A New Type of Carbon Yarn for Artificial Muscle and Other Multifunctional Applications

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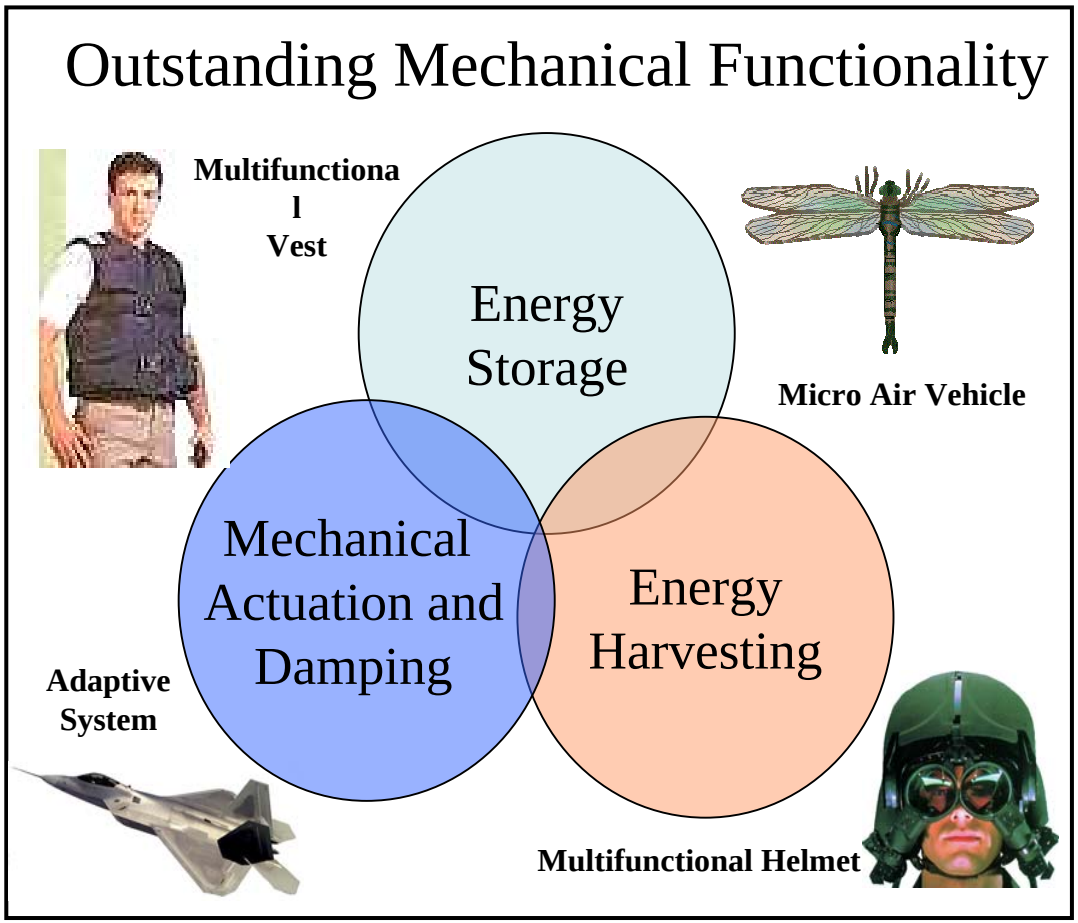
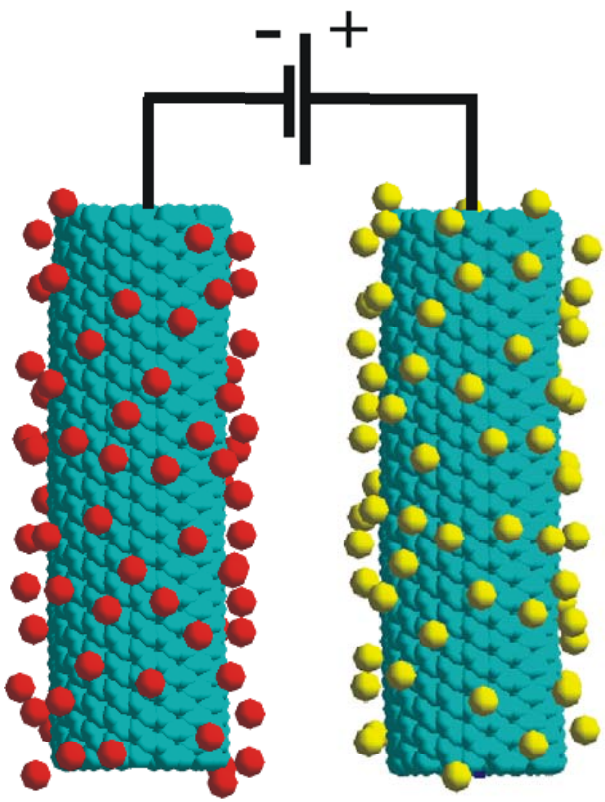
Multifunctionality Provides Opportunities



Carbon nanotube fibers combining mechanical functionality with

(a) **mechanical actuation,**
(b) **energy storage,**
(c) **mechanical dampening,**
(d) **energy harvesting**,
(e) **sensing**

The Actuator, Energy Storage, and Energy Harvesting Functions Use Electrochemical Charge Injection



ENERGY STORAGE

C= charge/voltage

C= Area × dielectric constant /d

Area/weight is above 300 m^2/gm; d is in nanometers

ACTUATION

Charge injection causes change in fiber length, which does work.

Work/cycle $\propto$ *(strain)*^{2} × Y

or *Work/cycle* $\propto$ *strain* × $\sigma_{failure}$

Y, $\sigma_{failure}$, and strain are all large.

Success of our original Spinning Technology: YARNS STIFFER, STRONGER, AND TOUGHER THAN SPIDER SILK

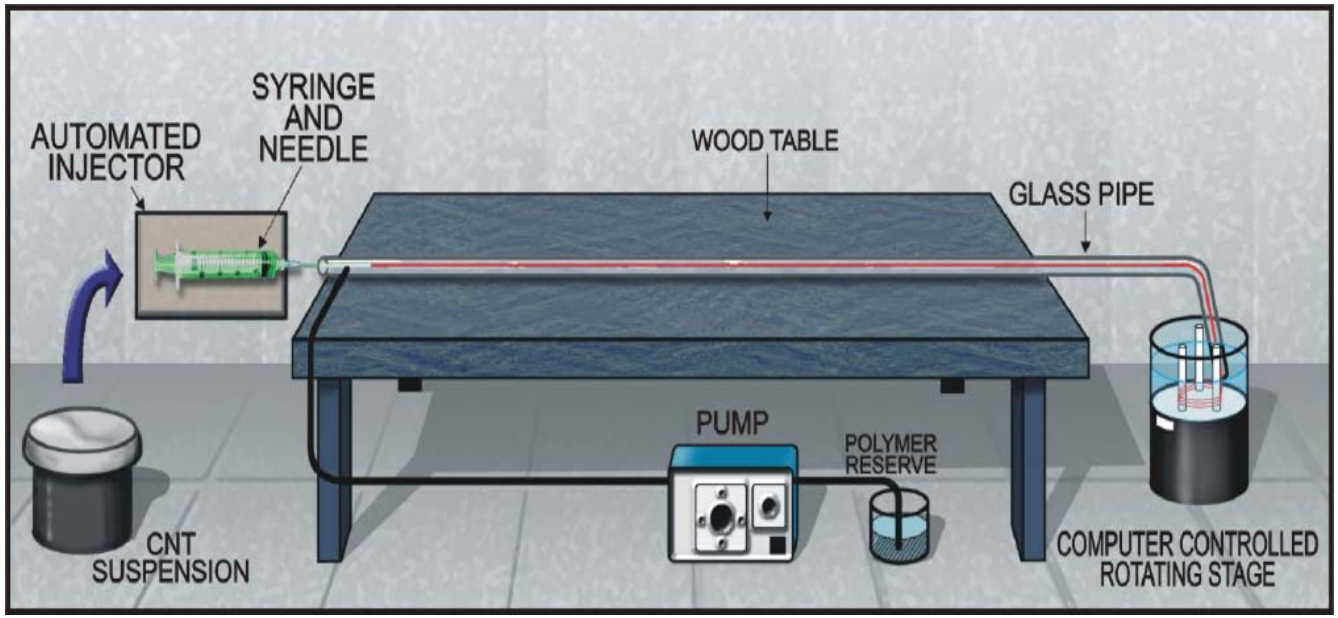
Spider silk properties evolved over 400 Million years to catch missiles (flying insects).

The energy absorption capability (energy-to-break) is called toughness.

By weight, spider silk is five times tougher that steel wire, leading to century-old commercialization attempts.

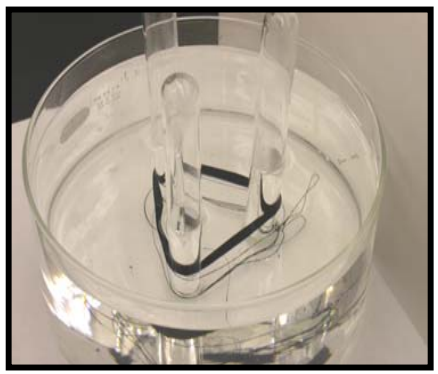
We can spin continuous nanotube composite fibers that are tougher than any known material – five times that of spider silk.

UTD Continuous Flow Spinning Process

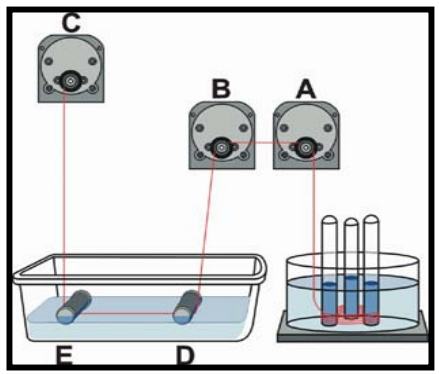


NT Spinning Solution

NT Gel Fiber

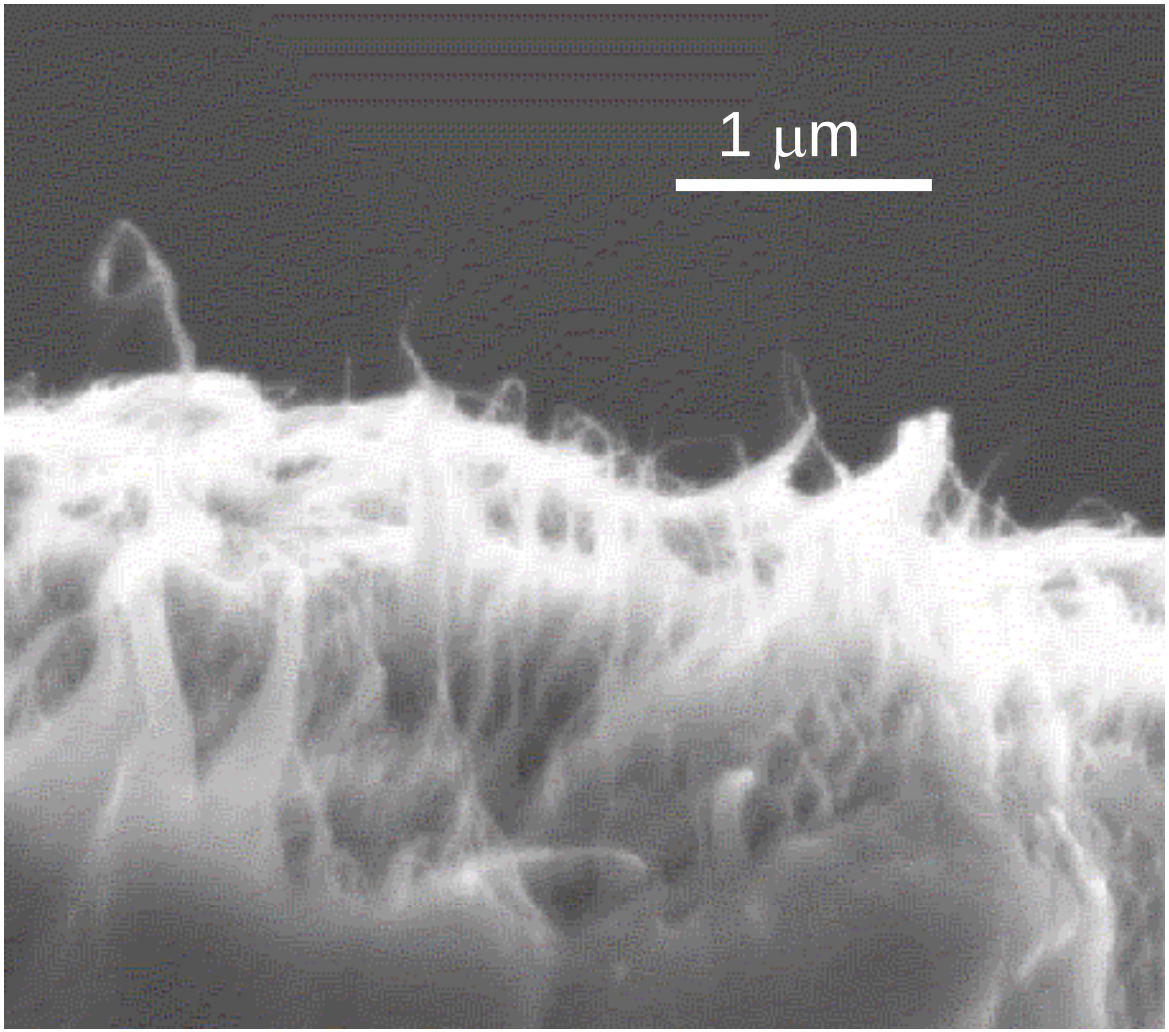


Gel fiber to solid fiber



NT fiber

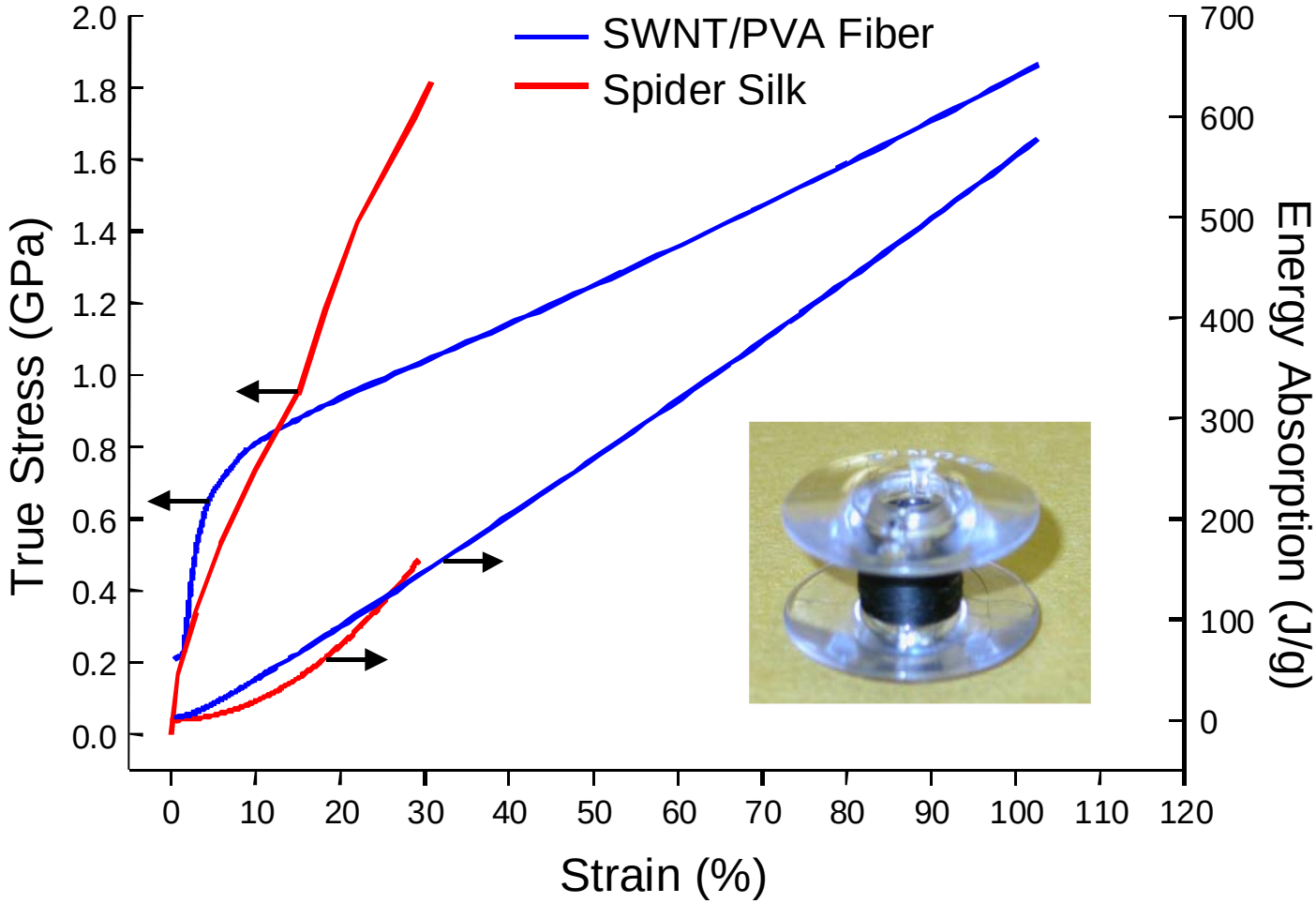
TOUGH FIBERS COMPRISE ~60% BY WEIGHT HiPco NANOTUBES AND ~40% POLYVINYL ALCOHOL



SEM micrograph showing end of undrawn carbon nanotube fiber (broken in liquid N_2).

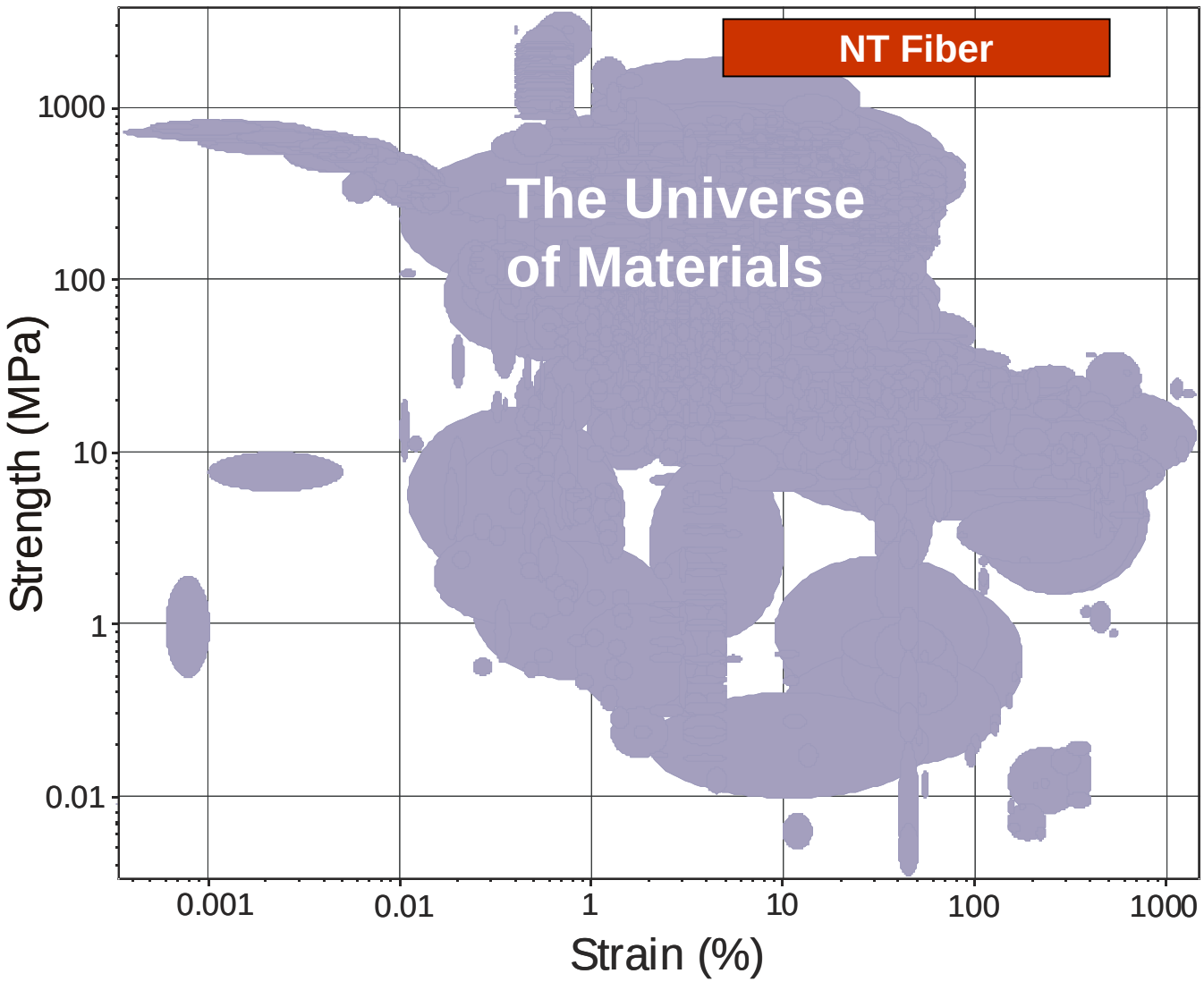
Nanotube fibers are coated with the polyvinyl alcohol matrix polymer.

OUR NANOTUBE COMPOSITE FIBERS ARE MUCH TOUGHER THAN SPIDER SILK OR ANY OTHER MATERIAL



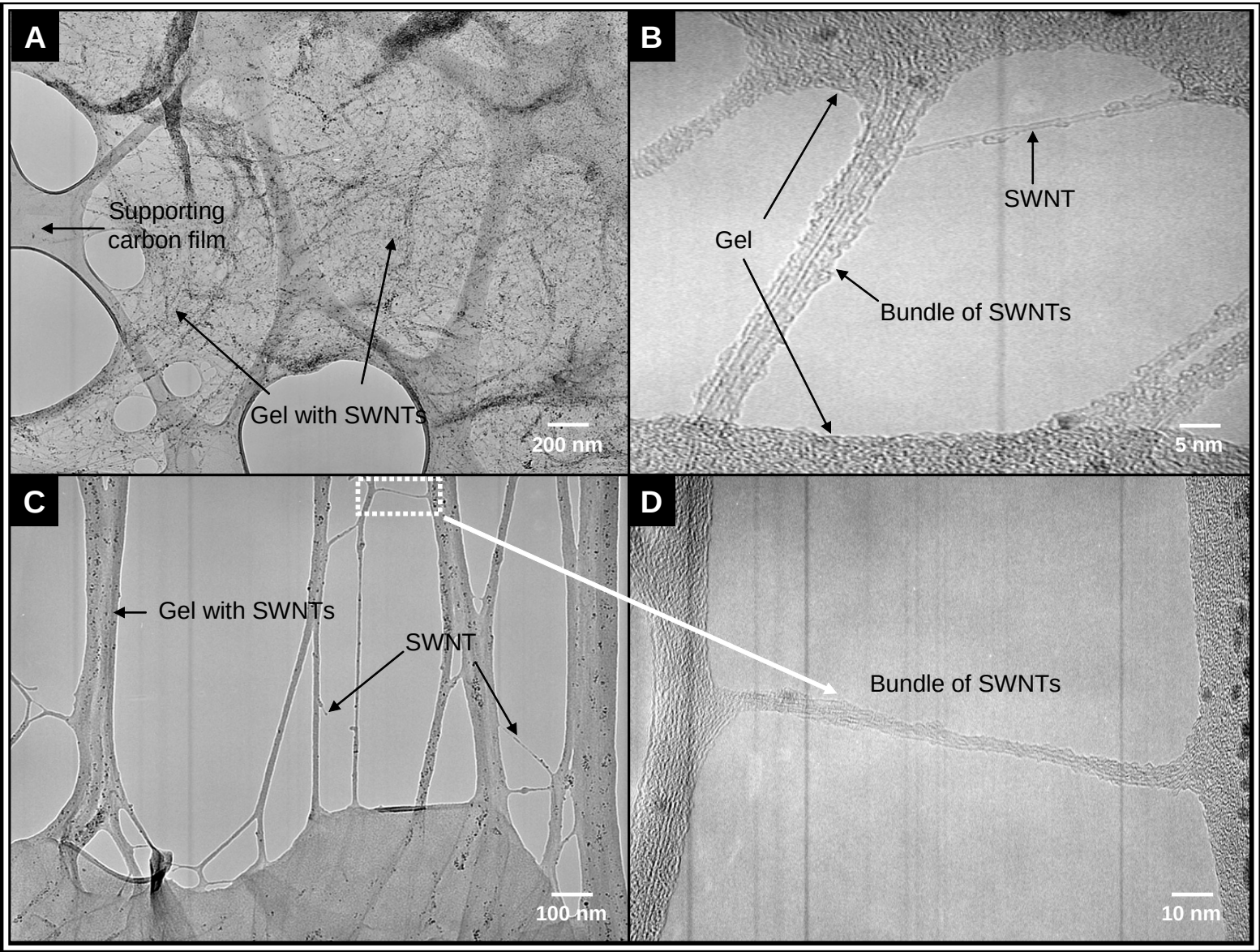
Tensile strength matches spider silk and modulus (80 GPa) is much higher than spider silk. Max obs. strength is 3.2 GPa.

Tougher Than Any Other Material

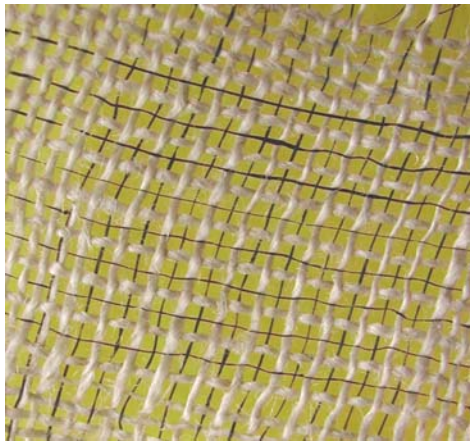


GEL NANOSTRUCTURE

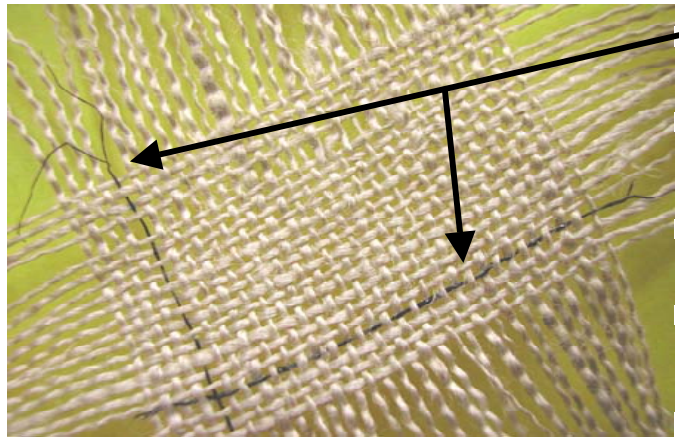
Micrographs by Yury Gogotsi's group



ELECTRONIC TEXTILES:
SUPERCAPACITORS IN FABRICS



CNT fiber woven into fabric



CNT fiber supercapacitor woven into fabric

Supercapacitor of electrolyte-separated helically-wound CNT fibers

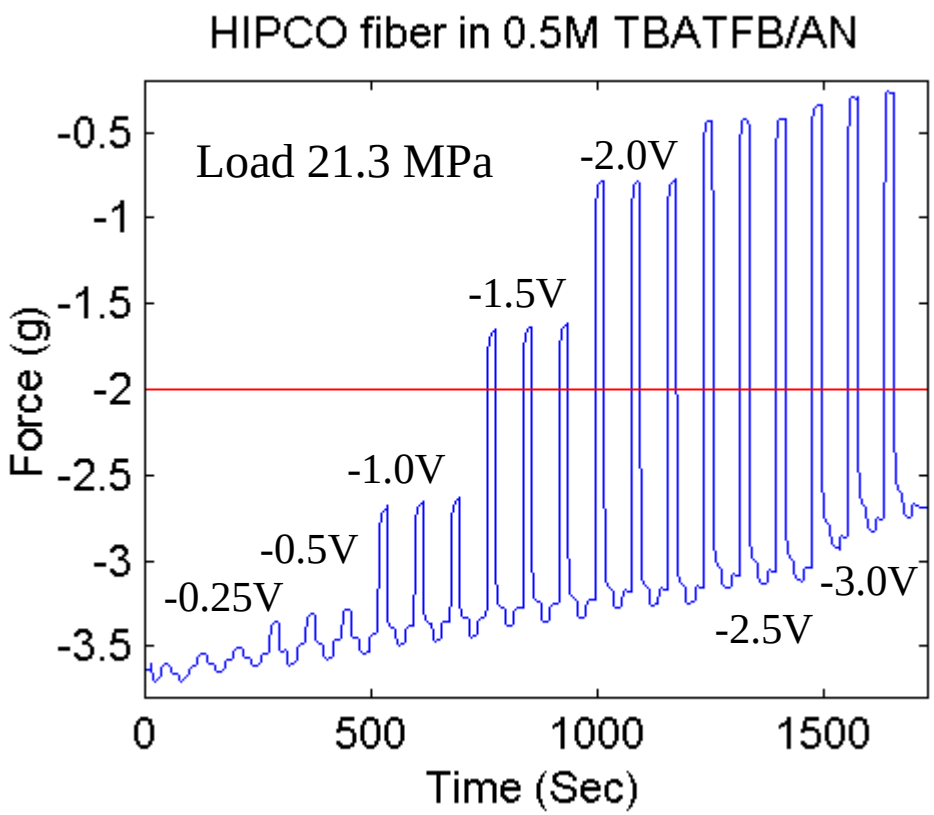
0.6 Wh/kg (1 V charge) and 1200 cycles demonstrated for supercapacitor.

Some possible additional functionalities for fabrics

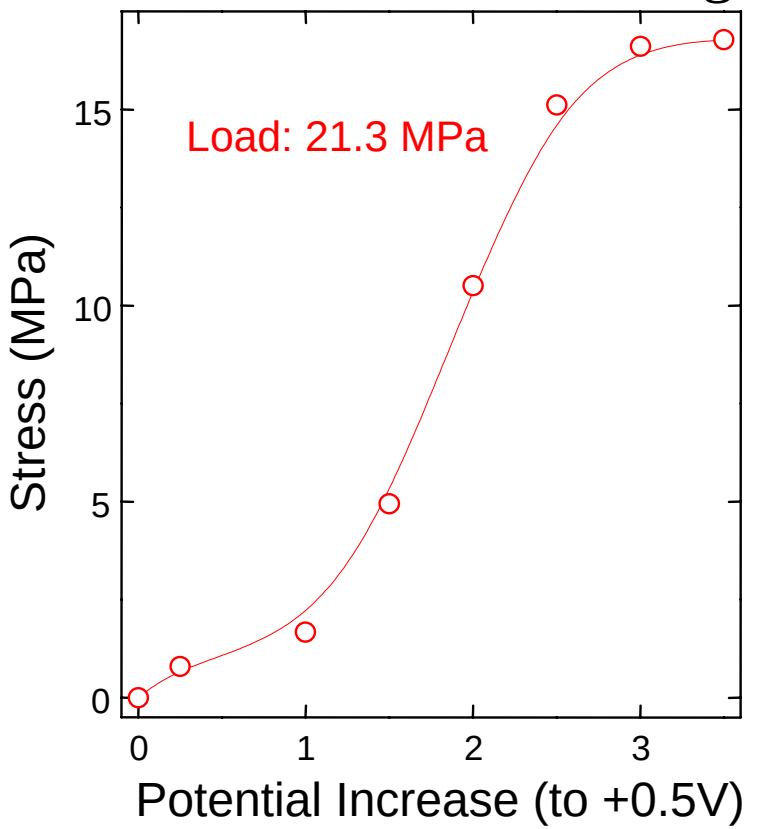
- Sensing (chemical and mechanical stress)
- Woven electronic interconnects
- Textile actuation (including porosity control)
- Thermal conductivity
- Camouflage and electromagnetic shielding

Actuation of HiPco Fiber (45mm diameter) in Organic Electrolyte:

Force vs. Potential (Ag/Ag^+)



Stress vs. Potential Change



Maximum Stress Generated is 26 MPa, about 100 times that of natural muscle.

OUR NANOTUBE ACTUATORS ALREADY GENERATE 100 TIMES THE FORCE OF NATURAL MUSCLE.

(3 times the max. stress of natural muscle in 6 msec)

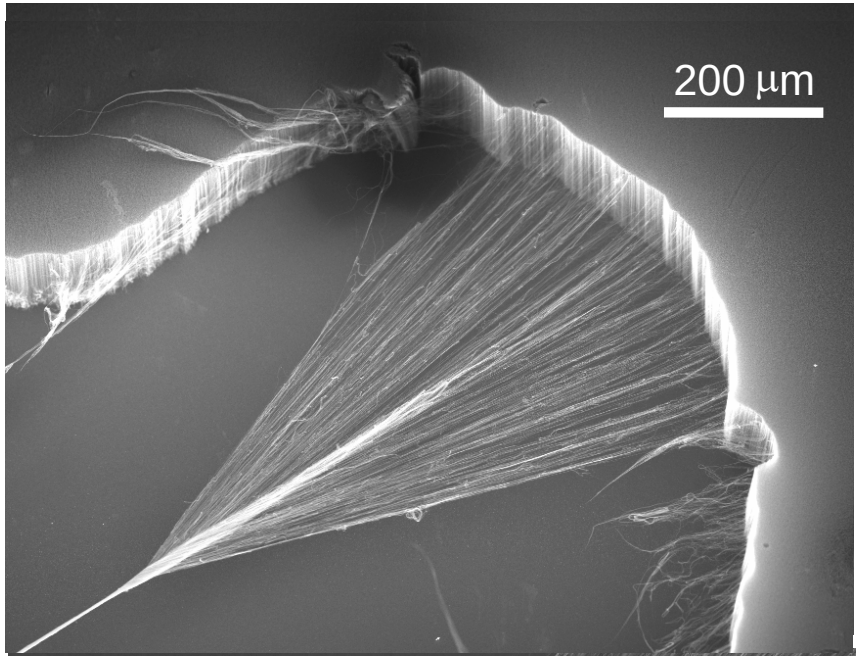
STRAIN RATE (20%/s) IS TWICE NATURAL MUSCLE.

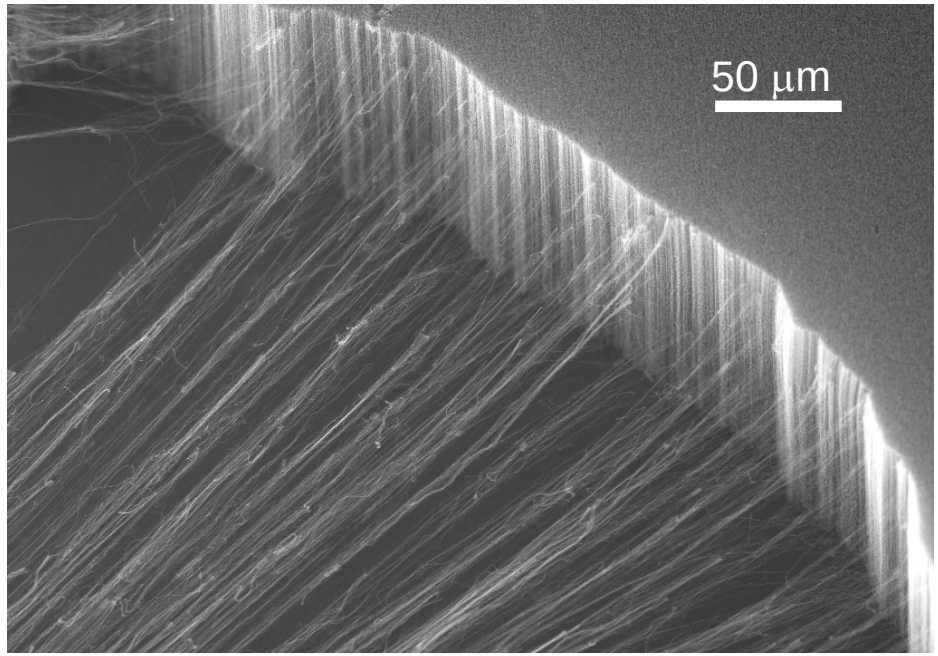
ARTIFICIAL MUSCLES: Our Twist-Drawn Nanotube Yarns Will Likely Solve Problems Found for Our Coagulation-Spun Yarns

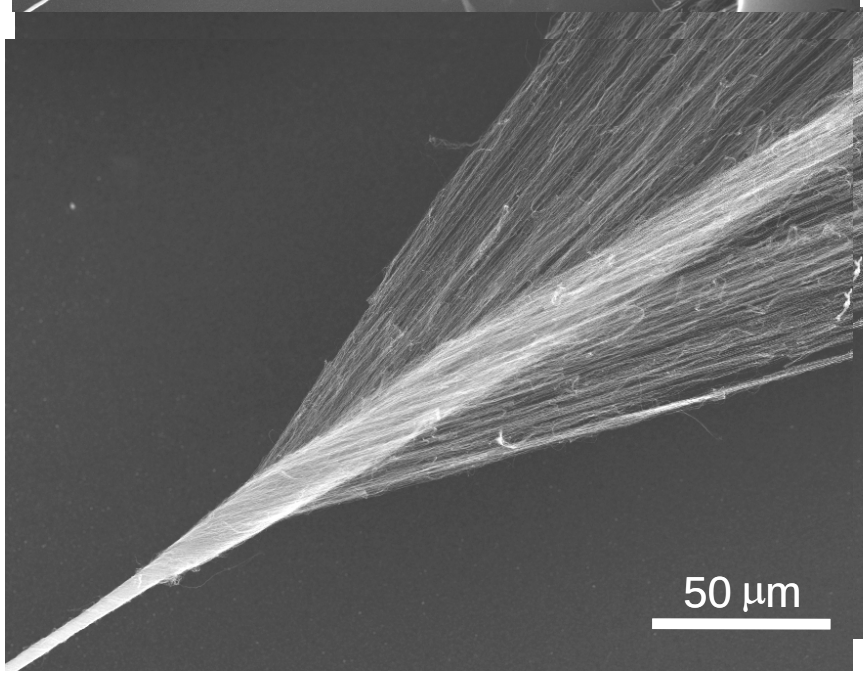
- Coagulation-spun yarns obtain strength from polymer binder. Converting this binder to high conductivity electrolyte degrades inter-fiber binding.

- We obtain impressive actuator properties by pyrolizing the polymer binder, which makes the yarns WEAKER and VERY BRITTLE.

- Twist drawn yarns are STRONGER than any other polymer-free nanotube yarns, EXTREMELY FLEXIBLE, and should provide exceptional rate performance (RC decreased by small yarn diameters, HIGH FIBER CONDUCTIVITY, and use of HIGH IONIC CONDUCTIVITY gel or liquid electrolytes).







SEM pictures of our new spinning process in which MWNTs are draw-twist spun from a forest.

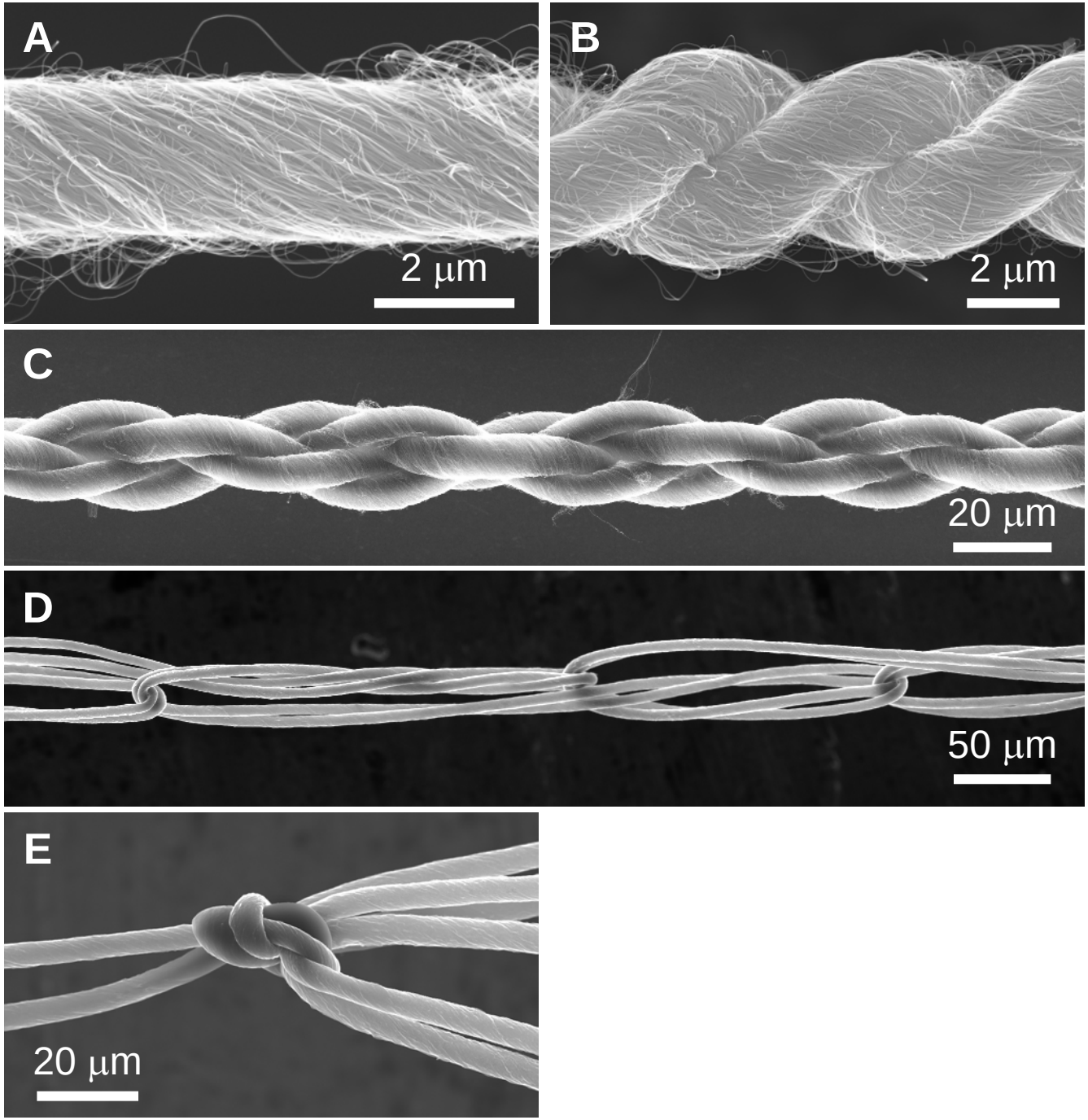
M. Zhang, K. Atkinson, R.H. Baughman, *Science* **306**, 1358-1361 (2004)

Twist increases strength > 1000X compared with earlier process.

Jiang *et al.*, Nature **419**, 801 (2002)

OUR 2nd SPINNING METHOD PROVIDES STRONG, TOUGH, PURE MWNTs!

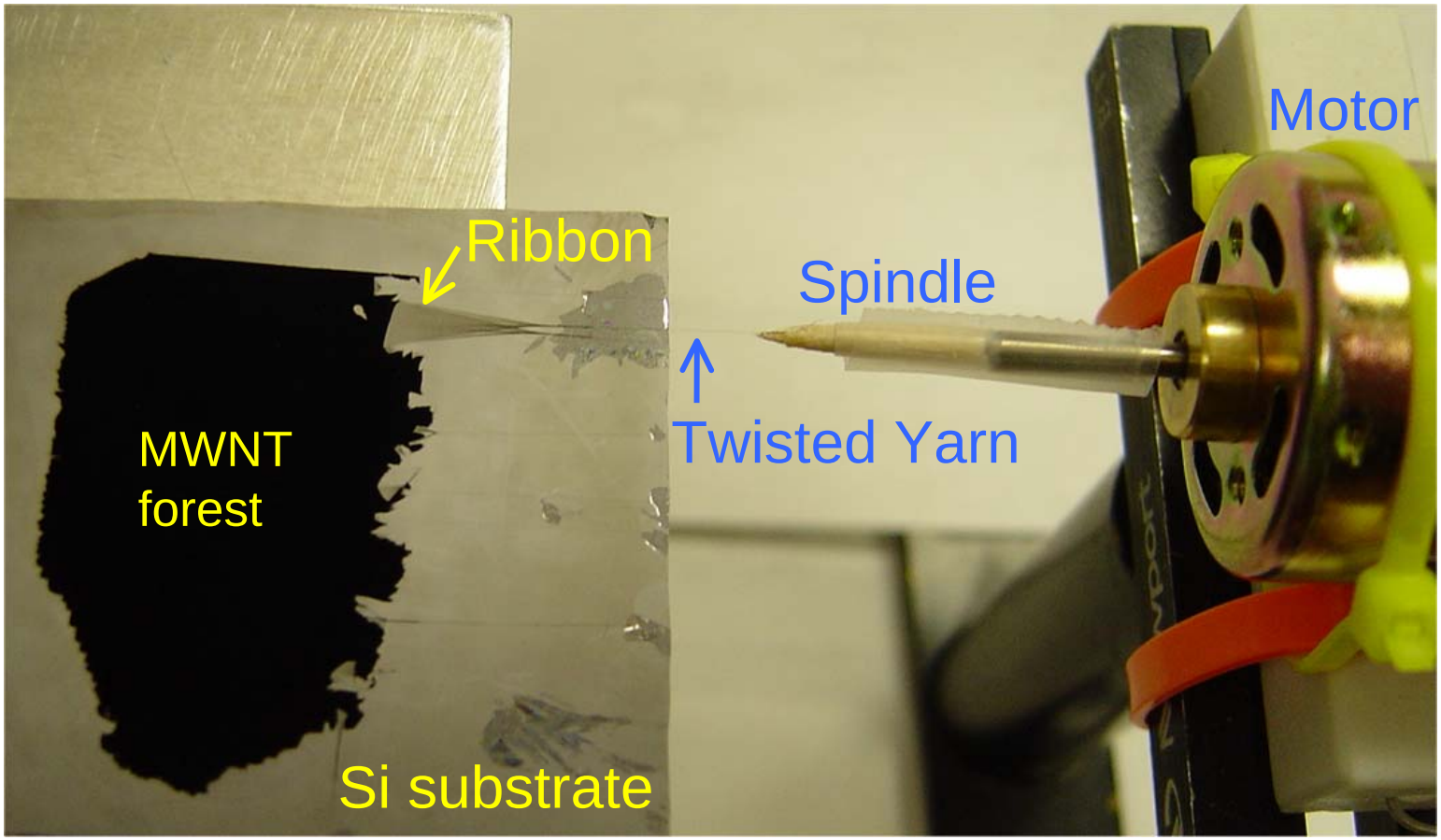
Fibers are micro denier – promising for electronic textiles!



Properties of Our Twist-Drawn MWNT Fibers

- Strength: 460 MPa (850 MPa with PVA binder).
- Modulus: up to 20 GPa.
- Toughness: 20 J/g (vs. 12 J/g for graphite and 33 J/g for Kevlar). Strain-to-failure: 13%. Reversibly absorbs up to 48% on input mechanical energy per cycle.
- Conductivity: 300 S/cm (little changed by PVA addition). Usual SWNT/PVA fiber has >150 lower conductivity.
- Unlike Kevlar and Spectra, knotting does not decrease strength. Also, abrasion resistant.
- Strength retained after heating one hour in air at 450°C.
- Poisson ratio giant (up to 4.2) $\Rightarrow$ stretch densified by $\Delta V/V = -7.4\ \varepsilon$. Linear compressibility is negative.

Twist-Based Yarn Spinning from a MWNT Forest



The yarn diameter depends on the width of the ribbon, the amount of twist, and the height of the forest.

Some Important Issues

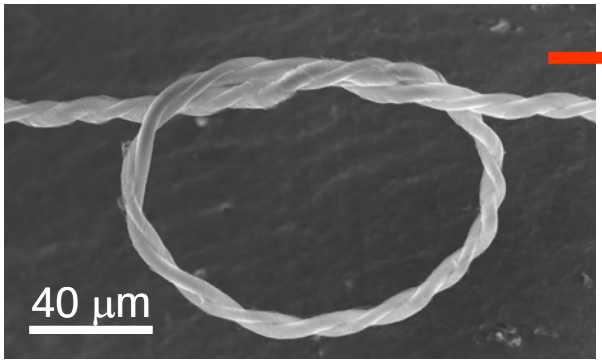
- About 100,000 MWNTs (10 nm diameter) pass through the cross-section of a 5 μm diameter yarn (~100,000 X higher areal density that usual yarns).

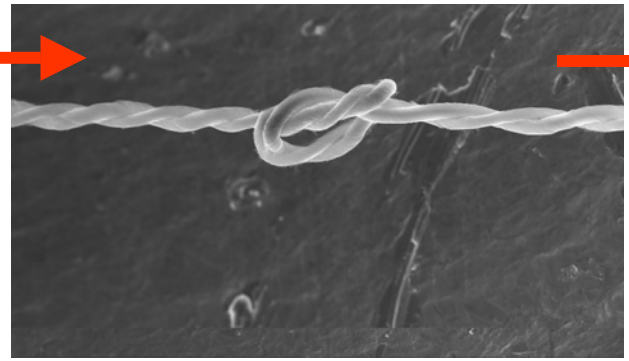
- MWNT aspect ratio is > 10,000 (meandering in forest provides lateral connectivity for spinning).

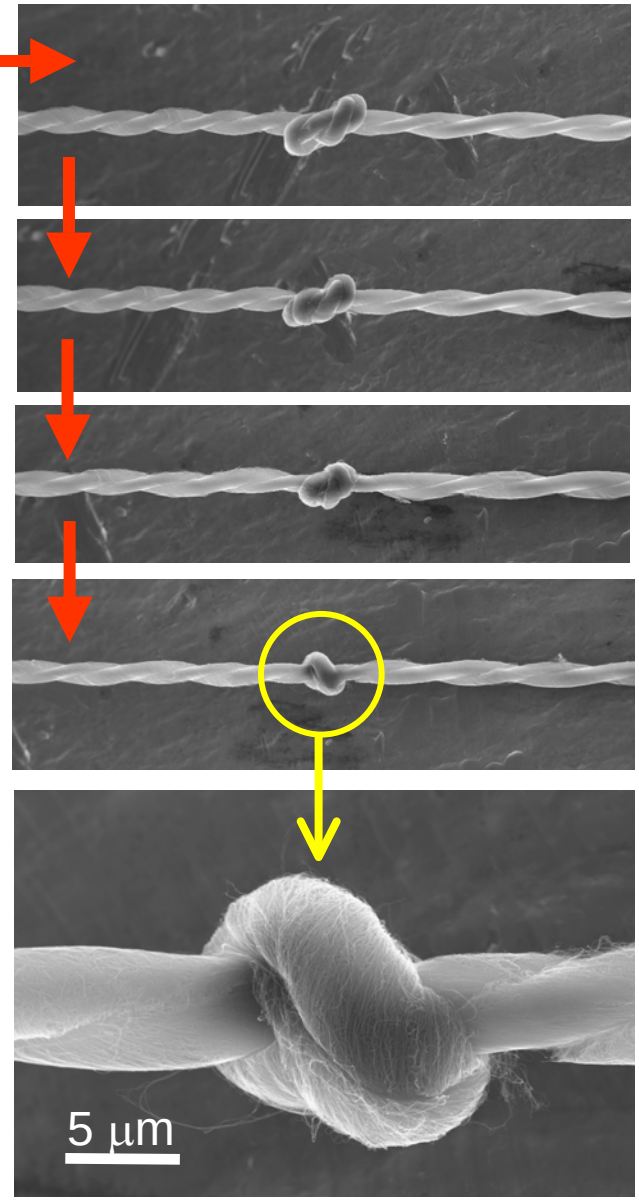
- Since the MWNT length is ~300 μm, we spin 1-10 μm diameter yarns.

- Twist needed to provide helix angle α in yarn of diameter D is tan $\alpha/\pi D$, so we insert giant twist (~80,000 turns/m vs. usual 1,000 turns/m for 80 times smaller yarns).

Tying Knots in MWNT Yarn and Knot Effects







Amazingly, the yarns do not break at knots – even the above overhand knot!

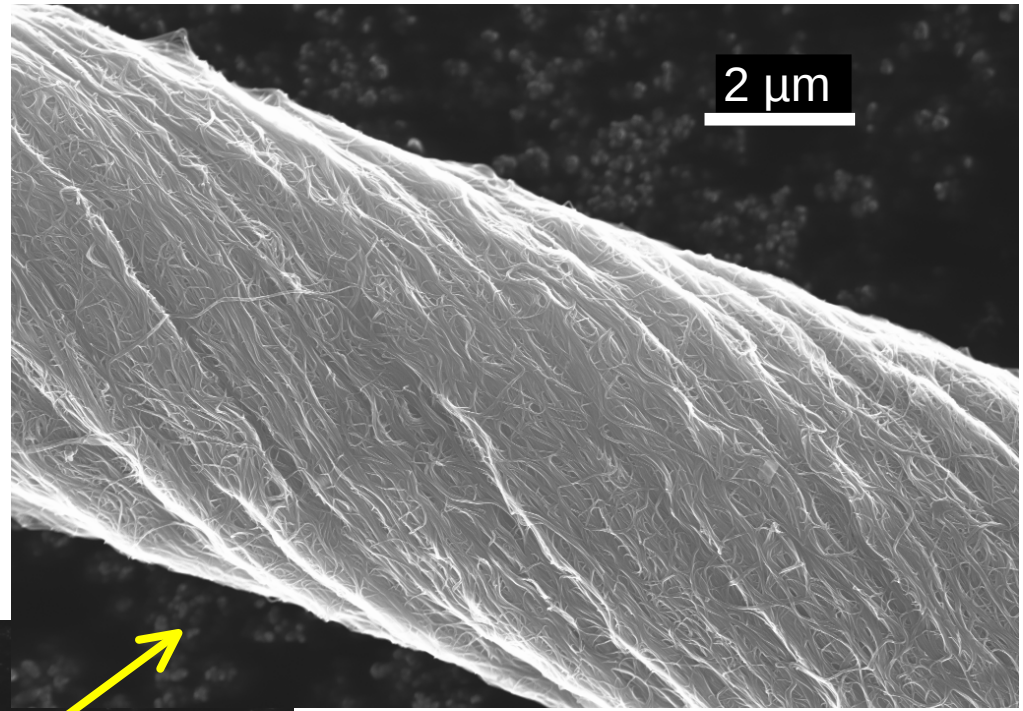
Kevlar, Spectra, DNA, and conventional yarns have greatly reduced strength when similarly knotted.

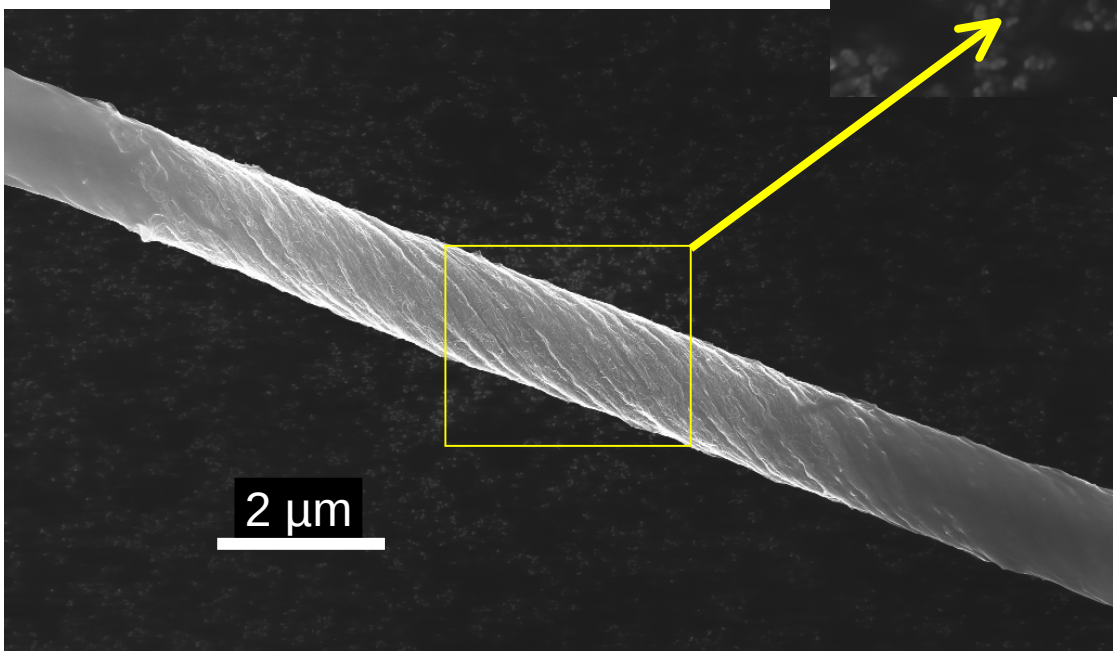
Likely explanation: Bending strains are 2000X higher for bending a 20 μm to the same radius as a 100Å nanotube.

Polyvinyl Alcohol Infiltrated Twisted MWNT Yarn

Mechanical strength of singles yarn increases to 850 MPa upon PVA infiltration.

Electrical conductivity is about 300 S/cm, >150X higher that for usual NT/polymer composites





Strain-to-failure is ~3-4%, compared with ~500% for our super tough SWNT/PVA fibers (σ ~0.1 – 2 S/cm).

Likely Reason: Inter-tube interconnects broken by Poisson ratio incompatibly.

The Toughness of the Twist-Drawn Nanotubes Yarn is Important

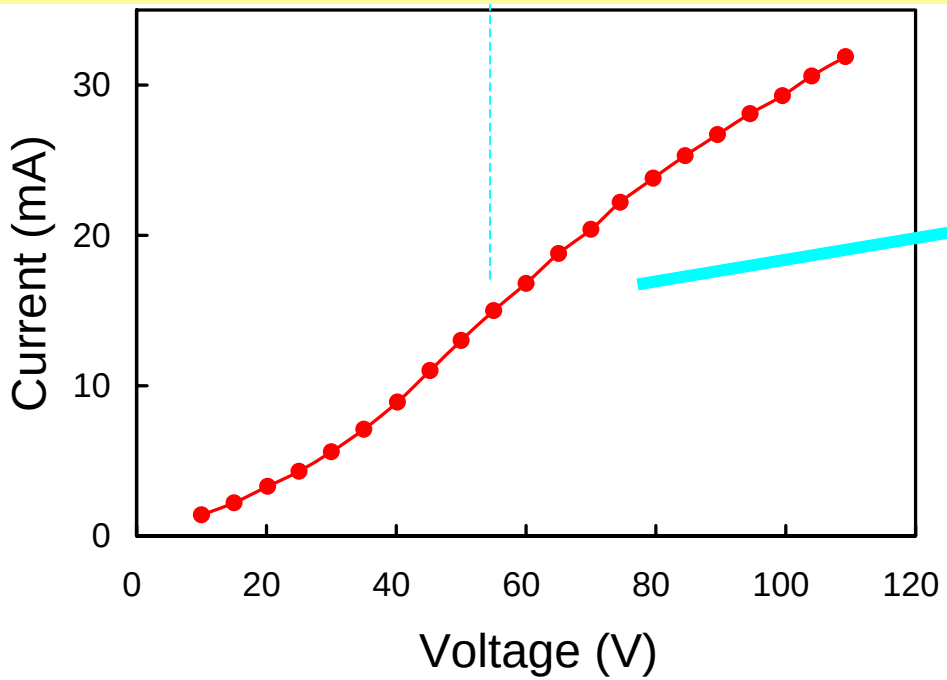
- Our present unoptimized yarns have a slightly lower toughness than Kevlar at room temperature (~20 J/g vs. ~33 J/g).

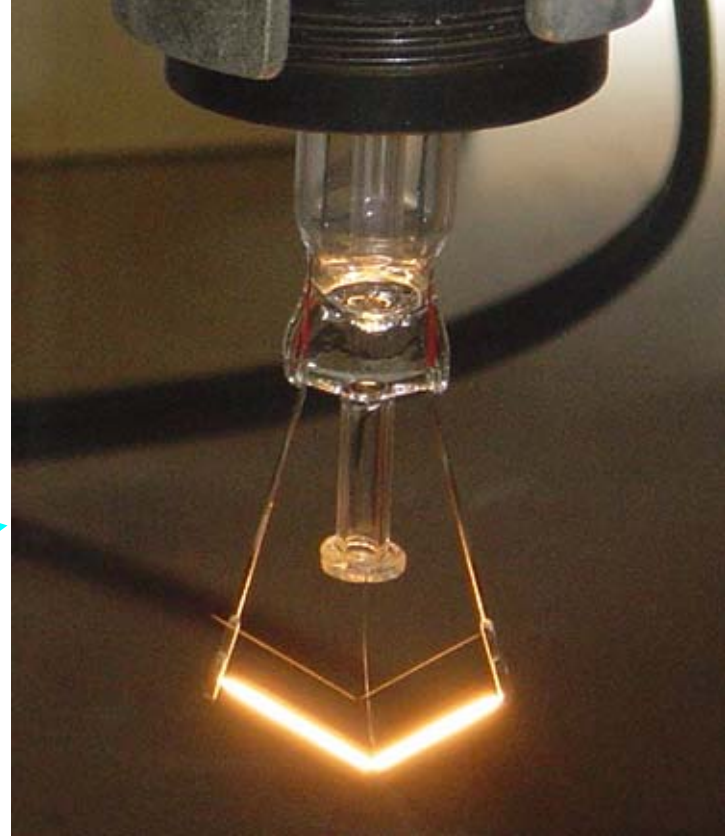
- However, Kevlar presumably loses toughness at either low or high temperatures.

- The toughness of carbon fibers (~12 J/g) is lower than for our MWNT yarns, and elastic – so released elastic energy helps further fragment the structure.

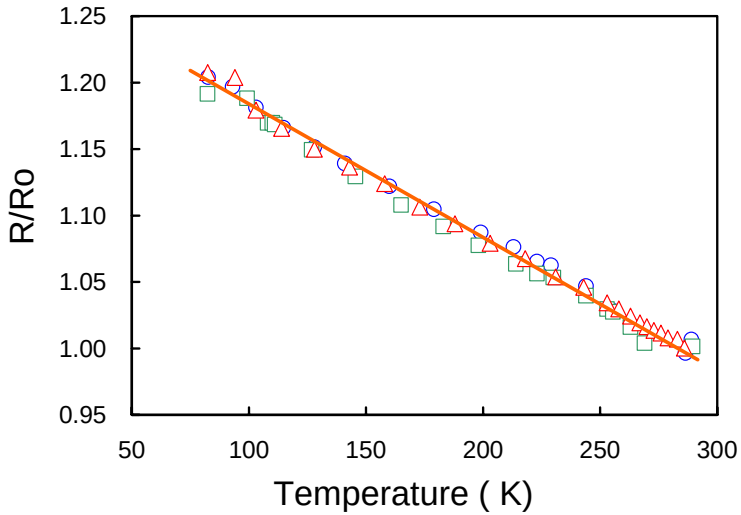
- While our coagulation-spun SWNT yarns have 10X the toughness of Kevlar and our MWNT yarns, the electrical conductivities are 150 X lower and polymer pyrolysis limits high temperature application.

Toughness might yield incandescent lights that survive mechanical abuse.





A yarn incandescent light



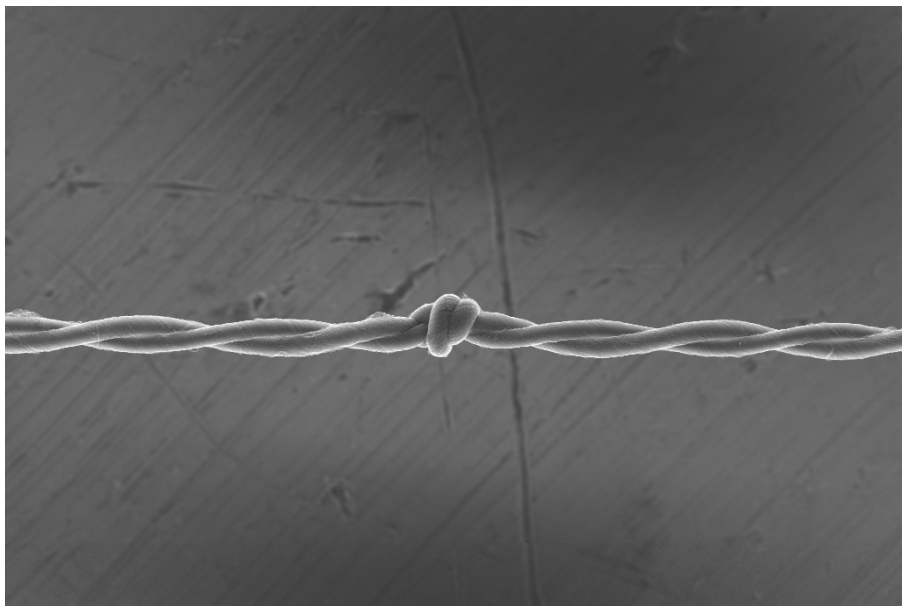
Previous filaments were neither strong or tough.

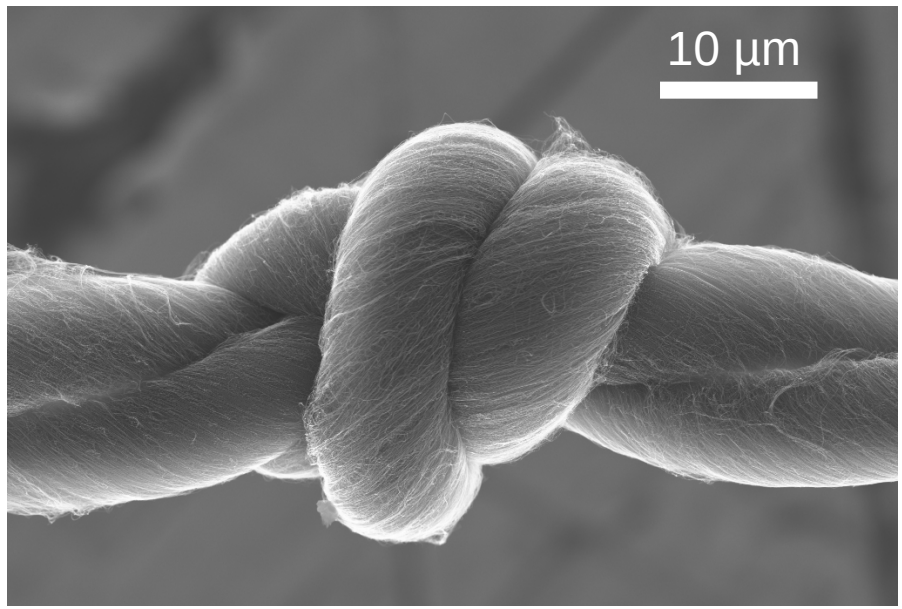
Conductivity: ~300 S/cm at RT.

Resistance decreases ~0.1% per degree K.

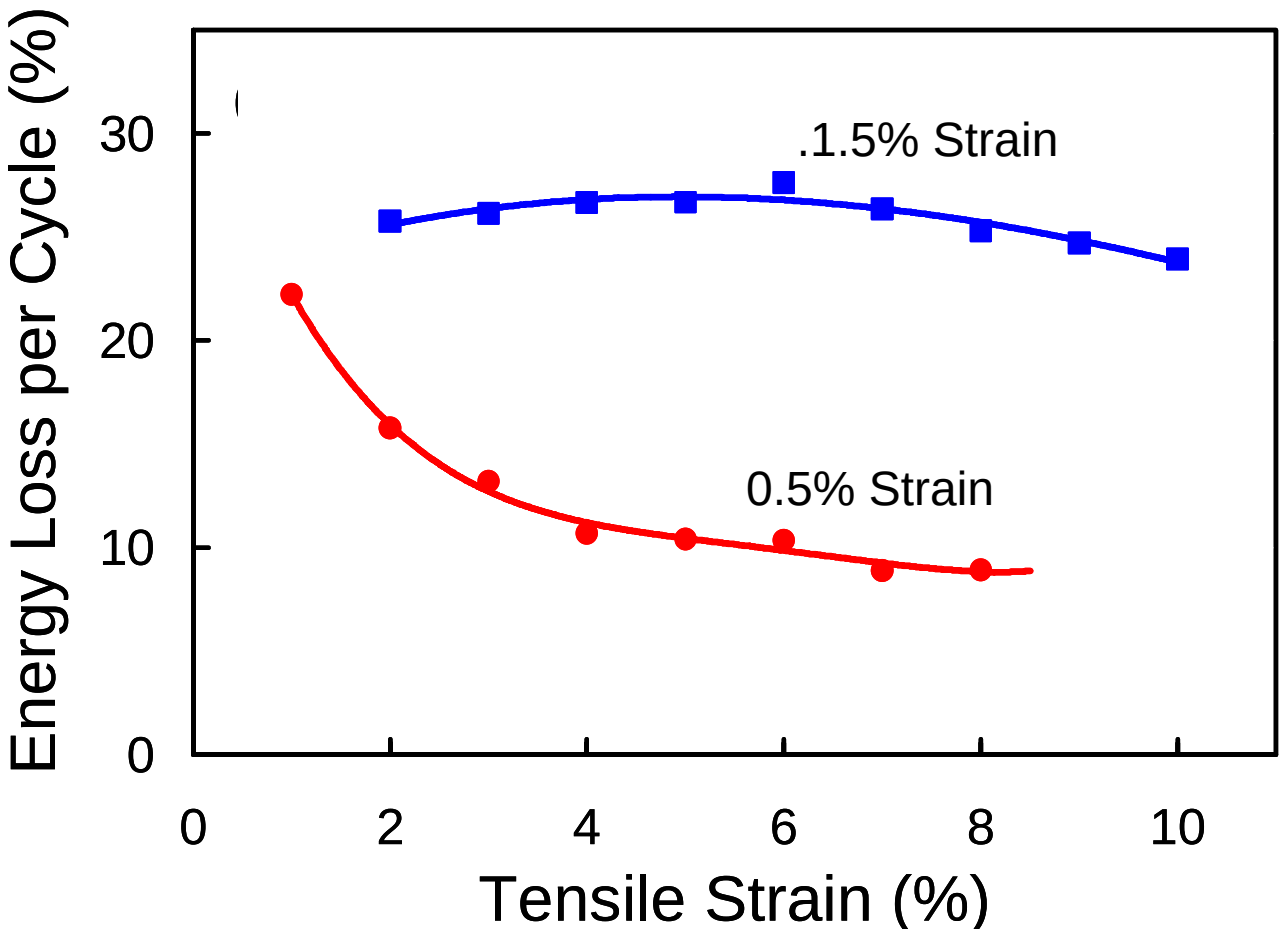
Unlike for Most Organic Polymers, No Loss of Flexibility Occurs At Low Temperatures

Knot tied in liquid nitrogen:





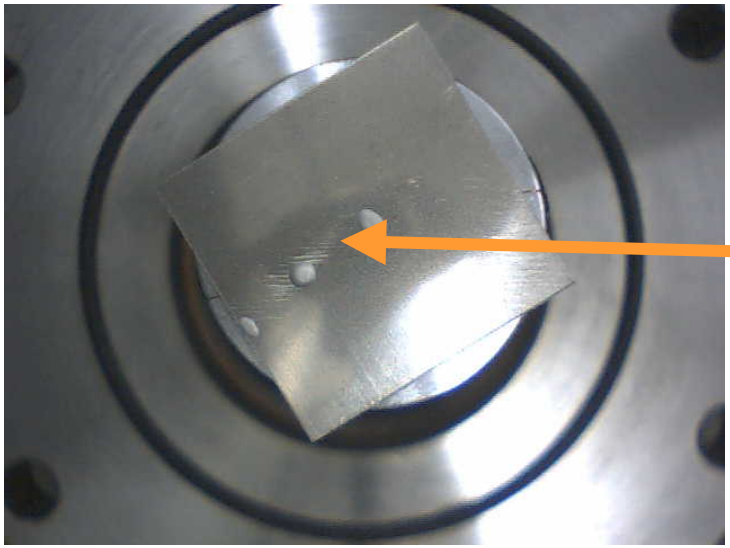
Yarns Reversibly Dissipate Mechanical Energy

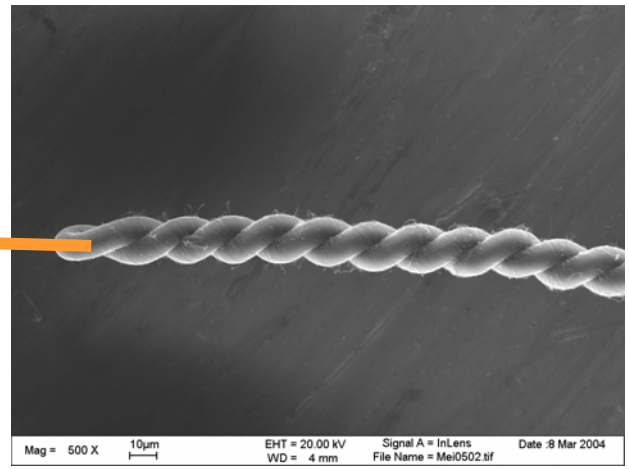


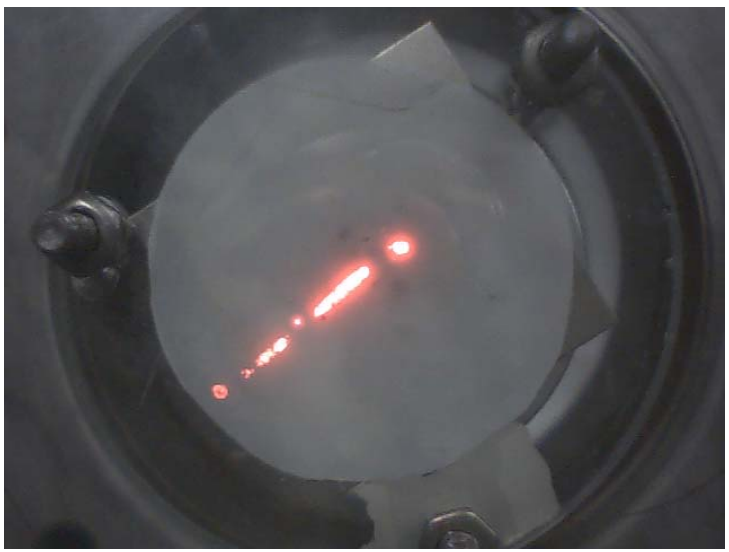
Energy dissipation per cycle increases to 39-48% per cycle for 2%-3% strain.

Enhanced Field Emission from MWNT Yarns:

Field emission light or x-ray source for catheter







On-set potential decreased by both yarn level and nanofiber level field enhancement.

Hearle's Approximate Eqn. is Useful For Understanding Twist-Induced Structural Reinforcement:

$\sigma_y/\sigma_f \approx \cos^2\alpha\ (1\text{-}k \operatorname{cosec} \alpha)$, where

$\sigma_y/\sigma_f \equiv$ ratio of yarn strength to fiber strength

$\alpha \equiv$ helix angle that fibers make with the yarn axis

$k \equiv (dQ/\mu)^{1/2}/3L$ $\quad$ $d \equiv$ fiber diameter

$\mu \equiv$ coefficient of friction $\quad$ $L \equiv$ fiber length

$Q \equiv$ fiber migration length (yarn length over which the fiber migrates from surface to deep interior and back again)

The $(1\text{-}k \operatorname{cosec} \alpha)$ term describes the locking of fibers together by transfer of tensile stress to transverse stress.

Increasing coefficient of friction and nanofiber length and decreasing nanofiber diameter and migration length needed.

The Game to Increase Strength and Modulus is to:

Decrease k in $\sigma_y/\sigma_f \approx \cos^2\alpha\ (1\text{-}k \operatorname{cosec} \alpha)$ by:

- ↑ Friction (using phys. or chem. friction aids)
- ↑ Nanofiber Length (cm lengths reported)
- ↓ Fiber Diameter (? SWNTs or MWNTs)
- ↓ Fiber Migration Length (↓ yarn diameter)

Present 460 MPa strength (850 MPa with PVA binder) for 300 μm MWNTs is encouraging, especially when combined with high toughness, knot and creep resistance, and high thermal stability (450° C for one hour in air).