

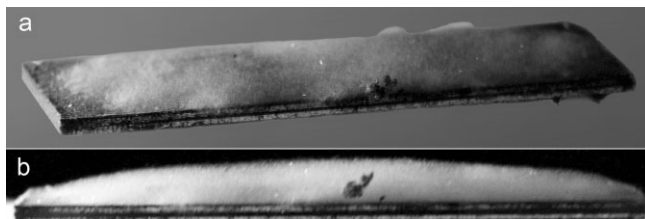
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## Carbon-Nanotube Cotton for Large-Scale Fibers\*\*

By Lianxi Zheng, Xiefei Zhang, Qingwen Li, Satishkumar B. Chikkannanavar, Yuan Li, Yonghao Zhao, Xiaozhou Liao, Quanxi Jia, Stephen K. Doorn, Dean E. Peterson, and Yuntian Zhu\*

Carbon nanotubes (CNTs) are much stronger than any existing material. To fully utilize their extremely high strength, carbon-nanotubes must be spun into continuous fibers.<sup>[1–3]</sup> The most efficient way to produce commercial-scale CNT fibers is by the five-thousand-years-old cotton-based spinning technology.<sup>[4]</sup> Therefore, it is technologically attractive to produce CNT materials that have spinning properties similar to cotton. Here we report a new form of CNT material, CNT cotton, that is made of ultralong individual CNTs. This CNT cotton is analogous to conventional cotton in many aspects including the color and fluffiness, and is found favorable for spinning. It is found that the CNT cotton is hydrophobic, and is composed of low spatial density and ultra-long individual CNTs.

Figure 1a is a photograph of fluffy and gray CNT cotton on a quartz support (15 mm × 35 mm). The CNT cotton has very low density with large space between individual CNTs, mak-

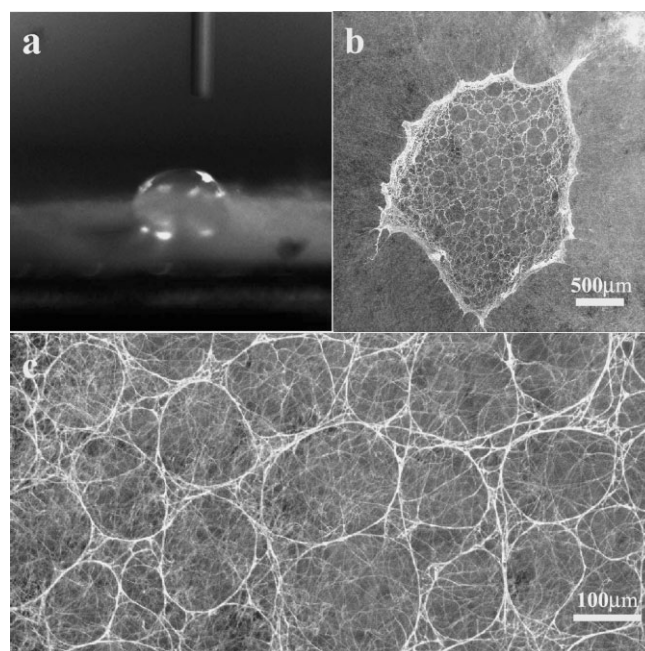


**Figure 1.** Carbon-nanotube (CNT) cotton on a 35 mm long quartz support. a) Top view; b) Side view.

ing it very similar to conventional cotton in terms of structural form. The gray color is surprising because all other CNT materials are black. This gray color is caused by the unique low spatial density of nanotubes in the CNT cotton, as well as a light-scattering effect. From the side view (Fig. 1b), we can

see a 2 mm thick CNT cotton above the support, indicating that the CNT cotton is composed of long (at least millimeters) individual CNTs.

The CNT cotton is also found to be hydrophobic. As shown in Figure 2a, a water droplet with a diameter of 2.5 mm was suspended on the CNT cotton. It sank into the CNT cotton because of its weight, but maintained a quasi-spherical shape. After the water-droplet was completely evaporated, the mor-



**Figure 2.** Hydrophobic nature of the CNT cotton. a) A water droplet suspended on CNT cotton; b) Web-like mesh formed after water is evaporated; c) Cotton form retained beneath the web.

phology of the CNT cotton was examined by scanning electron microscopy (SEM). The CNTs in the area that supported the water droplet were rearranged into a web-like mesh (see Fig. 2b), but the CNTs underneath the web still retained the cotton form (Fig. 2c), further confirming the hydrophobic behavior of CNT cotton.

Catalytic chemical vapor deposition (CVD)<sup>[5]</sup> was used to synthesize the CNT cotton. The catalyst precursor solution was prepared by dissolving  $\text{CoCl}_3$  and  $\text{FeCl}_3$  in ethanol to reach a concentration of 0.05 M Co + 0.05 M Fe. With a sharp-tip pen, this catalyst solution was then applied to one edge of a 5 mm × 10 mm Si substrate that had a 0.1  $\mu\text{m}$  thick  $\text{SiO}_2$  layer on its surface. The substrate was in turn placed on the

[\*] Dr. Y. T. Zhu, Dr. L. X. Zheng, Dr. X. F. Zhang, Dr. Q. W. Li, Dr. S. B. Chikkannanavar, Dr. Y. Li, Dr. Y. H. Zhao, Dr. Q. X. Jia, Dr. S. K. Doorn, Dr. D. E. Peterson  
Los Alamos National Laboratory  
Los Alamos, NM 87545 (USA)  
E-mail: yzhu@lanl.gov

Dr. X. Z. Liao  
School of Aerospace, Mechanical & Mechatronic Engineering  
The University of Sydney  
Sydney, NSW 2006 (Australia)

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surface and in the area center of a quartz plate with a dimension of 15 mm × 35 mm. The substrate and the quartz plate were placed into a 1-inch quartz tube furnace. The furnace was purged for 0.5 hour with forming gas (94% Ar + 6% H<sub>2</sub>), and then heated at a rate of 60 °C min<sup>-1</sup> to 900 °C and held at this temperature for 1 hour, with a flowing gas mixture of 4 cm<sup>3</sup> min<sup>-1</sup> of forming gas bubbling through ethanol, 8.5 cm<sup>3</sup> min<sup>-1</sup> of forming gas bubbling through acetone, and 10.5 cm<sup>3</sup> min<sup>-1</sup> forming gas for dilution.

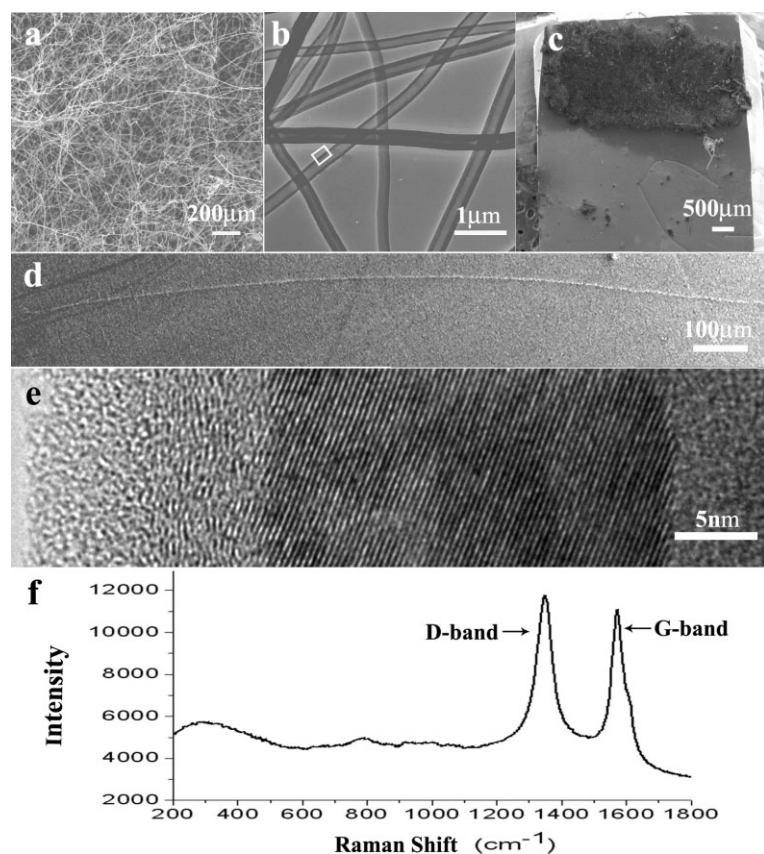
The as-synthesized CNT cotton was characterized by SEM and transmission electron microscopy (TEM). Figure 3a is a typical SEM image, showing very clean and long CNTs. Since this SEM image presents the as-grown morphology of the cotton sample, it clearly shows very low density. From higher resolution SEM images (not shown), we find that the average space between individual CNTs in our CNT cotton is about 10 μm, indicating a 2D density of 10<sup>4</sup> mm<sup>-2</sup>, which is much lower than that of vertically aligned CNT arrays (~10<sup>9</sup> mm<sup>-2</sup> in our normally grown arrays). In Figure 3b we show a TEM image of long multi-walled nanotubes in the cotton. The nanotube diameters are in the range of 100–380 nm, with an average diameter around ~250 nm.

In order to understand the growth mechanism, we examined under SEM the Si substrate, on which catalyst was applied, after removing the topmost CNT cotton. As shown in Figure 3c, there are two distinct areas: the catalyst area (upper area) is covered by a vertical CNT array, while other areas (lower area) have no CNT at all, indicating that all CNTs in the cotton were initially grown from catalyst area. This also suggests that individual CNTs could be more than 1 cm long because they covered the surface of the whole quartz plate. However, it is hard to directly measure their length because of their entangled nature. We pulled out several individual nanotubes from the CNT cotton and measured their length as 1–3 mm. The SEM image in Figure 3d shows an isolated nanotube with a length around 1.5 mm. It is likely that these individual CNTs were broken during the pulling, caused by the heavy entanglements (see Fig. 3a).

The detailed microstructure of the CNTs is revealed by the high resolution TEM image (see Fig. 3e, a magnification of the boxed area shown in Fig. 3b). In contrast to the normally observed structure of multi-walled CNTs that show graphene layers parallel to the CNT axis, the graphene layers in our CNTs stack in parallel but with a relatively large angle to the CNT axis. This characteristic stacking of graphene layers around the nanotube hollow region is referred to as ‘herringbone’ type stacking.<sup>[6]</sup> A similar stacking has been reported in other catalytically grown carbon fibers.<sup>[6]</sup>

It is found that the CNT walls are composed of well-ordered graphite layers, with not much extraneous amorphous carbon in the samples. Raman spectroscopic characterization of CNT cotton revealed the D-band and G-band features around 1349 cm<sup>-1</sup> and 1573 cm<sup>-1</sup>, respectively (see Fig. 3f). Consistent with the ‘herringbone’ structure of the stacked graphite layers, the G and D band frequencies and relative intensities are more similar to those found for graphitic structures than observed in typical CVD-grown nanotubes.

Large diameter CNTs reported previously<sup>[7]</sup> were believed to have grown via self-catalytic growth, i.e., CNTs themselves adsorb free carbon species at their open edges and sidewalls and thus grow axially and radially in the absence of metal particles. However, we believe that our CNT cotton was grown via the traditional catalytic growth mechanism. In particular, our steady CVD environment and extreme long length of CNTs in CNT cotton grown over a long duration corroborate such a mechanism. It is hard to imagine that CNTs can be self-grown with uniform diameter for such a long length over such a long time (1 hour) without the assistance of metal catalyst. In addition, the ‘herringbone’ type structure found for the graphene sheets firmly supports such a statement. Otherwise, a cone-structure instead of the tube-structure should



**Figure 3.** Characterization of CNT cotton. a) SEM image of CNT cotton; b) TEM image of individual CNTs; c) SEM image of Si substrate after pulling away the CNT cotton; d) SEM image of an isolated CNT pulled from CNT cotton; e) High-resolution TEM image of CNT wall (from the boxed area in b); and f) Raman spectrum of CNT cotton shows the G-band and D-band features arising from the carbon nanotubes.

have been resulted, i.e., the diameter of the CNT would change along its length.

In catalytic CVD, it has been established that the catalyst particles will aggregate together at high temperature and large size catalysts usually favor the growth of graphite sheet instead of CNTs. Therefore, high temperature CVD normally results in very low density of individual long CNTs lying on the substrate surface.<sup>[5]</sup> It is also reported that a small amount of oxygen atoms can prevent the formation of amorphous carbon and thus keep catalyst effective for a longer growth time and/or keep the CNTs clean.<sup>[8,9]</sup> Further study on the growth mechanism is still under progress, but we believe that the existence of oxygen atoms in our carbon precursors, ethanol and acetone, helps the nucleation of CNTs from large catalyst particles. Nevertheless, not every nucleated CNT can survive the whole growth time in a highly competitive process of amorphous carbon formation. Only some of them can grow to millimeter to centimeter long while others stop the growth at early time due to the catalyst encapsulation, resulting in the observed low special density in the CNT cotton. As a result of this low density, CNTs in the cotton are randomly arranged rather than vertically aligned, because neither the support force from adjacent nanotubes is enough to align them up nor the stiffness of individual CNTs is large enough to support their free-standing up to centimeter high. However it might be possible to grow centimeter long vertical CNT array if we can preserve the small catalyst size at high temperature.

The CNT cotton was spun into fibers using a spinning set-up built in-house. A speed-adjustable drill equipped with a 25  $\mu\text{m}$  metal tip was used to spin continuous fibers out of the CNT cotton. The tip was first coated with a layer of glue for initial attachment to a CNT sliver, which was pulled from the CNT cotton. Then the drill was pulled away from CNT cotton at a speed of 10  $\text{mm min}^{-1}$  while the drill was rotating at 1000–2000 rpm. As shown in Figure 4a and b, individual CNTs in the cotton were easily collected during fiber spinning, with alignment along the pulling direction. We can routinely spin 10 cm long fibers from the CNT cotton.

Figure 4c is a plot of stress versus strain for a typical spun fiber, showing very good mechanical strength. The failure mechanism was studied by imaging the ends of the fractured fiber using SEM. As shown in Figure 4d, individual CNTs slide against each other, instead of structural breakage, so the fiber became thinner and thinner until the final failure. The loose attachment between CNTs and the long length of individual CNTs are believed to be responsible for such a breaking behavior of the CNT fiber because longer CNTs can slide for a longer distance. The CNTs did not show any obvious fracture during tensile tests, suggesting that the strength of CNT fibers can be further increased by optimizing the structural arrangements of CNTs in the fiber. The strength can also be en-

hanced by improving CNT quality through, for example, decreasing the diameter of CNTs in the cotton.

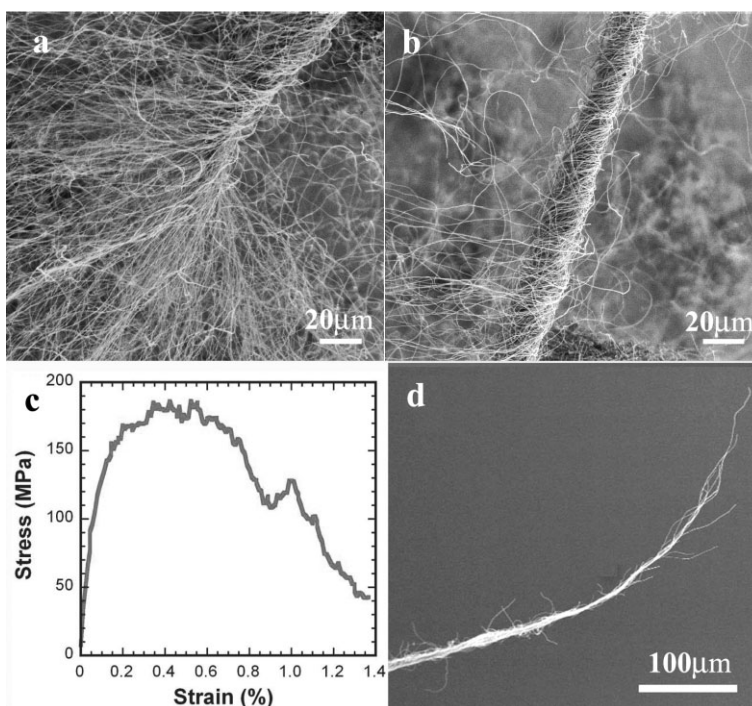
Other forms of CNT materials reported so far have various limitations for fiber spinning. For example, aerogels formed directly in the synthesis chamber contain a large amount of catalyst particles and relatively short nanotubes.<sup>[2,10]</sup> CNT solutions are suitable for spinning only when the nanotubes are relatively short.<sup>[3,11,12]</sup> Spinning fibers from CNT arrays<sup>[1]</sup> or forests<sup>[13]</sup> have been demonstrated, and 1 mm arrays were successfully used for fiber spinning in our previous paper.<sup>[14]</sup> However, CNT arrays longer than 1 mm have not been reported conducive to spinning. The CNT cotton reported here is the easiest form of CNT materials for fiber spinning, and importantly, has the potential to adapt for commercial cotton-spinning technologies for large-scale production of nanotube based fibers.

In conclusion, CNT cotton has been synthesized using CVD approach. The structure characterization indicates the presence of millimeter to centimeter long individual CNTs, which exhibit interesting microstructure. The CNT cotton shows hydrophobic characteristics. We have been successful at pulling CNT fibers from the CNT cotton. This form of CNT material shows the great potential for large-scale fiber production.

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**Figure 4.** a) SEM images illustrate that CNT cotton can be easily spun into fibers; b) A segment of a CNT fiber spun from the CNT cotton; c) A plot of stress versus strain for a typical spun CNT fiber; (d) The failure mode of the CNT fiber: gradual thinning due to inter-nanotube sliding.

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