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Abstract

The first-ever well-aligned continuous macroscopic neat single-walled carbon nanotube (SWNT) fibers were produced using conventional spinning techniques. Neat SWNT fibers, containing no surfactant or polymer, were made by spinning dispersions of SWNTs in 102% sulfuric acid into different coagulants. The critical role of sulfuric acid in dispersing and aligning SWNTs during fiber formation has been explored. Characterization shows alignment greater than any other macroscopic neat SWNT material reported to-date while providing insight into the fundamental hierarchy and nature of SWNT fiber formation. Electrical, thermal, and mechanical measurements indicate that neat SWNT fibers hold tremendous potential for future applications.

Individual SWNTs have been shown to possess remarkable mechanical (1 – 3), electrical (4 – 6), and thermal (7, 8) properties that equal, or even surpass, other benchmark materials (e.g. steel, copper, and diamond, respectively). Applications involving SWNTs on the micrometer and nanometer scale are progressing rapidly (9, 10). To truly take advantage of SWNTs' potential, processing methods must be developed that successfully translate these impressive properties from the microscopic to the macroscopic scale. To-date, SWNT composite fibers have been produced that show notable mechanical reinforcement (11 – 13) or improvements in otherwise marginal transport properties (14). However, they still fall far short of the impressive properties of individual SWNTs. Neat SWNT fibers have only been produced in relatively short centimeter lengths using laboratory processes with limited industrial scalability (15, 16), or have been produced in continuous lengths during the nanotube synthesis process with high levels of impurities and marginal alignment (17). Here we report the first well-aligned continuous macroscopic fiber consisting of only SWNTs, without any supporting surfactant or polymer structure. Fibers were made from concentrated dispersions of SWNTs in 102% sulfuric acid via an industrially viable wet spinning technique.

Because of the high temperature stability of SWNTs, melt spinning is not an option for SWNT fibers. Wet spinning is the only viable approach—as is the case for conventional rigid rod polymers such as poly(p-phenylene benzobisoxazole) (PBO), poly(p-phenylene terephthalamide) (PPTA), and poly(*p*-phenylene benzobisthiazole) (PBZT). The main challenge to the production of neat SWNT fibers is dispersing the SWNTs at high enough concentrations suitable for efficient alignment and effective coagulation. However, due to their chemical inertness and strong inter-tube van der

Waals attractions, SWNTs aggregate into ropes with limited solubility in aqueous, organic, or acidic media. Even in stable organic (e.g. dimethyl formamide, dichlorobenzene) or surfactant-aided aqueous (e.g. sodium dodecyl sulfate, Triton-X 100) dispersions, SWNTs are typically limited to concentration less than 0.5 wt%, and even then exist as dispersions of nanotube bundles and not true solutions of individual tubes. At such low concentrations: (a) it is difficult to order the SWNTs in the spinning process; (b) the coagulation stage becomes prohibitively arduous, as the fiber would have to shrink in diameter by approximately fifteen-fold without collapsing or disordering. If a surfactant is used to disperse the SWNTs, there is the added complication of removing the surfactant from the fiber during post-processing. Fortuitously, our recent studies of the behavior of SWNTs in sulfuric acid (18, 19) provided the insight into a viable route for spinning continuous fibers of pristine SWNTs. At very low concentration in superacids (100+% sulfuric acid), SWNTs dissolve as individual tubes which behave as Brownian rods (19). At higher concentration (> 0.03 wt%), in addition to the dissolved individual tubes, SWNTs also exist as SWNT Spaghetti – "swollen" ropes, readily intercalated by sulfuric acid molecules through the formation of energetically stable charge-transfer complexes of individual, protonated nanotubes surrounded by a finite number of negatively charged sulfuric acid anions (18). At even higher concentration (> 4wt%), these acid-intercalated ropes are mobile and can be readily dispersed and aligned into ordered domains (19) similar to the nematic liquid crystalline behavior of rigid rod polymers. Using conventional fiber spinning techniques, this ordered SWNT dispersion can be extruded and coagulated in a controlled fashion to produce continuous lengths of macroscopic neat SWNT fibers.

The SWNT/sulfuric acid dispersions were mixed in and extruded from a robust custom-built apparatus (Fig. 1a). SWNTs used in this study were produced using the HiPco process (20, 21) and purified to remove excess metal catalyst using a modified standard protocol (22, 23) (Fig. 2a). An 8 wt% dispersion of purified SWNTs in 102% sulfuric acid (2 wt% excess SO_3) was prepared in a nitrogen-purged dry box. The mixture was briefly manually mixed and then transferred to the mixing apparatus via a stainless steel syringe. The dopant remained fastidiously dry during transfer and mixing to prevent the formation of discrete tactoid structures (18) or changes to the acid's protonating ability due to minute water exposure. Extensive mixing was accomplished by two alternating pneumatic pistons which pushed the SWNT dope back and forth through an actively rotating shear cell within an evacuated housing (24). The speed of the mixing pistons under a constant applied pneumatic pressure allowed for relative changes in dope viscosity to be monitored. When the viscosity reached a steady state, the SWNT material was extruded through a small capillary tube (dia. < 125 μm) into a coagulation bath (Fig. 1b). Fibers were produced under a variety of conditions including different dope temperatures (0 to 100 ºC), coagulants (diethyl ether, 5wt% aq. sulfuric acid, water), and coagulation bath temperatures (0 ºC and room temperature). In the case of aqueous coagulants, fibers were washed for several hours before collection onto a Teflon™ drum (Fig. 1c). To remove water and residual acid, water-coagulated fibers were dried in a vacuum oven at 100 ºC followed by annealing in a flow of H_2/Ar (1:1) at 1 atm and 850 ºC for 1 hour. Fibers extruded into diethyl ether dried quickly in air. Prior to conductivity and XRD measurements, all fibers were further annealed in vacuum at ~1100 ºC.

The resulting fibers were dense, highly aligned macroscopic fibers consisting of only SWNTs without any surface contaminants or impurities (Fig. 2c and 2d). As in rigid rod polymer spinning, the morphology of the fibers was strongly determined by their coagulation conditions. Fibers spun into diethyl ether possessed a collapsed structure, commonly referred to as "dog-bone", due to the rapid flux of sulfuric acid leaving the fiber during the coagulation process. A dense, rigid skin formed which collapsed upon evaporation of the ether resulting in a fiber of density 0.87 ± 0.08 g/cc. When spun into dilute sulfuric acid or water, the fiber retained its circular shape and coagulated in a more uniform manner (Fig. 2c). These fibers possessed a density of 1.11 ± 0.07 g/cc, which is consistent with more uniform coagulation and fewer internal voids. The fact that the water-coagulated fibers had a density 77% that of the theoretical close-packing density for 1.0 nm nanotubes (i.e. 1.5 g/cc) is encouraging. In addition to overall morphology, all of the neat fibers possessed an interesting substructure of nanotube super-ropes (Fig. 2d), approximately 200 – 600 nm in diameter. These super-ropes were typically well packed together and possessed connectivity between one another. A closer examination of these super-ropes shows that they are themselves comprised of a dense packing of smaller ropes approximately 20 nm in diameter. Similar to the elemental microfibrils commonly observed in many rigid rod polymer fibers, they are believed to be formed during the coagulation of liquid crystalline samples during the extrusion process (25). As shown in Figure 2, the most striking result was the transformation of the starting purified SWNTs, which consisted of randomly oriented ropes with diameters less than 30 nm, into uniaxially oriented fibers of highly aligned, coalesced super-ropes with diameters of 200 nm or more. This dramatic transformation illustrates our observation that acid-intercalated SWNT ropes are mobile and can be easily aligned during the extrusion process; and furthermore, once their alignment becomes pervasive during the mixing/extruding process, the ropes coalesce into super-ropes due to formation of the energetically favorable charge-transfer complexes of SWNTs and sulfuric acid.

In addition to the qualitative alignment information that SEM analysis provided, polarized Raman spectroscopy and X-ray diffraction (XRD) have been used to probe the degree of alignment of SWNT fibers. A Renishaw MicroRaman System 1000 with 780 nm diode laser was used to collect Raman spectra. A multi-angle diffractometer equipped with Cu rotating anode, double-focusing optics, evacuated flight path, and 2D wire detector was used for XRD measurements (26). Due to the anisotropic polarization of SWNTs, the ratio of a SWNT sample's G-band intensity (parallel vs. perpendicular) provides a useful probe of the relative degree of alignment and has been used to probe other SWNT objects (16, 27). The neat SWNT fibers possess a Raman ratio greater than 20:1. XRD analysis has also been performed in detail and reveal both ether-coagulated and water-coagulated fibers to be highly aligned with a Full Width Half Maximum (FWHM) mosaic angle of $\phi = 31°$ and an unaligned fraction less than 10%. These analyses indicate the fibers to be the best aligned of any previously reported macroscopic neat SWNT material (28 – 30).

Physical characterization of the neat SWNT fibers reveals them to be a promising multifunctional macroscopic material. Mechanical, electrical, and thermal measurements of the fibers have been performed. The neat SWNT fibers possess good mechanical properties, with a Young's Modulus of 120 ± 10 GPa and a tensile strength of 116 ± 10 MPa. The strength is limited by the presence of defects, voids, and rope-rope interfaces,

but the fact that the strength of our recent SWNT fibers has seen a 30 fold improvement over our initial fibers is very encouraging. Electrical and thermal transport measurements have been performed in detail and also show interesting behavior (31). Electrical resistivity of the fibers has been found to be around $\rho = 0.2$ m$\Omega\circ$cm, with an order of magnitude increase upon high temperature annealing. The fibers are initially p-doped by residual acid, which is removed during annealing. Thermal measurements of ether-coagulated fibers have given a conductivity of $\kappa = 21$ W/K$\circ$m. Both of these conductivities are two orders of magnitude higher than those reported for other SWNT fibers that involve polymers in their production process (12), but are on the same order as both the randomly oriented (32) and aligned mats of SWNTs (28). Given that the connectivity between SWNTs within a given fiber is critical for transport properties and the presence of more than 20% voids, these values are not unexpected. These properties support neat SWNT fibers as valuable multifunctional materials with interesting scientific and commercial potential.

Beyond their novel production and properties, these neat SWNT fibers represent an important chapter in an overarching story that includes the dispersion of SWNTs in superacids (18), their formation into ordered domains (19), and now their continuous spinning into highly aligned macroscopic fibers. As discussed previously, the demonstrated success of this research is predicated on the unique intercalation of individual SWNTs inside each rope by sulfuric acid molecules (Fig. 3a – b), which imparts the mobility, high dispersity, and ease of alignment of ordered phases in SWNT dopes. This model is further supported by the swelling behavior of SWNT fibers in sulfuric acids. Inside a dry glove box, lengths of neat SWNT fiber were sealed in a quartz cell with sulfuric acid of varying concentrations and observed under an optical microscope. Fiber re-exposed at room temperature to 102% or 120% sulfuric acid quickly swelled and sank to the bottom of the cell while fiber exposed to 96% sulfuric acid (i.e. concentrated) floated at the top. However, upon heating to 60 ºC, the fiber in concentrated sulfuric acid swelled and sank to the bottom. The ratio (R) of diameters before and after exposure to sulfuric acid was used to quantify the degree of swelling. In 102% sulfuric acid, ether-coagulated fiber was found to swell to $R = 1.9 \pm 0.1$, while the denser, water-coagulated, dried and annealed fibers swelled to $R = 1.66 \pm 0.11$ and 1.33 ± 0.1, respectively (Figures 3c – d). In 120% sulfuric acids, $R = 1.96 \pm 0.11$ and 1.44 ± 0.09 for the water-coagulated, dried and annealed fibers, respectively. The difference in fiber porosity accounts for the different ratios.

Given the considerable difference in density between SWNT fibers (< 1.11 g/cc) and sulfuric acid (~1.9 g/cc), the sinking behavior of a swollen fiber indicates that the sulfuric acid within the fiber has formed a dense phase. Sulfuric acid molecules intercalate nanotube ropes within the fiber, forming charge-transfer complexes with individual nanotubes. The fact that solid sulfuric acid possesses a density of 2.13 g/cc (33), suggests that there is a similar increase in density for the ordered layer of sulfuric acid molecules surrounding the nanotubes (Fig. 3b). Since the swelling ratios were less than two, there were probably less than three acid layers between adjacent nanotubes. X-ray diffraction data further supports this interpretation.

In addition to XRD performed on dry fiber samples, data was also collected for a swollen SWNT fiber sample sealed in a glass capillary with 102% sulfuric acid. The pattern no longer shows the distinct Bragg reflections associated with SWNTs in the neat

fibers and the scattering intensity at small angles diminishes (Fig. 4), indicating that a) the intercalation of SWNTs by sulfuric acid smears out the triangular lattice; b) the density, and therefore, the electron density of the acid-swollen fibers has become similar to that of the superacid. Instead, the scattering profile shows only highly anisotropic scattering from the pure 102% sulfuric acid (Fig. 4d), but with about the same degree of orientation (FWHM = 32.1º) as the dry fibers. This means that some of the acid molecules must be aligned with respect to the fiber axis and that the anisotropic scattering is from a cylindrical shell of perhaps three acid monolayers in which the mass density is somewhat enhanced with respect to the bulk liquid due to interactions with the nanotubes. These striking results further affirm our model of acid-intercalated SWNT ropes in superacids with individual nanotubes surrounded by ordered layers of sulfuric acid.

We have reported the first-ever continuous spinning of well-aligned macroscopic neat single-walled carbon nanotube fibers without the assistance of any surfactant or polymer. The nature of concentrated dispersions of SWNTs in 102% sulfuric acid to form aligned ordered domains was exploited through conventional, commercially available wet spinning techniques to form dense highly aligned fibers. The resulting fibers possessed good mechanical, electrical, and thermal characteristics. In addition, this research has yielded a greater, more unified understanding of the behavior of nanotubes in superacids. Intercalated SWNT ropes disperse in superacids at high concentrations due to protonation, and readily form an ordered phase, which can be spun into dense, aligned macroscopic fibers. This work is the first, critical step towards achieving many of the applications envisioned for SWNTs since their discovery, in particular, light-weight structural fibers and macroscopic quantum wires of all metallic nanotubes. Both of these will require macroscopic objects of aligned nanotubes that can be produced on a commercial scale and this work helps contribute significantly towards these goals.

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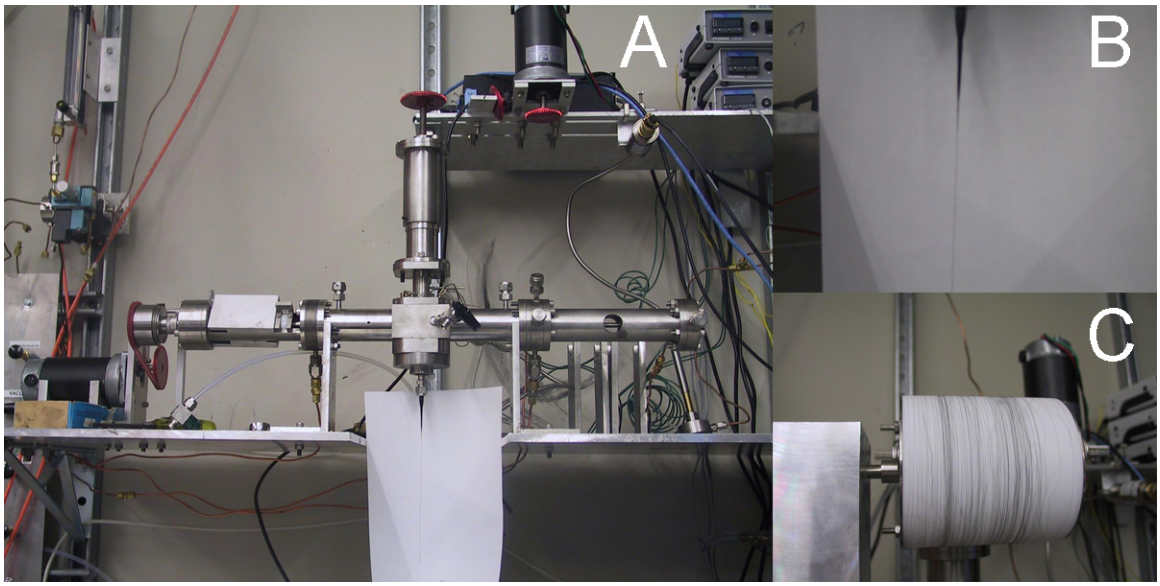

Fig. 1. The spinning process for SWNT in 102% sulfuric acids. **(A)** The custom-built apparatus used for mixing and extruding neat SWNT fibers. **(B)** A jet of SWNT dispersion being extruded out a capillary tube. **(C)** A 30 meter spool of water-coagulated fiber.

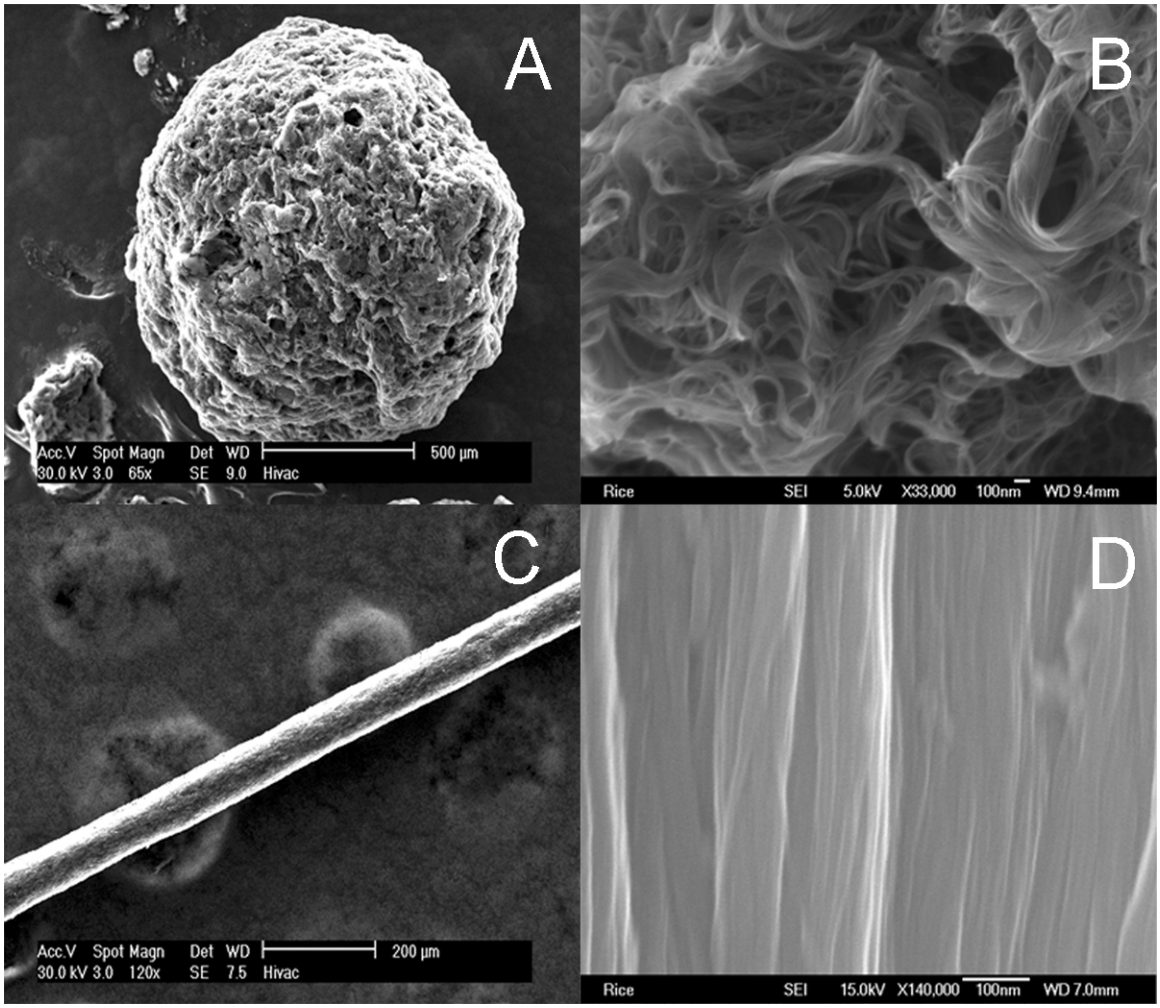

Fig. 2. Scanning electron microscopy details the evolution of purified SWNTs into continuous fiber. **(A)** SWNTs after the purification process (23). **(B)** Inside the purified SWNTs shows a tangled mass of SWNT ropes of 20 – 30 nm diameter. **(C)** An annealed neat SWNT fiber spun from 8 wt% dispersion in 102% sulfuric acid and coagulated in water. **(D)** Higher magnification of the neat fiber surface shows all the ropes have coalesced into highly aligned super-ropes of 200+ nm in diameter.

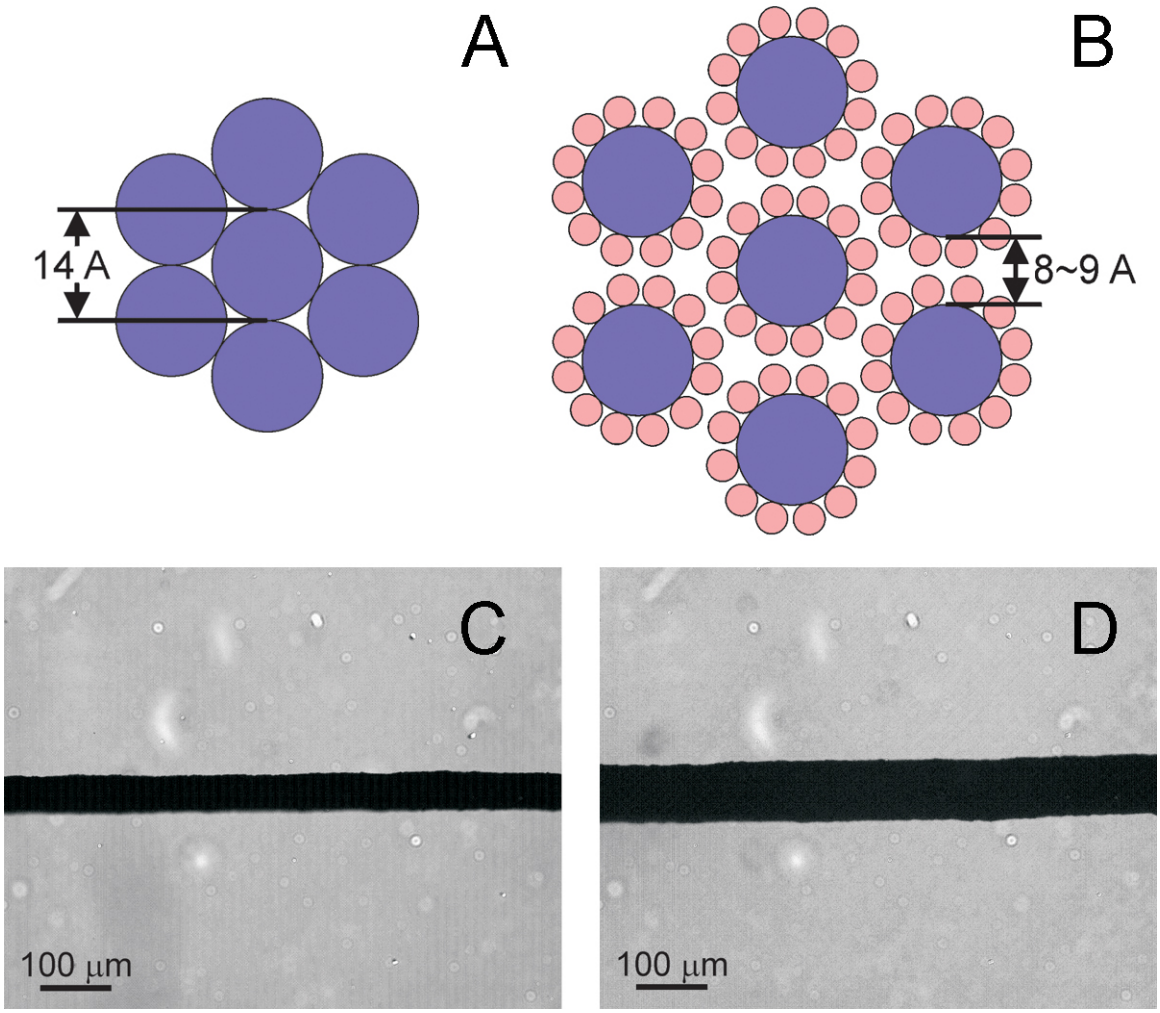

Fig. 3. A model illustrating the swelling of SWNT ropes in sulfuric acid. **(A)** A cartoon of SWNTs in van der Waals contact within a neat fiber. **(B)** The same SWNT fiber after re-exposure to sulfuric acid. A dense layer of sulfuric acid anions (red) surround the individual nanotubes forming an energetically favorable charge-transfer complex. **(C)** A neat fiber (dia. = 52.7 μm) within a quartz cell **(D)** swells to d = 87.4 μm (R = 1.66) upon exposure to 102% sulfuric acid.

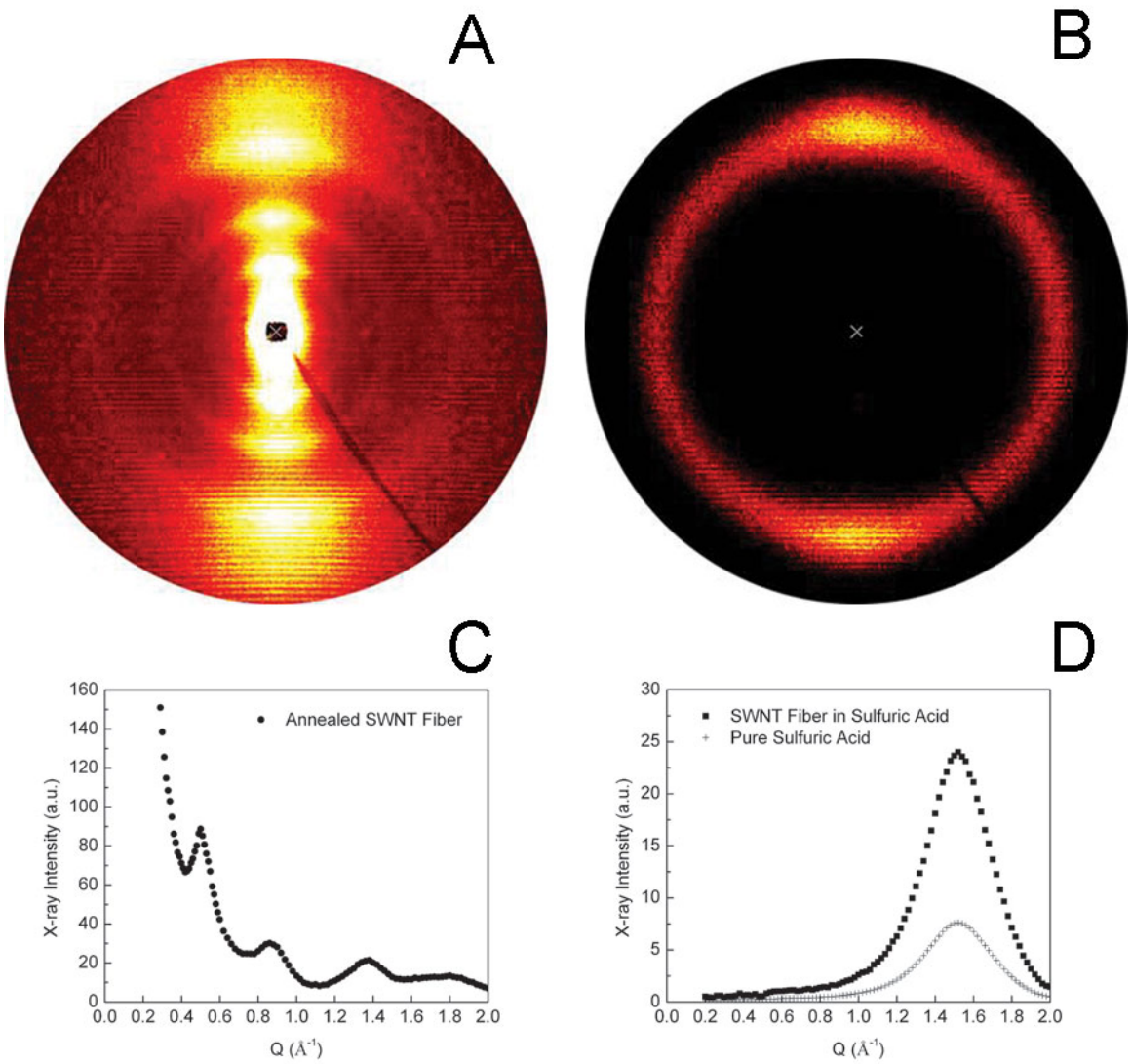

Fig. 4. Wide-angle x-ray scattering data. (A) Two-D detector image of dry annealed SWNT fibers. The intensity maxima indicate high degree of alignment of triangular SWNT crystallites. (B) Similar to (A), obtained from swollen SWNT fibers in a glass capillary with 102% sulfuric acid. The diffuse ring is mainly from isotropic acid molecules in solution. Strong anisotropy is also observed, indicating the presence of anisotropic "shells" of acid surrounding the SWNTs. (C) Integrated scattering profile derived from (A). (D) Scattering profiles of a fiber in acid (solid squares) and pure acid (pluses). Scattering from nanotube bundles is no longer detectable due to lack of x-ray contrast.