Tough Materials: Shear Bands & Crazes

Polycarbonate

Images removed due to copyright restrictions.

Please see, for example,
http://www.doitpoms.ac.uk/miclib/micrograph.php?id=559

http://www.doitpoms.ac.uk/miclib/micrograph.php?id=592

Applied stress is vertical:
horizontal ***Crazes*** and 45 deg
Shear Bands

Fatigue crack propagation in polycarbonate

Craze and crack moving to the right,

Generating shear bands at the craze tip

The Future -SWCNTs:

the ultimate polymer ?

Space Tether

$E = 1$ TPa
(expt and calc)

$\sigma_f \sim 50$ GPa
(calc)

Values for individual tubes

Image removed due to copyright restriction.

Please see the cover of *American Scientist*, July/August 1997.

SWNTs: The Perfect Material

- SWNTs are unique:
  - Polymers of pure carbon
  - High aspect ratio (>1000:1)
  - Unique electron configuration
- SWNTs have extraordinary properties
  - Strength (~100x steel)
  - Electrical conductivity (~Copper)
  - Thermal conductivity (~3x Diamond)
  - Accessible surface area (theoretical limit)
  - Thermal stability (~500 °C air, ~1400 °C anaerobic)
- SWNTs can be customized via organic chemistry
  - Modification of properties
  - Compatibilization with other materials

A new backbone polymer

The most inherently conductive organic molecule

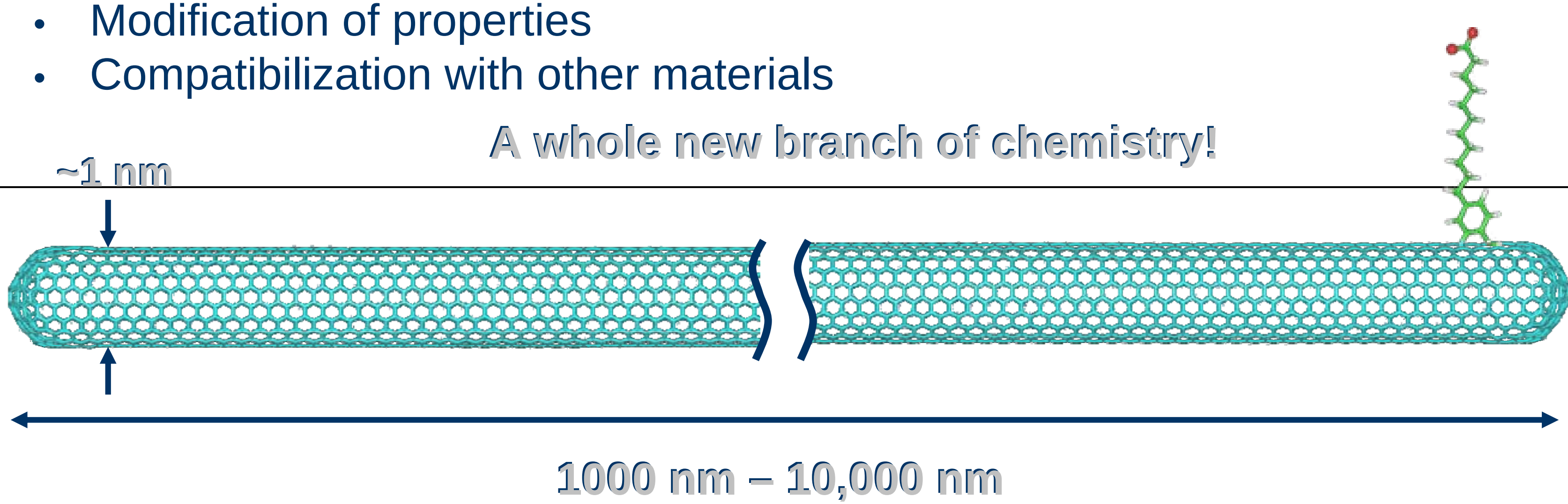
The most thermally conductive material

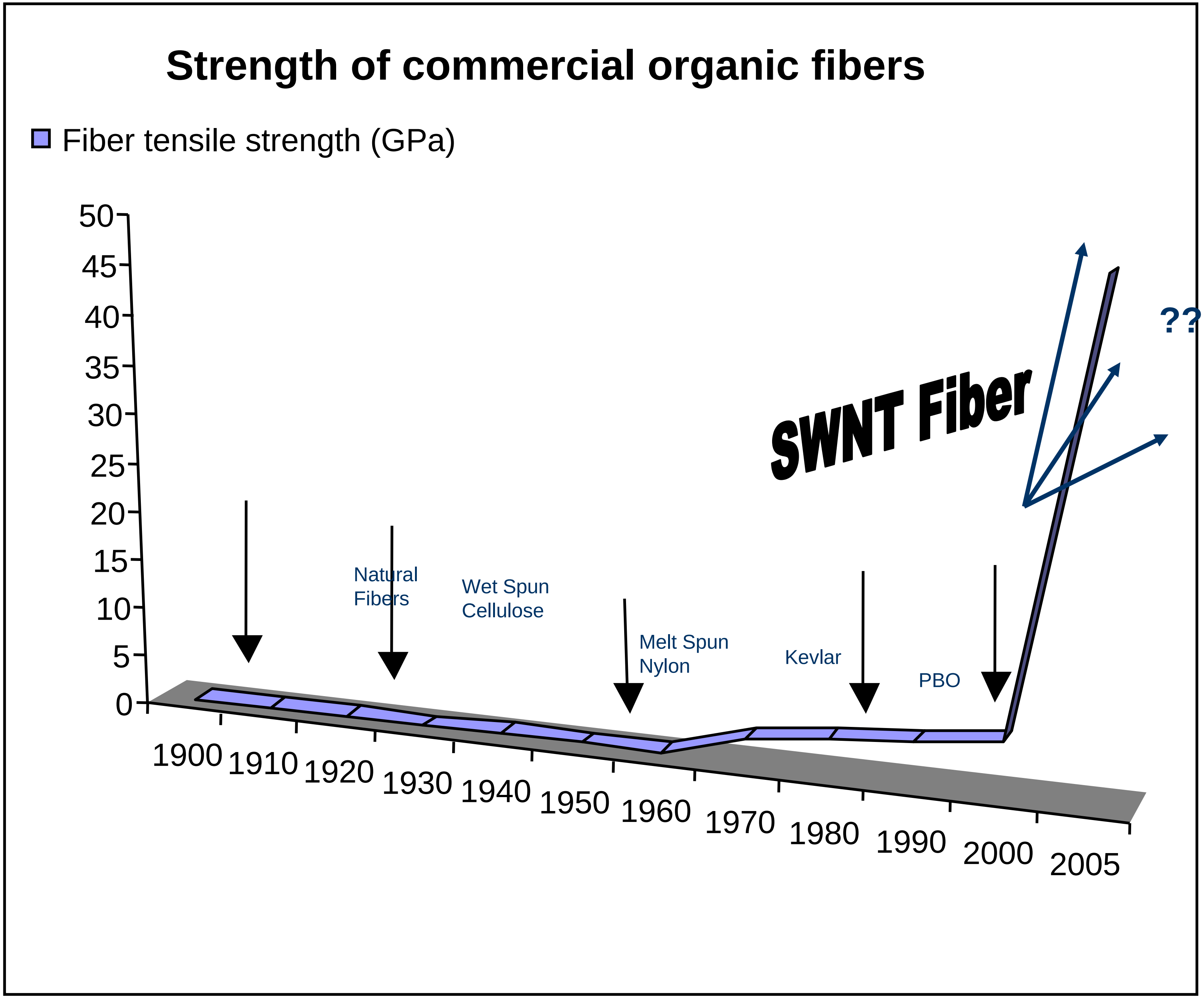
The strongest, stiffest, toughest molecule there will ever be

The best field emitter

The ultimate engineering polymer

A whole new branch of chemistry!





Adapted from NRC Report NMAB-458, April 1992.

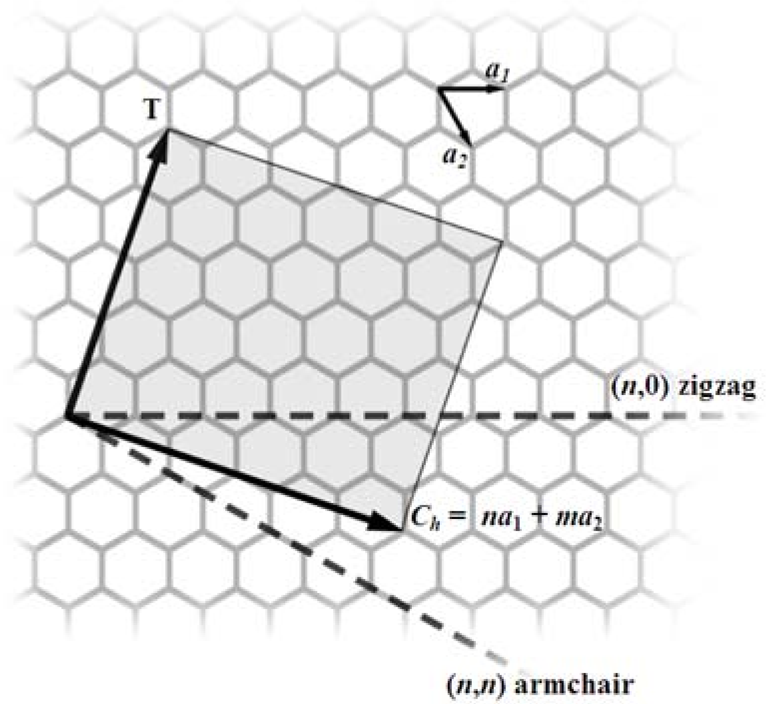
TYPES OF NANOTUBES

Carbon nanotubes are basically sheets of graphite rolled up into a tube. Hence, the hexagonal two dimensional lattice of graphite is mapped on a one-dimensional cylinder of radius R with various helicities characterized by the **rolling vectors (n,m).**

(n,0) zigzag nanotube

(n,n) armchair nanotube

(n,m) chiral nanotube



Fibres or Molecules?

	Diameter (nm)
Conventional Carbon Fibres	~10,000
Carbon Nanotubes (Multi-walled)	~10
Carbon Nanotubes (Single-walled)	~1
Polymethylmethacrylate (PMMA)	~0.7

Aspect ratio L/D: C60 ~ 1; SWNT ~ 1000; MWNT ~ 2000

Credit:

A. Windle, Cambridge University - about the next 15 slides

Electrical Conductivity of Carbon

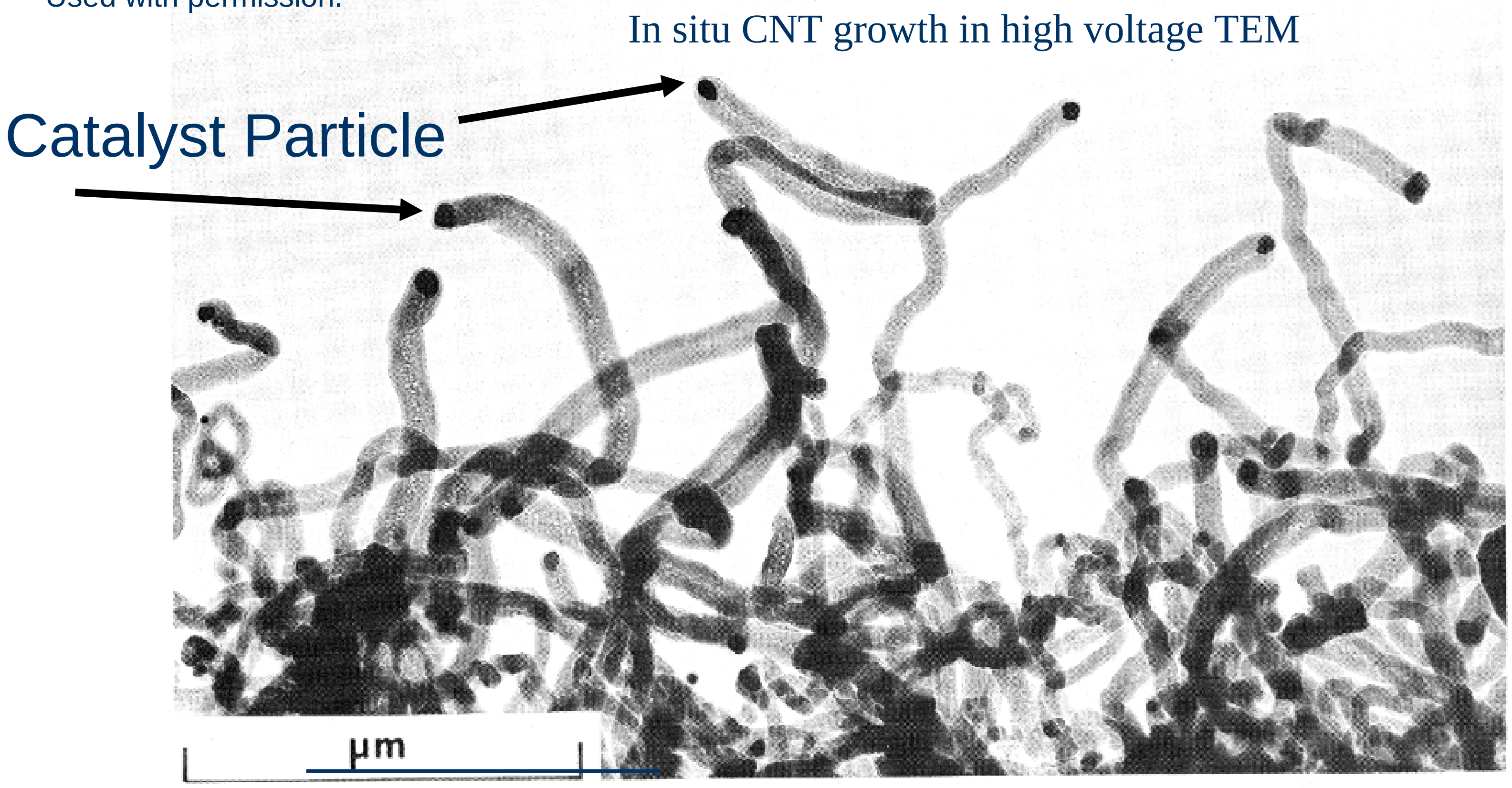
- CNT Fibre: $2.9 - 8.3 \times 10^5\ \Omega^{-1}m^{-1}$

- Conventional Carbon fibre: $\sim 1 \times 10^5\ \Omega^{-1}m^{-1}$

- Commercial graphite: $0.3 – 2 \times 10^5\ \Omega^{-1}m^{-1}$
- Copper: $6.0 \times 10^7\ \Omega^{-1}m^{-1}$

Source: Intro. To Mat. Sci. and Eng, W.D. Callister

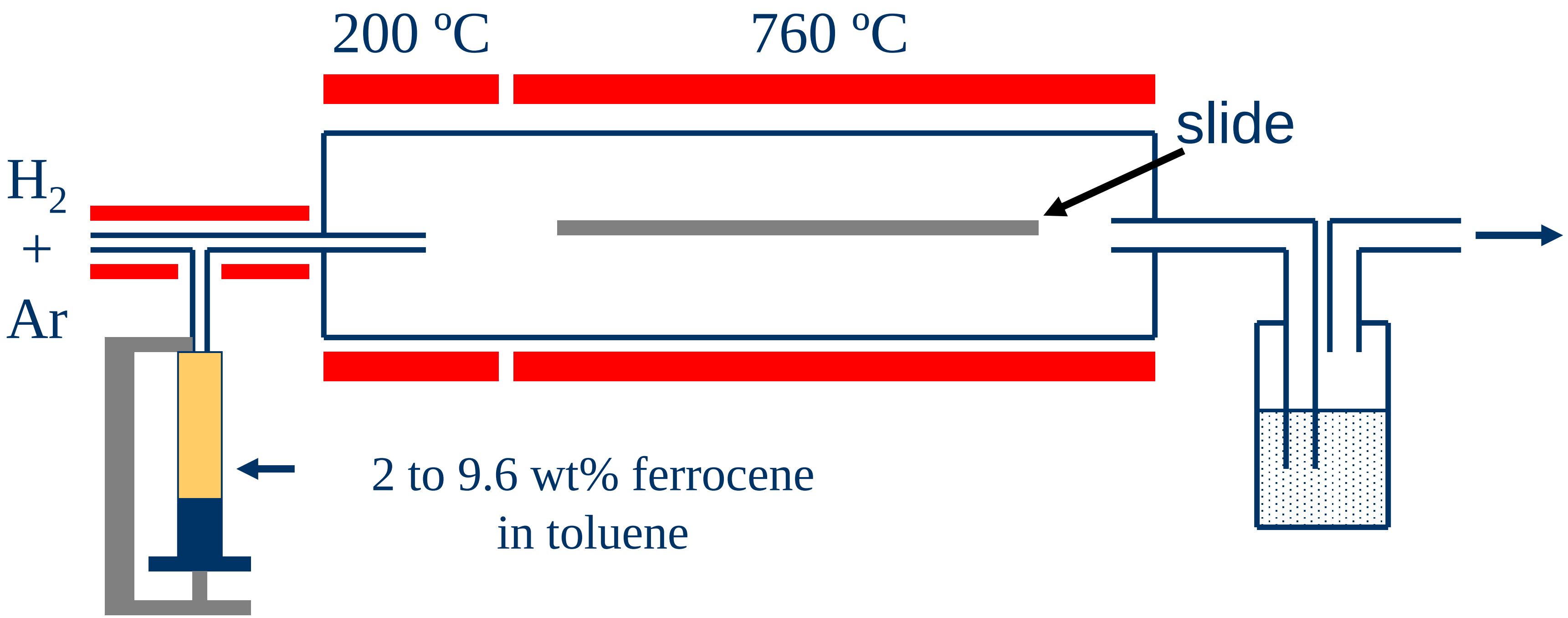
Carbon Nanotubes
long before the 'nano' word



T. Baird, J R Fryer and B Grant, *Carbon* 12, 591 (1974)

n.b. Endo (1976) C_{60} (1985) Iijima (1991)

Synthesis of MWCNT "carpets"



- Quartz reaction tube and substrates
- 14 mm and 65 mm diameter reactors
- Quartz slide inserted to collect carpet
- Reaction time 0 to 10 hrs: Longer experiment → longer carpet

Catalyst on substrate: MWCNT Carpet

Images removed due to copyright restrictions.

Please see Fig. 2 in Chen, S. Y., et al. "Fabrication and field emission property studies of multiwall carbon nanotubes." Journal of Physics D: Applied Physics 37 (2004): 273-279.

Multi-walled nanotubes: MWCNT

Large Hollow Core plus nested graphene shells

Images removed due to copyright restrictions.

Please see http://endomoribu.shinshu-u.ac.jp/research/cnt/images/mwcnt.jpg

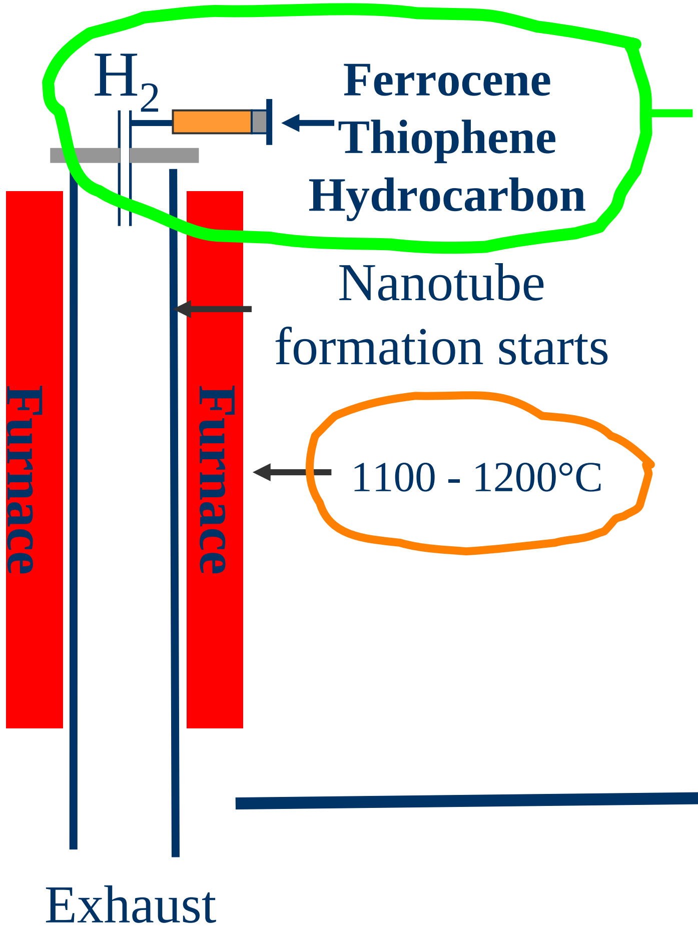
TEM: beam perpendicular to nanotube axis

TEM : beam parallel to nanotube axis (chance)

Direct CNT Fibre Process (A. Windle)

- Continuous process
- Wide range of organic feed stocks work
- Feedstock to product in 10cm at 1200°C
- Both MWNT's and SWNTs
- Never have to handle nanotube powder, therefore reduced health risks
- Mechanical properties, so far average but for high volume fractions of highly aligned nanotubes prospects are good
- Feedstock costing 0.1cents/gram converted continuously to CNTs currently marketing at $100/gram: mark-up of 10^5

High Temperature Continuous Film Process

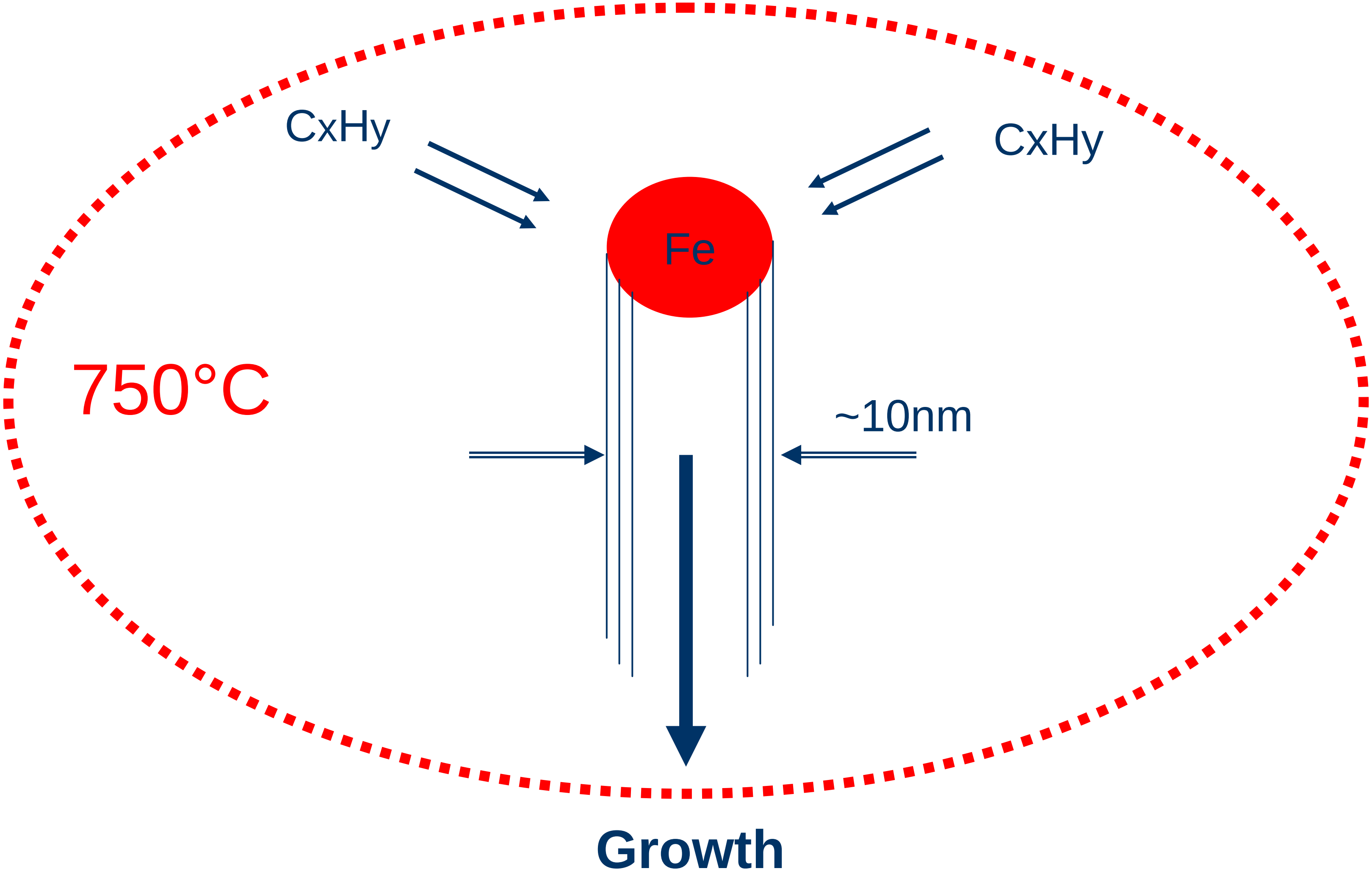


Fairly standard 1970s technology for vapour grown carbon fibres (10 μm)

Product:

@ 1100 C, clean walls, nanotubes only stick below 200°C

CVD synthesis of Carbon Nanotubes



Continuous Wind Up: Film

Feedstock

Images removed due to copyright restrictions.

Please see Fig. 1 in Li, Ya-Li, et al. "Direct Spinning of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis." *Science* 304 (April 9, 2004): 276-278.

Hydrocarbon Feedstock + Thiophene + Ferrocene
1100 to 1200 °C
H_2 carrier gas

Fibre process: Product

Images removed due to copyright restrictions.

Please see Fig. 3a in Li, Ya-Li, et al. “Direct Spinning of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis.” *Science* 304 (April 9, 2004): 276-278.

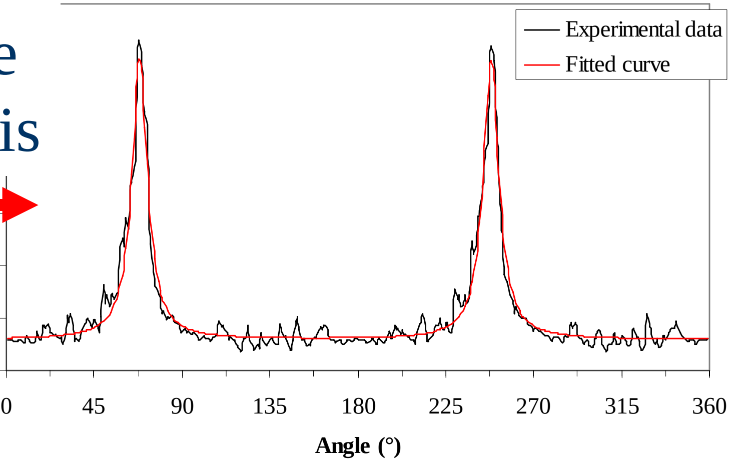
Ya-Li Li, Ian Kinloch and Alan Windle, ***Science***, **304**, p 276, 9 April 2004

Multi-wall CNTs: Variable Product Microstructure

Images removed due to copyright restrictions.

Please see Fig. 3b, c, d in Li, Ya-Li, et al. “Direct Spinning of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis.” *Science* 304 (April 9, 2004): 276-278.

Image analysis



Fibre diameter of 20 to 50 μm

Reaction conditions: Ethanol feedstock

- MWNTs
  - 2.3 wt% ferrocene
  - 1.5 % thiophene
  - H_2 flow 400 to 800 ml/min
  - Temperature 1100 to 1180 °C

- SWNTs
  - 2.3 wt% ferrocene
  - 0.5 wt% thiophene
  - 1200 ml/min H_2
  - 1200 °C

SWNTs need greater dilution of Fe by carrier gas

SWNT (and DWNTs):
~ often mixed in with some MWNTs

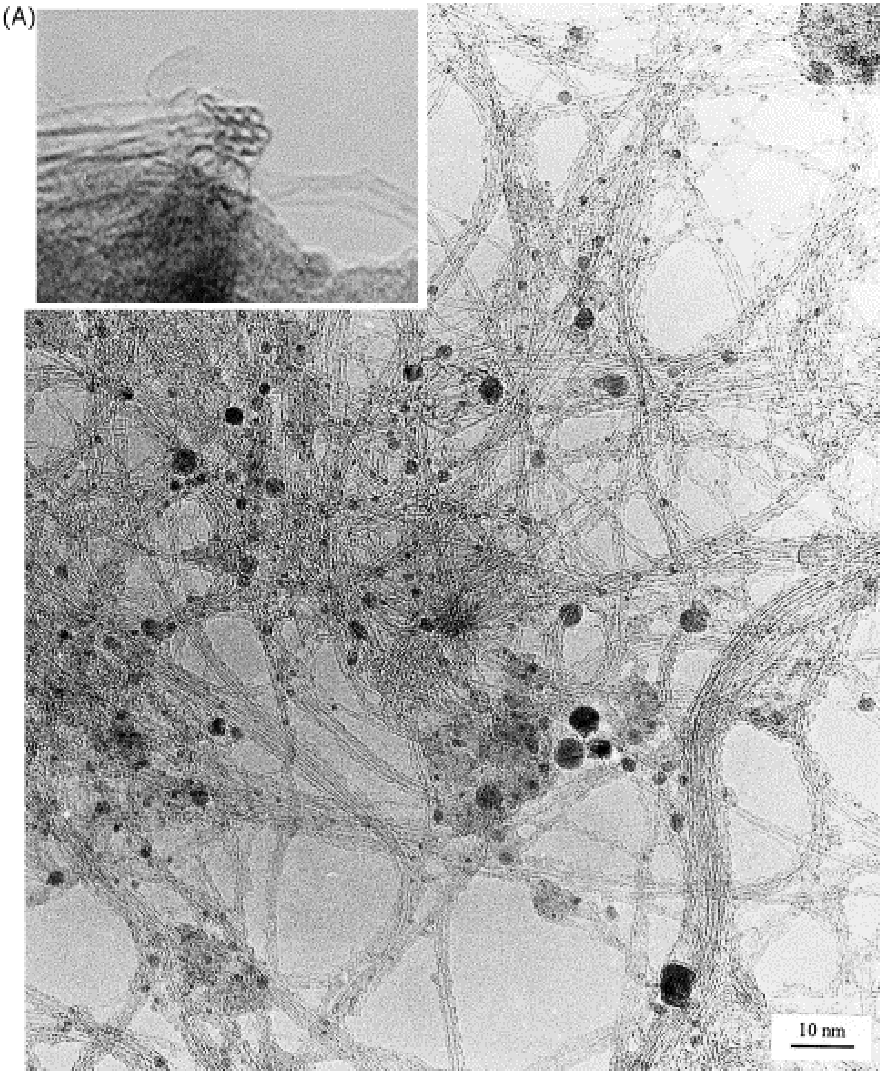
Diffraction Contrast

Catalyst Particles

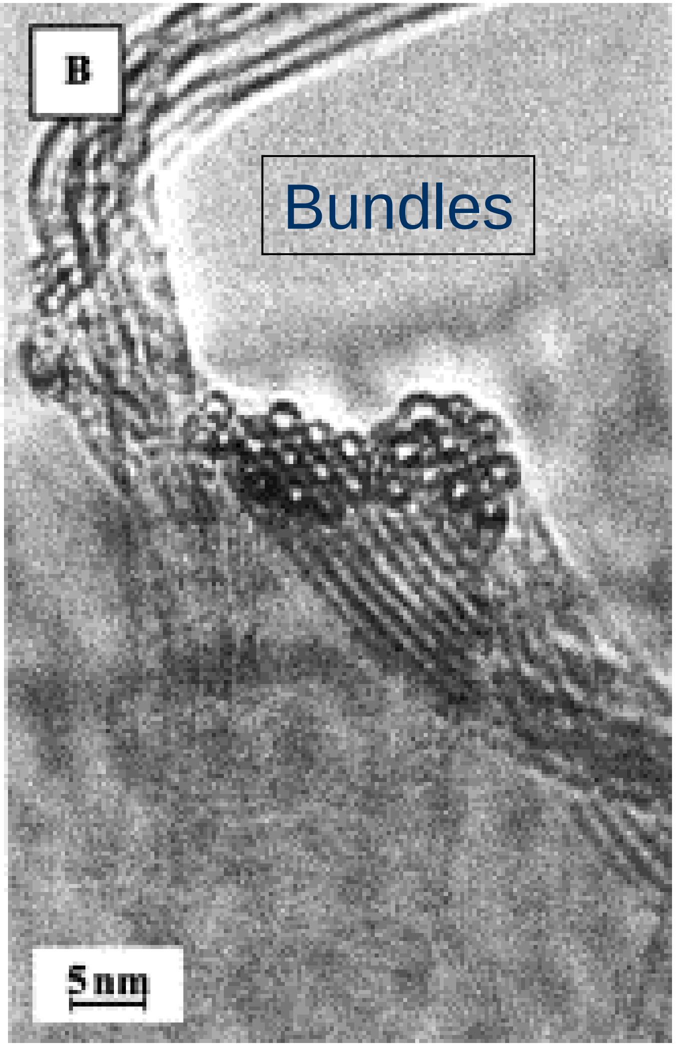
Images removed due to copyright restrictions.

Please see Fig. 2c and d in Motta, Marcelo, et al. “Mechanical Properties of Continuously Spun Fibers of Carbon Nanotubes.” *Nano Letters* 5 (August 2005): 1529-1533.

Single Wall CNT Fibres



Courtesy of Alan Windle. Used with permission.



Courtesy Elsevier, Inc., http://www.sciencedirect.com. Used with permission.

Mechanical Properties

Images removed due to copyright restrictions.

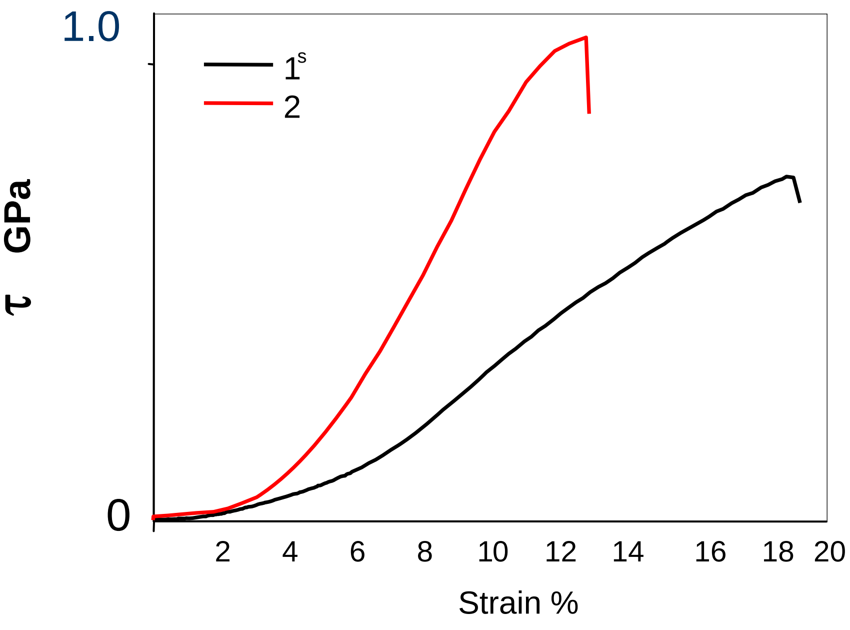
Please see Fig. 1 in Motta, Marcelo, et al. "Mechanical Properties of Continuously Spun Fibers of Carbon Nanotubes." *Nano Letters* 5 (August 2005): 1529-1533.

The range of diameters along a fibre occurs due to differences in the local packing density of nanotubes and/or instabilities in the gas-phase reaction.

100 μm

$$TEX = \frac{g}{km}$$

$$\frac{Force}{TEX} * Density = Stress$$



Direct CNT Fibre Process (A. Windle)

- Continuous process
- Wide range of organic feed stocks work
- Feedstock to product in 10cm at 1200°C
- Both MWNT's and SWNTs
- Never have to handle nanotube powder, therefore reduced health risks
- Mechanical properties, so far average but for high volume fractions of highly aligned nanotubes prospects are good
- Feedstock costing 0.1cents/gram converted continuously to CNTs currently marketing at $100/gram: mark-up of 10^5