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Multiscale mechanisms of twisted carbon nanotube yarns probed *in situ* by soft X-rays during tensile loading

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ABSTRACT

Piecing together carbon nanotubes (CNTs) into assemblies has so far failed to achieve the same elite strength performance metrics as individual CNTs, highlighting a critical deficiency in understanding of the effects that the processing of individual nanostructures has on the performance of their derived macroscale assemblies, thereby hindering the development of a process-structure-performance map for these materials. In this work, we propose a method to decouple the distribution orientation of nanoscale tortuosity and the microscale twist of CNT dry-spun yarns under applied loads via *in-situ* soft X-ray probing at high energy (1200 eV) and low energy (280 eV), respectively. With this decoupling enabled by *in-situ* soft X-ray scattering, we acquired a deeper understanding of the deformation mechanisms of these yarns. We found that for untreated yarns, the twist angle of collective CNT bundles at the macroscale is more sensitive to applied stress than the nanoscale alignment distribution. We also found that increasing nominal twist densities of yarns as well as increased strengthening via plasma treatments and polymer infiltration act to decrease the yarns' sensitivity to realignment at the nanoscale and prevent failure by the slip mechanism.

KEYWORDS: X-ray scattering, carbon nanotube yarns, micromechanics, in situ, tensile loading, soft X-rays

Carbon nanotubes (CNTs) are known as the strongest 1D material due to their covalent sp^2 carbon bonds and hexagonal lattice; an individual CNT at the nanoscale can have a Young's modulus and tensile strength up to ~ 1 TPa and 100 GPa, respectively.^{1, 2} To realize the potential of CNTs in ultrastrong, flexible, conductive structures in a variety of applications such as low-Earth orbit conductive cables,³ nano-mechanical energy harvesting,^{4, 5} wearable elastic strain sensors,^{6, 7} and artificial torsional muscles,^{8, 9} they need to be assembled continuously at the macroscale level. For example, mass-produced arrays, or vertically aligned forests, of μm -to-mm long CNTs can be first grown via chemical vapor deposition (CVD) on catalyst-activated substrates, and then these forests can be mechanically drawn out into webs to form cm-scale sheets and twisted yarns or fibers.^{10, 11} However, the mechanical strength of such CNT assemblies do not meet the same elite performance metrics as the individual, nanoscale constituents due to weak van der Waals bonding in between tubes and insufficient physical interconnection.^{12, 13} Depending on exact processing conditions, as-fabricated yarns exhibit tensile strength in the ranges of $\sim 0.1 - 2$ GPa,^{14, 15} which is three orders of magnitude less than the strength of individual nanoscale performance. Under a tensile load, the weak bonds and interconnectivity in between tubes in twisted CNT yarns results in failure by slippage, where CNT bundles slide past each other as the yarn unravels and loosens. The slippage mechanism occurs when the shear stress between CNT bundles overcomes the static frictional force between them.^{13, 16, 17}

Recently, our group showed that the vapor phase polymerization of crosslinkable poly-glycidyl methacrylate (PGMA) was a viable strategy for reinforcing the weak bonds between individual CNTs and enabling a better distribution of tensile load throughout the larger assembly; the treatment allowed for a 300% increase of elastic moduli of $2.3 \mu\text{m}$ diameter yarns, and a 1000%

increase for cross-hatched sheets.² Compared to pristine yarns, small angle X-ray scattering (SAXS) revealed that the CNT bundles within polymer-treated yarns underwent limited rearrangement and alignment at the nanoscale when subjected to tensile stress. We later showed with scanning transmission X-ray microscopy that the vapor phase polymer coating and subsequent crosslinking process results in near perfect filling of the void space between CNTs within spun yarns.¹⁸

In addition to realizing scalable and cost-effective methods of strengthening CNT assemblies for commercial use, a fundamental understanding of the multiple length-scale mechanisms during mechanical testing is also critical. SAXS is a popular, non-destructive technique to elucidate the nanoscale morphology of CNT arrays and assemblies, both statically¹⁹⁻²² and *in situ* during tensile loading.^{2, 16, 23} Obtained as a function of the scattering vector q , scattering data contains quantitative structural information of a greater number and larger volume of CNTs than imaging techniques such as scanning or transmission electron microscopy.^{24, 25} Typical SAXS configurations with sample-to-detector distances (SDD) and beam energies around ~ 2 m and greater than 10 keV, respectively, allow scattering related to the inner and outer diameter distribution of a CNT population as well as tube alignment to be observed. The alignment, or orientation of the CNTs describes their tortuosity at the nanoscale, and in twisted CNT yarns, the orientation distribution has been observed using SAXS to narrow as the yarns experience increased tension.¹⁶ I.e., it is understood that individual CNTs, which typically are less than 10 nm in outer diameter, within a larger twisted yarn or fiber structure will straighten in response to an applied tensile stress. However, to achieve a more complete comprehension of the multiscale, morphological changes experienced by CNT yarns under tensile stress, it is imperative to

understand the structural response of larger, microscale agglomerate features such as the collective twisted CNT bundles which are on the order of a few tens of nanometers to sub-micron in size. Typically, the microscale twist angle and response are not decoupled from the nanotube alignment orientation distribution when only the high beam energies for probing nanoscale features are used.

In this work, we utilized soft X-ray scattering at 280 eV and 1200 eV instead of typical SAXS beam energies to probe the microscale twist structure and the nanoscale alignment distribution, respectively, of CNT yarns during *in situ* tensile testing. The soft X-ray energies enabled access to a wide range in reciprocal q space and larger scattering angles compared to conventional SAXS. We note that the 280 eV beam energy used in this work is close to the X-ray absorption edge for carbon as is important in the chemically sensitive technique of resonant soft X-ray scattering (RSoXS),^{26, 27, 28} but this feature was not used. Instead, the choice of 280 eV and 1200 eV X-ray energies in this work were selected primarily to achieve differences in scattering length scale and spatial distribution during *in situ* tensile testing. By decoupling the nanotube alignment distribution from that of the microscale twist angles within the yarns, we sought to develop a full picture of the multiscale morphological responses of such twisted assemblies to applied stress. We found that the twist angle of collective CNT bundles at the microscale is more sensitive to applied stress than the alignment distribution; i.e., the collective bundles untwist to a greater degree than the nanotubes realign themselves at the nanoscale. We also found that increasing nominal twist densities of yarns as well as increased strengthening via plasma treatments and polymer infiltration work to decrease the yarns' sensitivity to realignment at the nanoscale and prevent failure by the slip mechanism.

Results and discussion

Figure 1 outlines our typical experimental setup (discussed in further detail in the Methods section), where within the ALS 11.0.1.2 vacuum chamber, a twisted CNT yarn was affixed on both ends via UV curable epoxy resin to a paper frame and mounted onto a tensile stage. Tension was applied to the yarns by elongating them in 20 μm increments, up until yarn failure. At each elongation step, specific X-ray beam energy (E) and sample-to-detector-distance (SDD) settings were applied to access various length scales of the CNT yarns via X-ray probing. In particular, the $[E, SDD]$ condition pairings of [280 eV, 150 mm] and [1200 eV, 70 mm] were utilized at each elongation step in order to probe the microscale twist structure of the yarns and nanoscale orientation distribution of the CNT bundles within the yarns, respectively, as a function of stress.

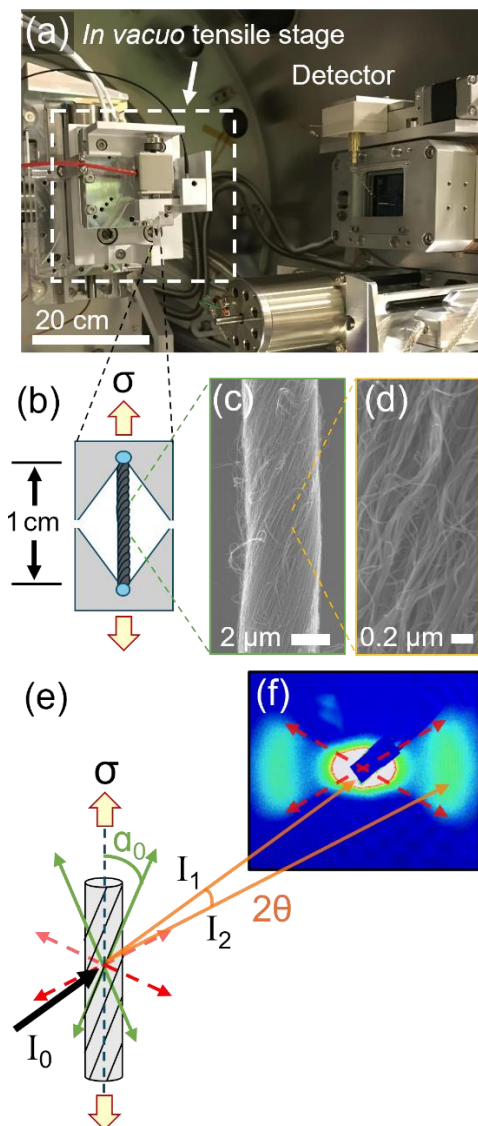


Figure 1: Experimental set-up for soft X-ray probing of CNT yarns during in-situ tensile loading.

(a) Photograph of vacuum chamber of the ALS 11.0.1.2 beamline, showing the *in vacuo* tensile stage and detector; (b) schematic illustration of a CNT yarn mounted on a paper frame for tensile testing; representative scanning electron microscopy (SEM) images of (c) an untreated yarn showing its microscale twist, and (d) nanoscale tortuosity; (e) schematic depiction of incident X-ray beams probing the twisted CNT yarn and (f) the resulting characteristic X-ray scattering pattern.

We assume for this work that a twisted CNT yarn can be modeled as a succession of coaxial cylinders wherein an individual CNT bundle or assortment of tangled bundles follows a spiraling path along the circumference of each cylinder, as depicted in the schematic shown in Figure 2(a). At the microscale, the CNT bundles lie at some twisted bias angle α relative to the yarn axis. The value of α is at a minimum at the center of the yarn where the yarn radius r is small, and increases with each succession of coaxial cylinder of increasing r . Thus, the maximum α of a twisted yarn is observed at its surface since that is where r is at a maximum. The value of α also depends on the nominal twist density (T) of the fabricated yarn; α is related to r and T through the equation $\tan(\alpha) = 2\pi rT$. At the nanoscale, CNT bundles lying on the helical paths of the cylinders are comprised of individual, tortuous CNTs which are situated at some alignment, or orientation angle θ with respect to the axis of the bundle.

Figures 2(b) and (c) show typical X-ray scatter patterns of a twisted CNT yarn with a twist density of $45\text{k turns}\cdot\text{m}^{-1}$ at incident beam energies of 280 eV and 1200 eV, respectively, prior to any tensile loading. In each pattern, the dashed and dotted lines represent the paths of the equatorial scattering and the azimuthal directions, respectively. At a low energy of 280 eV and SDD of 150 mm, the scattering in the macroscale range of $q = \sim 10^{-2} - 10^{-1} \text{ nm}^{-1}$ becomes observable when soft X-rays are incident upon a CNT yarn oriented perpendicular to the beam. At this microscale range of q , we can resolve within the twisted yarn structure the associated real space features of CNT – CNT separation and the bundling of several CNTs²² which are in the size range of $0.1 - 1 \text{ }\mu\text{m}$. The type of scattering associated with these real space features is generally classified as structure factor scattering.²⁰ Scattered X-rays at this low energy of 280 eV and SDD produce an “x”-like pattern with maximum intensities appearing as streaks at ca. $\pm 45^\circ$ relative to the equatorial direction, as

shown in Figure 2(b). The shape of the pattern results from the fact that the low energy beam probes the CNT bundles which are twisted at some bias angle relative to the yarn axis, and that the resultant scattering is perpendicular to the orientation of the bundles. In Figure 2(d), an intensity profile of equatorial scattering as a function of the magnitude of the scattering vector q reveals a broad, decaying shoulder without a defined peak, which is indicative of structure factor scattering.^{20, 22} At a high beam energy of 1200 eV and SDD of 70 mm, scattering in the nanoscale range of $q = \sim 10^{-1} - 10^0 \text{ nm}^{-1}$ instead becomes observable in the scattering pattern which is shown in Figure 2(c). The maximum intensity features in the high energy X-ray pattern appear as lobes lying along the equatorial direction, perpendicular to the axis of the CNT yarn. The intensity profile of the equatorial scattering at 1200 eV is shown in Figure 2(e), where a prominent and distinct peak can be observed in the range of $q = \sim 0.6 - 1 \text{ nm}^{-1}$. This peak derives from the hollow-cylinder form factor of CNTs, which contains information about the inner and outer diameter distributions²⁹ as well as the quantifiable nanoscale alignment of a CNT population.^{19, 24, 30}

Scattering from the structure factor and the form factor can be further analyzed to extract quantifiable information about the twist structure of CNT yarns at the macroscale and the orientation of CNTs within individual bundles at the nanoscale, respectively, by plotting the azimuthal intensity distribution at relevant positions of q at both length scales. The azimuthal intensity distributions as a function of the azimuthal angle Φ , from -90° to $+90^\circ$, are plotted at 280 eV and 1200 eV in Figures 2(f) and (g), respectively. We found that for both X-ray scan conditions, a double-Gaussian model (see Supplementary Information, Eq. (S1)) works well to fit the experimental azimuthal intensity distribution data;¹⁶ in Supplementary Figure S1, we show that the R^2 values of double-Gaussian model fittings of the azimuthal intensity distributions recorded at each elongation step of a tensile test of a typical CNT yarn in this study are greater than 0.97.

In Figure 2(f), the relevant peak feature is the peak center position a of a single Gaussian subpeak, which we postulate represents the average microscale twist angle of all bias angles α that twisted CNT bundles make with the yarn axis, from the center to the circumference of the yarn. We will discuss this idea further below. In Figure 2(g), the relevant peak feature is the full-width-at-half-max (FWHM, herein referred to as w), of a single Gaussian subpeak, which at the high energy of 1200 eV represents the nanoscale orientation alignment distribution of CNTs within the twisted bundles.

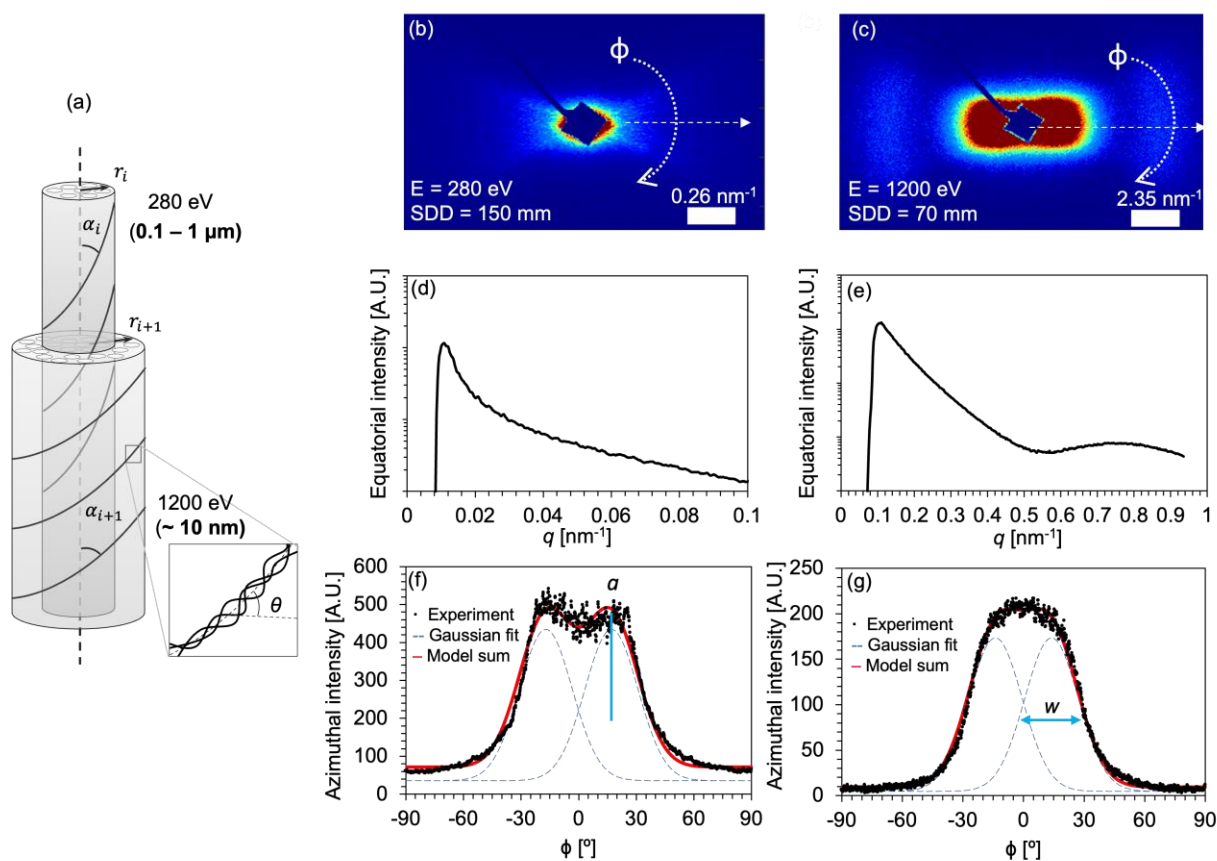


Figure 2: (a) Schematic of coaxial cylinders for the twisted fiber model. Typical X-ray scatter patterns of a twisted CNT yarn with a twist density of $45\text{k turns}\cdot\text{m}^{-1}$ at $[E, \text{SDD}]$ conditions of (b) $[280 \text{ eV}, 150 \text{ mm}]$ and (c) $[1200 \text{ eV}, 70 \text{ mm}]$, respectively, prior to any tensile loading. The broken

and dashed arrows represent the azimuthal and equatorial directions, respectively. Intensity profiles of equatorial scattering from the X-ray scatter patterns collected at the (d) [280 eV, 150 mm] and (e) [1200 eV, 70 mm] conditions. The azimuthal intensity distributions as a function of the azimuthal angle Φ , from -90° to $+90^\circ$, for the X-ray scatter patterns collected at (f) [280 eV, 150 mm] and (g) [1200 eV, 70 mm], respectively. The azimuthal directions indicated in (a) and (b) represent the integration paths for the azimuthal intensity distributions plotted in (f) and (g), respectively. In both (f) and (g) plots, the black dots, blue dashed line, and the solid red line, are the experimental data, Gaussian fits, and model sum, respectively.

Figures 3(a) and (b) show the SEM images of uncoated yarns with 45k and 90k turns·m⁻¹ nominal twist density, respectively. In both images, the twist angle α of the yarns are drawn, which corresponds to the angle that an inclined CNT bundle observed along the circumference of the yarn makes with the yarn axis. These angles were measured to be $30 \pm 1^\circ$ and $42 \pm 3^\circ$ for the 45k and 90k turns·m⁻¹ yarns, respectively. As discussed above, the bias twist angle α is at a maximum at the outer surface of the yarn and decreases toward the center. Thus, the SEM measurements provide information only about the maximum α (α_{max}) of the yarns at the outer surface and nothing about the distribution of the α values that exist within the volume of the yarns. Figure 3(c) shows α plotted as a function of yarn diameter as calculated using the aforementioned coaxial cylinder model for the twist densities of 45k and 90k turns·m⁻¹. Red vertical dashed lines are drawn to mark the measured diameter of the pristine 45k and 90k turns·m⁻¹ yarns, which were 3.96 and 3.43 μm , respectively. The diameters correspond to calculated α_{max} values of 31.3 and 46.5°, respectively, at the 45k and 90k turns·m⁻¹ twist densities, and they closely agree with the values measured via SEM. Also displayed in Figure 3(c) is the average twist angle $\bar{\alpha}$, obtained by

averaging all α values along the $\tan(\alpha) = 2\pi rT$ curve up to the measured diameters for both yarns; $\bar{\alpha}$ was calculated to be $15.4 \pm 0.6^\circ$ and $24.7 \pm 0.6^\circ$ for the 45k and 90k turns·m⁻¹ yarns, respectively. Figure 3(d) shows the azimuthal intensity distribution collected at 280 eV and $q = 0.06 \text{ nm}^{-1}$ for uncoated yarns of 45 and 90k/m twist density just prior to any tensile loading. The experimental data points for both samples are fitted with the double Gaussian distributions, from which the ϕ peak positions of $17.1 \pm 0.1^\circ$ and $23.6 \pm 0.1^\circ$ are observed for the 45k and 90k turns·m⁻¹ yarns, respectively. As the intensity distributions contain information about the entire cross section of the yarns and not just the outer surface, the peak position at this beam energy and q position should correspond to the average twist angle of all twist angles contained within each yarn. Thus, the discrepancy from SEM twist angle measurements stems from accounting for the outer surface of the yarn, which can only provide α_{max} , whereas $\bar{\alpha}$ extracted from the twisted fiber model provides a different value that accounts for all of the CNT bundles within the yarn and their varying twist angles as a function of yarn radius. Figure 3(e) compares the average twist angles estimated from the twisted fiber model to those measured via the azimuthal intensity distributions, and we can see that these values closely agree.

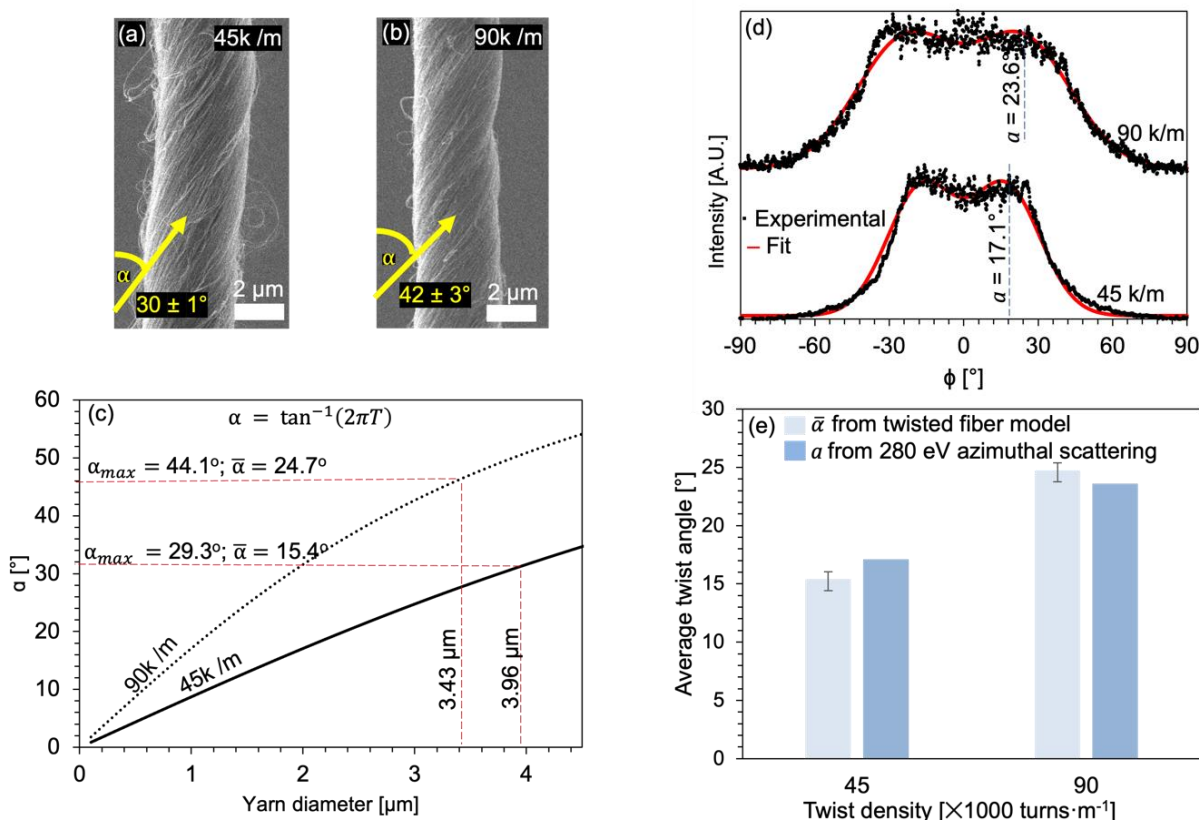


Figure 3. SEM images of untreated yarns with (a) 45k and (b) 90k turns·m⁻¹ nominal twist densities. (c) A plot of twist angle at the outermost surface of the yarn as a function of yarn diameter according to the twisted fiber model. The solid line and dotted line represent the curves for twist densities of 45k and 90k turns·m⁻¹, respectively. For each twist density, both the maximum twist angle (α_{max}) at the outer surface of the yarns as well as the average of all twist angles ($\bar{\alpha}$) from the core to the surface are listed in the plot. (d) Azimuthal intensity distributions collected at [280 eV, 150 mm] of untreated yarns with 45k and 90k turns·m⁻¹ nominal twist densities prior to tensile loading. The black dots and red solid lines are the experimental data points and the double-Gaussian model-fitted sums, respectively. The vertical dashed lines indicate the peak centers whose values are labeled and that which we postulate represent the average twist angle of the entire CNT population within the yarns probed by X-ray scattering. (e) A bar chart comparing the average

twist angle values of the yarns at both twist densities, prior to tensile loading, obtained from the twisted fiber model with that of soft X-ray scattering.

We can now show the results of a full experiment that measures the low and high energy X-ray features of a multiscale CNT yarn assembly during *in situ* tensile testing. Figure 4(a) shows the force vs time curve for an untreated yarn with a nominal twist density of 45k turns·m⁻¹. This yarn had an initial length of 6.06 mm and diameter of 3.964 ± 0.179 μm. From this temporal force data, the measured initial yarn parameters, and the known nominal elongation steps of the tensile stage (20 μm), the engineering stress-strain curve for this yarn was calculated and is shown in Figure 4(b). At each step of yarn tensile elongation, the yarn was measured at 280 and 1200 eV synchrotron X-ray energy to examine the evolution with stress of the macroscale twist and the nanoscale orientation distribution, respectively. Figures 4(c) and 4(d) show the azimuthal intensity distributions at select nominal values of yarn elongation at X-ray energies of 280 and 1200 eV, respectively. These data show that with increasing yarn elongation, or tensile stress, that both the average twist angle and the nanoscale orientation decrease. I.e., with increasing stress, the yarn increasingly untwists at the microscale and at the nanoscale, individual CNT bundles tend to straighten. Figure 4(e) shows the average twist angle and the orientation distribution with respect to their initial values (a/a_0 and w/w_0 , respectively) as a function of stress on a single plot, as collected from the 280 and 1200 eV X-ray energy analyses. Up to about 80 MPa, both a/a_0 and w/w_0 have roughly the same slope and thus a similar response to applied tensile stress. Beyond ~ 80 MPa, a/a_0 responds more greatly to increasing stress than does w/w_0 , implying that at the microscale, the untwisting of the yarn occurs more easily than does the realignment of CNT bundles at the nanoscale. Thus, the decoupling of the microscale twist from the nanoscale

tortuosity allows us to observe that for this untreated CNT yarn, slippage during applied stress occurs more easily between tube bundles than for individual nanotubes. These results strengthen the understanding that for untreated yarns under applied stress, lack of interaction between CNT bundles cause them to slide past each other more easily, while CNTs within the bundles are more densely tangled and thus more resistant to realignment than the microscale structure.² Thus, for untreated CNT yarns, the mechanical load is not well transferred to the ultrastrong, individual CNTs within bundles, and such yarns will fail as their bundles untwist and slip. The following section contains results on surface modification and polymer reinforcement to better distribute the load to individual CNTs, thus mitigating CNT yarn failure via the slip mechanism.

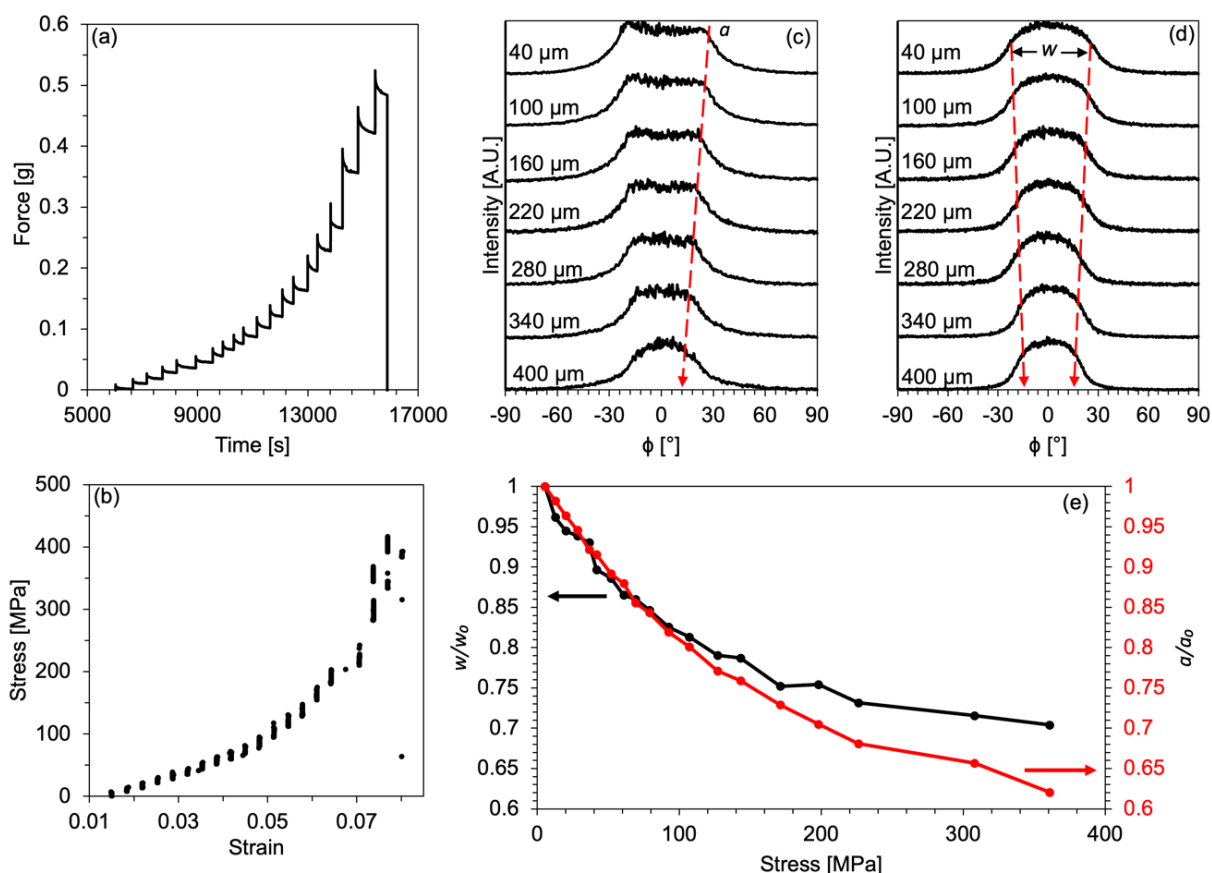


Figure 4. Full analysis of *in situ* tensile testing at [280 eV, 150 mm] and [1200 eV, 70 mm] of an

untreated yarn with a nominal twist density of $45\text{k turns}\cdot\text{m}^{-1}$. (a) Force load on the yarn as a function of time. X-ray measurements were conducted after the force load had stabilized to mitigate the effects of creep. (b) Stress-strain curve of the yarn during the experiment. Sequence of azimuthal intensity distribution plots collected at (c) [280 eV, 150 mm] and (d) [1200 eV, 70 mm] for increasing nominal yarn elongations as the tensile load is applied. Changes in the microscale average twist angle a and the nanoscale orientation distribution w are noted with the red dashed arrows in (c) and (d), respectively. (e) The changes in a and w plotted with respect to their original, pre-tensile load values a_0 (16.6°) and w_0 (30.0°) as a function of stress.

We have shown in previous work² that the incorporation of covalent bonds and cross-linking between CNT bundles within yarn assemblies helps to prevent the straightening and subsequent slipping of CNTs under tensile load. How strongly the CNT bundles resist straightening during tensile loading was quantified via 1200 eV soft X-ray measurements by extracting the w value of the azimuthal intensity integrated at the CNT core shell form factor peak position in q space. Figure 5(a) shows the FWHM with respect to its initial value (w/w_0) of untreated yarns as a function of applied stress for increasing initial twist densities. Smaller changes in w/w_0 indicate a higher resistance to nanoscale alignment as stress is applied to the yarn. As expected, the alignment distribution decreases as stress increases and nanotube bundles straighten. The yarns with 45k and $60\text{k turns}\cdot\text{m}^{-1}$ initial twist densities fail at ~ 435 and 460 MPa, respectively. The $60\text{k turns}\cdot\text{m}^{-1}$ yarn also failed at a smaller w/w_0 (~ 0.71) as compared to the $45\text{k turns}\cdot\text{m}^{-1}$ one (~ 0.66), indicating that larger twist density yarns are more resistant to alignment at the nanoscale. Further, the resistance to alignment at the nanoscale during loading can be quantified by the rates of change (in $\% \text{ MPa}^{-1}$) of the w/w_0 vs stress curves. The alignment of the $45\text{k}\cdot\text{turns m}^{-1}$ yarn relative to its

initial value decreases at a rate of 0.20% MPa⁻¹ before transitioning to a much shallower decline of 0.03% MPa⁻¹, while that of the 60k turns·m⁻¹ yarn falls a rate of 0.19% MPa⁻¹ before transitioning to 0.02% MPa⁻¹. The change in the slopes indicates a change of the failure mechanism of the yarns; larger, weakly coupled CNT bundles begin to translate past each other, followed by the slower slippage between individual CNTs which are more densely woven. The yarn with an initial twist density of 90k turns·m⁻¹ failed at a much lower stress (~ 200 MPa) compared to that of the 45k and 60k turns·m⁻¹ yarns, but also at a much larger w/w_0 (~ 0.78). The resistance to nanoscale alignment of the 90k turns·m⁻¹ yarn is further evidenced by its much shallower and singular rate of change in w/w_0 of 0.12% MPa⁻¹. Although the 90k turns·m⁻¹ yarn is more resistant to nanoscale realignment during tensile loading, it was shown by Mirzaeifar *et al.*³¹ that increasing the twist angle of a CNT yarn bundle will enhance intertube interactions to certain point through the increase of interaction area between tubes, but that beyond a critical twist angle, the cross sections of tube bundles experience enhanced deformation, thereby weakening the shear strength between tubes and causing yarn failure.

Figure 5(b) shows w/w_0 as a function of applied stress for air plasma-treated yarns of 45k turns·m⁻¹ initial twist density which either have been not coated with PGMA polymer, coated, or both coated and crosslinked. The plasma-treated, uncoated yarn exhibits a similar trend in w/w_0 as that of the 45k turns·m⁻¹ yarn in Fig. 5(a), except that the uncoated plasma-treated yarn fails at a higher stress (~ 580 MPa). Further, the w/w_0 vs stress curve of the uncoated plasma-treated yarn resists nanoscale realignment more strongly than the 45k turns·m⁻¹ not treated with plasma from Fig. 5(a), as evidenced by its shallower slope of 0.12% MPa⁻¹ before transitioning to 0.03 % MPa⁻¹. We show via XPS measurements in Figure S2 that as a function of air plasma treatment time of CNT yarns

that the O at.% increases relative to C at.%, and that the at.% of -C-O-C- ³² and >C=O ^{32, 33} increases at the expense of $\text{sp}^2\text{-C}$ as indicated by deconvolution of the C 1s shift. Complementary Raman data in Fig. S3 show that the D/G ratio of CNT yarns increases with air-plasma treatment time. These supplementary results together indicate that air plasma of CNT yarns induces point defects in the sp^2 lattice of CNTs which are the introduction of functional groups on the CNT surface such as -C-O-C- and >C=O . These functional groups allow covalent bonding to begin between CNTs³² in yarn assemblies which would explain the stronger resistance to nanoscale realignment of the plasma-treated yarn at $45\text{k turns}\cdot\text{m}^{-1}$ relative to the untreated one.

In Fig. 5(b), it can further be seen that the coating and infiltrating an air plasma-treated yarn with PGMA via iCVD results in an even stronger resistance to nanoscale alignment of CNT bundles under tensile loading, as evidenced by the singular, shallower rate of decline in w/w_0 of $2.27\times 10^{-2}\%$ MPa^{-1} . Further, the air-plasma treated yarn that was PGMA coated and underwent crosslinking exhibits a singular and the shallowest declining slope w/w_0 of $1.64\times 10^{-2}\%$ MPa^{-1} . Through PGMA coating and subsequent crosslinking of yarns, the extent of covalent bonding between CNT bundles increases. Whereas the uncoated yarns typically underwent nanoscale alignment, or straightening, and failed by the slipping of loose CNT bundles, the coated and crosslinked yarns, due to the increased covalent bonding between bundles, were able to resist such nanoscale alignment more strongly. The absence of a second slope in w/w_0 vs stress for the coated and crosslinked yarns indicates that the severance of the polymer-induced covalent bonds and CNT bundle slipping occurs simultaneously.² In this way, the tensile load is better transferred to the CNT bundles in treated yarns than in untreated yarns. These observations of enhanced load bearing effects of surface modification of CNT structures and their subsequent incorporation into composite

materials agree with those found in literature. For example, Kim *et al.*³⁴ found that a sulfuric-nitric acid treatment followed by Ar plasma exposure of multiwall CNTs created oxygen-containing surface functional groups which led to the CNTs being well dispersed in a polymer matrix resin. The high quality of the dispersion allowed for increased interfacial bonding between the matrix resin and the CNTs which resulted in enhanced mechanical properties for epoxy composites with surface-modified CNTs compared to those with untreated CNTs.³⁴ Similarly, Park *et al.*³⁵ showed that gamma radiation of CNT yarns also creates oxygen-containing functional groups on CNT surfaces which induced crosslinking in between CNTs; unidirectional epoxy laminates based on the irradiated yarns were stronger than that of the untreated yarns.

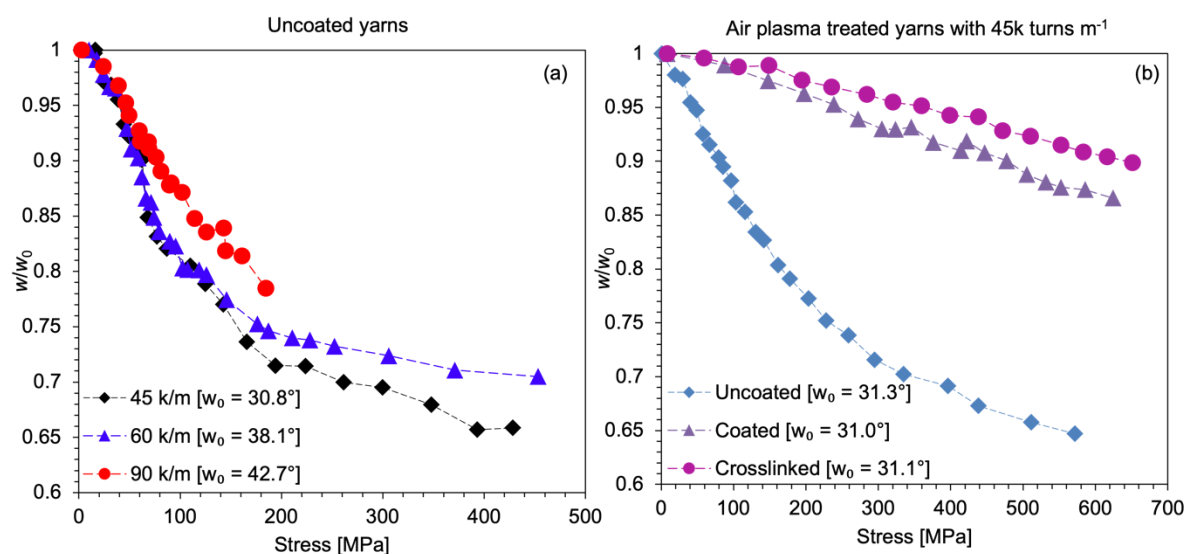


Figure 5. Changes in the nanoscale orientation distribution (w/w_0) as a function of tensile stress for (a) untreated yarns of varying twist density and (b) air-plasma treated yarns that are either uncoated, coated, or cross-linked at the same nominal twist density of 45k turns·m⁻¹. The initial orientation distribution w_0 for each sample are indicated in the legend of each plot.

Conclusions

In this study, we described a process for evaluating the twist structure of untreated CNT yarns during *in situ* tensile loading using soft X-ray synchrotron energy. In this way, we decoupled changes of the average microscale twist angle of aggregate CNTs within the yarn from that of the nanoscale orientation distribution of individual CNTs. We found that the untwisting of the yarn occurs more easily than does the realignment of CNT bundles at the nanoscale under applied stress, which is a critical understanding for the development of scaled fabrication of CNT yarns. We believe that the proposed soft X-ray technique can be used to decouple the structural morphology of multiple length scales of hierarchical assemblies based on other non-carbon and non-twisted materials systems, such as metallic nanowires,³⁶ whose assembly into macroscale structures will scale up their excellent properties optoelectronic transport, or hierarchically assembled biocompatible and biodegradable nanofibers in three-dimensional scaffolds for use in regenerative medicine.³⁷ Additionally, we observed changes of the nanoscale orientation only in treated yarns, varying both the nominal initial twist densities as well as the post-fabrication process conditions such as air-plasma exposure, PGMA polymer coating, and subsequent polymer crosslinking. We found that increasing the nominal initial twist density of yarns allowed for an increased resistance to nanoscale realignment during tensile loading, but that too large of a twist density can weaken the shear strength between tubes and cause premature failure. For a single twist density of 45k turns·m⁻¹, we found that air-plasma treated yarns exhibited a stronger resistance to nanoscale realignment and larger failure stress than untreated yarns. Subsequent PGMA coating and cross-linking further improved on that nanoscale realignment resistance and failure strength, as well as prevented mechanical failure due to the slip mechanism because of the increasing degrees of covalent bonding between CNTs. The CNT yarn reinforcement via air-plasma surface treatment

and PGMA infiltration allow for the advancement of CNT yarns in several applications such as laminate composites for load bearing, strain sensors, and smart and impact-resistant textiles.

Methods

CNT synthesis and fabrication of yarns

The details for synthesis of spinnable CNT forests and subsequent yarn fabrication can be found in our previous work.^{2, 18, 38} In short, CNT forests were first grown on Si substrates via near-atmospheric chemical vapor deposition (CVD) at 700 °C using acetylene (C₂H₂) as the carbon-containing precursor in a 12 vol % atmosphere of Ar/H₂. The Si substrates were pre-deposited with an electron-beam evaporated iron (Fe) thin-film catalyst layer to promote the growth of CNT forests during CVD. At these conditions, synthesized CNTs were typically multiwalled (~8 walls) with an outer diameter of ~ 11 nm and forest heights of ~ 250 μm.

The as-grown CNT forests were then dry-spun by first pulling a controlled track width (of 600 μm) of CNTs, patterned by laser machining, from the forest and fixing its end to the rotating axis of a motor. The forest and the motor were then linearly displaced in opposite directions during twist insertion to form yarns with prescribed twist densities of 45k to 90k turns·m⁻¹. Spun yarns had a typical total length of ~ 50 cm and diameters less than 10 μm. Shorter lengths between 1 – 2 cm of each yarn were sectioned by cutting and transferred onto paper-holder frames for safe and convenient manipulation before and during testing. On the paper-holder frames, the yarns, with their extremities fixed to the ends of the frames with UV-cured epoxy resin, were free-standing along a ~ 1 cm central aperture. Each yarn specimen diameter was measured at several positions along its length using SEM (Phenom Pro X).

iCVD polymer infiltration, crosslinking, and air plasma treatment

For mechanical reinforcement, fabricated yarns were infiltrated with polymer using a vapor-phase synthesis approach and subsequently cross-linked by a short thermal treatment. Details of the polymer infiltration chamber and conditions can be found in our previous work.^{2, 18} In short, PGMA was deposited onto yarns via initiated-CVD (iCVD) (GVD Co. *iLab* coating system) at a chamber pressure of 20 mtorr. Glycidyl methacrylate (GMA, Sigma-Aldrich, 97%) was used as the monomer while *tert*-butyl peroxide (TBPO, Sigma-Aldrich, 98%) was used as the polymerization initiator. Within the chamber, a hot filament was held at ~ 155 °C to break the initiator molecule and promote the polymerization reaction, while the yarn sample was held close to room temperature via active cooling of the substrate chamber. The PGMA coating thickness was monitored *in situ* during the deposition process by interferometry of a He–Ne laser ($\lambda = 632.8$ nm) incident on the surface of a Si reference wafer which was placed directly on top of the chamber substrate surface. Typical PGMA deposition rates as observed on the Si reference wafer were ca. $4 \text{ nm} \cdot \text{min}^{-1}$. To induce self-crosslinking in the PGMA, the PGMA-coated yarns were subjected to a thermal treatment in a vacuum furnace at 150 °C for 30 min under a continuous N₂ flow bleed at a pressure of 40 torr. To evaluate the impact of chemical functionalization on the CNT sidewall on polymer-load mechanical transfer, only when specified, we pre-treated CNT yarns and free-standing sheet assemblies with an air plasma for 60 s (1 mbar, 30 W, 13.56 MHz, Diener Femto Plasma Cleaner) immediately before CVD polymer deposition infiltration. Unless otherwise stated, yarns that were not subject to any post-processing treatment for reinforcement will be referred to as *untreated*; yarns subjected to PGMA coating and infiltration but without crosslinking will be referred to as *coated*; and yarns subjected to the PGMA coating, infiltration and

crosslinking will be referred to as *crosslinked*. Similarly, we add the prefix *plasma* to the *coated* and *crosslinked* CNT assembly that were pre-treated with plasma.

Characterization

Chemical analysis of treated CNT assemblies

The surface composition and chemical binding states of air-plasma treated sheet assemblies were probed using a Thermo-Fisher K-Alpha Plus X-ray photoelectron spectroscopy (XPS) system. XPS measurements utilized a monochromatic Al K α X-ray source (1.486 eV), a hemispherical analyzer, a multi-channel detector, and an electron flood source for charge neutralization. The probing X-ray beam had a spot-size of 400 μm . The analyzer was set to a pass energy of 50 eV and the energy step-size was 0.100 eV. For each sample, scans were performed at three different locations within the center of the sheet assembly. The three sets of data for each sample were then averaged and analyzed to determine O 1s/C 1s composition relationships as well as the O 1s and C 1s chemical binding states. Spectra were calibrated to the sp²-C state of C 1s at 284.4 eV.^{39, 32} Quantification of each spectra for surface composition analysis was performed using Advantage Data System software (ThermoFisher Scientific) where a Shirley background was employed. To determine chemical binding states, C 1s and O 1s spectra were then deconvoluted with pseudo-Voigt functions in Fityk.⁴⁰ Micro-Raman spectroscopy of CNT sheet assemblies was performed using an inVia™ Qontor® confocal Raman microscope with an excitation wavelength of $\lambda = 633$ nm at 20 mW power, a 1200 lines/mm grating, and a 20 $\times$ objective lens. The system was calibrated with an internal Si wafer reference standard before each measurement. Single-point spectra were obtained in the 500 – 3500 cm⁻¹ range for 30 s exposure times averaged over 15 accumulations at 10% laser power. Each spectrum was baseline subtracted with an 11th order polynomial⁴¹ and normalized to the D-band (~ 1310 cm⁻¹) prior to data analysis.

In situ X-ray scattering under tensile load

To probe the micro- and nanoscale morphological responses of CNT yarn structures to *in situ* tensile loading, we performed nondestructive synchrotron experiments at the Advanced Light Source (ALS, Beamline 11.0.1.2). We were able to access the micro- and nano- length scales by collecting 2D X-ray scattering images in different q regimes, where q is defined as the magnitude of the scattering vector as follows:

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{2\theta}{2}\right) = \frac{4\pi E}{hc} \sin\left[\frac{1}{2} \tan^{-1}\left(\frac{\text{pixel size} \times \text{pixel \#}}{SDD}\right)\right] \quad \text{Eq. (1)}$$

where λ and E are the wavelength and energy of the incident X-rays, respectively, 2θ is the scattering angle, h is Planck's constant, c is the speed of light, and SDD is the sample-to-detector distance. A 1024×1024 charged couple device (0.027 mm square pixel) was used to detect scattered X-rays during experiments. In this work, we utilized $[E, SDD]$ condition pairings of [280 eV, 150 mm] and [1200 eV, 70 mm] to achieve observable q ranges between $\sim 0.008 - 0.1 \text{ nm}^{-1}$ and $\sim 0.1 - 1.0 \text{ nm}^{-1}$, respectively. Using the conventional $2\pi/q$ relationship, these ranges in q -space correspond to real-space ranges of $\sim 60 \text{ nm} - 0.8 \text{ }\mu\text{m}$ and $\sim 6 - 60 \text{ nm}$, respectively. We note in this work that the $\sim 6 - 60 \text{ nm}$ feature size range provided by the [1200 eV, 70 mm] condition potentially allows us to resolve information regarding the change in size of small CNT bundles from X-ray measurements during tensile loading as that range falls within that expected of bundle size (10 – 100 nm).²² However, the observed scattering feature is a broad slope in the measured scattering intensity, which is indicative of a broad size distribution. Although the CNT bundle size was outside the scope of this work, our group has previously measured this feature explicitly²² in multiwall CNT forests by analyzing the mesoscale structure factor^{20, 22} observed

from [284 eV, 50 mm] scattering. Verploegen *et al.*²⁰ were also able to explicitly resolve CNT bundle sizes using hard ultra-small X-ray scattering (SAXS). Using the scattering model described by Verploegen *et al.*²⁰, where the intensity is expressed as $I(q) = A \cdot F(q) \cdot S(q) + C(q)$ — with A as an independent scaling factor, $F(q)$ representing the form factor of individual CNT scattering cross-sections, $S(q)$ the structure factor capturing neighboring inter-tube scattering interactions, and $C(q)$ the Debye–Büche function accounting for scattering and characteristic CNT bundle size — we were able to estimate bundle sizes and assess their evolution under yarn strain within the 200–400 nm range. The analysis indicates that bundle sizes increase from approximately 200 nm to ~ 400 nm at intermediate strains, likely due to the unentangling and alignment of adjacent CNTs. As strain increases further, the bundle size decreases back to ~ 200 nm, suggesting that external forces eventually overcome frictional interactions, causing larger bundles to be pulled apart. However, due to limitations in the q -range accessible with our current dataset, we are unable to resolve contributions from larger bundles exceeding ~ 600 nm during the straining process.

Within the vacuum chamber connected to the beamline, we installed a custom-built tensile stage to incrementally elongate yarns (in repeatable, 20 μm steps) and measure their displacement, respectively, during *in-situ* X-ray scattering. This tensile stage integrates a UHV-compatible piezo precision linear stage (13 mm travel distance, PI Q-motion, and ESP302-2N Newport Controller) in series with a miniature load cell (10 g $\pm$, Futek LSB200) to measure the force. In this setup, the travel distance (z -displacement) was measured independently with a high precision displacement optical measurement sensor (0.25 μm resolution, spectral interferometer, Keyence Co. SI-F01). The stage was adjustable in the XY-plane and was attached to a vertical translator to perform yarn elongation along the Z-direction, i.e., along the yarns' longitudinal axis. Both ends of the paper frame supporting the yarn were fixed to the tensile stage with UV-curable epoxy resin. After

mounting the sample to the stage, the paper frame was cut on either side of the yarn in order to place the yarn under tension prior to the *in-situ* straining experiment. The exerted tensile force and displacement of each yarn was recorded and from knowing the original yarn diameter and length were then converted to engineering stress and strain, respectively. In this study, we utilized the [280 eV, 150 mm] and [1200 eV, 70 mm] conditions to probe the micro- and nanoscale morphological evolutions of untreated yarns only, which had nominal twist densities of 45k and 90k turns·m⁻¹. In a typical experiment, after chamber pump-down and beam alignment, the beam and tensile stage were first brought to the [1200 eV, 70 mm] condition where the high-energy X-ray shot is taken. The system was then brought to the [280 eV, 150 mm] condition where the low-energy X-ray shot is taken. Then, the elongation was increased by 20 μm and another shot at [280 eV, 150 mm] was taken. At this same step in elongation, the system was switched back to the [1200 eV, 70 mm] condition for measurement, and this process was repeated until yarn failure, which is observable as a distorted X-ray pattern. We note that creep was evident in the yarns upon incremental loading; to account for the creep, each X-ray measurement was conducted after the stretch force response stabilized. Prior to each X-ray measurement, a “blank” shot was taken where the sample was not in the field of view of the beam (by adjusting the lateral X position of the stage to a specified, repeated distance away from the beam center) so that there existed a background scan that could be subtracted from each measurement scan during analysis. A separate set of untreated, coated, and cross-linked yarns with nominal twist densities of 45k, 60k, and 90k turns·m⁻¹ were analyzed only at the [1200 eV, 70 mm] to observe their morphological evolution with stress at the nanoscale alone. Custom MATLAB scripts¹⁹ were used to reduce and analyze all scattering data.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Double Gaussian methodology for fitting the azimuthal intensity ($I(\Phi)$) of the distribution profiles and representative R^2 values from the fits; deconvoluted XPS and Raman spectra for both control and air-plasma treated carbon nanotubes. (PDF)

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The diagram illustrates the experimental setup for measuring the spin Hall effect of light. An incident beam with intensity I_0 and polarization σ_0 enters a cylindrical sample. The transmitted beam is split into two components, I_1 and I_2 , separated by an angle 2θ . An inset shows a false-color image of the beam profile. Two SEM images show the surface morphology at 280 eV (0.1-1 μm) and 1200 eV (~ 10 nm) scales.