Circumventing the Mechanochemical Origins of Strength Loss in the Synthesis of Hierarchical Carbon Fibers

Supporting Information

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S1. Tabular Data for Single-Fiber Carbon Fiber Tensile Tests

In this section, tabular summary data for the single-fiber carbon fiber tensile tests and calculated Weibull parameters are presented including fiber processing conditions, number of samples tested per condition, mean tensile strength $\overline{\sigma}$, standard deviation of mean tensile strength $S(\overline{\sigma})$, Weibull modulus α, mean tensile modulus $\overline{E}$, and standard deviation of mean tensile modulus $S(\overline{E})$. We note that the Weibull distributions presented here may be wider than the true distribution of fiber properties in a tow as they include all measurements regardless of fiber break point. Testing did not allow for identification of break location and it is anticipated that some fibers broke away from the center of the testing frame (e.g., at the fiber-epoxy interface). The asymmetric bias of the distributions towards lower tensile strength values with increasing number of samples tested supports this hypothesis, as more breaks at the mounting points would be included in the dataset. Weibull parameters derived from tensile tests of single alumina fibers used for CNT growth derived exclusively considering fibers with breaks in the middle of test

specimens result in a comparatively narrower Weibull distribution.[1] As is observed here

for carbon fibers, the Weibull distribution of alumina fibers narrows after CNT growth.

Nonetheless, single-fiber tensile tests performed by Qian *et al.* with similar carbon fibers

(unsized high-tenacity SGL Carbon C320.00A PAN-based fibers, ~7.5 μm diameter)

gave an average tensile strength of 3,500±170 MPa for a gage length of 25 mm, which is

very close to what we report here (~3,400 MPa mean tensile strength with a standard

deviation of 570 MPa, see Table 1).[2] Additionally, Hitchon and Phillips in

characterizing the tensile strength of high-tenacity carbon fibers (Courtalds reel 2CT

76B/11R, 7.9-9.5 μm diameter) reported a Weibull modulus ranging from 6.3-8.8, similar

to the range we report here (6.1-6.4).[3] Full stress-strain plots for all sample tests

performed is available elsewhere.[4]

Sample Description	Processed as	No. of Samples[1]	$\bar{\sigma}$ (GPa) (= β)	S($\bar{\sigma}$) (GPa)	Weibull Modulus α	$\bar{E}$ (GPa)	S($\bar{E}$) (GPa)
Unsized HTR40, never mounted (control #1)	Tow	24	3.44	0.57	6.05	204	9.62
Unsized HTR40, never mounted, (control #2)	Tow	12	3.26	0.51	6.37	206	12.8
Unsized HTR40, mounted in frame and then unmounted	Single fibers in frame	11	3.56	0.44	8.00	203	6.81
Unsized HTR40, CVD processed, mounted in frame	Single fibers in frame	19	2.25	0.50	4.48	184	11.4
Unsized HTR40, CVD processed, unmounted (processed as tow)	Tow	10	2.76	0.55	5.04	202	11.0
Unsized HTR40, 15 min dwell at 300°C in H_2, CVD processed, mounted	Single fibers in frame	9	1.71	0.55	3.09	183	12.3
Unsized HTR40, 15 min dwell at 350°C in H_2, CVD processed, mounted	Single fibers in frame	10	2.09	0.58	3.61	190	9.54
h-PSMA-coated HTR40, CVD processed, mounted	Single fibers in frame	10	2.16	0.36	6.01	197	8.91
h-PSMA/alumina/Fe^{3+}-coated HTR40, CVD processed, mounted	Single fibers in frame	22	1.62	0.38	4.21	194	9.61

[1]A minimum of 15 valid tests is required for calculation a valid Weibull distribution.[8]

Table S1. Summary of single-fiber tensile test data for carbon fibers as received, after thermal processing with H_2 and subsequent CVD process suitable for CNT growth, and coated and CVD-processed.

Sample Description	Processed as	No. of Samples[1]	$\bar{\sigma}$ (GPa) (= β)	S($\bar{\sigma}$) (GPa)	Weibull Modulus α	$\bar{E}$ (GPa)	S($\bar{E}$) (GPa)
Temperature Study, HTR-40							
Unsized HTR-40	Tow	19	4.49	0.75	5.96	223	7.88
Unsized HTR-40, 480°C in He, 10 min at set point	Tow	19	4.37	0.83	5.27	213	12.9
Unsized HTR-40, 580°C in He, 10 min at set point	Tow	18	2.50	0.34	7.42	211	11.9
Unsized HTR-40, 730°C in He, 10 min at set point	Tow	20	1.47	0.28	5.30	194	13.1
Temperature Study, AS4							
Unsized AS4	Tow	19	3.77	0.46	8.11	237	10.2
Unsized AS4, 480°C in He, 18 min ≥ 480°C	Tow	17	3.55	0.66	5.34	239	9.99
Unsized AS4, 580°C in He, 18 min ≥ 480°C	Tow	20	3.74	0.69	5.40	234	13.3
Unsized AS4, 730°C in He, 18 min ≥ 480°C	Tow	18	1.09	0.20	5.41	215	10.2
Temperature vs. Time Study							
Unsized HTR-40, 480°C in He, 18 min ≥ 480°C	Tow	20	4.49	0.94	4.76	217	7.54
Unsized HTR-40, 580°C in He, 18 min ≥ 480°C	Tow	20	3.56	0.36	9.97	212	8.96
Unsized HTR-40, 730°C in He, 18 min ≥ 480°C	Tow	20	3.09	0.52	5.94	205	14.0
Unsized HTR-40, 480°C in He, 36 min ≥ 480°C	Tow	20	4.20	0.95	4.44	212	12.6
Unsized HTR-40, 580°C in He, 36 min ≥ 480°C	Tow	19	2.61	0.43	6.11	200	13.3
Unsized HTR-40, 730°C in He, 36 min ≥ 480°C	Tow	18	1.94	0.63	3.07	192	12.2

[1]A minimum of 15 valid tests is required for computation of a valid Weibull distribution.[8]

Table S2. Summary of single-fiber tensile test data for carbon fibers thermally processed in He atmosphere as a function of temperature and time.

Sample Description	Processed as	No. of Samples[1]	$\bar{\sigma}$ (GPa) (= β)	$S(\bar{\sigma})$ (GPa)	Weibull Modulus α	$\bar{E}$ (GPa)	$S(\bar{E})$ (GPa)
Low Tension Study							
Unsized HTR-40, untensioned,730°C in He, 18 min ≥ 480°C	Tow on tension frame	20	3.91	1.07	3.66	214	17.6
Unsized HTR-40, tensioned ($\bar{\Xi}$ =0.12), 730°C in He, 18 min ≥ 480°C	Single fibers on tension frame	21	4.46	0.72	6.23	215	10.7
h-PSMA/alumina/Fe^{3+}-coated HTR40 tensioned ($\bar{\Xi}$ =0.12), CVD processed, mounted	Single fibers on tension frame	24	3.36	0.77	4.74	215	9.30
Moderate Tension Study							
Unsized HTR40	Tow	19	3.46	0.79	4.40	212	12.5
Unsized HTR40, tensioned ($\bar{\Xi}$ =0.45), 730°C in He, 18 min ≥ 480°C	Single fibers on tension frame	24	3.10	0.71	4.36	202	11.6

[1]A minimum of 15 valid tests are required for computation of a valid Weibull distribution.[8]

Table S3. Summary of single-fiber tensile test data for carbon fibers thermally processed in He atmosphere under tension as single fibers and control samples processed untensioned as tows.

Sample Description	Processed as	No. of Samples[1]	$\bar{\sigma}$ (GPa) (= β)	$S(\bar{\sigma})$ (GPa)	Weibull Modulus α	$\bar{E}$ (GPa)	$S(\bar{E})$ (GPa)
Unsized HTR-40[b]	Tow	19	3.46	0.79	4.40	212	12.5
K-PSMA/Fe^{3+} on HTR-40, CO_2/C_2H_2 CVD at 480°C	Tow	20	3.88	0.85	4.55	213	13.2

[a]A minimum of 15 valid tests is required for calculation of a valid Weibull distribution.[8]
[b]Repeat of listing from Table 3; served as control for moderate tension study and CNT growth study.

Table S4. Summary of single-fiber tensile test data for carbon fibers coated with Fe^{3+}-loaded K-PSMA CVD processed for CNT growth with CO_2/C_2H_2, and as-received control samples.

S2. Full Experimental Details

Preparation of h-PSMA

Aqueous solutions with varying concentrations of h-PSMA were prepared

according to the method of Stroock et al.[5] Solutions were prepared by dissolving 1.4 g,

4.2 g, or 7.0 g (corresponding to concentrations of 0.5, 1.5, and 2.5 wt%, respectively) of

PSMA (Sigma-Aldrich, 99%, M_w=350,000) in 25 mL of acetone with gentle heating.

The PSMA solution was then added to 300 mL of 0.3 M NaOH in deionized water with

stirring and allowed to react for 3 h, after which it was acidified with 0.1 M HNO_3 to a

pH of 8. The acetone in the solution was then removed with a rotary evaporator.

Non-covalent Functionalization of Carbon Fibers with h-PSMA

Unsized (i.e., never-sized), never-surface-treated carbon fiber tow (TohoTenax

product number HTR40 N00 24k 1550tex) was used for substrates. (Note: This product

was obtained through industrial liaisons and is not available commercially. The

equivalent commercial version, HTA40 F22 24k 1550tex, is surface-treated and sized.)

h-PSMA was coated over the fibers by dip-coating a tow in aqueous h-PSMA solution for

~5 min and subsequently allowing the tow to dry in air or blow-drying with cool air

(which took ~9 min). Upon removal of the tow from h-PSMA solution the tow became

noticeably stiff and difficult to peel apart. To improve coating of fibers in the inner tow,

the tow could be dabbed up and down in the h-PSMA solution (as is done to clean a

watercolor paintbrush) over the 5-min period.

Application of Alumina Barrier Coating to Carbon Fibers

The h-PSMA-coated fibers were coated with a sol-gel-derived alumina coating

and coated with catalyst for CNT growth. Two sol-gel processes for alumina deposition

were investigated, an alkoxide-based approach and an epoxide-assisted approach.[6]

Aluminum tri-*sec*-butoxide (ATSB, Sigma-Aldrich product number 201073, 97%), 2-

methoxyethanol (MeOEtOH, Sigma-Aldrich product number 185469, ≥99.0%),

acetylacetone (acac, Sigma-Aldrich product number 10916, ≥99.5%), nitric acid (Sigma-

Aldrich product number 438073, ACS grade), and analytical reagent grade deionized water (Ricca Chemical Company product number 9150-1) were used as received. In the alkoxide-based approach, a solution of 50 mL MeOEtOH, 1.25 mL ATSB, and 0.5 mL acac was prepared. Next, carbon fiber substrates were rinsed with acetone followed by 2-propanol and baked dry on a hot plate at 80°C. The carbon fibers were then soaked in the alkoxide solution and baked in air at 200°C. The process was repeated 3-6 times to build up a thicker (up to ~1 μm) alumina coating. In the epoxide-assisted approach, 2.96 g $AlCl_3 \cdot 6H_2O$ was dissolved in a mixture of 20.0 g (20.0 mL) deionized water and 20.0 g (25.4 mL) 2-propanol. The mixture was stirred until the salt had fully dissolved. Next, 7.86 g (9.5 mL) propylene oxide was added slowly into the solution via syringe with stirring. The solution was then stirred another 5 min and allowed to solify. Gel time was ~4 h. Alternatively, a solution of 10.0 g (10.0 mL) deionized water and 7.89 g (10.0 mL) absolute ethanol could be used. In this case the gel time was reduced to ~1 h 40 min. Gel time could be further adjusted for either of these processes by increasing the amount of solvent used, however this also results in an increase in porosity.

CVD Growth of CNTs on Alumina-Coated Carbon Fibers

Catalyst precursor was applied to h-PSMA/alumina-coated fibers. First, a catalyst solution of 0.050 M $Fe(NO_3)_3 \cdot 9H_2O$ in 2-propanol (IPA) was prepared and aged with stirring for 0-2 h. Solution aging time was examined as a parameter for controlling CNT diameter and density as iron oxide nanoparticles continually grow in the solution during this time frame and eventually precipitate. h-PSMA/alumina-coated fibers were subsequently dip-coated into this solution for ~5-30 min.

Finally, the h-PSMA/alumina/Fe^{3+}-coated fibers were CVD processed for CNT growth. CVD growth of CNTs was performed in a fused quartz tube (54-mm outer diameter, 50-mm inner diameter, 137-cm length) heated by a three-zone split-hinge tube furnace (Lindberg/Blue M model HT55667C, 30-cm heated zone lengths). (*Caution: Due to the distance between thermocouples and process tube in this furnace, reported temperatures may different from actual process temperatures substantially; calibration via in situ thermocouple measurement is advised for repeatable results*). In a typical process, specimens were placed in a fused quartz process tube at the center of the third zone. The tube was then flushed with a flow of 2070 sccm He for 10 min to displace oxygen from the tube. Next, a flow of 1040 sccm H_2 gas (Airgas, ultrahigh purity grade, >99.999%) was introduced and He was turned off. The sample was then heated to 650°C under H_2 gas over the course of ~8 min to reduce iron oxide nanoparticles on the specimen to catalytically-active iron. The sample remained at these conditions for an additional 7 min to further reduce remaining iron oxide nanoparticles. A flow of 316 sccm ethylene (Airgas, ultrahigh purity grade, >99.999%) was then added for 5 min to facilitate CNT growth. Lastly, the flow of He was increased to 2070 sccm, the H_2 and C_2H_4 were turned off, and the sample was allowed to cool to room temperature under He flow.

Improvements in adhesion to unsized carbon fibers and reduction in cracking of sol-gel-derived coatings were assessed by FE-SEM and spatial elemental analysis by Auger spectroscopy.

Preparation of K-PSMA Ion Exchange Polyelectrolyte

Various formulations for preparing K-PSMA were explored. In the method most optimal for CNT growth, a solution of 1.5 wt% h-PSMA is prepared as described above.

The h-PSMA polyacid is then neutralized by stirring solid K_2CO_3 (Sigma-Aldrich part number 209619, $\geq 99.0\%$) into the solution. At first, the K_2CO_3 simply dissolves in the solution, but upon further addition, evolution of a CO_2 fizz results. K_2CO_3 is added until CO_2 fizz no longer results upon further addition. This point corresponds to a solution pH of ~11 or ~0.79 g K_2CO_3/10.00 g 1.5 wt% h-PSMA solution. Alternative formulations were also explored. In one set of formulations, KOH was used instead of NaOH during hydrolysis of the PSMA precursor. In some of these formulations, the solution was only acidified to a pH of ~11 to test whether or not a K^+-rich solution at a pH of ~11 would result in K-PSMA or if neutralization with K_2CO_3 from a pH of 8 was required. The concentration of h-PSMA (and thus K-PSMA) can be varied from 0.5 wt% instead of 2.5 wt% to adjust to processing requirements (higher concentrations of h-PSMA and K-PSMA generally yield thicker polymer coatings over carbon fibers and can make carbon fiber tows stiffer but may also result in higher loading of catalyst onto the fiber).

Non-covalent Functionalization of Carbon Fibers with K-PSMA

Unsized (i.e., never-sized), never-surface-treated HTR40 carbon fiber tow was used for substrates. Carbon fiber tows (~10 cm long) were cut and taped at one end with masking tape (3M 2600) for ease of handling. K-PSMA was coated over the fibers by dip-coating a tow in aqueous K-PSMA solution for ~5 min and subsequently allowing the tow to dry in air or blow-drying with cool air (which took ~9 min). Upon removal of the tow from K-PSMA solution the tow became noticeably stiff and difficult to peel apart, but less so than when coating with h-PSMA. To improve coating of fibers in the inner tow, the tow could be dabbed up and down in the h-PSMA solution (as is done to clean a watercolor paintbrush) over the 5-min period.

K-PSMA-coated fibers were then dip-coated with iron catalyst precursor solutions. In one set of formulations, 0.050 M $Fe(NO_3)_3 \cdot 9H_2O$ in 2-propanol (Fe^{3+}/IPA) was used. In subsets of these formulations, the Fe^{3+}/IPA solution was aged for 30 min, 60 min, and 90 min prior to dip-coating. Some K-PSMA-coated fibers were dip-coated before the K-PSMA deposit was dry, others were dip-coated after it was dry. Alternatively, 0.1 M aqueous $Fe(NO_3)_3$ was used to dip-coat catalyst precursor. After dip-coating with catalyst, the masking tape at the end of the tow was cut off. At this point, the tow was sufficiently stiff from and held together by its K-PSMA coating that handling of the fibers was possible without tape.

CVD Growth of CNTs with K-PSMA-Coated Carbon Fibers

Fe^{3+}/K-PSMA-coated fibers were then CVD processed for CNT growth. CVD processing was performed. Temperature set points reported by Magrez *et al.* were calibrated against our system's set points by comparing the optimal temperature for CNT growth established for Fe/alumina-coated wafers via the CO_2/C_2H_2 process. The temperatures reported by Magrez *et al.* underestimate the optimal growth temperature for similar substrates in our system by ~80°C. As such, the optimal growth temperature for carbon-supported iron reported by Magrez *et al.* (400°C)[7] was converted to a set point of 480°C for our system. Samples were placed in a dedicated fused quartz process tube (25-mm outer diameter × 22-mm inner diameter × 30-cm length) and heated in an electric clam-shell tube furnace (Lindberg/Blue M MiniMite). Samples were positioned at 75% along the length of the heated zone. First, a flow of 750 sccm Ar (Airgas, ultrahigh purity grade, >99.999%) was introduced into the reactor for 2 min to displace oxygen from the process tube. Next, a flow of 400 sccm H_2 (Airgas, ultrahigh purity grade,

>99.999%) was added and the Ar flow lowered to 200 sccm Ar. The samples were then heated to a set point temperature of 480°C under H_2/Ar flow to reduce and coarsen iron ions adsorbed over the coated fiber surfaces to iron nanoparticles. Once at this temperature, a flow 17 sccm CO_2 (Airgas, ultrahigh purity grade, >99.999%) and 167 sccm 10% C_2H_2 in Ar (Airgas, ultrahigh purity grade, >99.999%, acetone-free) were introduced and the H_2 and Ar deactivated. The samples were soaked under these conditions for 15 min after which a flow of 750 sccm Ar was introduced and the CO_2 and C_2H_2/Ar mixture were deactivated. The furnace was then opened and the samples were allowed to cool to ambient conditions. Between CNT growths, the quartz process tube was baked in air at 750°C for ~20 min to remove deposited organics. In one variation of this process, samples were not treated with H_2 on ramp-up to the set point temperature.

Efficacy of various K-PSMA formulations and catalyst application methods for facilitating CNT growth was assessed by the presence, areal density, and length of CNTs on tows following from CVD processing as observed by SEM.

Preparation and Mounting of Carbon Fiber

The carbon fibers used in this investigation were unsized (that is, never sized, as opposed to desized), never-surface-treated TohoTenax HTR40 and Hexcel AS4. Unsized fiber was chosen in order to eliminate possible fiber damage associated caused by desizing procedures such as thermally decomposing the sizing under inert atmosphere or interaction of the fiber with unremoved sizing. Prior to use, fibers were rinsed with acetone and evaporatively dried in air. Single fibers were carefully extracted from the 24k tow using Q-Tips®, which gently latch onto the fibers and pull them out from the other fibers. Care was taken not to stretch fibers when pulling them out to avoid

pretensioning of the fiber. (Note that the force required to break a single carbon fiber is ~40-180 mN, or ~0.01-0.04 lbf, corresponding to a stretch of only ~150-300 μm.) The single fibers were then mounted into a rectangular two-piece milled graphite frame to hold them in place for handling and processing (Figure S1). Fibers were mounted into the frame by stringing lengthwise across the bottom half of the frame with slack on either side and then setting the top half of the frame on top. This held the fibers in place by compression. Up to five fibers could be mounted at a time. If coatings were to be applied to the fibers, masking tape was used to hold the frame together until ready for heat treatment at which point the masking tape was peeled off and any adhesive residue was gently scrubbed from the frame with acetone.
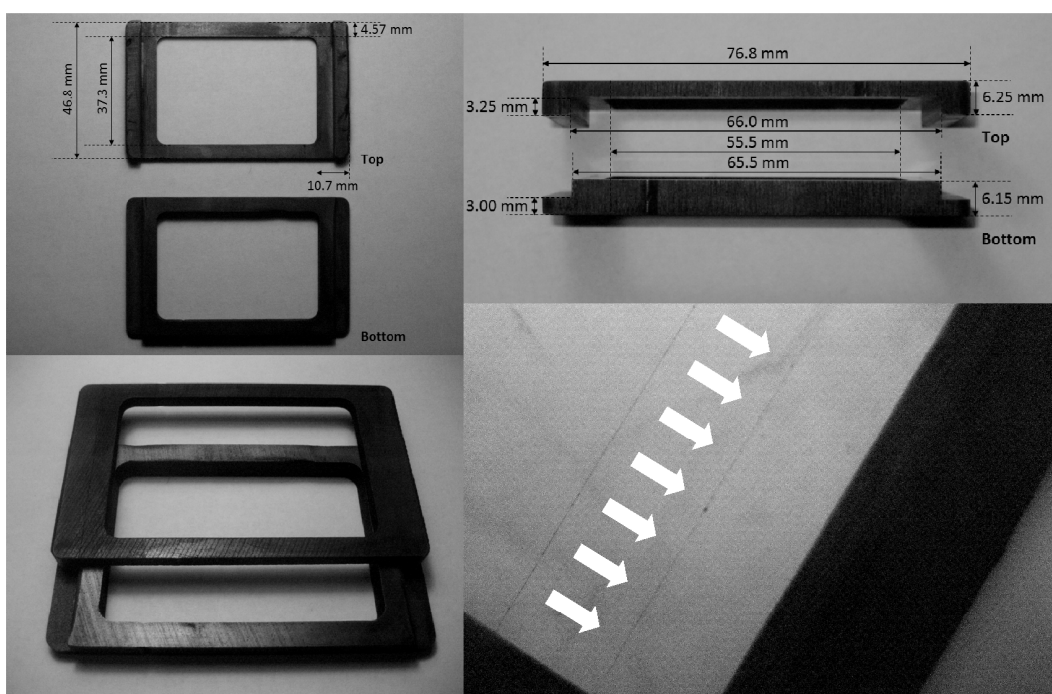
 Figure S1. Graphite frame developed for manipulating and thermochemically processing single 7-μm-diameter carbon fibers: *(top row)* dimensions of two-piece graphite frame; *(bottom left)* demonstration of top and bottom of graphite frame illustrating clamping concept; *(bottom right)* individual Fe^{3+}/alumina/h-PSMA-coated carbon fiber after CVD processing strung in graphite frame with visible CNT clusters.

Application of Coatings and CVD Growth of CNTs on Single Carbon Fibers

Fibers were prepared for CVD growth of CNTs using the coatings techniques described in the previous sections. A sol-gel-derived alumina barrier coating with iron catalyst was used to facilitate CNT growth. Sol-gel was selected as the method for depositing alumina to maximize ease of processing and probability of success. A coating of 2.5 wt% aqueous h-PSMA was put on the fiber to facilitate adhesion of the alumina coating. The alumina coating was deposited using cyclic baking of an alkoxide-derived sol as described.

A solution of 2.5 wt % aqueous h-PSMA was prepared as described. Briefly, 7.0 g of poly(styrene-*alt*-[maleic anhydride]) (PSMA, M_W=350,000, Sigma-Aldrich) was dissolved in 25 mL acetone with mild heating (up to 45°C). This solution was then added to 300 mL of 0.30 M aqueous NaOH. After 3 h, the pH was lowered to 8 with the addition of nitric acid. Finally, the acetone was removed from the solution using a rotary evaporator.

Graphite frames loaded with isolated single carbon fibers were placed into a "boat" of Parafilm[®] (wrapping all sides of the frame except the top) to allow for filling of the frame with liquid. Using a Pasteur pipette, 2.5 wt% aqueous h-PSMA solution was injected into the frame until the fibers were submersed (note that the frame is wetted in this process). The fibers were allowed to soak in the solution for 2 h, after which the solution was drained using a Pasteur pipette and the fibers were allowed to evaporatively dry in air overnight.

Graphite frames loaded with isolated single fibers were placed into a new Parafilm boat as described above. Using a Pasteur pipette, a solution containing 2.5 vol %

aluminum tri-*sec*-butoxide (ATSB, Sigma-Aldrich, 97%) in 2-methoxyethanol

(MeOEtOH, Sigma-Aldrich, 99%) was injected into the frame until the fibers were

submersed as described above. The fibers were allowed to soak for 5 min after which

they were heated at 200°C in a convection oven and cooled in air for 3 min. This process

was repeated three times. The coated fibers were then allowed to dry 30 min at room

temperature prior to further processing.

A solution of 0.050 M $Fe(NO_3)_3 \cdot 9H_2O$ in 2-propanol was prepared and stirred for

1-2 h. Graphite frames loaded with isolated single fibers were placed into a new Parafilm

boat as described above. Using a Pasteur pipette, the frames were then filled with the iron

nitrate solution aged no more than 2 h until the fibers were submersed. Shortly after (~5

min), the frame was drained, the fibers were allowed to dry overnight, and the Parafilm

boat was removed.

Atmospheric thermal CVD was performed in a three-zone Lindberg/Blue M

furnace with a 62-cm heated length using 54-mm outer diameter by 50-mm inner

diameter fused quartz process tubes with a length of 138 cm. (Note that due to the

distance between the thermocouples and samples inside a fused quartz process tube in

this furnace, the furnace set point may underestimate the actual process temperature by

~80°C.) Fiber-loaded graphite frames were slid into the quartz tube and positioned

between 50% and 75% of the heated length as measured from the gas intake end of the

furnace. Gases used were all ultrahigh purity grade (Airgas, >99.999%). The CVD

process was performed as follows. First, the tube was flushed at ambient temperature for

10 min with a flow of 2070 sccm He to displace air in the tube. Next, the flow of He was

dropped to 41 sccm and 1040 sccm H_2 was added. All three zones were then ramped to a

set point 650°C (corresponding to an actual process temperature of 730°C) over the course of ~7 min at which point the samples were allowed to soak under H_2 for an additional 7 min. A flow of 318 sccm C_2H_4 was then introduced for 5 min to enable CNT growth. Finally, the He flow was increased to 2400 sccm, the H_2 and C_2H_4 were turned off, and the samples were allowed to cool to ambient temperature and removed.

Thermochemical Processing of Single Fibers Under Tension

The role of tension during thermochemical processing of carbon fibers was evaluated using a special all-graphite tensioning frame (see Figure S2 left, Figure S3, and Figure S4) and screw-clamp weights. Photographs of the tensioning frame are shown in Figure S4. Due to concerns of chemical contamination, the frame and all fastening parts were machined exclusively out of polycrystalline graphite. Special clamp-on weights, also made of graphite, were used to impart up to 0.5 GPa of tension into single carbon fibers (Figure S5). A set of tungsten-core, graphite-shell weights was also produced (see Figure S2 right and Figure S6) and enabled application of tension up to 3.2 GPa.

A length of carbon fiber tow (~30 cm long) was cut and laid out on a clean sheet of copy paper. A "fiber grabber" tool was fashioned to extract fibers from the tow, made by rolling a piece of masking tape (3M 2600, tape type is important) onto the end of a thin wooden dowel (e.g., a toothpick) to make an ~0.5 x 1.0 cm "flag" of tape hanging off the end of the dowel with sticky side exposed. This tool was used to gently stick onto single carbon fibers in the bundle and pull them away from the tow through gentle application of torque rather than tension. This was done to minimize stretching or "pretensioning" of fibers during extraction from the tow. Next, with fiber attached to the fiber grabber, the fiber was drawn out and laid across two Parafilm-covered fiberglass

blocks (~5 cm x 2.5 cm x 4.3 mm, see Figure S7) separated by a distance of ~18-20 cm, to which the fiber could cling electrostatically (this is the desired result). White paper could optionally be placed between the translucent Parafilm and off-white fiberglass to improve contrast of fibers placed atop the blocks. Another, thinner fiberglass block (~12 cm x 5 cm x 2.9 mm) without Parafilm was placed nearby for the next step. With a gloved finger, the end of the fiber attached to the fiber grabber tool was pressed down onto its Parafilm-covered fiberglass block and the fiber grabber twisted away and detached. With fiber strung between, the two Parafilm-covered fiberglass blocks were then picked up and carefully placed down and over the larger, thinner fiberglass plate such that the larger plate sat between the two Parafilm-covered blocks lengthwise (12-cm length) with ~3 cm space between it and each Parafilm-covered block. Once set down, the Parafilm-covered blocks were gently pulled apart to tension the fiber, noting that the fiber is capable of slipping on the Parafilm which self-corrects for and reduces concerns for overtensioning.

Next, graphite clamp weights (or heavier tungsten-core/graphite-shell clamp weights) were readied for attachment to the fibers. The clamp weights were assemblies comprised of two small blocks with dimensions of 9.5 mm x 9.5 mm x 17.8 mm joined at one end with a graphite screw to form a sandwich structure. The screw could be tightened or loosened to open a gap between the two blocks, which sit parallel to each other and perpendicular to the screw thread. Two such weight assemblies, tightened such that an ~1 mm gap was left between the two weight blocks, were placed on either side of the long fiberglass plate and pushed against the plate with gap running parallel to and under the fiber, in preparation for the fiber to be laid down into them (Figure S7). The

two Parafilm-coated blocks were then carefully picked up and the taught fiber laid into the gaps of the two clamp weight assemblies. Once in place, the screws on the weight assemblies were screwed finger-tight resulting in clamping of the weights onto the fiber.
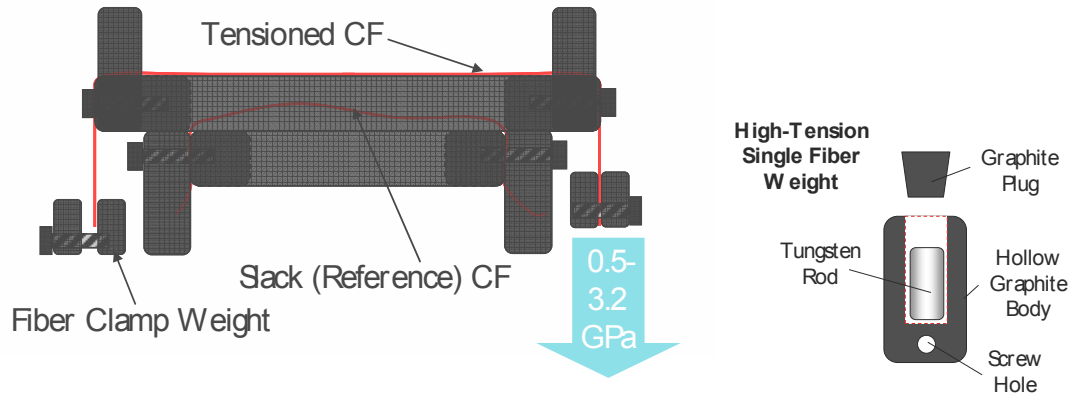

Figure S2. Diagram of all-graphite tensioning frame developed for thermal processing of single carbon fibers under tension *(left)* and tungsten-core/graphite-shell high-tension weight for enabling application of higher levels of tension to a fiber than with all-graphite weights.
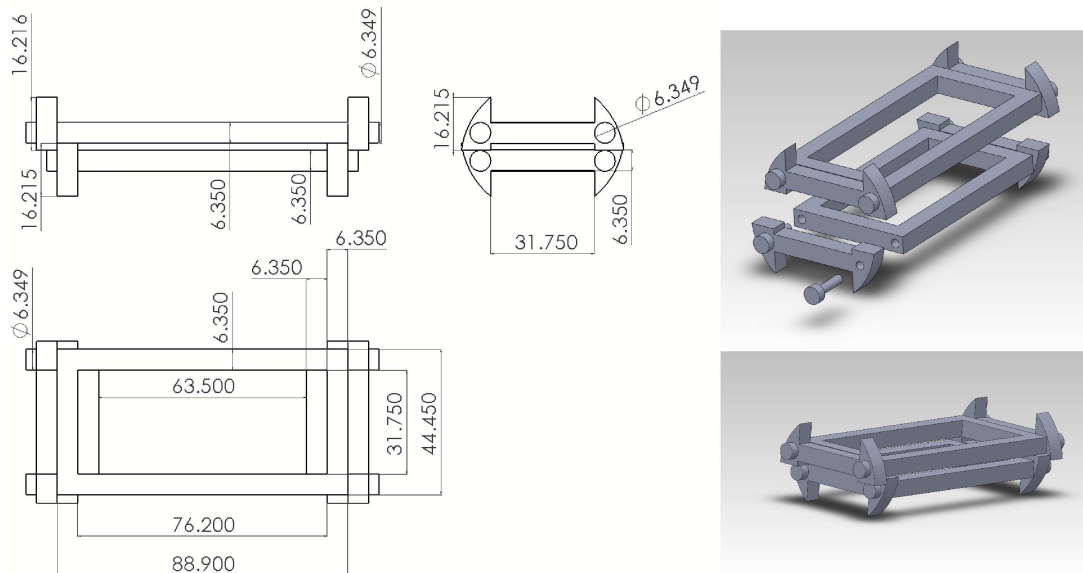
Figure S3. *(Left)* Dimensions (in mm) for all-graphite tensioning frame; *(upper right)* exploded view of tensioning frame components showing attachment of "horned bumpers" with threaded graphite screws; *(lower right)* assembled tensioning frame.
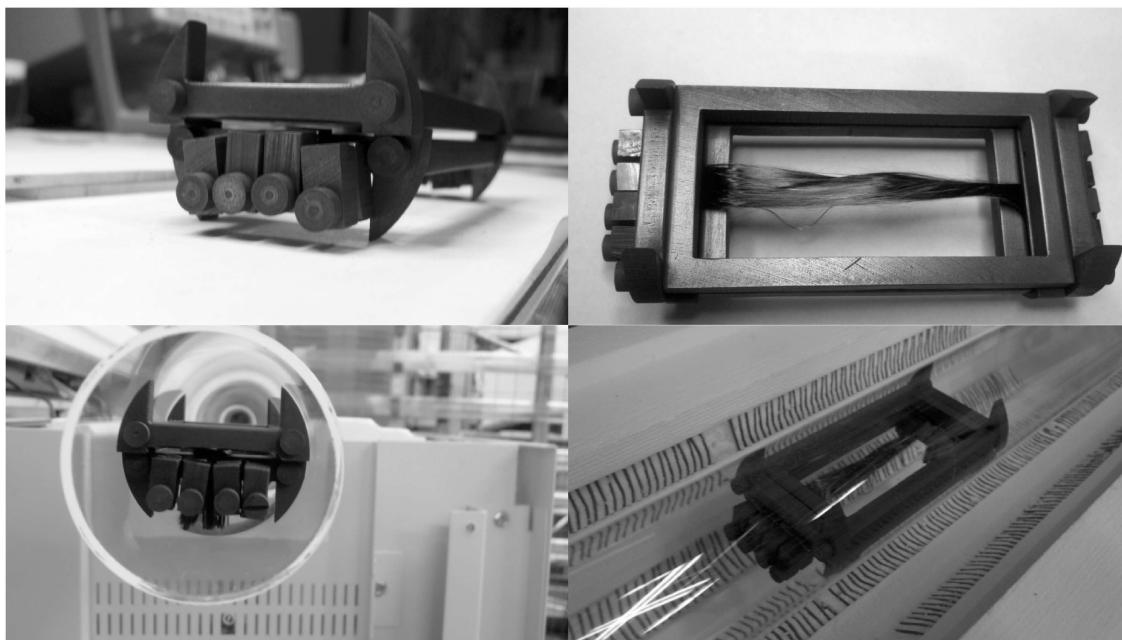
Figure S4. Photographs of all-graphite tensioning frame: *(upper left)* four separate 7-µm-diameter tensioned carbon fibers supporting dangling tungsten-core weights; *(upper right)* untensioned tow simultaneously clamped in lower level of frame to provide reference fibers after CVD processing; *(lower left and lower right)* tensioning frame positioned in fused quartz process tube inside electric clamshell furnace ready for CVD processing.
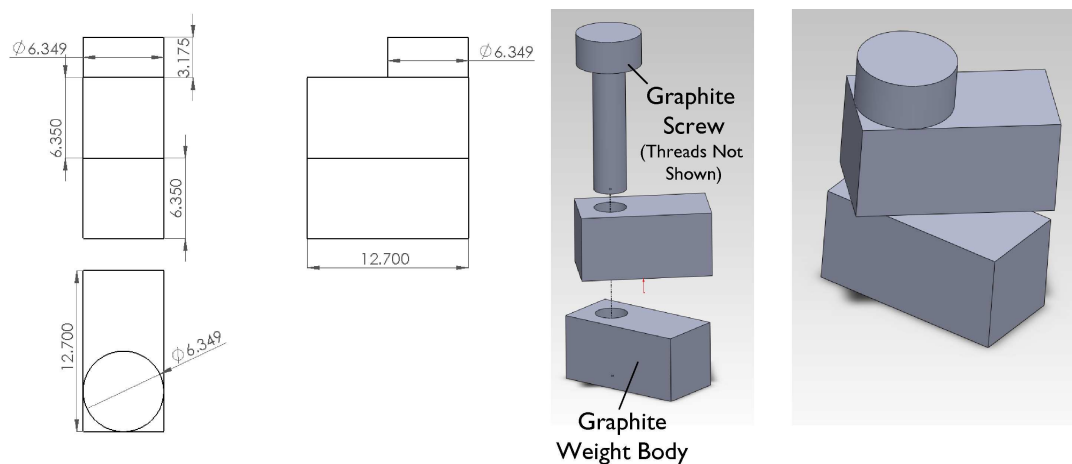

Figure S5. *(Left)* Dimensions (in mm) for two-piece graphite weight assemblies; *(middle)* exploded view of weight assembly; *(right)* assembled weight assembly.
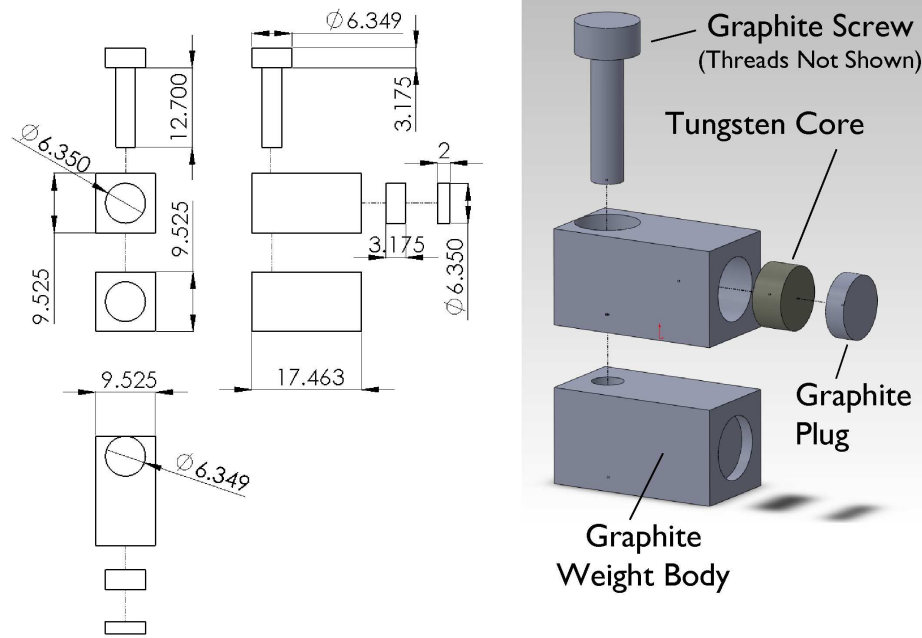
Figure S6. *(Left)* Dimensions (in mm) for tungsten-core weight assembly used for higher tension studies and screws used for both weight assemblies and tensioning frame; *(right)* exploded view of tungsten-core weight assembly.
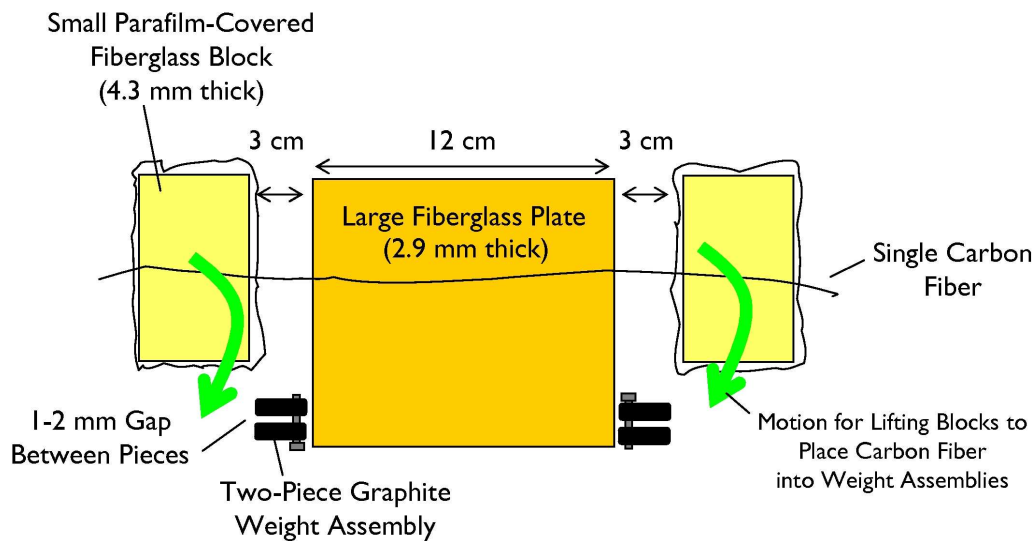

Figure S7. Transferring single carbon fiber into the graphite weight assemblies.

Once the clamp weights were attached, the fiber could be loaded onto the tension frame. The tension frame was placed on top of an adjustable-height lab jack to which a piece of clean white copy paper had been taped. The lab jack was then placed onto a cardboard tray which served as a semi-rigid carrying structure that helps to dampen

vibration from walking when moving the fiber-loaded frame (as described below). Two fiberglass plate "guide rails" were also taped down onto the paper to restrict sliding of the tension frame to one dimension. A 6.3-mm-thick prop block was then placed to the left of the tension frame. Pinching both of the clamp weights to pick up the fiber, the fiber-weight assembly was moved over the tension frame. Next, one clamp weight was propped up vertically (screw-side-up) on the prop block on the left side of the tension frame while the other weight was placed on its long edge atop the right side of the tension frame in such a way as to not twist the fiber. Finally (with care and skill), the right weight was carefully pulled and rotated over the right edge of the tension frame and then gently released. The prop block on the left was then carefully removed and the two weights were left dangling off either edge of the frame, holding the fiber in tension over the frame. The fiber loading process was repeated up to three more times, loading the frame with up to four fibers total. *Important: once loaded onto the frames, neither the fiber nor the weights should be touched until after processing.*

The cardboard tray under the lab jack was then carefully and slowly picked up and the lab jack with loaded tensioning frame on top was moved and placed in proximity of the tube furnace using extreme care (walking with baby steps) as to not impart dynamic loading onto the fibers. With a process tube inside the furnace, the lab jack was placed next to the furnace and raised to the height of the process tube so that the tension frame could be smoothly (but slowly) pushed into position with a push rod (see Figure S8).

Thermal processing was then performed per usual. Following thermal processing, the frame was pulled out of the furnace by one of its horns and placed back onto the lab jack and the fibers were removed by grabbing both weights of each fiber simultaneously,

slacking the fiber, and resting it on a surface with the weights. Some fibers were found to break spontaneously during thermal processing or from bumping or vibration during loading, observable by the presence of a dropped weight next to the frame. Such fibers were no longer considered valid for tensile tests. Each fiber on the frame could be cut in half to afford two tensile test specimens.

Single-Fiber Tensile Testing

Single-fiber tensile tests were performed in a universal testing machine (Nano-UTM, MTS Nano Instruments) according to the ASTM D3379-75 standard.[8] This standard was selected over the ISO 1156 standard,[9] another candidate single-fiber tensile test standard, because ASTM D3379-75 factors in strain rate, which we have observed can significantly impact the measured tensile strength values for single carbon fibers.

A baseline data set for as-received fibers was established each day that tensile tests were run to normalize variations arising from machine alignment and variations in materials properties along the tow spool. As an extra validation step, conclusions regarding a sample type are drawn based on differentials run against their respective baseline dataset.
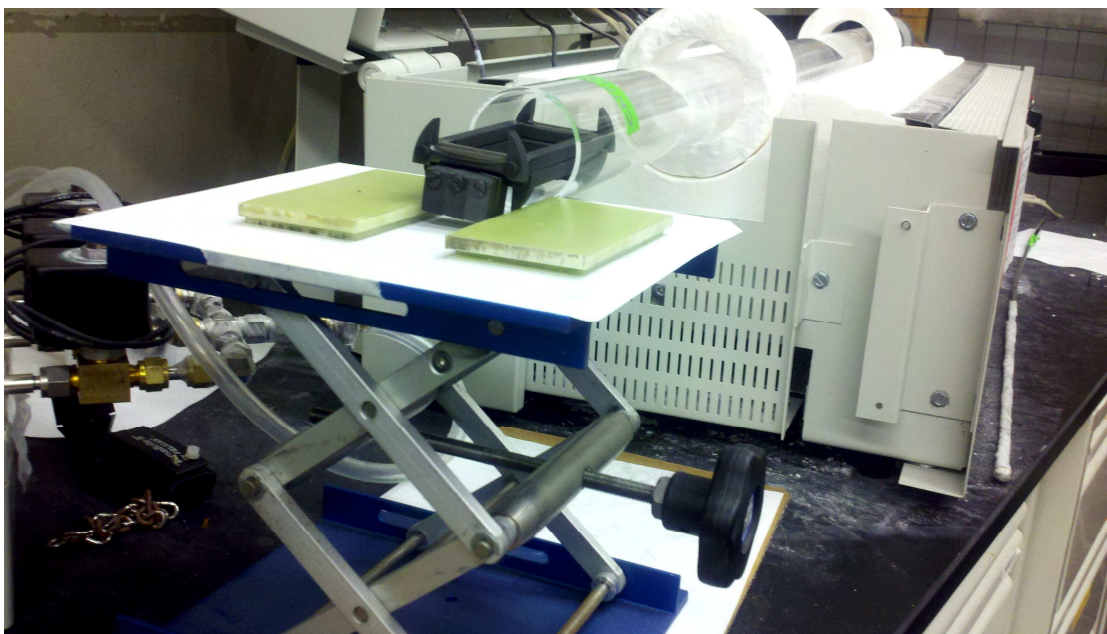
Figure S8. Transferring the graphite tension frame, loaded with three tensioned fibers, into the furnace via lab jack.

Testing tabs were laser-cut from tagboard to dimensions specified by the standard. Fibers were mounted on tagboard frames with epoxy. A gage length of 25 mm was used for all samples. First, a straight line was drawn down the center of the tagboard testing frame. A length of CF tow was cut and laid out on a smooth surface such as clean white copy paper. With gloved fingers, the ends of the tow were spread slightly apart. A "fiber grabber" tool was used to gently stick onto single carbon fibers in the bundle and pull them away from the tow as described earlier. The fiber grabber was used to draw a fiber over the line drawn on the testing frame. One end of the fiber was then taped down in this position on the testing frame. A second fiber grabber was then used to pull the fiber taught at other end. This end of the fiber was then taped down. Finally, each end of the fiber was glued in placed with dabs of 5-min epoxy (Devcon, product number 14250) applied by Q-Tip.

Fiber specimens were first mounted in the testing machine. *Proper vertical alignment of the tagboard frame is critical to ensure accurate and repeatable tensile measurements.* Tabs were gripped on the tagboard 25 mm away from the fiber-epoxy joints. Once mounted in the machine, the sides of the tagboard frame were separated into top and bottom halves by snipping twice on each side as to remove a section of tagboard—this ensures the top and bottom halves do not catch on each other during pulling and introduce a spike or offset in the force-displacement curve measured for the fiber from incorrect autotaring by the instrument software. Fibers were pulled at a strain rate of 400 µstrain/s which guaranteed no test took longer than 60 s to complete. A nominal fiber diameter of 7 µm was used for stress calculations (verified by SEM to be a consistent and reasonable value). Fibers typically broke at a load of ~40-180 mN and an extension of ~150-300 µm. While ideally fiber pulls would only be considered valid if the test resulted in a break in the middle of the test specimen, the extremely small diameter of the fibers and large amount of elastic energy stored at break almost always resulted in specimens springing off of the frame, making it exceedingly difficult to assess where fiber failure occurred. All fiber break test results are included in the presented data as a result and it is expected that some of the lower values of strength in particular are a result of fiber breakage near the fiber-tab interface. Elastic modulus was calculated by linear regression fit of all data points in the linear region of the stress-strain curve for a given test such that an R^2 value of 0.99 or better was obtained (data points from movement of the testing frame and non-linear behavior at the fiber break point were excluded). In some datasets, force-displacement curves exhibited a constant offset due to

misstarting of the load cell (arising from momentary collision of the tagboard frame top

and bottom); accordingly, this offset was subtracted from these datasets in postprocessing.

Supporting Information References

[1]   Garcia, E. J.; Hart, A. J.; Wardle, B. L.; Slocum, A. H. *Proceedings of the 47th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, 1-4 May 2006, Newport, Rhode Island.* **2006**.
[2]   Qian, H.; Bismarck, A.; Greenhalgh, E. S.; Kalinka, G.; Shaffer, M. S. P. *Chemistry of Materials* **2008**, *20*, 1862-1869.
[3]   Hitchon, J. W.; Phillips, D. C. *Fibre Science and Technology* **1979**, *12*, 217-233.
[4]   Steiner III, S. A. *Carbon Nanotube Growth on Challenging Substrates: Applications for Carbon-Fiber Composites*, PhD Thesis, MIT, 2011.
[5]   Stroock, A. D.; Kane, R. S.; Weck, M.; Metallo, S. J.; Whitesides, G. M. *Langmuir* **2003**, *19*, 2466-2472.
[6]   Baumann, T. F.; Gash, A. E.; Chinn, S. C.; Sawvel, A. M.; Maxwell, R. S.; Satcher Jr., J. H. *Chemistry of Materials* **2005**, *17*, 395-401.
[7]   Magrez, A.; Seo, J. W.; Smajda, R.; Korbely, B.; Andresen, J. C.; Mionic, M.; Casimirius, S.; Forro, L. *ACS Nano* **2010**, *4*.
[8]   ASTM International, *Standard Test Method for Tensile Strength and Young's Modulus for High-Modulus Single-Filament Materials*, ASTM D3379-75, 1989.
[9]   International Standards Organization, *Carbon Fibre—Determination of the Tensile Properties of Single-Filament Specimens*, ISO 11566, 1996.