

Continuous carbon nanotube composite fibers: properties, potential applications, and problems†

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Using solution spinning, which involves an intermediate gel-state, we obtained exceptionally strong carbon nanotube fibers that are tougher than either spider silk or any fiber used for mechanical reinforcement. We use these fibers to make 100 micron diameter supercapacitors and electronic textiles. Per weight, the energy needed to break these fibers is about $4 \times$ higher than spider dragline silk and $20 \times$ higher than steel wire. This article describes this advance, comparisons with the prior art, potential applications, and present barriers for large volume applications.

Over 400 million years of evolution, spiders developed the ability to spin a silk that is optimized for catching missiles (flying insects). Absorbing mechanical energy without breaking is key for this performance, which is characterized by fiber toughness (the total mechanical energy a specified fiber mass absorbs before breaking). The extraordinary toughness of spider silk (five times higher than the same weight steel wire) has inspired bio-based commercialization efforts, from pulling silk from spiders over a century ago to genetically engineering silk protein production in goat's milk today.^{1,2} Despite attempts by scientists to mimic the mechanical properties of spider silk

using synthetic materials, no alternative organic fibers with similar toughness have emerged until now.

We find that carbon nanotube fibers, comprising single walled carbon nanotubes in a polymer matrix (Fig. 1), have a toughness far exceeding that of spider silk. This discovery resulted from our efforts to solve a long standing problem in the carbon nanotube area: while individual carbon nanotubes have exceptional strength, high modulus, and exciting electronic properties, no one has effectively utilized these properties in long fibers or sheets comprising mostly carbon nanotubes. An impediment is that bulk synthesis methods produce carbon single wall nanotubes (SWNTs) as a low density, soot-like powder³⁻⁵ that is difficult to process. This processing difficulty restricts efforts to use carbon nanotubes as multifunctional

materials, in which the mechanical and electronic properties of nanotubes might be simultaneously exploited for such uses as artificial muscles,⁶ sensing,⁷⁻¹⁰ and electronic textiles.

A number of studies have used carbon nanotubes as fillers in polymer sheets and fibers.¹¹⁻¹⁵ While some successes have been achieved in the reinforcement of polymers using small amounts of nanotubes, no one has been able to achieve outstanding mechanical properties for continuous fibers that comprise mostly carbon nanotubes. One barrier is that the high viscosity of molten nanotube/polymer composites limits nanotube concentrations in melt-spun fibers to below $\sim 10\%$.¹⁶ The best prior-art technology for producing nanotube fibers involves spinning an aqueous dispersion of nanotubes into a rotating coagulation bath of aqueous

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From left to right: Alan Dalton, Steve Collins, Von Howard Ebron, Ray Baughman, Joselito Razal, John Ferraris (not shown: Edgar Munoz, Johnny Coleman, Bog Kim).

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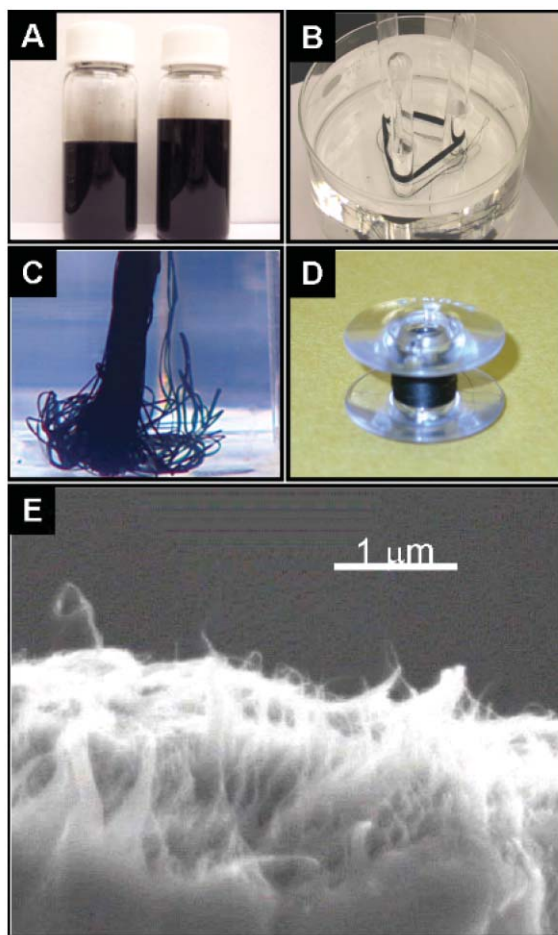


Fig. 1 (A) Stable SWNT suspension in a lithium dodecyl sulfate/dionized water solution. These suspensions are used as the “ink” for spinning nanotube gel fibers. (B) The ink in (A) is injected into a glass pipe (where the coagulation solution is coaxially flowing) to form the gel fiber, which travels along the glass pipe and is eventually collected on a rotating mandrel in a water bath. A hundred meters of gel state fiber tightly wrapped on a mandrel is shown. (C) These pictured gel fibers act like a rubber, reversibly elongating up to 400% before breaking. (D) The gel is subsequently drawn out of the bath, passed over a series of godets and through an acetone washing bath during a drying process, and finally wound onto a spool (pictured, with a wound nanotube fiber). (E) Scanning electron micrograph of the end of an undrawn composite carbon nanotube fiber, showing carbon nanotubes in a polyvinyl alcohol matrix.

polyvinyl alcohol to produce gel fibers (comprising about 90 weight percent water). Drawing these as-spun gel fibers is extremely slow ($\sim 1 \text{ cm min}^{-1}$) and solid fiber lengths reported in the literature are short (~ 10 centimeters).^{17–19} The gel fiber is too weak to be handled, except by a slow draw process, and the rotating bath method is unsuitable for obtaining long, untangled gel fiber. Moreover, the mechanical properties are relatively disappointing: a tensile strength of $\sim 300 \text{ MPa}$ and a Young's modulus of 40 GPa (respectively, factors of ~ 100 and ~ 10 below those of the component individual nanotubes).

Building on the pioneering work of Vigola *et al.*,^{16–18} we developed a modified coagulation-based method for spinning continuous nanotube fibers having record lengths, tensile strengths, and toughness (energy-to-break).²⁰ We obtained these advances by developing a continuous spinning apparatus for producing the gel fiber (involving

injecting the spinning solution into a coaxial flow of coagulation solution), optimizing the compositions of spinning and coagulation solutions and their relative velocities, and substantially avoiding extraction of the coagulant polymer (polyvinyl alcohol). The resulting gel fibers now have sufficiently high strength that they can be wound on mandrels, and subsequently unwound, passed over rollers through an acetone wash bath, and dried to produce solid fiber. We can now routinely make several hundred meter long reels of continuous nanotube-polymer composite fiber at $100 \times$ the prior-art rate and achieve fiber strengths higher than 1.8 GPa . These fibers (comprising 60% by weight nanotubes and 40% polyvinyl alcohol) are over $7 \times$ stronger, $300 \times$ tougher, and over $10,000 \times$ longer than any prior-art nanotube fibers containing mostly carbon nanotubes. Our drawn nanotube fibers match the energy absorption capability of the highest performance spider silk up to

the breaking strain of this silk (30%), and continue absorbing energy until reaching an energy-to-break of over 600 J g^{-1} , as compared with 165 J g^{-1} for the best spider silk, 50 J g^{-1} for Spectra fiber, 33 J g^{-1} for Kevlar fiber, and 1.7 J g^{-1} for prior-art solution-spun nanotube fibers.¹⁸ No tougher organic fiber has been previously reported. Normalized to density, the strength and Young's modulus of our nanotube composite fiber is over twice that of high performance steel wire and are over twenty times tougher.

Despite these advances, a number of problems must be overcome before commercialization of the spinning process is viable. These include: (1) sub-commercial spinning rates, (2) the present cost of the utilized SWNTs, and (3) problems of using the current fiber binding agent (polyvinyl alcohol) in the nanotube fibers for applications involving electrochemical charge injection — such as artificial muscles and fiber capacitors. While our advances increased the spinning rate to a hundred times the prior-art rate for solution spinning, our spinning rate of $\sim 100 \text{ cm min}^{-1}$ is much lower than for commercial specialty fibers. The present fiber cost (above 3 cents m^{-1} for $10 \mu\text{m}$ diameter fiber, based on SWNT content) is too high for other than very specialized applications, and phosphoric acid treatment of the polyvinyl alcohol to make an ionically conducting polymer (needed for supercapacitor, energy harvesting, and energy storage multifunctional applications) degrades mechanical properties.

Since the gel state is critical for making high performance fibers at increased overall spinning rates, deeper understanding is needed on how to manipulate the properties of the gel fibers that initially form during spinning, as well as the evolution of these properties during conversion of gel fibers to solid fibers. The gel state fiber acts like a rubber, elongating up to 400% before breaking for the optimized nanotube/polyvinyl alcohol gel.

The present cost of SWNTs (about $\$500 \text{ g}^{-1}$ for present kilogram scale production) is also a major barrier to commercialization for all but very specialized applications. Until SWNTs become available in commercial quantities at low cost, this problem could be mitigated by using multiwall nanotubes (MWNTs) as an alternative to SWNTs. MWNTs have long ago been up-scaled to industrial quantities by Hyperion. Mitsui projects a cost of about $\$80 \text{ kg}^{-1}$ for multi-wall nanotubes that will be produced in their plant, and an eventual price of about $\$10$ per pound seems eventually achievable.

While the mechanical properties that

we have so far demonstrated are quite spectacular, these properties result from inter-nanotube stress transfer *via* the binder polymer in our composite fiber. Also, the coagulation polymers that are best for spinning (like polyvinyl alcohol) lose some of their utility for inter-tube stress transfer when these polymers are converted to ionic conductors (which are needed for application of these fibers as supercapacitors, artificial muscles, and batteries). By extending our technology to other coagulation polymers, especially those having higher modulus and/or intrinsic high ionic conductivity, and by using longer nanotubes that are “welded” together, we believe that fiber performance can be further improved. Even after very recent increases in fiber tensile strength (from 1.8 GPa to 3.2 GPa, without sacrificing fiber toughness), our fiber strength and modulus are still factors of ~10 and ~8, respectively, below those for reasonably small diameter individual nanotubes. Hence, further major improvements in strength and modulus seem feasible.

Initial commercial applications are anticipated in low volume/high value applications, such as carbon nanotube actuators for microcatheters for microsurgery, for moving pins on dynamic brail displays, for inexpensive, three-dimensional optical fiber switches, and as a minority fiber component for electronic textiles. Using much lower modulus and strength nanotube strips, cheaply fabricated nanotube optical switches have been demonstrated that have a 30 ms switching time, and this switching time should be easily reduced.²¹ Since the cost of getting materials into space is quite high (about \$10,000 per pound), the combination of light weight and high performance suggests intermediate volume applications — including satellite tethers for large aperture satellite arrays and structures deployed in space. The extreme toughness of our nanotube fibers could be used for other medium volume applications, as long as the high toughness can be maintained at ultra-high deformation rates and the high failure strain can be either decreased or included in component design. These include anti-meteorite/anti-ballistic shields for satellites, anti-ballistic vests, explosion proof blankets for aircraft cargo bays, and safety belts for high performance applications. Longer term application targets, having from low-to-high volume possibilities, include actuators (artificial muscles) for prosthetic devices and for severe environments (planetary exploration, down-hole for oil exploration, and aircraft engines). Demonstrated performance for our actuators, using polymer-free nanotube fibers obtained by thermally annealing

coagulation spun fiber composites, includes a force generation capability that is a hundred times that of the same size natural muscle, and twice the response rate. Based on the known stability of carbon electrodes in electrolytes at high temperatures, they should be capable of operating in an oxygen free environment to above 1000 °C.

We show that the carbon nanotubes can be used to make fiber capacitors, which can be woven into textiles for providing both a structural function and the storage of electrical energy. These 100 micron supercapacitors provide high cycle life and comparable energy storage capabilities to large aqueous-electrolyte supercapacitors, but slower discharge rates — so we need to increase the achieved electrical conductivity of our fibers. Other electronic textile applications also seem promising for our composite carbon nanotube fibers, which are easily woven or sewn into textiles — such as distributed sensors, electronic interconnects, electromagnetic shielding, antennas, and batteries.

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