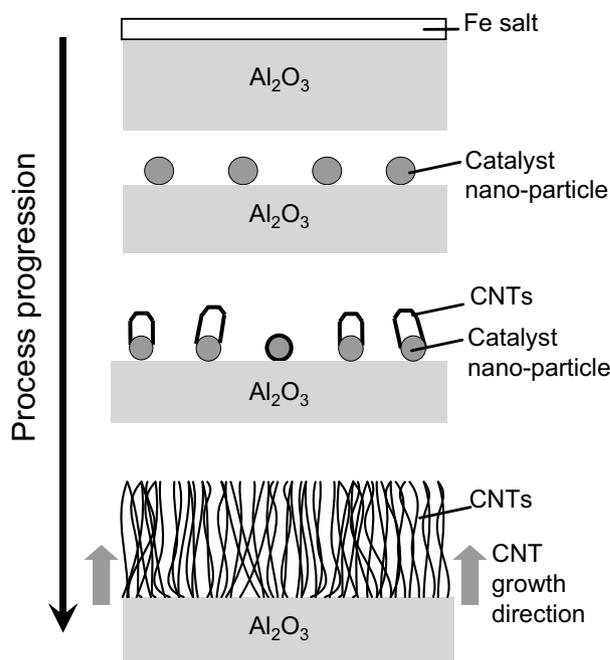

Fig. 1 – Critical stages of CNT forest growth from a salt precursor: catalyst deposition, catalyst reduction and formation of nano-particles, CNT nucleation, and CNT growth [29].

A cloth sample is placed in an atmospheric pressure quartz tube furnace (Lindberg, 22 mm inner diameter, 30 cm heated length). At room-temperature, the furnace is first purged with 920 sccm helium (He, Airgas UHP grade). After purging, the He flow is reduced to 75 sccm, and the furnace is heated for 10 min to 750 °C. This is the temperature reported by the control thermocouple which is located outside the tube, and corresponds to a temperature of 800 °C measured by placing a thermocouple in the center of the tube. After allowing the temperature to stabilize for an additional 10 min, 400 sccm of hydrogen (H_2, Airgas UHP grade) is introduced for a desired duration as discussed later. Finally, the carbon source gas, 110 sccm of ethylene (C_2H_4, Airgas 99.5%), is added to the H_2/He mixture and maintained for 5 min.

In this study we varied the parameters listed in Table 1. The concentration of $Fe(NO_3)_3 \cdot 9H_2O$ in the 2-propanol solution determines the amount of Fe deposited on fiber surfaces. The duration of H_2 treatment before introduction of C_2H_4 influences formation of suitable catalytic sites for CNT growth. The location of the cloth substrate in the tube furnace is also important, as thermal decomposition of C_2H_4 in the flow along the tube determines the activity of the CVD atmosphere for high-yield CNT growth.

Table 1 – Variable process parameters for study of CNT forest growth on Al_2O_3 fiber cloth.	
Concentration of $Fe(NO_3)_3 \cdot 9H_2O$ in 2-propanol (mM)	10, 25, 50
Duration of pre-treatment in H_2 (min)	0, 2, 5
Sample position downstream of control thermocouple at the furnace center (cm)	0–3, 3–6, 6–9

The cloth samples are imaged by scanning electron microscopy (SEM, JOEL 5910 and Philips XL30). Energy dispersive X-ray spectroscopy (EDX) with a 90 s collection time is used to determine the elemental composition on samples processed only through the H_2 annealing period. Transmission electron microscopy (TEM) is performed using a JOEL 2011, operating at 200 keV. To prepare samples for TEM, the CNT-coated cloth is immersed in 2-propanol and ultrasonicated in a bath (VWR, 150D). This to detaches the CNTs from the cloth, and a drop of the solution is deposited on carbon-coated copper grids (Ladd Research, 40750), and dried in ambient air.

Due to capillary action as the cloth is wet by the salt, the edges of the cloth showed much darker iron salt color than the middle section, possibly indicating higher Fe concentration. Thus, although the sample length is ∼ 4 cm, these edge sections are not considered in the subsequent discussions. At least three points on the inner 3 cm wide area of each cloth were examined to determine the uniformity of the growth results across one sample. At least three samples were fabricated under each set of conditions to confirm repeatability of the growth process. To quantify the CNT yield, each cloth sample is weighed using a microbalance (Sartorius ME36S,

1 μg resolution), both after catalyst coating and after CNT growth.

3. Results

Within the parameter space established by Table 1, the growth process was tuned to achieve cloth samples having fibers coated with uniform and dense CNT forests, as shown in Fig. 2. The best results were observed on samples prepared using 50 mM salt solution and 2 min H_2 treatment time at 3–6 cm downstream of the furnace center. As shown in Figs. 2b and Fig. 2c, the cloth expands considerably because CNT growth expands the space among the fibers; forest growth generates an extrusive force [17] which pushes the fibers apart. Fiber bundles were manually removed from the cloth and were inspected under SEM and TEM to confirm growth throughout the interior of the weaves. As shown in Fig. 3, although some CNTs detached from the fibers during the unraveling process, relatively aligned growth was confirmed. TEM images verify the parallel wall structure of the CNTs. Averaged over 30 CNTs, the inner and outer diameters are ∼9.7 nm (standard deviation 1.8 nm) and ∼17.1 nm (standard deviation 3.3 nm) respectively. From these diameters, the
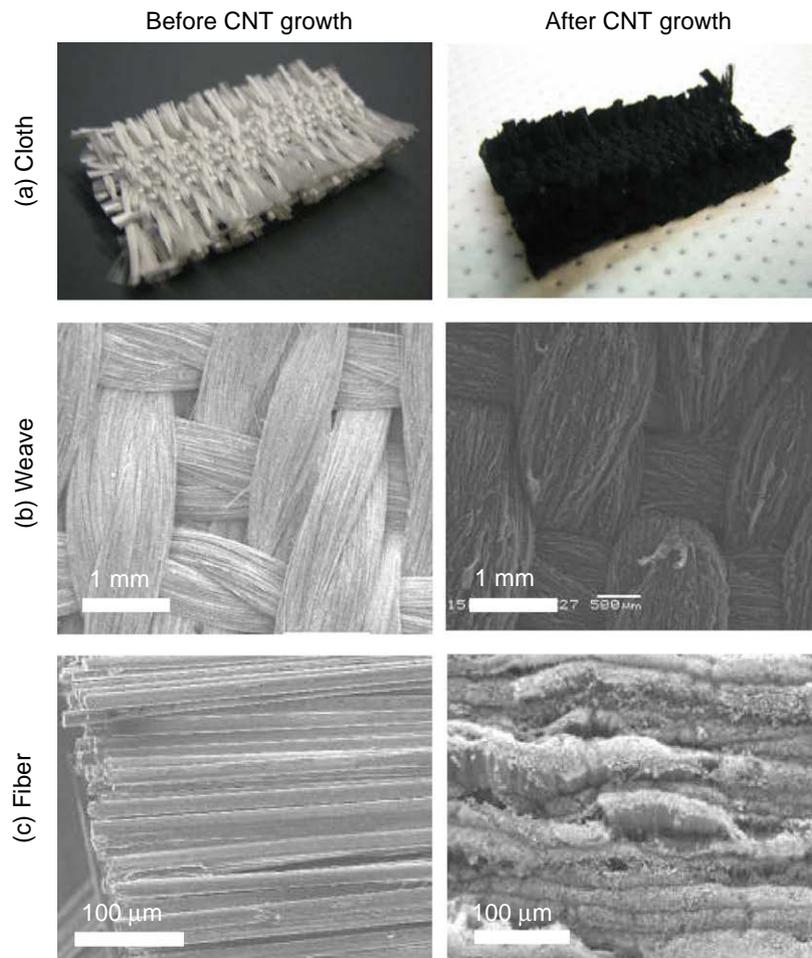

Fig. 2 – Alumina fiber cloth before and after CNT growth: (a) optical photos of cloth, (b) SEM images of fiber weave, (c) SEM images of fiber bundles.
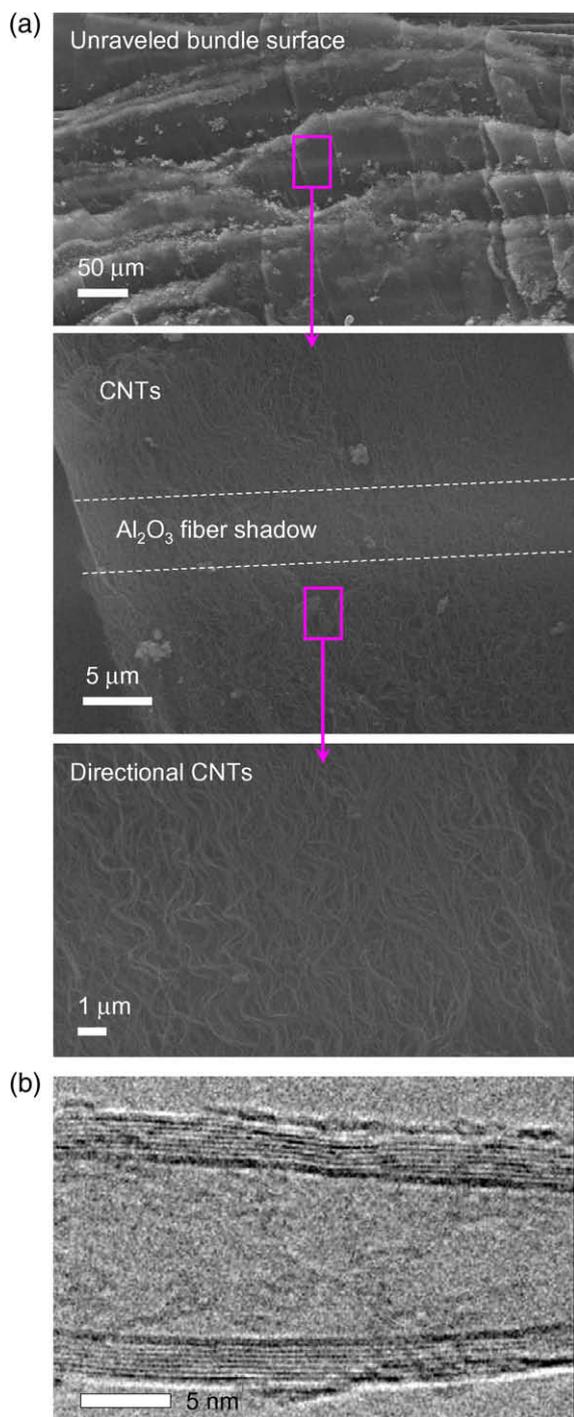
Fig. 3 – CNTs grown on Al₂O₃ fibers (50 mM Fe solution, with 2 min H₂ pre-treatment time, and at 3–6 cm downstream of the furnace center): (a) SEM images of aligned CNTs uniformly grown on alumina fibers inside the weave, and (b) TEM image of an individual multi-wall CNT taken from the fiber surface.

density of CNTs grown on the fibers is calculated as ~0.8 mg/mm³, based on the 1.4 mg/mm³ density of 1 nm-diameter SWNT [18]. At the best conditions, the CNT growth rate (forest thickness) was typically ~0.3 μm/s.

We define the yield of CNTs on the cloth as weight gain of the cloth during the growth process. CNTs add $2.6 \pm 1.4\%$ (averaged over 29 samples) to the sample weight with 2 min growth, and up to $3.8 \pm 1.2\%$ (8 samples) with 5 min growth. The catalyst coating process adds $\sim 0.7\%$ to the original cloth mass. Assuming uniform growth over the fiber surfaces and an effective CNT density of 0.8 g/cm³, the spacing between CNTs at the root on the Al₂O₃ fiber surfaces is calculated as 170–200 nm. This gives an areal density of 2×10^9 CNTs/cm² on the fiber surfaces. We assume that the catalyst mass does not decrease during the heating and pre-treatment stages; however, since organic elements in the salt layer vaporize when heated, our calculation of CNT yield is therefore a lower-bound value.

3.1. Effect of catalyst precursor concentration

The effect of the Fe solution concentration is shown in Fig. 4. A uniform coating of aligned CNTs is found only on samples prepared with 50 mM Fe solution. On samples prepared with 10 or 25 mM Fe solution, CNTs are locally-aligned, but the coverage of aligned regions is patchy. Therefore, an appropriately high concentration of Fe is needed for uniform CNT forest growth on the fiber surfaces.

3.2. Effect of hydrogen pre-treatment duration

The effect of varying the duration of H₂ pre-treatment is shown in Fig. 5. In this study, 2 min H₂ pre-treatment time always gives the most uniform growth coverage of CNT forests, for all catalyst concentrations and sample locations tested. Alternatively, CNTs grown after 0 or 5 min H₂ pre-treatment time exhibit poor coverage.

The observed trends of CNT growth coverage can be correlated to the formation of nano-particles during the pre-treatment stage. To further understand the effect of pre-treatment on catalyst particle size and coverage, cloth samples were processed identically to the CNT growth experiments, except the process was terminated and the furnace was cooled rapidly at the end of the pre-treatment step. This sequence attempts to "freeze" the surface structure of catalyst so the morphology which exists at the start of CNT growth (when C₂H₄ is introduced) can be observed. SEM images and accompanying EDX spectra of these samples are shown in Fig. 6. While it is difficult to obtain quantitative comparisons of elemental composition using EDX, the relative intensities of elemental signals may be used to qualitatively compare the presence of Fe on the fiber surfaces.

With no H₂ pre-treatment time, a highly non-uniform surface morphology is observed: fibers have both areas with a smooth morphology which give a low-intensity Fe signal (Fig. 6a) and areas with large clusters which give a strong Fe signal (Fig. 6b). This surface morphology is analogous to the initial structure of the Fe salt layer after dip-coating, and the non-uniformity can be directly related to the non-uniform CNT growth on samples without H₂ pre-treatment (Fig. 5a). After 2 min of H₂ pre-treatment time, a uniform surface morphology was observed. Nanoscale clusters with ≈ 100 nm average lateral dimension were observed on most surfaces
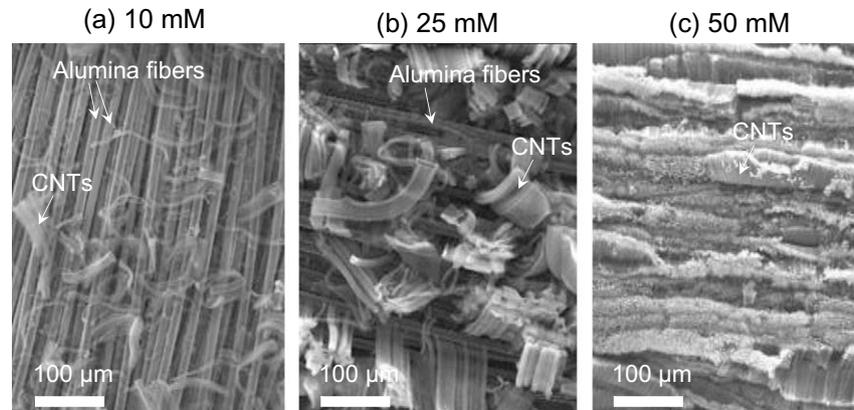
Fig. 4 – Effect of catalyst solution concentration on CNT growth on alumina cloth. All experiments used 2 min H_2 pre-treatment time, and the sample location was 3–6 cm downstream of the furnace center.
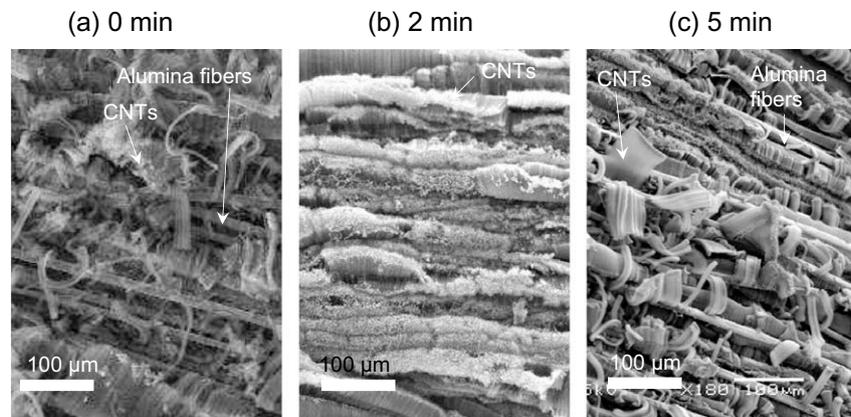

Fig. 5 – Effect of H_2 pre-treatment duration on CNT forest coverage and morphology. All experiments used 50 mM catalyst concentration, and the sample location was 3–6 cm downstream of the furnace center.

of the fibers (Fig. 6c). As a result, this pre-treatment condition results in uniform growth of CNT forests on the fiber surfaces (Fig. 5b). With longer durations of H_2 pre-treatment (e.g., 5 min), the clusters coarsen [19] into larger size particles (Fig. 6d), de-wetting Fe from the rest of the fiber surfaces (Fig. 6e). Thus, the corresponding coverage of CNTs on the fibers is once again non-uniform (Fig. 5c).

Experimentally as shown in Fig. 6c, well conditioned nano-particles sizes are a couple of 100 nm, much larger than the grown MWCNT diameter of 17.1 nm. This is the same order of magnitude as previous work on the correlation between nano-particles sizes and the resulting single-walled CNTs [20,21]. The spacing of several 100 nm between the nano-particles in Fig. 6c correspond well with the CNT spacing of ≈200 nm estimated above assuming uniform radial growth over the surfaces and CNT density.

3.3. Study of sample location

The location of the samples inside the quartz tube also influences growth as shown in Fig. 7. In our system, placing the sample 3–6 cm downstream of the furnace center (the location of the control thermocouple) gives the best CNT alignment and coverage. This position is best for all catalyst concentrations tested, although only the 50 mM concentration gives uniform and complete coverage. Growth results depend on sample position because the reactant mixture decomposes into a plurality of active species [22] as it is heated in the tube furnace. While we have not identified the chemical composition of the most active compounds, thermal decomposition of C_2H_4 is clearly essential for high-yield CNT forest growth from ethylene [23], and this determines a "sweet-spot" for growth in a tube furnace. When the sample is placed farther downstream (6–9 cm), excessive thermal decomposition has occurred, and the atmosphere is less favorable for CNT growth.

4. Discussion

This study achieves growth of uniform CNT forests on the surfaces of woven fibers using a simple, low-cost, and scalable catalyst preparation and deposition technique.

Overall, we demonstrate that three conditions must be satisfied to achieve uniform dense CNT growth on surfaces when a salt-based precursor is used, as listed below.

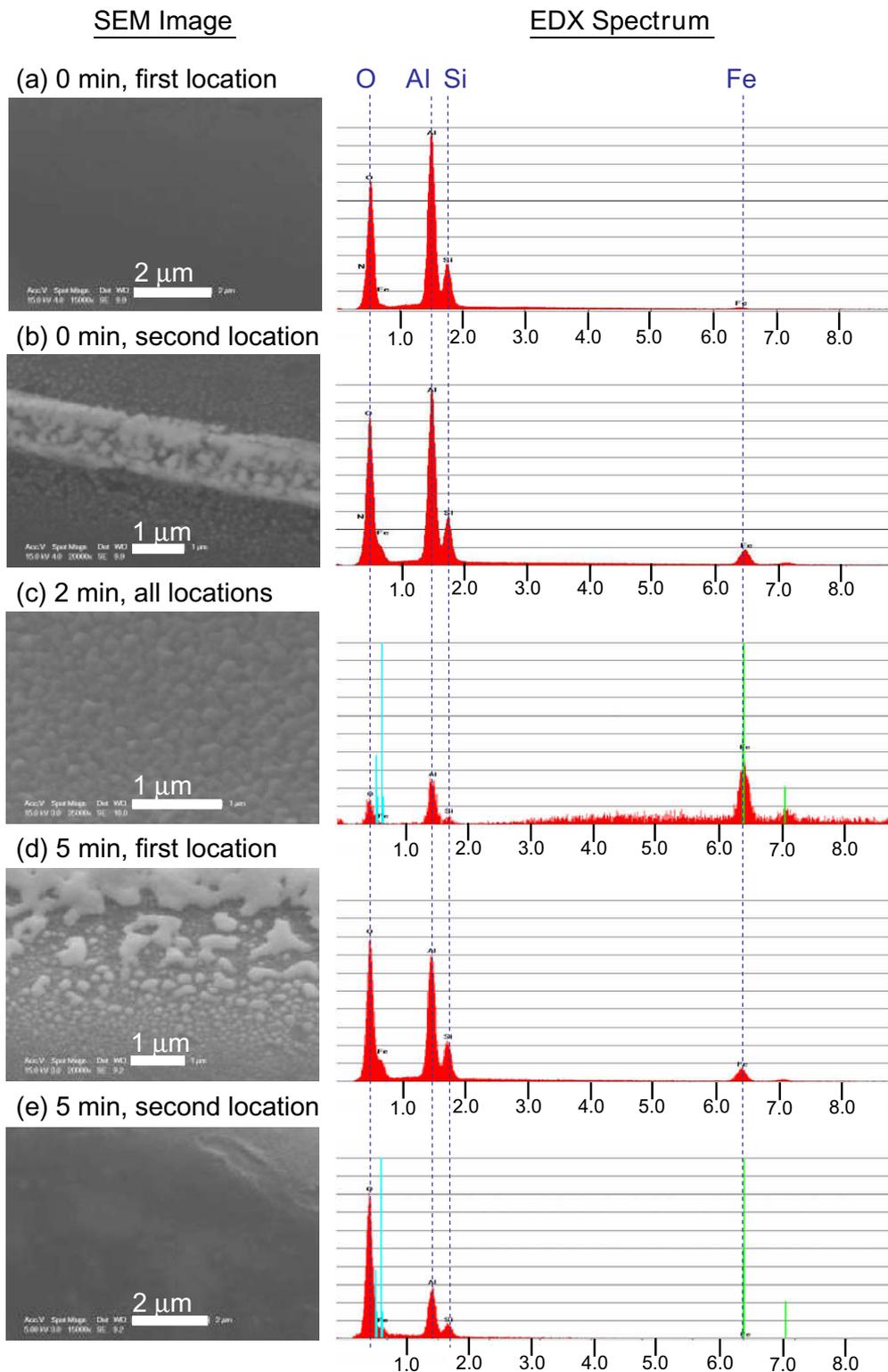- The catalyst concentration must be sufficient to fully coat the fiber surfaces.

Fig. 6 – Evolution of surface structure of catalyst-coated Al_2O_3 fiber surfaces at varying durations of H_2 pre-treatment time. All experiments used 50 mM catalyst concentration, and the sample location was 3–6 cm downstream of the furnace center.

- The H_2 pre-treatment time must be sufficient to create a uniform coating of nanoscale clusters which catalyze CNT growth, while not causing excessive coarsening which leads to non-uniform growth.

- Thermal decomposition of the reactant mixture must be sufficient to nucleate and supply carbon to a high density of CNTs.
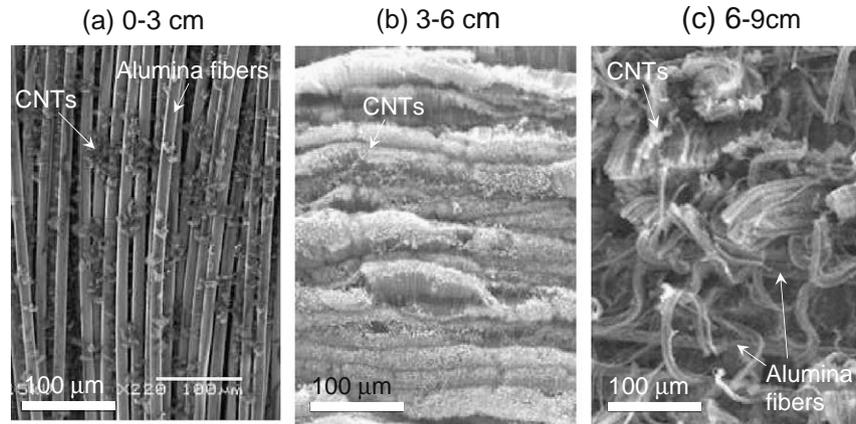
(a) 0-3 cm   (b) 3-6 cm   (c) 6-9cm

Fig. 7 – Dependence of CNT growth due to sample location in tube furnace. All samples were grown with 50 mM catalyst concentration and 2 min H$_2$ pre-treatment time.

Upon variations in these critical process parameters, we observe various morphologies of CNT organization on the fiber surfaces (Fig. 8). Tangled or locally-grouped growth (Fig. 8a–c) happens when the catalyst coating and/or activation (particle size, pre-treatment) is non-uniform. When the catalyst nano-particles are well-distributed, growth is dense and uniform, aligned perpendicular to the fiber surfaces (Fig. 8d–f). When CNT length is less than or comparable to the fiber diameter ($\approx$10 μm), the CNT coating has a uniform radial morphology (Fig. 8d). When the CNTs are larger than the fiber diameter, a "mohawk" morphology is

observed as the radial coating splits into two or more distinct groups (Fig. 8e and f). This is determined by competition between the extrusive forces of CNT growth and van der Waals forces among nearby CNTs. Similar CNT organization has been observed for growth on ceramic spheres [10,24].

While our initial experiments were conducted in a 22 mm ID quartz tube, larger samples are needed for preparation of ASTM standard composite samples for mechanical property tests, and also to eventually achieve industrial applications of CNT-reinforced composites. As a result, we more recently transferred our process to a larger furnace (Lindberg,
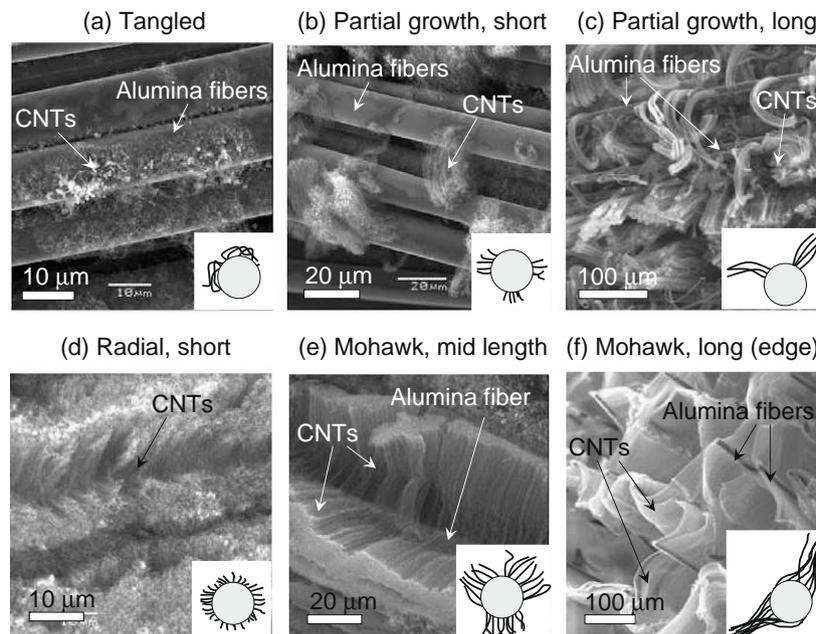

(a) Tangled   (b) Partial growth, short   (c) Partial growth, long
(d) Radial, short   (e) Mohawk, mid length   (f) Mohawk, long (edge)

Fig. 8 – Control of CNT morphology on fiber surfaces: (a) tangled CNTs grown with 50 mM catalyst concentration with 5 min H$_2$ pre-treatment time at 0 cm position, (b) partial coverage of short aligned CNTs (50 mM, 5 min H$_2$ pre-treatment, 0 cm), (c) partial coverage of long aligned CNTs (50 mM, 2 min H$_2$ pre-treatment, 8 cm), (d) radial coverage short aligned CNTs (25 mM, heated in air prior to 5 min H$_2$ pre-treatment, 0 cm), (e) "mohawk" aligned CNTs (25 mM, pre-treated in H$_2$ from room-temperature until growth begins, 3–6 cm), and (f) very long mohawk CNTs (50 mM, 2 min H$_2$ pre-treatment, 3–6 cm). All growth times are 5 min.

102 mm ID heater coils, 61 cm heated length) with a 51 mm ID quartz tube. Compared to the initial setup, this furnace tube is twice the diameter, and the furnace has three independently-controllable temperature zones.

First, CNTs were grown for 10 min in the larger furnace at the same setpoint temperature (750 °C) used in the smaller furnace, while quadrupling the gas flow rates to maintain the same gas residence time. As shown in Fig. 9a, growth was very poor in terms of both coverage and CNT length. However, at this setpoint temperature, the actual temperature inside the larger quartz tube was measured to be 40 °C higher (840 °C) than the temperature of 800 °C measured inside the smaller furnace. This is due to the larger diameter of the heater coils in the new furnace. Accordingly, a series of experiments studied the effect of the individual zone setpoint temperatures and sample position on the coverage and length of CNTs on the fibers. Finally, zone 1 was set at 850 °C to increase gas-phase decomposition of the reactants, zone 2 was set at 600 °C to isolate zone 1 from zone 3, and zone 3 was set at 700 °C to pre-condition catalyst nano-particles for CNT growth and give a suitable growth temperature. In addition, the flow rate of each gas was decreased by 20% to increase the residence time and therefore move the location of growth closer upstream in the furnace. This condition gives uniform aligned CNT growth on the fiber surfaces throughout an extended range of the larger furnace tube, enabling preparation of CNT-coated cloth samples as large as 5×10 cm^2.

Radial and dense CNT growth on fiber surfaces throughout woven fabrics is useful for multifunctional enhancement of traditional structural composites, where the CNTs act to mechanically, thermally, and electrically bridge the matrix region between adjacent fibers. After CNT growth, hybrid composites (advanced fibers, CNTs, and epoxy) were fabricated by immersing and curing the alumina fiber cloth with aligned CNTs ($\approx$100 μm length) on its fiber surfaces in room-temperature curable epoxy (West Systems) [2]. CNTs radially grown on the surfaces stay attached during matrix application, maintaining CNT uniform dispersion of CNTs in a matrix that is
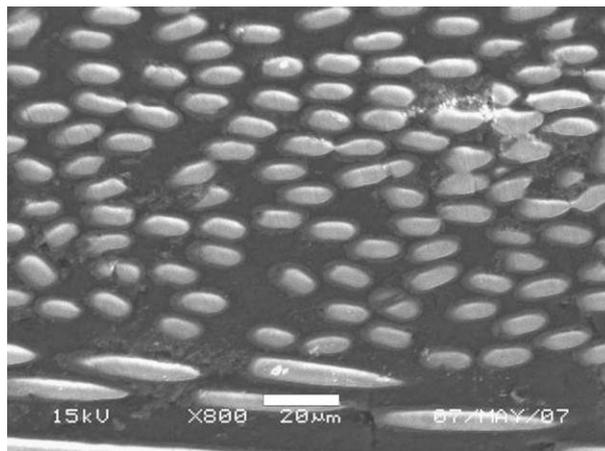

Fig. 10 – **Cross-section of Al$_2$O$_3$ fiber/CNT/epoxy composite, exhibiting uniform wetting of epoxy into aligned CNT coatings on ceramic fibers. The electrical conductivity of the CNTs causes charge contrast in the SEM image, giving the halos observed around the fiber-CNT/epoxy interfaces.**
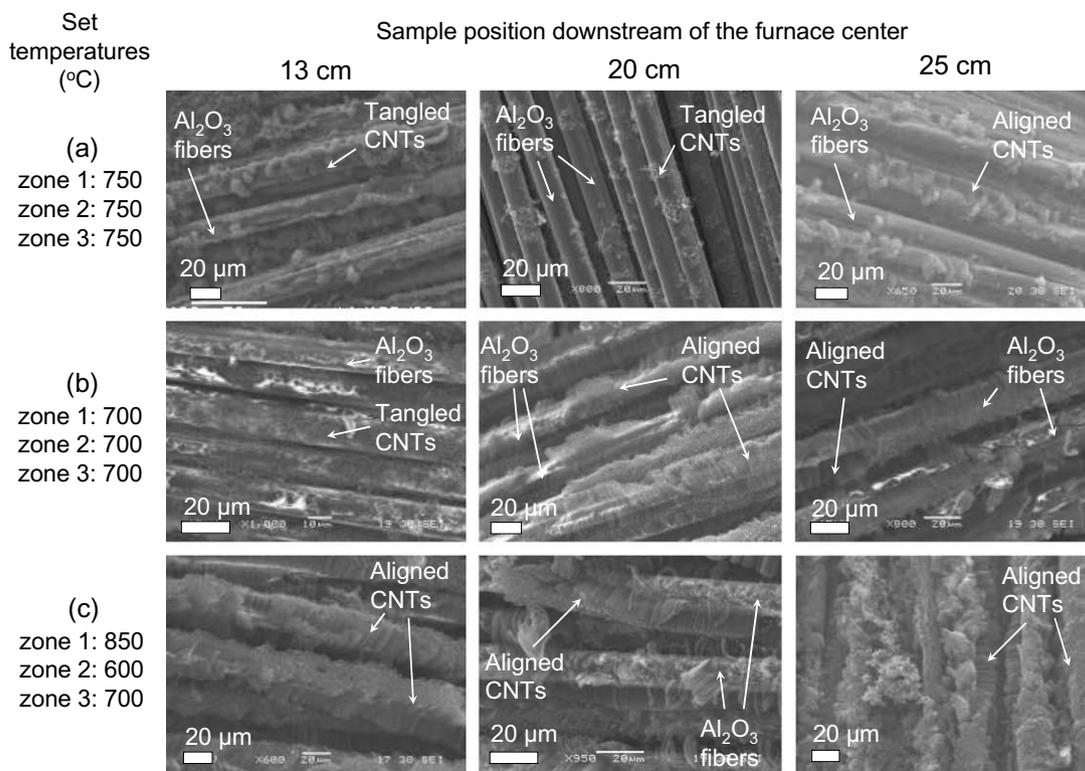

Fig. 9 – **Tuning of CNT growth process to achieve uniform results over large areas in 51 mm diameter tube furnace. Results are shown for various combinations of zone temperatures, at otherwise identical catalyst coating and treatment conditions.**

difficult to achieve when CNTs and matrix are mixed in bulk [25,26]. Due to the strong capillary forces among the aligned CNTs [27,28], the epoxy uniformly wets the CNTs inside the composite matrix Fig. 10, leaving no noticeable voids. Formation of an electrical network among the CNTs is confirmed by measuring an electrical conductivity enhancement of 10^6 (through-thickness) and 10^8 (in-plane) at 1% CNT volume fraction. The interlaminar shear strength is increased by 69% with ~1% CNT volume fraction [2], which is a significant improvement attractive to many structural applications.

5. Conclusion

We created a scalable process for growth of uniform radially-aligned CNTs on fibers within woven alumina cloth, by varying key process factors which govern the distribution and formation of catalyst nano-particles, along with the activity of the CVD reaction atmosphere. This study demonstrates uniform growth can be achieved throughout a pre-woven fiber cloth, using a low-cost and scalable catalyst deposition process starting with a metal salt solution. This a vital development for commercial feasibility of CNT-enhanced fiber composites. Further, the catalyst coating and growth process conditions can be tuned to control the morphology of CNTs on the fibers, and uniform radially-aligned CNTs are targeted for our current applications. The resulting CNT-enhanced cloth can be incorporated into traditional composite manufacturing and can significantly enhance multifunctional properties by way of nano-scale physical networks formed by CNTs on adjacent fibers. Applications of such CNT-reinforced hybrid composites include integral armors with enhanced impact resistance. Future work includes extending this growth process to carbon fiber composite systems for a wider set of applications in vehicle structures.

Acknowledgements

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