TÉCNICO LISBOA

Nanostructured Materials and Nanotechnology
2022-2023

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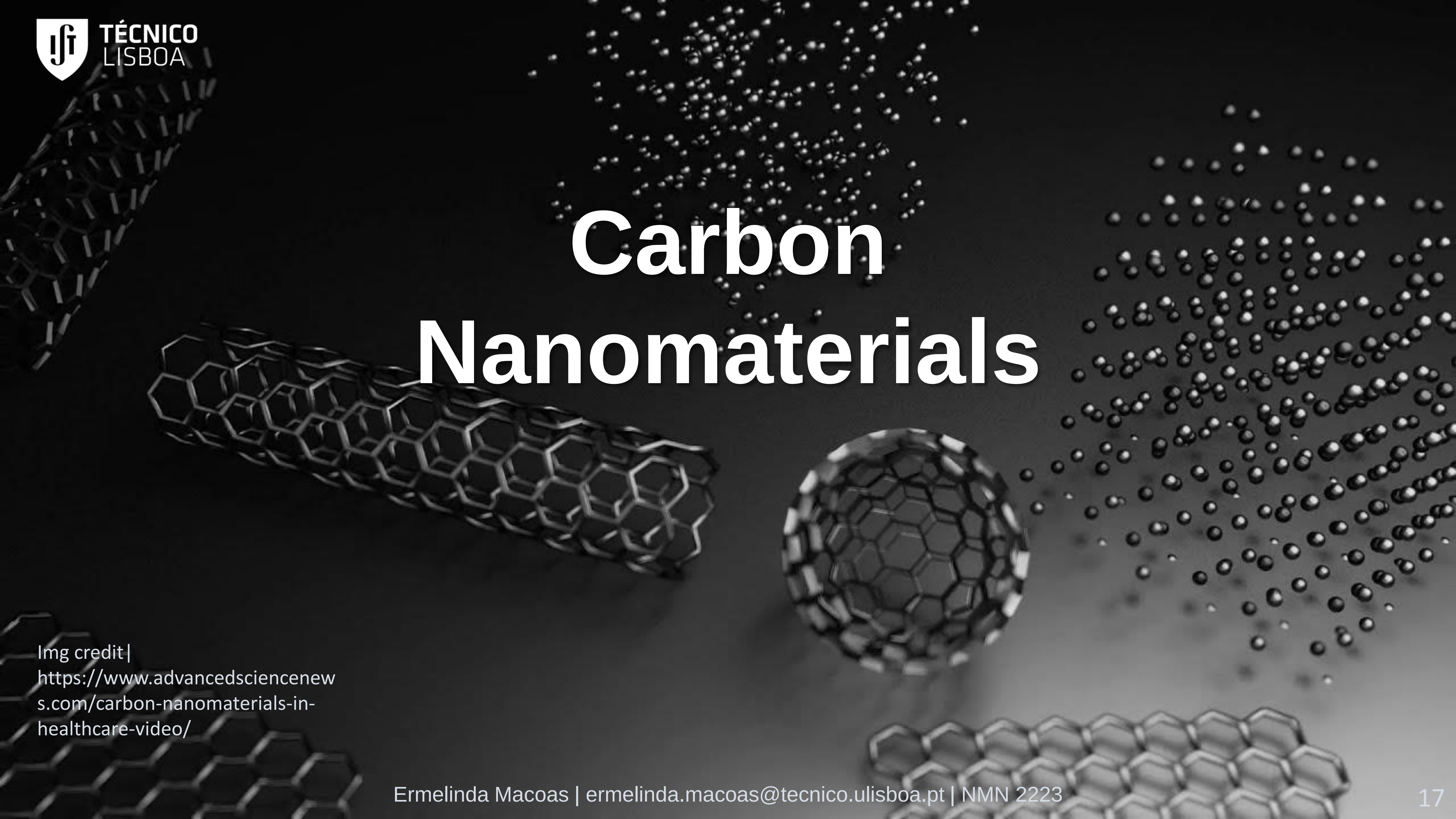

Carbon Nanomaterials

Img credit| https://www.advancedsciencenews.com/carbon-nanomaterials-in-healthcare-video/

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Content

1. Brief introduction to carbon nanomaterials
2. What is so special about carbon? Carbon hybridization
3. Fullerenes, 1st 0D carbon nanomaterial
4. Carbon nanotubes:

    SWNT, MWNT

    Chiral vector and characterization according to the electrical conductivity properties (metal and semi-conductor),

    Fabrication & purification methods

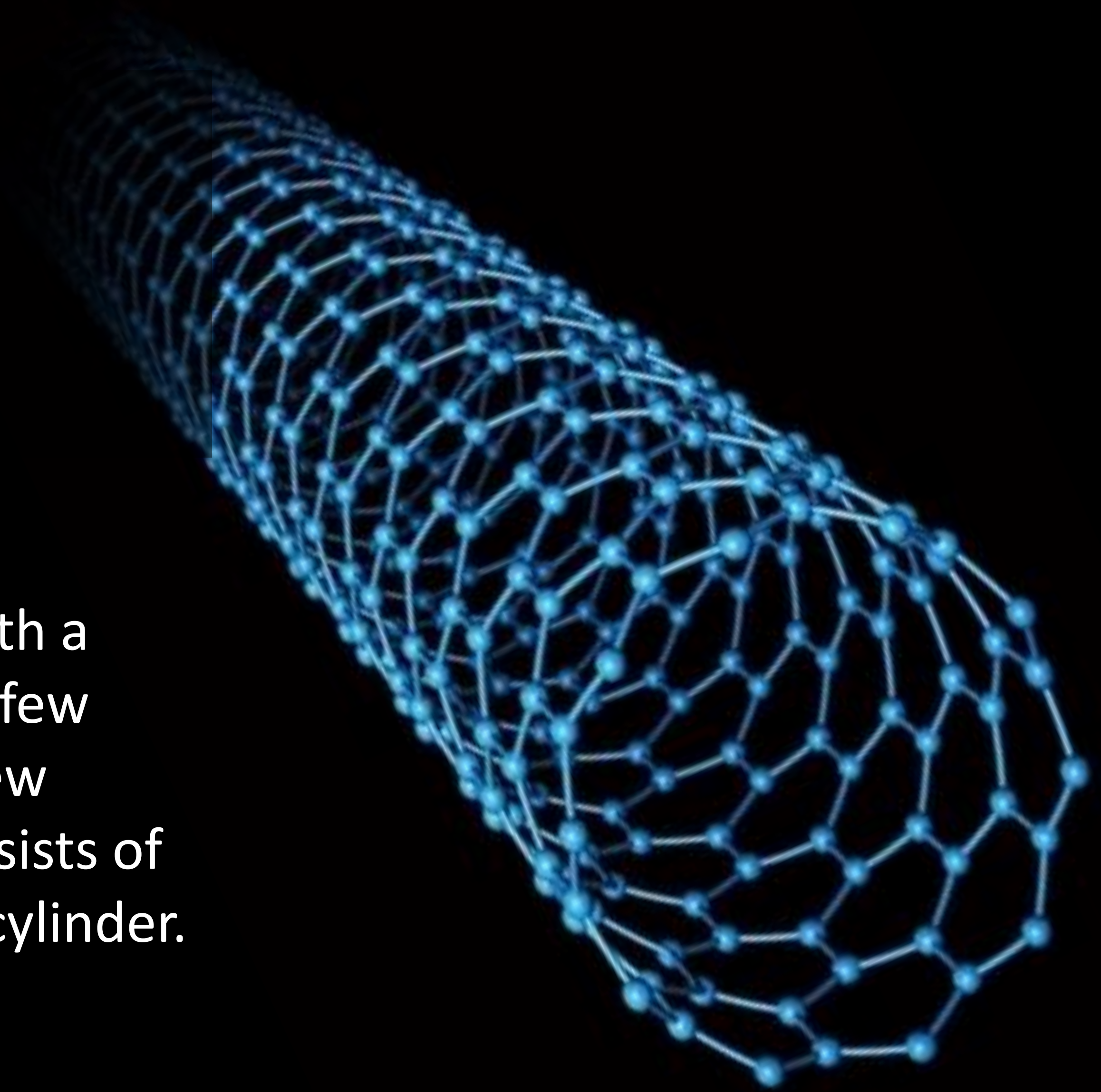
    Characterization techniques,

    Properties,

    Applications

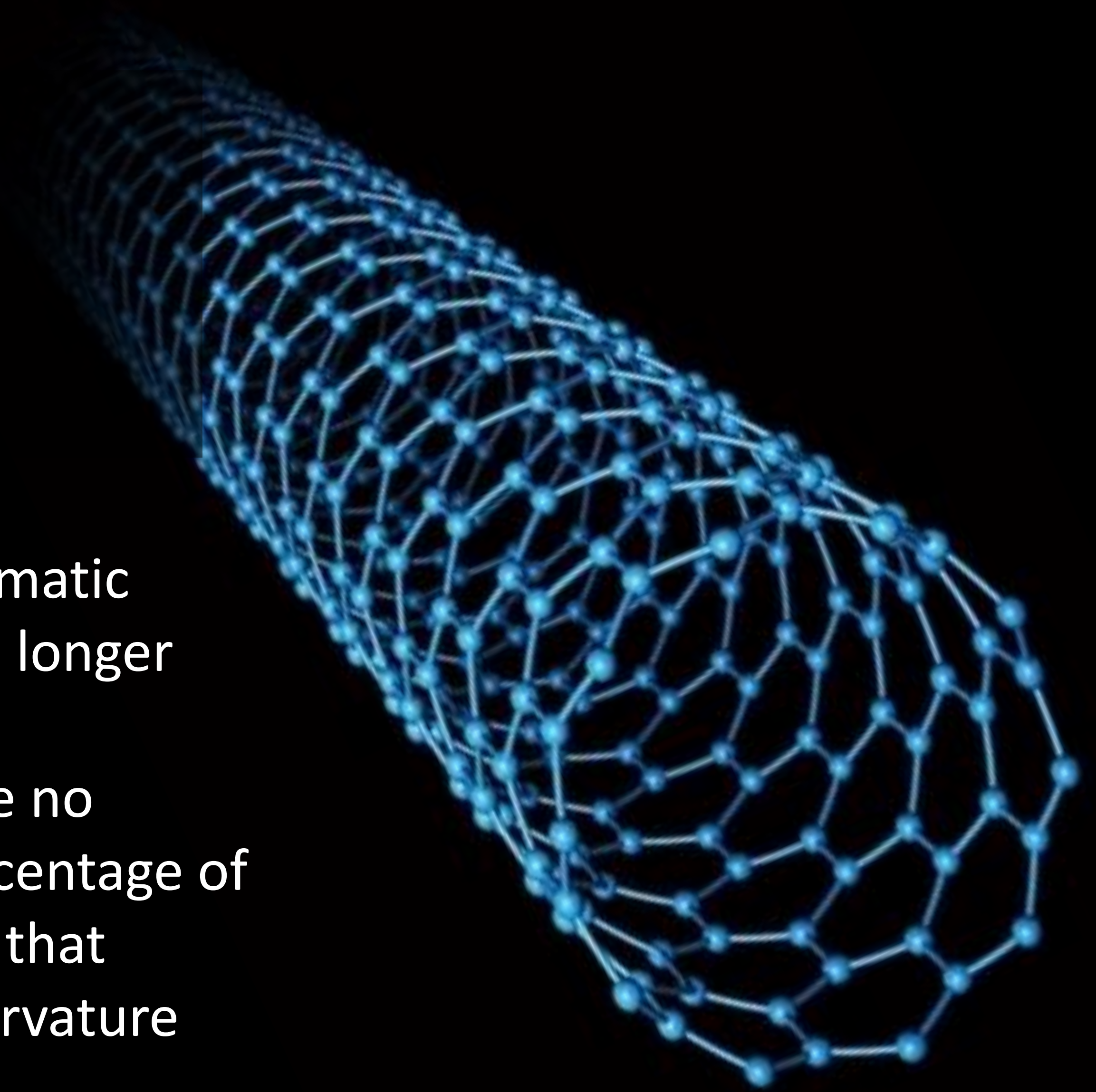
    Market overview

Carbon NanoTubes



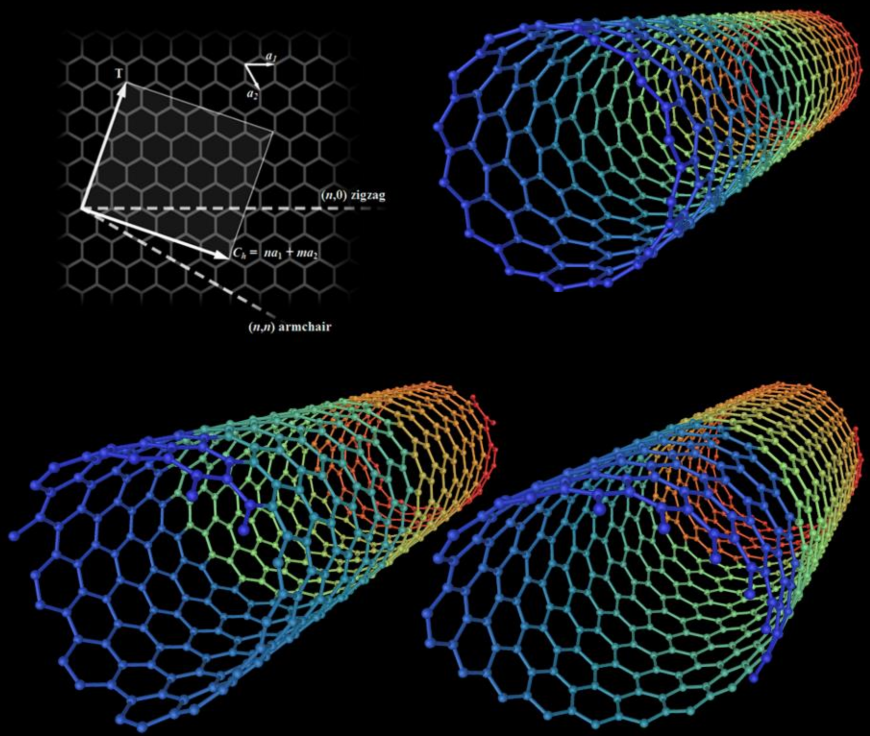
CNTs are cylindrical molecules with a diameter ranging from 1 nm to a few nanometers and length up to a few micrometers. Their structure consists of a graphite sheet wrapped into a cylinder.

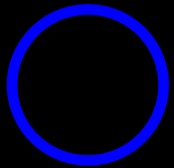
Carbon NanoTubes

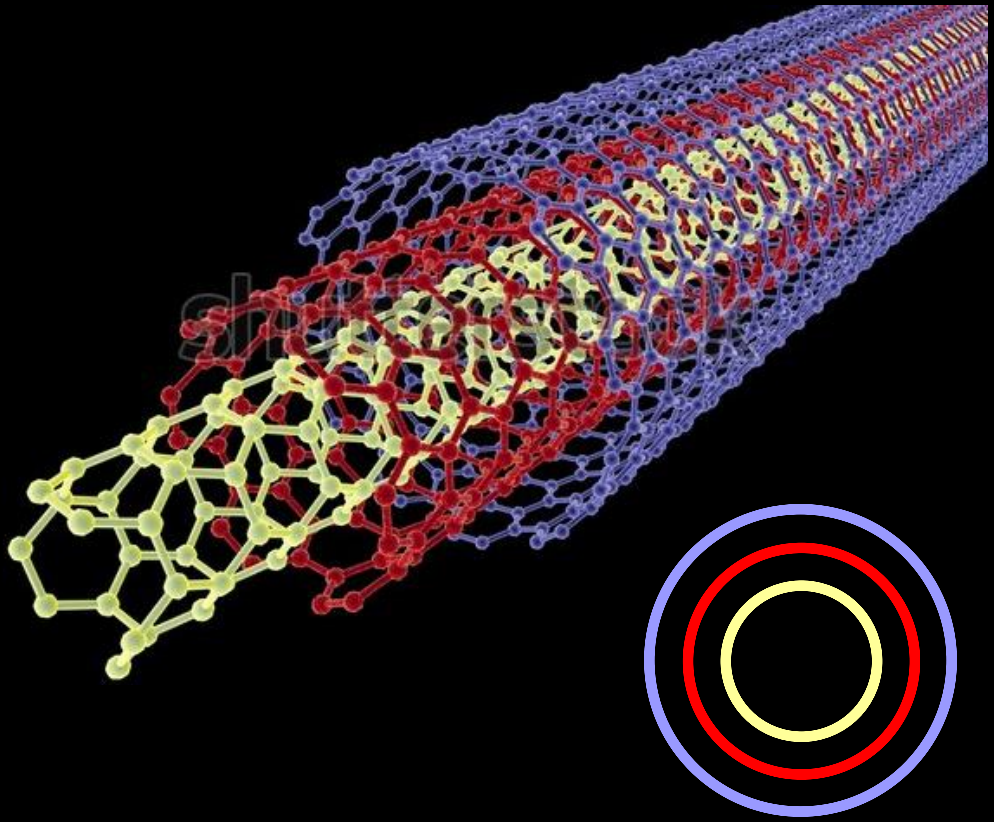


Carbon atoms are involved in aromatic rings, the C=C bond angles are no longer planar as they should ideally be. Hybridization of carbon atoms are no longer pure sp^2 but get some percentage of the sp^3 character, in a proportion that increases as the tube radius of curvature decreases

Single Wall and Multiwall CNTs







- Controlled synthesis
- Poor purity
- More pliable

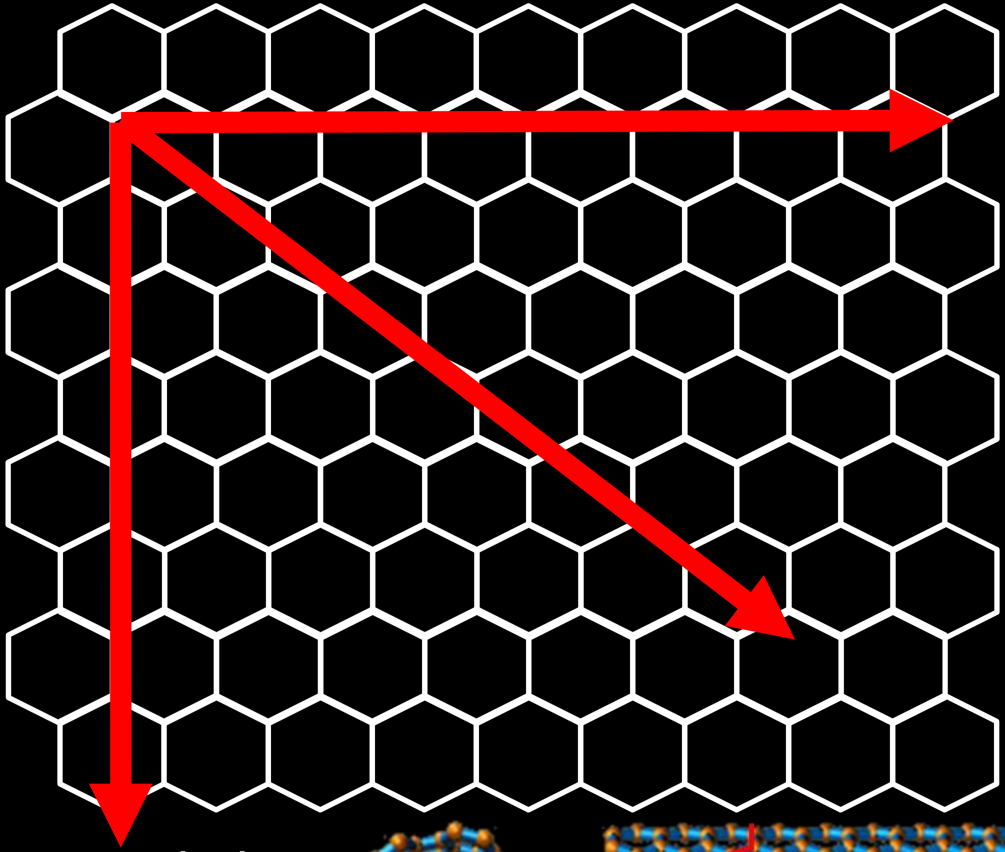
- One layer
- Diameter ~0.4 - 3 nm

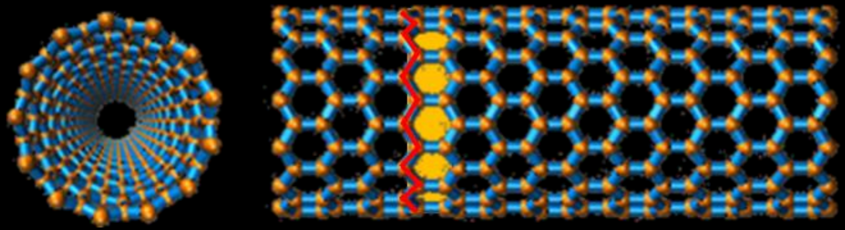
- Simple synthesis
- High purity
- More rigid

- Multiple layers
- Diameter ~3 - 100 nm
- Inter-layer spacing 0.35 nm

SWNT

Properties depend on the orientation of the hexagonal network with respect to the nanotube long axis, a property known as chirality

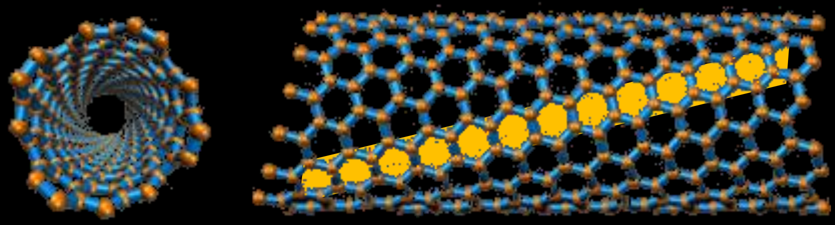




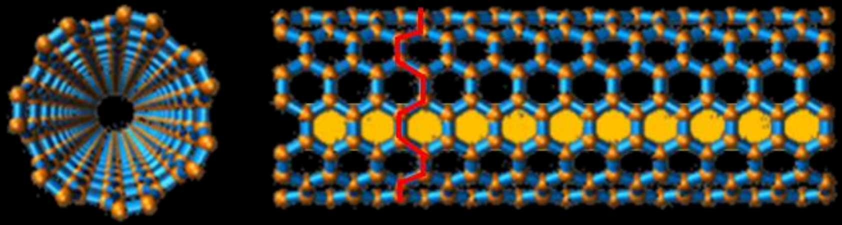
Zigzag
semiconductors

High current on/off
High carrier mobility for FETs

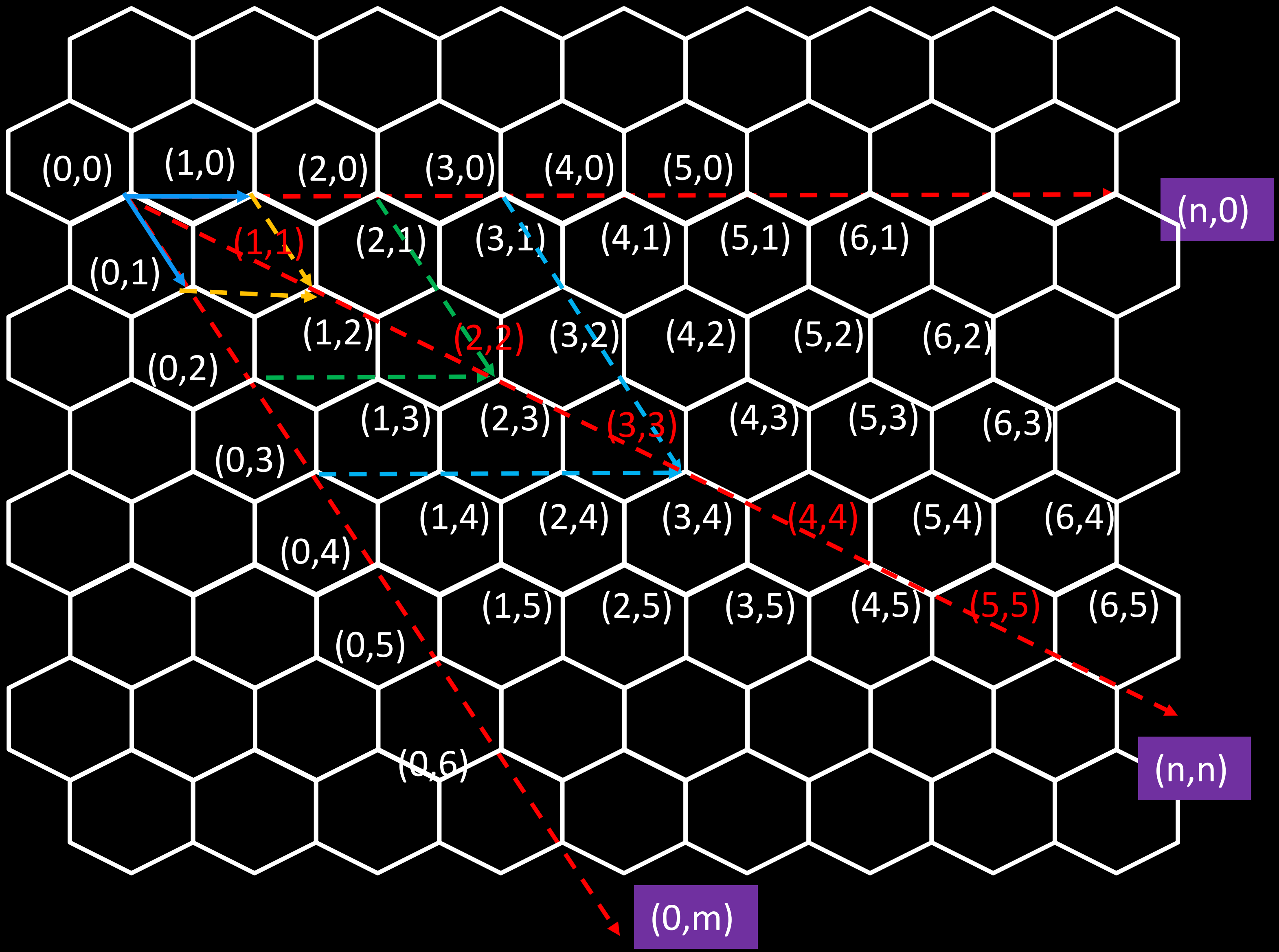
chiral



Armchair
metallic



Ballistic transport, ultrahigh current densities for interconnectors in circuits and conductive films



Lattice vectors

$a_1 = a_2 = a = 0.246$ nm

(a, lattice constant of graphite)

Chiral Vector

Direction for rolling the sheet so that the origin of the vector coincides with the end point

$\mathbf{Ch} = n\,\mathbf{a}_1 + m\,\mathbf{a}_2$

Nanotube diameter

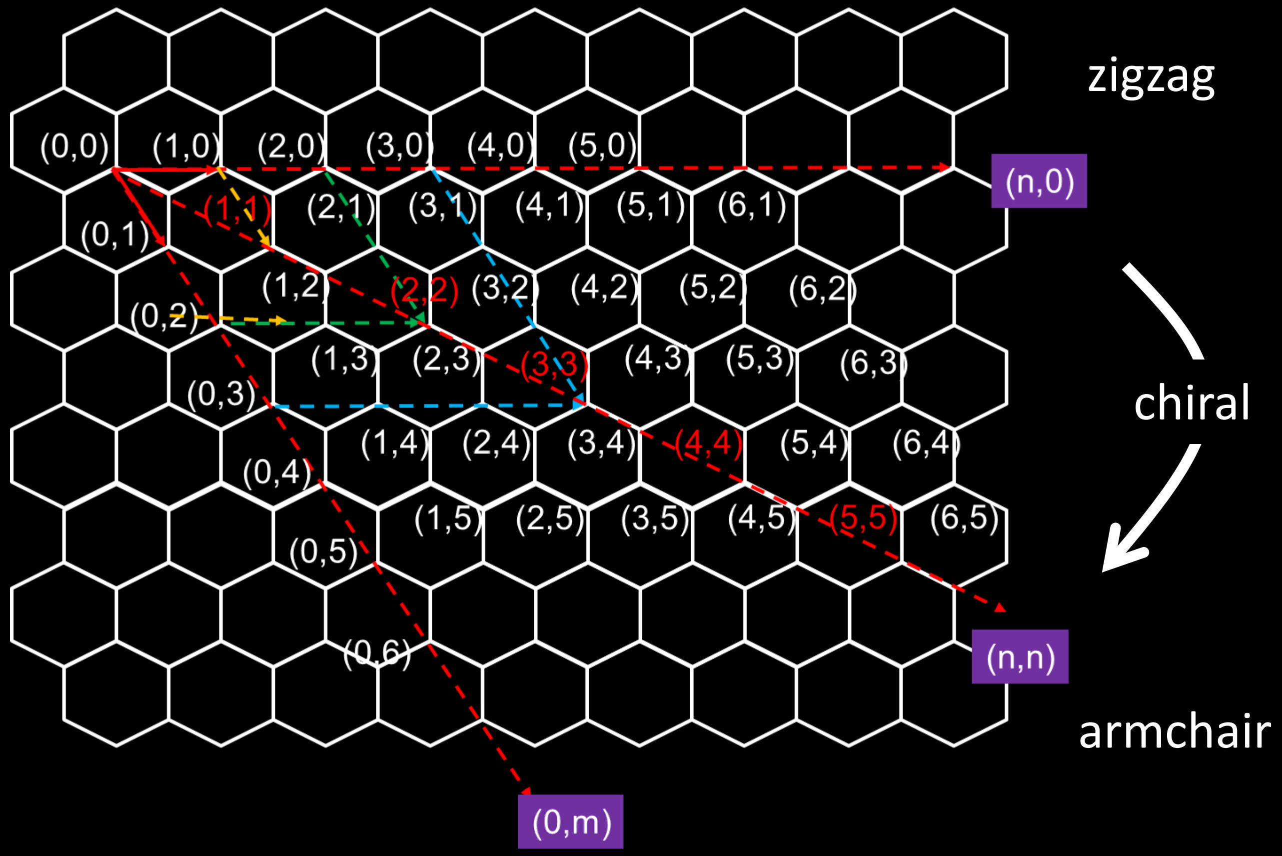
$$d = \frac{a\sqrt{m^2 + mn + n^2}}{\pi}$$

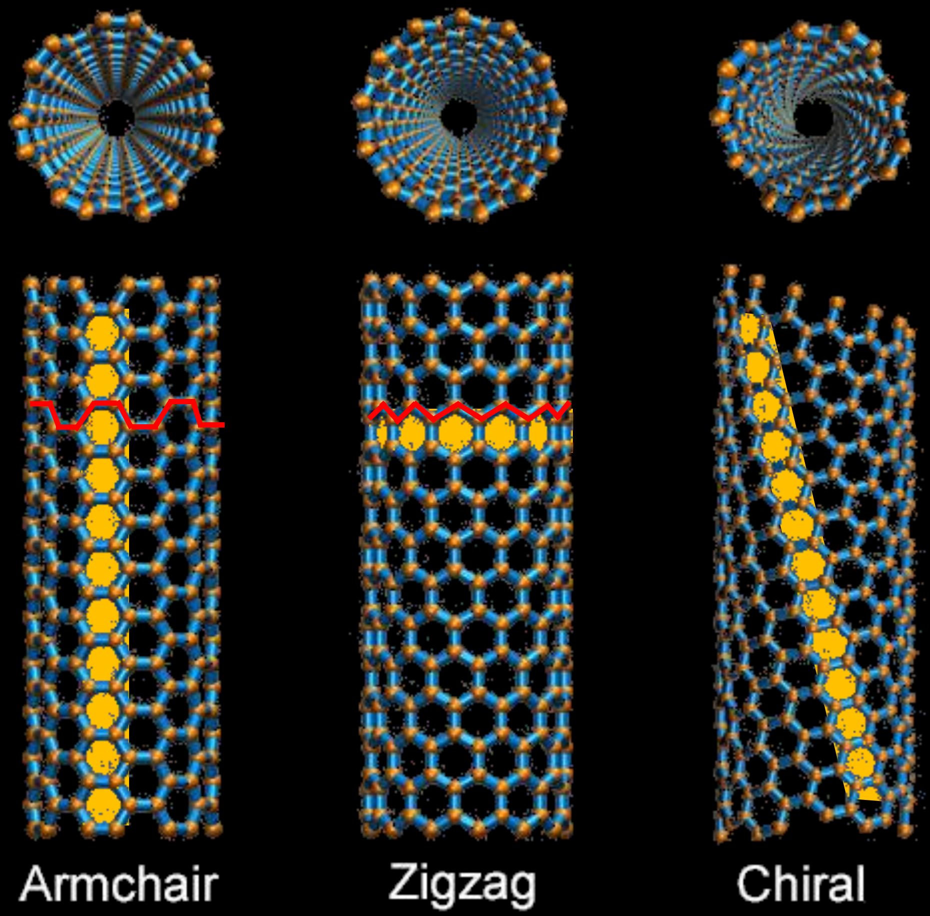
Chiral angle

$$\theta = tan^{-1}\left(\frac{m\sqrt{3}}{m + 2n}\right)$$

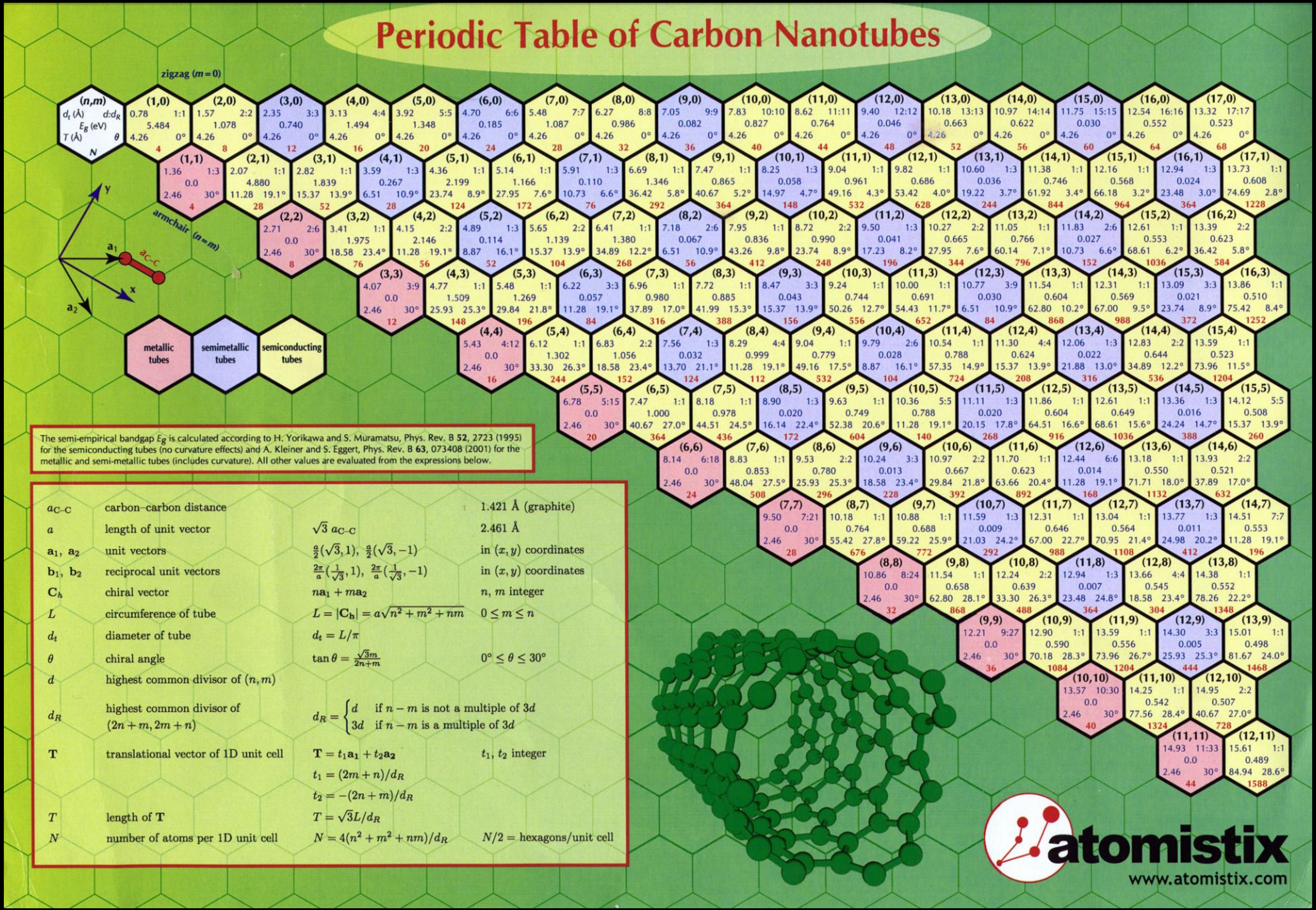
Armchair nanotubes and those where *n*−*m* is a multiple of 3 are metallic

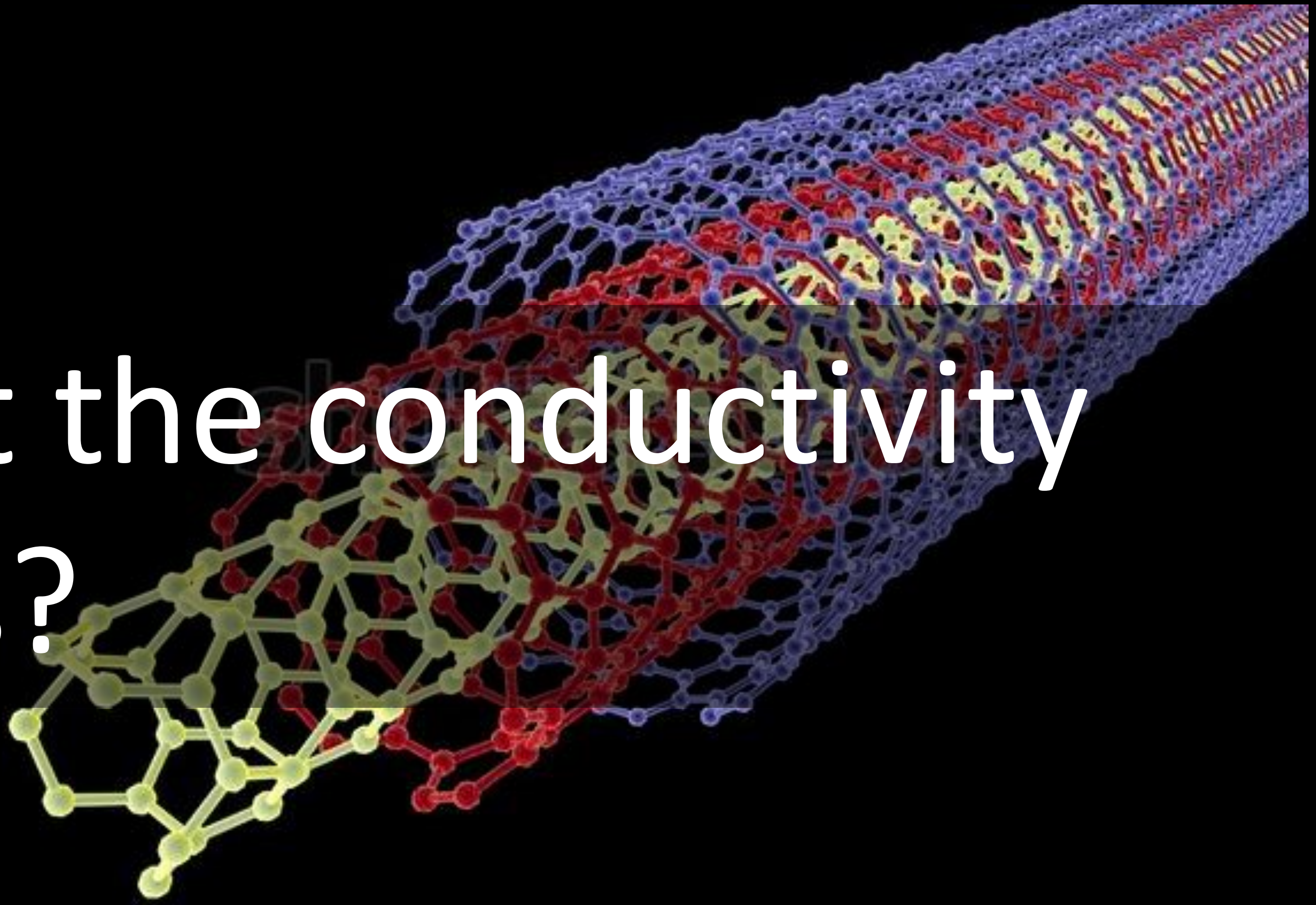
Other forms are semiconductor





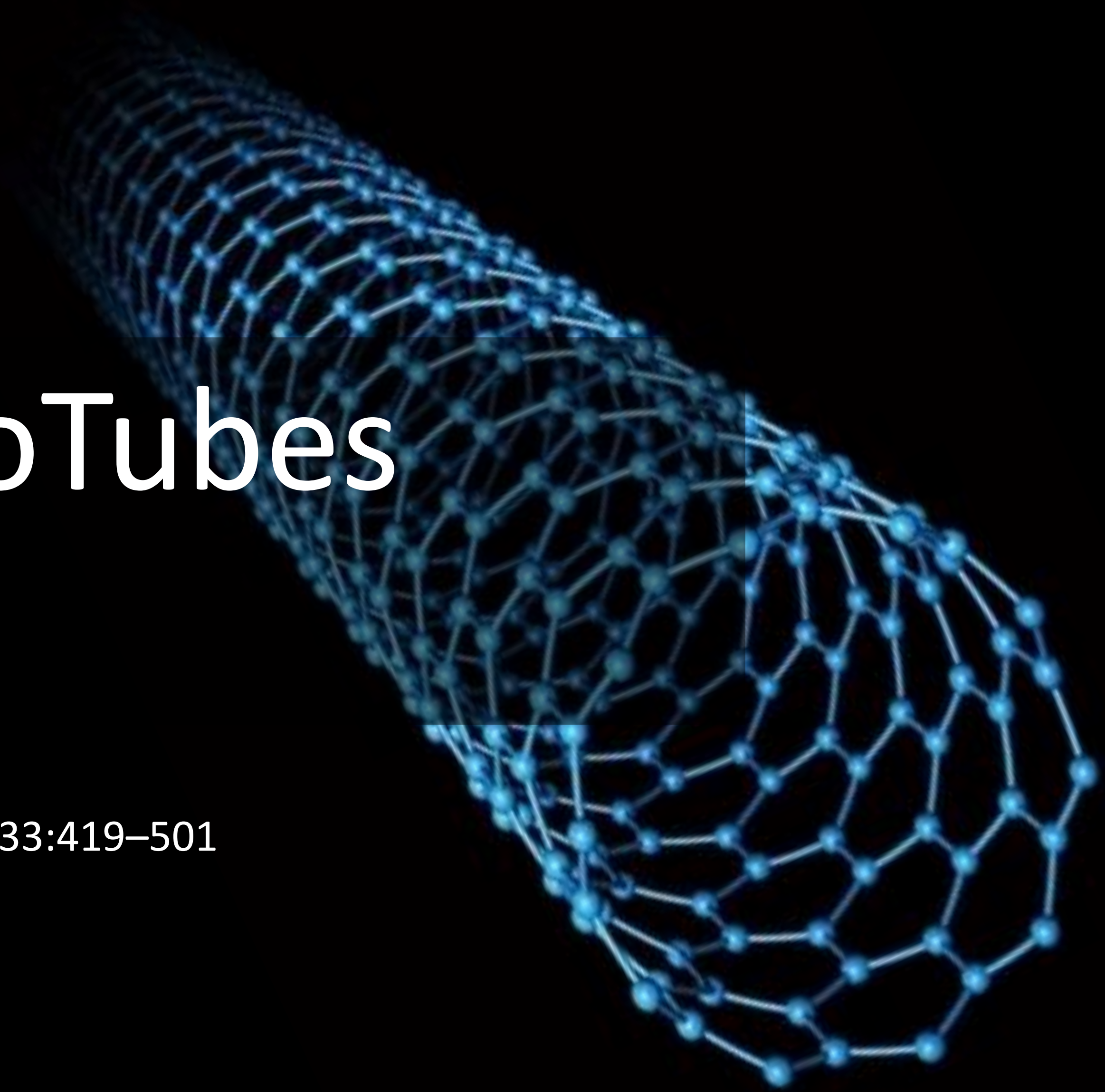
$n=m$ $\theta = 30^0$ $m=0$ $\theta = 0^0$ $0^0 < \theta < 30^0$


Periodic Table of Carbon Nanotubes
zigzag (m = 0)
armchair (n = m)
(n,m)
d_t (Å) $d{:}d_R$
E_g (eV)
T (Å) θ
N
metallic tubes
semimetallic tubes
semiconducting tubes
The semi-empirical bandgap E_g is calculated according to H. Yorikawa and S. Muramatsu, Phys. Rev. B 52, 2723 (1995) for the semiconducting tubes (no curvature effects) and A. Kleiner and S. Eggert, Phys. Rev. B 63, 073408 (2001) for the metallic and semi-metallic tubes (includes curvature). All other values are evaluated from the expressions below.
a_{C-C} carbon–carbon distance 1.421 Å (graphite)
a length of unit vector $\sqrt{3}\,a_{C-C}$ 2.461 Å
$\mathbf{a}_1, \mathbf{a}_2$ unit vectors $\frac{a}{2}(\sqrt{3},1)$, $\frac{a}{2}(\sqrt{3},-1)$ in (x,y) coordinates
$\mathbf{b}_1, \mathbf{b}_2$ reciprocal unit vectors $\frac{2\pi}{a}(\frac{1}{\sqrt{3}},1)$, $\frac{2\pi}{a}(\frac{1}{\sqrt{3}},-1)$ in (x,y) coordinates
$\mathbf{C}_h$ chiral vector $n\mathbf{a}_1 + m\mathbf{a}_2$ n, m integer
L circumference of tube $L = |\mathbf{C_h}| = a\sqrt{n^2+m^2+nm}$ $0 \le m \le n$
d_t diameter of tube $d_t = L/\pi$
θ chiral angle $\tan\theta = \frac{\sqrt{3}m}{2n+m}$ $0° \le \theta \le 30°$
d highest common divisor of (n,m)
d_R highest common divisor of $(2n+m, 2m+n)$ $d_R = \begin{cases} d & \text{if } n-m \text{ is not a multiple of } 3d \\ 3d & \text{if } n-m \text{ is a multiple of } 3d \end{cases}$
$\mathbf{T}$ translational vector of 1D unit cell $\mathbf{T} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2$ t_1, t_2 integer
$t_1 = (2m+n)/d_R$
$t_2 = -(2n+m)/d_R$
T length of $\mathbf{T}$ $T = \sqrt{3}L/d_R$
N number of atoms per 1D unit cell $N = 4(n^2+m^2+nm)/d_R$ $N/2$ = hexagons/unit cell
atomistix
www.atomistix.com



What about the conductivity of MWCNTs?

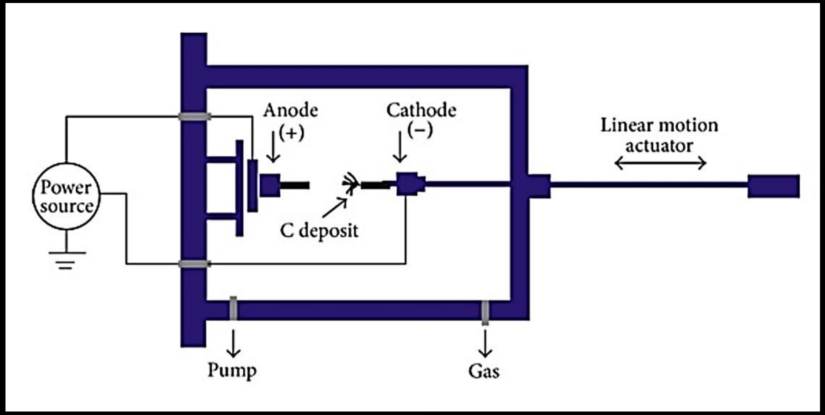
Carbon NanoTubes Fabrication



M. Terrones, Annu. Rev. Mater.Res. 2003. 33:419–501

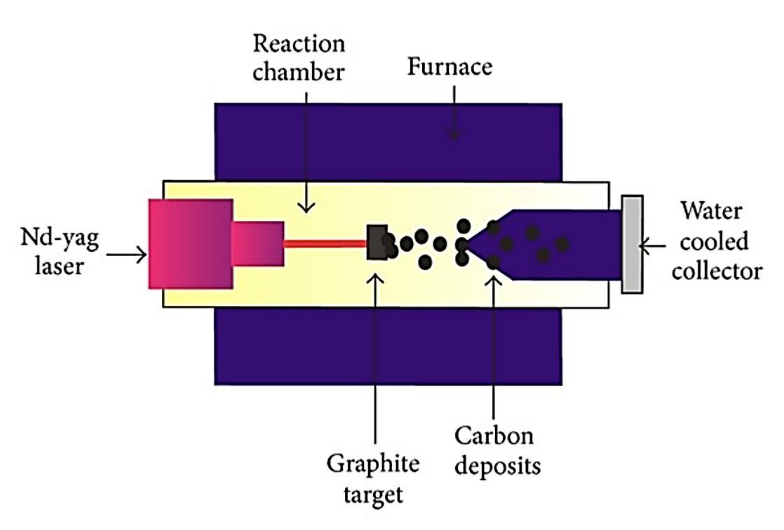
Production methods

Electric arc discharge (1st observation)

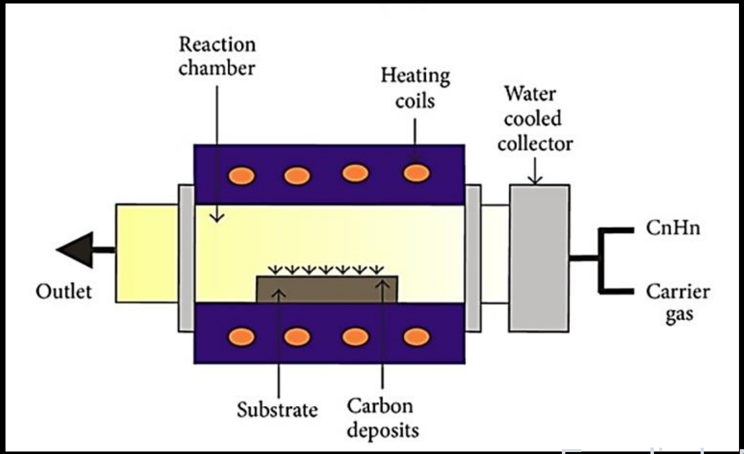


Carbon atoms are generated through an electric arc discharge at T> 3000ºC between two graphite rods. Nanotubes are formed in the presence of suitable catalyst metal particles (Fe, Co or Ni)

Laser ablation



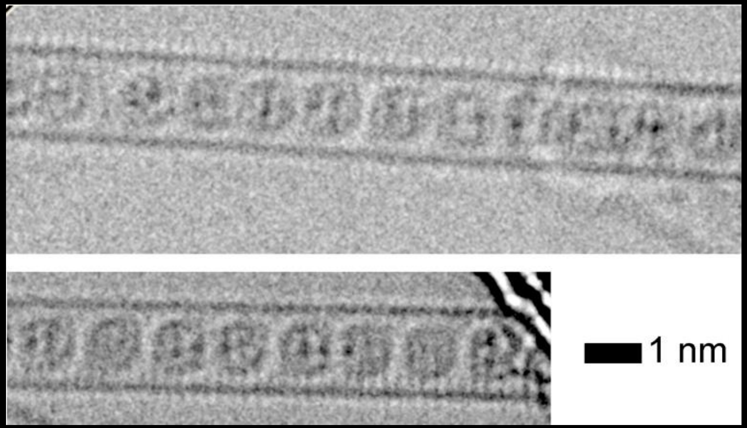
Generation of atomic carbons at T>1200ºC through laser irradiation of graphite containing appropriate amounts of catalyst particles (Fe, Co or Ni) is followed by formation of nanotubes

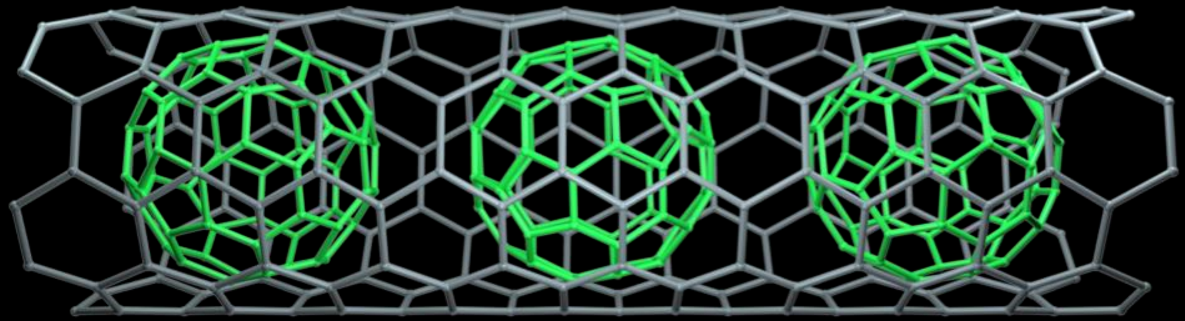


CVD with catalytic decomposition of hydrocarbon

Decomposition of a gaseous hydrocarbon source (acetylene, ethylene, ethanol or methane) is catalyzed by metal nanoparticles (Co or Fe). Particles can be prepared by pyrolysis of suitable precursors ($Fe(CO)_5$) at 1000-1100 ºC under high pressure and placed inside the chamber

Peapod methods for DWNTs





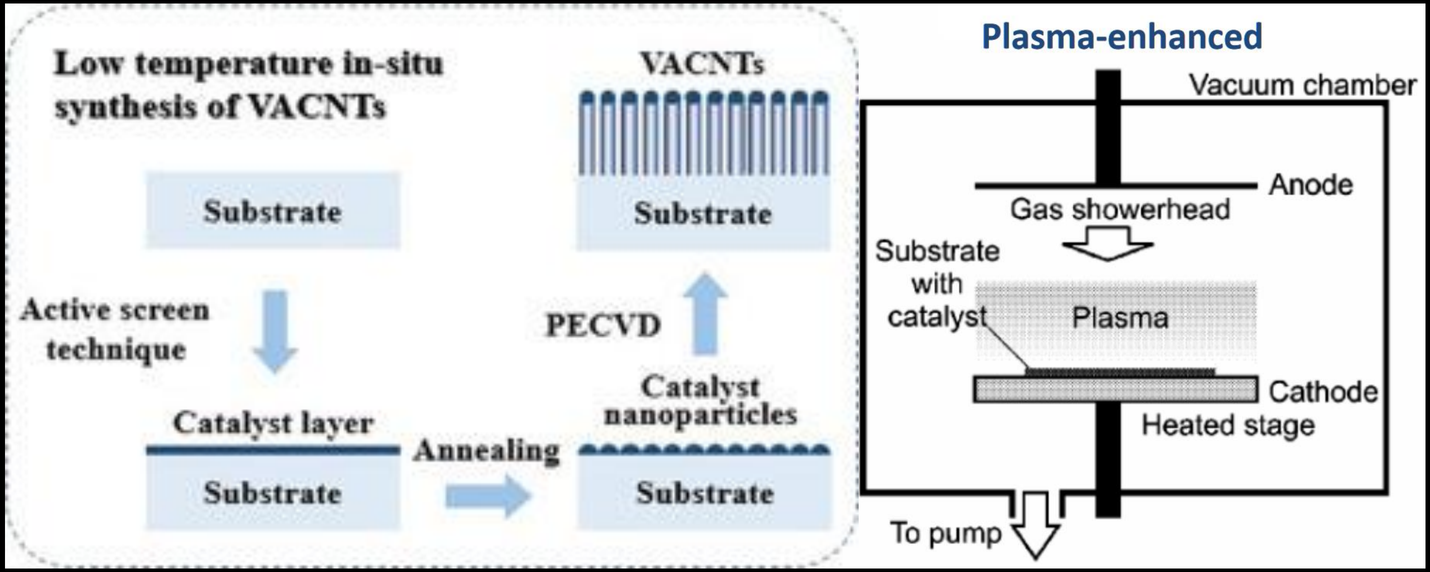
Fullerene filled SWNTs are known as ‘‘peapods’’

DWNTs are selectively produced by annealing carbon peapods in vacuum or inert gas atmosphere

Nanoscale, 2011, 3, 503–518. doi: 10.1039/c0nr00620c


WomenInNano
WomenInNano
in collaboration with
nano2hybrids
Nano2Hybrids
and
Vega Science Trust
VEGA
presents
http://vega.org.uk

Production methods: VANTAs

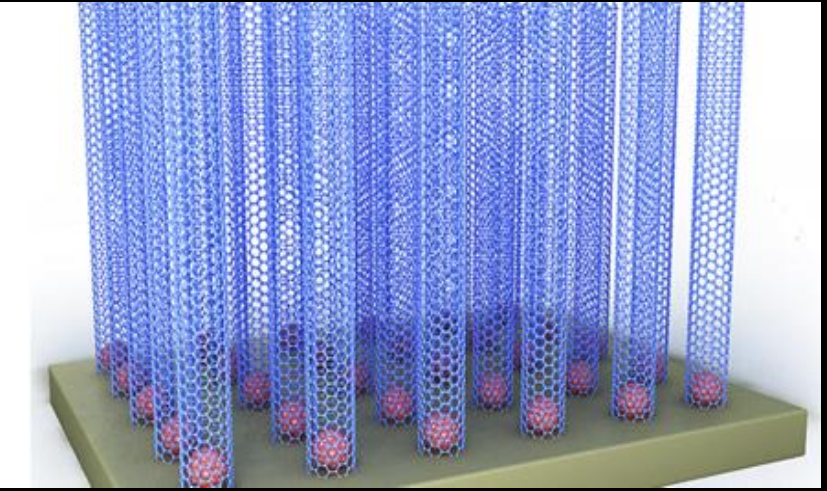


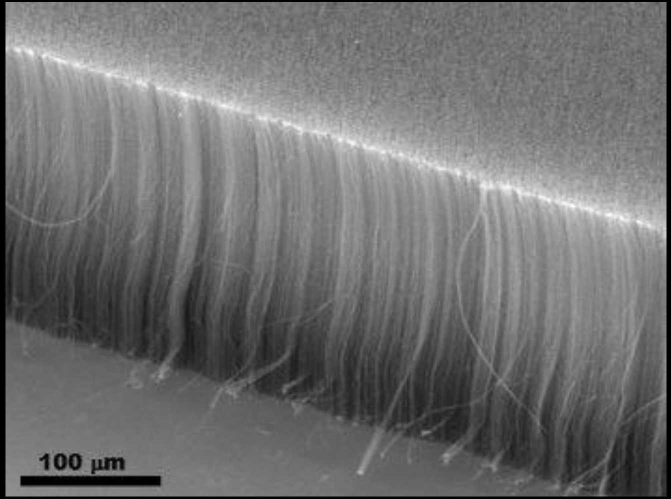
Catalyst nanoparticle deposition followed by Plasma Enhanced CVD

In VACNT carbon nanotubes are grown in an array oriented along their longitudinal axis normal to the surface

A sputtered thin film of catalyst (e.g. 1 nm of Fe) is applied. During heating, the film de-wets, creating islands of iron that nucleate nanotubes. The support must be conductive
C_2H_2 is typically the carbon source

In DC-PECVD a typical procedure is conducted at a pressure of 8 Torr in NH_3 and at a growth temperature in the range of 450–600º
High purity (99.98% carbon) VANTAs consisting of SWNTs have been grown as long as 0.5 cm





https://www.youtube.com/watch?v=fg2x0L4YAuU

The blackest black (Vantablack)

“It absorbs 99-plus percent of light. There are virtually no reflections. Seen against a black background, the car appears two-dimensional.”

Purification

Remove catalyst, carbon particles/amorphous carbon, unvaporized graphite
Tips opening
Introduction of functional groups

Thermal oxidation in air (350ºC)

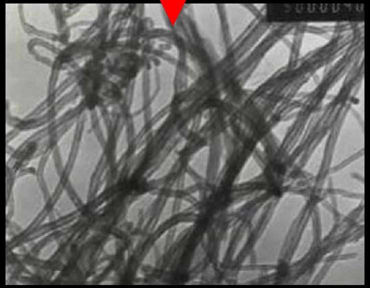
Oxidation of carbonaceous impurities

Acid Reflux (HCl)

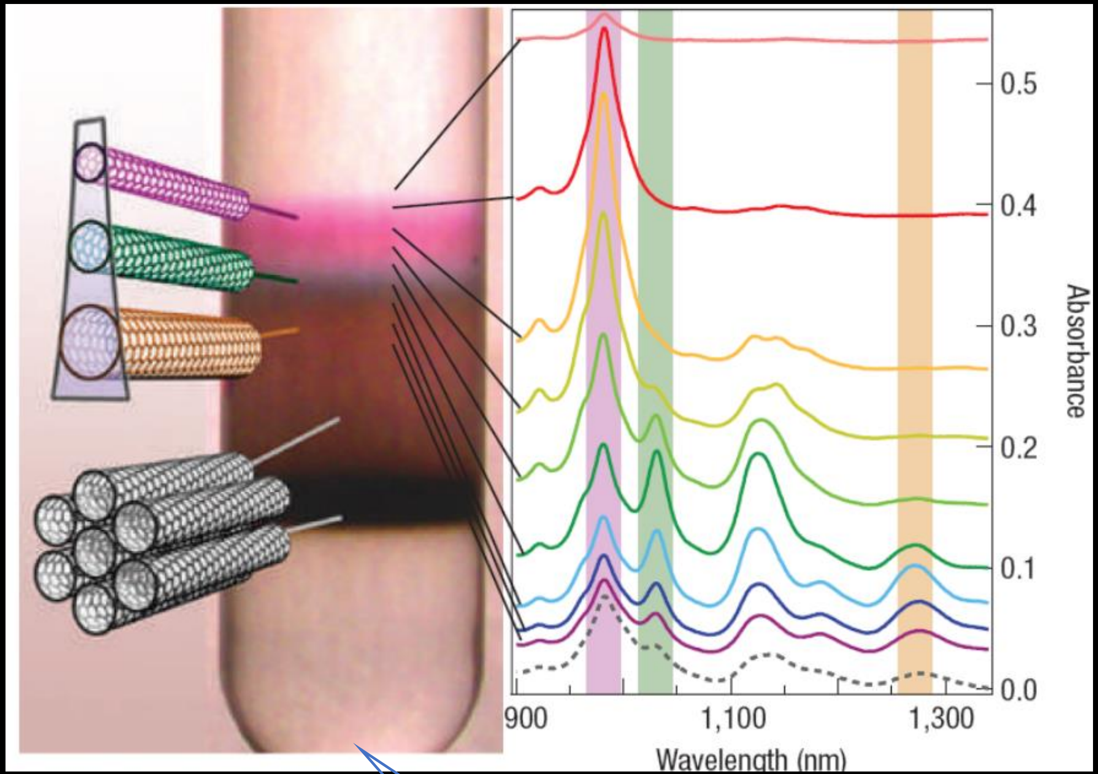
Dissolution of metallic impurities

Filtration

Thermal annealing (1100ºC)

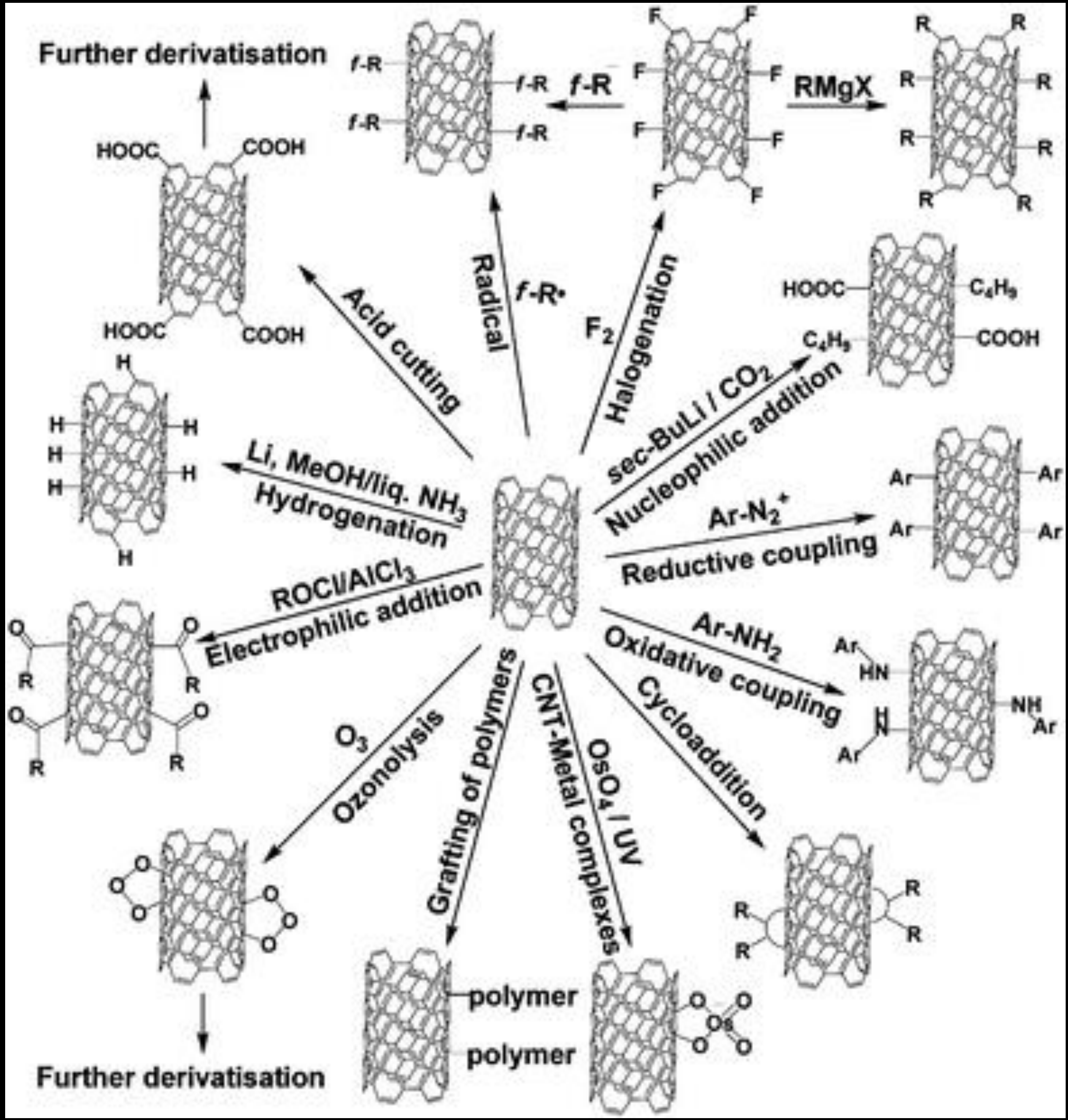


Carbon, 2008, 46(15) 2003



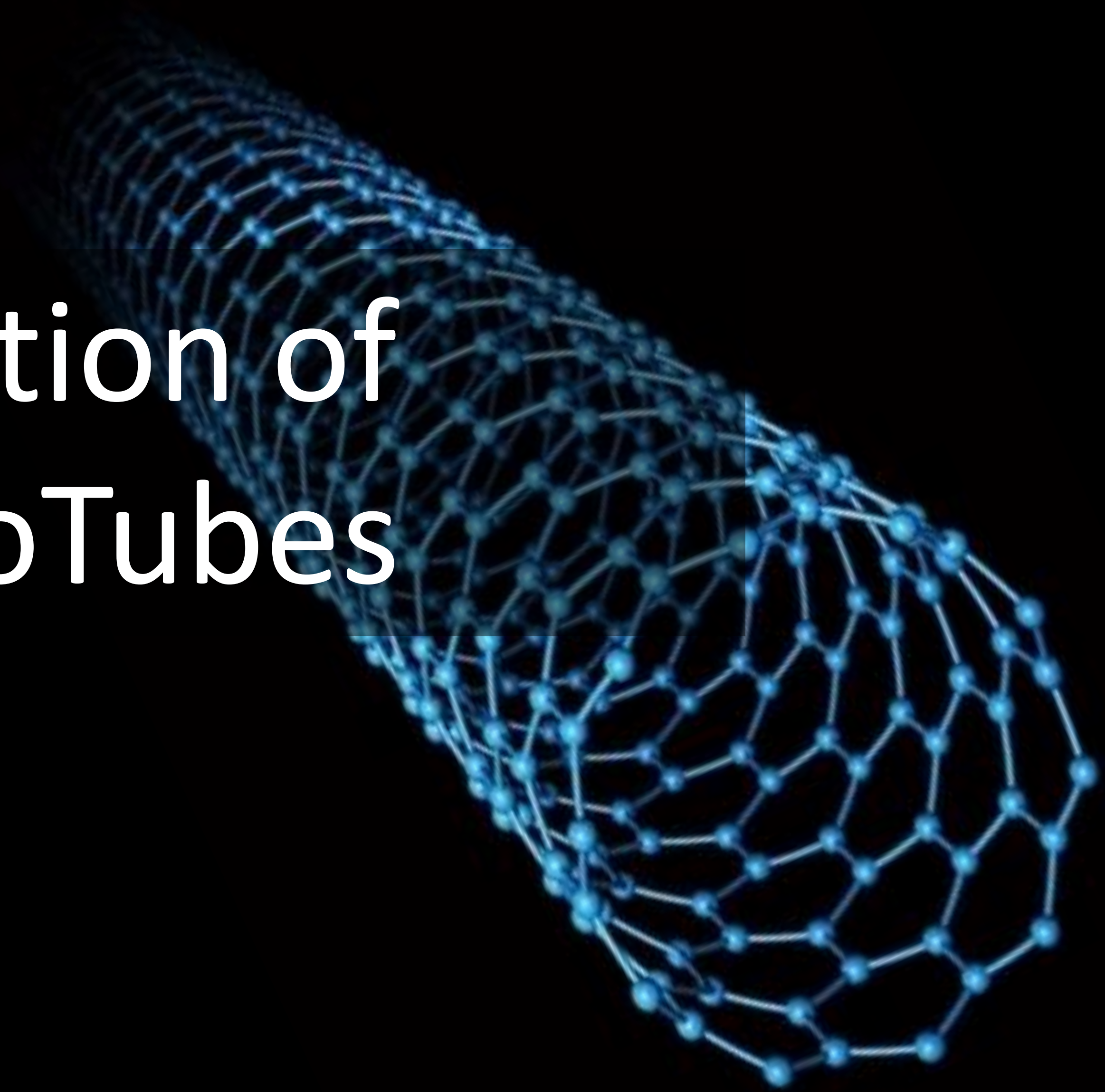
Ultracentrifuge (≈50000 rpm, ≈12h) in a density gradient

Chemical Modification

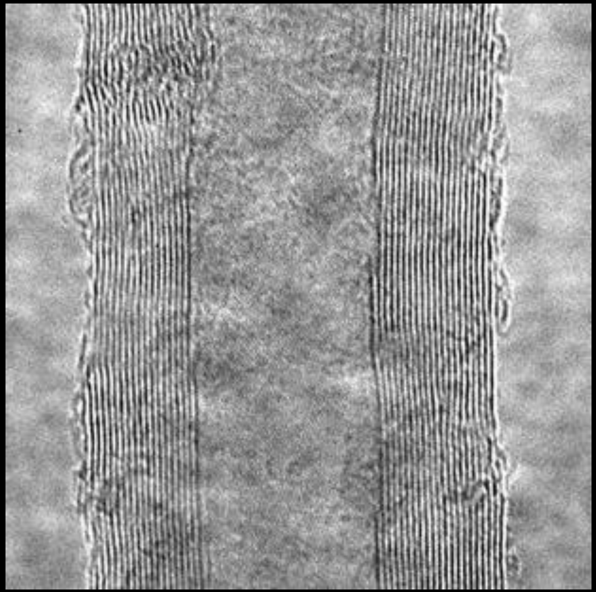


Nature Nanotechnology 2006, 1, 60

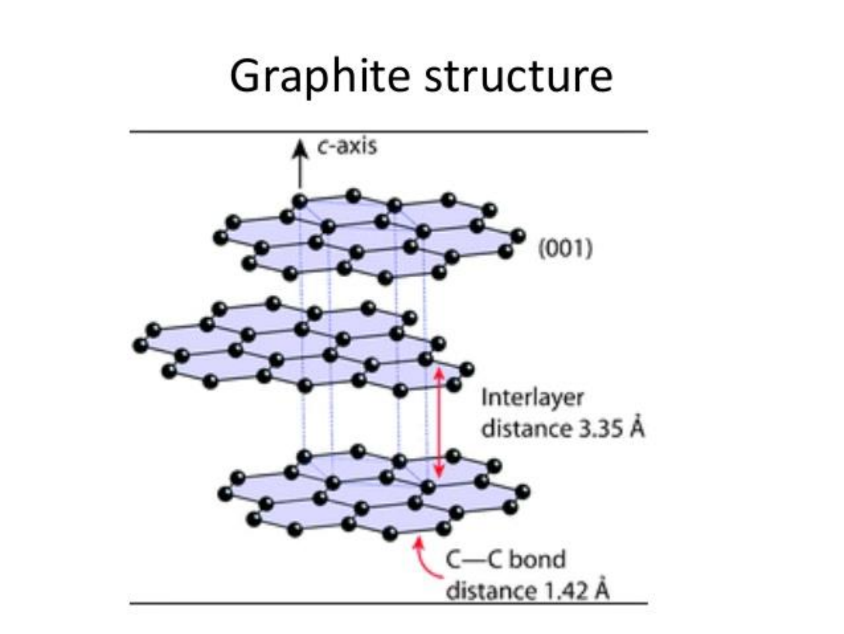
Characterization of Carbon NanoTubes

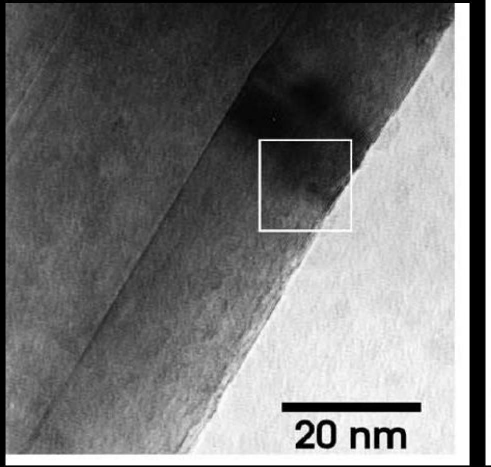


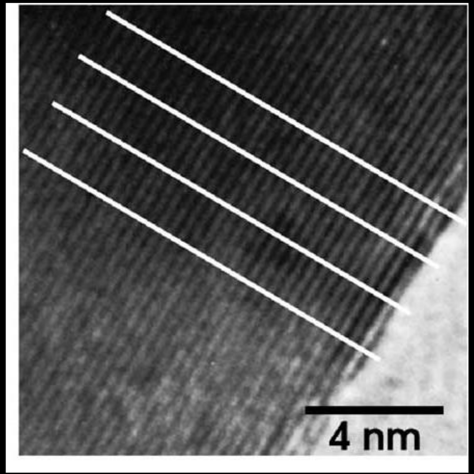
Transmission Electron Microscopy

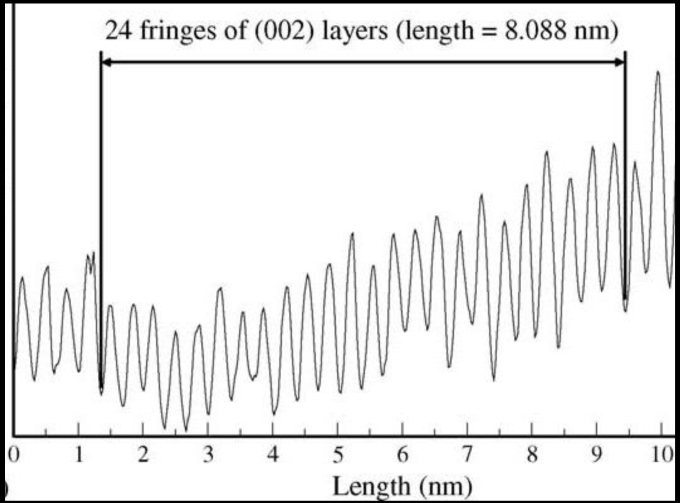


MWNT





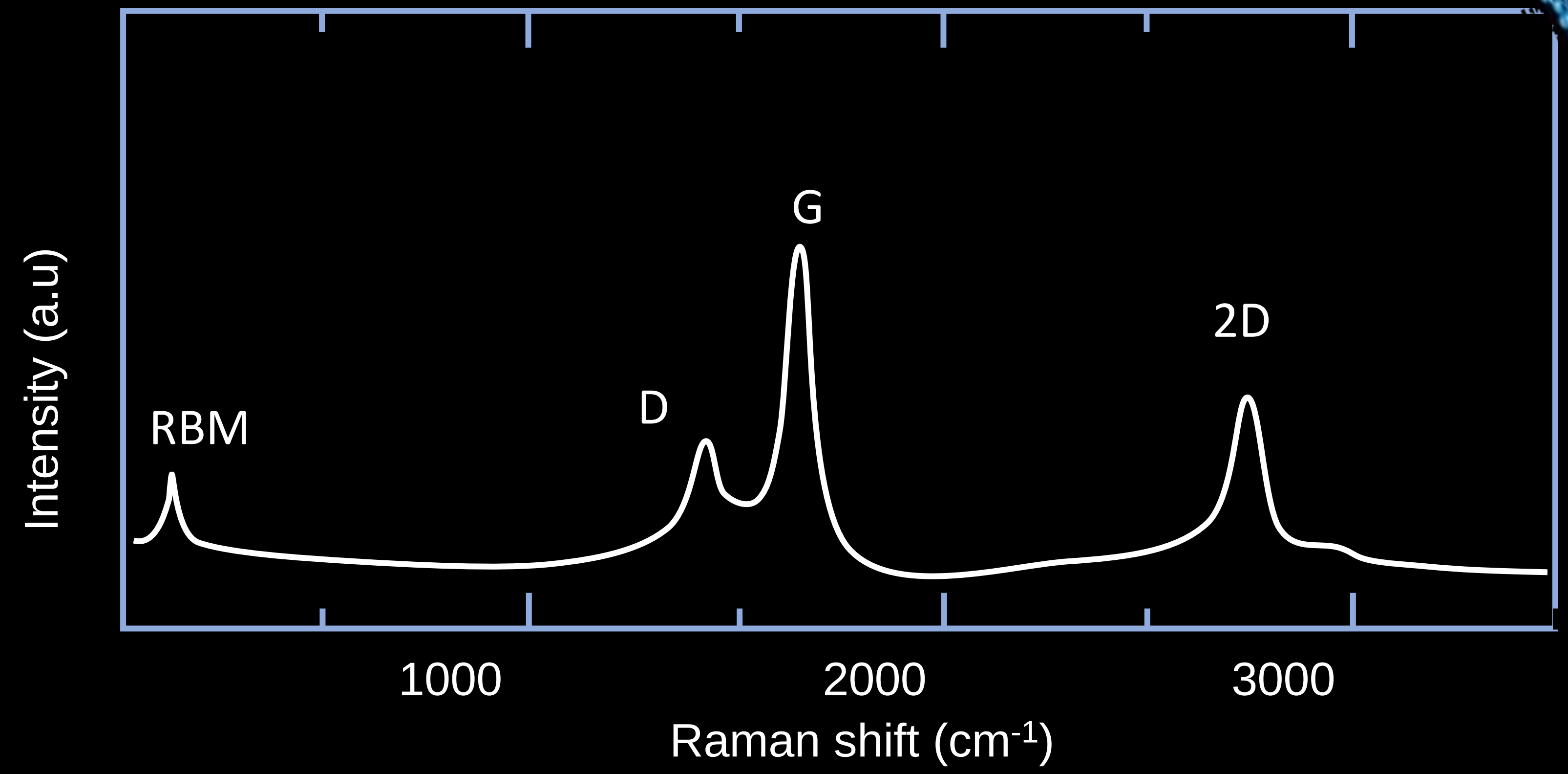


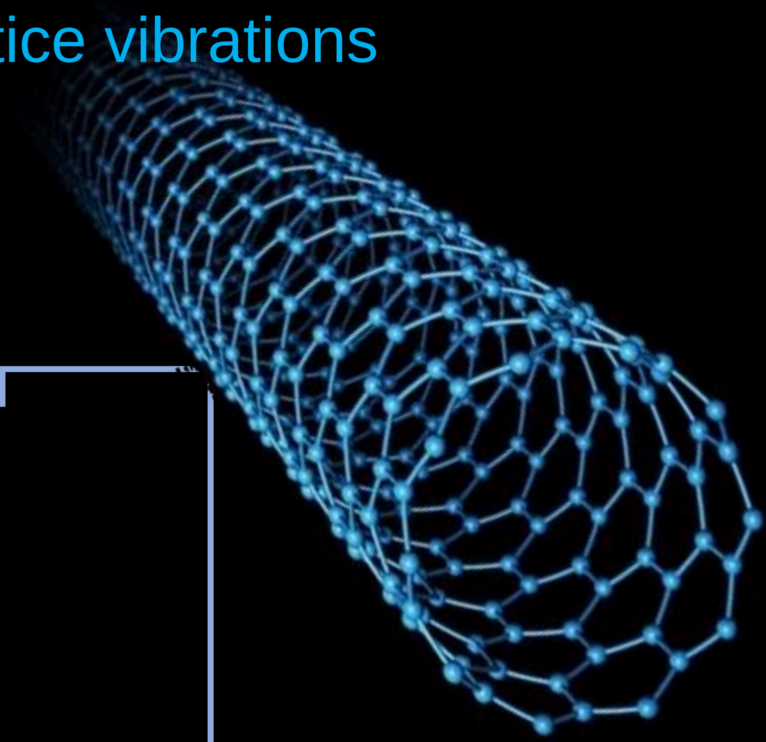


Raman Spectroscopy

Inelastic scattering due to molecular and lattice vibrations

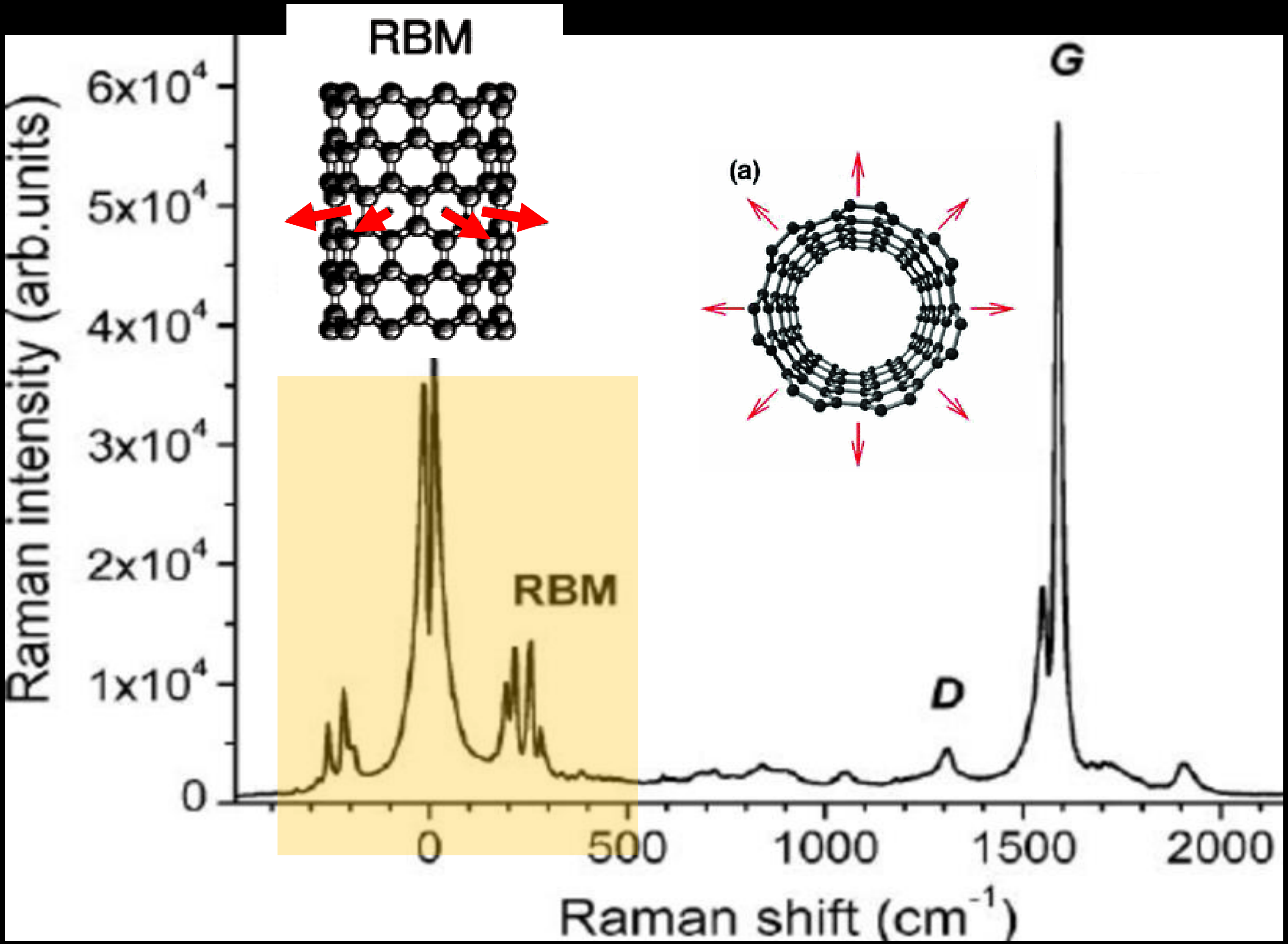
RBM: Distinguish, SWCNT, DWCNT, MWCNT
I_D/I_G : amount of defects
Shape of G band: metallic vs semiconducting

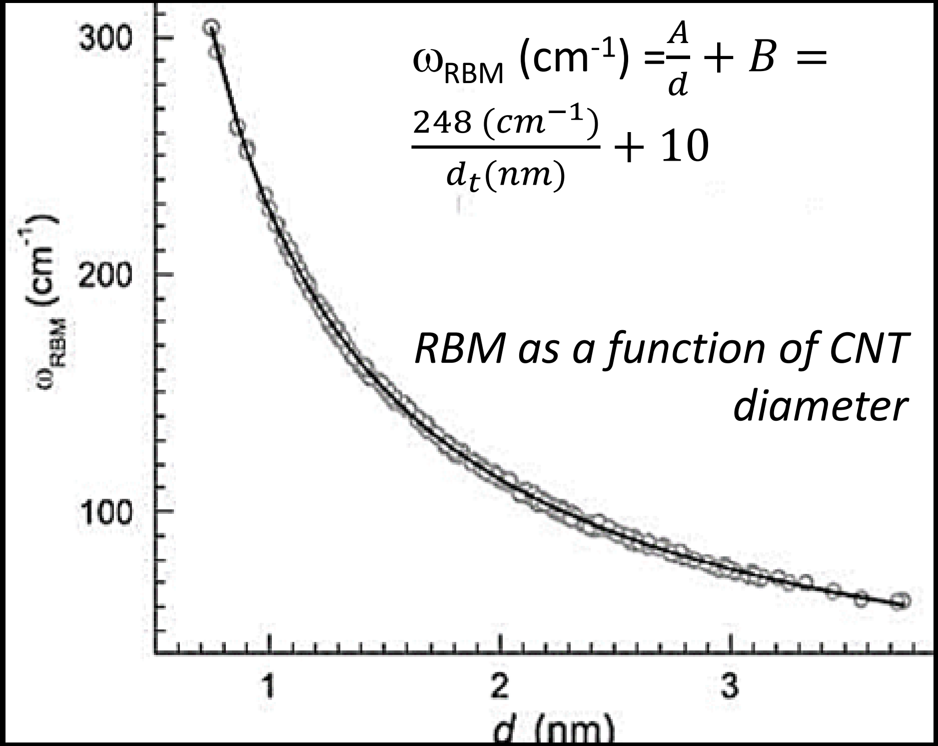




https://www.spectroscopyeurope.com/system/files/pdf/Raman-24-6.pdf

Raman Spectroscopy





ω_{RBM} (cm^{-1}) $= \frac{A}{d} + B = \frac{248\ (cm^{-1})}{d_t(nm)} + 10$

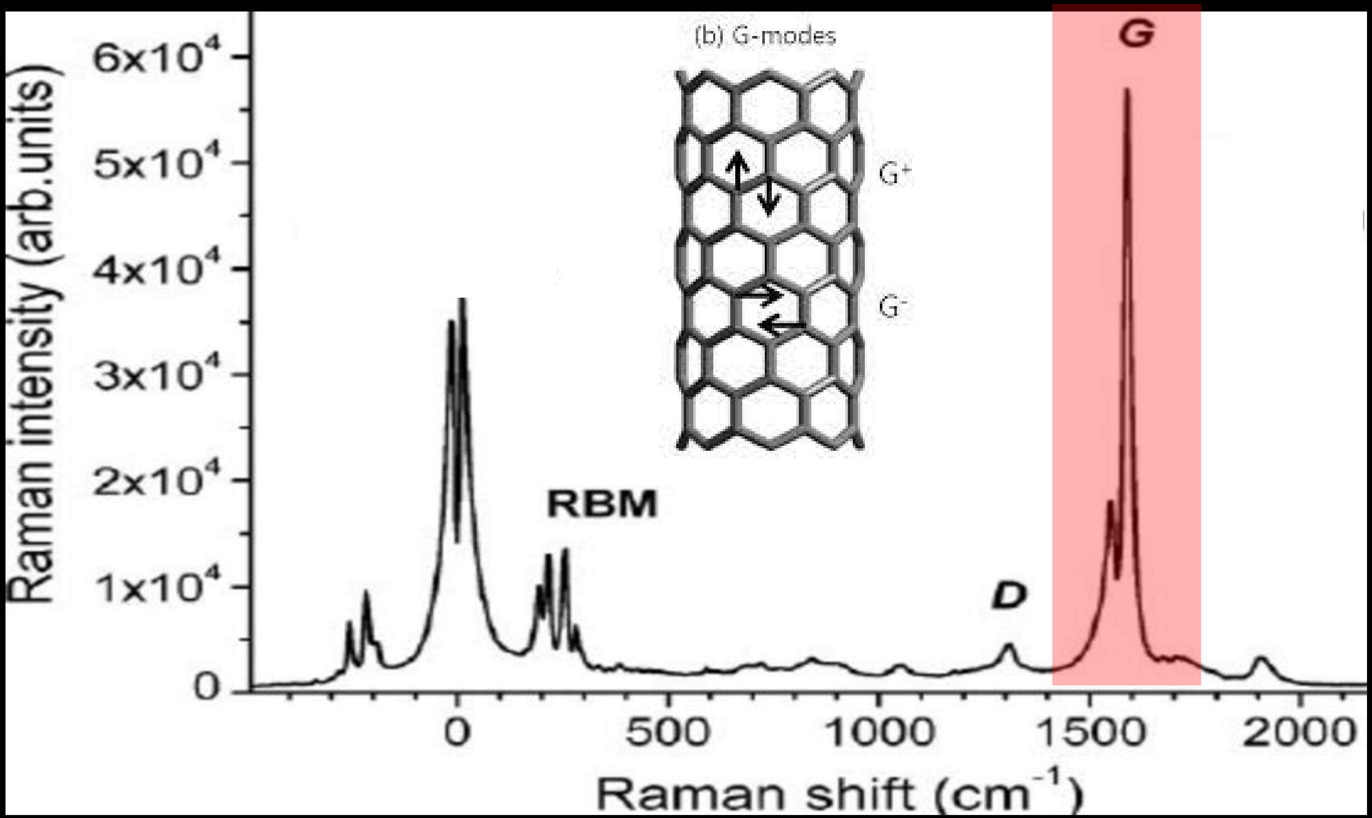
RBM as a function of CNT diameter

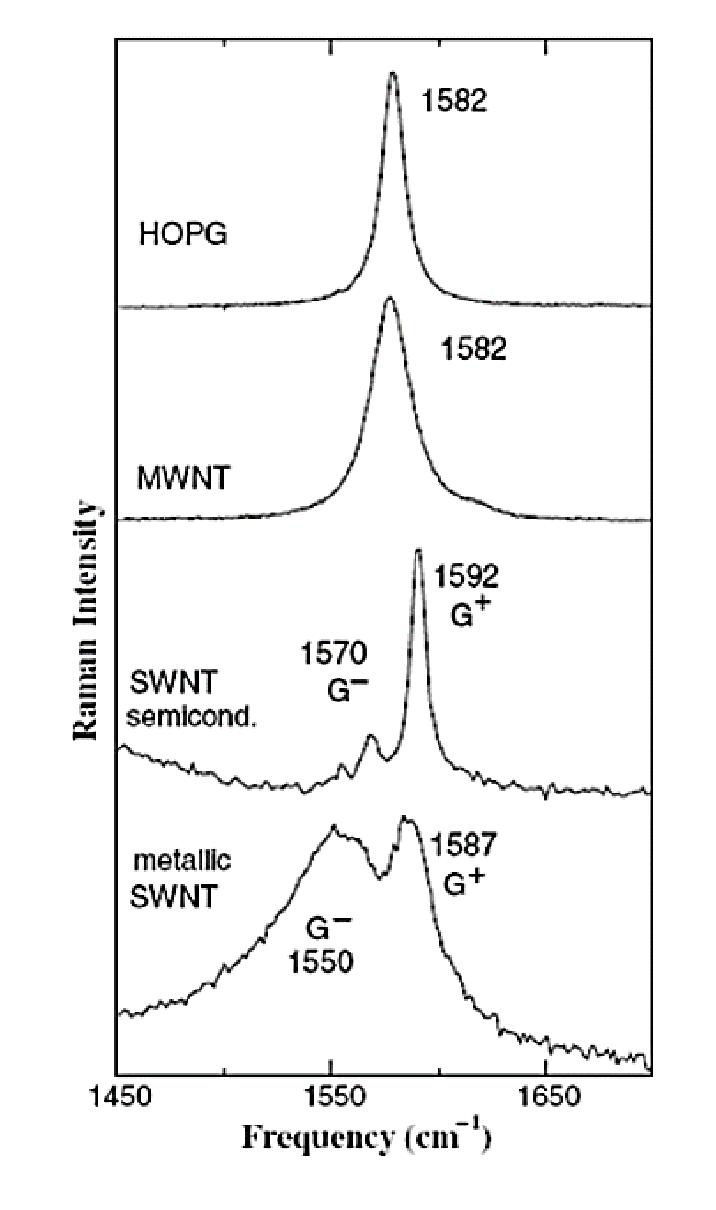
- Radial breathing mode (RBM) – exists only in SWNTs and DWNTs (ω_{RBM} depends on SWNT diameter)

M.S. Dresselhaus et al. / Physics Reports 409 (2005) 47–99

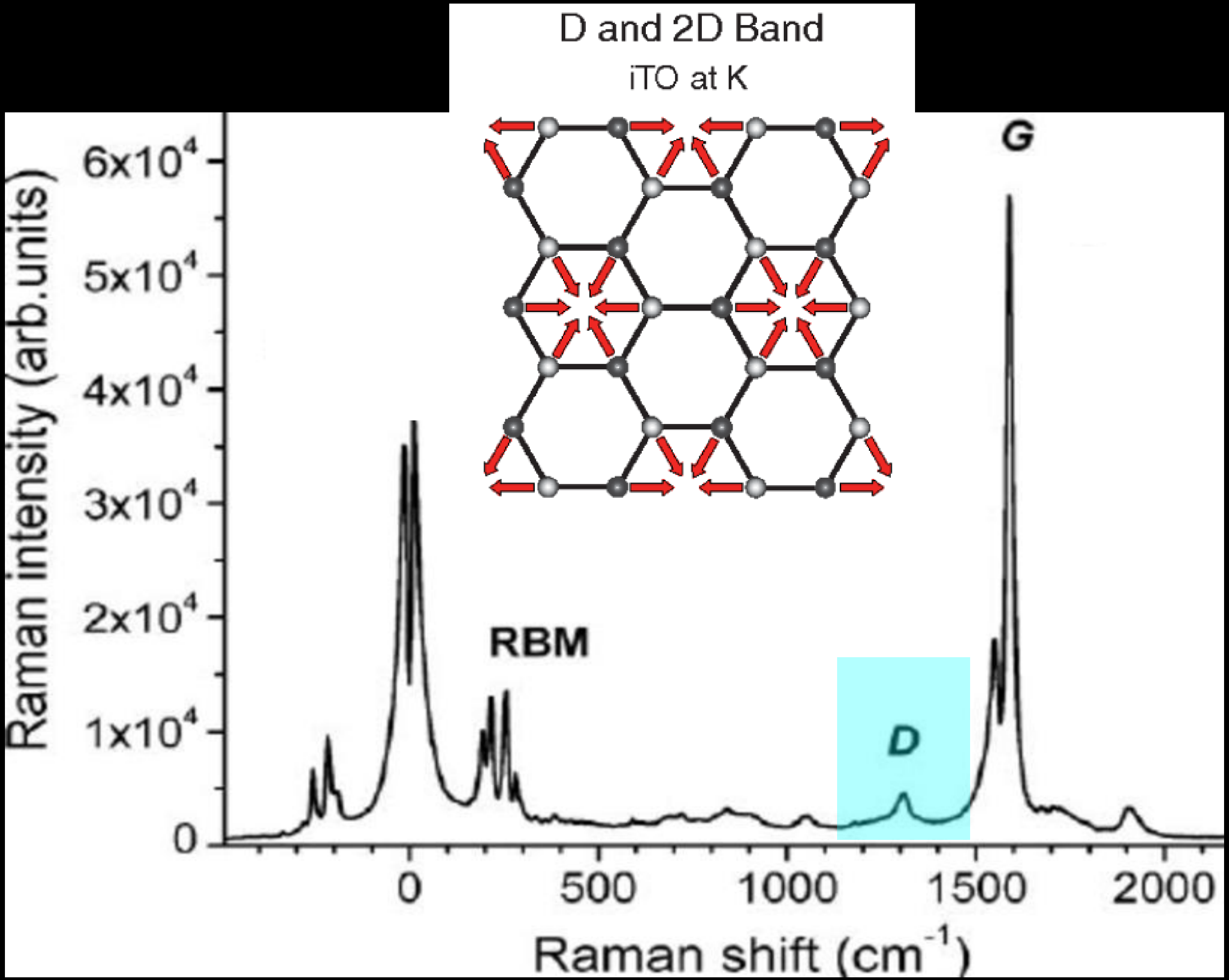
Raman Spectroscopy

- G mode/ tangencial – in graphite-like materials (distinguish metallic or semiconductor SWNT)
- G^- is downshifted, broader and depends on diameter in metallic tubes (phonon-plasmon interaction)





Raman Spectroscopy

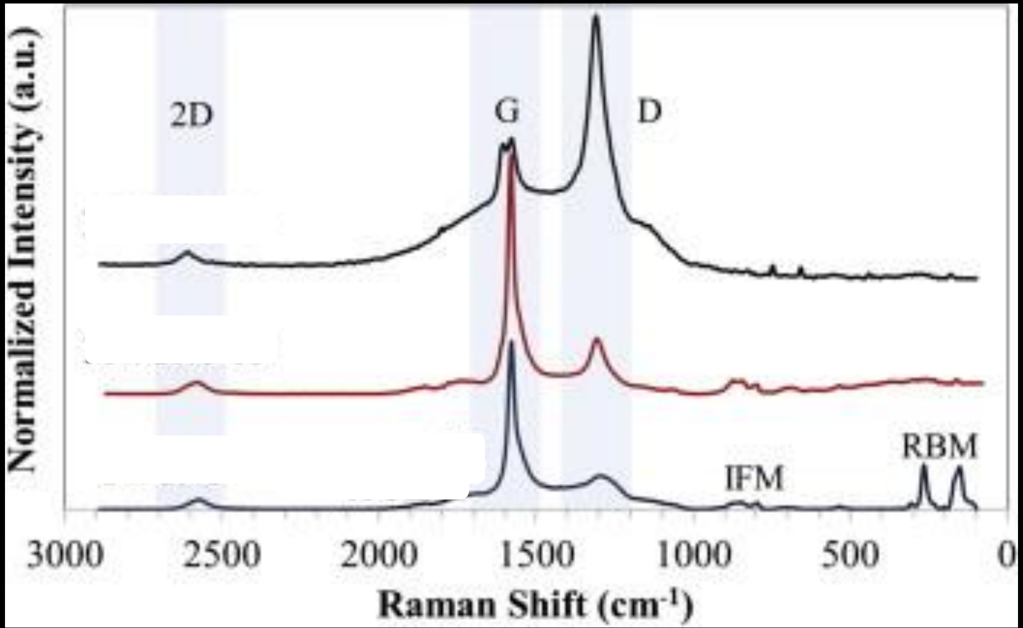


D mode – Highly symmetric ring breathing mode

Disorder induced mode requires a defect to appear in Raman
(G/D measures quality of the CNTs)

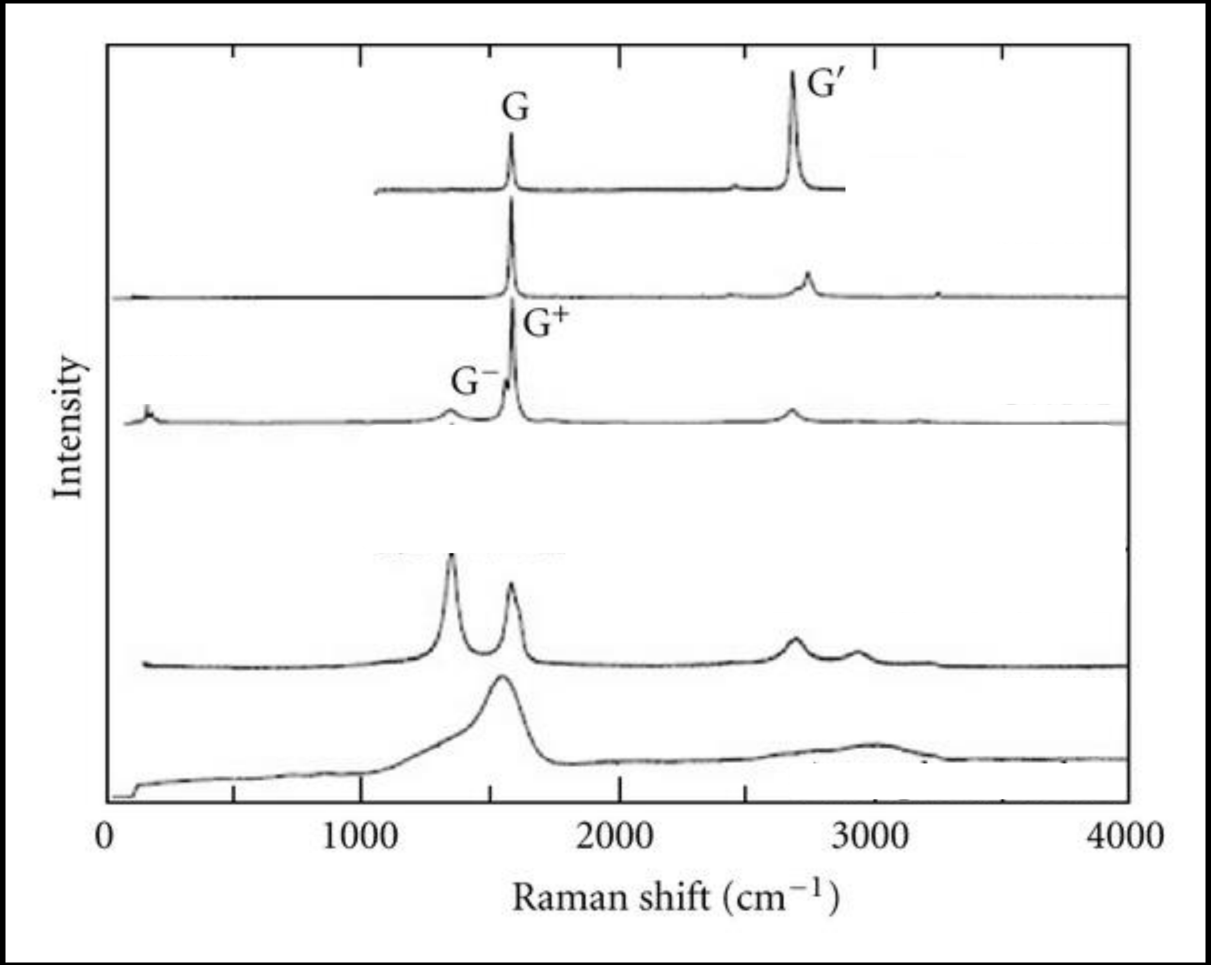
Raman Spectroscopy

Can you tell what type of tubes are here?



Raman Spectroscopy

Can you tell which one corresponds to SWCNT?



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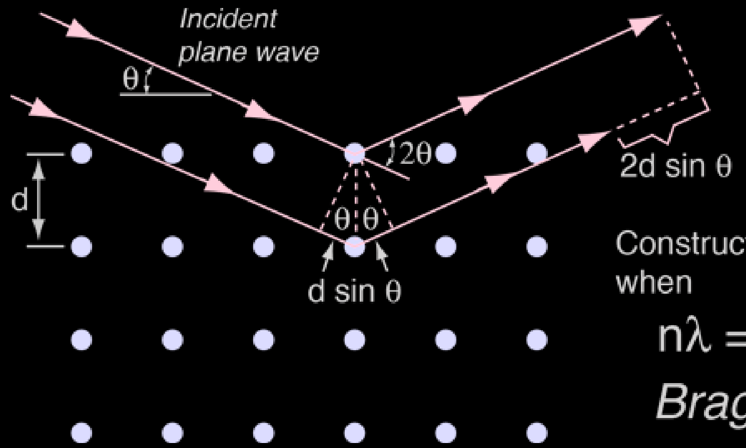
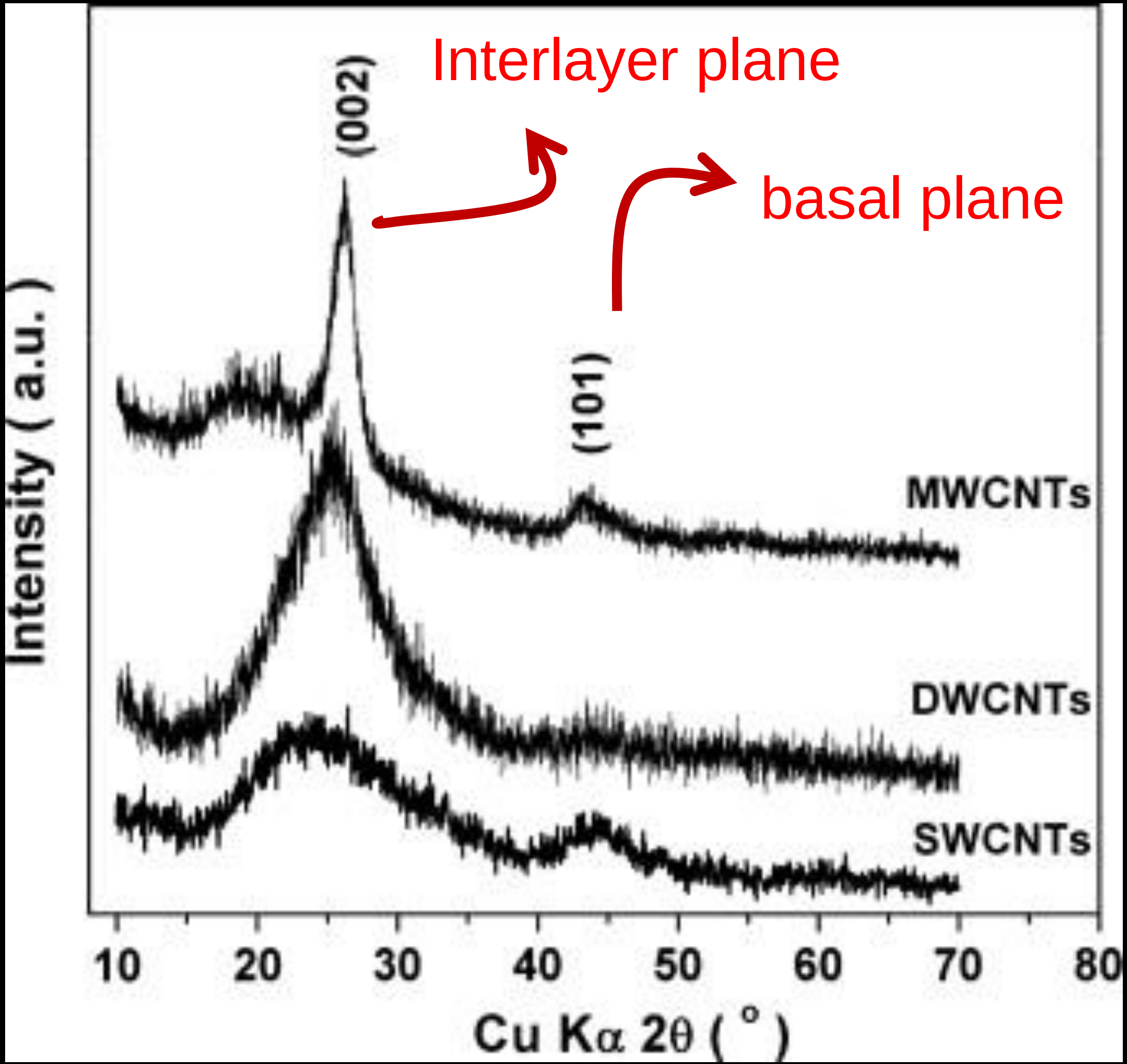
X-ray diffraction



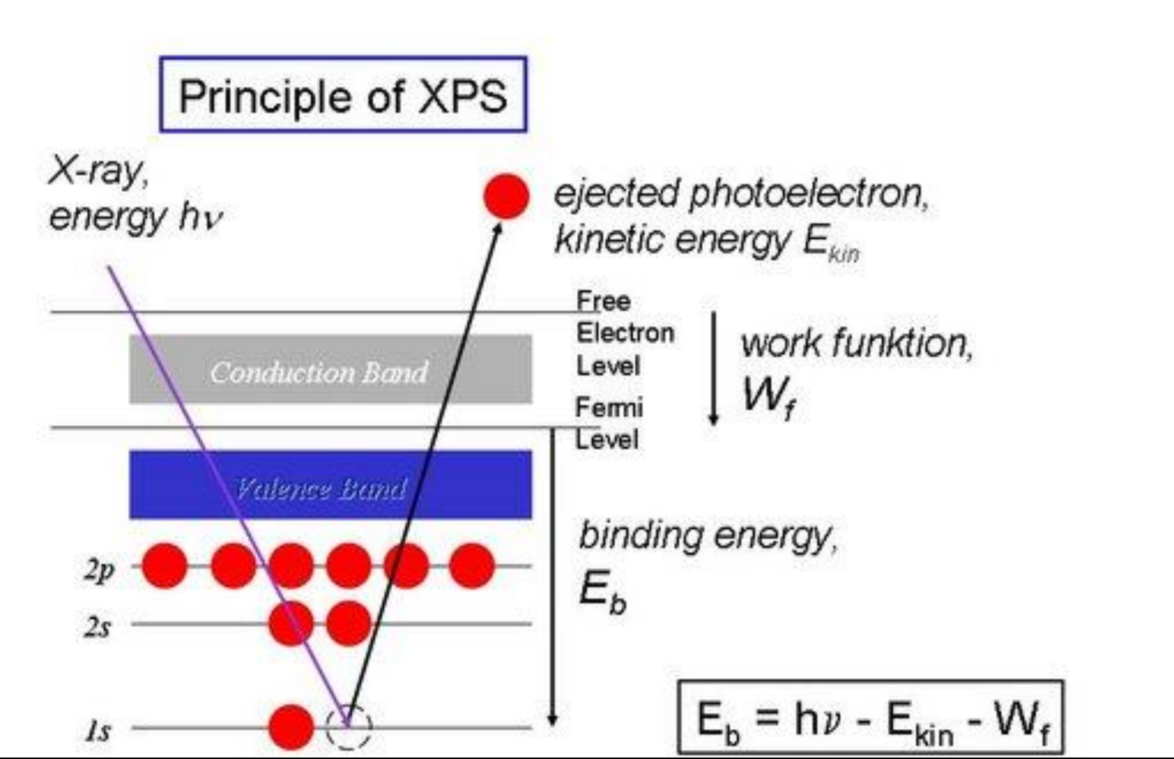
Constructive interference when

$n\lambda = 2d \sin\theta$

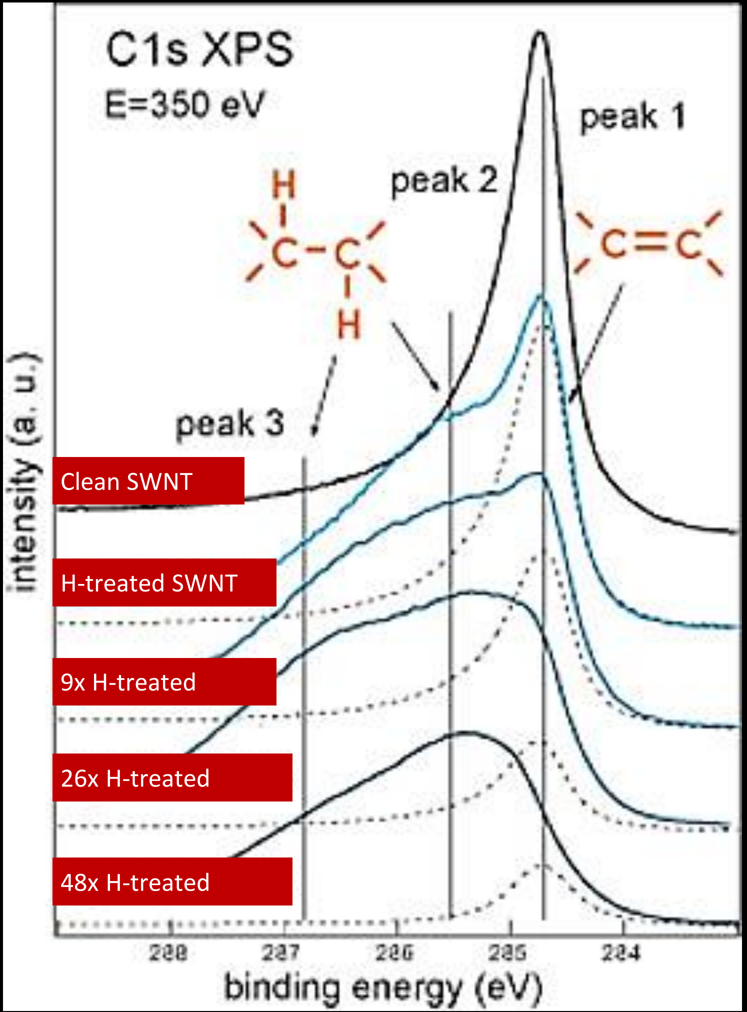
Bragg's Law



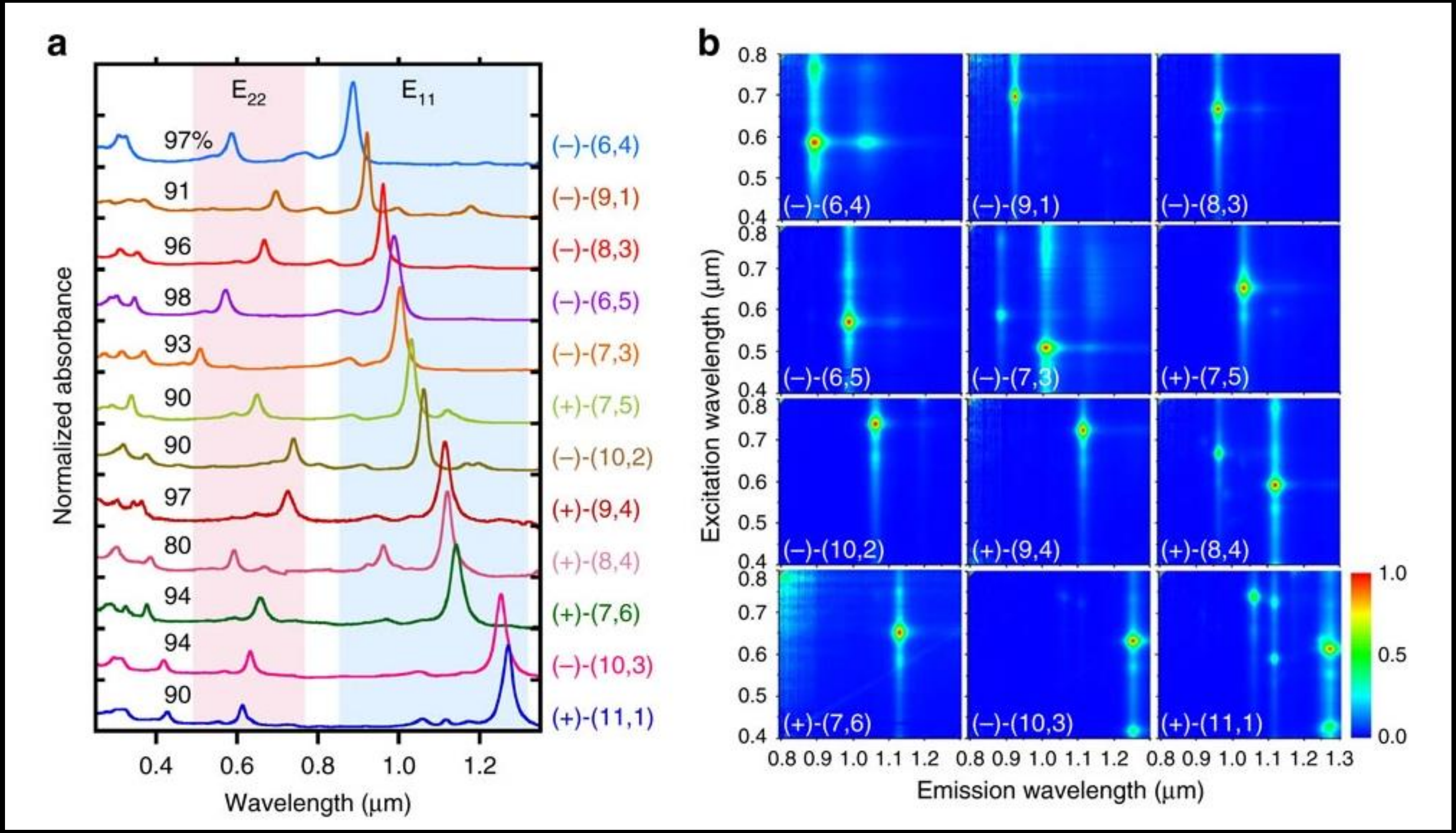
X-ray photoelectron spectroscopy



Hydrogenation of CNT followed by XPS
sp^2 carbon (peak1) vs sp^3 carbons (peak2)



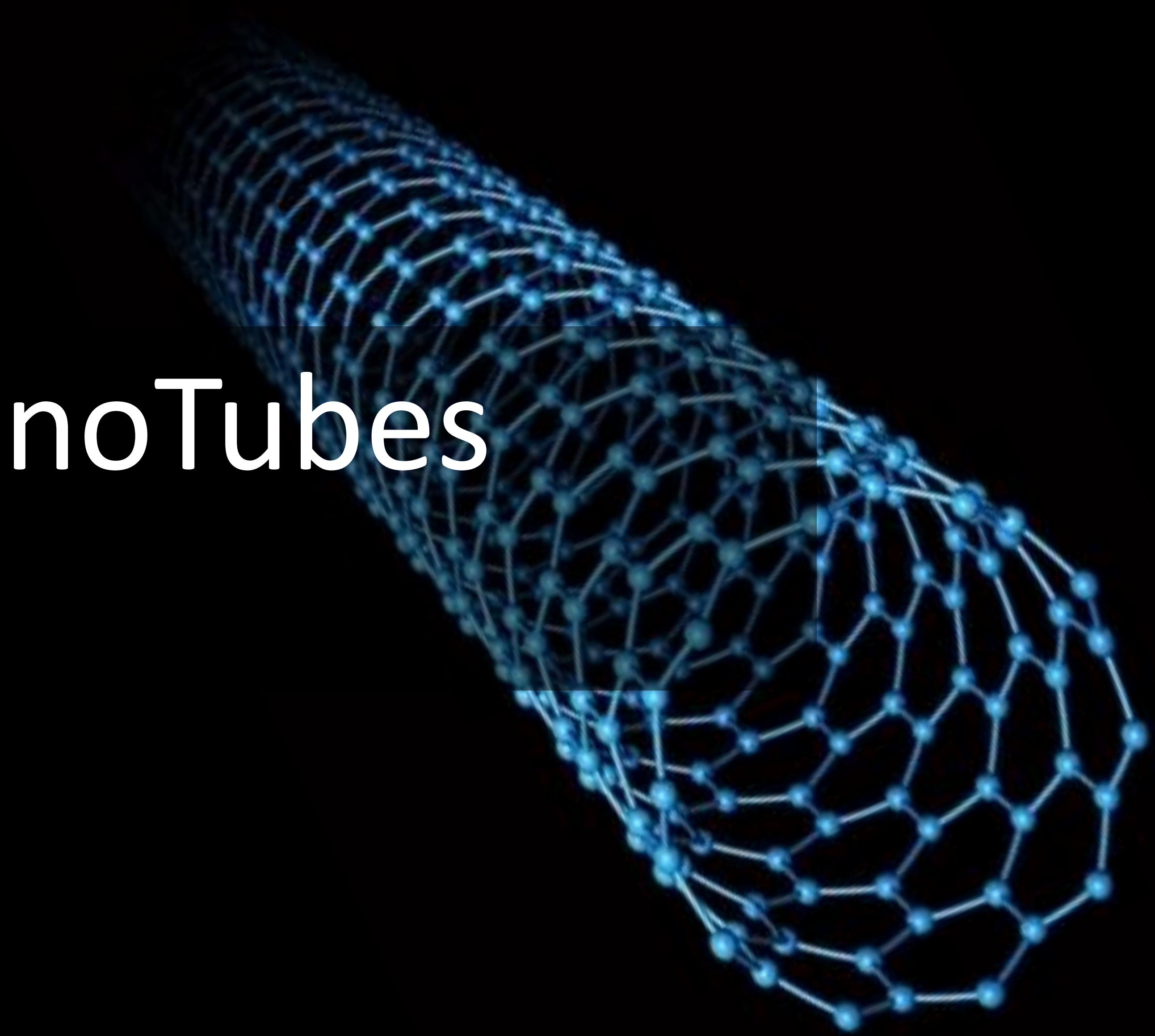
Optical characterization



Optical absorption spectra (**a**) and photoluminescence contour maps (**b**) of the 12 sorted (*n*,*m*) semiconducting SWCNTs

Wei, X., Tanaka, T., Yomogida, Y. *et al. Nat Commun* **7,** 12899 (2016). https://doi.org/10.1038/ncomms12899

Carbon NanoTubes Properties



SWNT Properties

Very low density

Excellent mechanical properties (up to 100x stronger than steel)

Young's modulus

SWNT ≈ 1 TPa

MWNT ≈ 1.28 TPa

Tensile strength >20 GPa

Conducting CNTs estimated to carry 1000 times higher current density than copper

Current density $1x10^9$ A/cm^2

High thermal conductivity

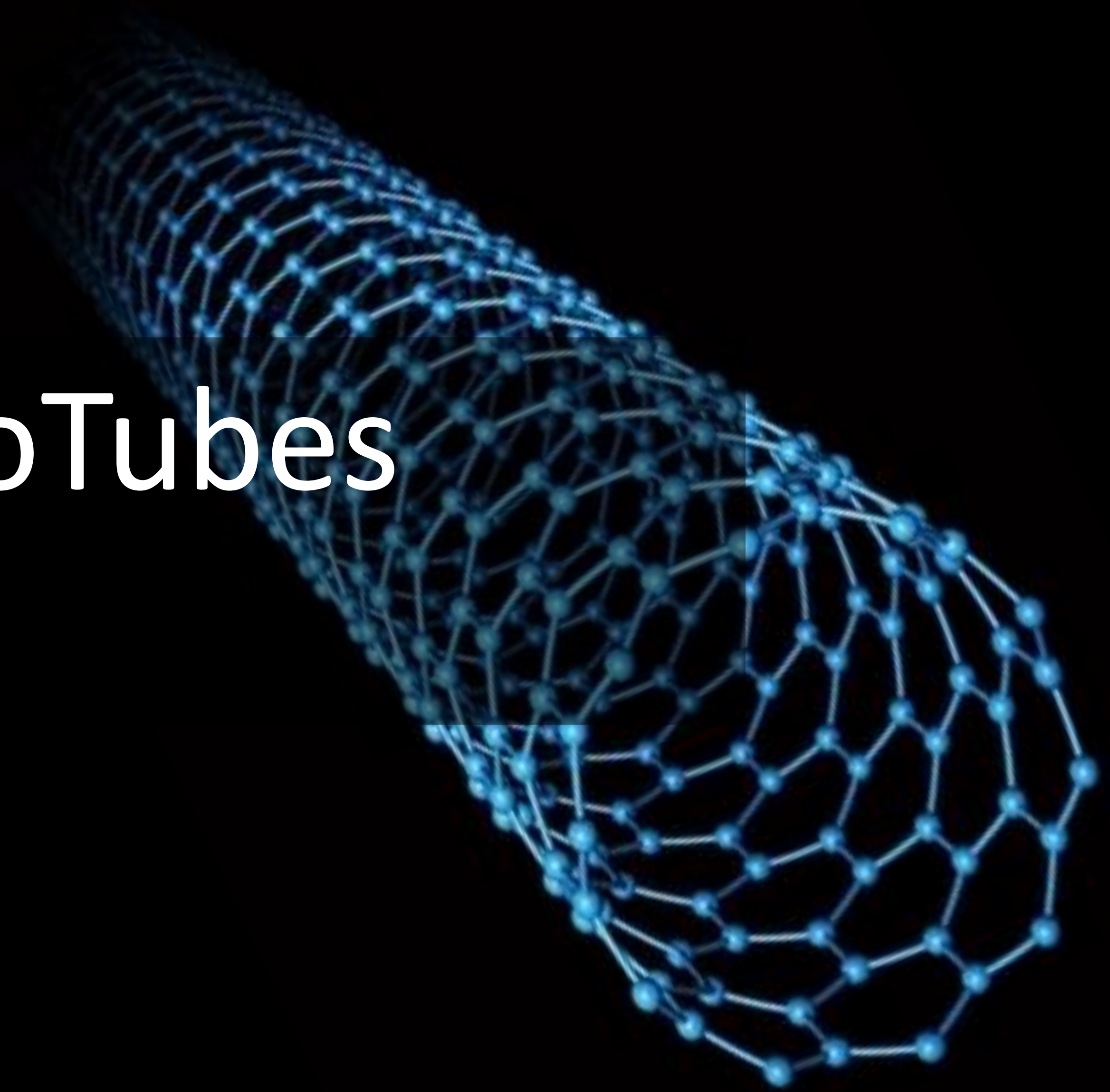
Thermal conductivity 6000 W/m.K

Cost 1-700 k€/g SWCNT (gold is 60€/gram)
1-100 €/g MWCNT

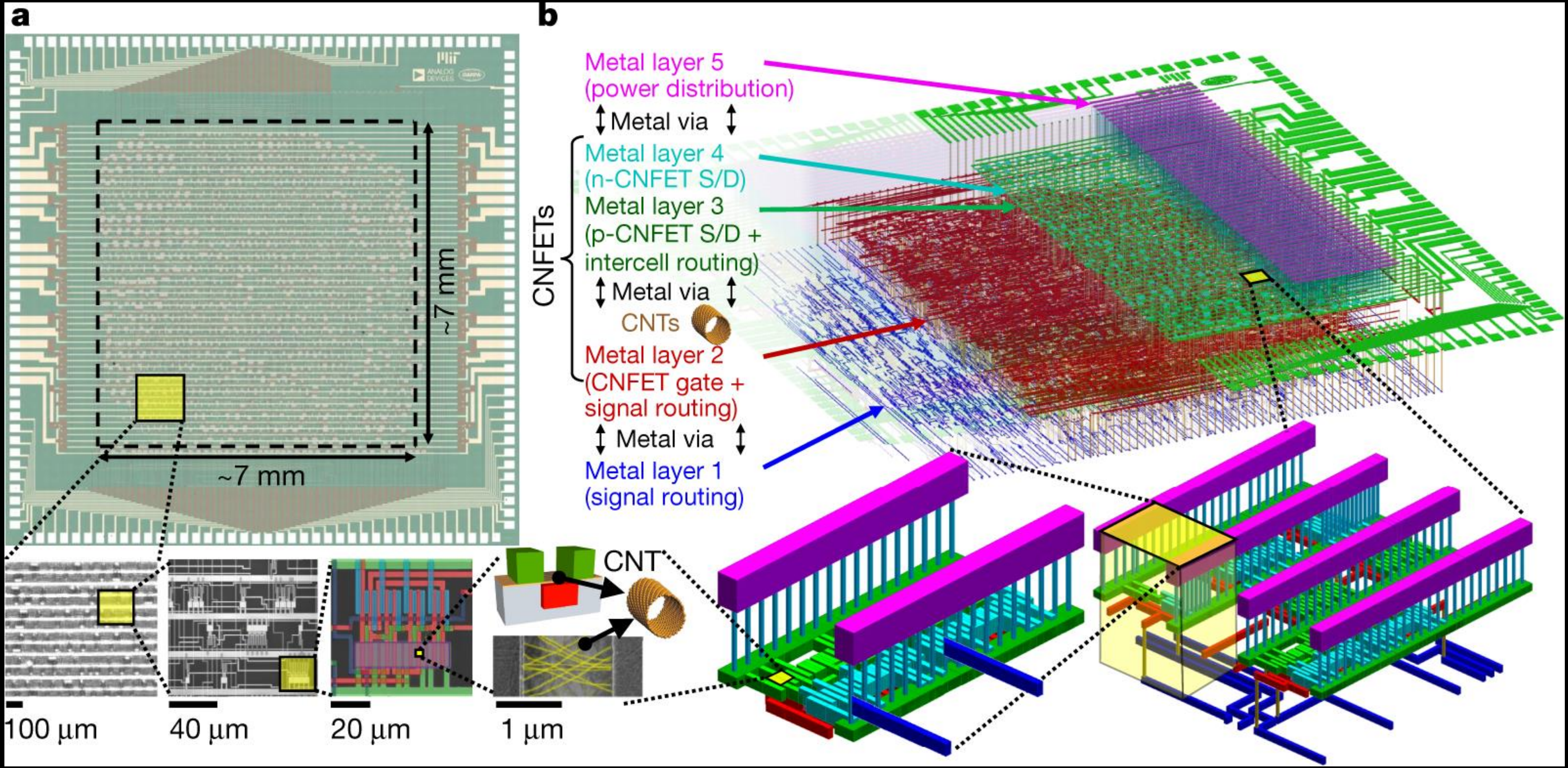
Property	Single-Walled CNT	By Comparison
Size	0.6 - 1.8 nm in diameter	Electron beam lithography can create lines 50 nm wide and a few nm thick
Density	1.33 – 1.40 g/cm^3	Aluminum has a density of 2.7 g/cm^3
Tensile Strength	$\approx 45 \cdot 10^9$ Pascals	High-strength steel alloys break at $\approx 2 \cdot 10^9$ Pascals
Resilience	Can be bent at large angles and re-straightened without damage	Metals and carbon fibers fracture at grain boundaries
Current Carrying Capacity	$\approx 1 \cdot 10^9$ A/cm^2	Copper wires burn out at $\approx 1 \cdot 10^6$ A/cm^2
Field Emission	Can activate phosphors at 1 – 3 V if electrodes are spaced 1 micron apart	Molybdenum tips require ≈ 50 – 100 V/micrometer with very limited lifetimes
Heat Transmission	≈ 6,000 W/m·K at room temperature	Nearly pure diamond transmits ≈ 3,320 W/m·K
Temperature / Thermal Stability	Stable up to 2,800 C in vacuum and 750 C in air	Metal wires in microchips melt at ≈ 600 – 1,000 C
Cost	≈ 1,500 $/g	Gold sells for ≈ 40 $/g
Preservation of the Quantum Property of Electron Spin	Optimal; Very high	Low in regular conductors
Power Consumption	Very low	Higher in metal wires
Speed	Very high $\geq 1 \cdot 10^{12}$ Hertz nanoscale switch	≥ 1,000 times as fast as processors available today
Electron Scattering (Resistance)	Almost none	Comparatively high
Energy Band Gaps	Easily tunable; Depends on CNT diameter and thus wide range of band gaps can be obtained: ≈ 0 (like a metal), as high as band gap of Silicon, and almost anywhere in between	No other known material can be so easily tuned

FACTA UNIVERSITATIS Ser: Elec. Energ. Vol. 25, No 1, April 2012, pp. 15 - 30 DOI: 10.2298/FUEE1201015A

Carbon NanoTubes Applications



MIT engineers have built a modern microprocessor from carbon nanotube field-effect transistors (pictured), which are seen as faster and greener than silicon transistors. The new approach uses the same fabrication processes used for silicon chips



Nature 2019, 572, 595–602 (2019)

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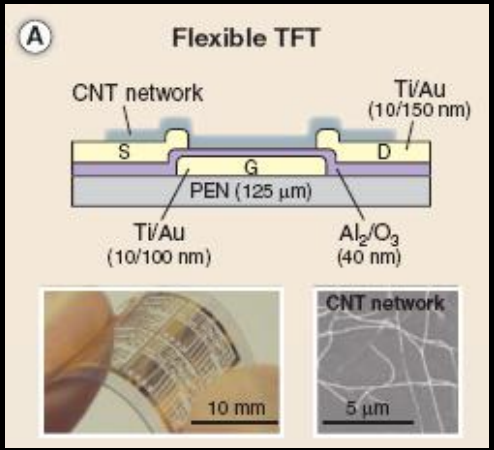
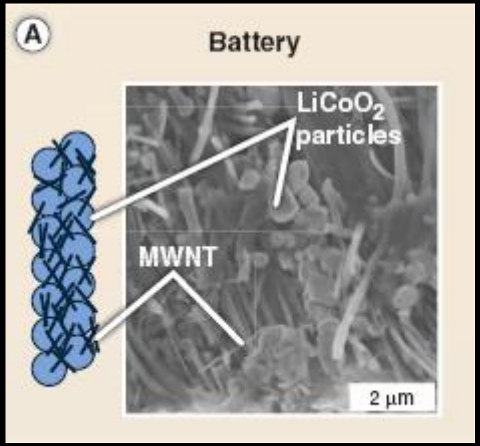
Energy and microelectronics

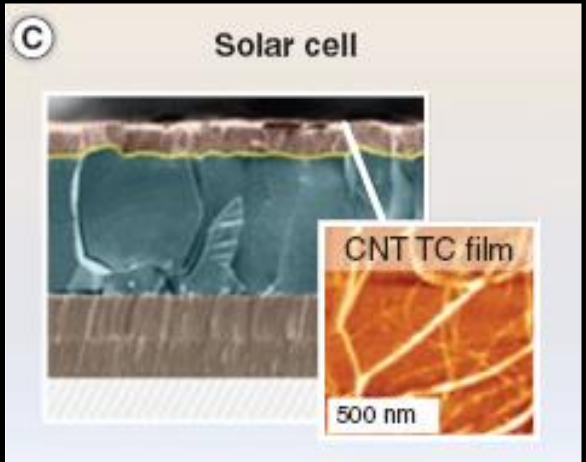
Transparent electrodes for displays, batteries and solar cells

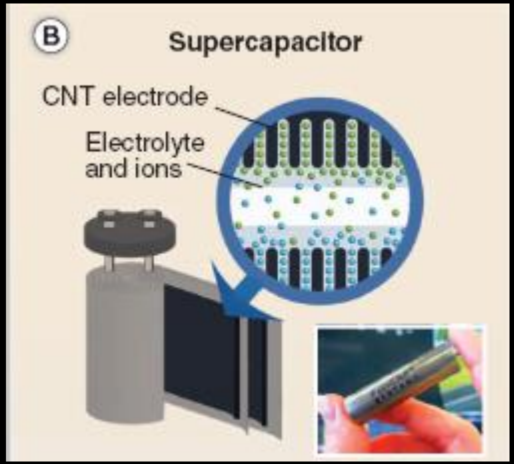
Super-capacitors for energy storage

Transistors and connectors for integrated circuits





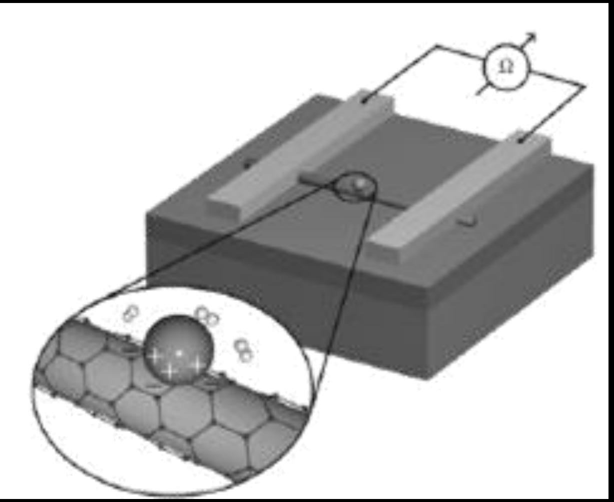




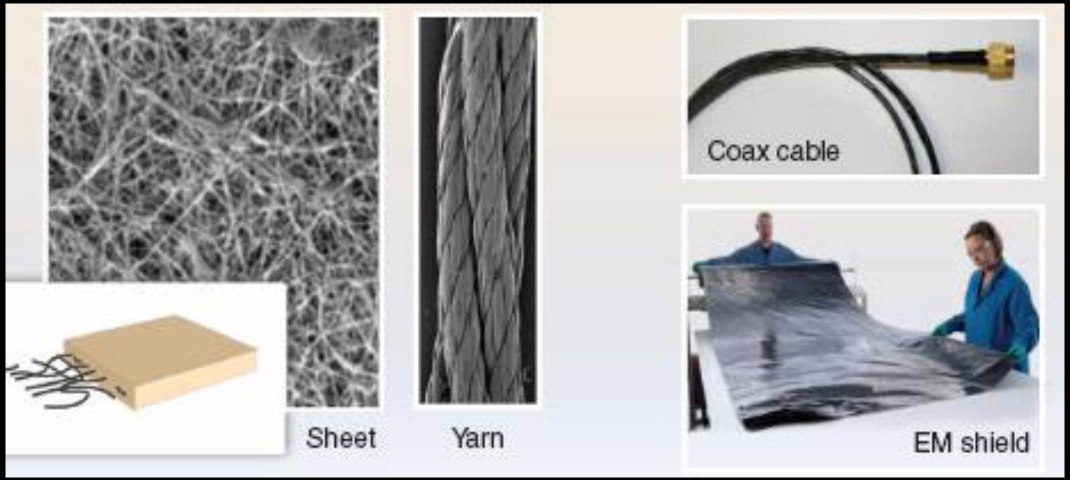
MWNTs are widely used as electrodes in lithium ion batteries for notebook computers and mobile phones, marking a major commercial success

- Sensors (change in electrical resistance)

hydrogen sensor from a nanotube decorated with palladium nanoparticles



- EM shielding



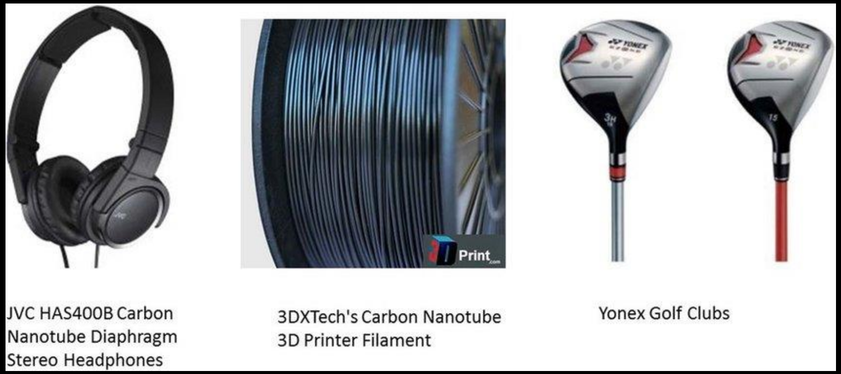
- Environment

Prototype portable water filter using a functionalized tangled CNT mesh in the latest stage of development

Volder et al, Science, 2013, 339, 535

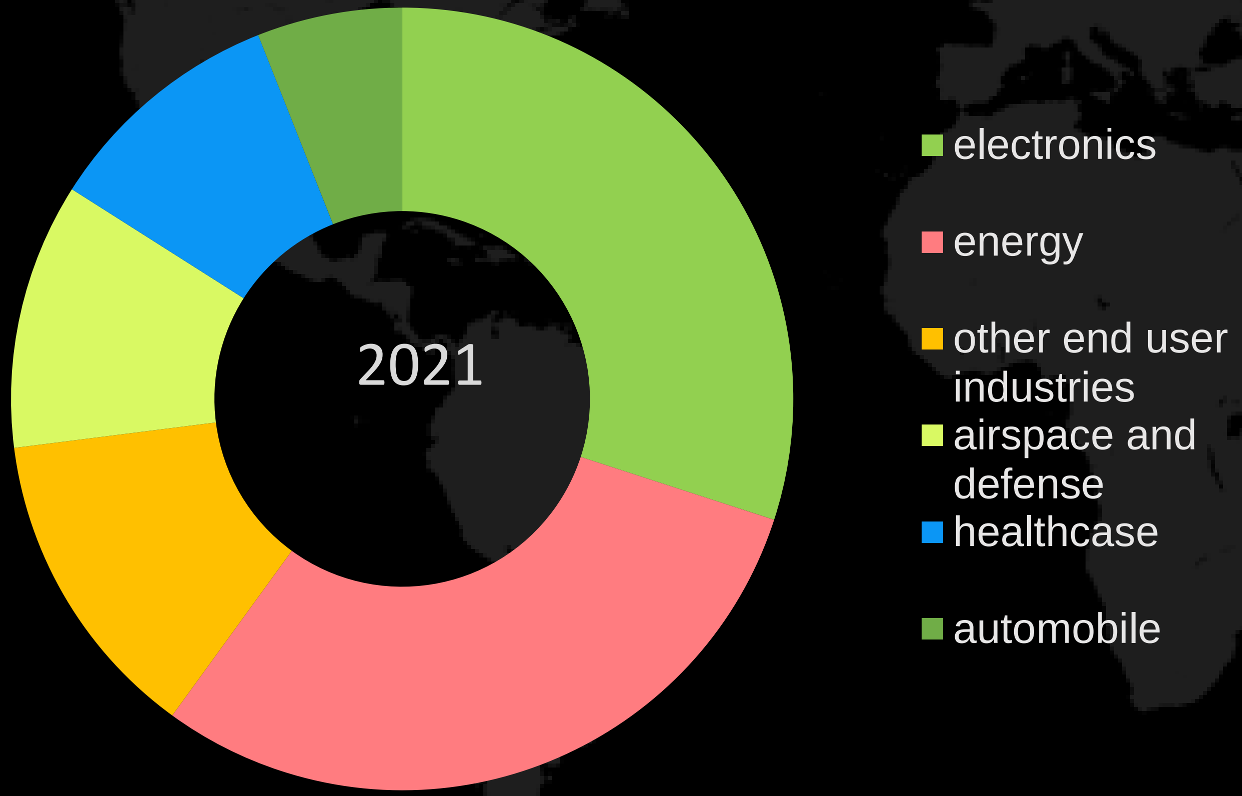
- Nanocomposites (polymer reinforcement)

Sports equipment, headphones, soft body armor and much more made out of carbon nanotubes



The Beautiful Molecule: 30 Years of C60 and Its Derivatives, Acquah et al, ECS Journal of Solid State Science and Technology, 6 (6) M3155-M3162 (2017)

Global CNT Market Segmentation



Drivers
•Superior chemical and mechanical properties
•Emerging demand from APAC
•High growth in end-use industries such as electrical & electronics and automotive
•Increasing demand for lightweight and low carbon emitting vehicles

Restraints
•Environmental concern and health & safety issues

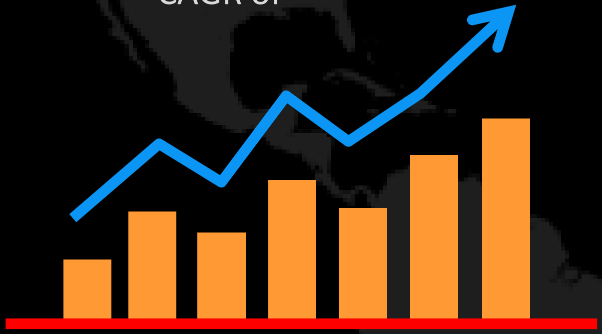
Challenges
•Maintaining quality
•Stringent and time-consuming regulatory policies
•High price & processing difficulties

Global CNT Market Trends

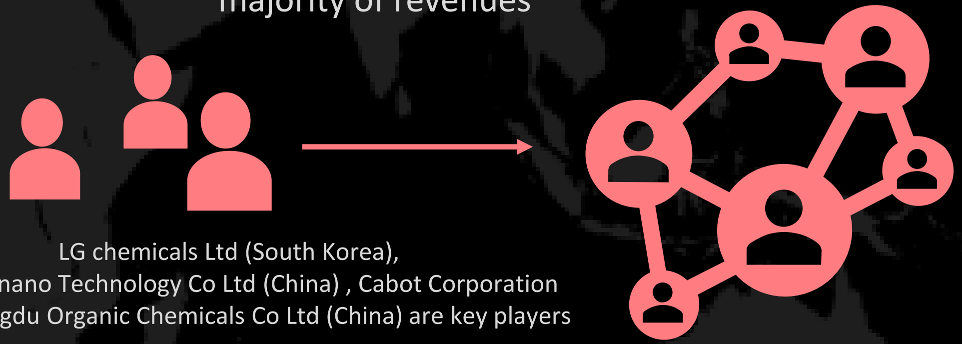
876 USD Millions 2021

1.714 USD Millions 2026

Market growth CAGR of 14.9 %



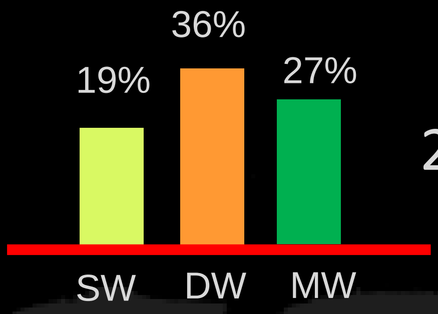
The market is CONSOLIDATED with few players accounting for the majority of revenues



LG chemicals Ltd (South Korea),
Jiangsu Cnano Technology Co Ltd (China) , Cabot Corporation (US), Chengdu Organic Chemicals Co Ltd (China) are key players

32.6 %

of global market revenues generated by APAC in 2021



2027

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Nanostructured Materials and Nanotechnology 2022-2023

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