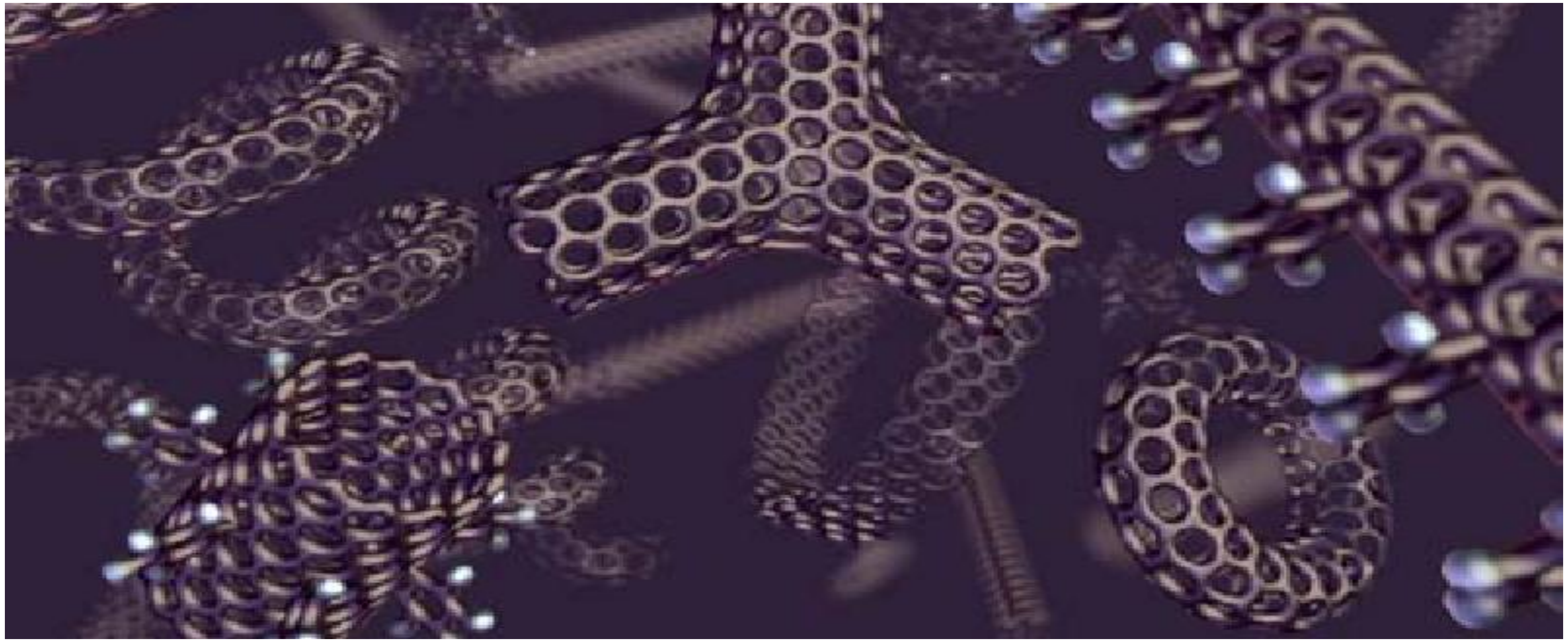
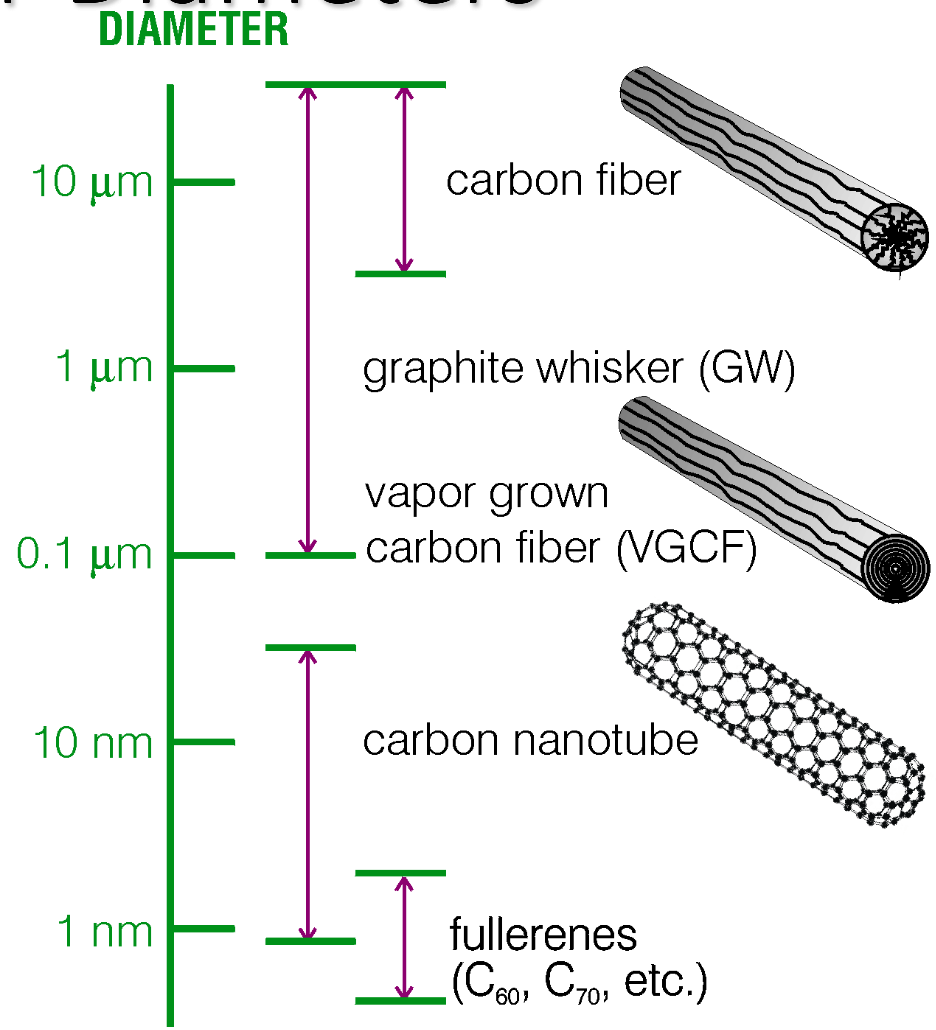
# Carbon Nanotubes



- Introduction
- Applications
- Growth Techniques
- Growth Mechanism

Based on a presentation by *Shishir Rai. University of Notra Dame*

# Carbon Fiber Diameters



# High Strength to Weight Materials

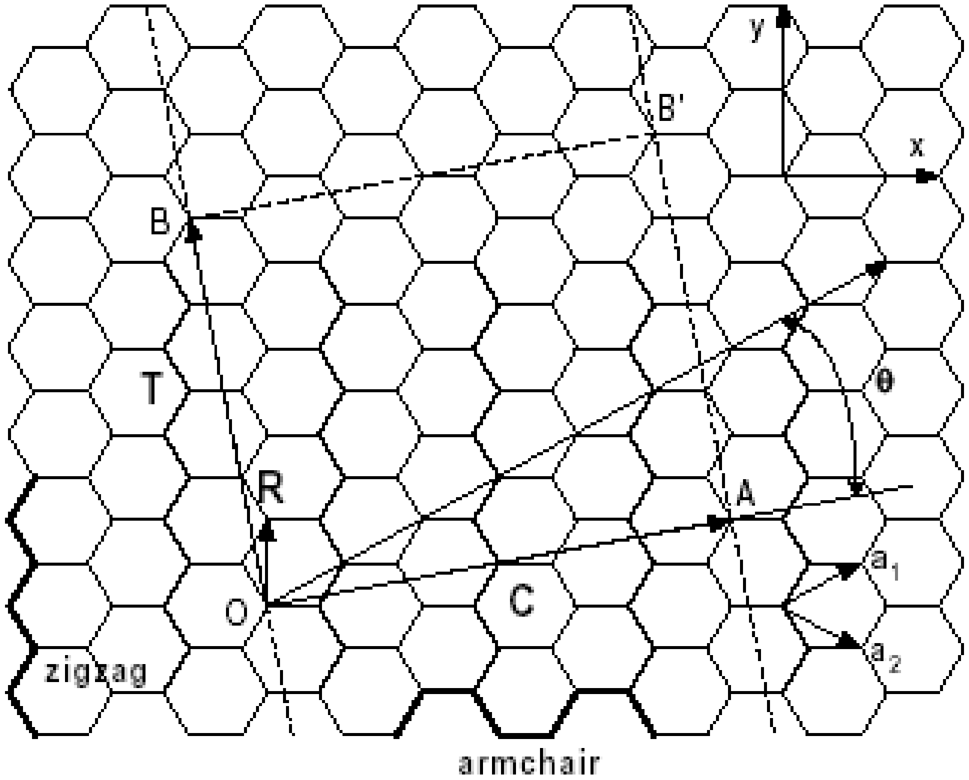
| | Graphite Crystal | Carbon Fibers | MWNT | SWNT | Steel |
|---|---|---|---|---|---|
| Tensile Strength - GPa | 100 | 3-7 | 300-600 | 300-1500 | 0.4 |
| Elastic Modulus - GPa | 1000 | 200-800 | 500-1000 | 1000-5000 | 200 |
| Specific Strength - GPa | 50 | 2-4 | 200-300 | 150-750 | 0.05 |
| Specific Modulus - GPa | 500 | 100-400 | 250-500 | 500-2500 | 26 |
| Strain to Failure - % | 10 | 1-3 | 20-40 | 20-40 | 25 |

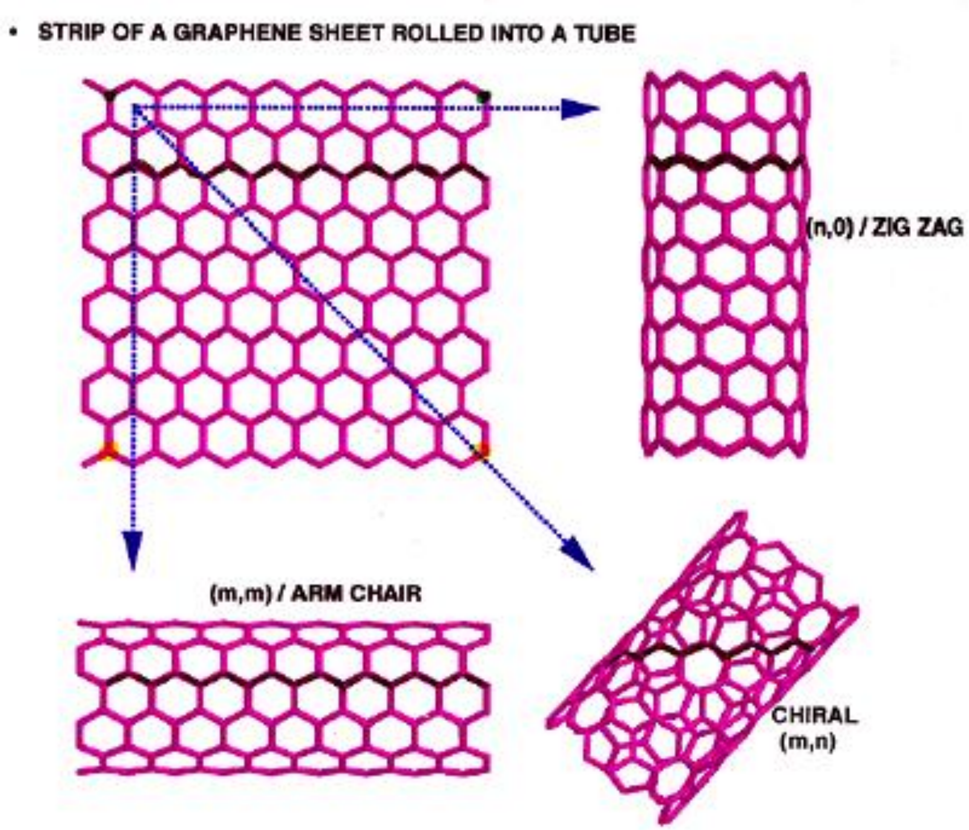
# What is a Carbon Nanotube?

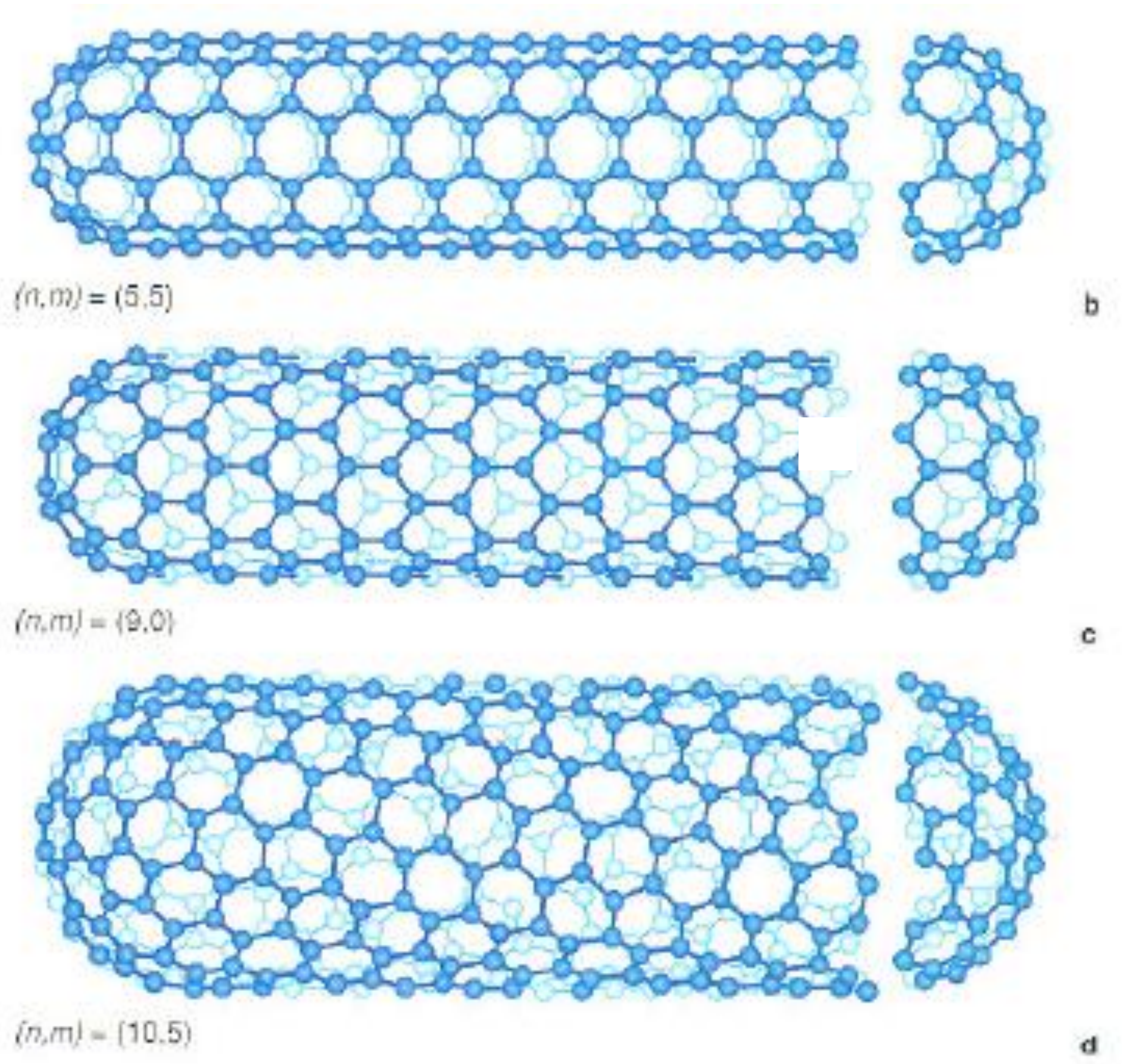
CNT is a tubular form of carbon with diameter as small as 1nm. Length: few nm to microns.

CNT is configurationally equivalent to a two dimensional graphene sheet rolled into a tube.

A CNT is characterized by its Chiral Vector: $\mathbf{C}_h = n\,\hat{a}_1 + m\,\hat{a}_2$, $\theta \rightarrow$ Chiral Angle with respect to the zigzag axis.






Armchair (n,m) = (5,5)
$\theta = 30^\circ$

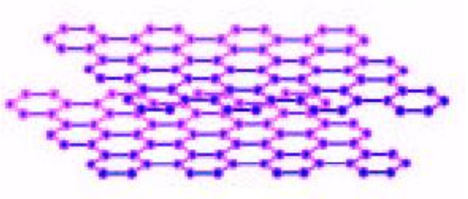
Zig Zag (n,m) = (9,0)
$\theta = 0^\circ$

Chiral (n,m) = (10,5)
$0^\circ < \theta < 30^\circ$

# Why do Carbon Nanotubes form?

Carbon → Graphite (Ambient conditions)

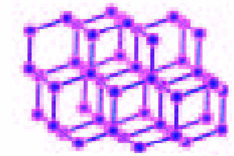
sp$^2$ hybridization: planar



graphite

→ Diamond (High temperature and pressure)

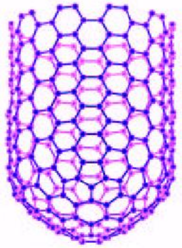
sp$^3$ hybridization: cubic



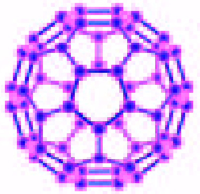
diamond

→ Nanotube/Fullerene (certain growth conditions)

sp$^2$ + sp$^3$ character: cylindrical



(10, 10) nanotube



$C_{60}$ fullerene

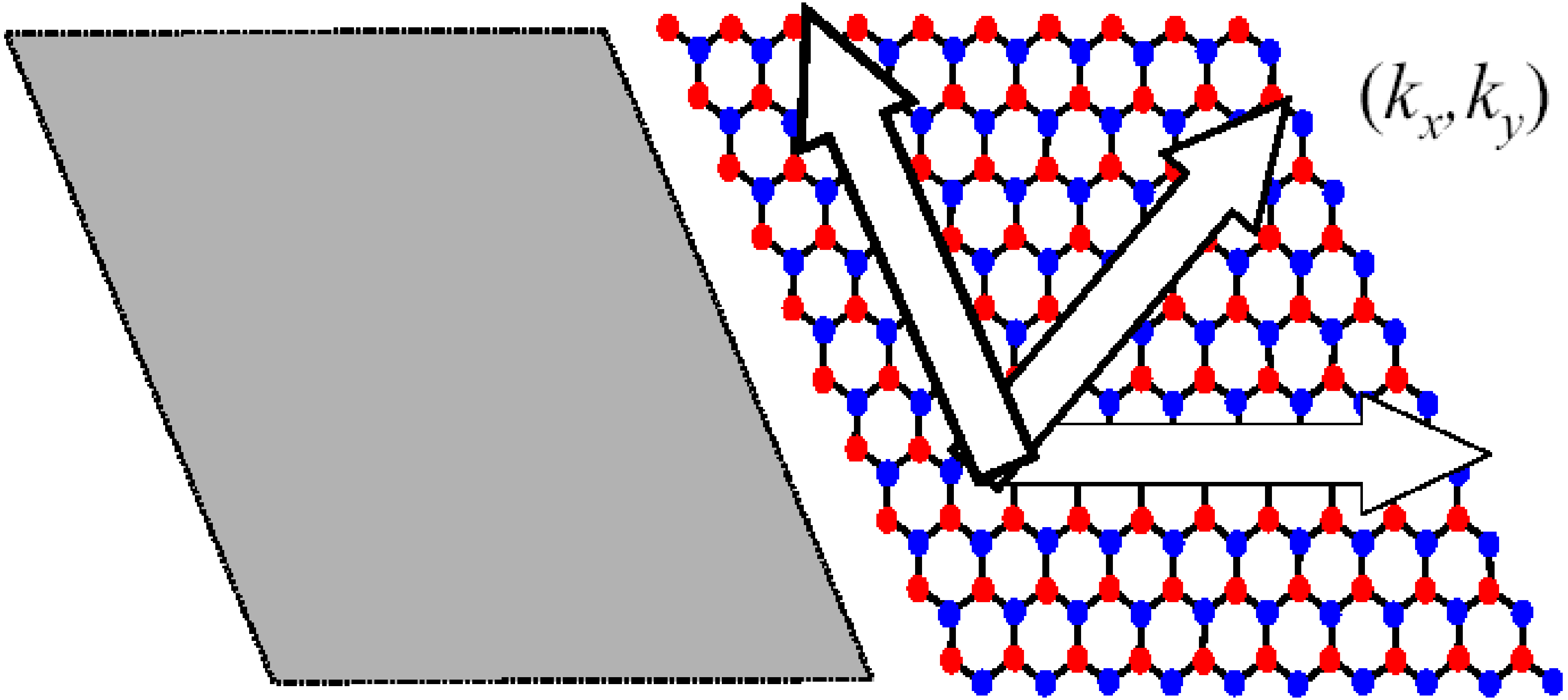
Finite size of graphene layer has dangling bonds. These dangling bonds correspond to high energy states.

Nanotube formation → Eliminates dangling bonds + Increases Strain Energy → Total Energy Decreases

# Types of CNTs

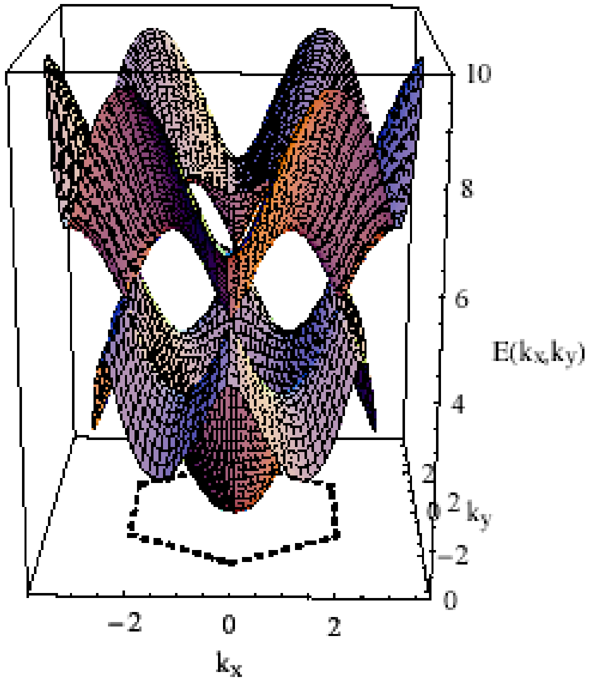
- Single Wall CNT (SWCNT)
- Multiple Wall CNT (MWCNT)
- Can be metallic or semiconducting depending on their geometry.

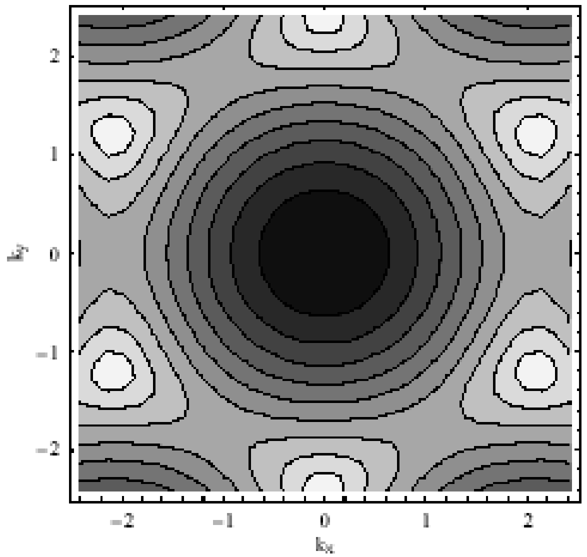
# The Graphene sheet

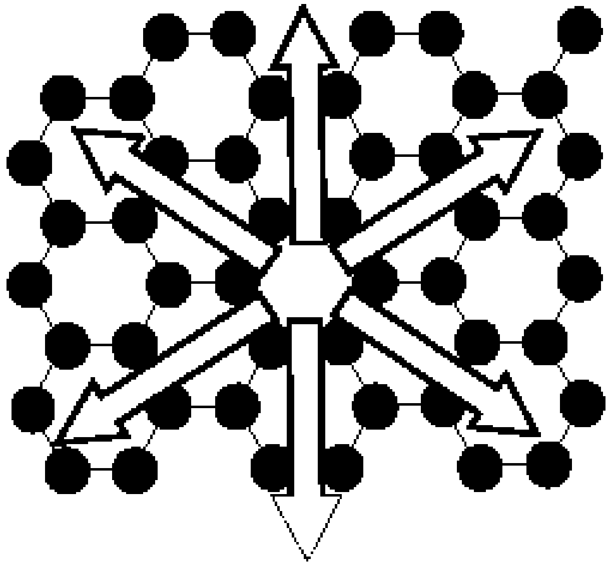


# "Metallic directions"



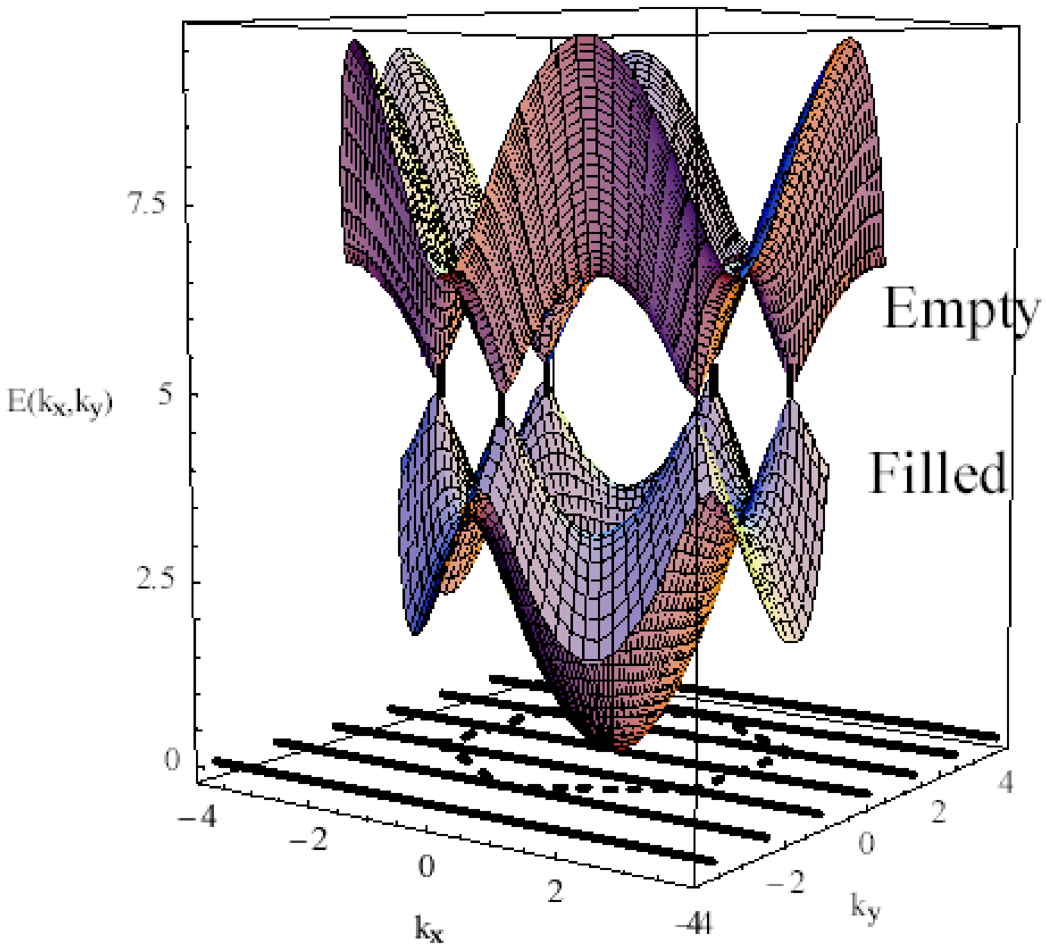


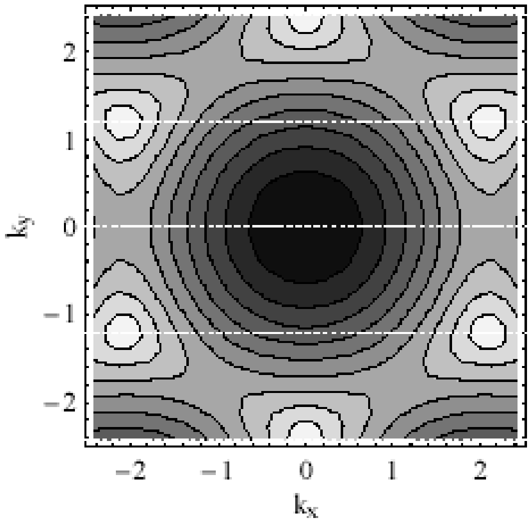



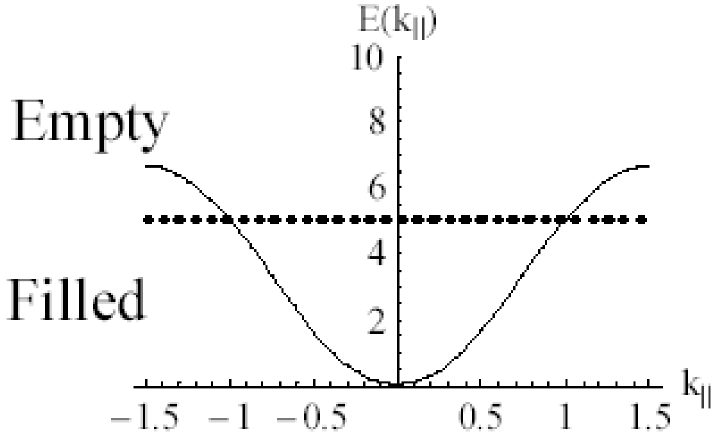



# Nanotube: Metallic

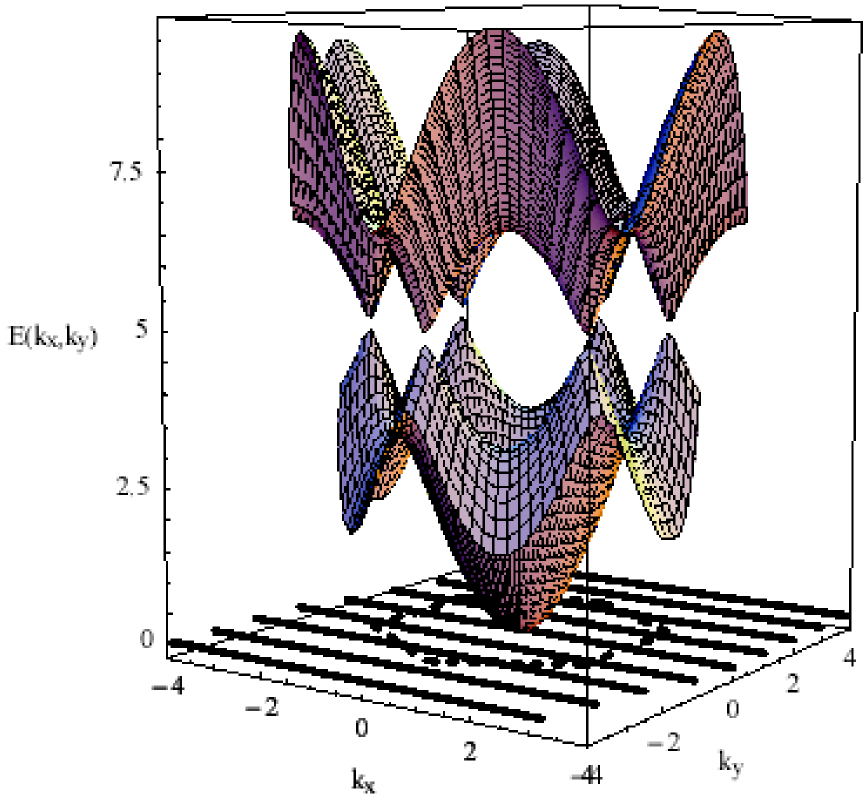


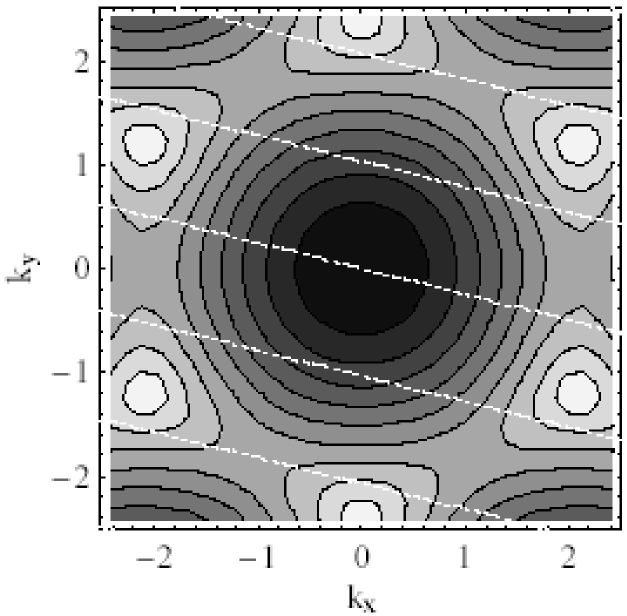


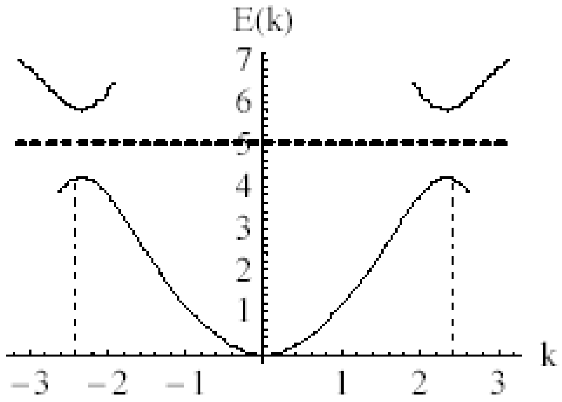



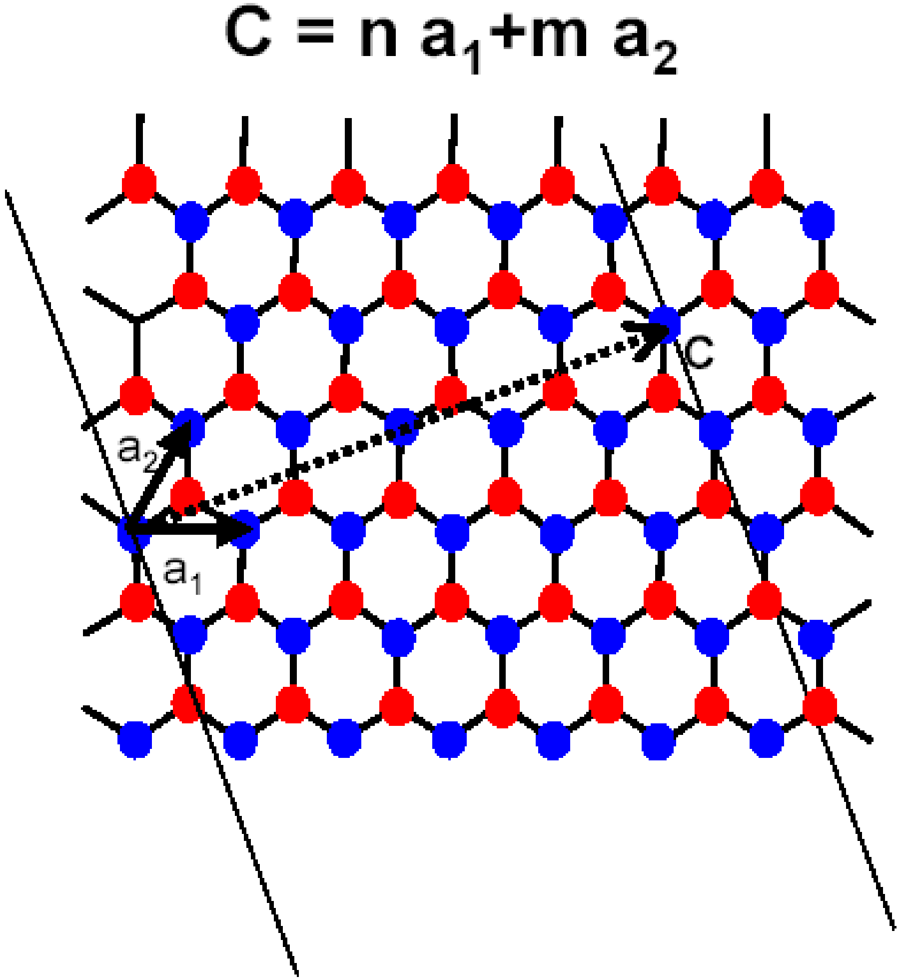
# Nanotube: Semi-conductor

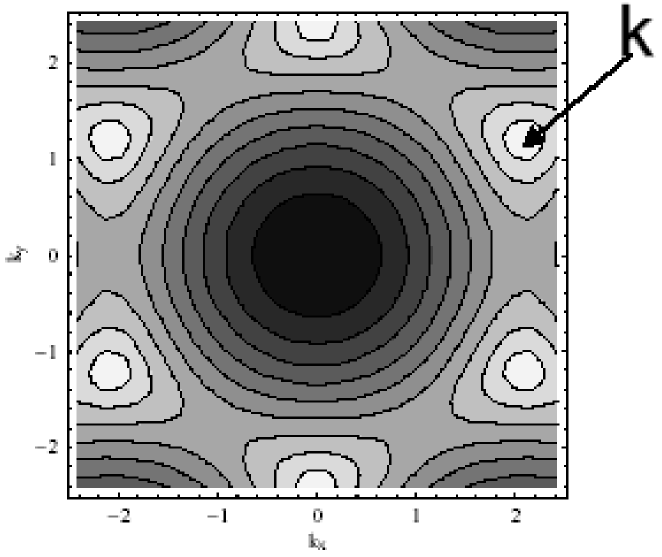


# Metallic: $n - m = 3j$

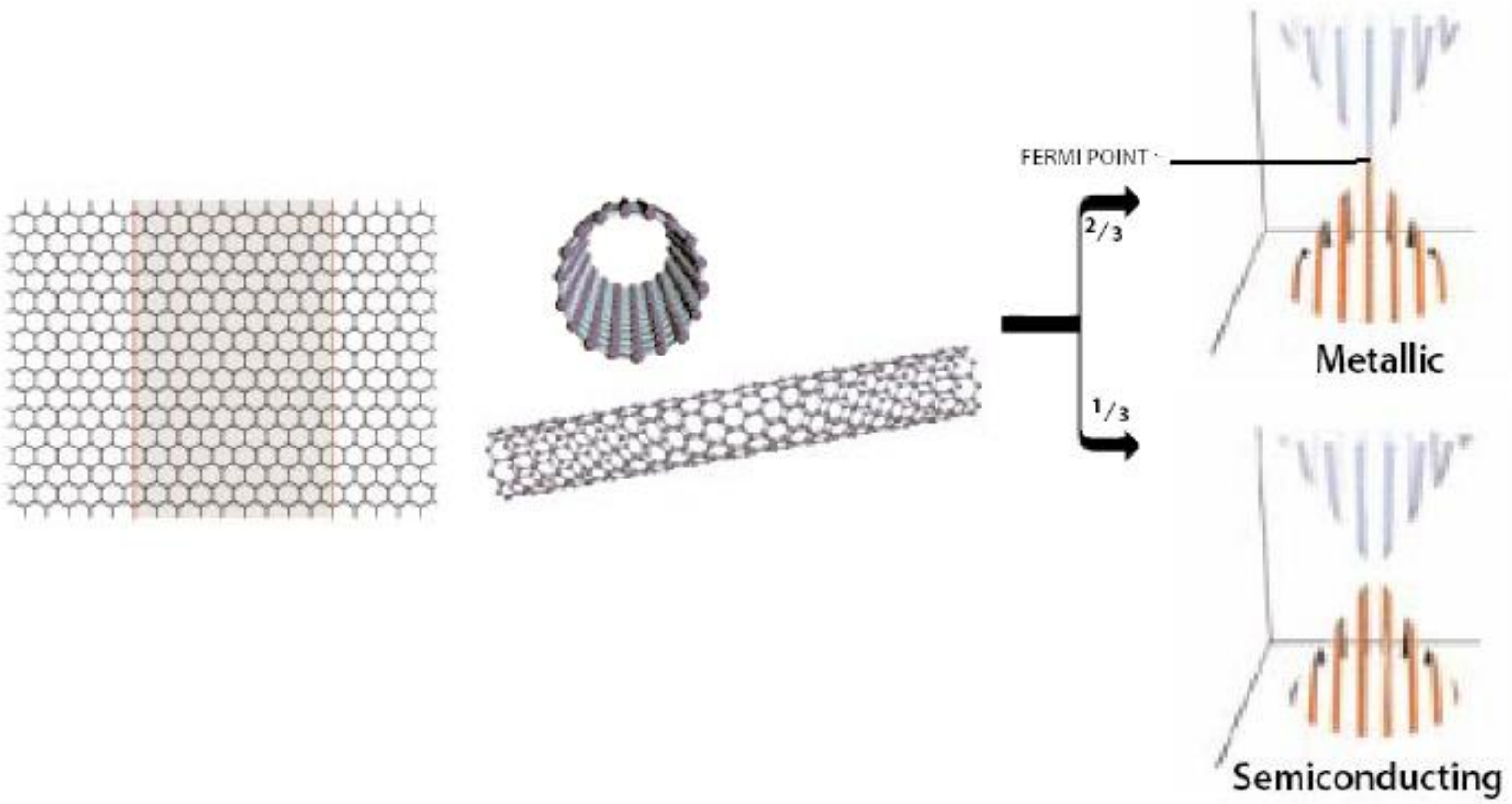



$$\mathbf{C} \cdot \mathbf{k} = 2\pi j$$

# Non-chiral ("Straight") nanotubes

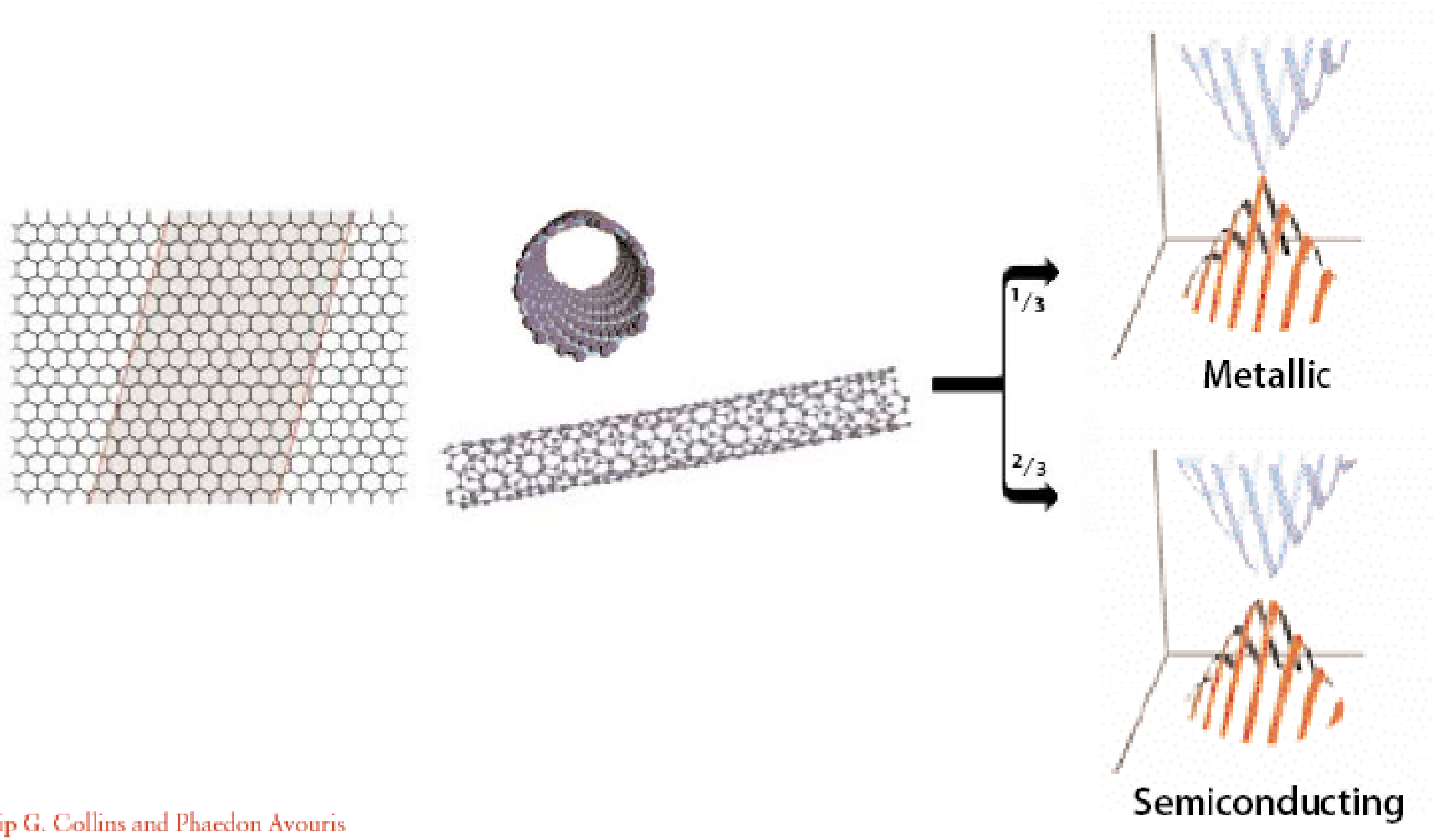





Philip G. Collins and Phaedon Avouris

SCIENTIFIC AMERICAN December 2000

# Chiral (”Spiral”) Nanotubes




Philip G. Collins and Phaedon Avouris

Scientific American December 2000

To know more, go to:

Crystal Structure Analysis Presentation pp 259 y 270 :

BRAGG’S LAW OF DIFFRACTION: pp 230

THE RECIPROCAL LATTICE: pp 259

FIRST BRILLOUIN ZONES: pp 270

**K** and LATTICE PLANES: pp 276

ELECTRON DENSITY MAPS: pp 319

Crystal dynamics

https://www.slideshare.net/chinkitkit/crystal-dynamics

# Growth Mechanisms

- Electronic and Mechanical Properties are closely related to the atomic structure of the tube.
- Essential to understand what controls the size, number of shells, helicity & structure during synthesis.
- Mechanism should account for the experimental facts: metal catalyst necessary for SWNT growth, size dependent on the composition of catalyst, growth temperature etc.

- MWNT Growth Mechanism:
    - Open or close ended?
    - Lip Lip Interaction Models

- SWNT Growth Mechanism:
    - Catalytic Growth Mechanism

# Open-Ended Growth of Multi Walled Nanotube

- Role of Hexagons, Pentagons & Heptagons

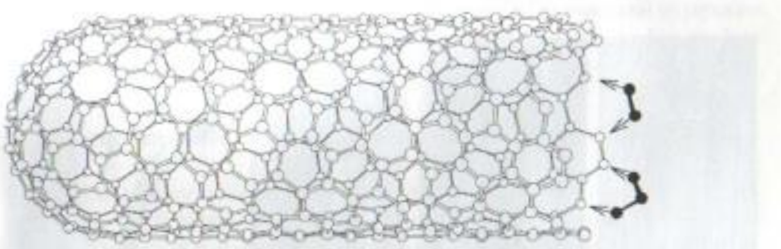
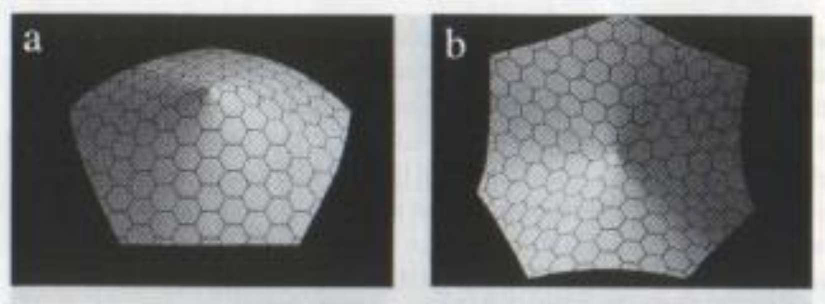
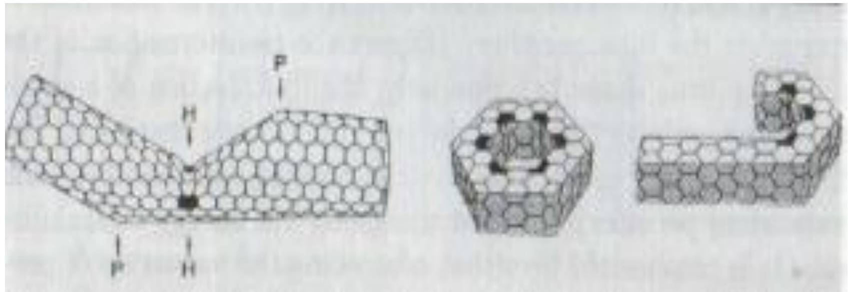
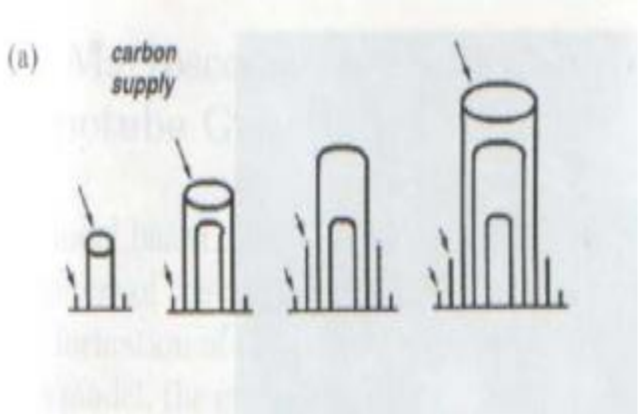


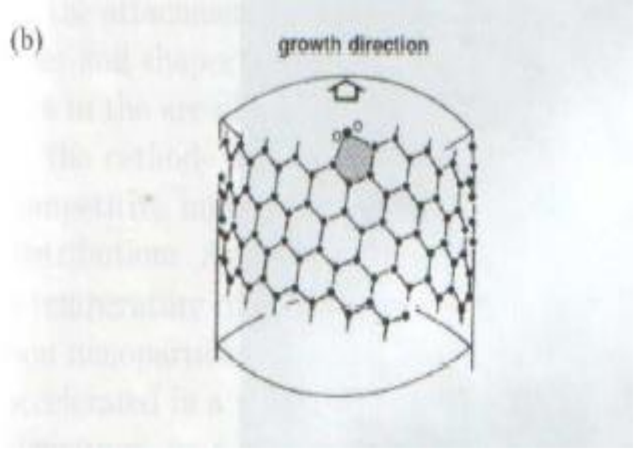
**Fig. 2.** Growth mechanism of a carbon nanotube (white ball-and-stick atomic structure) at an open end by the absorption of $C_2$ dimers and $C_3$ trimers (in *black*), respectively [14]

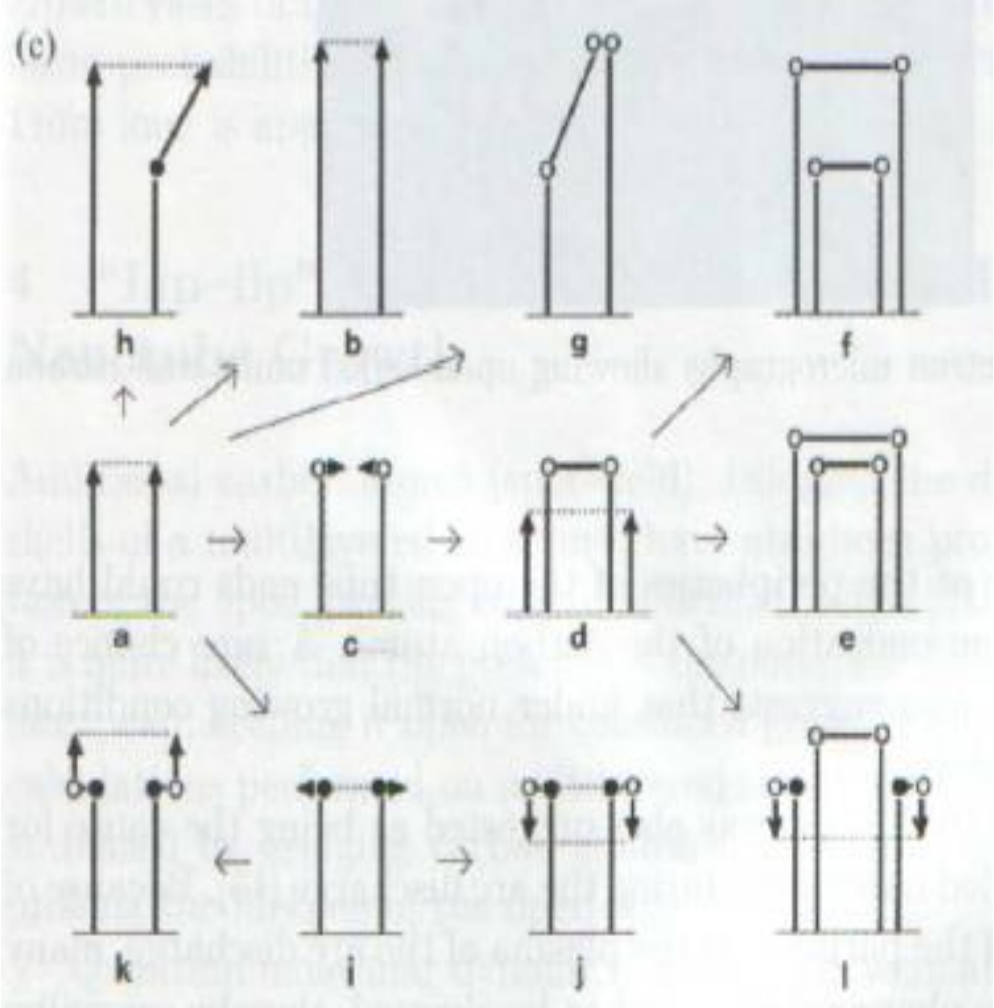


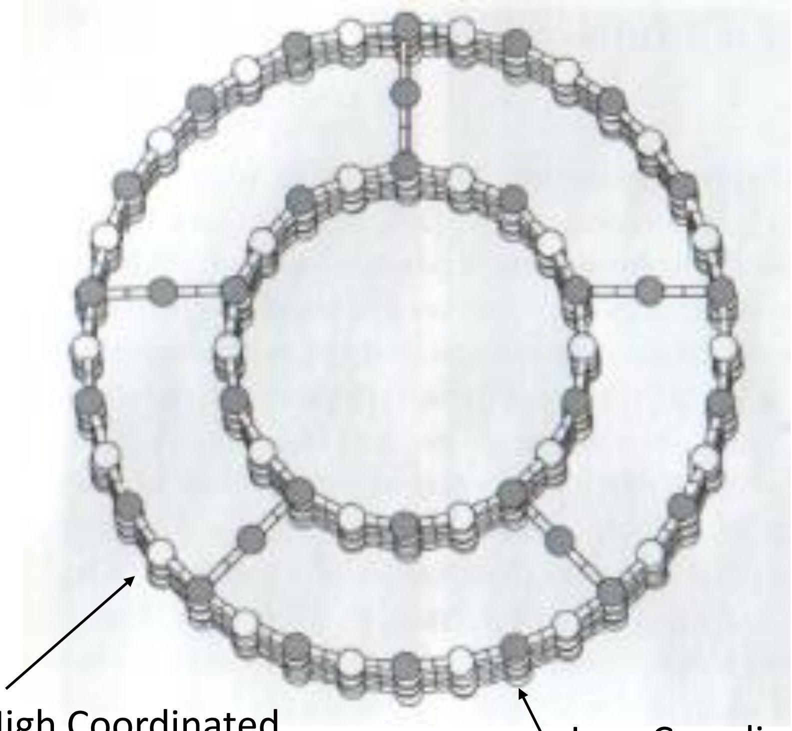
# MWNT: The possibilities



# MWNT: Lip-Lip Interaction Model



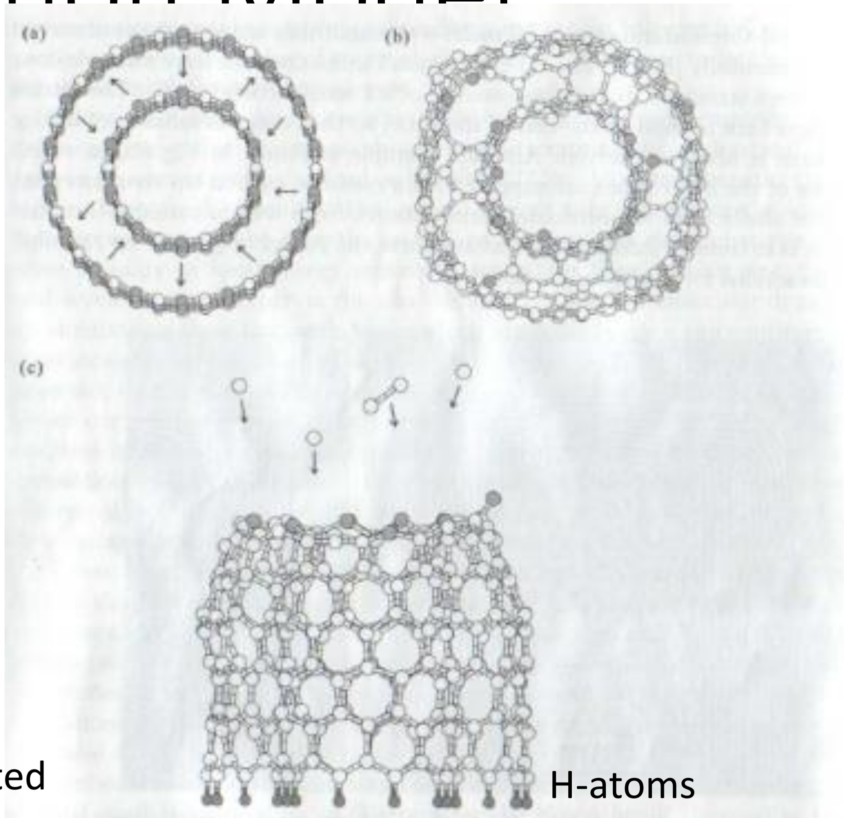



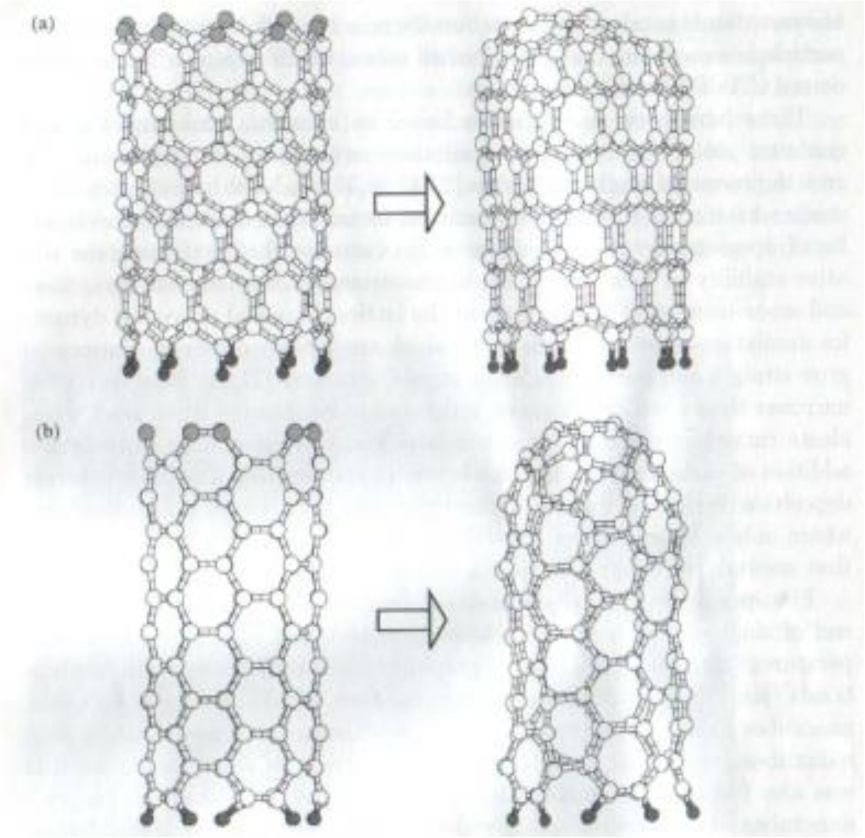

**Fig. 6.** Schematic ball-and-stick representation of the top of a multiwall nanotube with an open zigzag edge. Only two of many layers are shown for clarity. Three-coordinated carbon atoms are represented by white spheres, while low coordinated carbon atoms (dangling bonds and bridging atoms) are represented as light grey spheres on the top of the structure. Several "spot-weld" adatoms are shown occupying sites between doubly coordinated edge atoms of adjacent layers. The nanotube growth is enabled by these adatom spot-welds which stabilize the open configuration [21]

**Fig. 7.** Creation (**a**) and stabilization (**b**) of a double-walled (10,0)@(18,0) nanotube open edge by "lip–lip" interactions at ~3000 K. The notation (10,0)@(18,0) means that a (10,0) nanotube is contained within an (18,0) nanotube. The direct incorporation (c) of extra single carbon atoms and a dimer with thermal velocity into the fluctuating network of the growing edge of the nanotube is also illustrated [22,23]. The present system contains 336 carbon atoms (large white spheres) and 28 hydrogen atoms (small dark grey spheres) used to passivate the dangling bonds on one side of the cluster (bottom). The other low coordinated carbon atoms (dangling bonds) are represented as light grey spheres on the top of the structure

# SWNT Growth Mechanism

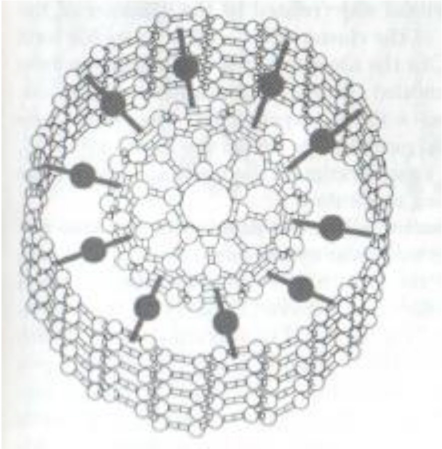
## Is uncatalyzed growth possible?

- Simulations & Observations $\Rightarrow$ **No!**
- Spontaneous closure at experimental temperatures of 2000K to 3000K.
- Closure reduces reactivity.

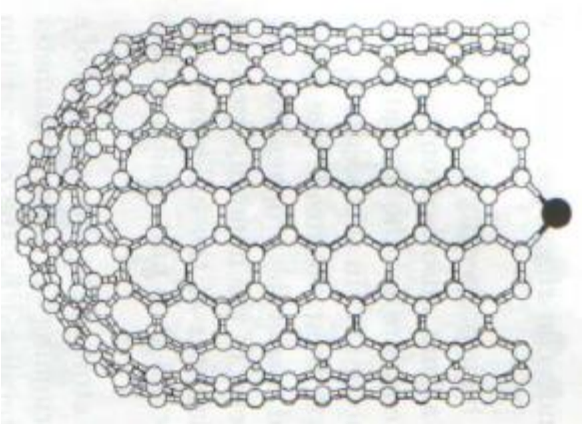


# Catalytic SWNT Growth Mechanism

- Transition metal surface decorated fullerene nucleates SWNT growth around periphery.

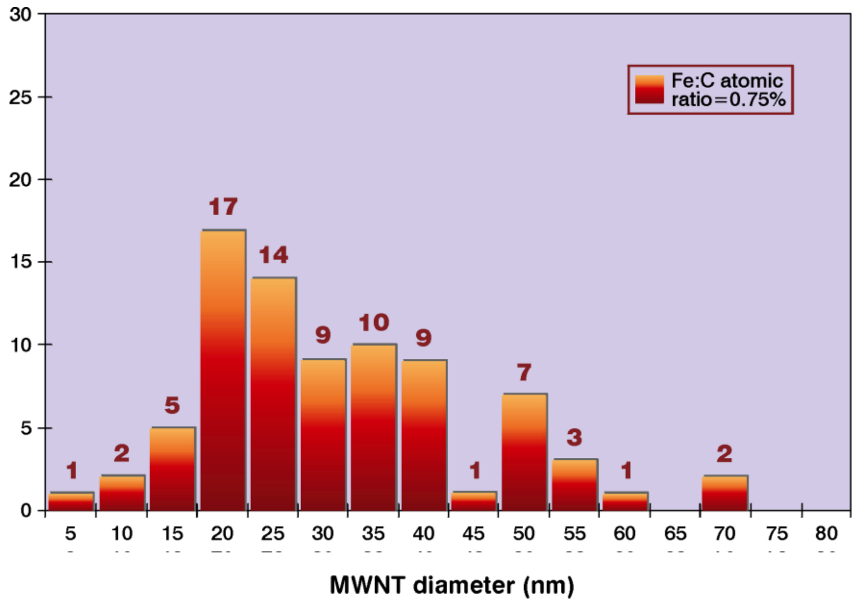


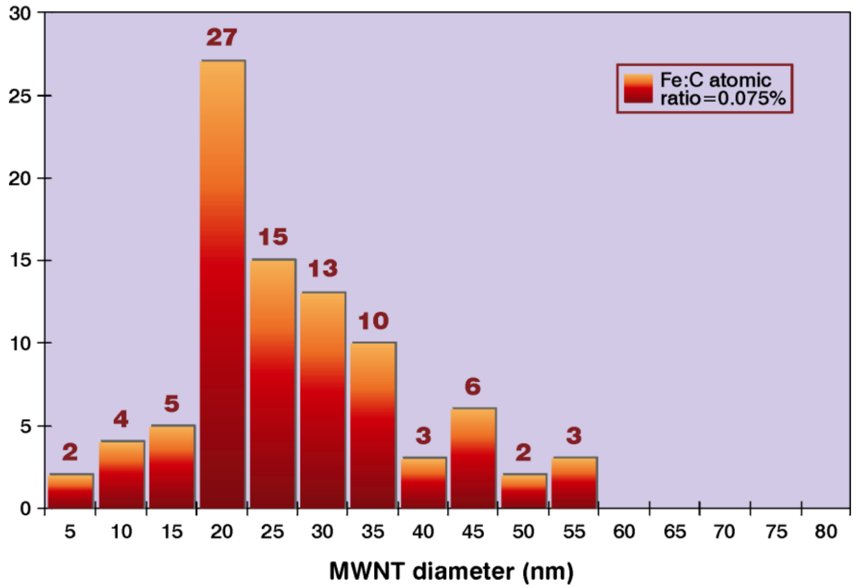
- Catalyst atom chemisorbed onto the open edge. Catalyst keeps the tube open by scooting around the open edge, ensuring and pentagons and heptagons do not form.



# Catalyst Loading

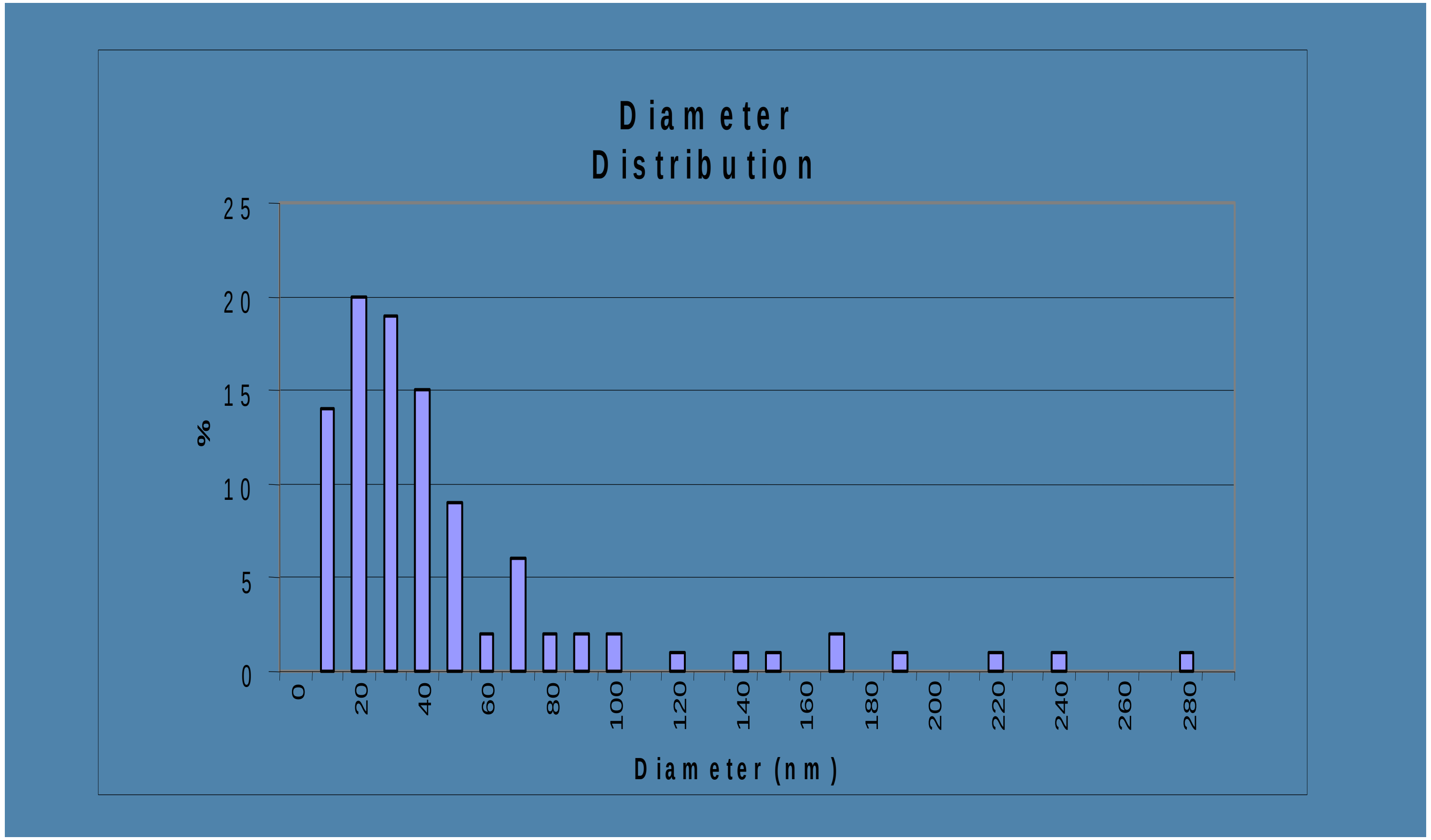
- Production rate increases with Fe:C ratio
- Diameter distribution widens



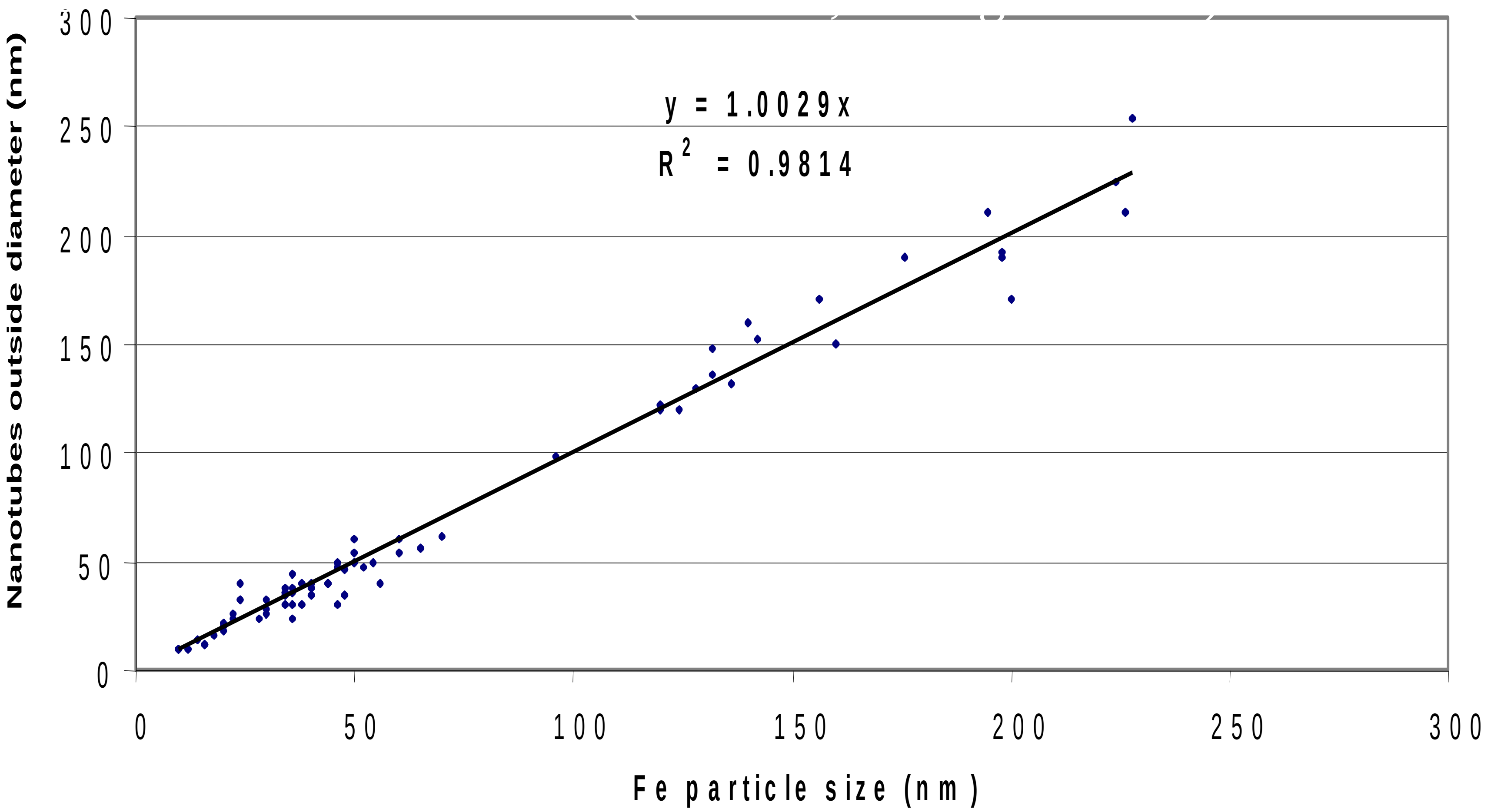



# Distribution of MWNT Diameters

Diameter function of temperature, partial pressure and time.



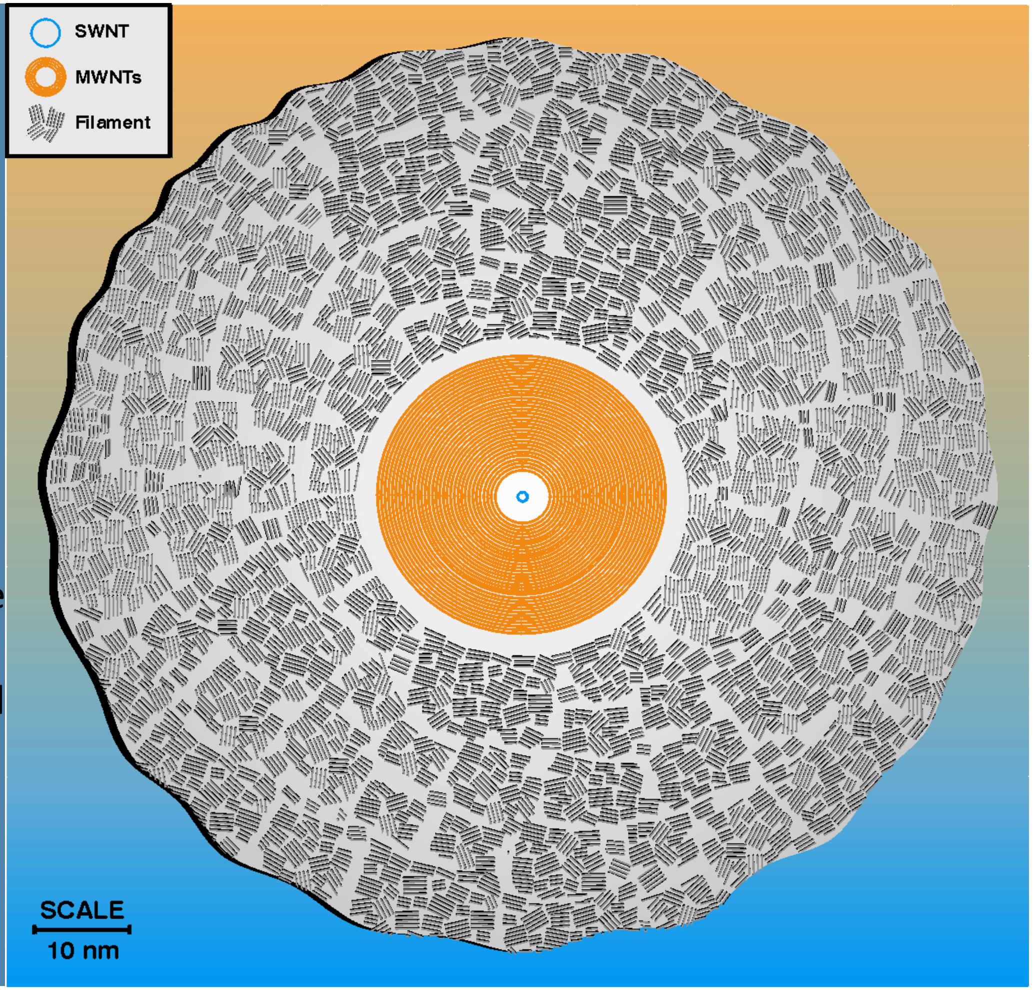
# Outer diameter relates to particle size.



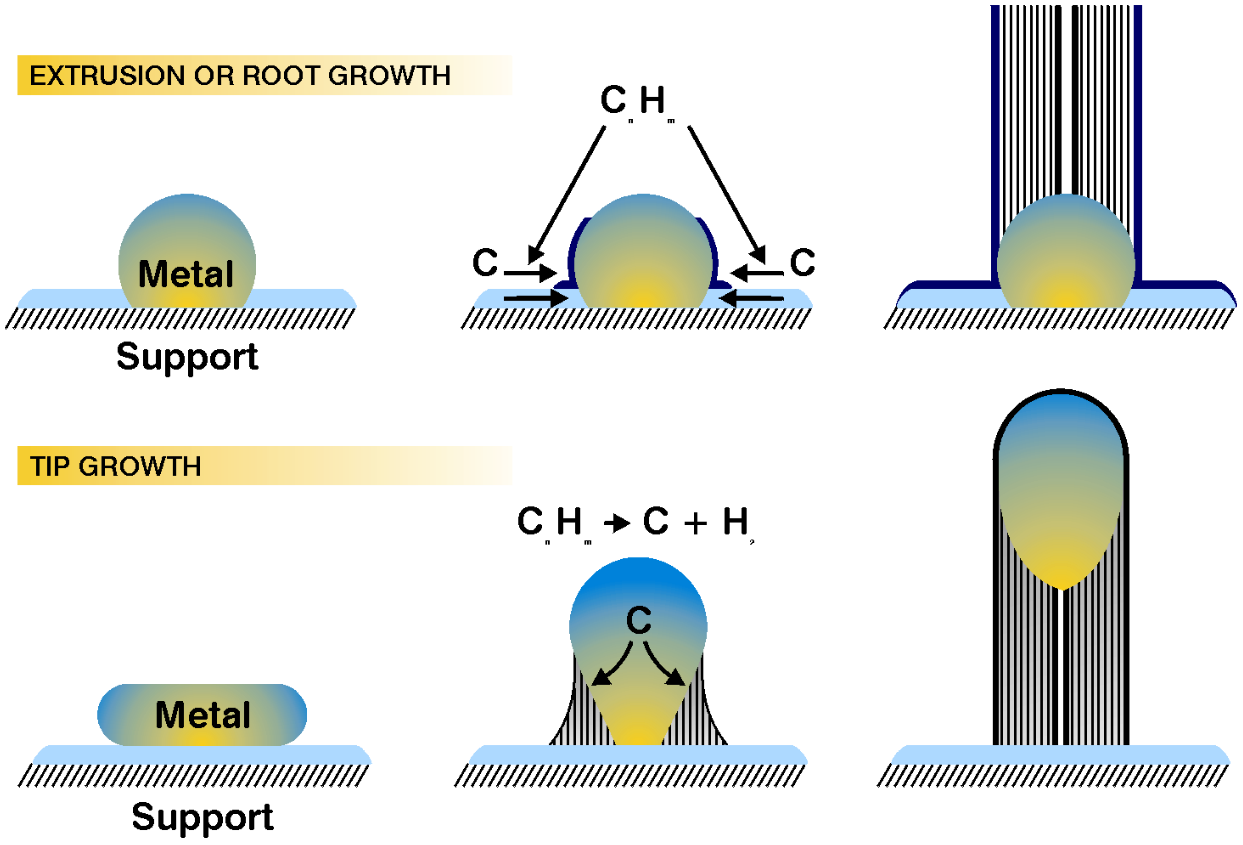
# Growth Mechanism

- Form of carbon depends on metal particle size
  - graphite
  - graphite whiskers (VGCF)
  - nanofibers
  - MWNT
  - SWNT

- As metal becomes smaller
  - curvature is eventually favore (MWNT)
  - ultimately, SWNT is only stabl form



# ‘Lawn’ Growth Mechanism



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*Review*

# An Overview of the Recent Progress in the Synthesis and Applications of Carbon Nanotubes

**Gul Rahman [1,*], Zainab Najaf [1], Asad Mehmood [2], Salma Bilal [3], Anwar ul Haq Ali Shah [1], Shabeer Ahmad Mian [4] and Ghulam Ali [5]**

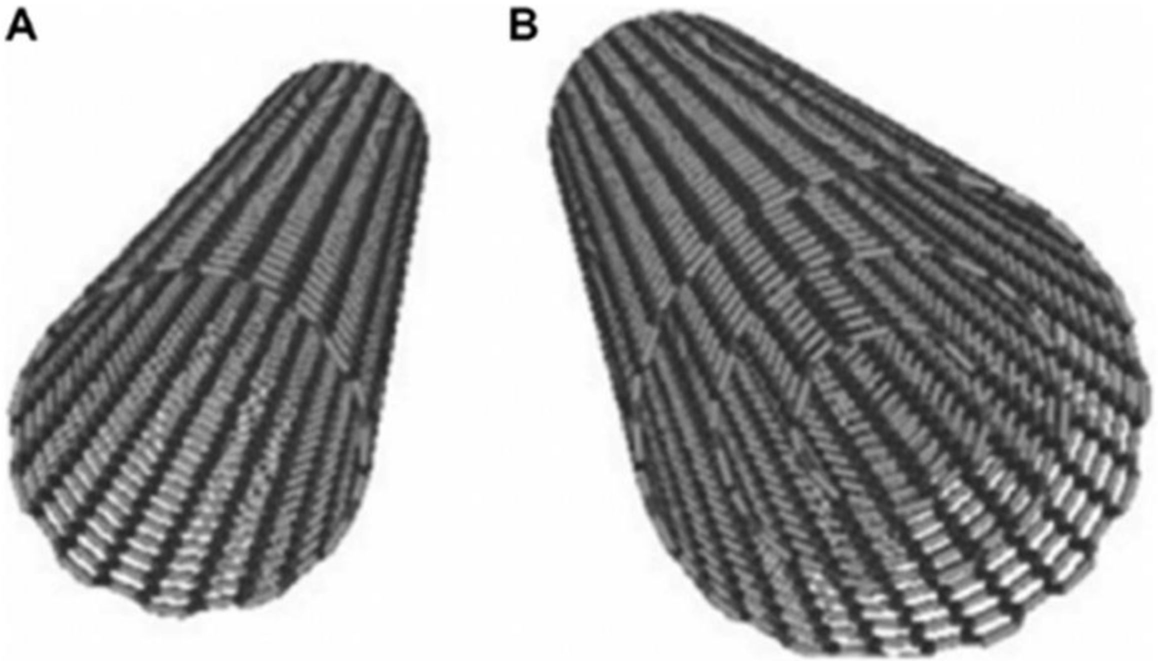


**Figure 2.** (**A**) Structure of SWCNT; (**B**) MWCNT. Reproduced with permission from [22]. Copyright DOVE Medical Press, 2016.

**Table 1.** Comparison between SWCNTs and MWCNTs [23].

| SWNT | MWNT |
|---|---|
| Single graphene layer | Multiple graphene layers |
| Synthesis requires catalyst | No catalyst is required |
| Difficult bulk synthesis due to the requirement of appropriate growth and atmospheric condition. | Easy bulk synthesis |
| Poor purity | High purity |
| Greater chances of defects during functionalization | Lesser defect chances but when this occurs, it is hard to recover |
| Aggregation in the body is less | Aggregation in the body is greater |
| Easy assessment and characterization | Structure is complicated |
| More pliable and easily twisted | Twisting is not easy |

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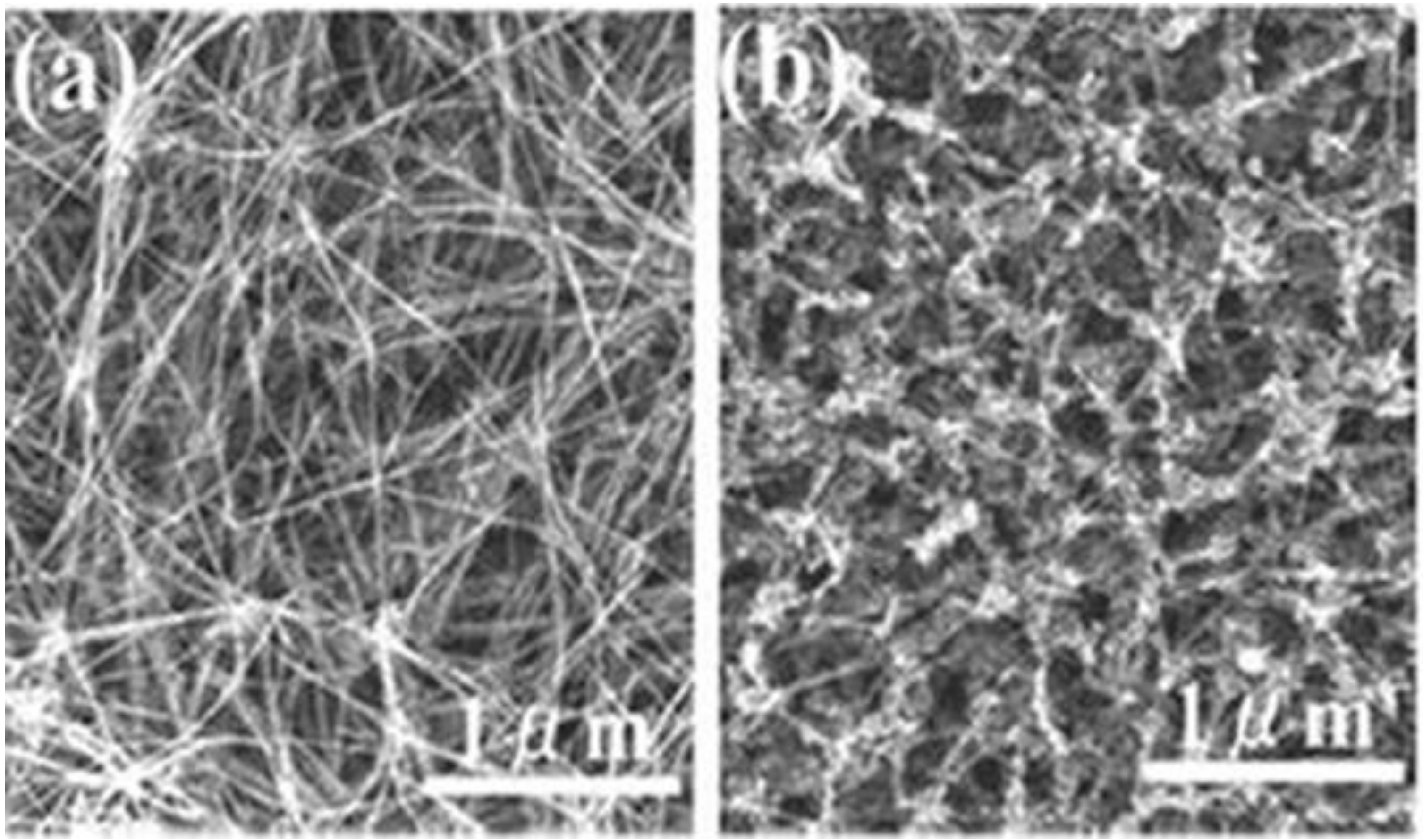


**Figure 4.** SEM images of MWCNTs (**a**) in the presence of and (**b**) in the absence of a magnetic field. Reproduced with permission from [29]. Copyright AIP, 2002.

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# Shapes of CNT

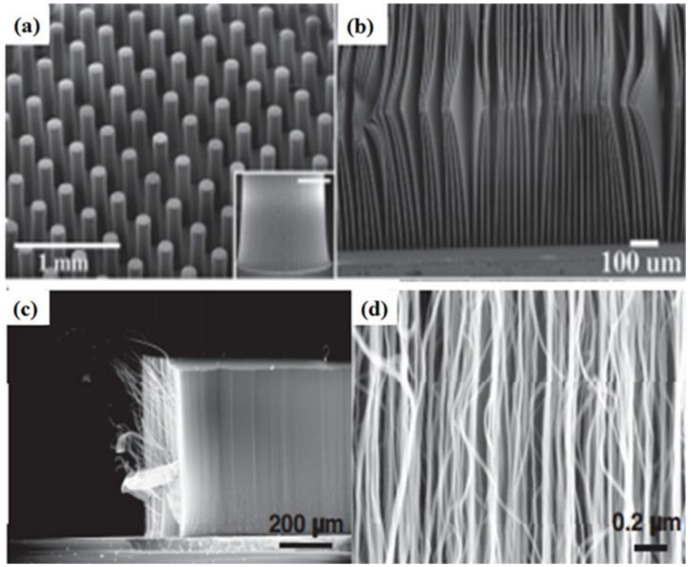


**Figure 7.** (**a**) SEM micrograph of cylindrical pillars of SWCNTs; (**b**) SEM images of 10 µm thick SWCNT sheets. Reproduced with permission from [73]. Copyright AAAS, 2004. (**c**,**d**) super-aligned MWNT array with different magnifications. Reproduced with permission from [84]. Copyright Elsevier, 2009.

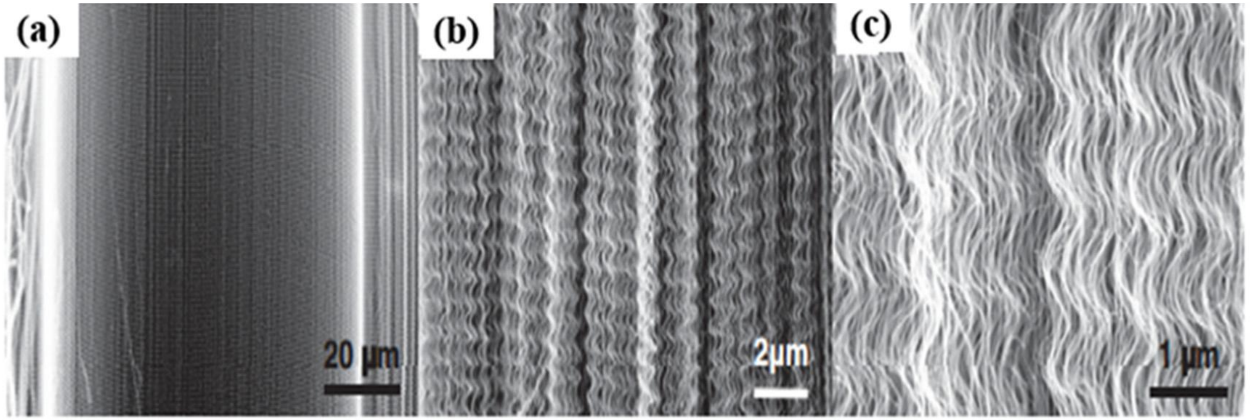


**Figure 8.** SEM images of a MWNT array with wavy structures at various magnifications (**a**–**c**). Reproduced with permission from [84]. Copyright Elsevier, 2009.

Furthermore, helically coiled shape CNTs consisting of pentagon–heptagon paired atomic rings have been reported in literature (Figure 9) [87].They were first detected in the 1990s [88,89]. They can be synthesized in large amounts by catalytic CVD [90–93]. The unusual morphology of coiled CNTs impart them some functionalities such as the high-efficiency of electromagnetic wave absorbers capacity, electrical inductors, resonators, sensors, nanostructured mechanical springs, and magnetic beam generators [84,94].

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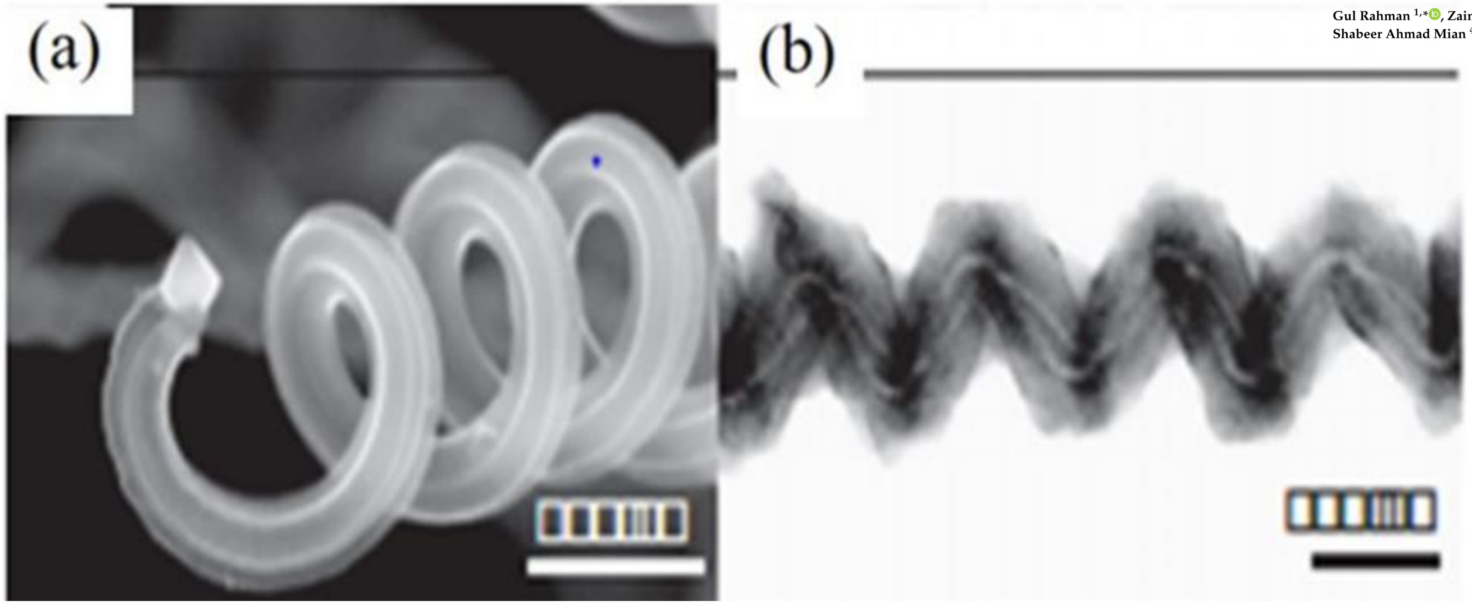
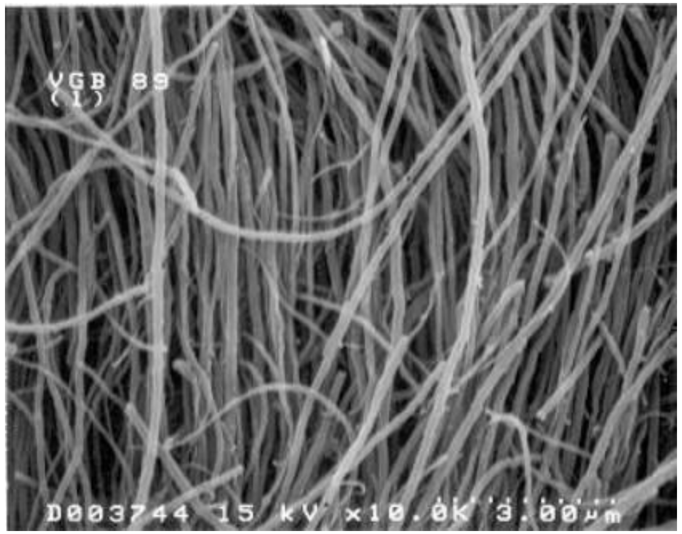
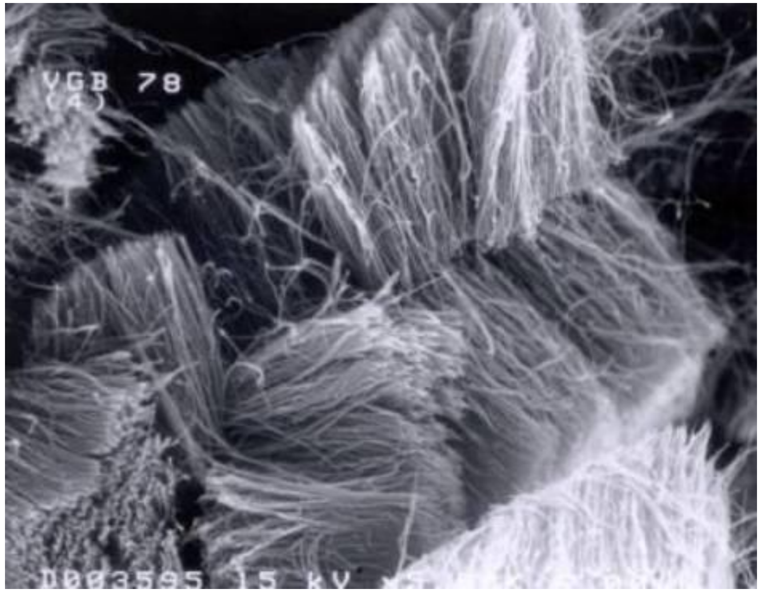



**Figure 9.** SEM image of helically coiled CNTs (**a**) Tip of a coil. The scale bar is 600 nm; (**b**) TEM image of two tubules, forming a coil with different diameters, but the similar pitch, and a small alteration in phase. The scale bar is 100 nm. Reproduced with permission from [84]. Copyright Elsevier, 2009.

# MWNT Materials

- CVD synthesis
  - xylene / ferrocene
  - low temperature, 725 $^{o}$C
  - high purity,  > 95%



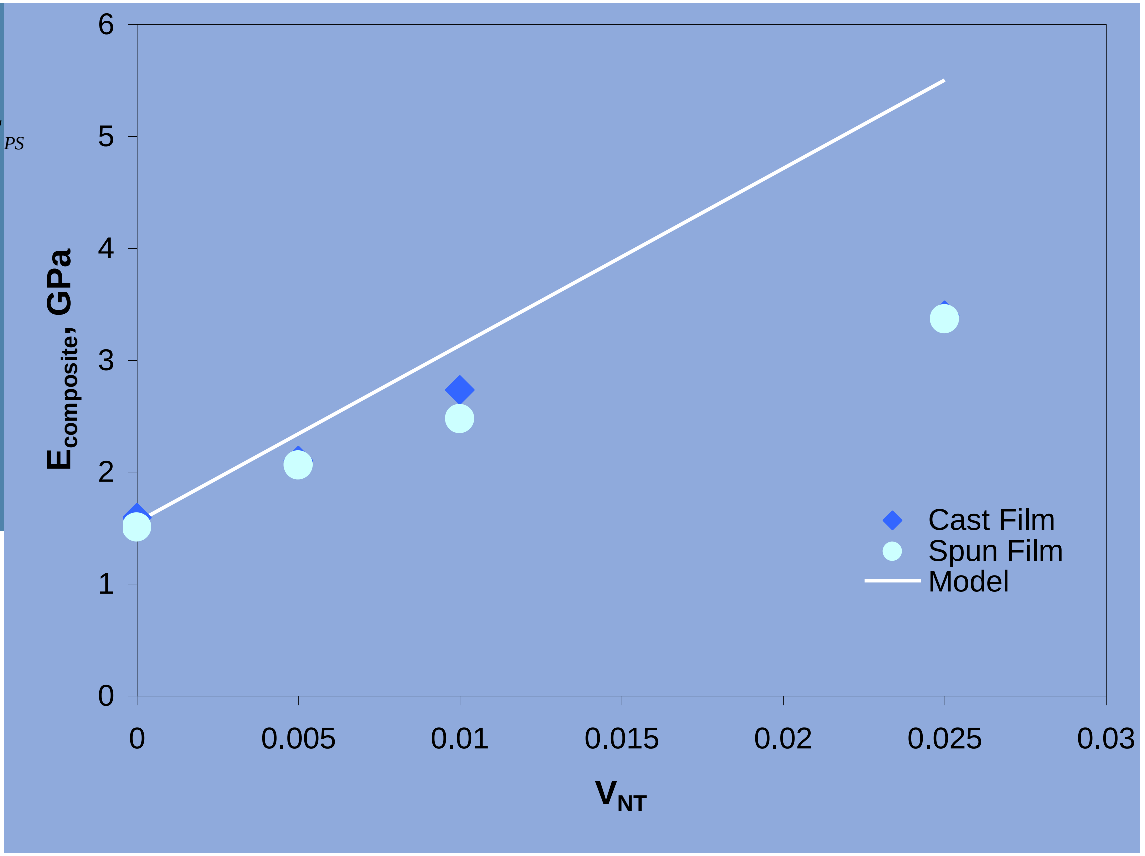

- aligned normal to substrate
- easily dispersed

# Experimental and Theoretical Moduli

$$E_c = \left[ 3/8 \frac{1 + 2(l_{NT}/d_{NT})\eta_L V_{NT}}{1 - \eta_L V_{NT}} + 5/8 \frac{1 + 2\eta_T V_{NT}}{1 - \eta_T V_{NT}} \right] E_{PS}$$

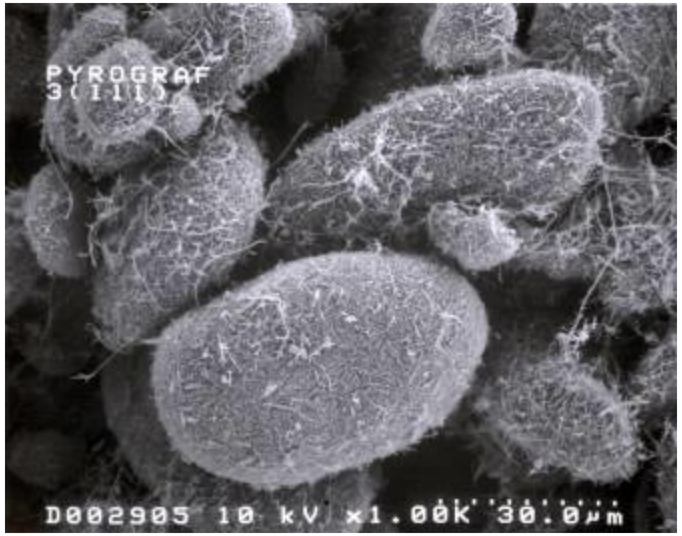
$$\eta_L = \frac{(E_{NT}/E_{PS}) - 1}{(E_{NT}/E_{PS}) + 2(l_{NT}/d_{NT})}$$

$$\eta_T = \frac{(E_{NT}/E_{PS}) - 1}{(E_{NT}/E_{PS}) + 2}$$



# Pyrograf III

- Nanofibers
  - Applied Sciences, Inc.
  - entangled
  - some pyrolytic carbon



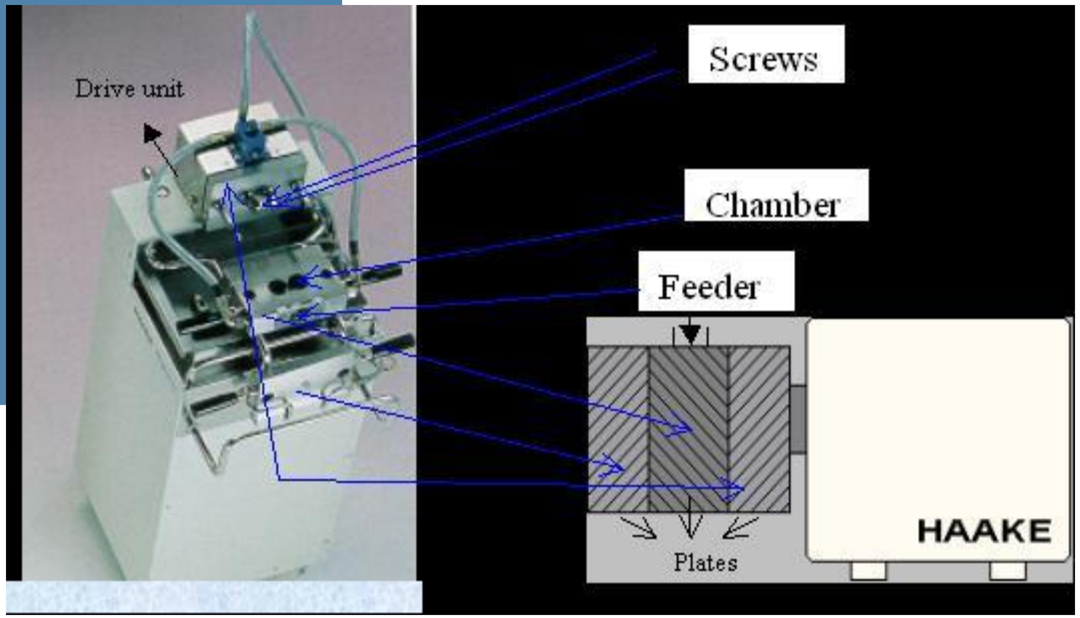


– commercially available

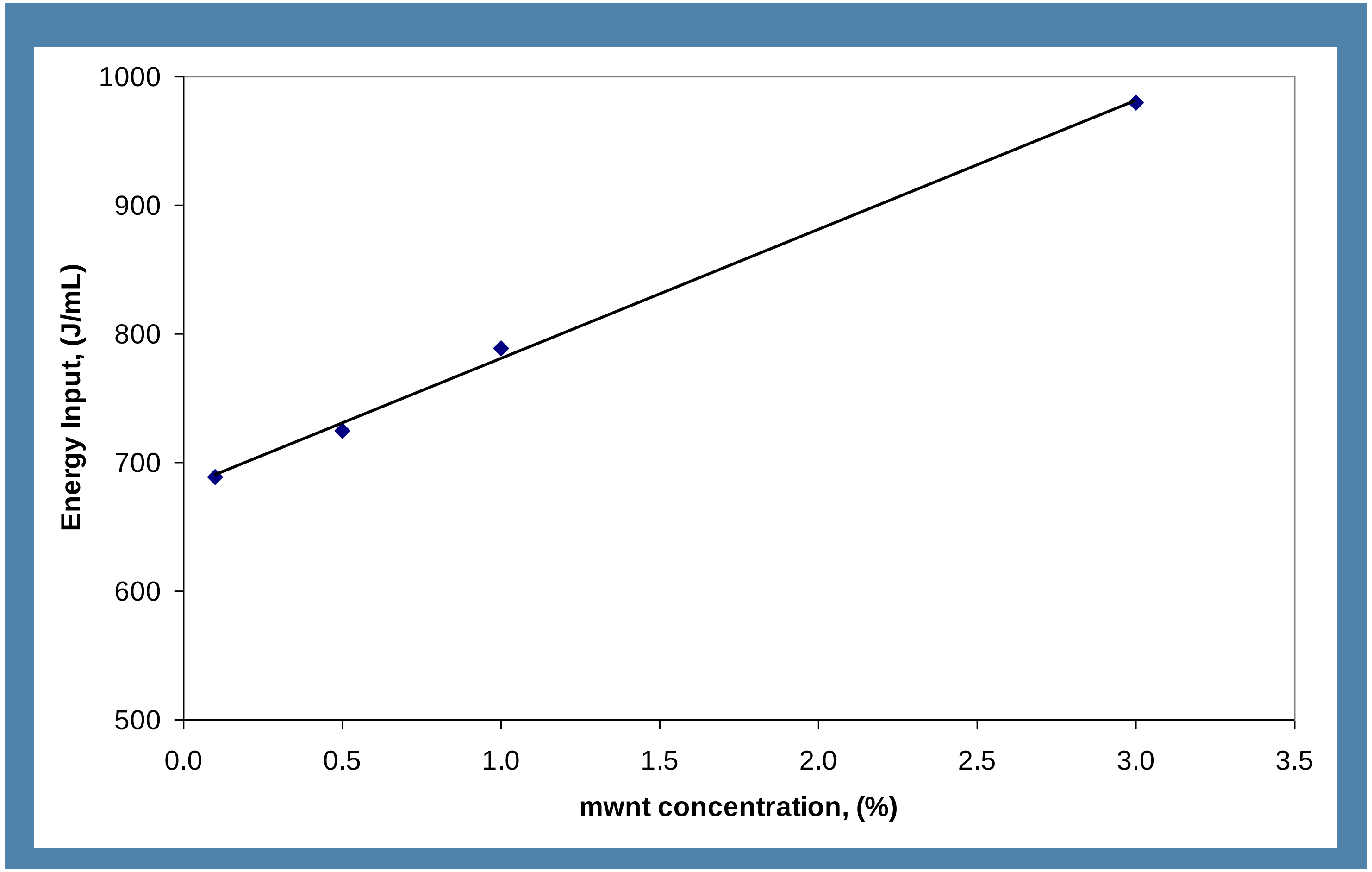
# Melt Processing: Shear Mixing

# Shear Mixing of MWNT into Polymers

- Haake Polylab Shear Mixer
  - 50 gram charges
  - 0 - 25 wt% fiber
  - Matrices:
    - HIPS
    - PP
    - ABS
    - Pitch
- Mixing Energy



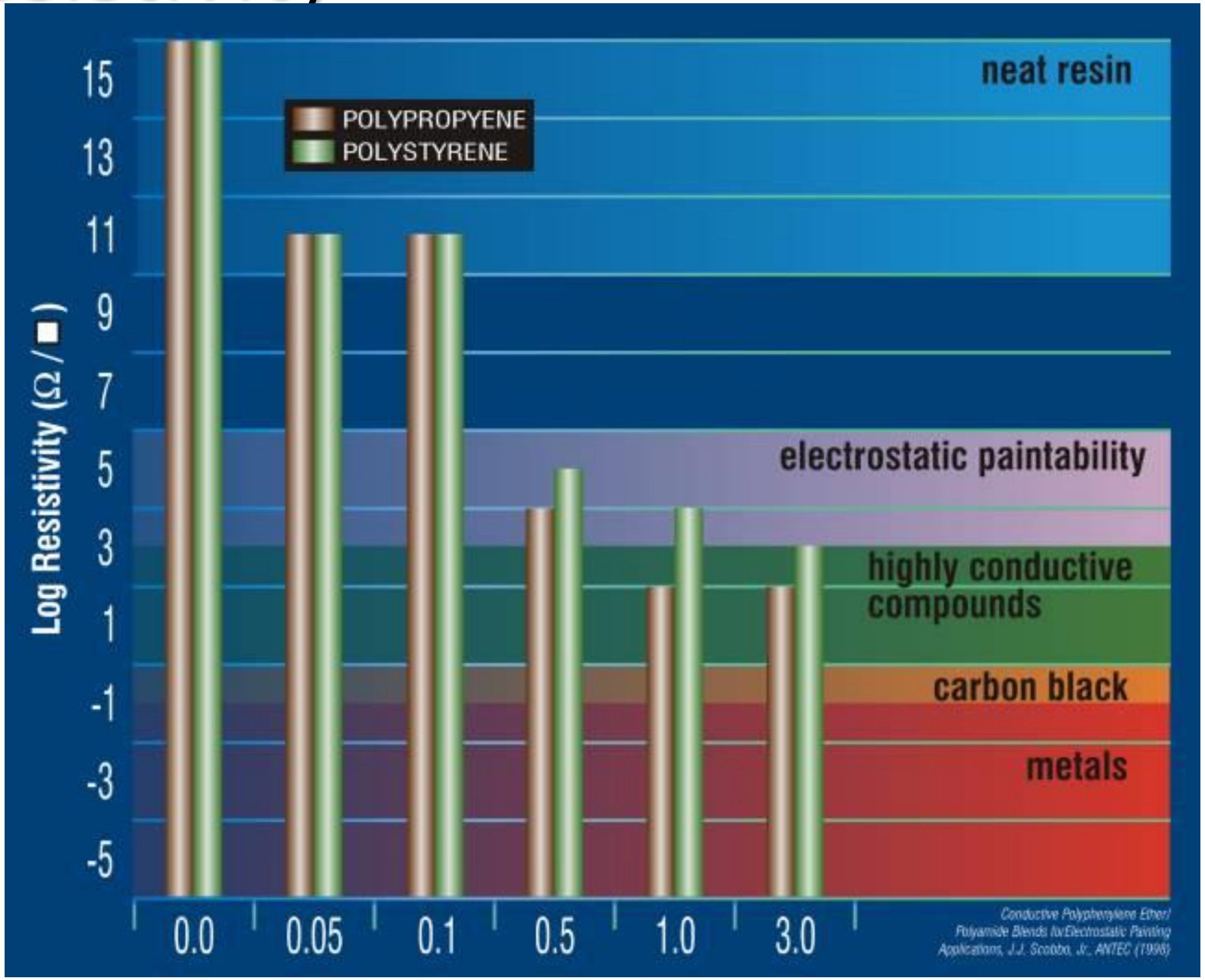
# Mixing Energy Increases with Loading



# Melt Processing

Thin Films

# Surface resistivity



# Conclusion

- Their phenomenal mechanical properties, and unique electronic properties make them both interestingas well as potentially useful in future technologies.

- Significant improvement over current state of electronics can be achieved if controllable growth is achieved.

- Growth conditions play a significant role in deciding the electronic and mechanical properties of CNTs.

- Growth Mechanisms yet to be fully established.

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- Carbon Nanotubes: Introduction to Nanotechnology 2003, Mads Brandbyge.

# Chemical treatments of carbon nano-fibers and their effects on the rheological, electrical and morphological properties of their polypropylene composites

**Dr. Jaime Bonilla Ríos, (ITESM, Campus Monterrey**

**Dr. Enrique Barrera (Rice University)**

**Dra. Karten Lozano (UT-Panam)**

Based on

**Effects of Nanofiber Treatments on the Properties of Vapor-Grown Carbon Fiber Reinforced Polymer Composites**

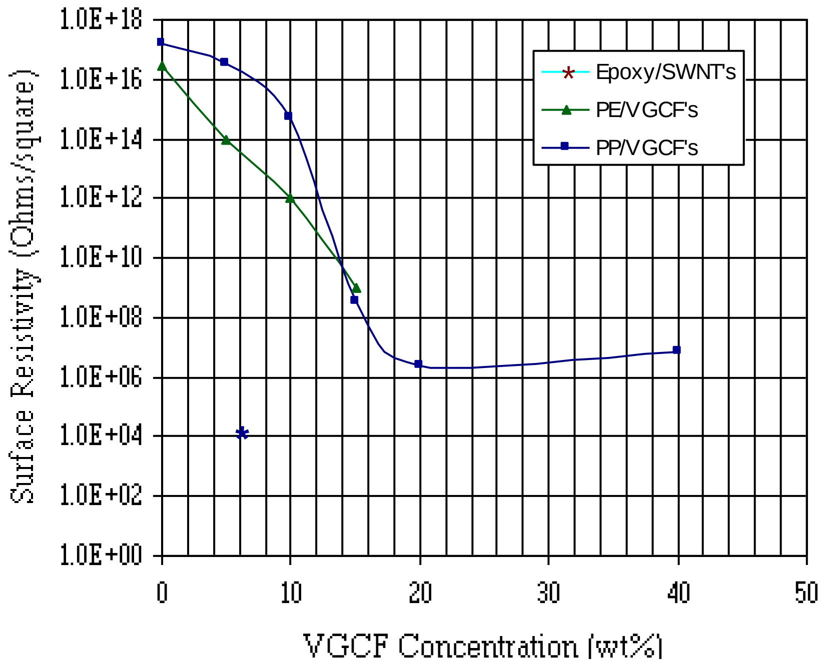
**P. Corte´s,[1] K. Lozano,[2] E. V. Barrera,[3] J. Bonilla-Rios[1]**

Journal of Applied Polymer Science, Vol. 89, 2527–2534 (2003) 

# Comments

| ESD Material | Surface resist range (Ω/square) |
|---|---|
| ESD Nylons [18] | $10^6 - 10^{12}$ |
| Thermoplastic resin/chopped linear carbonaceous fibers [11] | $10^4 - 10^{10}$ |
| PC 85% / PAN 10% / Gr fiber 5% [4] | $10^3 - 10^4$ |
| Nylon 85% / 6/6/15% fiberglass [4] | $10^3$ |
| Carbon black filled PP, PE, PC [4] | $10^7$ |
| Carbon Black/ Nylon 6/6 [4] | $10^7$ |
| Carbon black/PP/20% fiber glass [4] | $10^5$ |

- Previous studies by Bonilla, Barrera and Lozano showed that the concentration of VGCF to achieve ESD materials requires concentrations of around 12% by weight of VGCF and that the mechanical properties of the composites were very similar to those of polypropylene.
- In this study, the VGCF were washed with dichloromethane and then treated with nitric and sulfuric acid for their "functionalization".



# Objective

To evaluate the effects of different chemical treatments on VGCF on the mechanical, rheological, electrical and morphological properties of the PP-VGCF composite.

# Materials

| *Material* | *Carácterísticas* |
| --- | --- |
| Cu * | En polvo, malla 3/23 |
| $HNO_3$ | Soluciones normales 5.06 N y 11.2 N |
| VGCF ** | Pelletizadas |
| PP | MFI 4, homopolímero |

* The copper was mixed with the PP resin in a C.W. Brabender at the following concentrations: 0.1 %, 0.5 % y 1.0 %

** The fibers were mixed with the PP resin in a C.W. Brabender at a concentration of 5%

# Methodology

- VGCF
  - No treatment
    (Control 1)
  - Treatment
    - $H_2O$
      (Control 2)
    - Nitric acid
      - No electrodeposition
        (A, B, C y Control 3)
      - Cu Electrodeposition
        (D y E)

# Metodología

| Tratamiento | Interacción de componentes | Identificación | Condiciones |
|---|---|---|---|
| | | | |
| Sin tratamiento | VGCF | Control 1 | ------ |
| | | | |
| Agua destilada | Agua + VGCF | Control 2 | 4 hrs. |
| | | | |
| Ácido nítrico | Ac. nitrico + VGCF + cobre en polvo* | Control 3 | 4 hrs. 11.2 N |
| | Ac. nítrico + VGCF | A | 4 hrs. 5.06N |
| | Ac. nítrico + VGCF | B | 4 hrs. 11.2 N |
| | Ac. nitrico + VGCF | C | 64 hrs. 11.2 N |
| | Ac. nitrico + VGCF | E | 64 hrs. 11.2 N |
| | | | |
| **Electrodepositación @** | | | |
| | Ac. Nítrico + VGCF del tratamiento A + cobre** | D | 4 hrs. 5.06 N |
| | Ac. Nítrico + VGCF del tratamiento E + cobre*** | E | 4 hrs. 11.2 N |

* 0.05 moles de cobre

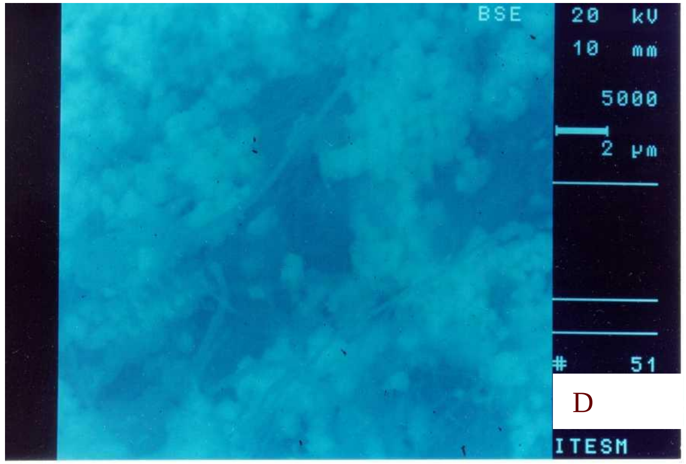
** 0.008 moles de cobre electrodepositado

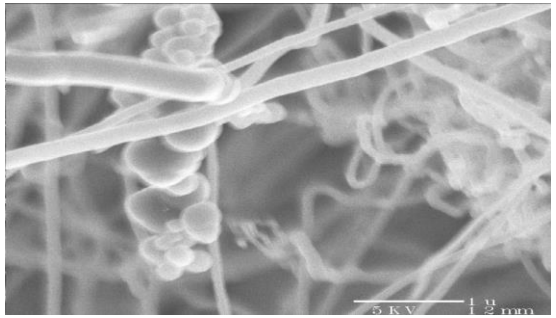
*** 0.010 moles de cobre electrodepositado

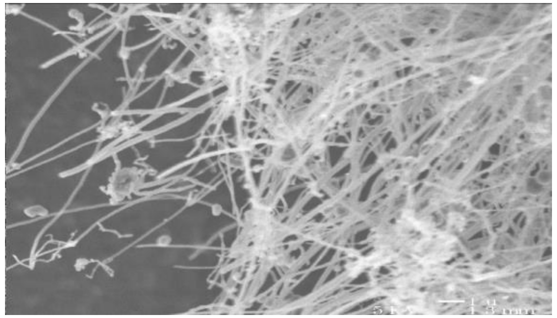
@ 1.3 Amperes, 5 Volts

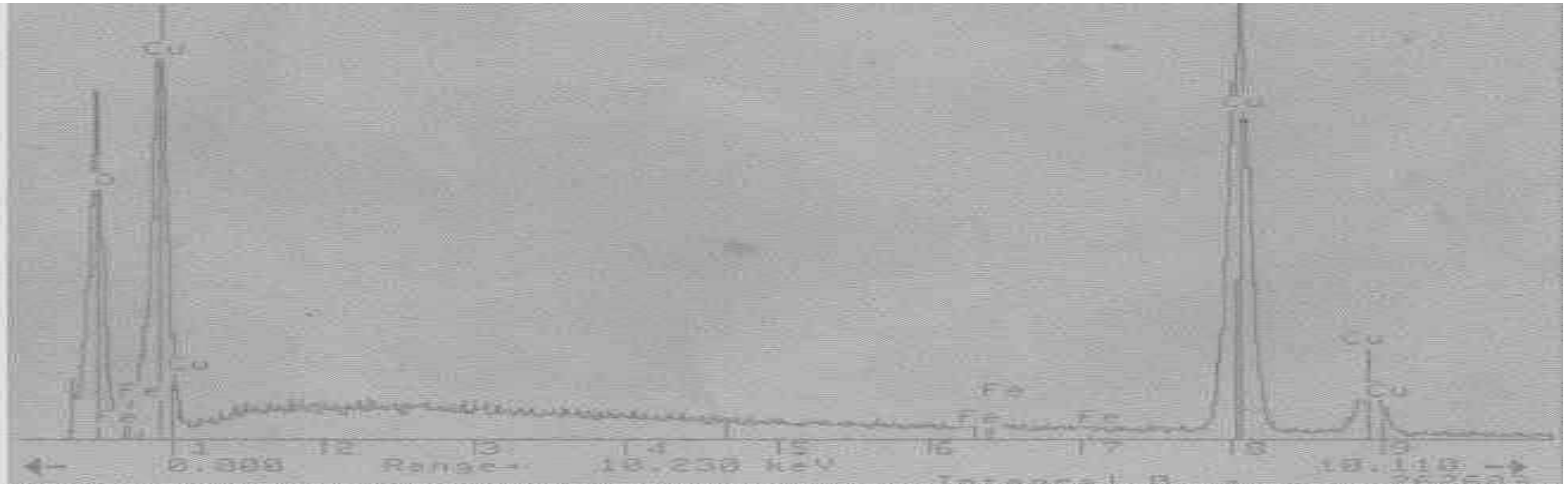
| Compositos | Abreviatura |
|---|---|
| PP ("Pellets" tal y como se reciben) | PPLL |
| PP puro (Pasados por el mezclador) | PPP |
| PP/Cu 0.1% | PPC.1 |
| PP/Cu 0.5% | PPC.5 |
| PP/Cu 1% | PPC1 |
| PP/VGCF 5% | Control 1 |
| PP/VGCF 5% (Tratamiento con agua 4hrs.) | Control 2 |
| PP/VGCF 5% (Tratamiento con ácido 11.2N + Reposo en una solución de Cu por 4 hrs. sin electrodepositación) | Control 3 |
| PP/VGCF 5% (Tratamiento con ácido 11.2N 4hrs. sin electrodepositación) | Composito B |
| PP/VGCF 5% (Tratamiento con ácido 11.2N 64hrs. sin electrodepositación) | Composito C |
| PP/VGCF 5% (Tratamiento con ácido 5.06N 4hrs. y electrodepositación) | Composito D |
| PP/VGCF 5% (Tratamiento con ácido 11.2N 64hrs. y electrodepositación) | Composito E |

# Results



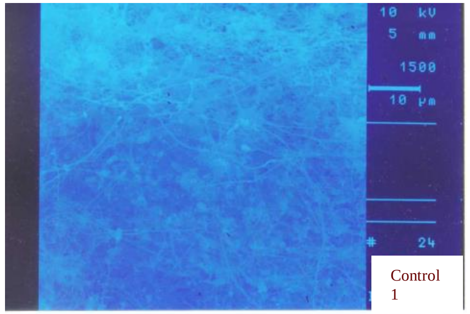




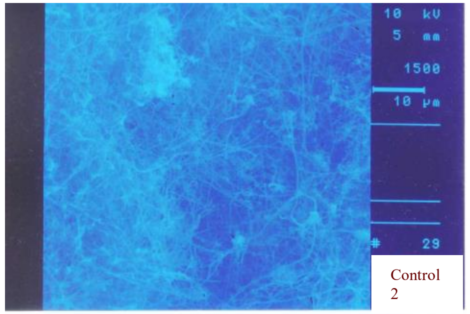

Cu on VGCF was found by XSD

# Results

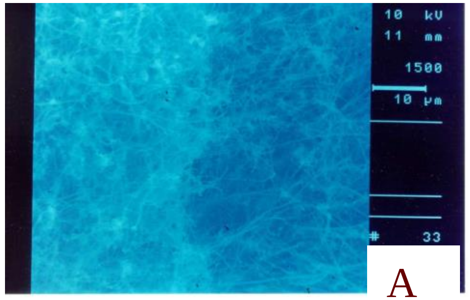
Observación morfológica de las VGCF en un miroscopio electrónico de barrido Zeiss DSM 960



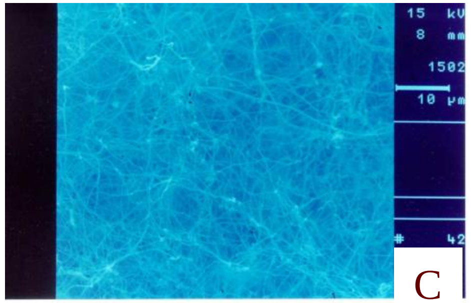

Control 1



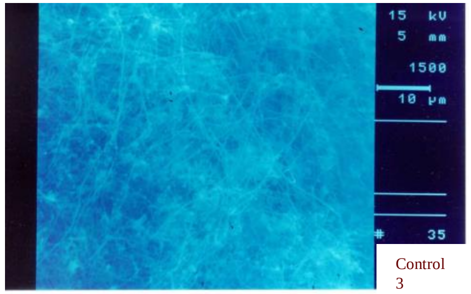

Control 2



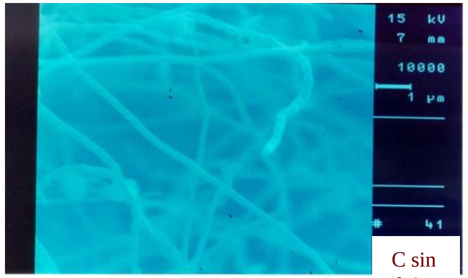

A




C




Control 3

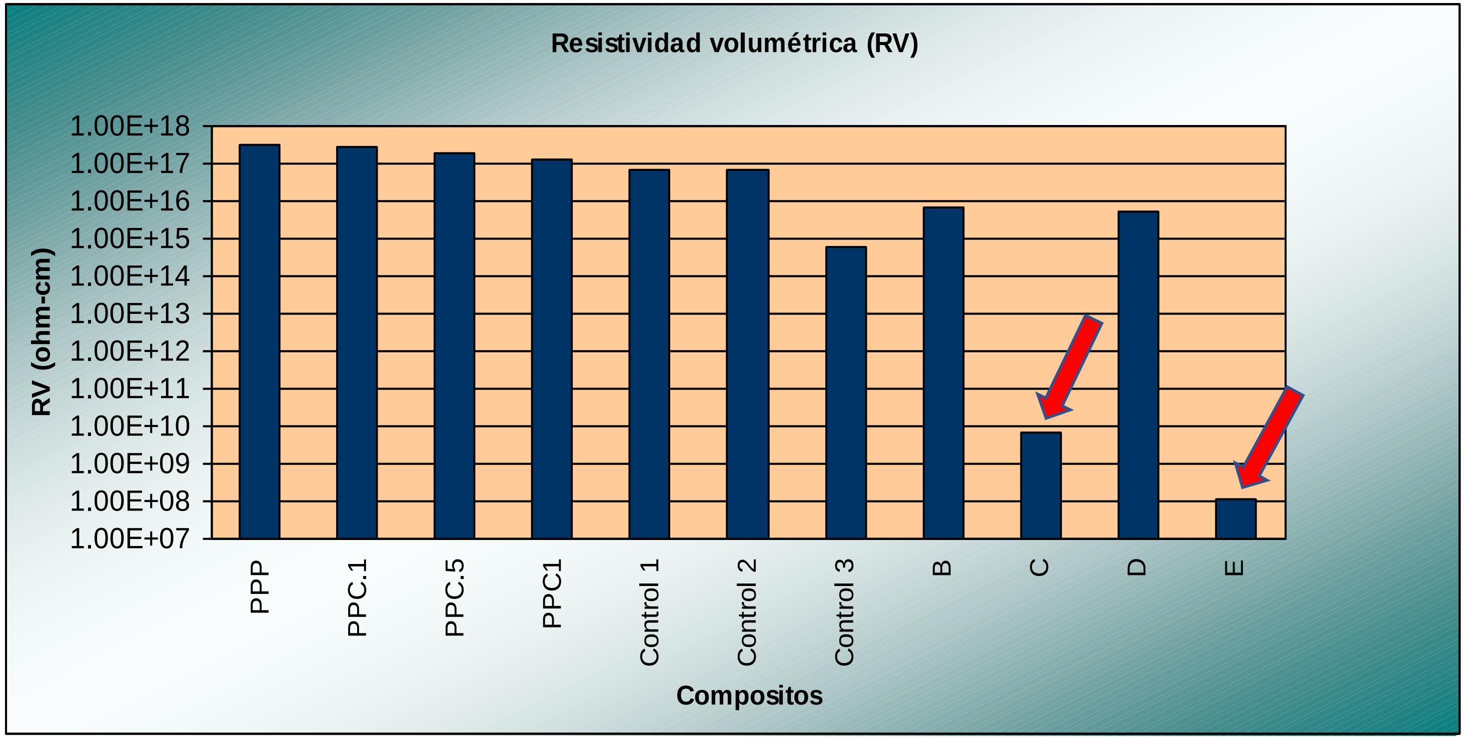



C sin daño s

- VGCFs, as received, have a large amount of amorphous carbon.
- The treatments with water and ac. Nitric 5.06 N did not help to remove amorphous carbon (cleaning) from VGCF.
- Treatment with ac. Nitric 11.2 N cleans VGCFs without apparent damage, therefore this is the best treatment to clean them.

# Results

AntiStatic Values between: 1X10$^5$ a 1x10$^{11}$




Elaborado bajo la norma ASTM-257. En un Keithley instruments, INC. 6105 resistivity adapter.

| Composit o | Lado | RS (ohms/por superficie cuadrada) Medición inicial con una humedad relativa del 50%. | RS (ohms/por superficie cuadrada) Segunda medición después de 48 horas con una humedad relativa menor al 28%. |
|---|---|---|---|
| C | 1 | 1x10$^{13}$ to 1x10$^{14}$ | 1x10$^{13}$ to 1x10$^{14}$ |
| | 2 | 1x10$^{11}$ to 1x10$^{14}$ | 1x10$^{12}$ to 1x10$^{14}$ |
| E | 1 | 1x10$^{9}$ to 1x10$^{11}$ | 1x10$^{9}$ to 1x10$^{11}$ |
| | 2 | 1x10$^{10}$ to 1x10$^{12}$ | 1x10$^{9}$ to 1x10$^{11}$ |

Under the Norm ANSI/EOS/ESD-S11.11-1993.

# Conclusions

- Chemical treatment is a process that allows obtaining clean VGCF without altering its structure.

- The electrodeposition of copper on the VGCF results in composites with high conductivity that allows achieving the conductivity threshold with a lower concentration of VGCF.

- The electrodeposition of copper, as well as ac treatments. Nitric is a successful process for increasing the conductivity of composites without significantly altering their rheological and mechanical properties.

Ministry of Environment and Food of Denmark
Environmental Protection Agency

# Carbon nanotubes

## Types, products, market, and provisional assessment of the associated risks to man and the environment

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# Environmental

- *“In chapter 4 we demonstrated that there is a potential environmental release during especially CNT production and handling as well as discard of waste and accidents during transport (Tables 4-1 and 4-2). Air and waste stream pathways were both important for the release to the environment. However, no monitoring data were available on the environmental release and exposure to the general public.”*

- *“7.6 Provisional Integrated Risk assessment*

*Due to the still very limited knowledge on the CNT exposure to workers and consumers, an integrated risk assessment is highly uncertain. We are aware of no measured data on the environmental release and exposure in environment. Similarly, the human and environmental toxicity of CNT is far from being fully investigated. Therefore, combining the uncertain data-sets into a valid integrated risk assessment will be associated with even greater uncertainty.”*

*“7.7 Concluding remarks*

- *It is evident that there is still a lack of publically available systematic toxicological studies on CNT that can be applied for establishment of exposure limits and applied for regulatory purposes. Hypotheses have been established proposing that the toxicity of CNT should vary with the side-wall topology (i.e. type of CNT), their persistence in biological compartments, their length and diameter, contents of impurities, and (bio-)chemical reactivity. There is clearly a need to improve the material and exposure characterization for all of these endpoints in a harmonized manner and implement such information in toxicological studies. Especially, it may be of crucial importance to improve our understanding of the biological interaction, both for CNT within and outside the scope of high- aspect ratio nanomaterials.*
- *Based on scientifically derived occupational exposure limits and results from reviews, the proposed inhalation exposure limits are one to three orders of magnitude lower than the currently regulatory enforced exposure limits for CNT. The highest exposure limit was derived by Kobayashi et al 107 who suggested that an exposure yo be 210 µg /m3 was acceptable for working 8 hours/day 5 days a week. Pauluhn has suggested an occupational exposure limit of 50 µg/m3 166 based on his own OECD guideline inhalation experiment 167. In 2010, NIOSH proposed a recommended exposure limit (REL) of 7 µg/m3 of CNT or carbon nanofibers in air as an eight-hour, time-weighted average, respirable mass concentration (www.cdc.gov/niosh/docket/review/docket161A/). This value was re-adjusted to be 1 µg carbon/m3 in April, 2013 (http://www.cdc.gov/niosh/docs/2013-145). “*