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Ultrastrong, Stiff, and Lightweight Carbon-Nanotube Fibers**

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From the stone ages to modern history, new materials have often been the enablers of revolutionary technologies.[1] For a wide variety of envisioned applications in space exploration, energy-efficient aircraft, and armor, materials must be significantly stronger, stiffer, and lighter than what is currently available. Carbon nanotubes (CNTs) have extremely high strength,[2–5] very high stiffness,[6,7] low density, good chemical stability, and high thermal and electrical conductivities.[8] These superior properties make CNTs very attractive for many structural applications and technologies. Here we report CNT fibers that are many times stronger and stiffer per weight than the best existing engineering fibers and over twenty times better than other reported CNT fibers. Additionally, our CNT fibers are nonbrittle and tough, making them far superior to existing materials for preventing catastrophic failure. These new CNT fibers will not only make tens of thousands of products stronger, lighter, safer, and more energy efficient, but they will also bring to fruition many envisioned technologies that have been to date unavailable because of material restrictions.

Strong, stiff, and lightweight are critical property requirements for materials that are used in the construction of space shuttles, airplanes, and space structures. These properties are assessed by a material's specific strength and specific stiffness, which are defined as the strength or stiffness (Young's modulus) of a material divided by its density.[9] The combination of high strength, high stiffness, and low density affords CNTs with extremely high values for specific strength and specific stiffness. The most effective way to utilize these properties is to assemble CNTs into fibers. However, despite extensive worldwide efforts to date, the specific strength and specific stiffness of CNT fibers that have been reported by various research groups are much lower than currently available commercial fibers.[10–22] In early studies, researchers attempted to reinforce polymer fibers with short CNTs, but the reinforcement was limited by several issues, including poor dispersion, poor alignment, poor load transfer, and a low CNT volume fraction.[10–15] Recently, pure CNT fibers (also called yarns) were reported with and without twisting.[16–22] For example, Zhang et al.[20] demonstrated that spinning from aligned CNT arrays could significantly improve the strength of CNT fibers by twisting them. However, to date no breakthrough has been reported in the specific strength and specific stiffness of CNT fibers.

Here we report CNT fibers with values for specific strength and specific stiffness that are much higher than values reported for any current engineering fibers as well as previously reported CNT fibers. As shown in Figure 1, the specific strength

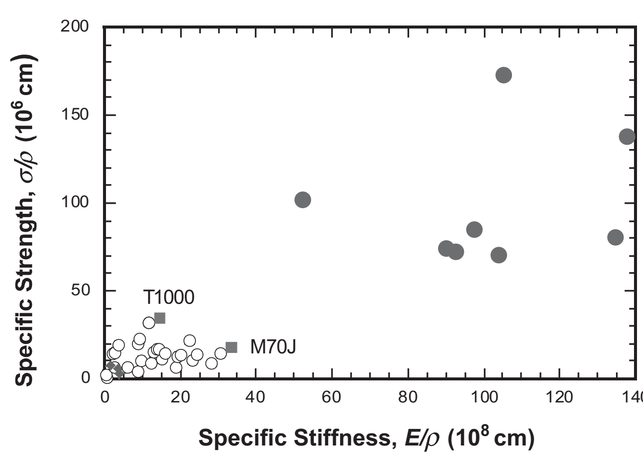

Figure 1. Comparison of the specific strength and specific stiffness (stiffness is defined as Young's modulus) of our CNT fibers (filled circles) to other existing engineering fibers (unfilled circles) [9], the strongest and stiffest carbon fibers (filled squares) [23], and CNT fibers reported previously (filled diamonds) [20–22]. For more information on these data points, see Figure S1 in the Supporting Information.

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of our strongest CNT fiber is 5.3 times the specific strength of the strongest commercial fiber (T1000), and the specific stiffness of our stiffest CNT fiber is 4.3 times the specific stiffness of the stiffest commercial fiber (M70J).[23] Furthermore, the specific strength and specific stiffness of our CNT fibers are more than 23 and 35 times higher, respectively, than values for CNT fibers reported previously.[20–22] Details on the preparation of our CNT fibers are given in the Supporting Information.

The key to the superior properties of our CNT fibers is the ultralong (1 mm) and ultralight individual CNTs comprising the arrays used for spinning. The synthesis of the long, light, CNT arrays was reported previously.[24] The CNT fibers were spun either using a hand-held spindle[7] or an automatic spinning machine (see Fig. S2 in the Supporting Information). Scanning electron microscopy (SEM) images of an as-spun CNT fiber are shown in Figure 2a and b. Figure 2c and d show

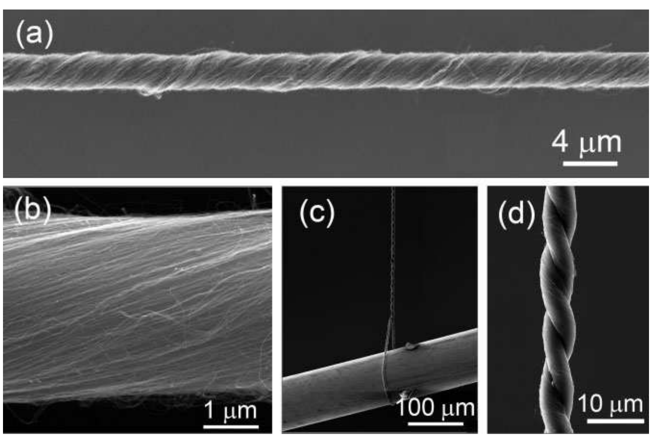

Figure 2. SEM images of CNT fibers. a) CNT fiber at low magnification. b) CNT fiber at high magnification. c) CNT fiber forming a loop around a Ni wire and then twisted. d) Twisted two-ply section of the fiber in (c).

the images of a CNT fiber holding a 0.1 mm diameter Ni wire and the enlarged image of the two-ply CNT fibers twisted together. These images clearly demonstrate the high quality of our CNT fibers.

Our CNT fibers have an extremely low density, (0.2 ± 0.01) g cm^{-3}, which is one-tenth the density of a commercial carbon fiber and about one-fortieth the density of steel. In fact, they are so light that we lost many fibers during their handling because of the air circulation in our laboratory. The density was determined using two methods, both of which yielded a consistent value of (0.2 ± 0.01) g cm^{-3}. The first method involved calculating the fiber density from the density of individual CNTs and the packing density of CNTs inside the fiber, whereas the second method involved measuring the weight of CNT fibers using a quartz crystal microbalance. More details are described in the Supporting Information. The low density of our CNT fiber was derived from two factors: first, the individual CNTs had a large average diameter of 7 nm (Fig. 3a) and were double-walled (Fig. 3b) and second, the CNT fibers had a very low packing density (see Fig. 3c and d). As shown in Fig. 3d, the CNTs tended to cluster as strands inside the CNT fiber, and there were large spaces between strands.

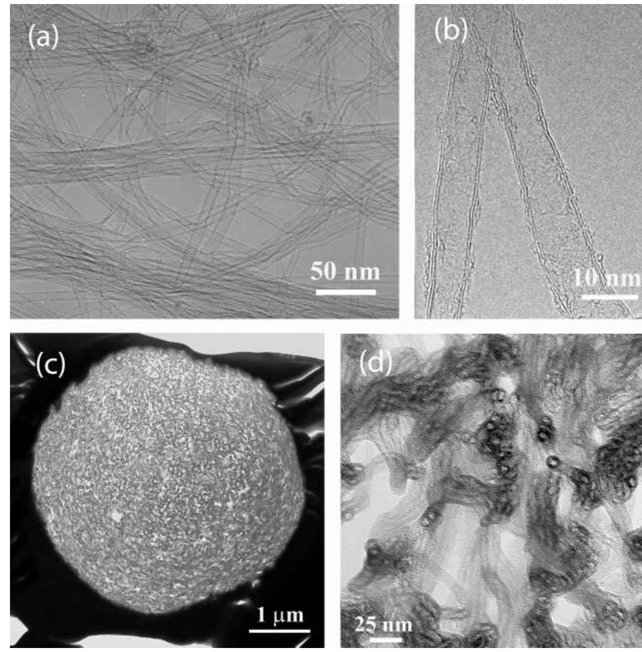

Figure 3. a) TEM image showing CNTs with relatively large diameters and thin walls, b) high-resolution TEM image revealing the CNTs as double-walled, c) TEM image showing the cross section of a CNT fiber encased in platinum (the black surrounding), and d) enlarged area from (c) showing the low packing density of the CNT fiber. The circles are where CNT strands exit the specimen top or bottom surfaces.

The tensile strength and stiffness of our CNT fibers were measured in the range 1.35 to 3.3 GPa and 100 to 263 GPa, respectively (see Table S1 and the testing procedure in the Supporting Information). The tensile strength and stiffness were calculated using the initial fiber diameter, which was directly measured using a laser diffraction method. The scatter in the data was from variations in spinning parameters, such as the helix angle that CNTs make with the fiber axis, the CNT array quality, and the CNT fiber diameter. These strength values were higher than values reported previously.[7,20–22] Coupled with an extremely low density, they yielded the ultrahigh specific strengths and specific stiffness values shown in Figure 1. More importantly, we found that some of the CNT fibers did not fracture at the highest load, as was observed for other advanced fibers as well as for CNT fibers reported previously.[20–22] An example of the nonbrittle behavior of our CNT fibers is demonstrated in Figure 4a. From the area under the stress–strain curve, we calculated the toughness (the work needed to break the fiber) of a CNT fiber as (975 ± 49) J g^{-1}, which is comparable to the toughness of a recently reported single-walled nanotube/poly(vinyl alcohol) (SWNT/PVA) composite fiber (870 J g^{-1});[15] higher than the toughness of a similar fiber reported previously (570 J g^{-1});[13] and much higher than carbon fibers

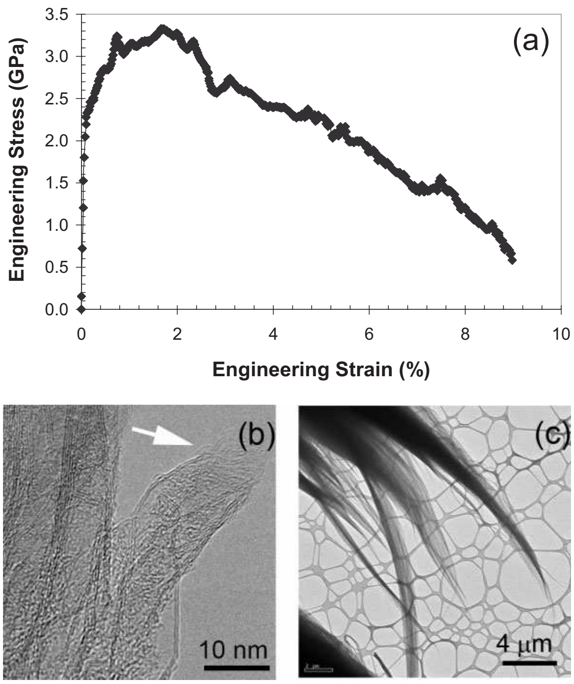

Figure 4. a) Stress–strain curve of a CNT fiber under tension shows non-brittle behavior. b) TEM image shows broken CNT ends (marked by an arrow) after tensile testing. c) TEM image of the fracture morphology of a CNT fiber indicates sliding between CNT strands. The background in (c) is supporting carbon foil.

(12 J g^{-1}),[20] Kevlar fibers (33 J g^{-1}),[25] and CNT fibers reported previously (14–20 J g^{-1}).[20] The toughness of our CNT fibers ranged from (110 ± 5) to (975 ± 49) J g^{-1} (see Table S1 in the Supporting Information) with an average toughness of (309 ± 15) J g^{-1}. The ultrahigh toughness of our CNT fibers will increase the safety factor of CNT fiber composite structures by preventing catastrophic failure.

Transmission electron microscopy (TEM) images of a fractured section of the CNT fibers reveal evidence of both fractures in individual CNTs (Fig. 4b) and the sliding of CNT strands against each other (Fig. 4c). From the stress–strain curve and the fracture morphology in Figure 4, we envision the following fiber failure process: under increasing load, some CNT strands initially break because all CNT strands are not under the same tension. This breakage results in an immediate stress relaxation (stress drop), which was observed in the stress–strain curve in Fig. 4a, because the tensile test was carried out under a constant displacement speed. As a result, the load carried by the broken strand is transferred to neighboring strands that are under less tension initially, which leads to a partial stress recovery. At the same time, the broken strand may slide against its neighbors. As this process repeats itself, more strands are broken, leading to a lower load-carrying capacity by the fiber until the final failure, as demonstrated by the rough and gradual stress drop in Fig. 4a.

We also monitored the fiber diameter in situ during a tensile test and found that the diameter could shrink by as much as 10 %, indicating that the maximum true stress could be ca. 20 % higher than the strength listed in Table S1. Similar behavior was also observed by Zhang et al,[20] who attributed it to a "giant Poisson ratio." We believe that this giant Poisson ratio was caused by the low packing density of CNTs in the fiber. As shown in Figure 3c, there are large spaces between CNT strands inside the fiber, and individual CNT strands appear wavy. Therefore, under a tensile load, these CNT strands will straighten and tightly twist around each other, leading to large shrinkage in fiber diameter. This observation raises a processing issue on how to improve the packing density of CNT fibers.

The high strength of our CNT fibers was derived from the long length of our CNT arrays. The strength of our CNT fibers increased with increasing CNT array length (see Fig. S4, Supporting Information). The dependence of fiber strength on array length can be explained by two possibilities. First, as shown in Figure 3c, the CNT strands are not in close contact with each other, which makes the load transfer between strands very weak. Therefore, a significant length near a strand end may not carry much load. Longer CNT arrays yield longer strands and have a larger length fraction that carries load. Second, the ends of CNT strands are also where CNT ends cluster, giving rise to flaws that weaken the CNT fiber at certain points because the strand ends do not carry load. This problem is especially severe if the ends of several CNT strands are located close to each other because it gives rise to an even bigger flaw that will break the fiber under a relatively low tensile stress. We have indeed observed CNT end clustering in CNT ribbons drafted from a CNT array (see Fig. S5 in the Supporting Information). With increasing CNT array length, the probability that such big flaws exist in a fiber of certain length decreases and the strength of the fiber increases. We expect that the CNT fiber strength will continue to increase with even longer CNT arrays (>1 mm) and eventually reach a saturation higher than values reported here.

In summary, we have spun CNT fibers with ultrahigh specific strength, specific stiffness, and toughness values, which are derived from two unique characteristics of our CNT arrays: they have long spinnable length and are lightweight. The specific strength and stiffness of our CNT fibers are much higher than commercially available engineering fibers. Our results suggest that these properties can be significantly improved by using even longer CNT arrays and by improving the packing density of CNTs in the fiber.

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