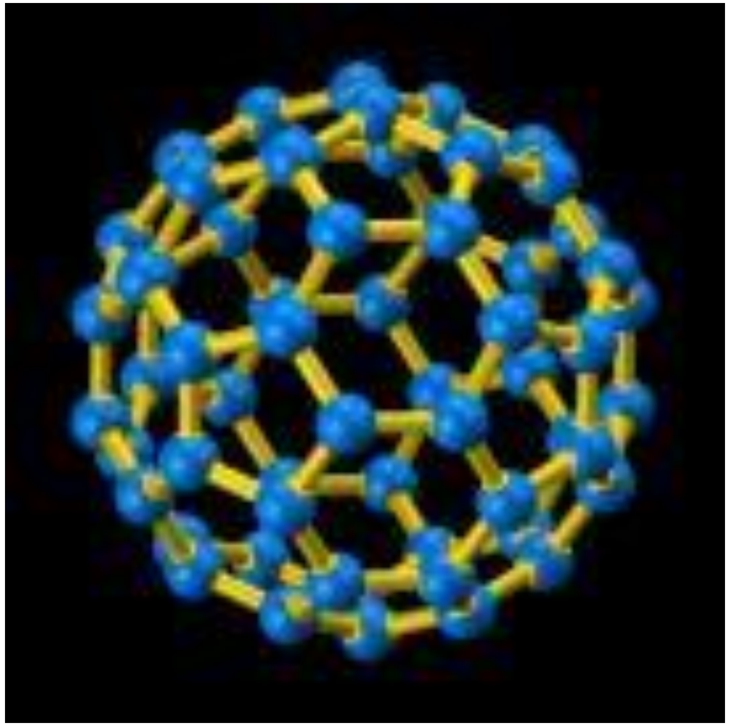
Carbon Nanotubes

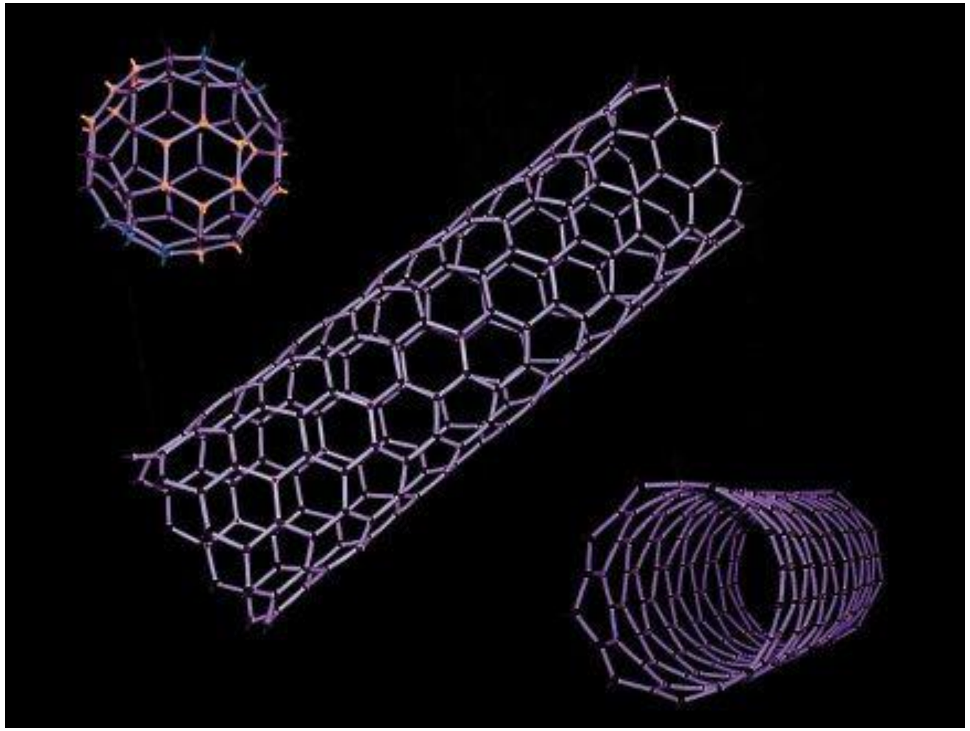
Session 11

May 18th, 2020

Carbon based nano structures



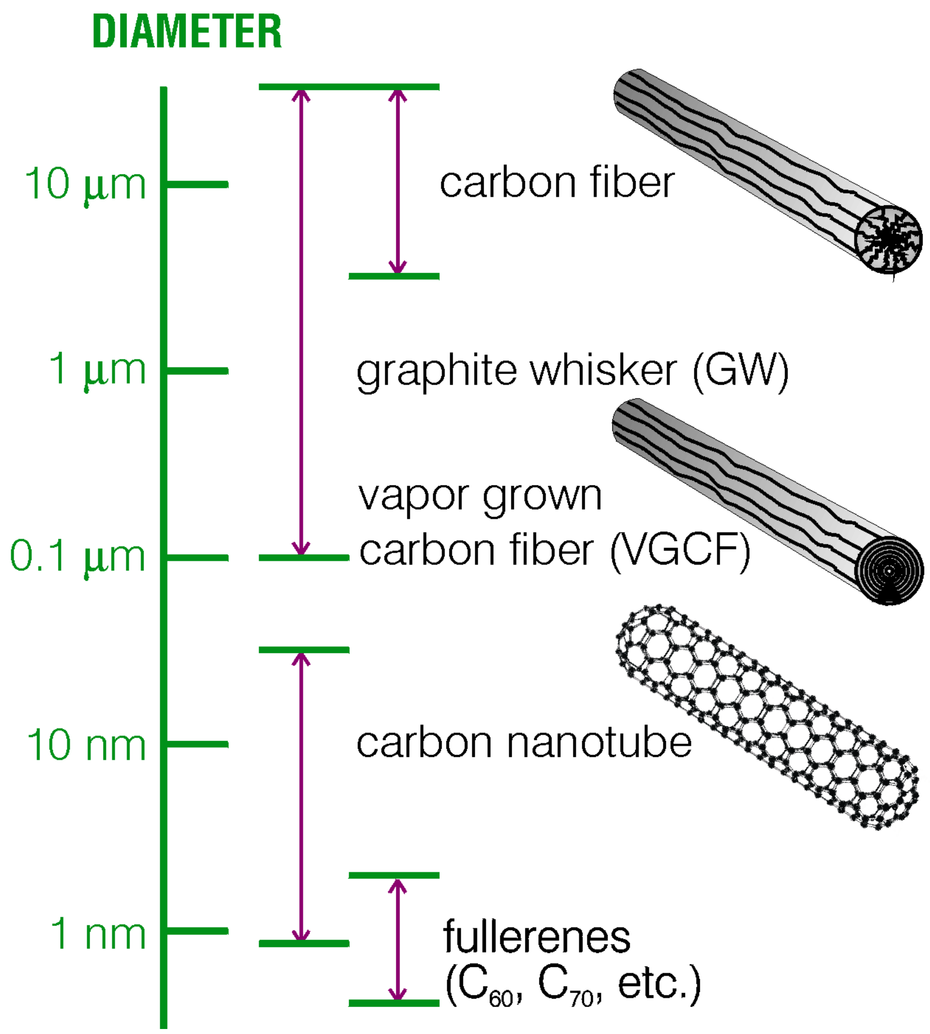
Bucky ball



Carbon nano tube

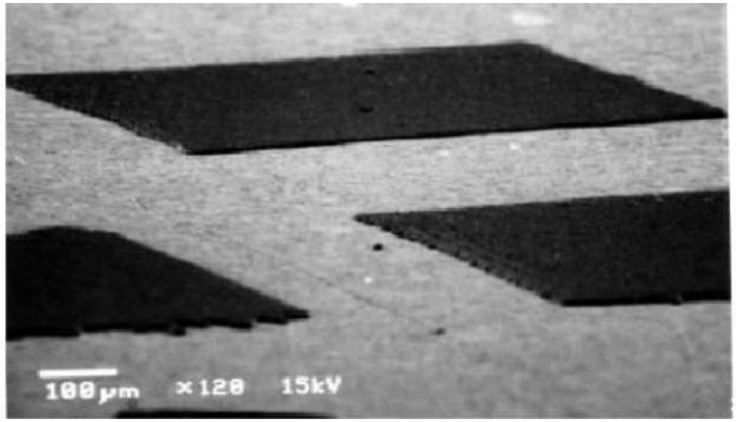
http://www.nccr-nano.org/nccr/media/gallery/gallery_01/gallery_01_03

Carbon Fiber Diameters



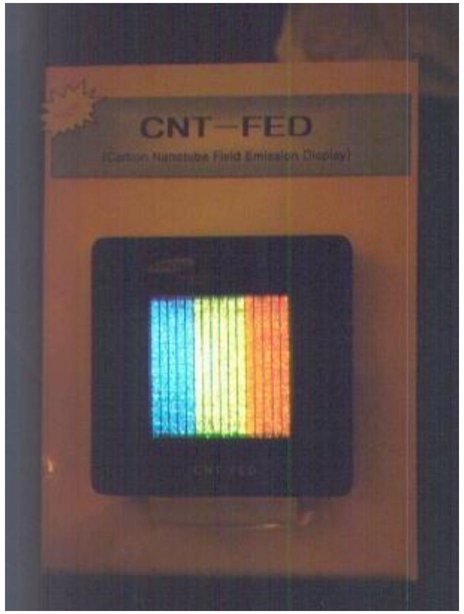
Nanotube Applications

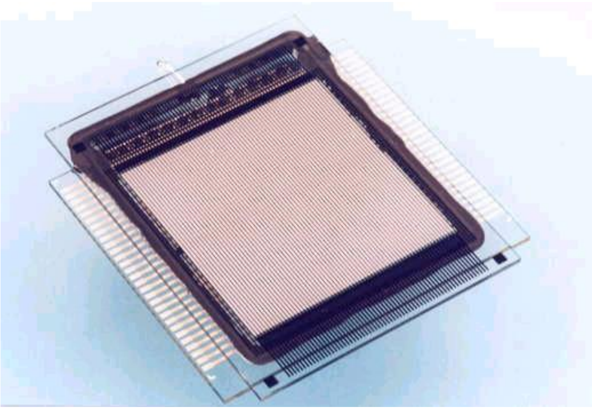
- Nano-electronics
  - Metallic and semi-conducting varieties
  - Molecular circuits
- Electromagnetic interference shielding
  - ‘Stealth’ composites and coatings



Nanotube Applications

- Energy Storage
  - Hydrogen storage
  - Super-capacitors and batteries
- Field emission devices
  - Flat panel displays





High Strength to Weight Materials

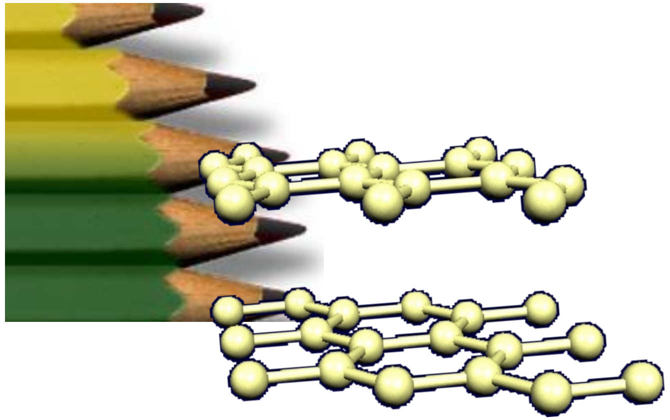
	Graphite Crystal	Carbon Fibers	MWNT	SWNT	Steel
Tensile Strength - GPa	100	3-7	300-600	300-1500	0.4
Elastic Modulus - GPa	1000	200-800	500-1000	1000-5000	200
Specific Strength - GPa	50	2-4	200-300	150-750	0.05
Specific Modulus - GPa	500	100-400	250-500	500-2500	26
Strain to Failure - %	10	1-3	20-40	20-40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

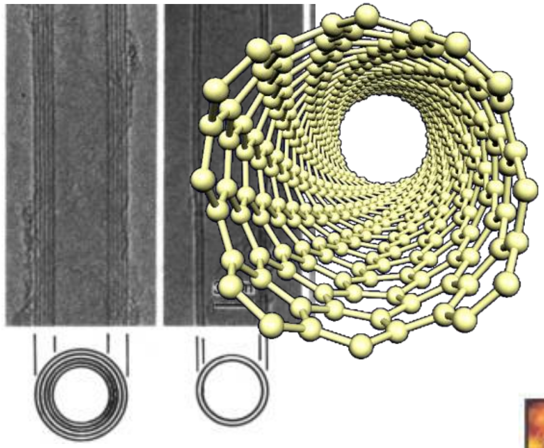
Freie Universität Berlin

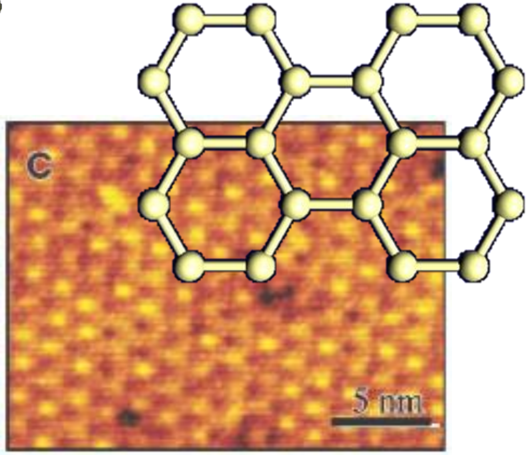
Carbon nanotubes

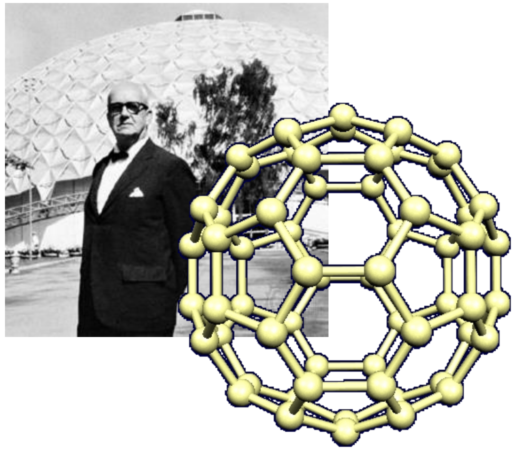
Stephanie Reich
Fachbereich Physik, Freie Universität Berlin

Pure sp^2 & sp^3 carbon

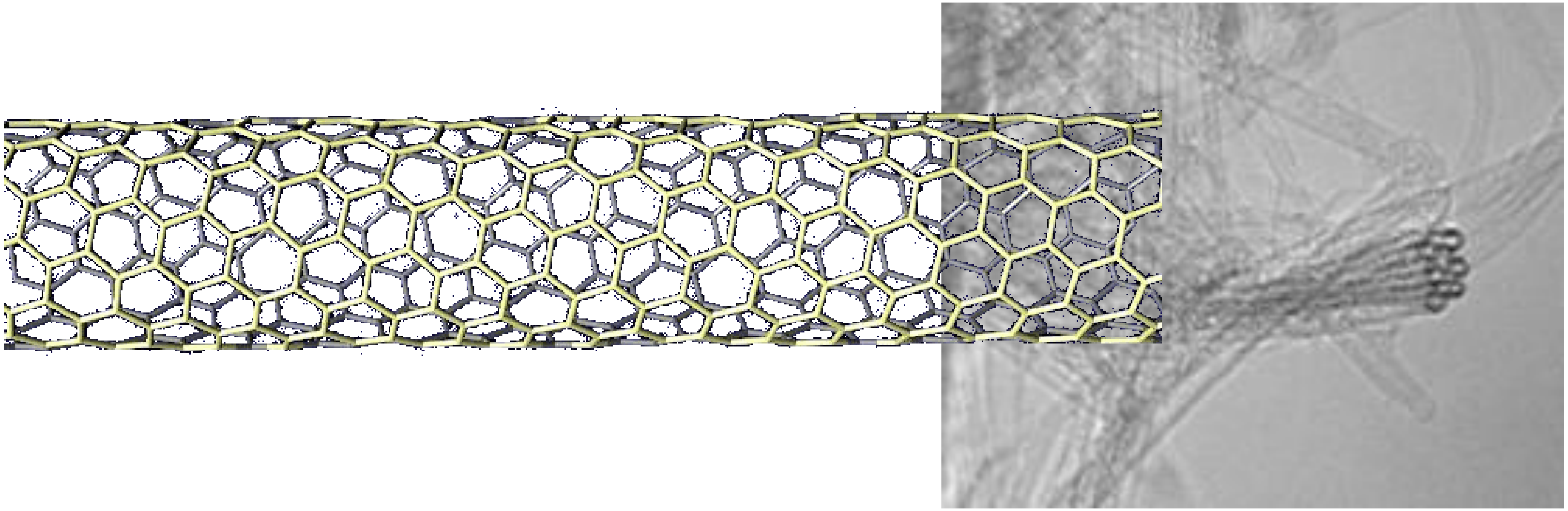








Single-walled carbon nanotubes



- Nanotubes are not one, but many materials
- **Nanotubes consist only of surface atoms**

Single-walled carbon nanotubes

Topics

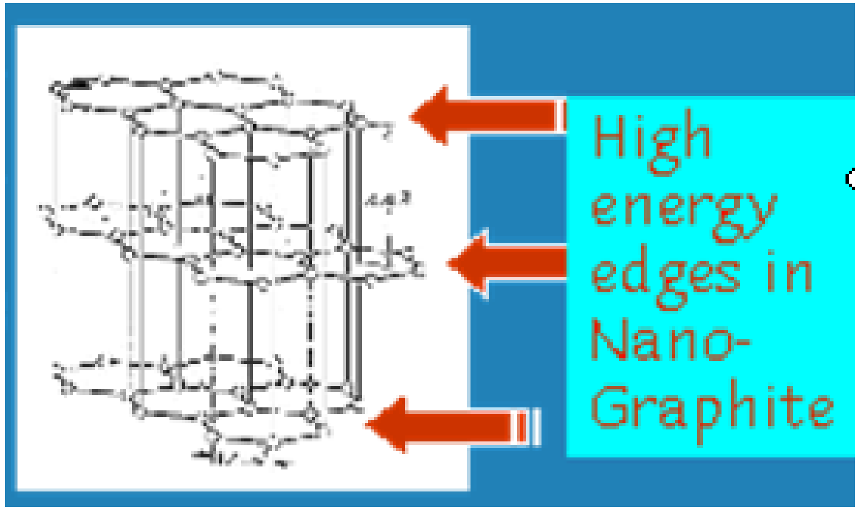
- Growth of carbon nanotubes
- Zone folding & fundamentals
- Electronic properties
- Optical properties
- Nanotube vibrations
- (Functionalization)

Why Ball and Tube Shape?

- In Nano Material Science, high surface and even edge energy matters.

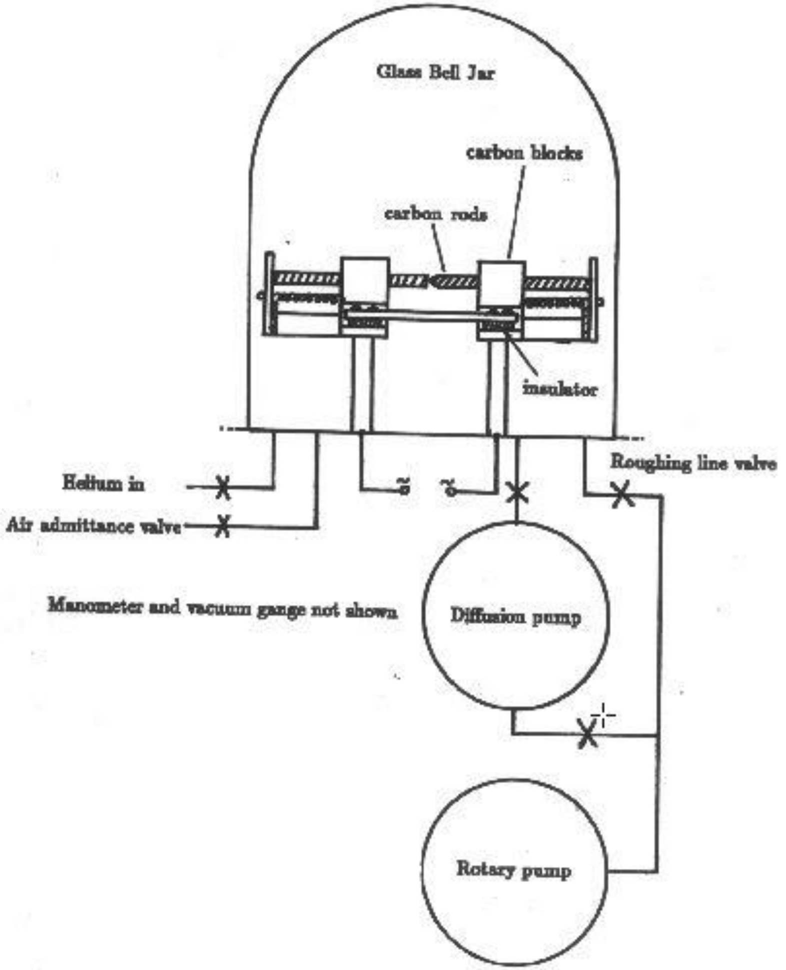
- As we previously discussed, a tiny piece of graphite would have a lot of atoms at its edge which is unstable.

- Giving opportunities, nano solids would roll them self up to bucky balls or tubes to minimize the total energy



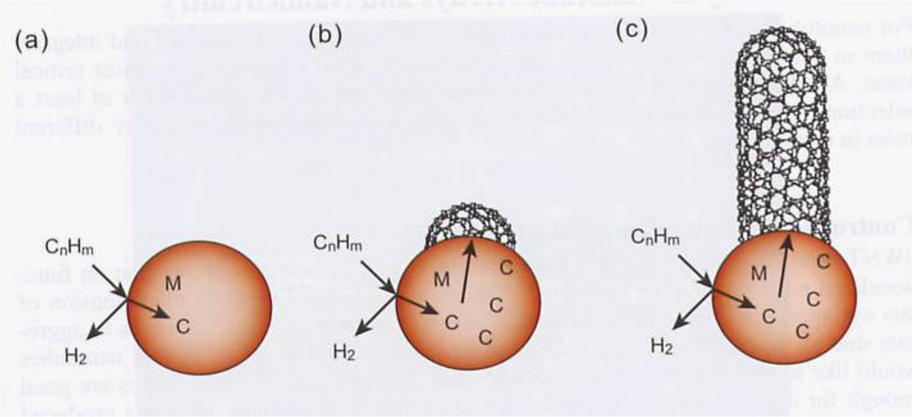
http://nanonet.rice.edu/intronanosci/sld005.html

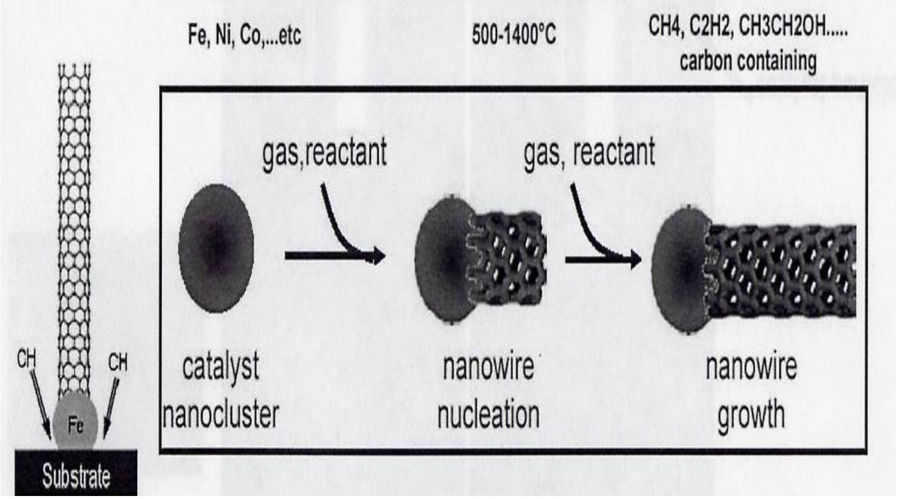
Making Buckminsterfullerene



- Carbon Arc Experiments
  - -- Two Carbon robs arcing in He at 100 Torr.
  - -- Can now be reproduced in gram level at a time
- First discovered in 1985, it is most known nano particles
- The round cage like structure of the fullerenes was reminiscent of the dome structures designed by the architect Richard Buckminster Fuller, and so it was named Buckminsterfullerene

Mechanisms of Carbon Nano tube



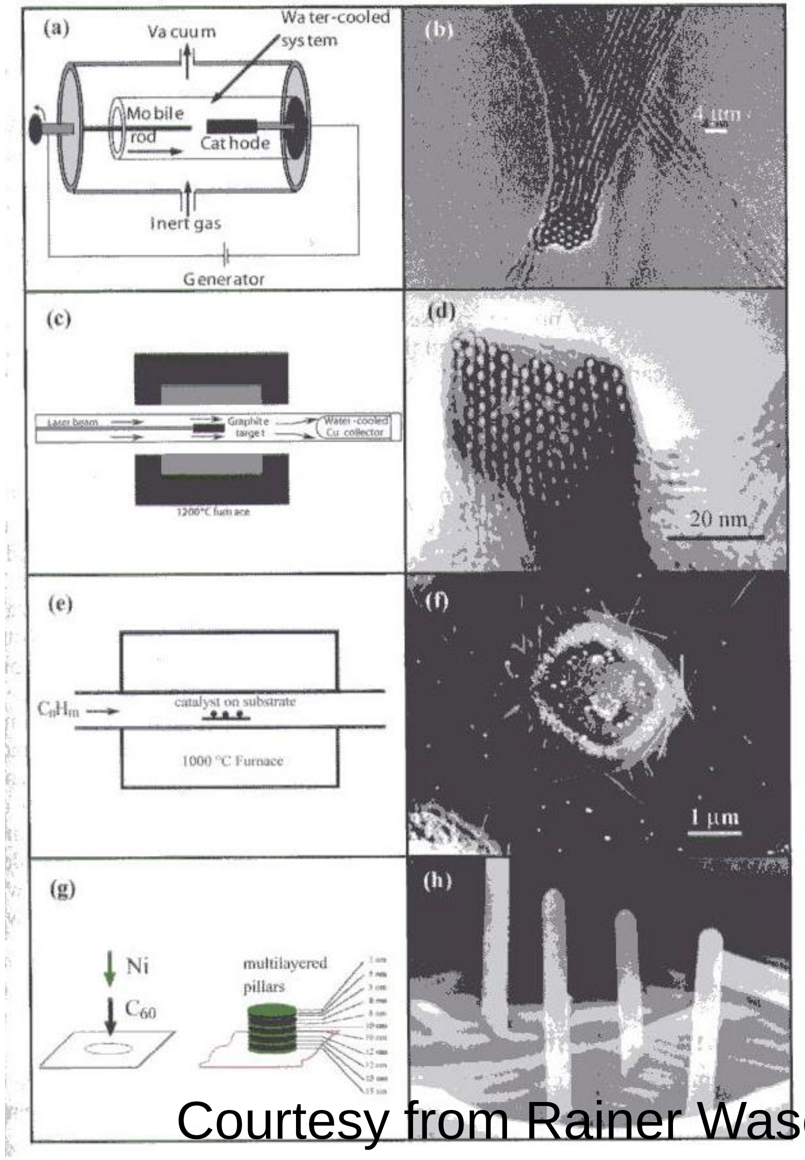


Root Growth Mechanism:

- Transition metal as catalyst
- Hydrocarbon dissociate at metal surface into H and C.
- Once surface saturated with C, it starts to form as graphite sheet with fullerene cap
- More C atoms can be inserted into Metal-C bond so the tube get growing longer.

Courtesy from Rainer Waser Nano-electronics and Information technology

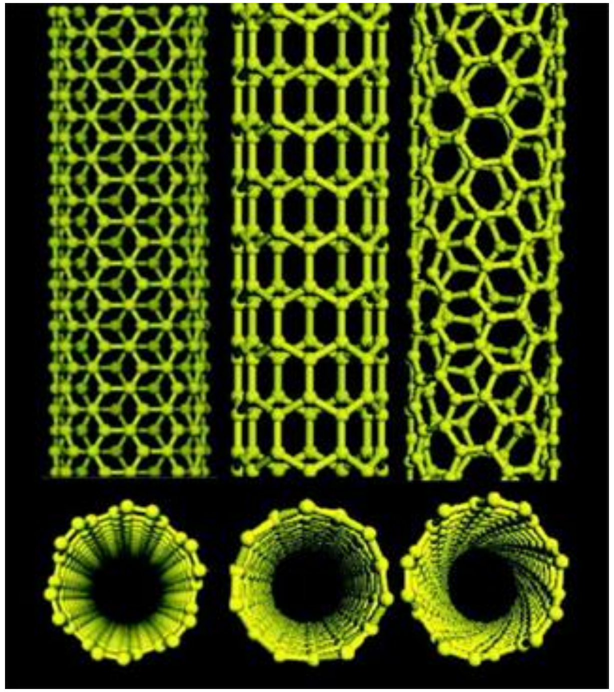
Synthesis Methods for CNT

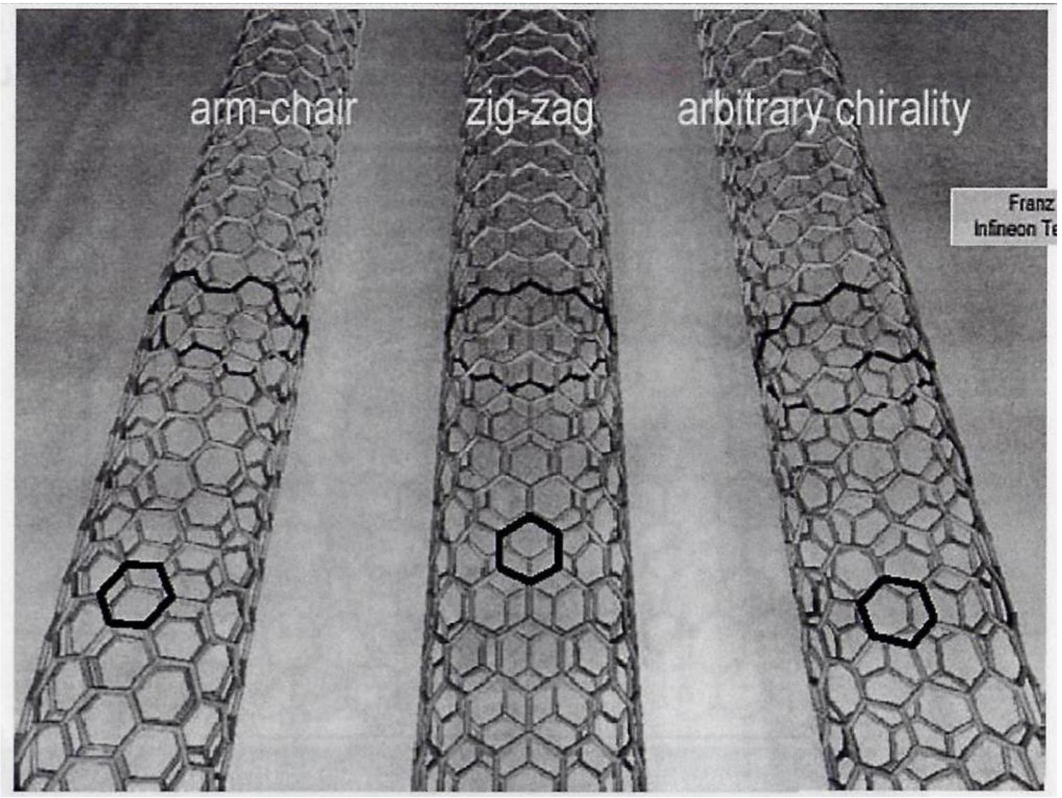


1. Electric Arc Discharge: similar with the one for Bucky Ball
2. Laser Vaporization: Graphite target with Co, Ni powders sitting in 1200C furnace and hit by laser pulse. CNT collected downstream at cold finger.
3. CVD: pre-patterned structure with Fe, Mo nano particles in a tube furnace at 1000C and methane as precursor of carbon
4. Fullerene recrystallization: depositing Ni and C60 multi-layers and recrystallize at 900C

Courtesy from Rainer Waser Nanoelectronics and Information technology

Properties of Carbon Nano Tube





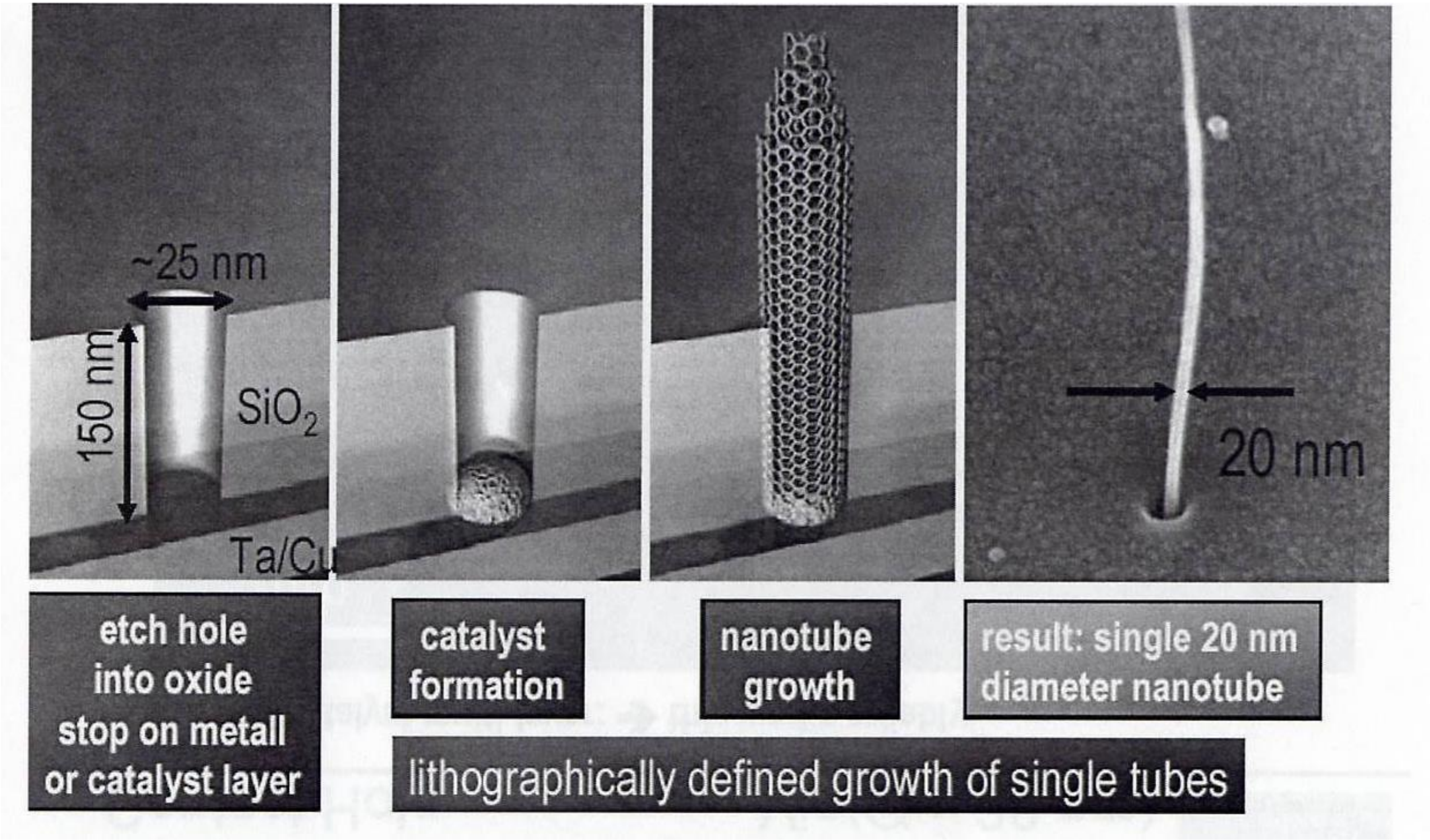
- There are different ways to roll up the graphite sheet to form carbon nano tube. This configuration is defined as Chirality

- The electronic properties of carbon nano tube are determined by its chirality.

- It can be semiconductor, semimetals or metals

Courtesy from Stanley Wolfe: Advanced Silicon Processing

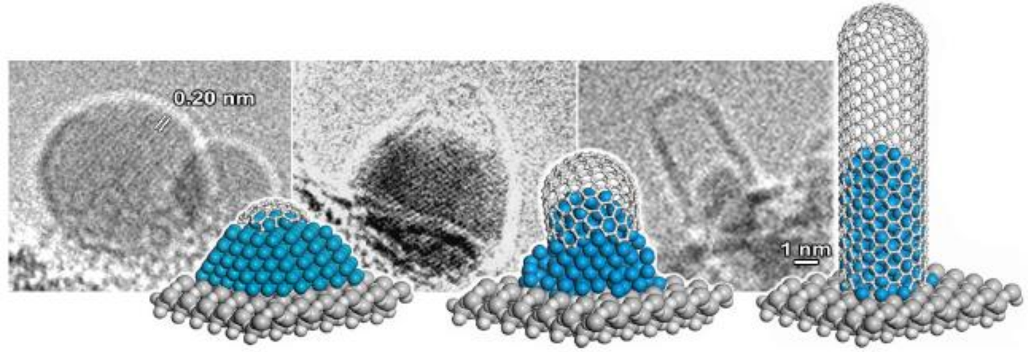
Self Assembly of Carbon Nano Tube as interconnect (Metal)

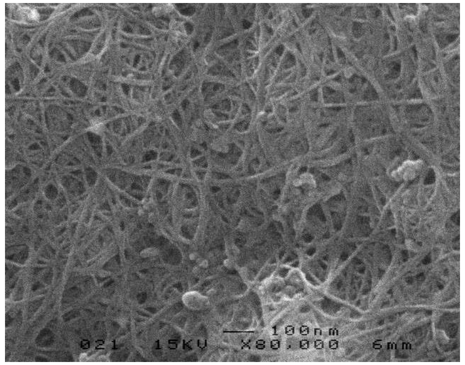


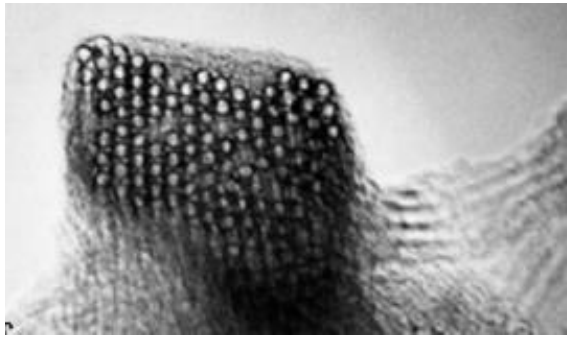
Courtesy from Stanley Wolfe: Advanced Silicon Processing

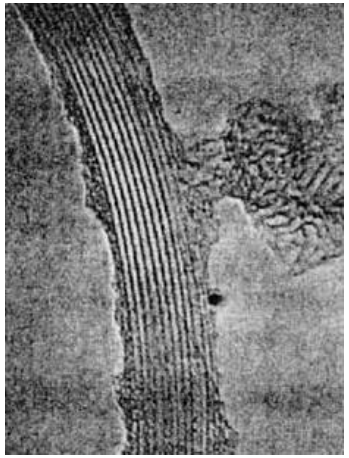
Nanotube growth

- grow out of a carbon plasma
  - laser ablation
  - arc discharge
  - chemical vapor deposition
- metal catalysts
  - nickel, cobalt, iron …
- carbon tubes
  - diameter ~ 1 nm
  - length 500 nm – 4 cm
- industrial scale production
  - started 2005
  - since 2009 large scale



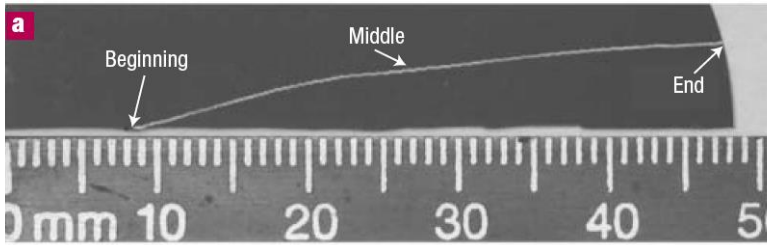


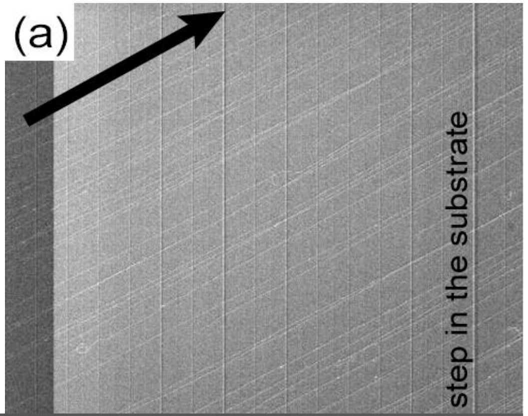


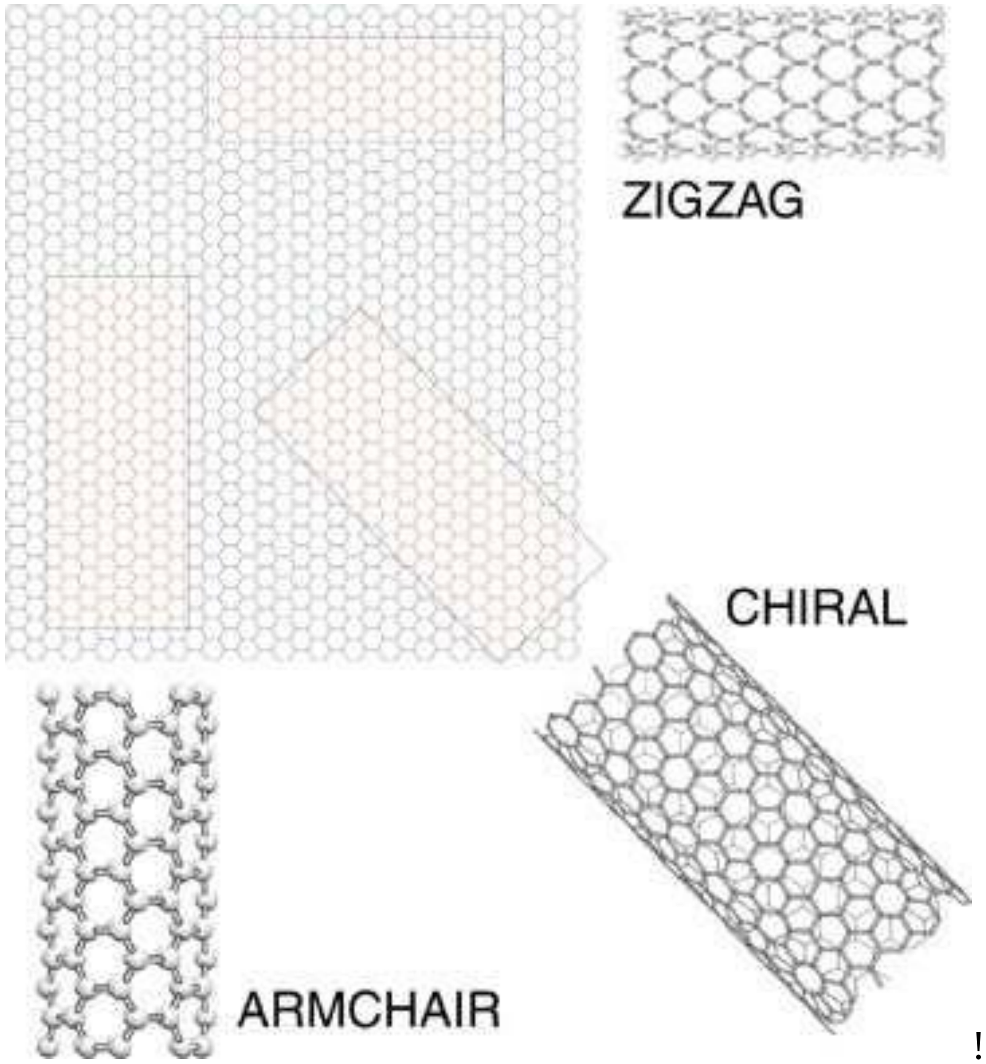


Chemical vapor deposition

- ☐ long tubes & high yield
- ☐ high quality
- ☐ high degree of control during growth

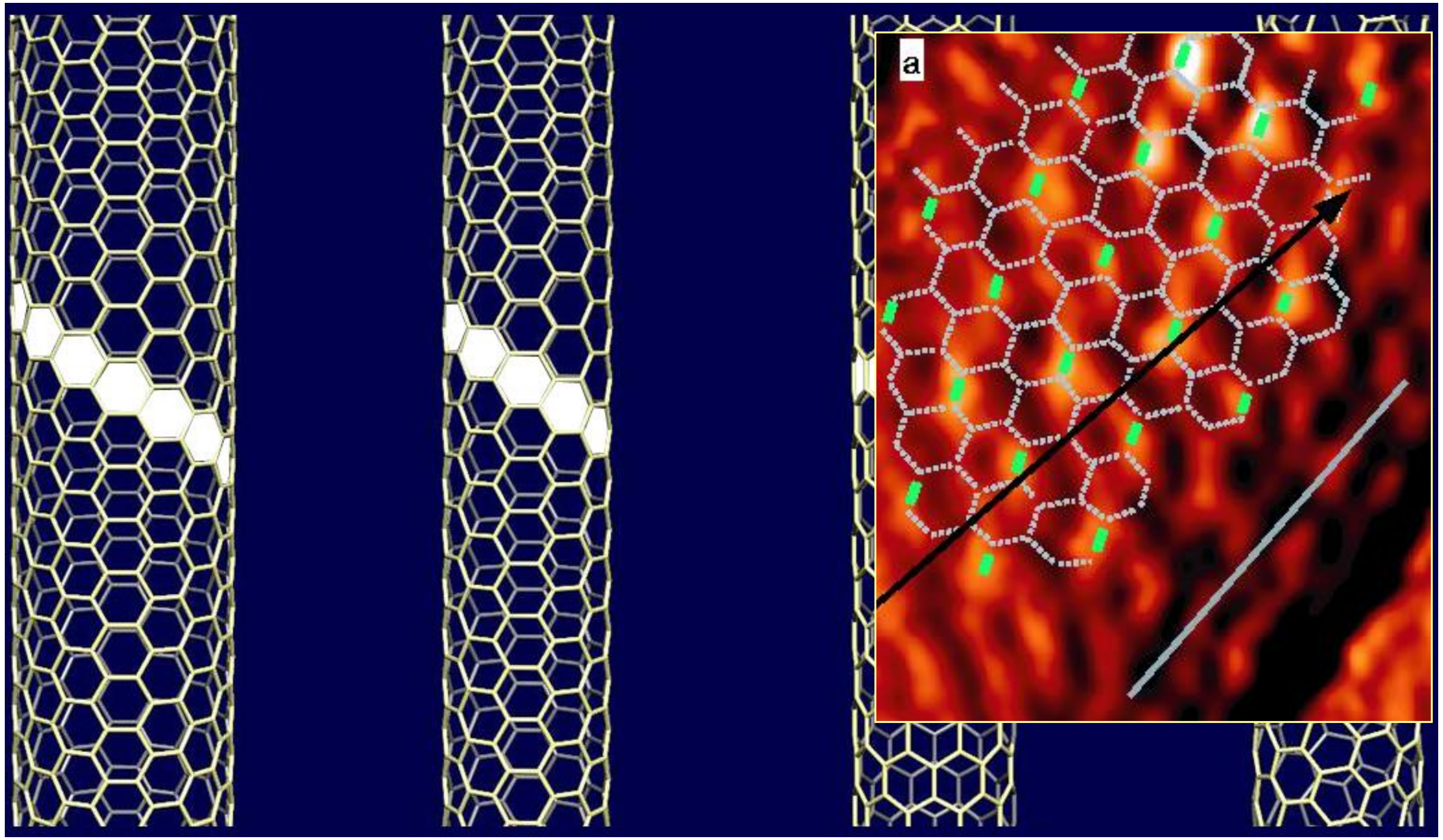






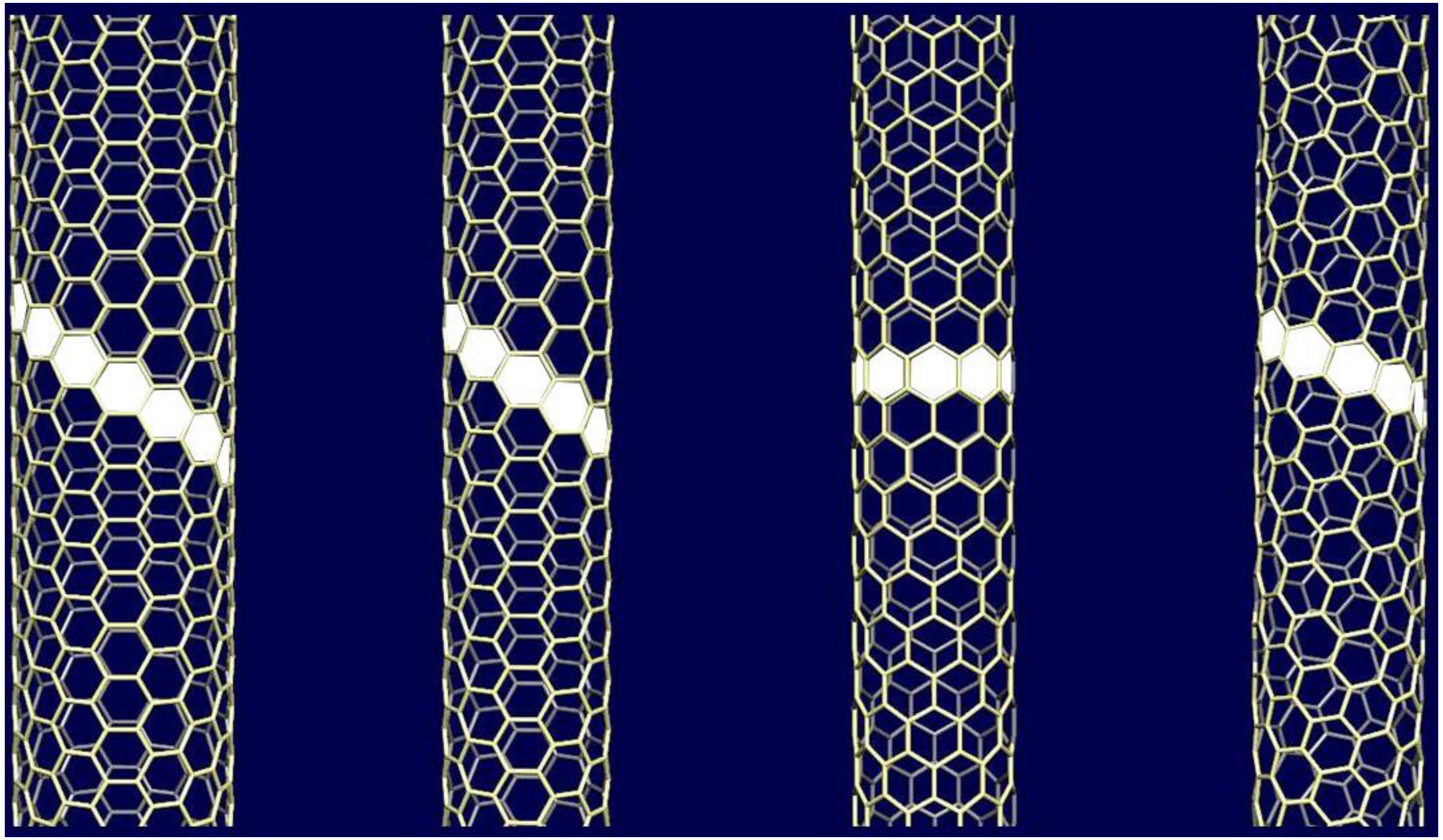
a'-?,%!` 8!Z +0. A!(%!: . 05-?,+A! 0&!jJk!

Nanotube structure



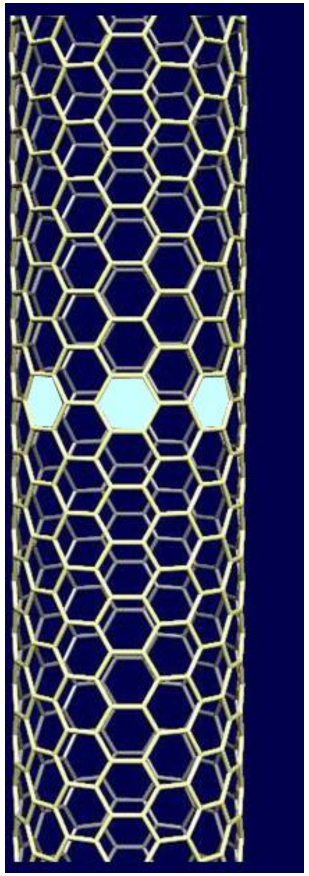
- nanotube diameter *d* & chiral angle Θ determine microscopic structure

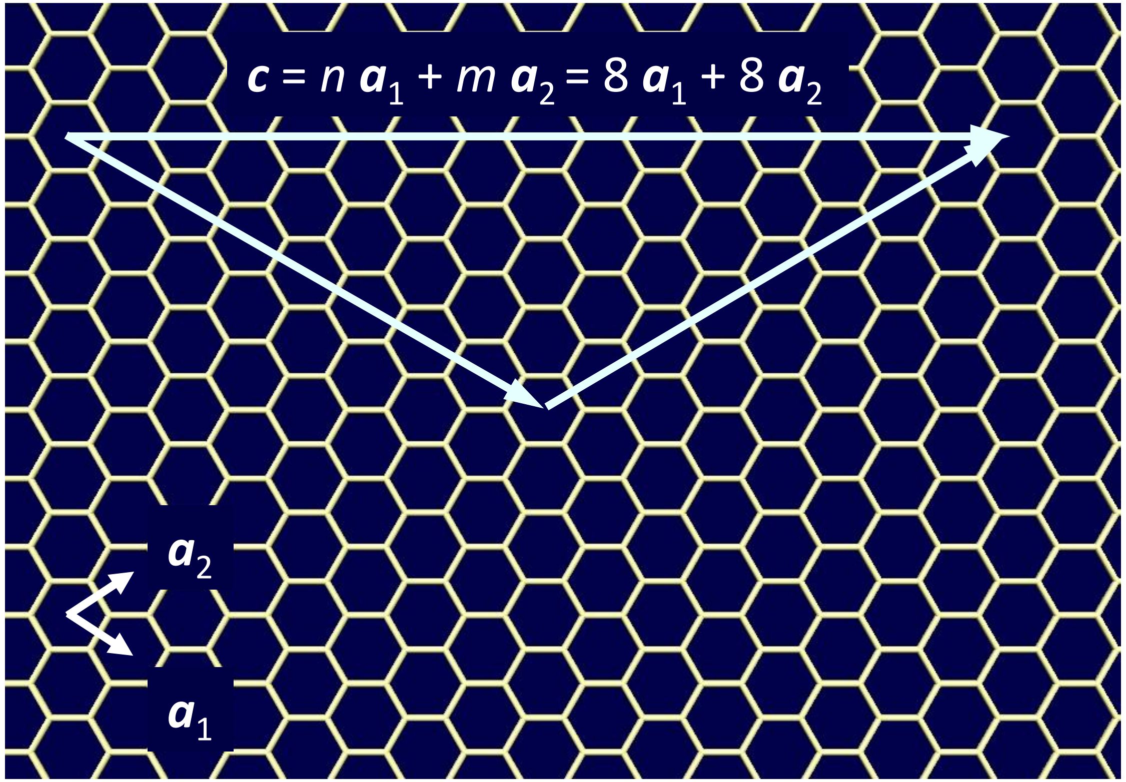
Nanotube structure



- nanotube diameter *d* & chiral angle Θ determine microscopic structure

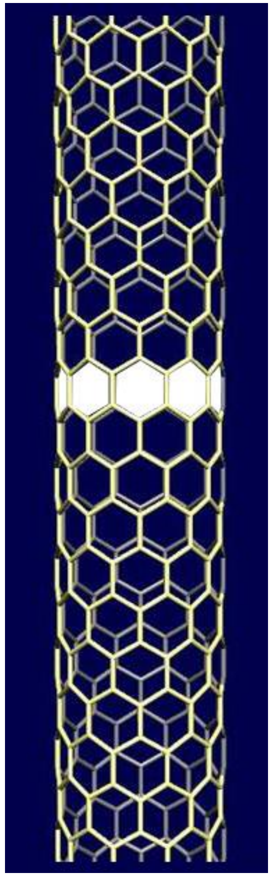
Chiral vector - (n,m) nanotube

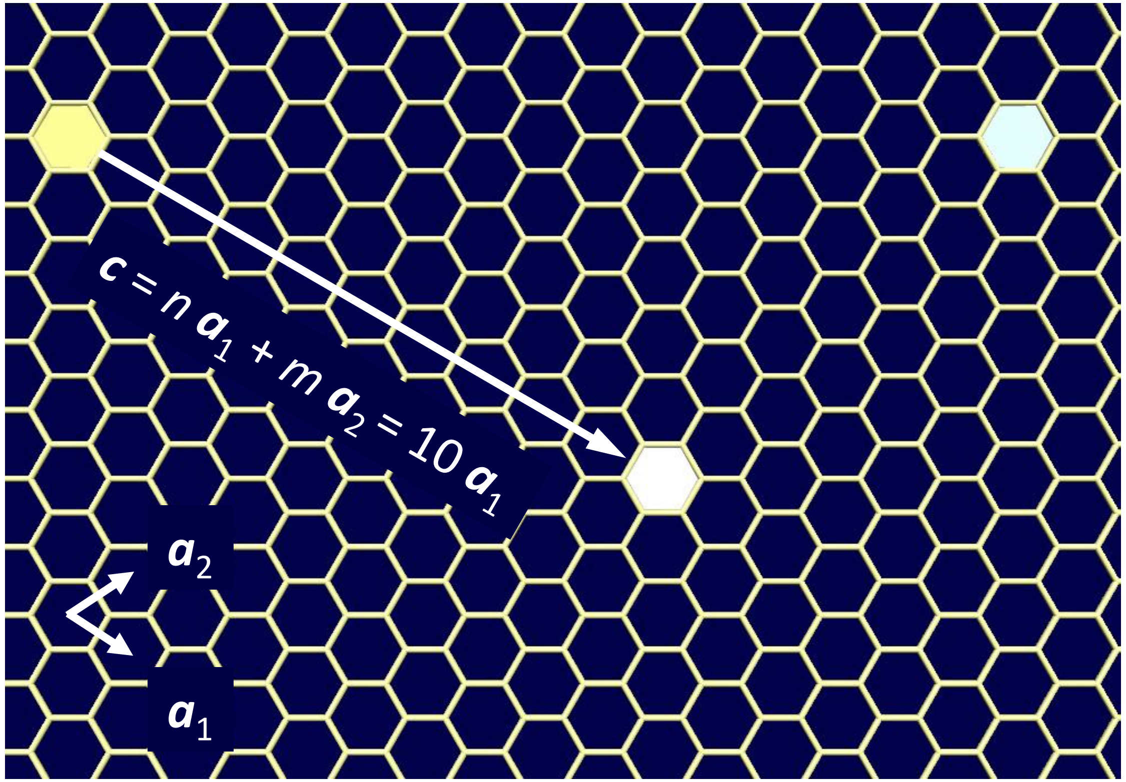




- nanotube diameter d & chiral angle Θ determine microscopic structure
- specified by the chiral vector $\boldsymbol{c}$ around the circumference

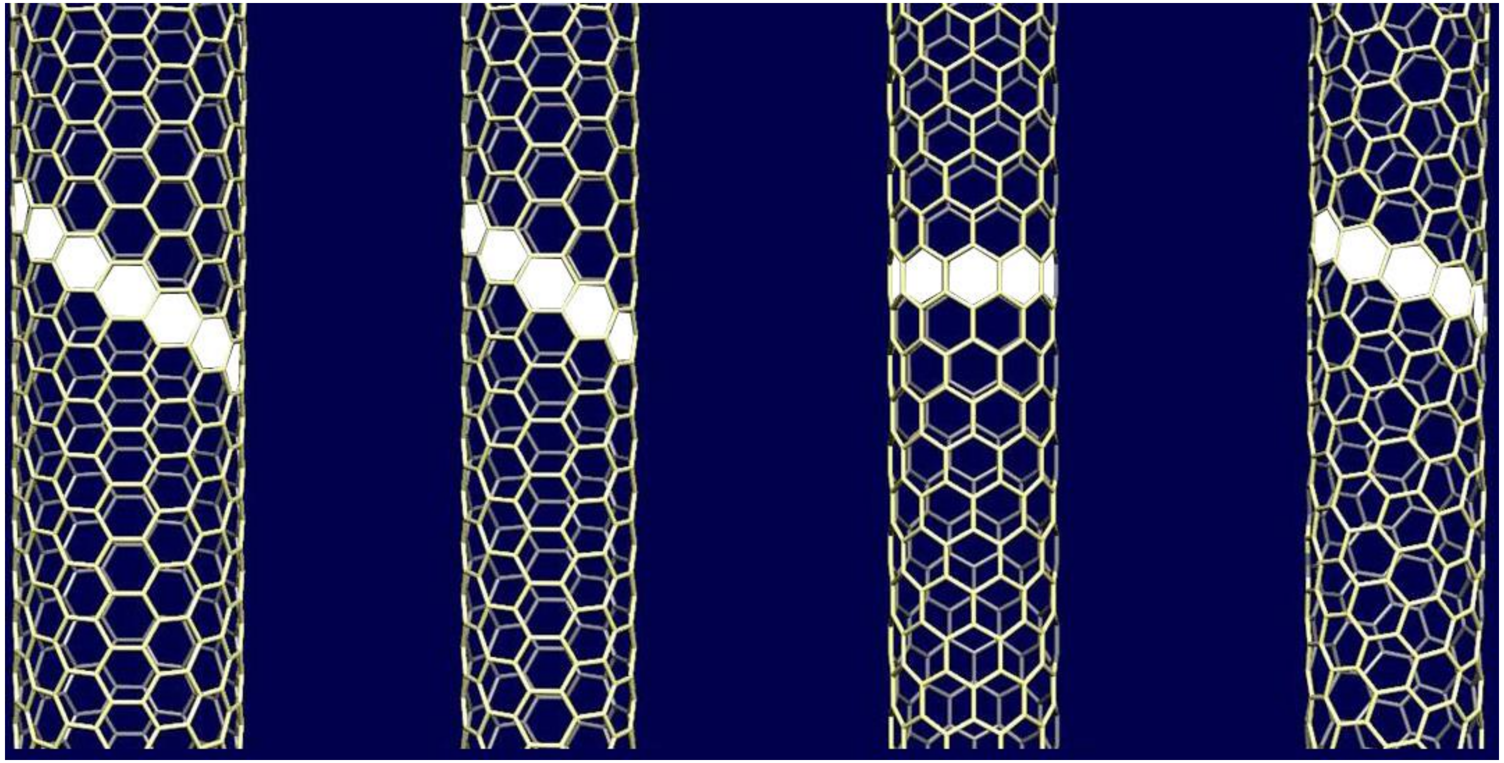
Chiral vector - (10,0) nanotube





- nanotube diameter d & chiral angle Θ determine microscopic structure
- specified by the chiral vector $\boldsymbol{c}$ around the circumference

Nanotube structure

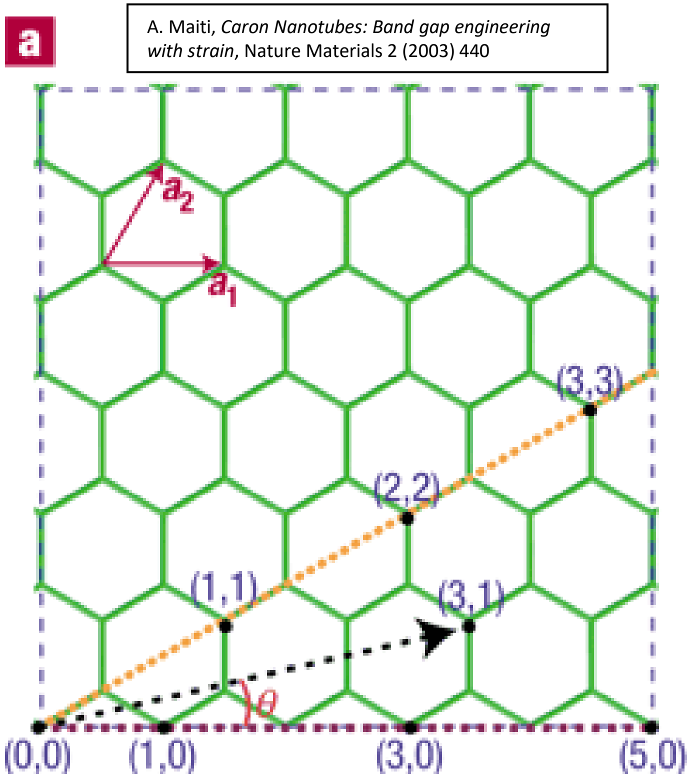


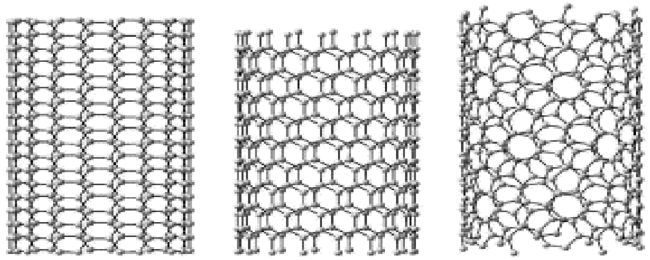
- typical samples contain 40 – 100 different chiralities
- controlling chirality during growth is impossible

Properties: Foundation

- Nanotubes are fully described by their chiral vector
  - $C_h = n\,\hat{a}_1 + m\,\hat{a}_2$
- Important parameters
  - $d_t = (\sqrt{3}/\pi)a_{c\text{-}c}(m^2 + mn + n^2)^{1/2}$
  - $\Theta = \tan^{-1}(\sqrt{3}n/(2m + n))$
- Grouped according to θ
  - Armchair: n=m, θ=30°
  - Zigzag: n or m=0, θ=0°
  - Chiral: 0°<θ < 30°

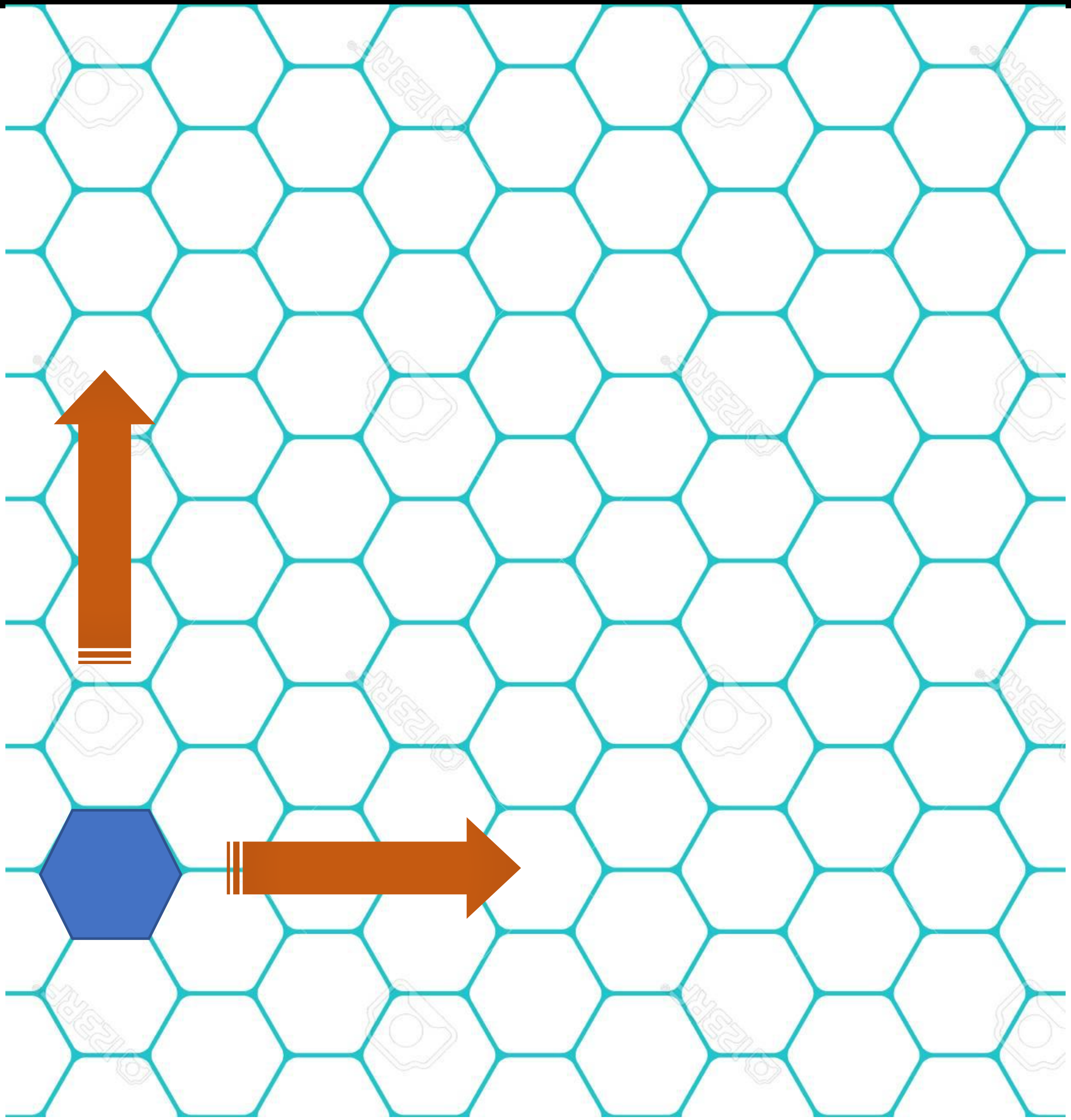
A. Maiti, *Caron Nanotubes: Band gap engineering with strain*, Nature Materials 2 (2003) 440



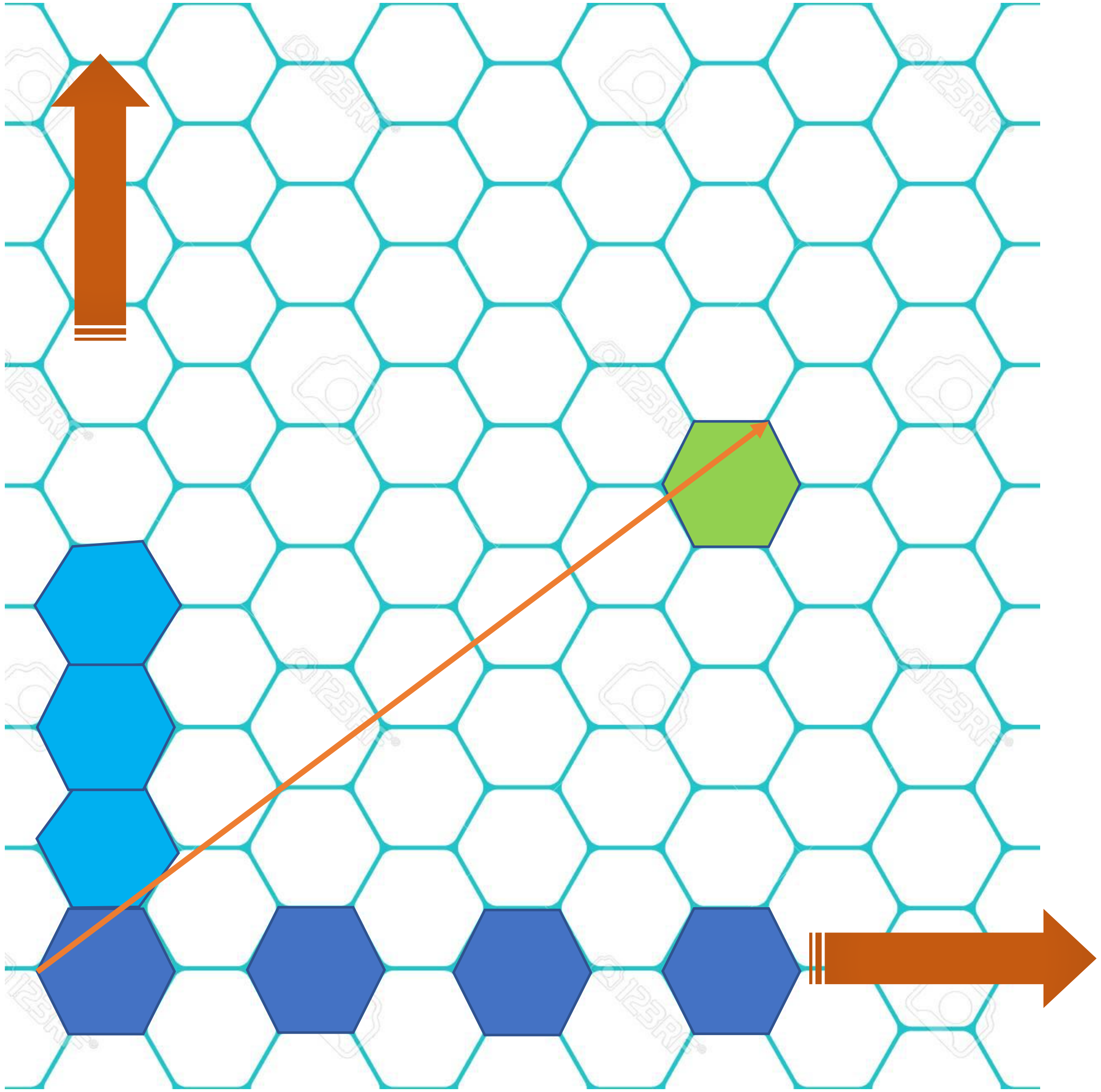


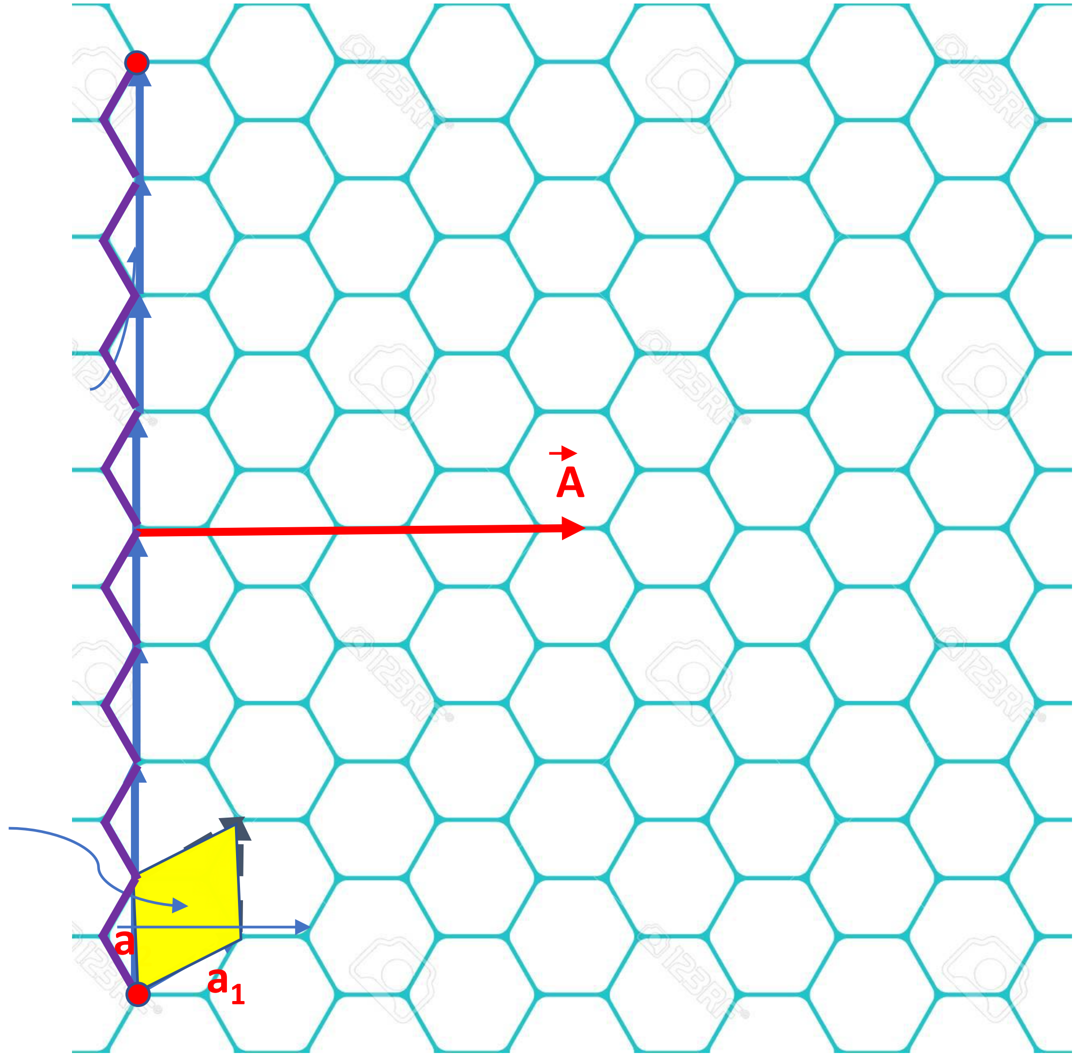
V. Popov, *Carbon nanotubes: properties and applications*, Materials Science and Engineering R 43 (2004) 61-102

Equivalent

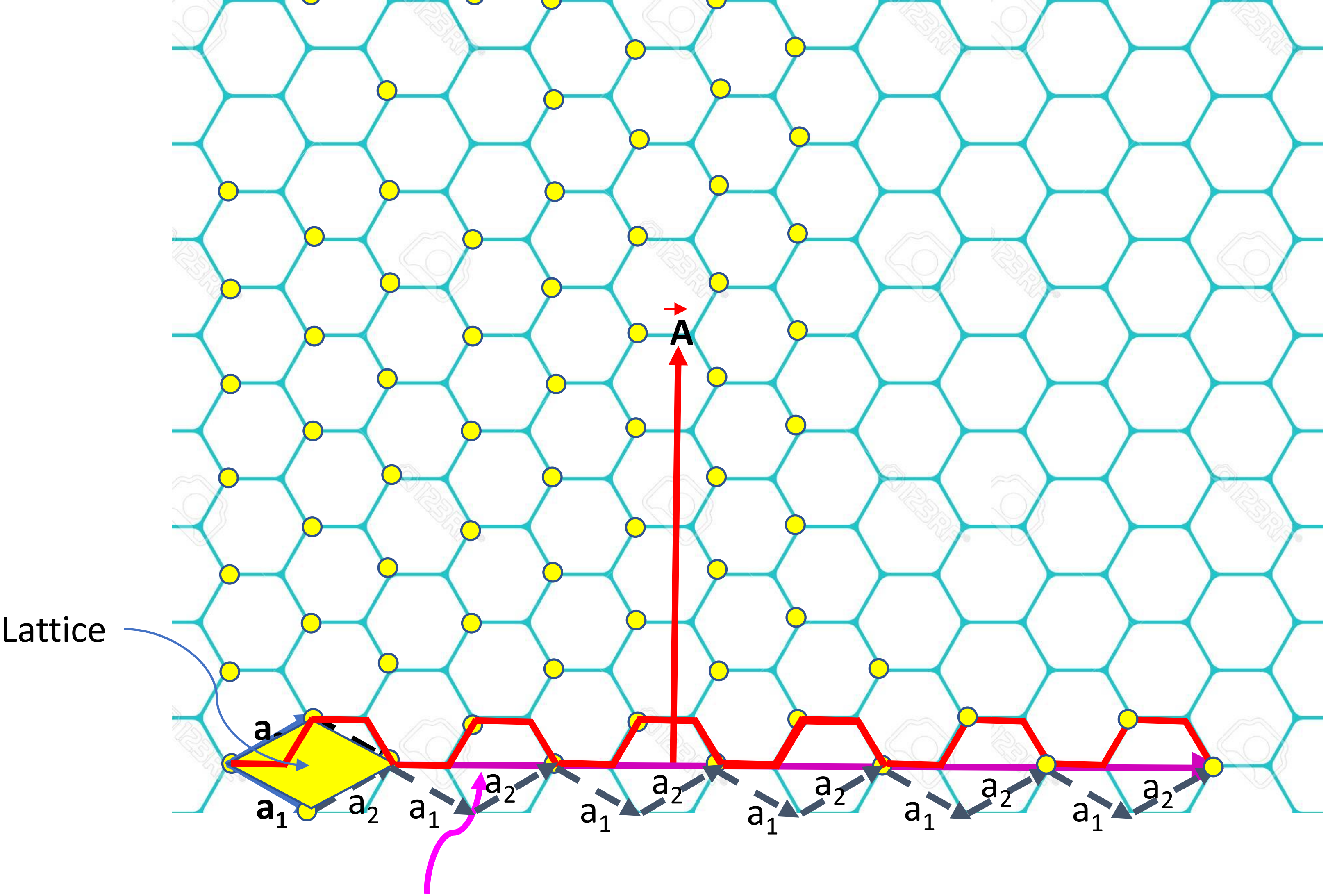


Equivalent





$\vec{A}$
a
a_1

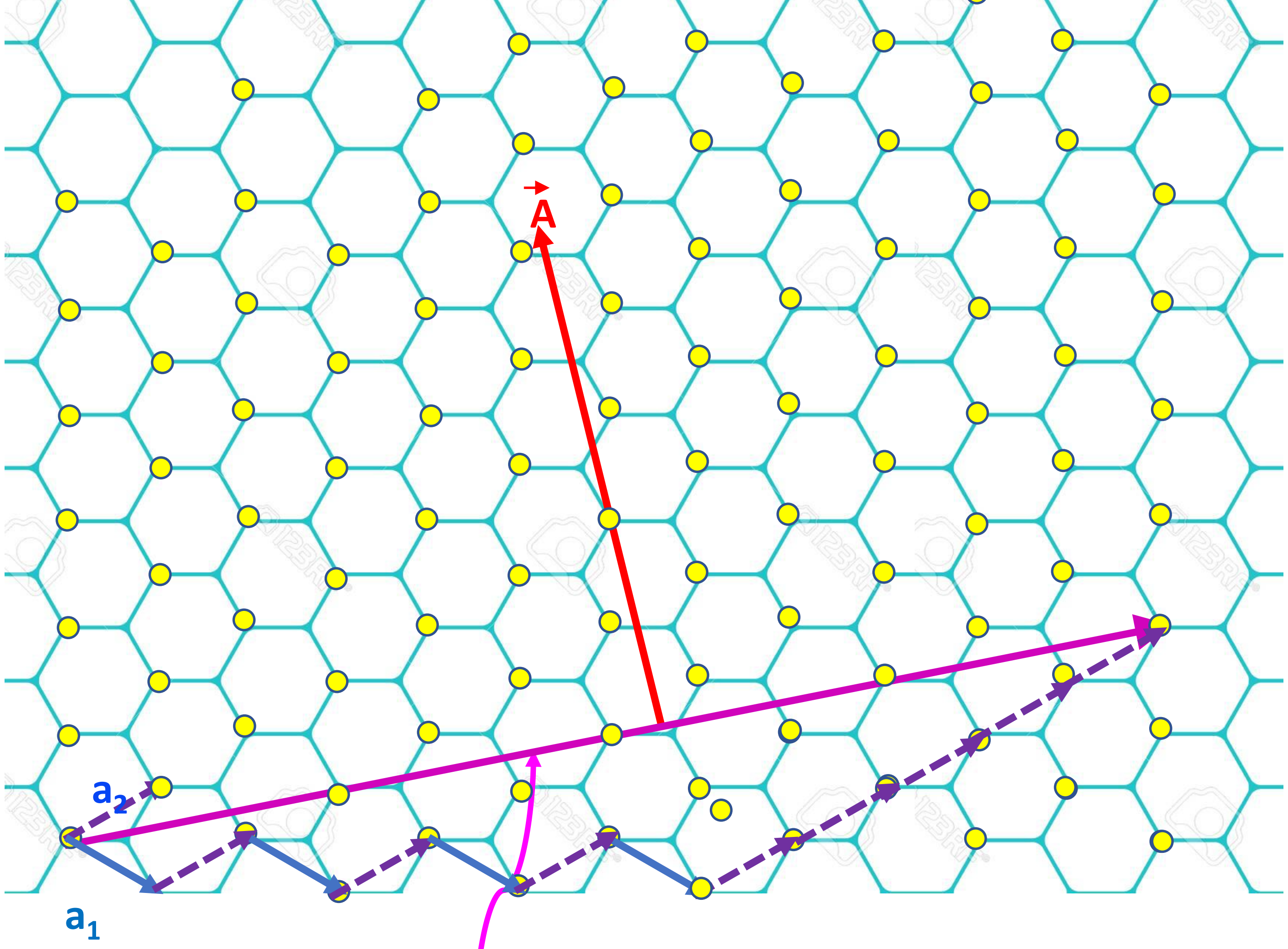


Chiral Vector

(circumferential vector)

It is lattice vector

$\vec{C} = \mathbf{6a_1+6a_2}$

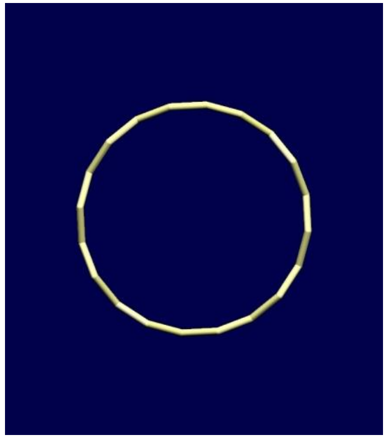


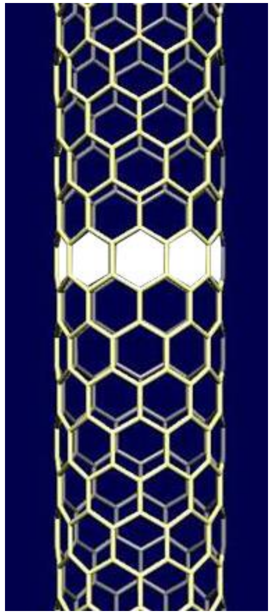
Chiral Vector

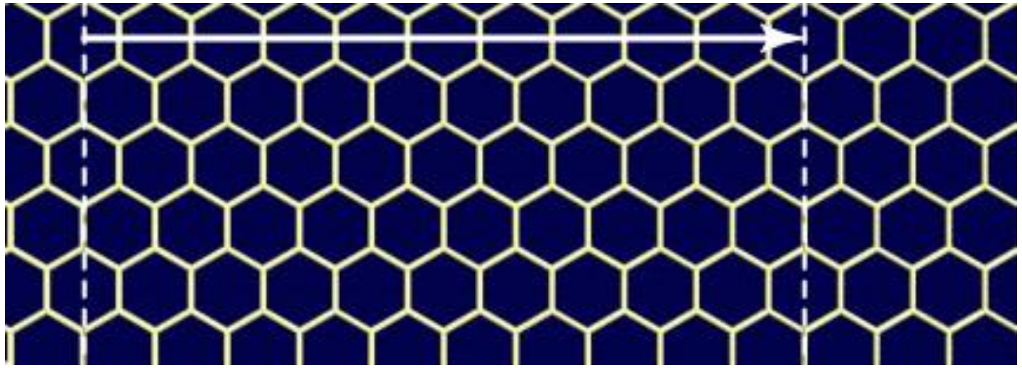
(circumferential vector)

It is lattice vector

Quantum confinement

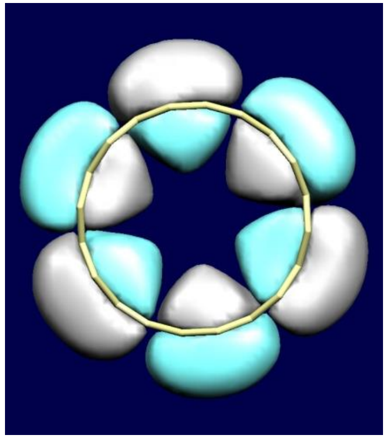


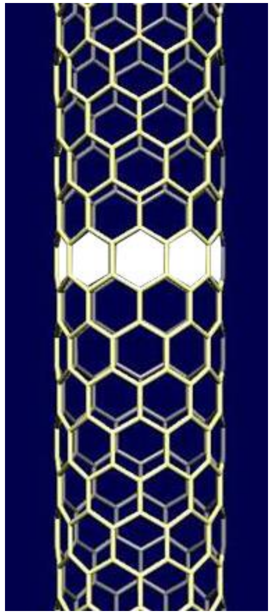


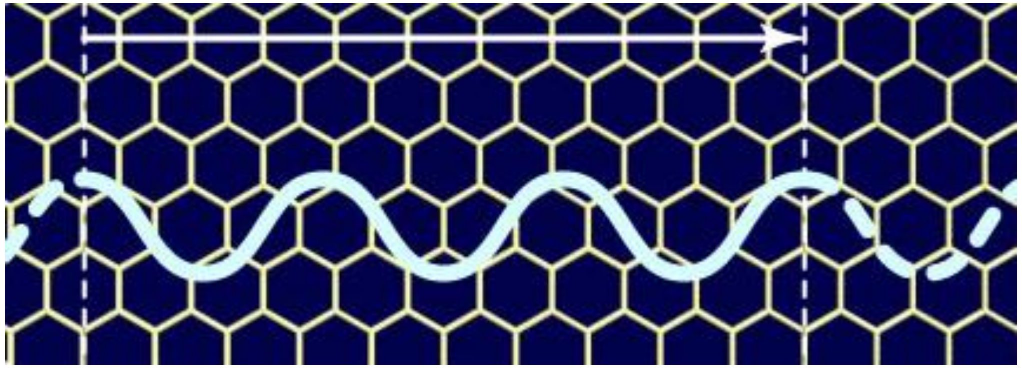


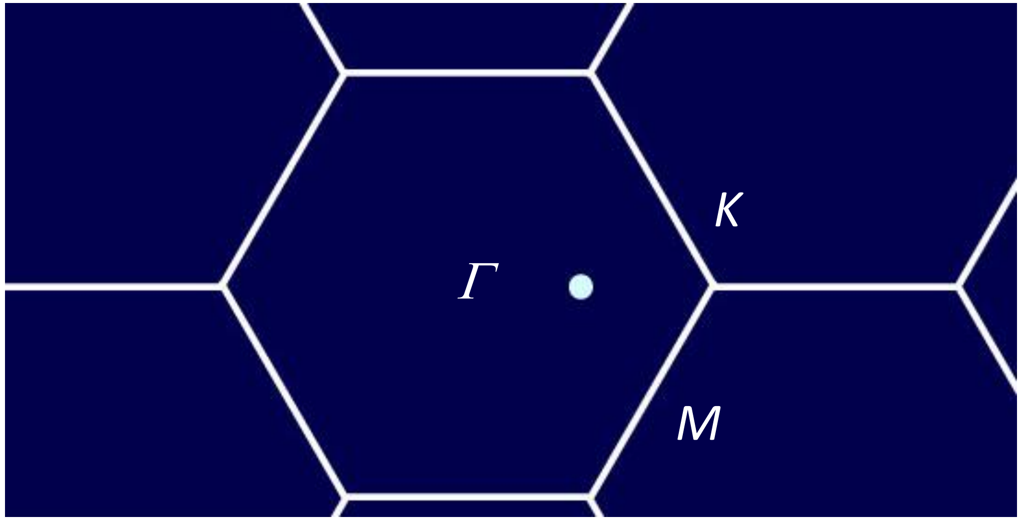
- circumference – periodic boundary conditions
- $\lambda = \pi$ diameter/p (*p* integer)

Confined phase space

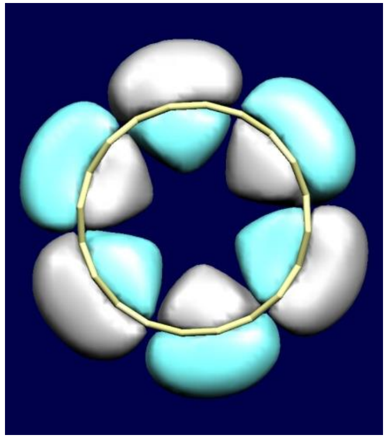


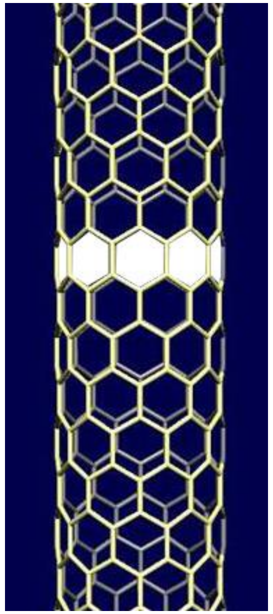


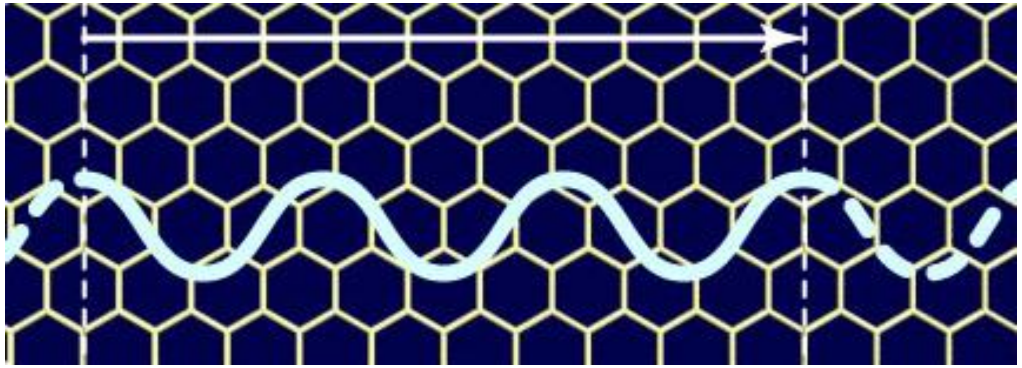


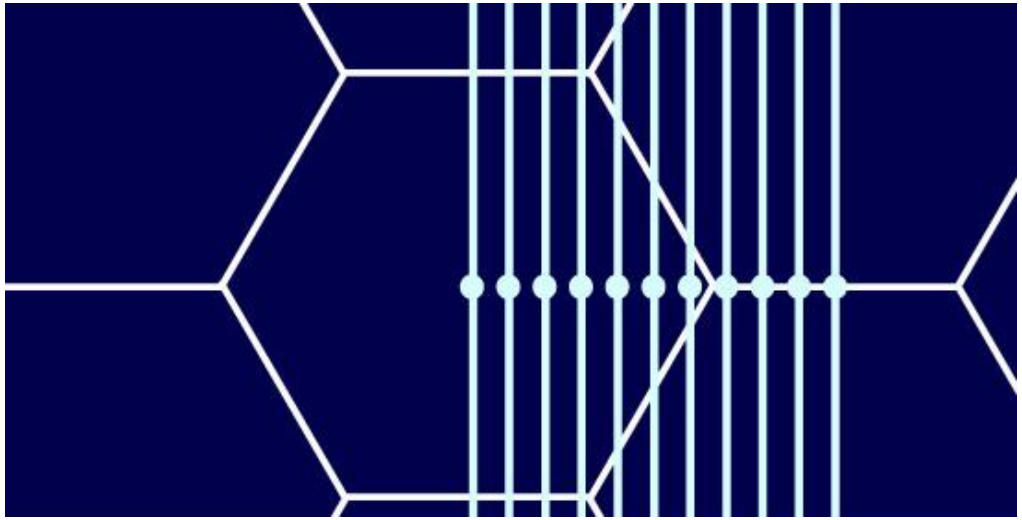


One-dimensional Brillouin zone

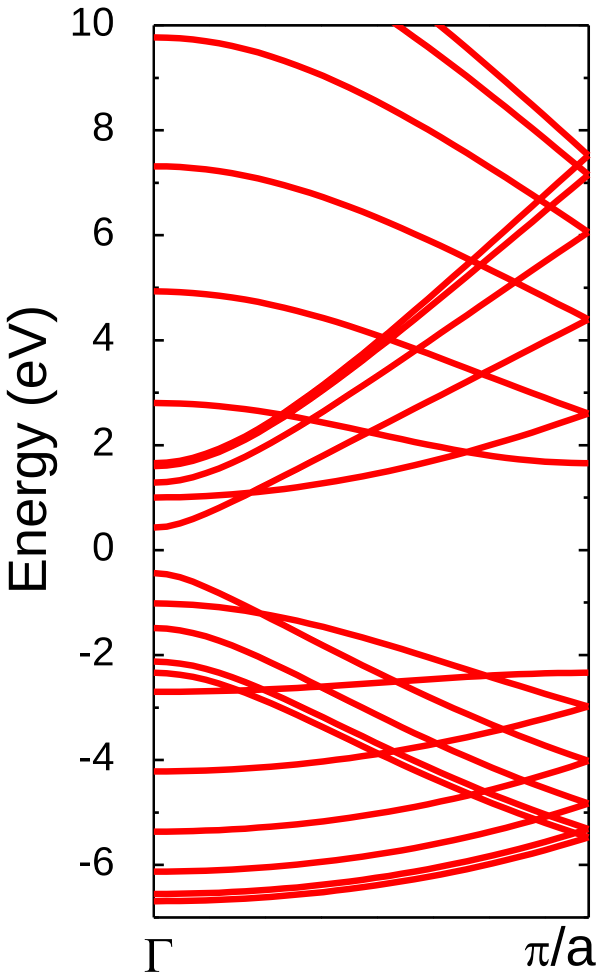


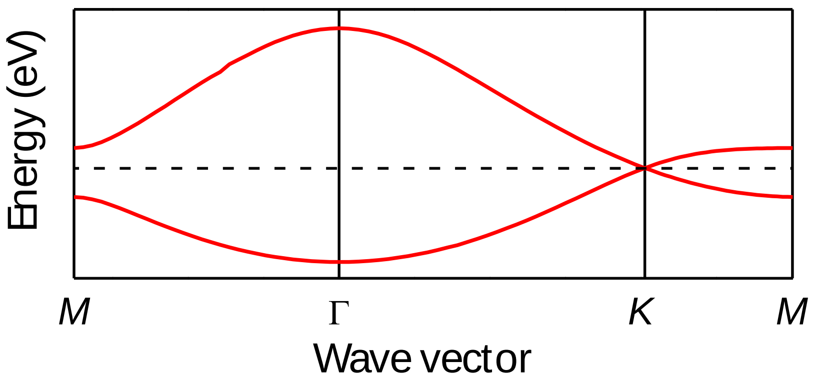


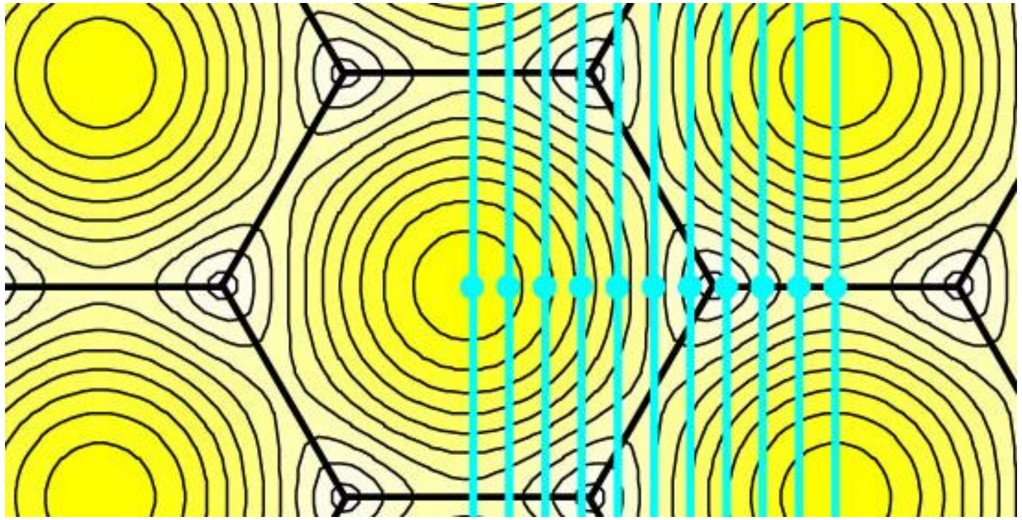




Band structure (10,0) tube

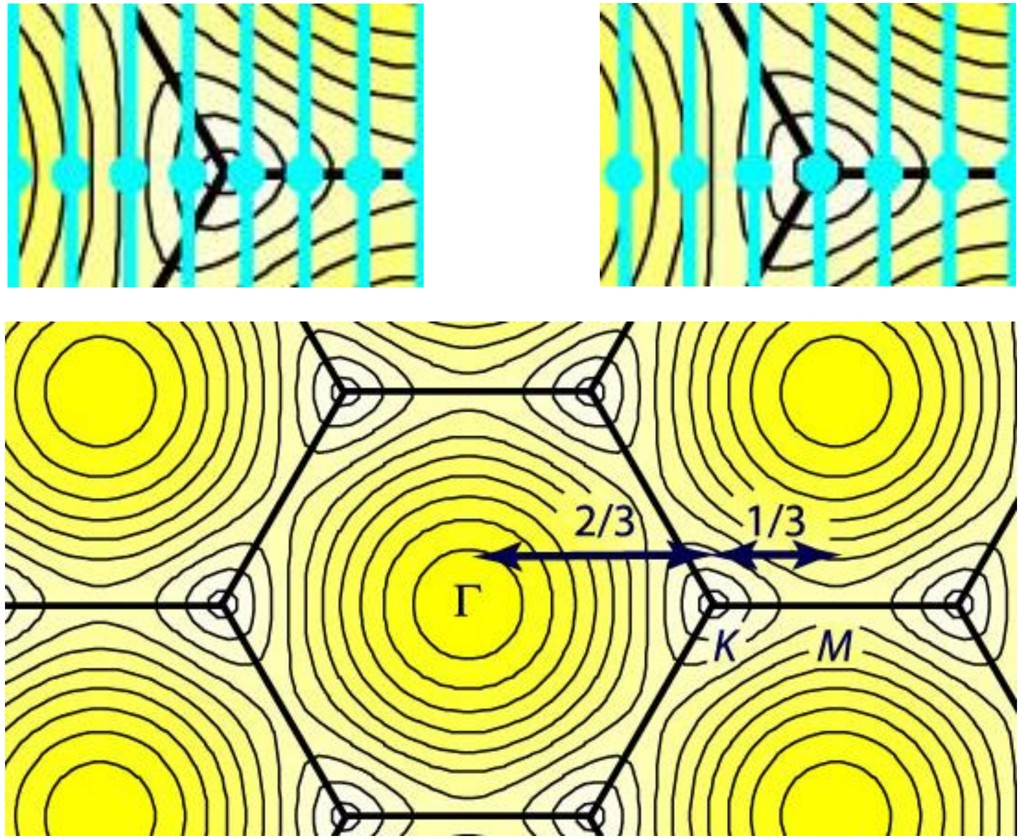




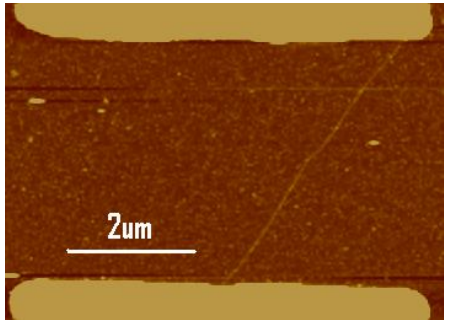


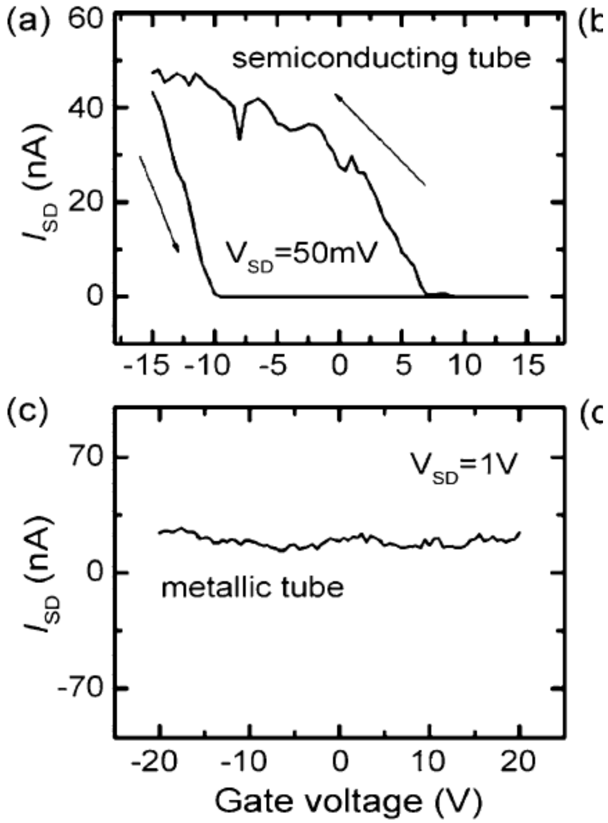
Metal or semiconductor? – (n-m)/3

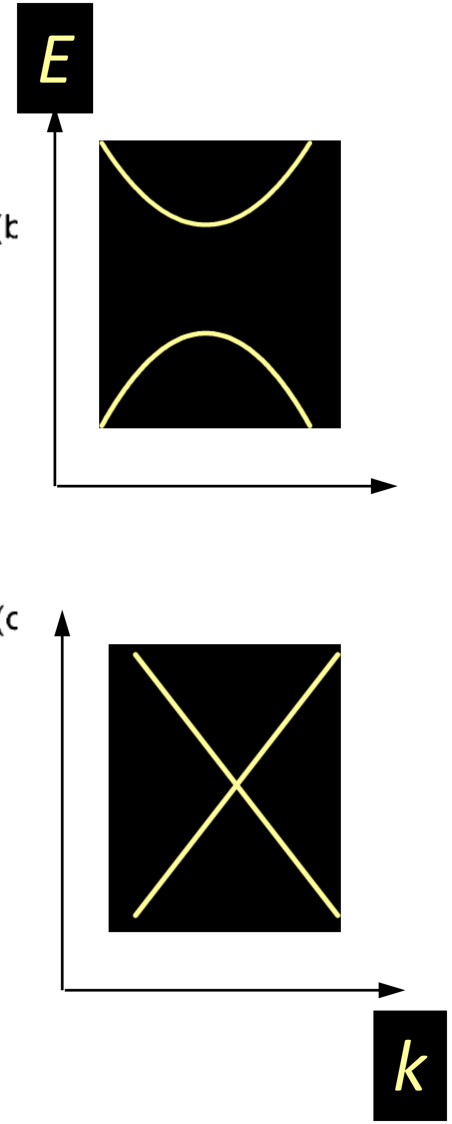
- quantization in (n,0)
  - n+1 allowed lines between Γ and M
- ΓK = 2/3 KM = 1/3
- metals
  (3,0), (6,0), (9,0), (12,0) …
- semiconductors
  (2,0), (4,0), (5,0), (7,0) …
- general condition
  metallic if
  (n-m)/3 = integer



Metal & semiconductor in experiment



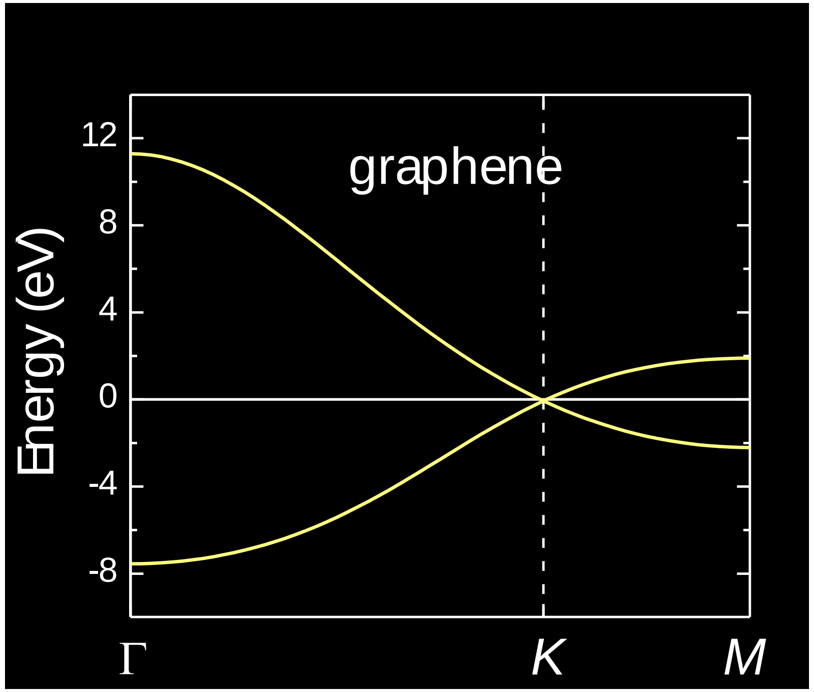


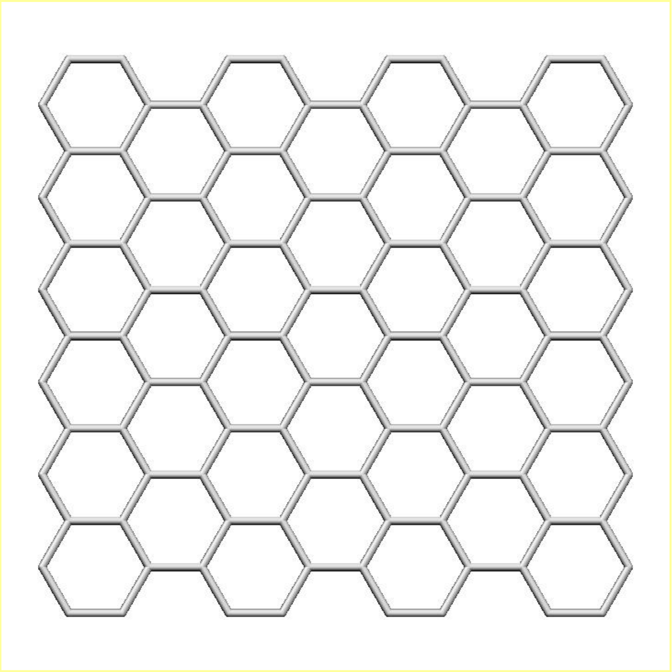


Concept of zone folding

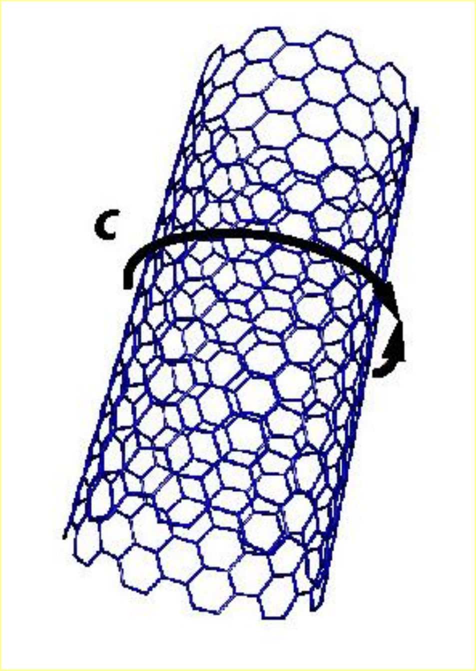
- quantization along the circumference
- reduced phase space
- find nanotube properties by reference to graphene
- works for
  - electrons, phonons, and other quasi-particles
  - interactions, e.g., electron-phonon coupling
- central concept of nanotube research

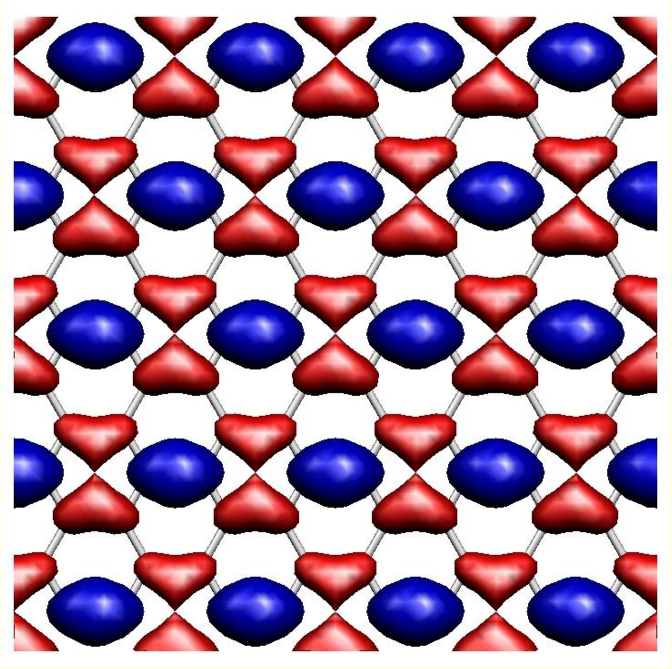
Graphene – a semimetal





HOMO & LUMO



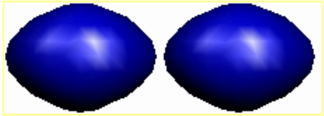


⇒ HOMO (highest occupied molecular orbital) & LUMO (lowest unoccupied molecular orbital) are degenerate

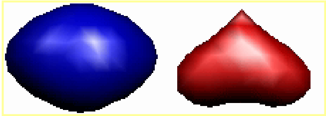
⇒ Nanotube chiral vector compatible with HOMO/LUMO wave function?

Metal or not?

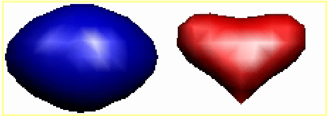
- three nanotube families



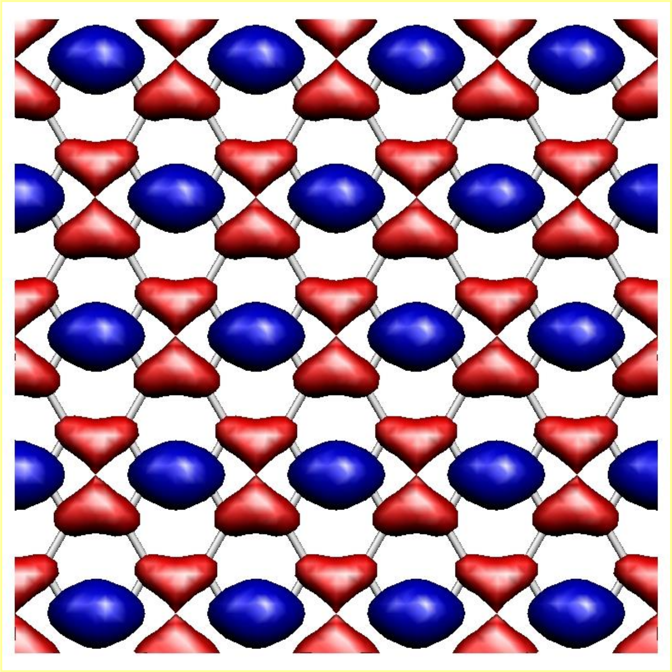
metal



semiconductor
small gap

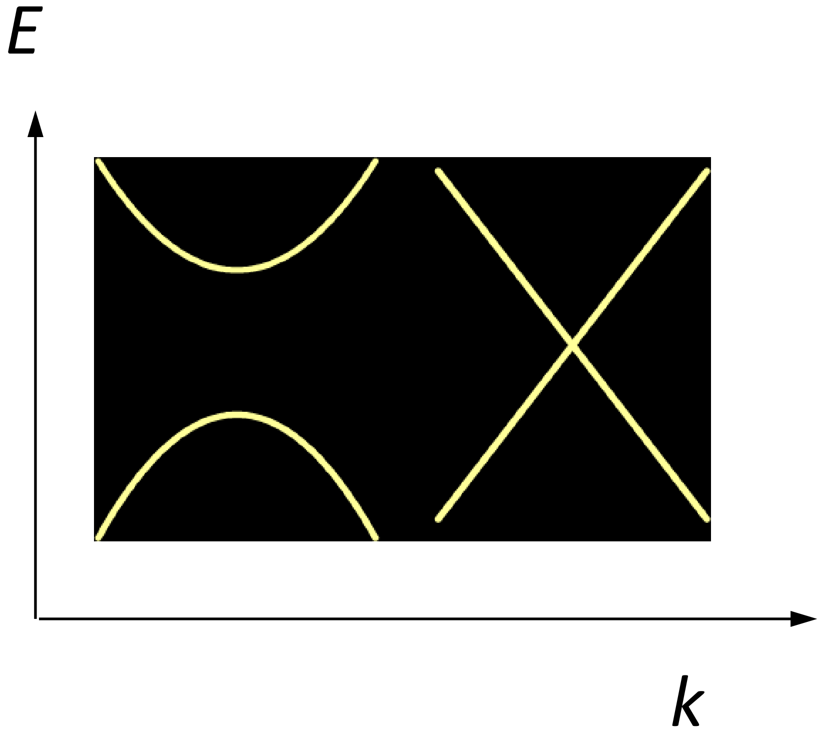


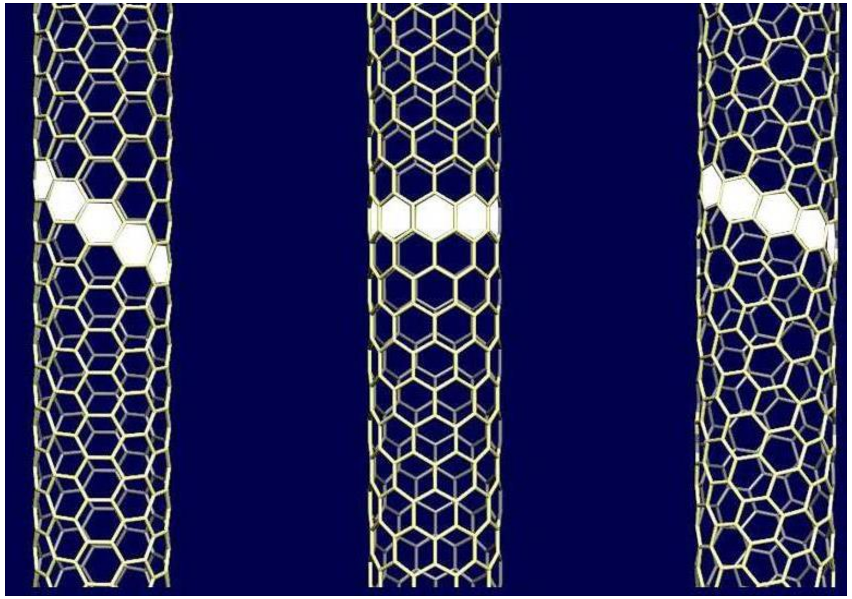
semiconductor
large gap



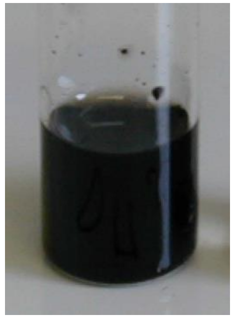
Electronic properties of nanotubes

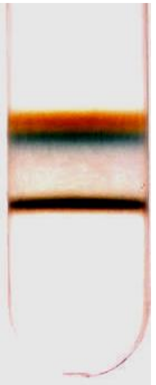
- quantum confinement
- band gap depends on structure
- most properties depend on band gap

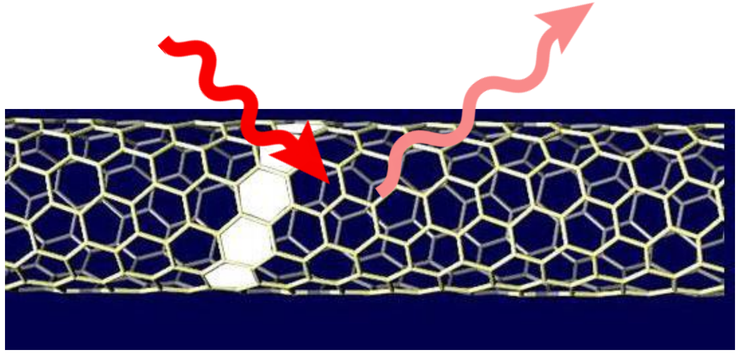


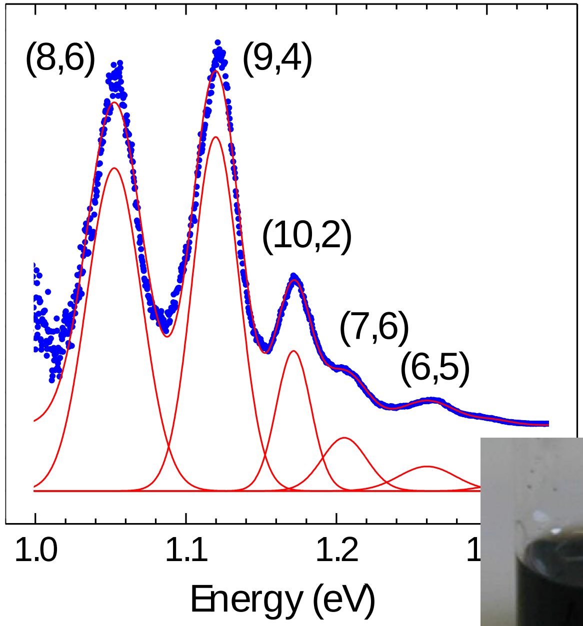


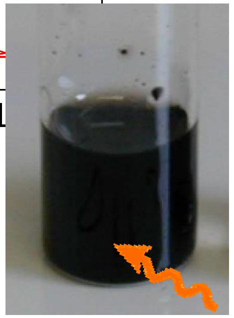
Optical properties of nanotubes





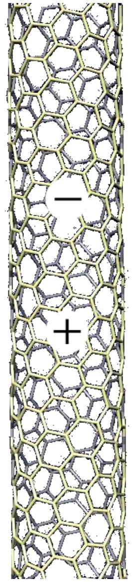


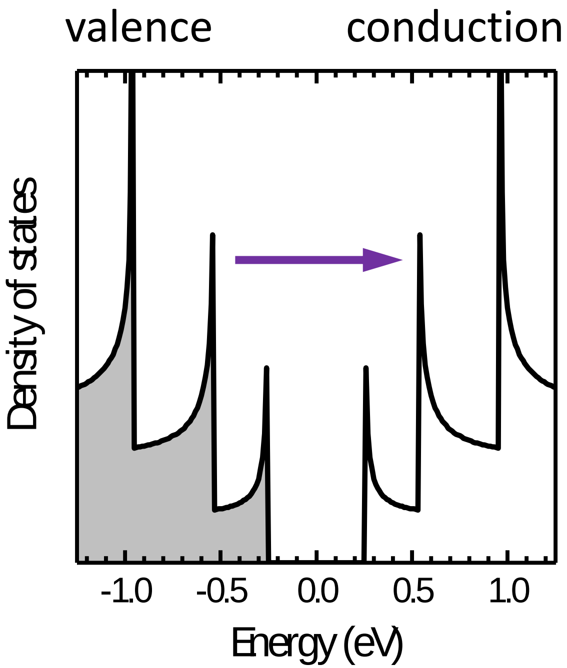


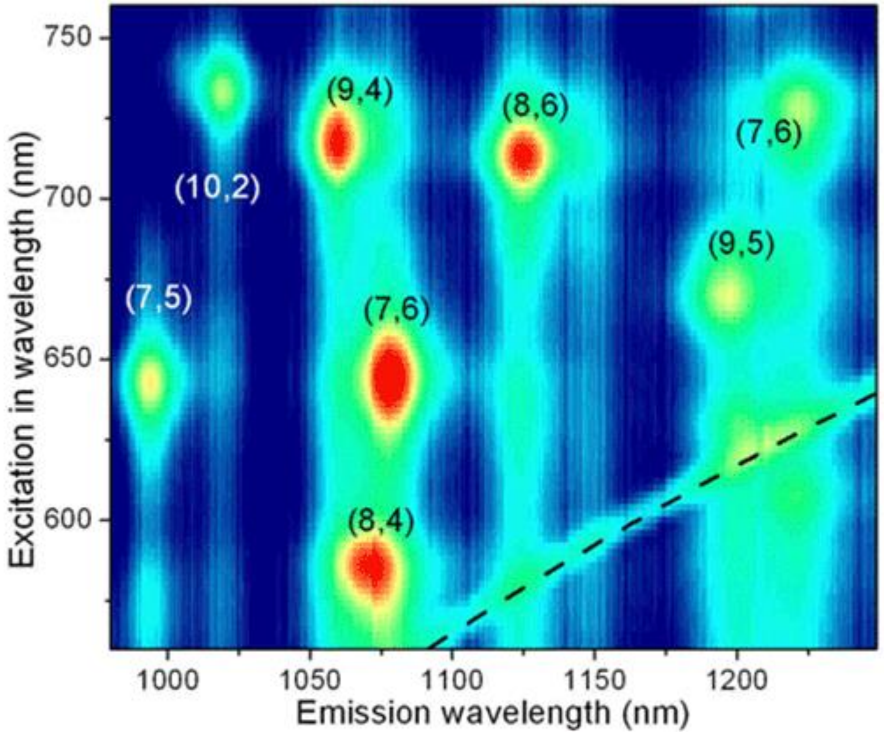


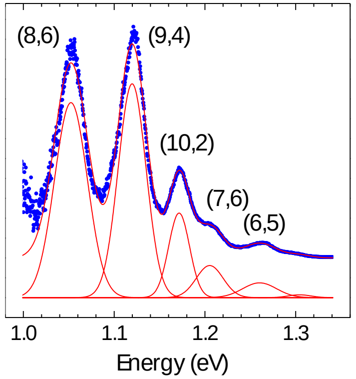
- Every nanotube – colorful
- Bulk nanotube samples – black

Transitions between subbands

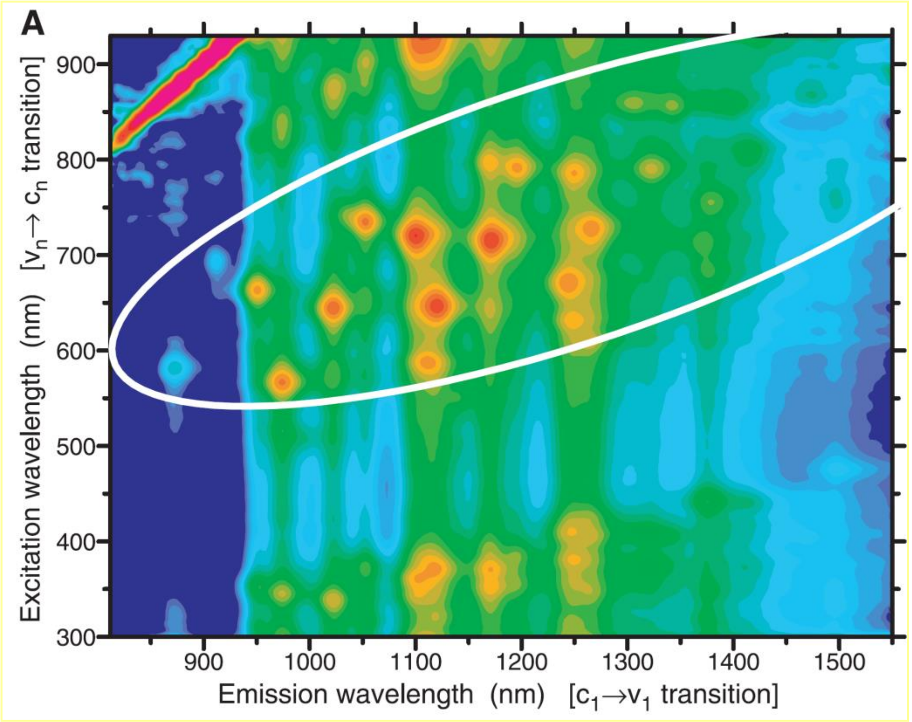


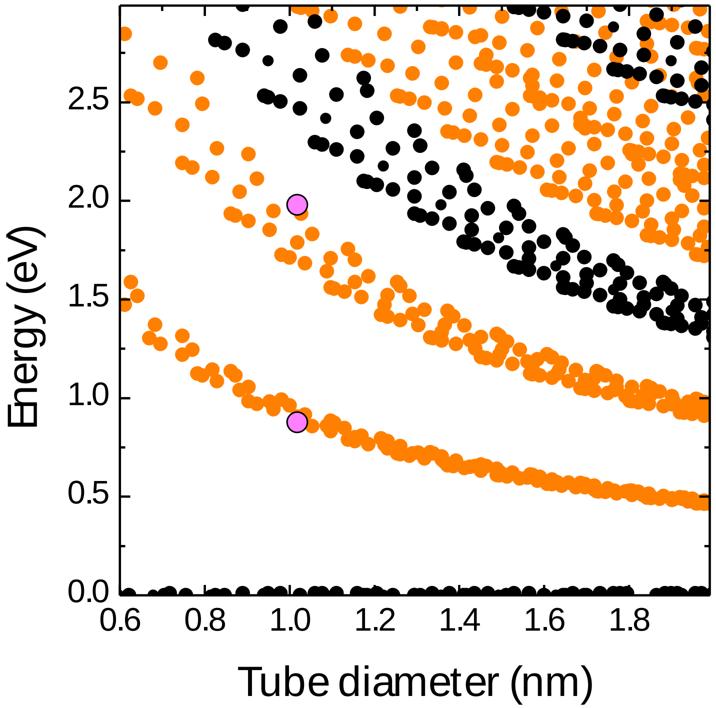




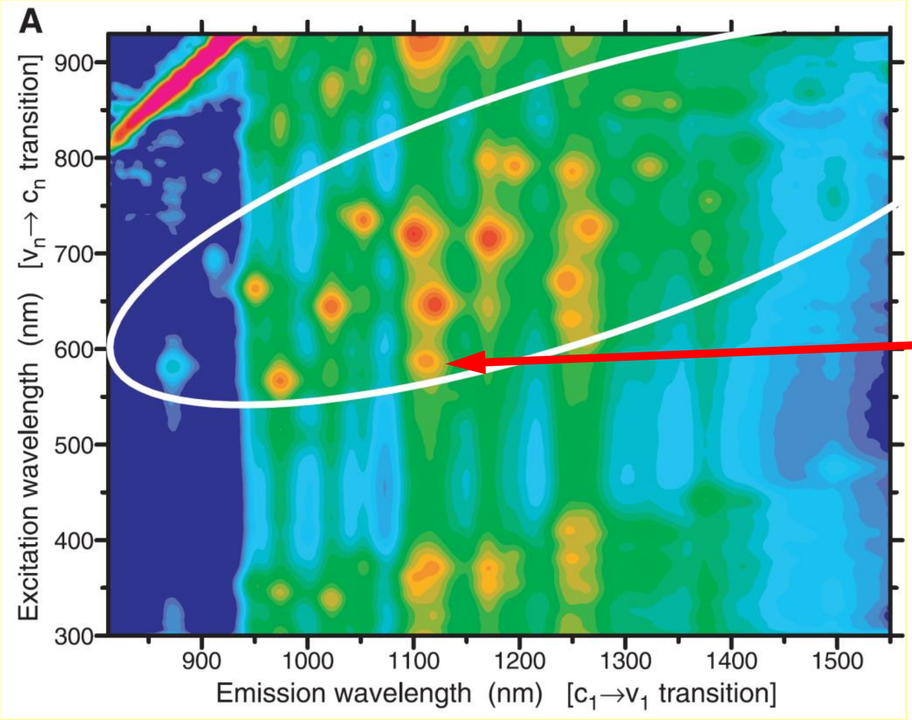


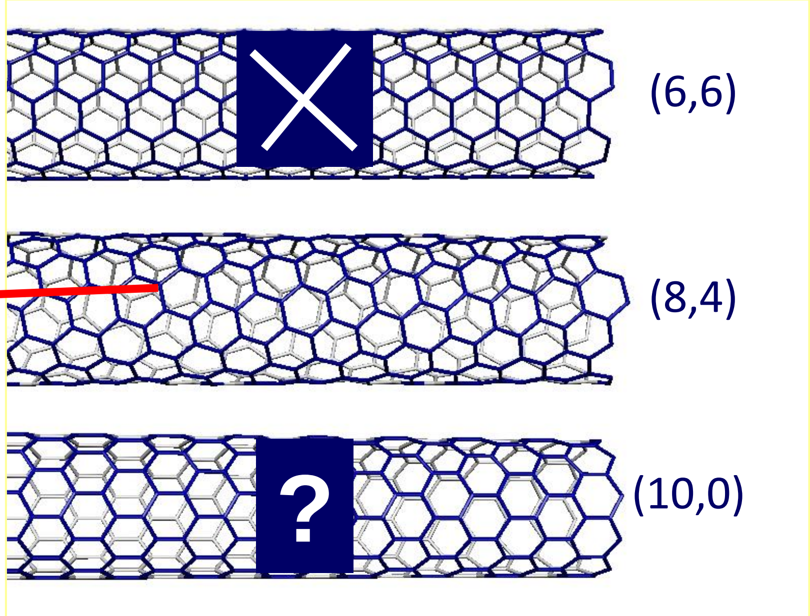
Chirality from luminescence



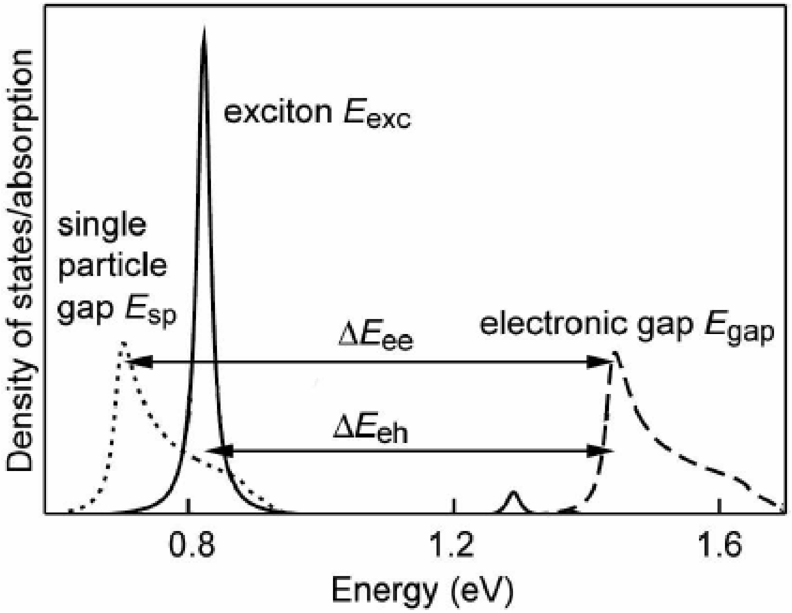


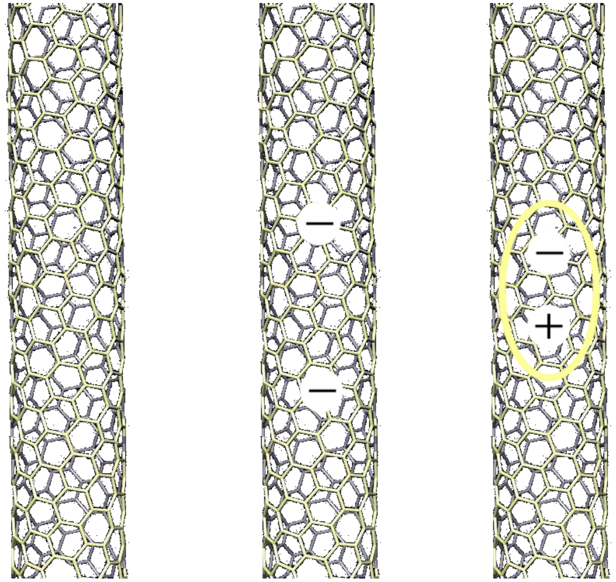
Chirality from luminescence





Nanotubes, optics & excitons

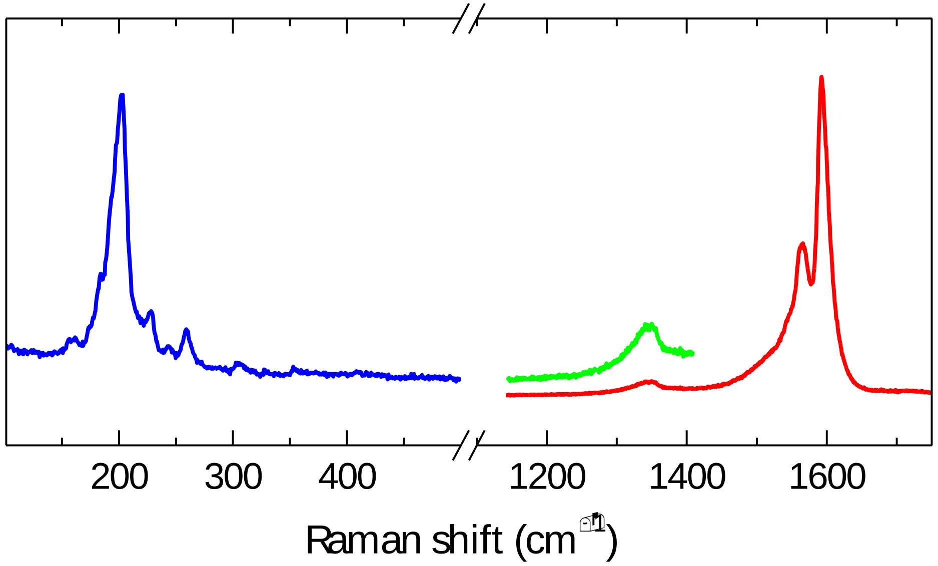


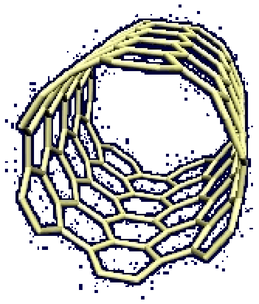


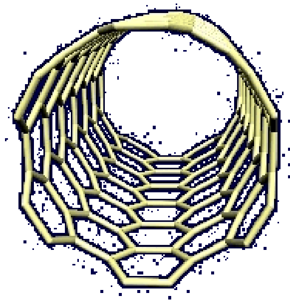
- chirality, electron-electron, and electron-hole interaction
- sensitive to environment

Phonons in carbon nanotubes

- 100 – 1000 vibrations
- strong coupling to electronic system
  - radial-breathing mode (RBM)
  - high-energy mode (HEM)
  - D mode
- twiston and low-energy phonons

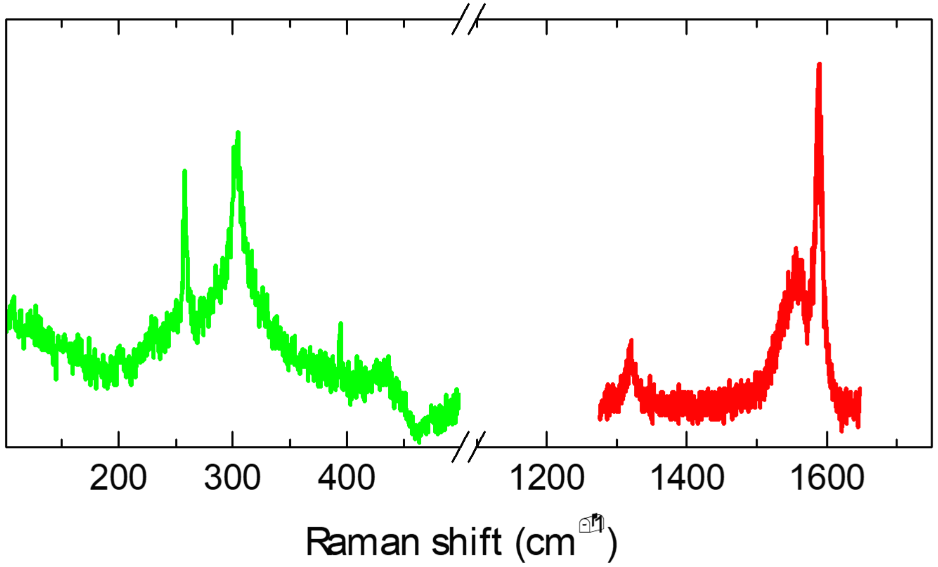






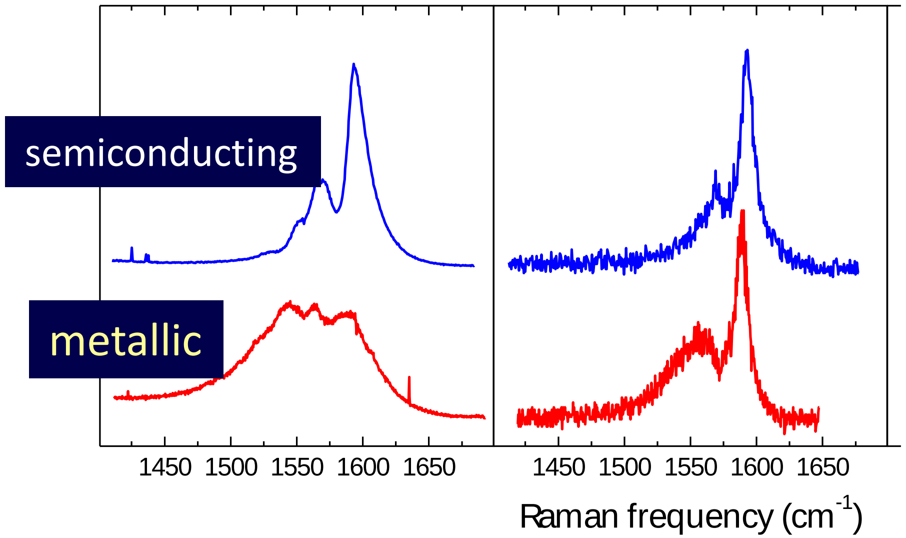
Phonons in carbon nanotubes

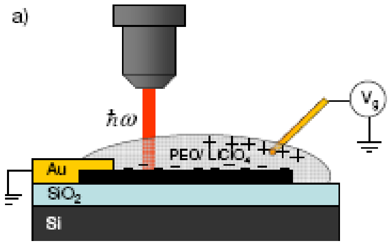
- 100 – 1000 vibrations
- strong coupling to electronic system
  - radial-breathing mode (RBM)
  - high-energy mode (HEM)
  - D mode
- twiston and low-energy phonons
- characterizie nanotubes
  - presence
  - metallic/semiconductor
  - chirality

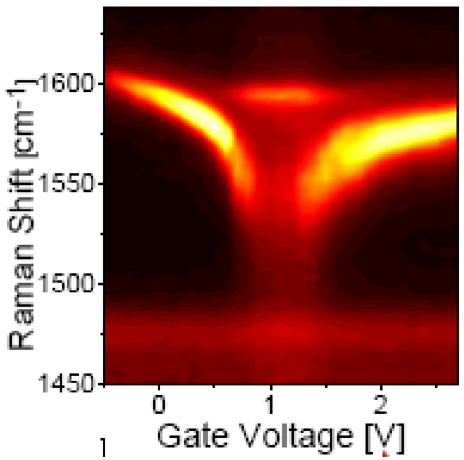


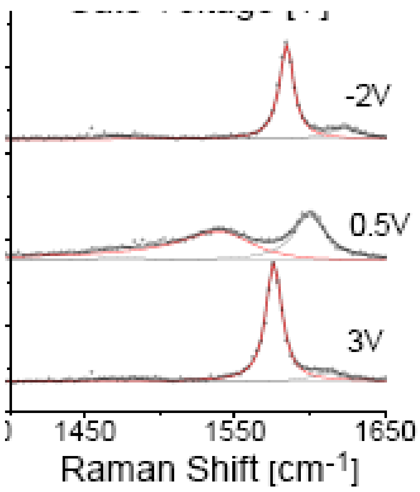
Electron-phonon coupling

- doping hardens phonon frequencies
- metallic into semiconducting spectrum?
- bundling effect?



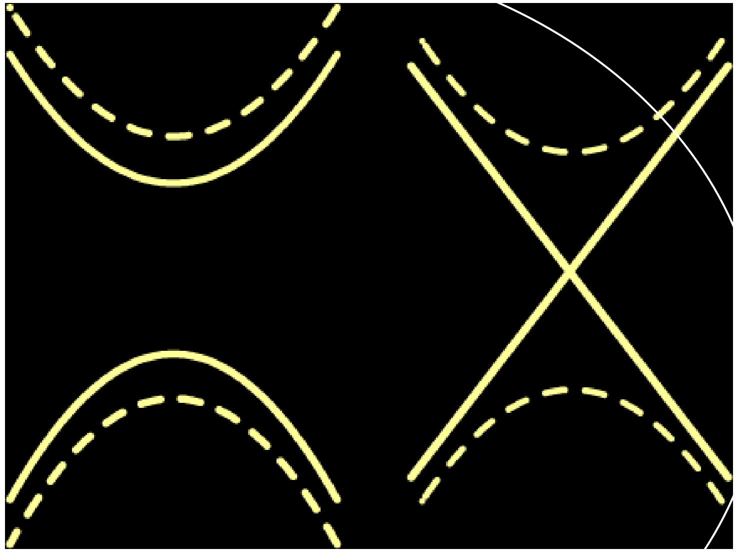


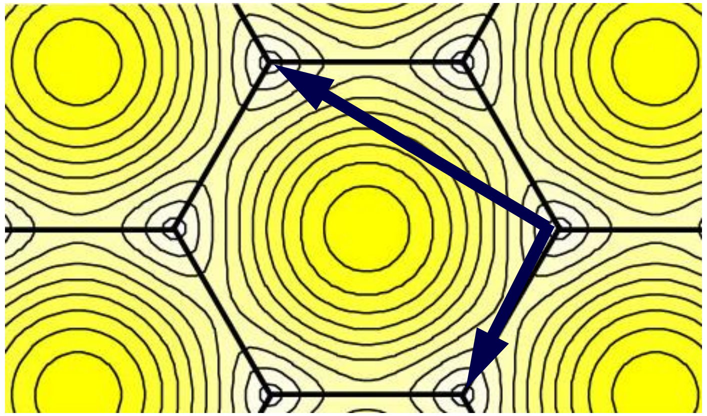




Phonon softening

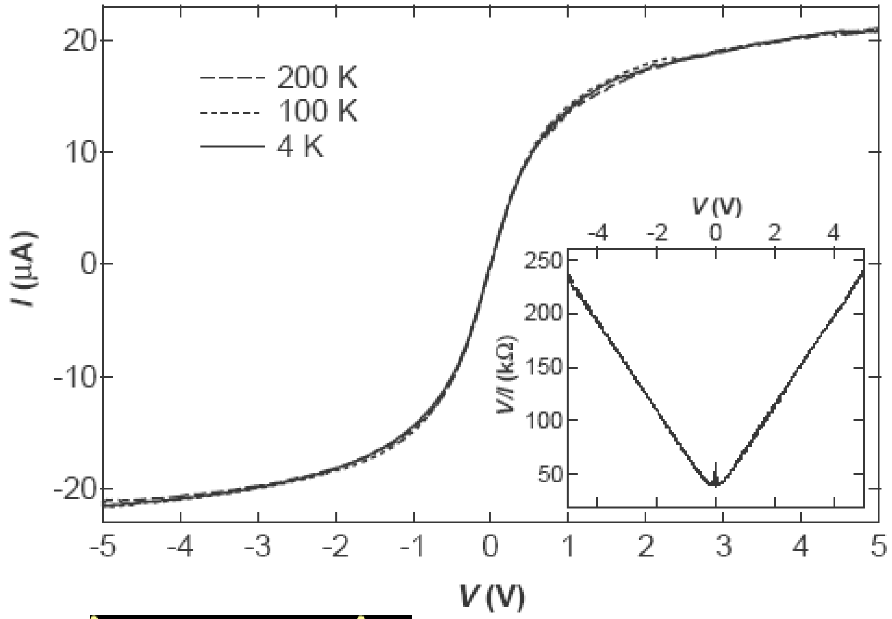
- vibration periodically opens and closes a band gap
- softening of the phonon frequencies
- phonon dispersion is singular
- $\boldsymbol{q} = \boldsymbol{k}_1 - \boldsymbol{k}_2$

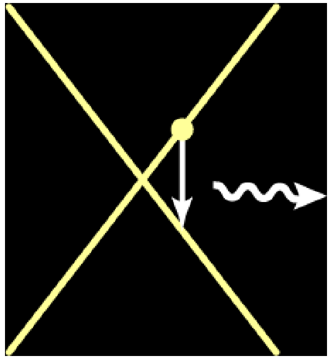




Phonons limit nanotube transport

- ballistic transport
  - resistance approaches quantum limit 13kΩ/channel
  - no scattering by defects
- ballistic transport breaks down by hot phonons
- phonon emission faster than decay





Yang PRL (2000); Javey Science (2003)

Functionalization

- change nanotube properties
  - solubility
  - composite materials
  - sensitivity & reactivity

- tune pristine properties
  - electron interaction
  - defects
  - vibrations

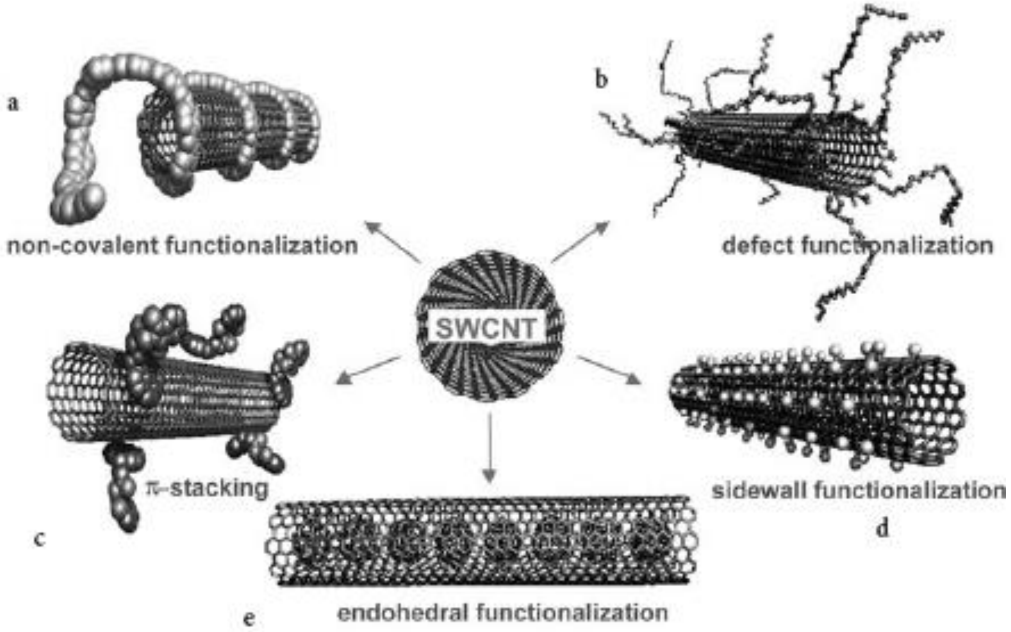


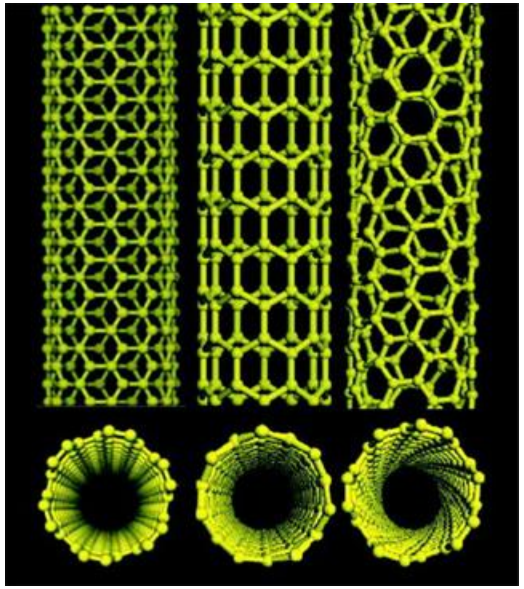
Fig. 2a–e Different possibilities of the functionalization of *SWCNTs*. a Noncovalent exohedral functionalization with polymers. b Defect-group functionalization. c Noncovalent exohedral functionalization with molecules through π-stacking. d Sidewall functionalization. e Endohedral functionalization, in this case C_{60}@SWCNT

Quintessential nanotubes

- Many different nanotube structures
- Properties differ vastly

Essential ingredients:

- Quantum confinement – pick properties
- Large surface area – manipulate properties
- *sp*^{2} carbon bond – ultra-strong material



- We cannot control the type of tube

Summary

- Nanotube properties depend on their structure;
  there is no „typical nanotube“
- Growth of carbon nanotubes produces many different tubes = different materials
- Nanotube absorb light & show infrared luminescence
- Particularly strong electron-phonon coupling
- Functionalize nanotubes for further tailoring

Thanks to…

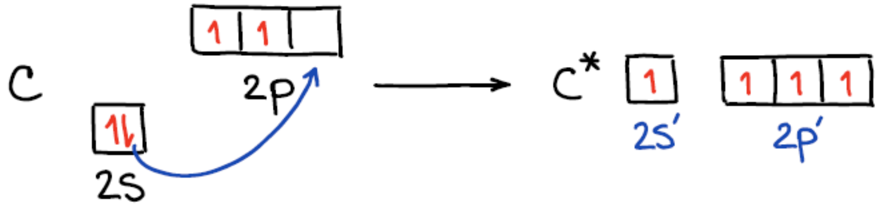
- Cinzia Casiraghi (AvH)
  Antonio Setaro (FUB)
  Vitalyi Datsyuk (BmBF)
- Rohit Narula (FUB)
  Sebastian Heeg (ERC)
  Oliver Schimek (DFG)
  Asaf Avnon (SfB)
  Thomas Straßburg (BmBF)
  Stefan Arndt (BmBF)
- Ermin Malić (SfB)
  Megan Brewster (MIT, NSF)

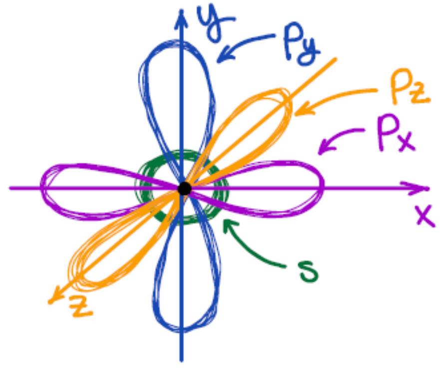
- ☐ TU Berlin
  Christian Thomsen
  Janina Maultzsch
- ☐ MIT
  Michael Strano
  Francesco Stellacchi
  Jing Kong
- ☐ KIT
  Frank Hennrich
- ☐ University of Cambridge
  Stefan Hofmann
  John Robertson

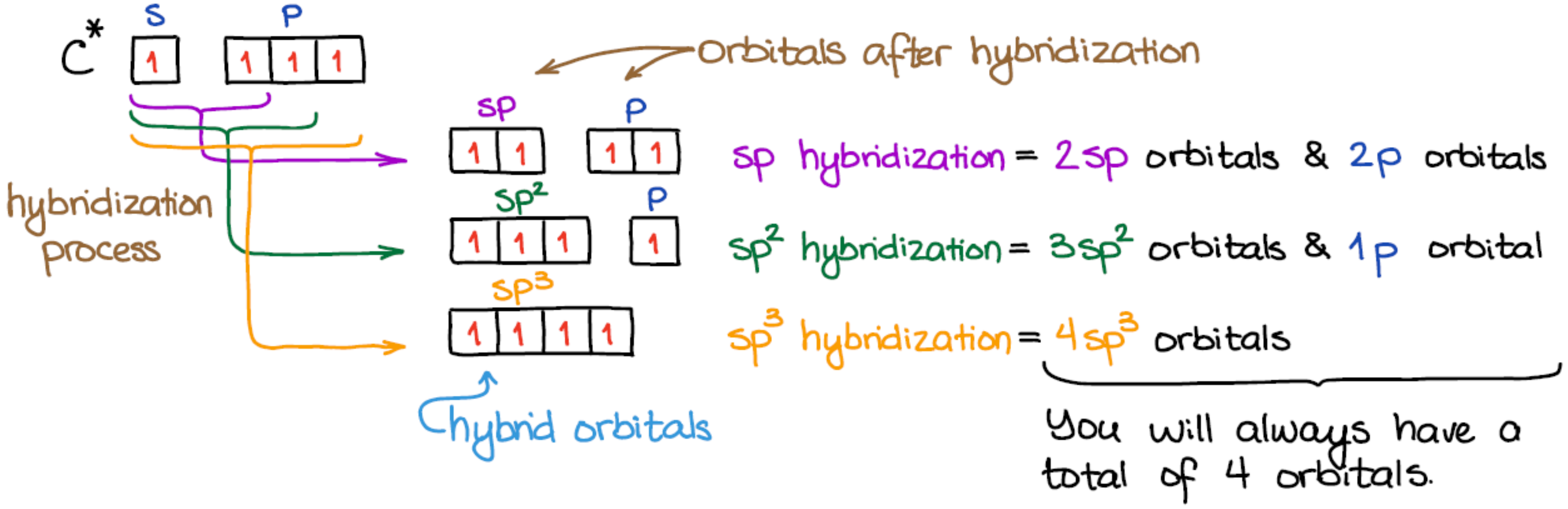
Annex

Hybridization

C | **1**s2 | **2**s2 | **2**px | **2**py

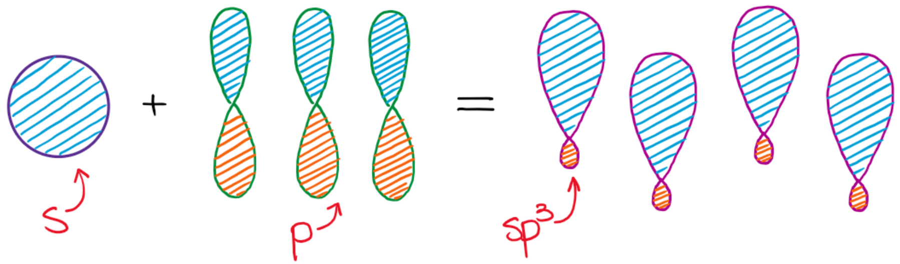


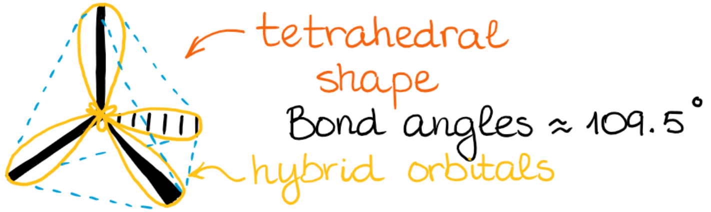


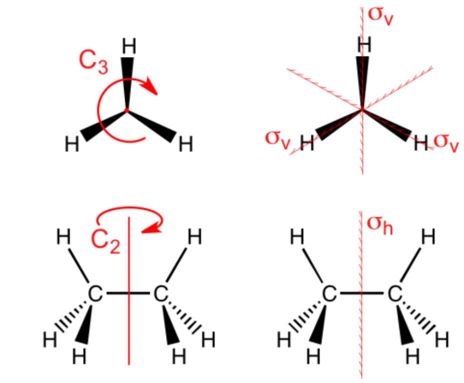


https://www.organicchemistrytutor.com/hybridization/

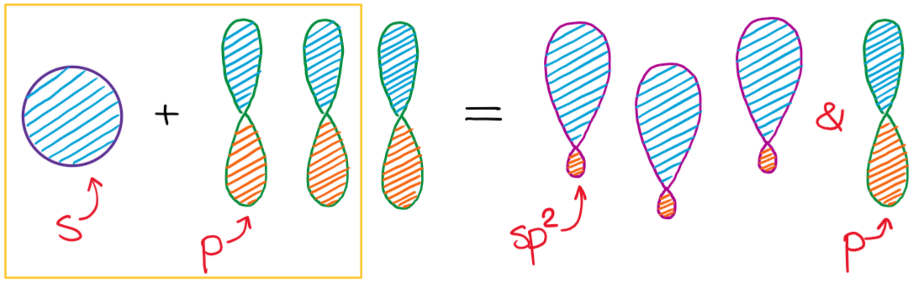
Hybridization

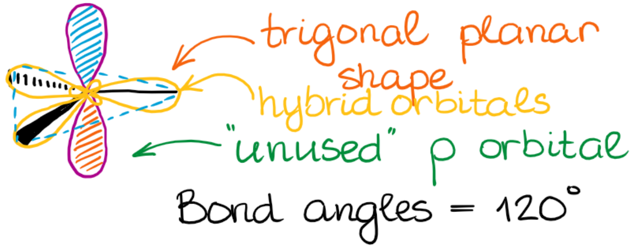


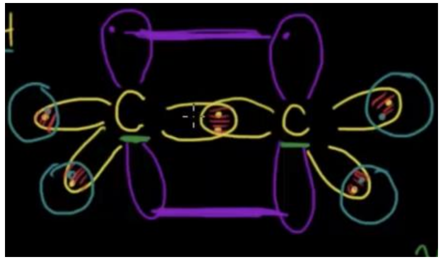


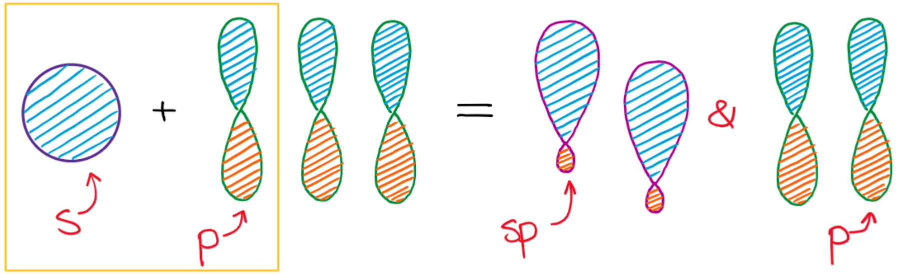


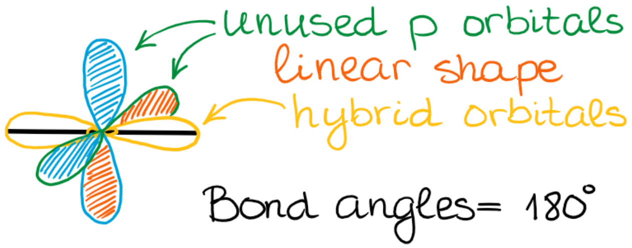
Show all 3 equivalent C_2 axis

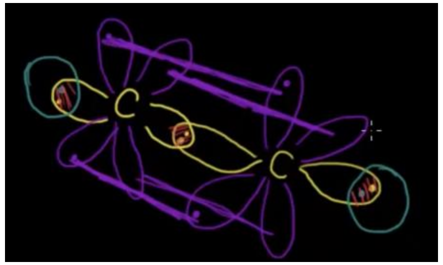








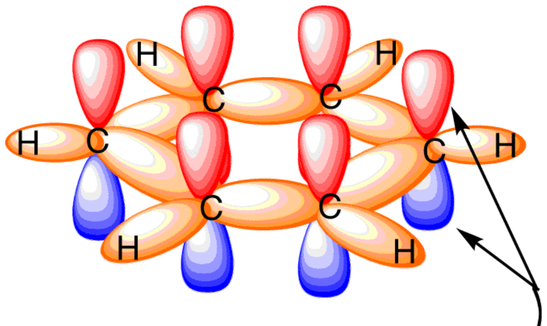




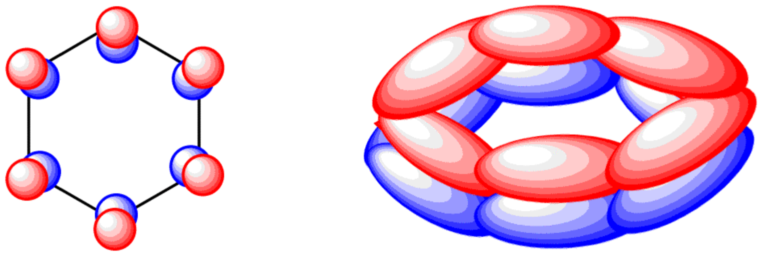
https://www.organicchemistrytutor.com/hybridization/ https://es.khanacademy.org/science/chemistry/chemical-bonds/hybridization-and-hybrid-orbitals-chemistry/v/sp2-hybridization-jay-final

Resonance

σ bonds shown in green



a single p orbital
different phases shown
in red and black



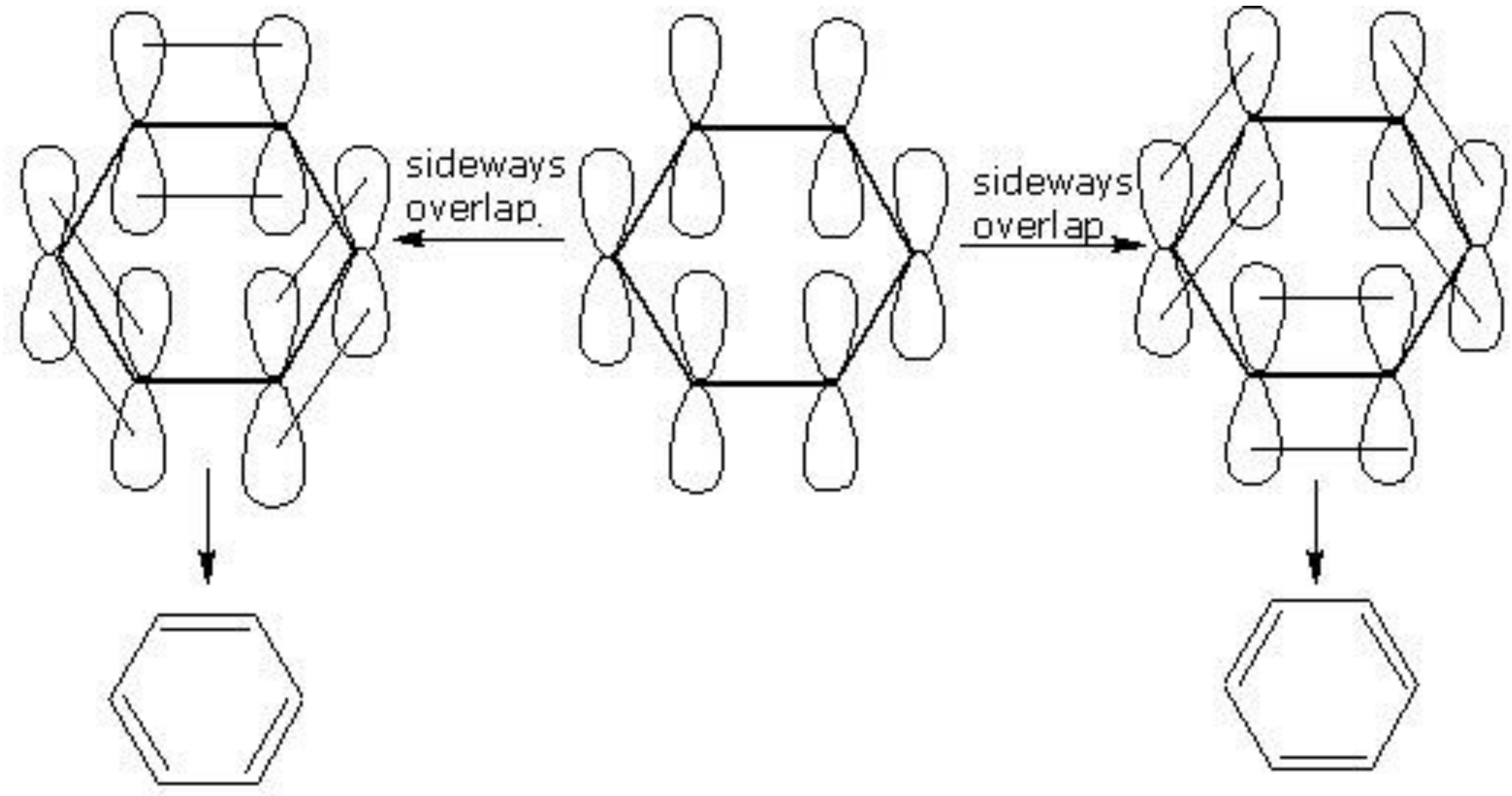
the lowest energy MO for benzene has
all the p orbitals combining in-phase

https://www.chemtube3d.com/orbitalsbenzene/

https://www.chemtube3d.com/vibrationsc6h6/

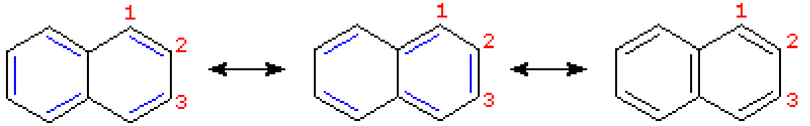
https://www.chemtube3d.com/diamond/

Resonance



Resonance Structures on Aromatic Fused Rings

Napthalene

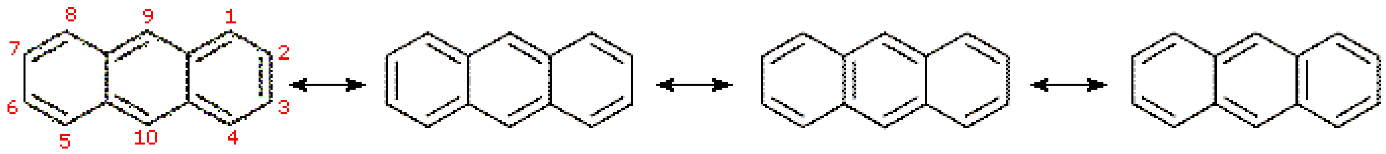


10 π-electron annulenes   2 benzene rings

Resonance Energy = 61 kcal/mole (less than twice benzene)
(30.5 kcal per ring)

The C–C bond lengths in benzene are all 1.40 Å
The C^1–C^2 bond length in naphthalene is 1.36 Å
The C^2–C^3 bond length in naphthalene is 1.42 Å

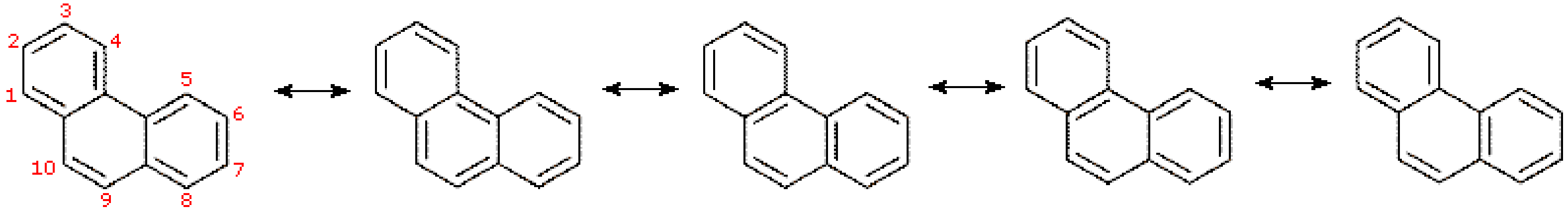
Anthracene



14 π-electron annulenes   benzene + 10 π-electron annulene

Resonance Energy = 83 kcal/mole
(27.7 kcal per ring)

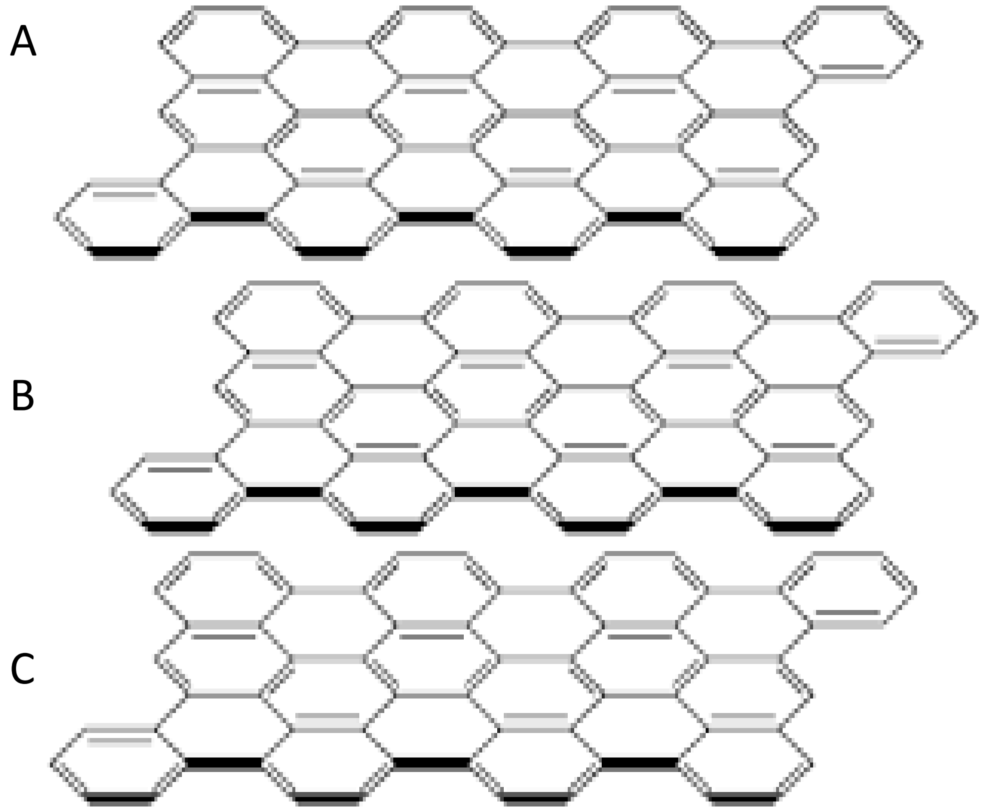
Phenanthrene

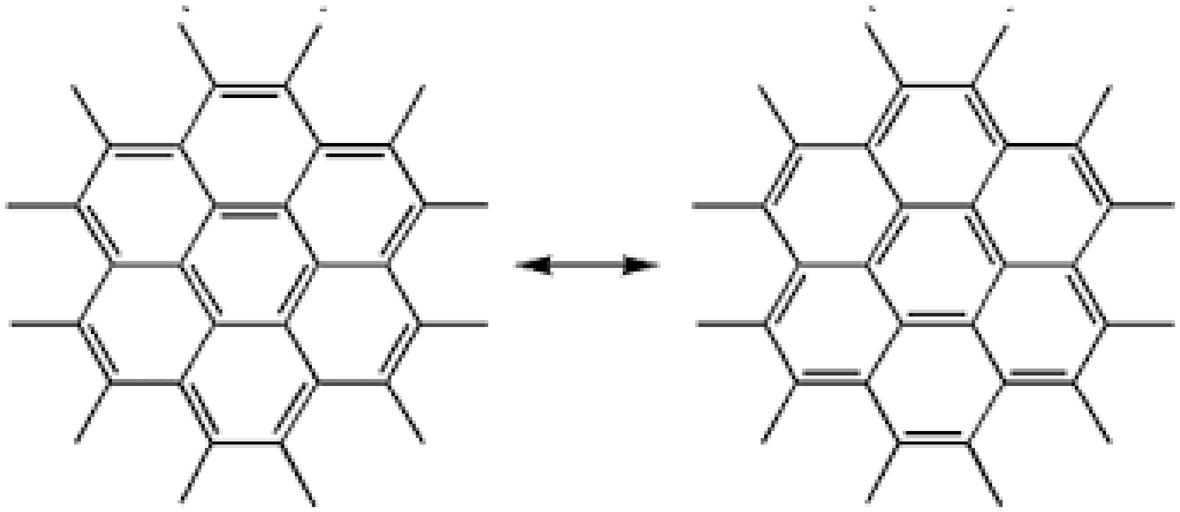


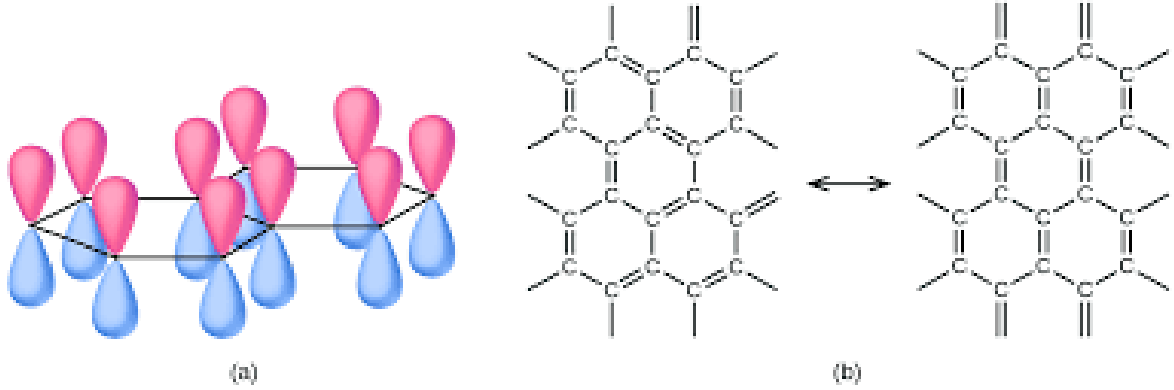
14 π-electron annulenes   3 benzene rings   benzene + 10 π-electron annulene

Resonance Energy = 91 kcal/mole
(30.3 kcal per ring)

Graphite

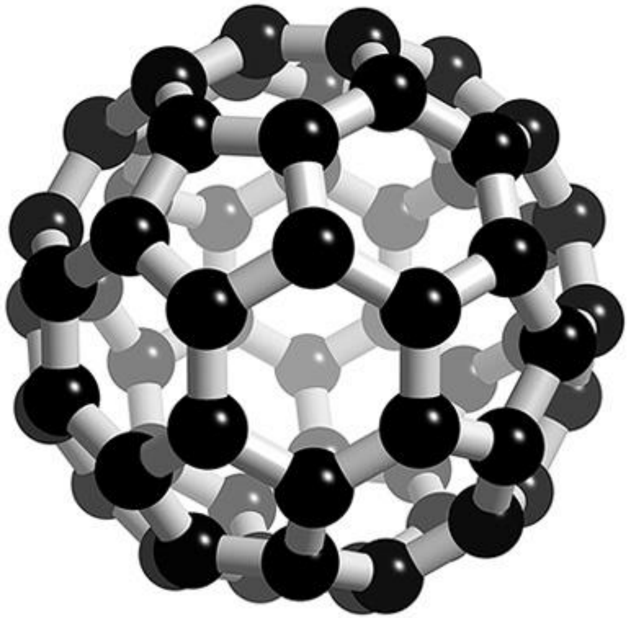






https://www.google.com/search?q=resonance+graphite&tbm=isch&ved=2ahUKEwiqla7sl77pAhVEfK0KHRpJCDcQ2-cCegQIABAA&oq=resonance+graphite&gs_lcp=CgNpbWcQAzoCCAA6BggAEAUQHlCT5iFY9_YhYOyFlmgAcAB4AIABogGIAawIkgEDMC44mAEAoAEBqgELZ3dzLXdpei1pbWc&sclient=img&ei=R-fCXurVIcT4tQWakqG4Aw&bih=361&biw=559&hl=en-US

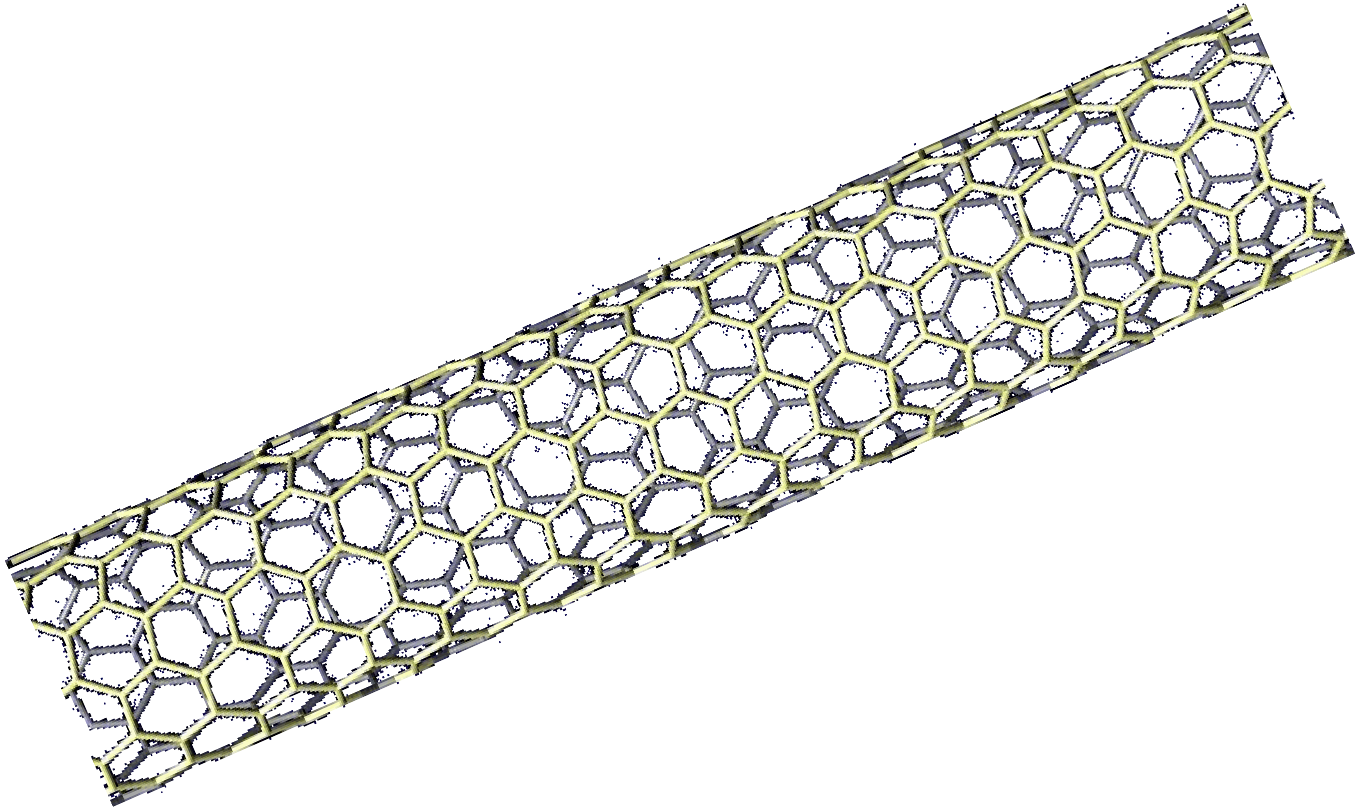
Carbon Fullerene
(an sp2 hybridized material)



https://www.chemtube3d.com/c60/

https://www.chemtube3d.com/ClaydenCarbonAllotropes/

Carbon Nanotube
(an sp2 hybridized material)



Applications

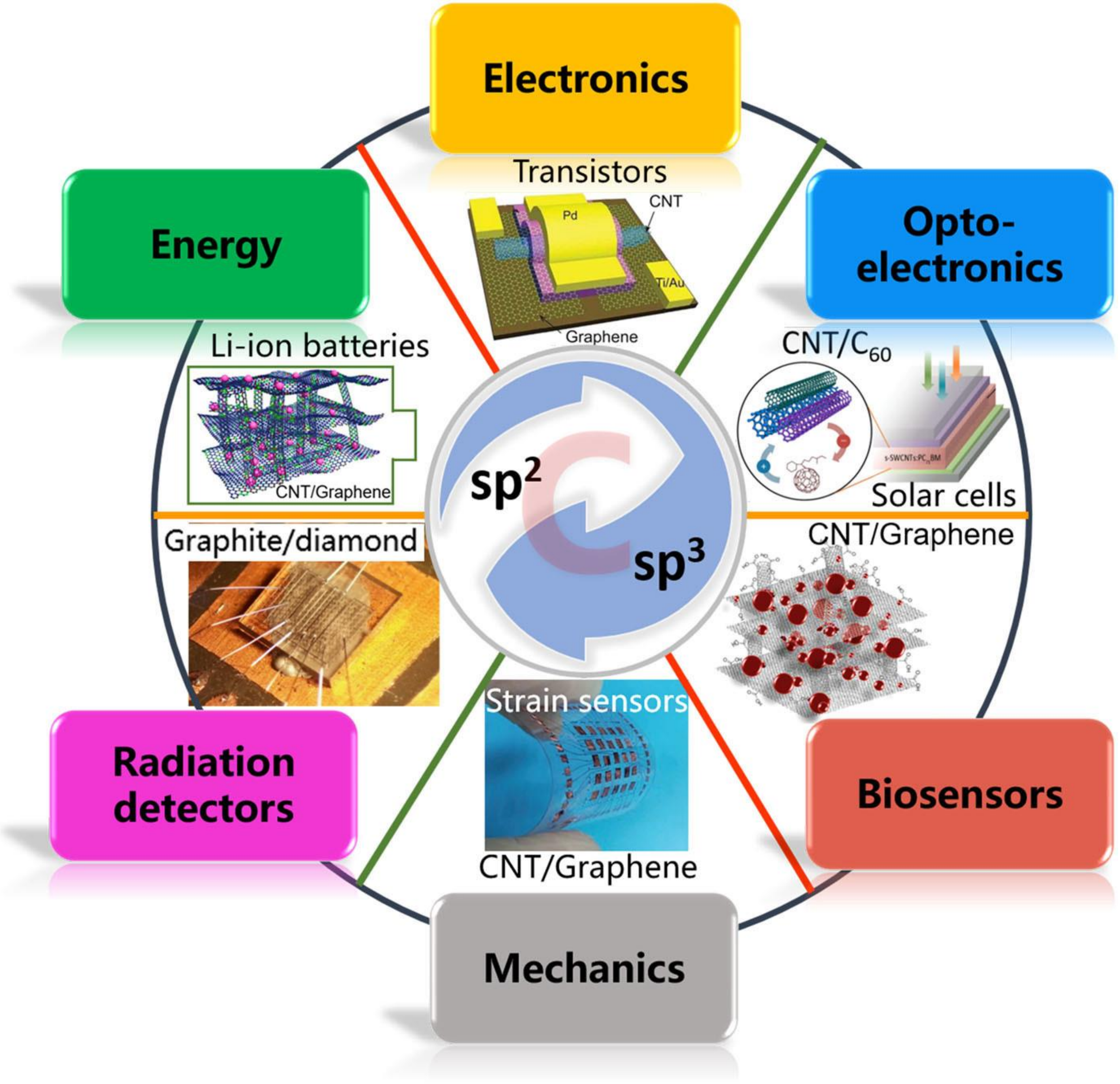


FIG. 2. Various fields of all-carbon device applications.

Published in: Qilong Yuan; Cheng-Te Lin; Kuan W. A. Chee; *APL Materials* **7,** 030901 (2019) DOI: 10.1063/1.5082767. Copyright © 2019 Author(s)

Thermal Conductivity

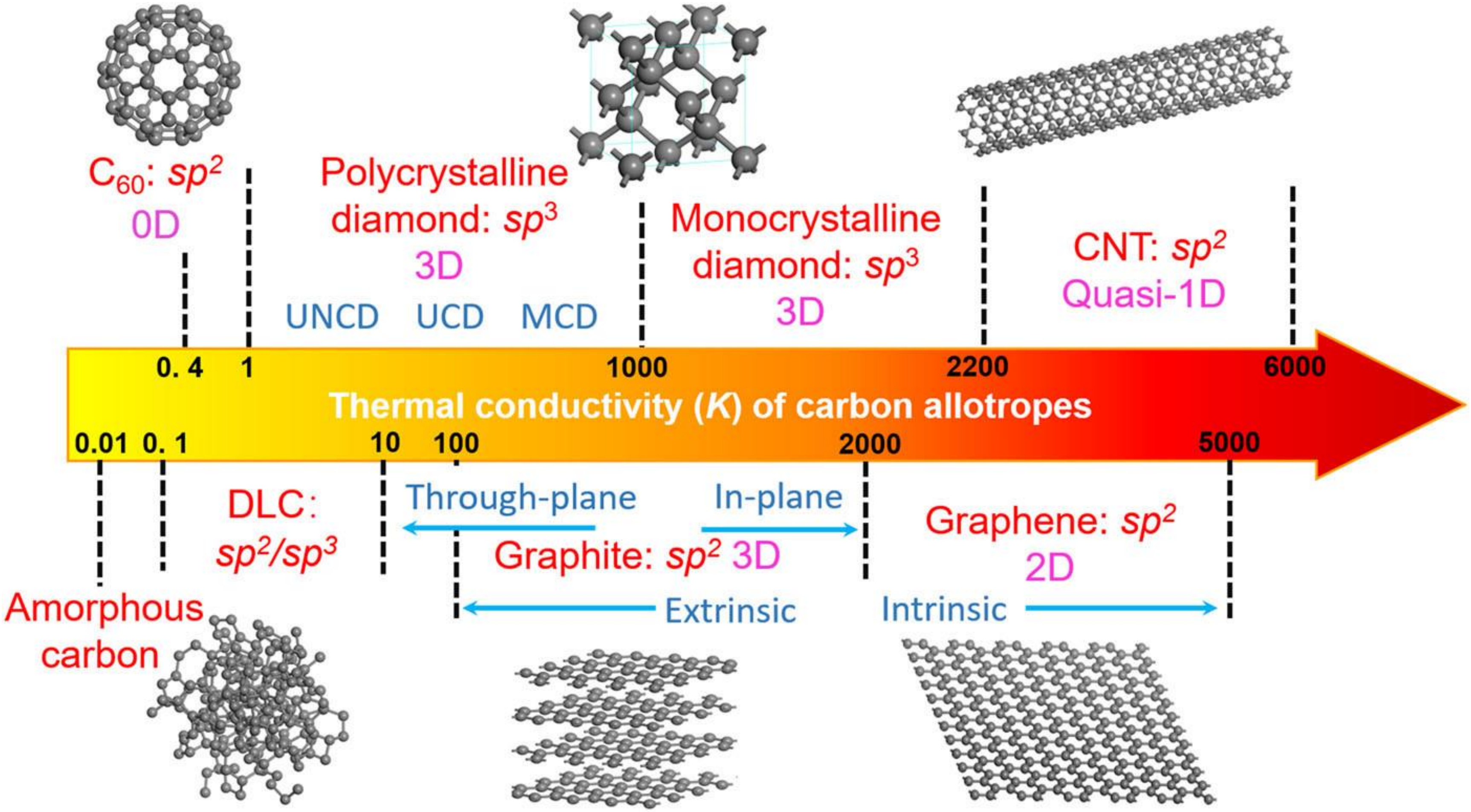
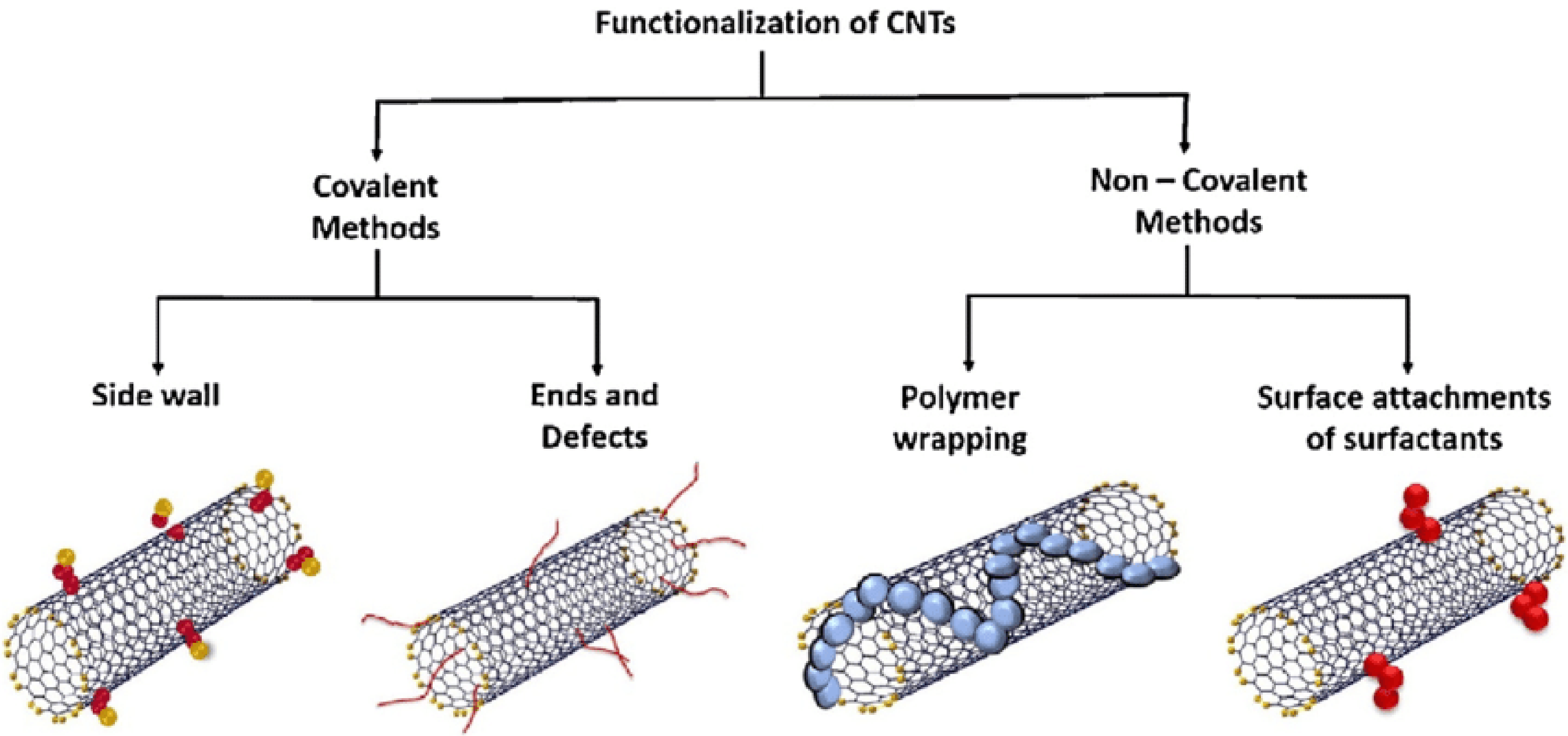
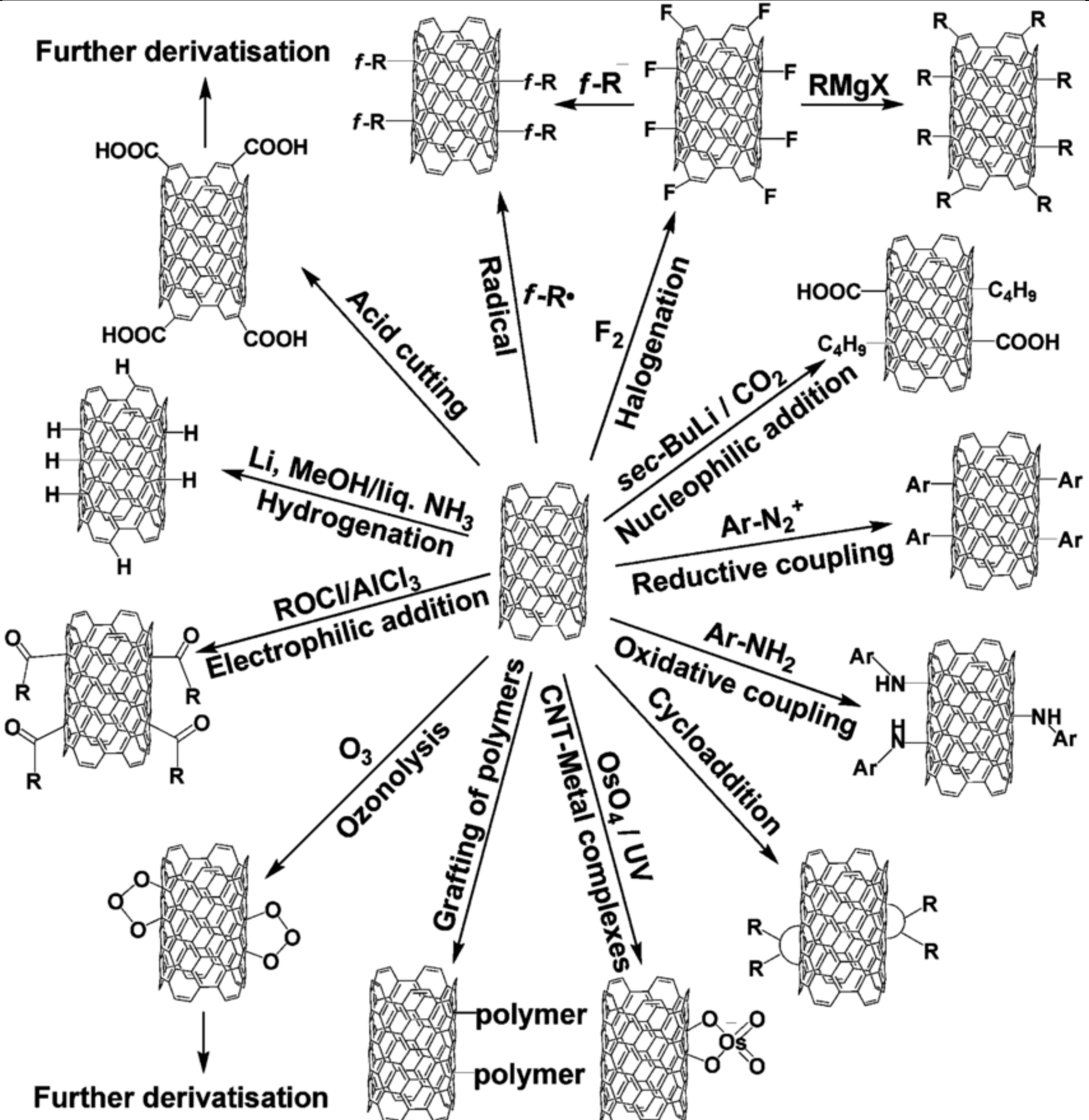


FIG. 1. Thermal conductivities of carbon allotropes (unit: W m^{-1} K^{-1}).

Published in: Qilong Yuan; Cheng-Te Lin; Kuan W. A. Chee; *APL Materials* **7,** 030901 (2019) DOI: 10.1063/1.5082767. Copyright © 2019 Author(s)


Functionalization of CNTs
Covalent Methods
Non – Covalent Methods
Side wall
Ends and Defects
Polymer wrapping
Surface attachments of surfactants


Further derivatisation
HOOC
COOH
HOOC
COOH
Acid cutting
f-R
f-R
f-R
f-R
f-R⁻
Radical
f-R•
F
F
F
F
F
F
F
F
F2
Halogenation
RMgX
R
R
R
R
R
R
R
R
HOOC
C4H9
C4H9
COOH
sec-BuLi / CO2
Nucleophilic addition
H
H
H
H
H
H
H
H
Li, MeOH/liq. NH3
Hydrogenation
Ar-N2+
Reductive coupling
Ar
Ar
Ar
Ar
ROCl/AlCl3
Electrophilic addition
R
R
R
R
Ar-NH2
Oxidative coupling
Ar
HN
H
N
Ar
NH
Ar
O3
Ozonolysis
Grafting of polymers
CNT-Metal complexes
OsO4 / UV
Cycloaddition
R
R
R
R
polymer
polymer
Os
Further derivatisation

Effect of Functioalization: An Example

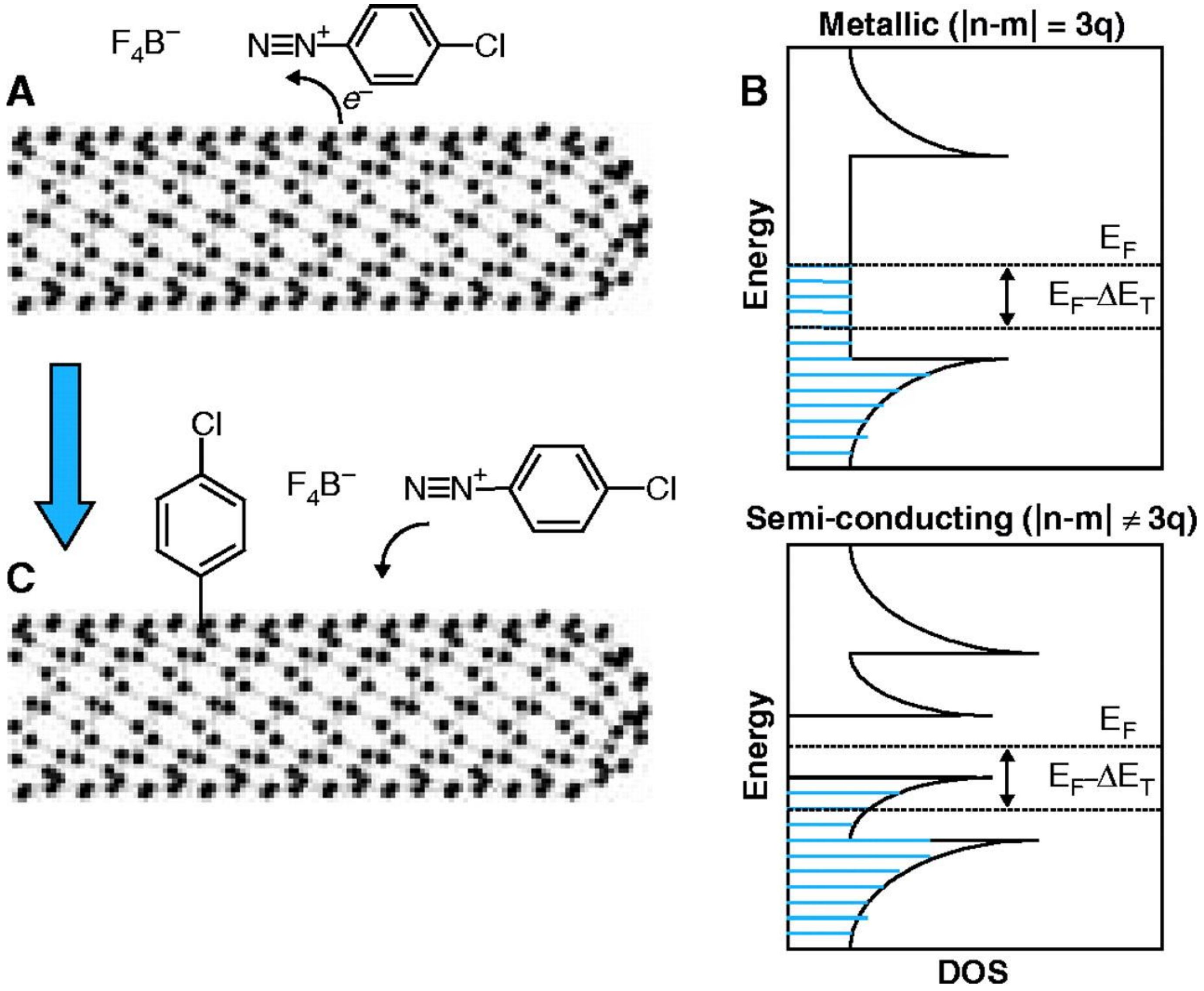


Fig. 1.
(**A**) Diazonium reagents extract electrons, thereby evolving N_2 gas and leaving a stable C -C covalent bond with the nanotube surface. (**B**) The extent of electron transfer is dependent on the density of states in that electron density near E_F leads to higher initial activity for metallic and semimetallic nanotubes. (**C**) The arene-functionalized nanotube may now exist as the delocalized radical cation, which could further receive electrons from neighboring nanotubes or react with fluoride or diazonium salts.

REPORT
Electronic Structure Control of Single-Walled Carbon Nanotube Functionalization
Science 12 Sep 2003:
Vol. 301, Issue 5639, pp. 1519-1522
DOI: 10.1126/science.1087691

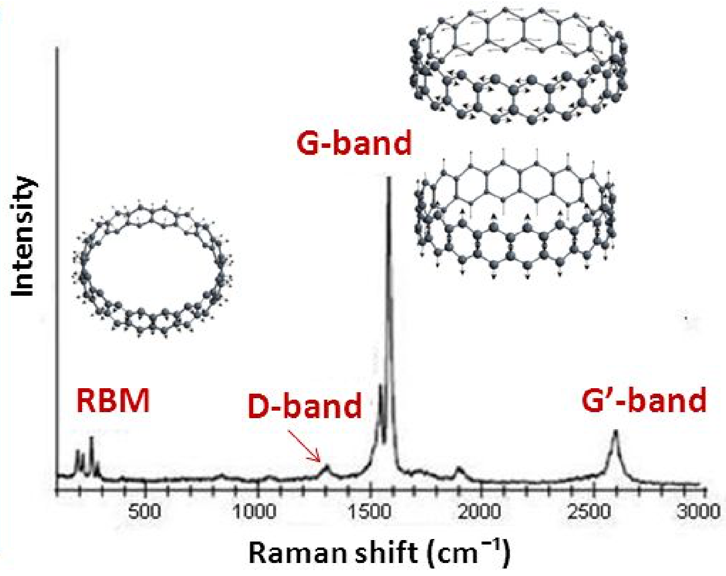
Raman Spectroscopy

Raman spectrum of SWNT

Raman spectrum gives us many information about the vibrational modes of carbon nanotubes.

Principal peaks:

- **RBM**: Radial Breathing Mode (150 - 350 cm^{-1})
- **D-band**: Disorder induced band (1350 cm^{-1})
- **G-band**: tangential (derived from the graphite like in-plane) mode (1560 – 1600 cm^{-1})
- **G'-band**: overtone of D-band



R. Graupner J. Raman Spectrosc. **38**, 673 (2007)

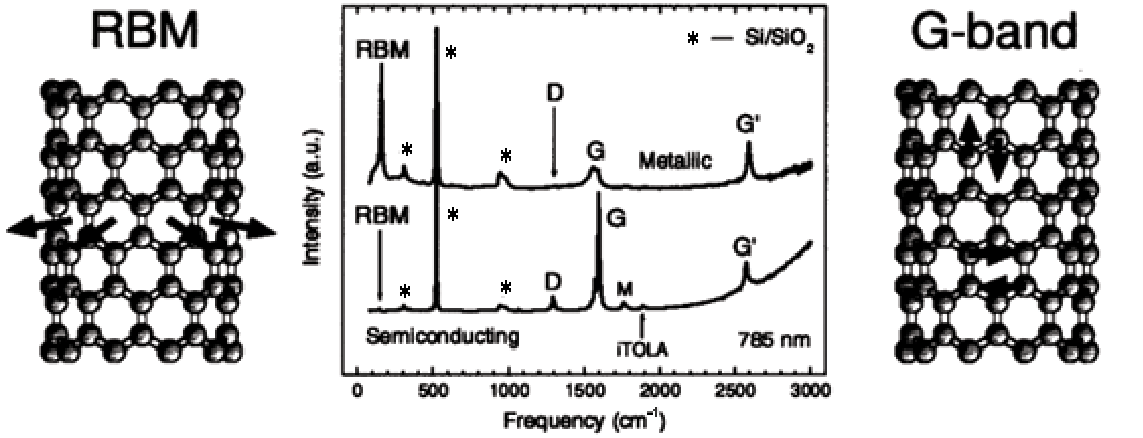


Fig. 2 – Raman spectra from a metallic (top) and a semiconducting (bottom) SWNT at the single nanotube level using 785 nm (1.58 eV) laser excitation, showing the radial breathing mode (RBM), *D*-band, *G*-band, and *G'* band features, in addition to weak double resonance features associated with the M-band and the iTOLA second-order modes. Insets on the left and the right show, respectively, the atomic displacements associated with the RBM and *G*-band normal mode vibrations. The isolated carbon nanotubes are sitting on an oxidized silicon substrate which provides contributions to the Raman spectra denoted by '*' which are used for calibration purposes.

Effect of treatment

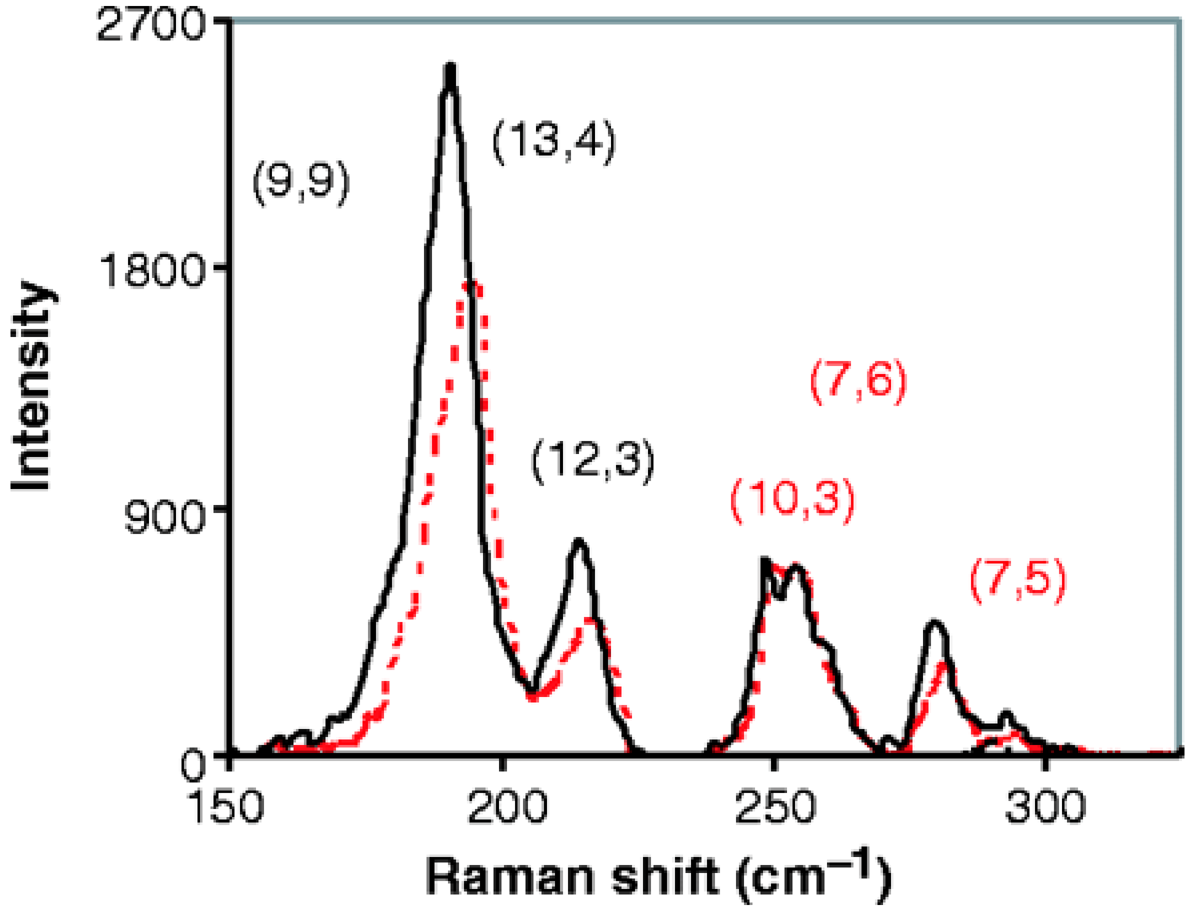


Fig. 5.
Raman spectra at 633 nm probing both metals and semiconducting nanotubes before reaction (solid line) and after recovery and thermal pyrolysis (dotted line). The reversibility of the chemistry implies that intrinsic electronic and optical properties of the pristine nanotubes can be recovered.

REPORT
Electronic Structure Control of Single-Walled Carbon Nanotube Functionalization
Science 12 Sep 2003:
Vol. 301, Issue 5639, pp. 1519-1522
DOI: 10.1126/science.1087691