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MATERIAIS NANOESTRUTURADOS E NANOTECNOLOGIAS

# THE CARBON AGE

M. Clara Gonçalves

# *Summary*

**Summary**

- **Introduction**
- **Carbon allotropic phases**
- **Fullerenes and Nanotubes Synthesis**
- **Applications**
- **Further Reading**

# Introduction

## PERIODIC TABLE

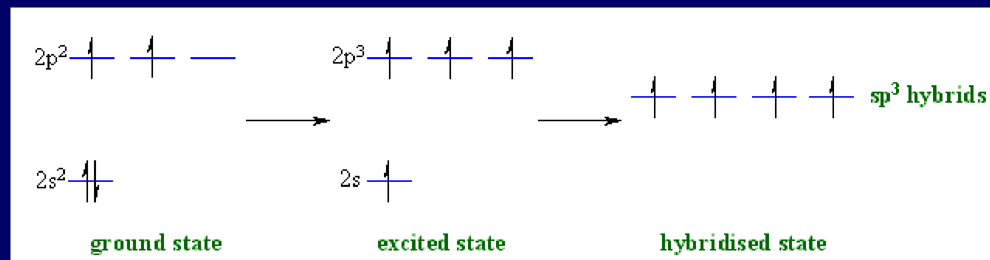
| IA | IIA | IIIB | IVB | | | | | | | | | IIIA | IVA | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | R | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Ti | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |

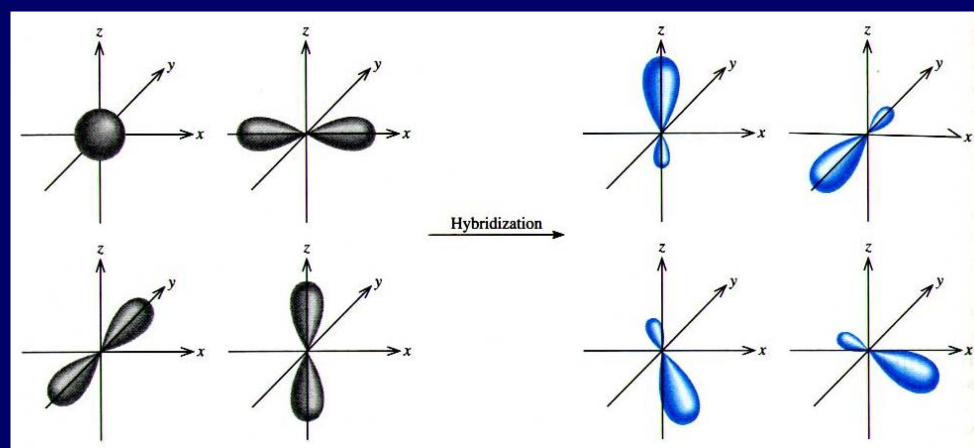
- Metais alcalinos
- Metais alcalino-terrosos
- La Lantanídeos
- Ac Actinídeos
- Metais de transição
- Metais não nobres
- Semi-metais
- Não metais
- Gases raros

# Carbon Allotropic Phases: Diamond

- **CARBON $sp^3$ HYBRIDIZATION**

**[C] = $1s^2\ 2s^2\ 2p^2$**



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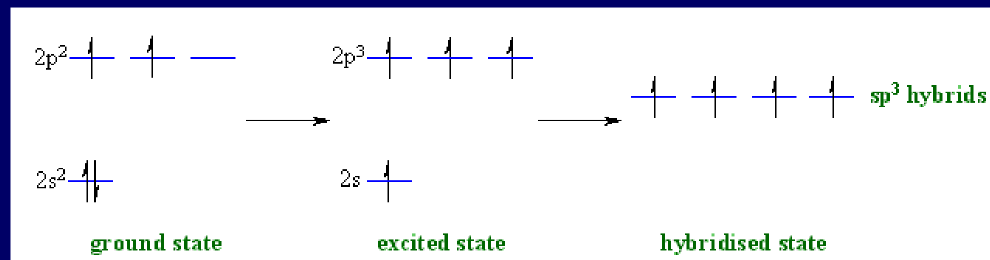
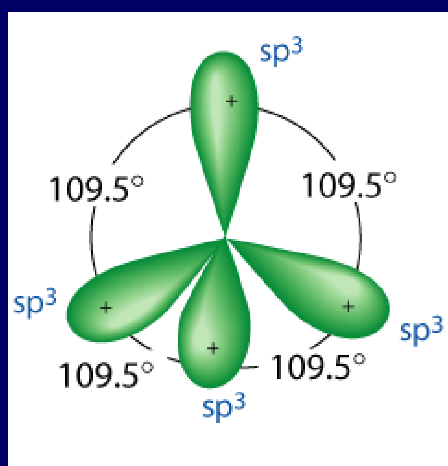


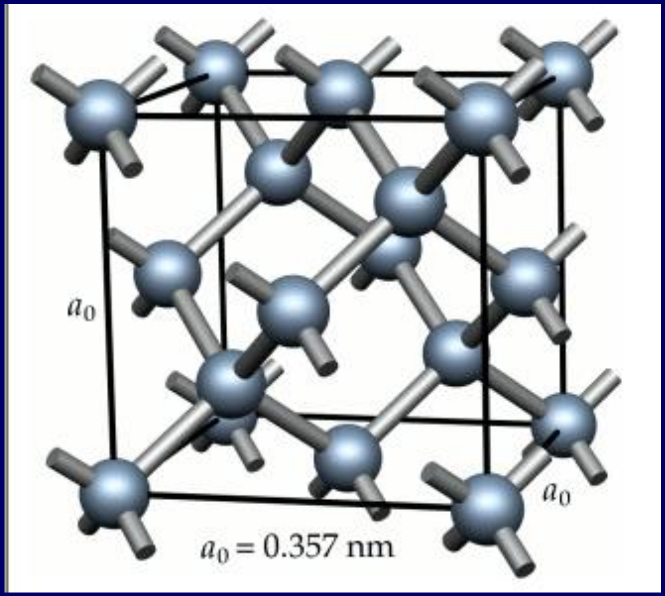

**Blend (i.e. hybridise) the s and the three p orbitals...**

- **Since we mixed 4 orbitals, we get a set of 4 $sp^3$ orbitals**
- **Each $sp^3$ hybrid contains a single unpaired electron**
- **The $sp^3$ ortbital looks like a distorted orbital with unequal lobes**
- **The 4 $sp^3$ hybrids points towards the corners of a tetrahedron.**

# Carbon Allotropic Phases: Diamond

• **CARBON ALLOTROPIC PHASES**

**DIAMOND**




**DIAMOND**

3D TETRAHEDRAL NETWORK

CN = 4 (GROUP IV ELEMENT)

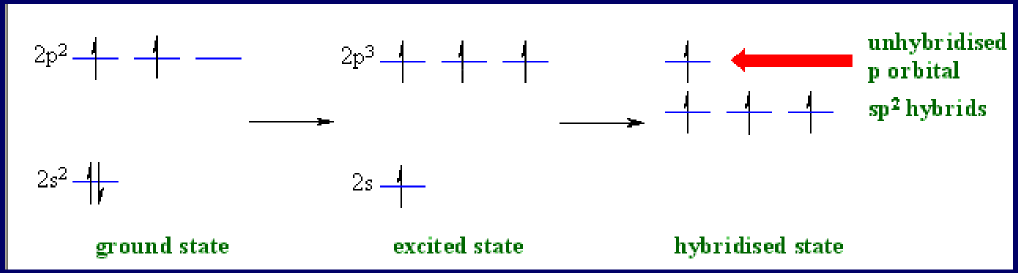
COVALENT BONDS

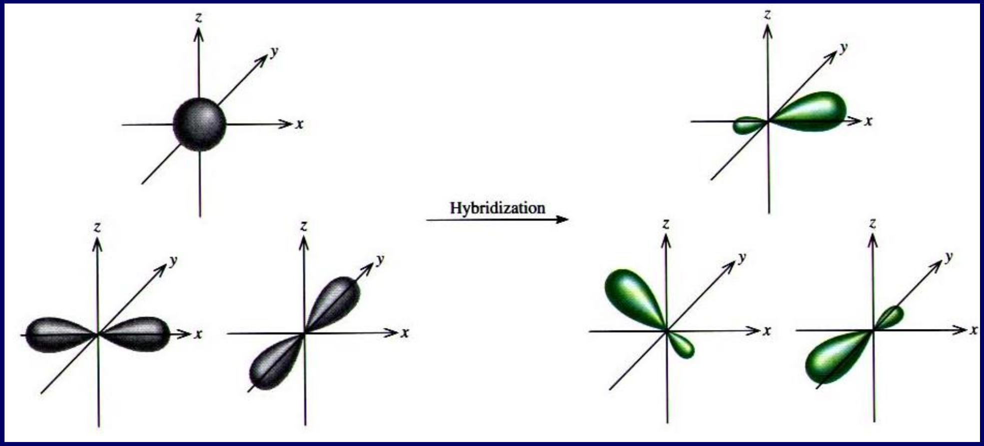
http://newton.ex.ac.uk/research/qsystems/people/sque/diamond/structure/

# Carbon Allotropic Phases: Graphite

• CARBON $sp^2$ HYBRIDIZATION

$[C] = 1s^2\ 2s^2\ 2p^2$



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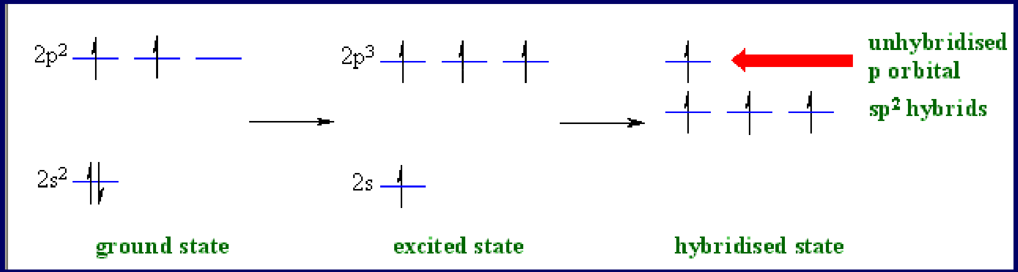
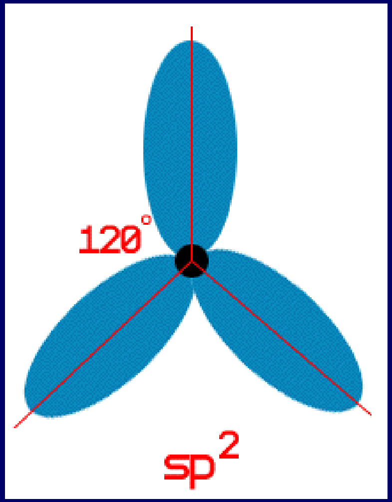


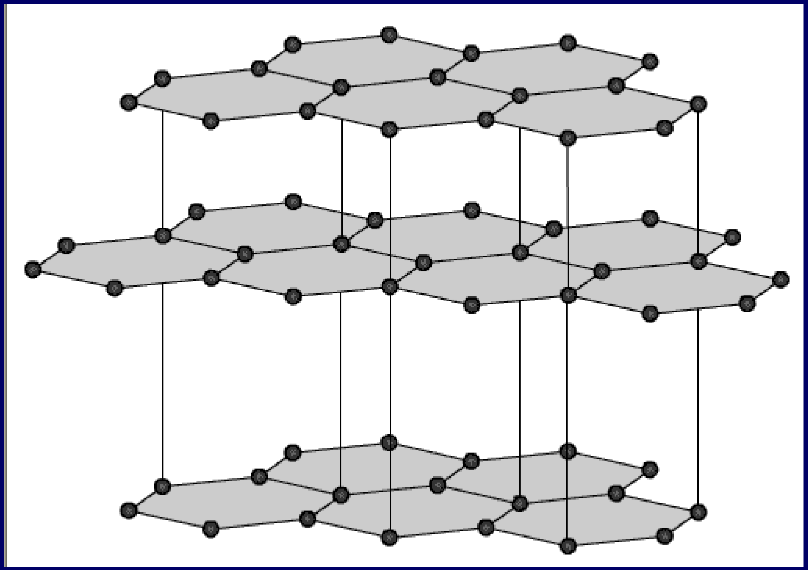

**Blend (i.e. hybridise) the s and the two p orbitals...**

- **Since we mixed 3orbitals, we get a set of 3 sp$^2$ orbitals**
- **The other p orbital remains unaffected**
- **Each sp$^2$ hybrid contains a single unpaired electron**

# Carbon Allotropic Phases: Graphite

• CARBON ALLOTROPIC PHASES

GRAPHITE



GRAPHITE

2D HEXAGONAL LAYERED STRUCTURE

CN = 3

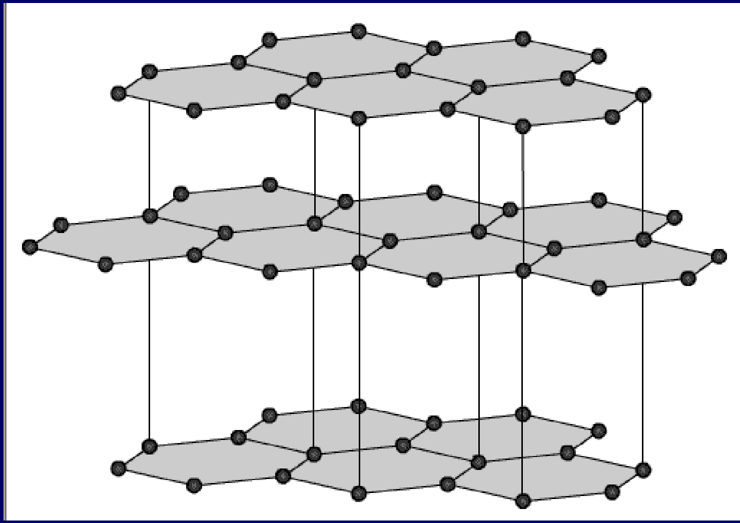
COVALENT BONDS (WITHIN EACH LAYER)

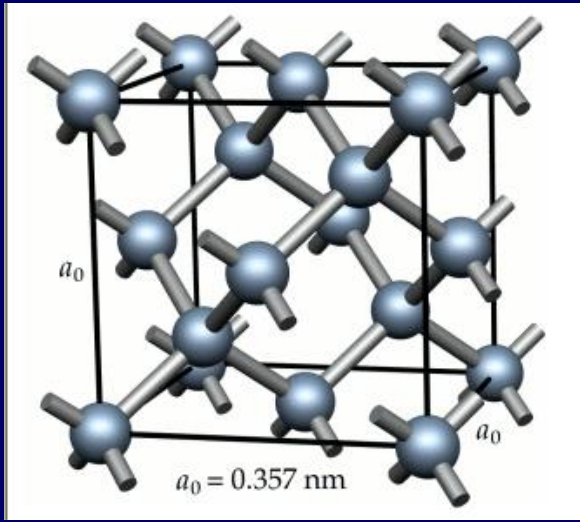
VAN DER WAALS (INTERLAYER FORCES)

# Carbon Allotropic Phases

• **CARBON ALLOTROPIC PHASES - 1980**

**GRAPHITE / DIAMOND**



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• **CARBON ALLOTROPIC PHASES - 1980**

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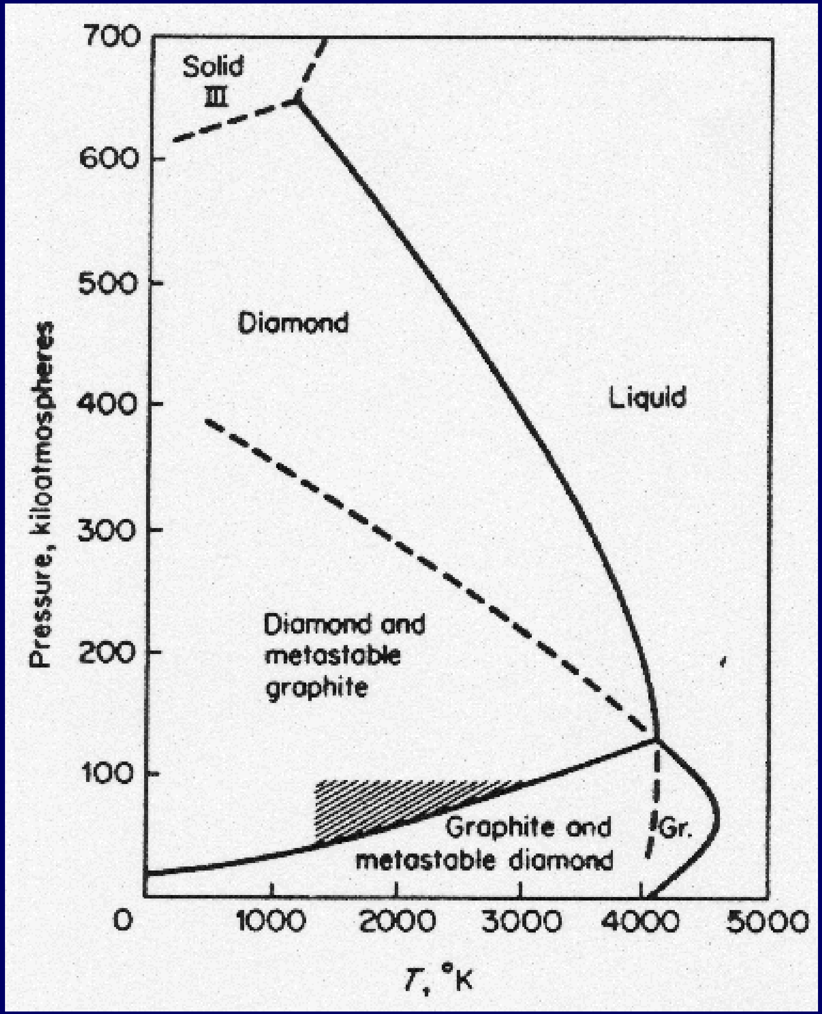


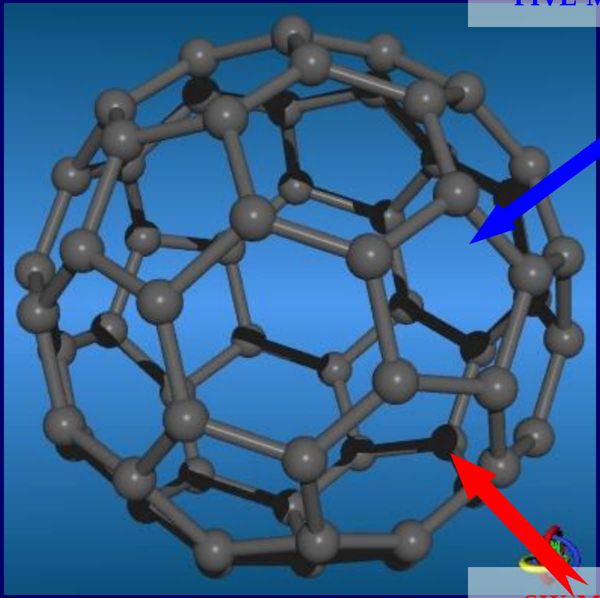
# Carbon Allotropic Phases

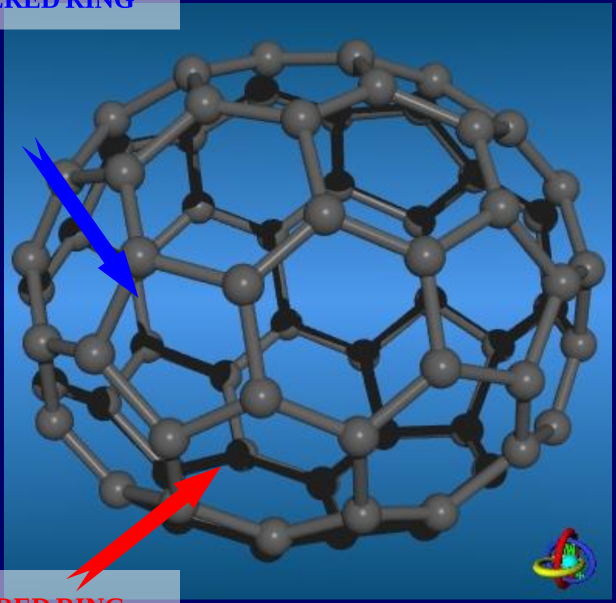

# Carbon Allotropic Phases: Fullerenes

• CARBON ALLOTROPIC PHASES - 1985

GRAPHITE / DIAMOND / CARBON NANOTUBES /FULLERENES

FIVE-MEMBERED RING





SIX-MEMBERED RING

$C_{60}$

SOCCER BALL SHAPE

$C_{70}$

RUGBY BALL SHAPE

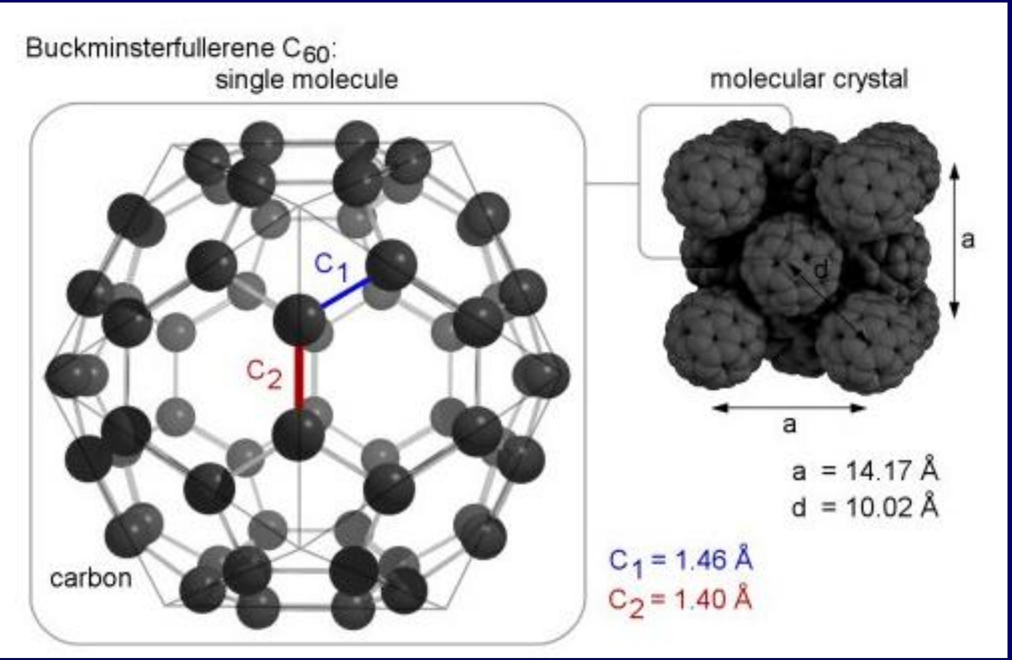
$C_{60}$ UP TO $C_{120}$

IT IS POSSIBLE TO DRAW LOTS OF STRUCTURES WITH FIVE AND SIX-MEMBERED RINGS IN DIFFERENT POSITIONS AND SOMETIMES TOGETHER

# Carbon Allotropic Phases: Fullerenes

• CARBON ALLOTROPIC PHASES

GRAPHITE / DIAMOND / CARBON NANOTUBES /FULLERENES




FULLERENES

$C_{60}$ -- BUCKYBALL

$C_{60}$ – FIRST SPHERICAL CARBON MOLECULE WITH C ARRANGED IN A SOCCER BALL SHAPE.

60 C ATOMS ($C_{60}$), ARRANGED IN A NUMBER OF FIVE-MEMBERED RINGS ISOLATED BY SIX-MEMBERED RINGS.

# Carbon Allotropic Phases: Fullerenes

• CARBON ALLOTROPIC PHASES

•GRAPHITE / DIAMOND / CARBON NANOTUBES /FULLERENES

**FULLERENES**

**(R. Buckminster Fuller)**

$C_{60}$ (1985)

2-BILLION-YEAR-OLD- IMPACT

CRATER SUDBURY, CANADA

**FULLERENES**

$C_{60}$

SOLID FORM OF $C_{60}$ IS ORIENTATIONALLY DISORDERED

AT ROOM TEMPERATURE $C_{60}$ MOLECULES SITTING

ON THE LATTICE SITES OF FCC LATTICE

**FULLERENES**

SUPERCONDUCTIVY (E.G. $K_3C_{60}$)

$C_{60}$ – USED TO PRODUCE DIAMOND FILMS

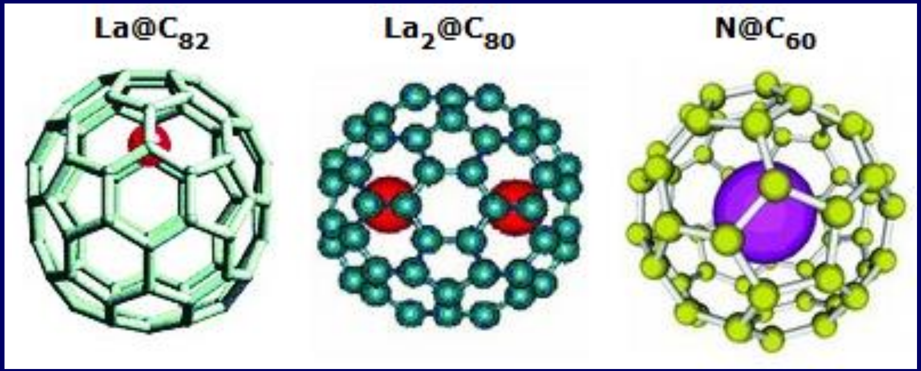
$C_{60}$(S) - YELLOW

$C_{60}$ (DISSOLVED BENZENE) - MAGENTA

# Carbon Allotropic Phases: Fullerenes

• CARBON ALLOTROPIC PHASES

GRAPHITE / DIAMOND / CARBON NANOTUBES /FULLERENES




**FULLERENES**

$C_{60}$ (1985)

ATOMS CAN BE PLACED INSIDE

THE FULLERENE BALL –

ENDOHEDRAL.

M@Cn –ex., $La@C_{82}$, $Y@C_{82}$

**FULLERENES**

$C_{60}$ (1985)

ATOMS CAN BE PLACED OUTSIDE

THE FULLERENE BALL AS SALTS,

FULLERENE GAIN $e^-$

EXAHEDRAL.

$M_X^+ C_{60}^{n-}$

# Carbon Allotropic Phases: Fullerenes

• CARBON ALLOTROPIC PHASES

GRAPHITE / DIAMOND / CARBON NANOTUBES /FULLERENES

**FULLERENES**

$C_{60}$

BULK OR THIN FILMS OF PURE $C_{60}$

SEMI-CONDUCTING

RESISTIVITY ~ 108 Wcm

**ADDITION OF ALKALI METALS AS SALTS**

EXAHEDRAL POSITIONS

$M_X^+C_{60}^{n-}$

RESISTIVITY ↓

MINIMUM X = 3

SUPERCONDUCTING

**ADDITION OF ALKALI METALS AS SALTS**

EXAHEDRAL POSITIONS

$M_X^+C_{60}^{n-}$

FURTHER INCREASING THE ALKALI METAL STOICHIOMETRY

RESISTIVITY ↑

INSULATOR, X = 6

# Carbon Allotropic Phases: Fullerenes

• CARBON ALLOTROPIC PHASES

GRAPHITE / DIAMOND / CARBON NANOTUBES /FULLERENES

**FULLERENES**

**OPTICAL PROPERTIES**

WHEN MORE INTENSE LIGHT SHINES ON $C_{60}$, LESS IT TRANSMITTED.

$C_{60}$ BECOMES A BETTER LIGHT LIMITER AT LONGER WAVELENGTHS, BECAUSE THE ABSORPTION CROSS SECTIONS OF THE GROUND STATE AND THE EXCITED STATE BOTH CHANGE WITH WAVELENGTH, BUT IN OPPOSITE DIRECTIONS.

THIS MAY LEAD TO USING $C_{60}$ FOR PROTECTION FROM LIGHT RADIATION, BUT FIRST MATERIALS SCIENTISTS HAVE TO WORK OUT A WAY TO PRODUCE STRONGER FILMS OF $C_{60}$ AND TO KEEP THEM FROM OXIDIZING.

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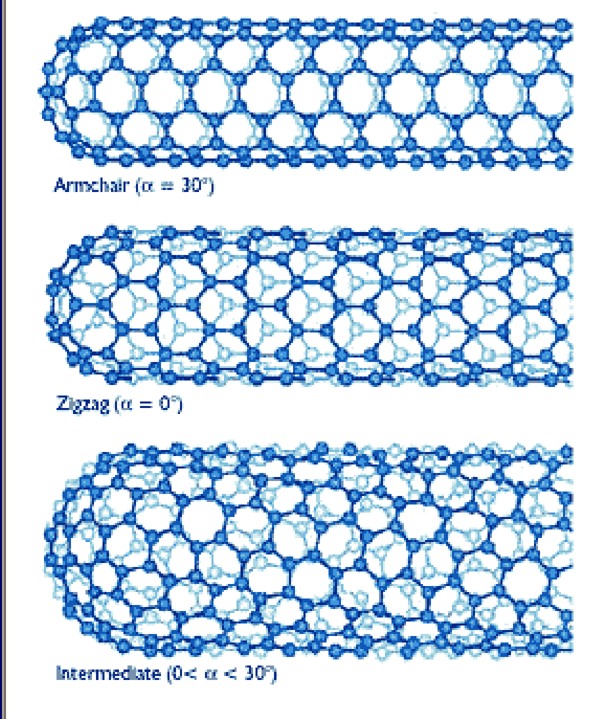
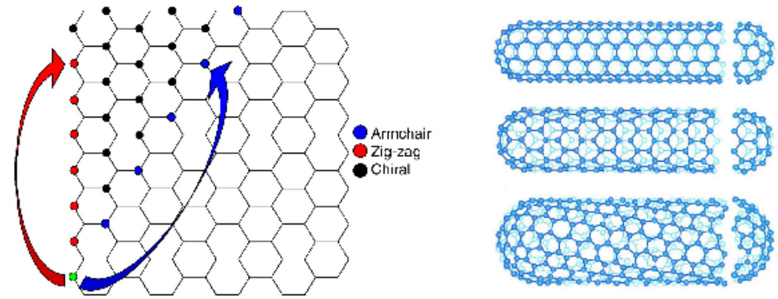
• **CARBON NANOTUBES**

**ARMCHAIR / ZIG-ZAG / CHIRAL**




Armchair nanotubes are metallic. Zig-zag and Chiral nanotubes can be either metallic or semiconducting.

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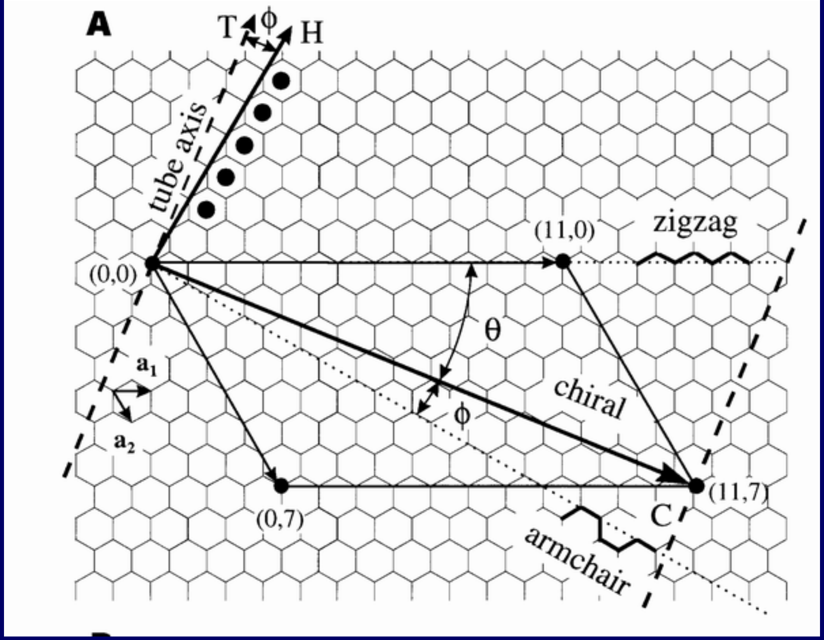
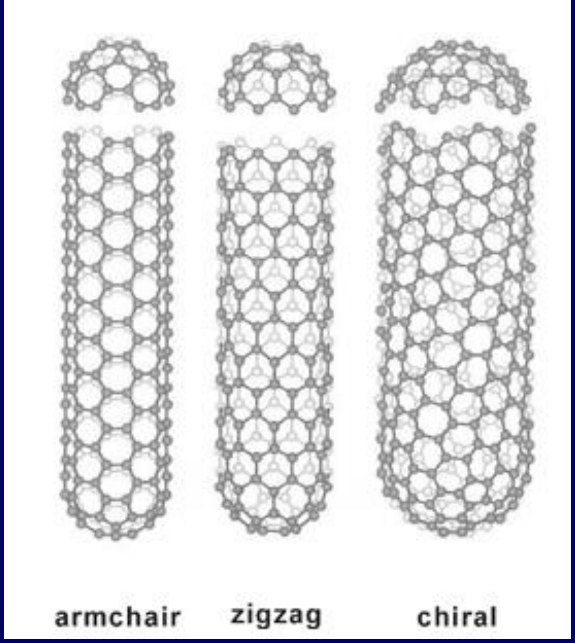
• **CARBON NANOTUBES**

**ARMCHAIR / ZIG-ZAG / CHIRAL**

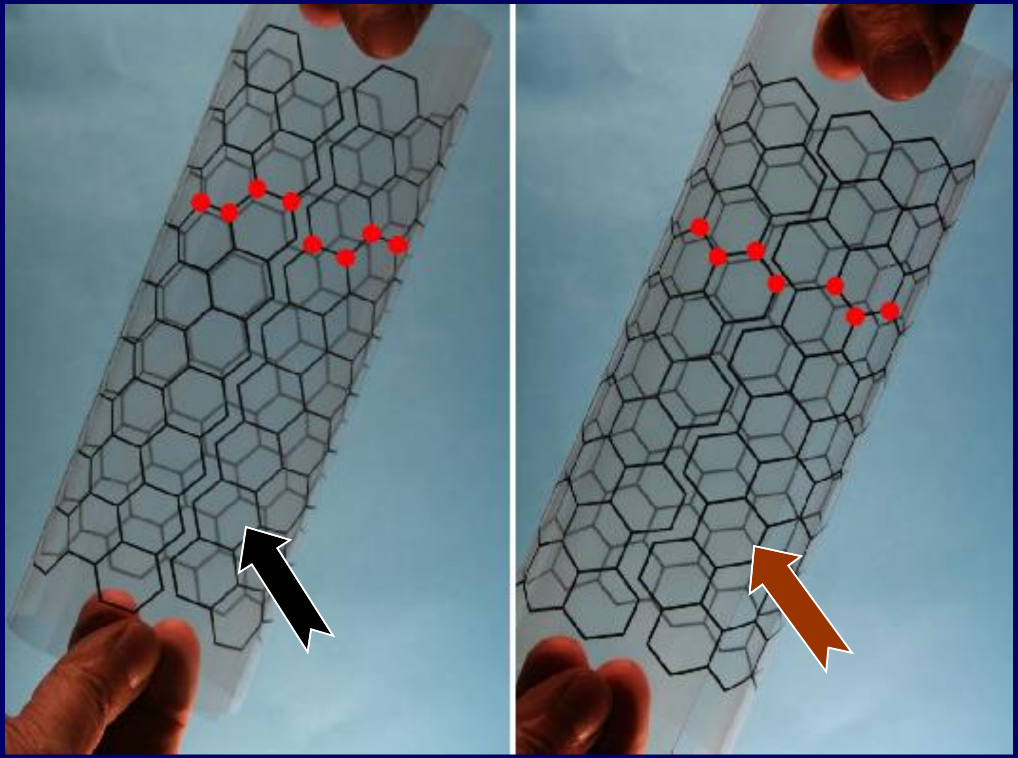


# Carbon Allotropic Phases: Nanotubes

**• CARBON NANOTUBES**

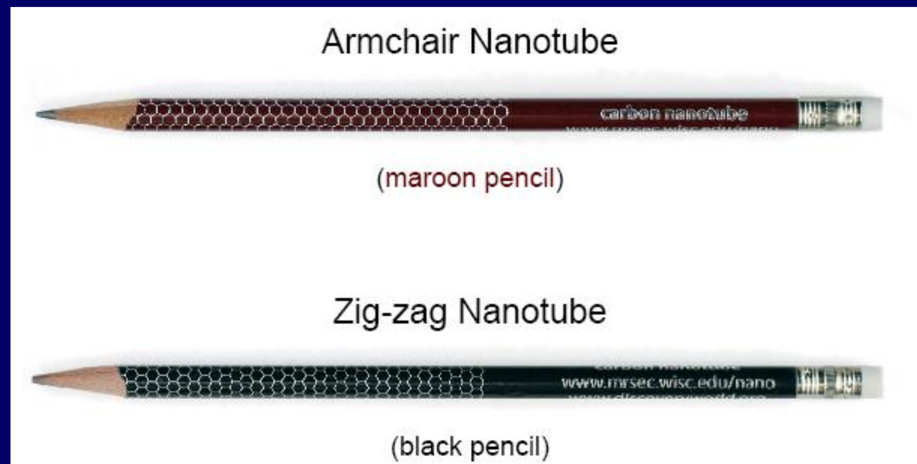
**ROLLING GRAPHENE SHEETS**

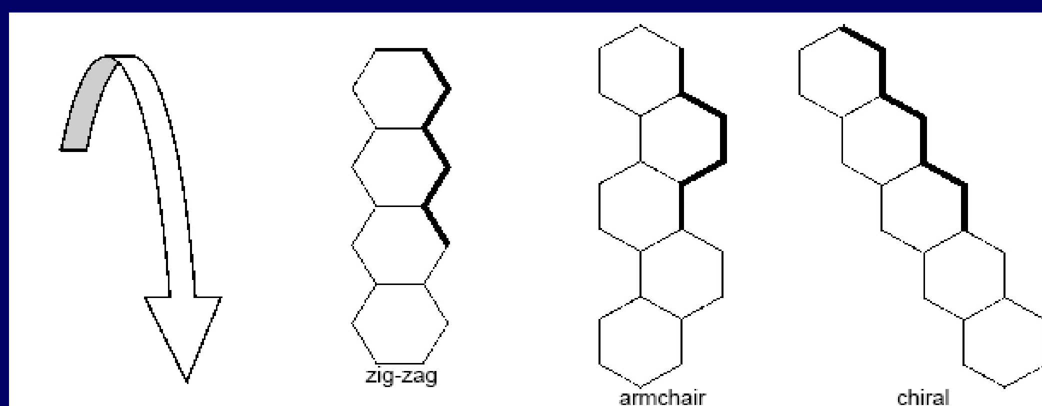


# Carbon Allotropic Phases: Nanotubes

• **CARBON NANOTUBES**

**ARMCHAIR / ZIG-ZAG / CHIRAL**



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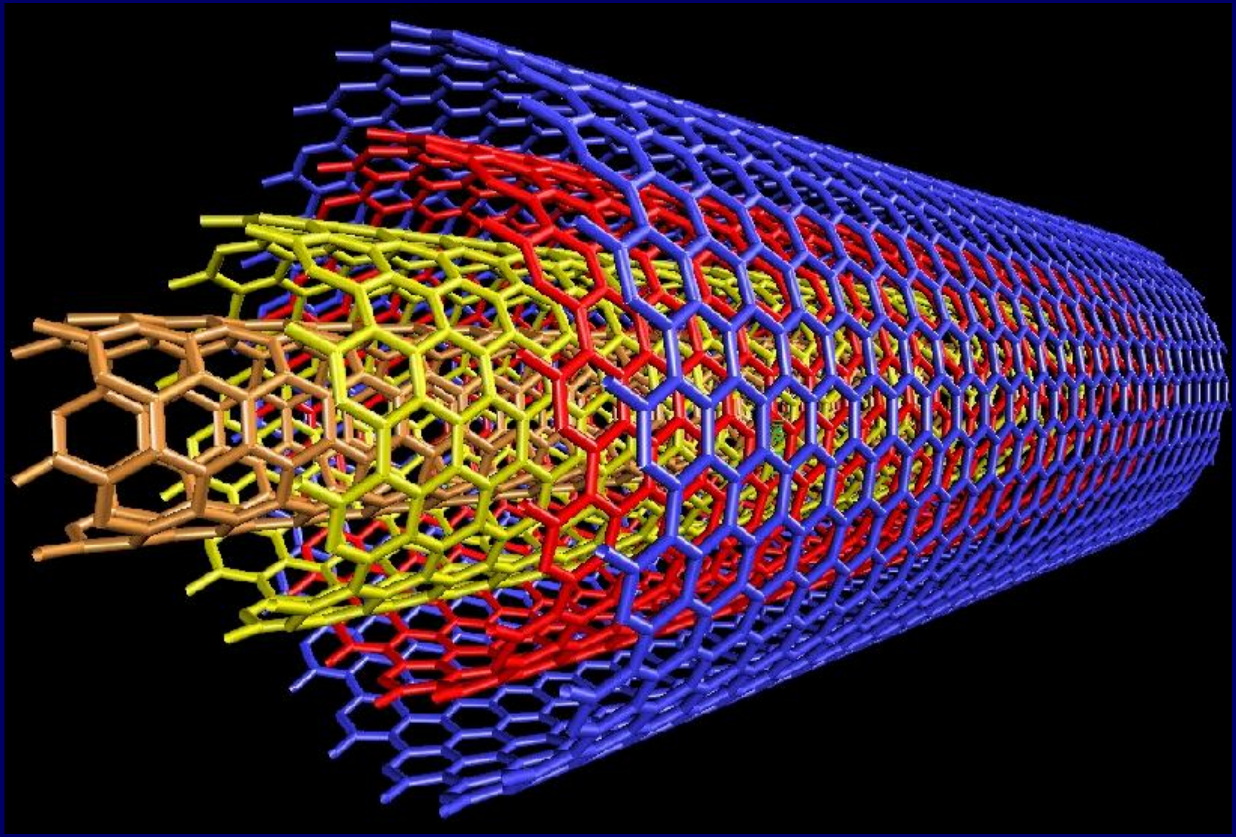
- **CARBON NANOTUBES**



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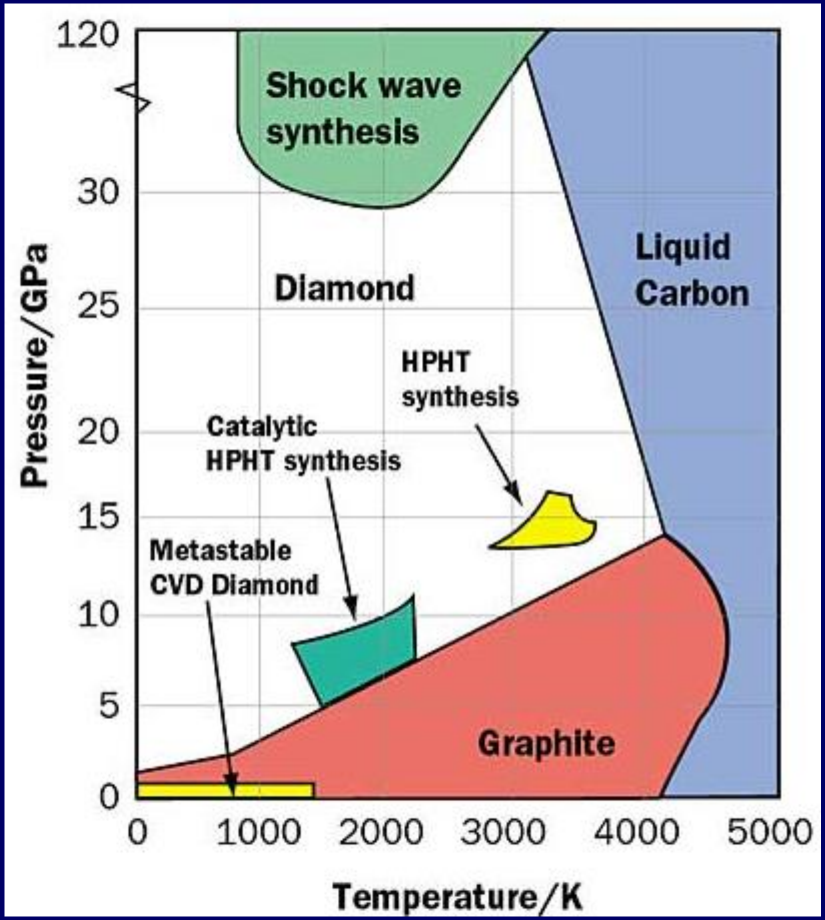
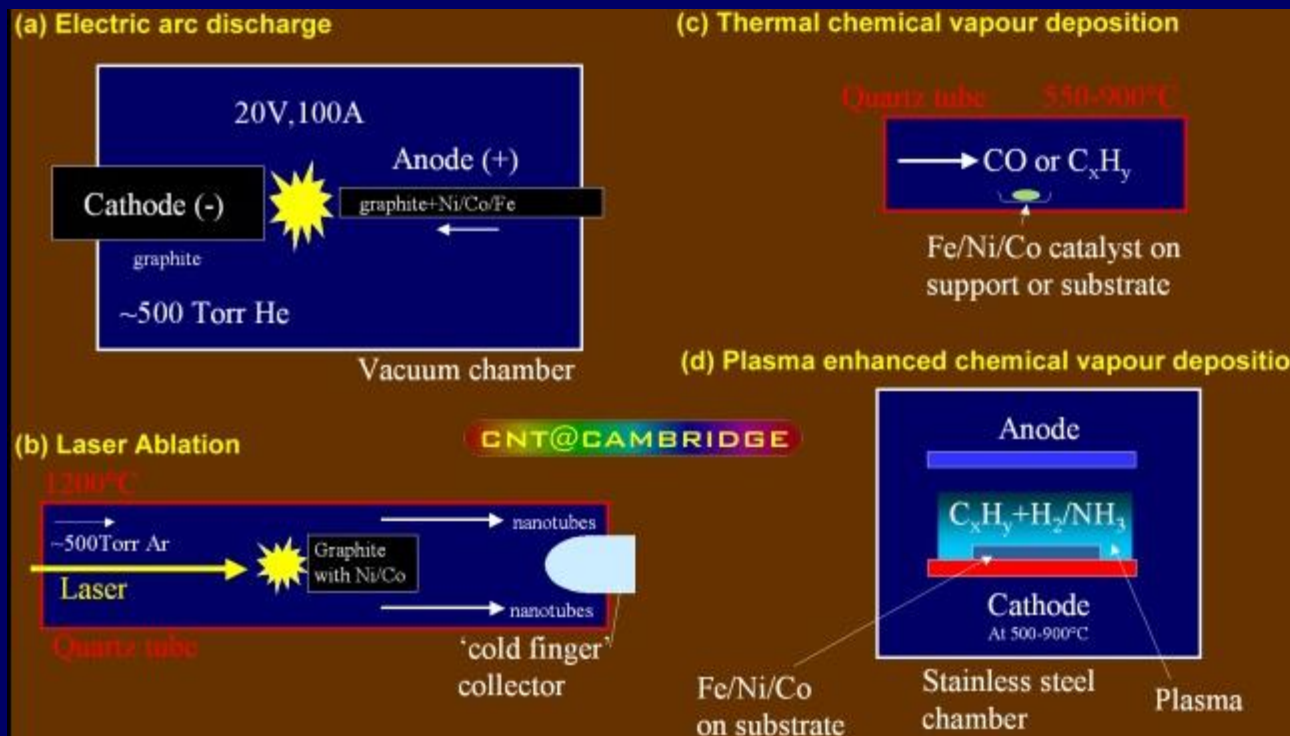
• **CARBON NANOTUBE SYNTHESIS**



# Carbon Nanotubes / Fullerenes Synthesis

• **CARBON NANOTUBE SYNTHESIS**

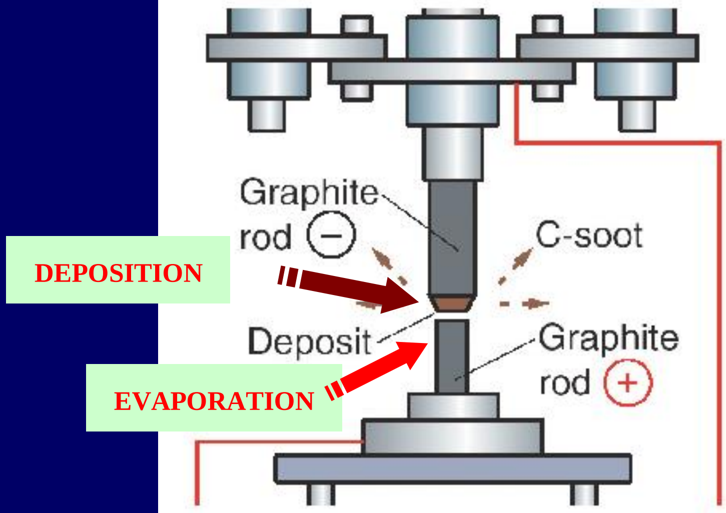


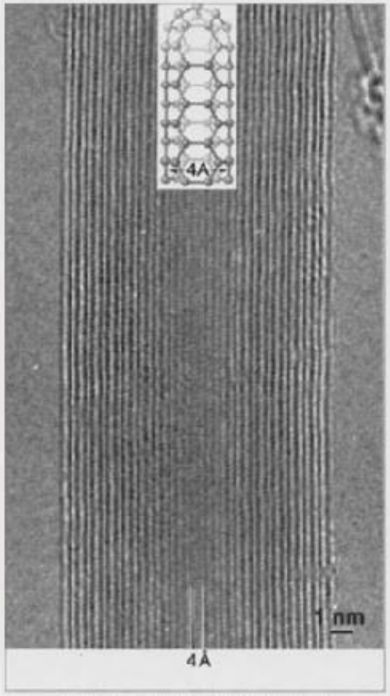
# Carbon Nanotubes / Fullerenes Synthesis

• **CARBON NANOTUBE SYNTHESIS**

**PLASMA ARCING**

Arc-discharge between graphite rods (low pressure)




L. C. Qin, *Nature* (2000) 408, 50

- Fullerenes deposited as soot
- SWNT in soot if anode contains metal catalyst (Fe, Co, Ni-Co, etc.)
- MWNT deposited on cathode under hydrogen gas (0.34 nm layer spacing)

Yoshinori Ando, Xinluo Zhao, Toshiki Sugai, and Mukul Kumar, "Growing Carbon Nanotubes," *Materials Today*, Oct 2004, pages 22-49.

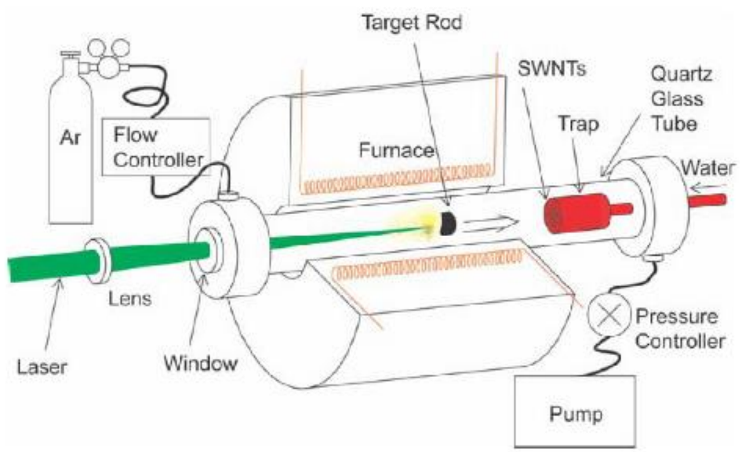
# Carbon Nanotubes / Fullerenes Synthesis

**• CARBON NANOTUBE SYNTHESIS**

**DUAL-PULSED LASER VAPORISATION**

## Laser Furnace

- YAG or $CO_2$ laser aimed at carbon target containing catalytic metals
- SWNT diameter depends on furnace temperature and catalyst (Ni-Y large, Rh-Pd small)

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# Carbon Nanotubes / Fullerenes Synthesis

• **CARBON NANOTUBE SYNTHESIS**

**PLASMA ARCING**

**DUAL-PULSED LASER VAPORISATION**

• **UNCLEAR HOW TO SCALE UP NANOTUBE PRODUCTION TO THE INDUSTRIAL LEVEL**

• **VAPORIZATION METHODS GROW NANOTUBES IN HIGHLY TANGLED FORMS MIXED WITH UNWANTED FORMS OF CARBON OR METAL SPECIES.**

• **NANOTUBES ARE DIFFICULT TO PURIFY, MANIPULATE, AND ASSEMBLE FOR BUILDING NANOTUBE-DEVICE ARCHITECTURES.**

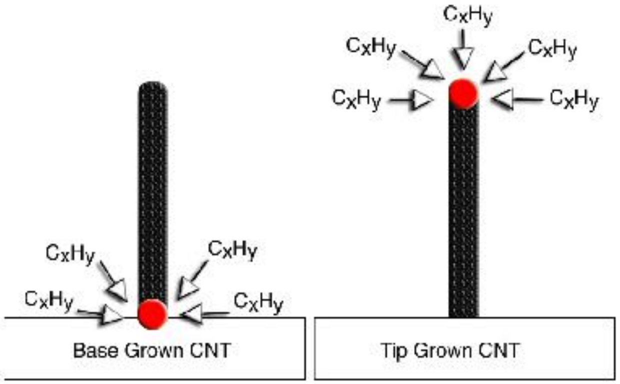
# Carbon Nanotubes / Fullerenes Synthesis

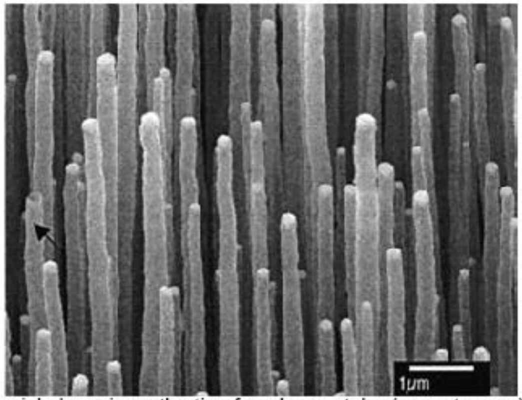
**• CARBON NANOTUBE SYNTHESIS**

**CVD**

## Chemical vapor deposition

- Hydrocarbon vapor passed through a tube furnace.
- SWNTs or MWNTs depends on size and temperature of catalyst (Fe, Ni with $NH_3$).
- Low-temperature (600-900°C) yields MWNTs, higher temperature (900-1200°C) favors SWNTs.



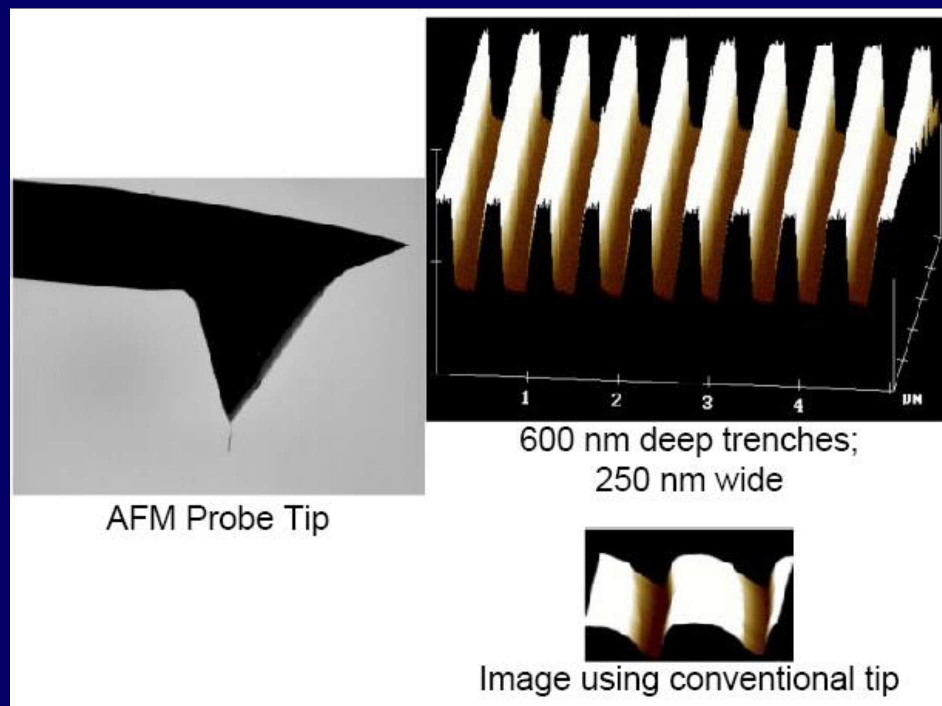

A nickel cap is on the tip of each nanotube (except arrow).

Yoshinori Ando, Xinluo Zhao, Toshiki Sugai, and Mukul Kumar, "Growing Carbon Nanotubes," *Materials Today*, Oct 2004, pages 22-49.

Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, P. N. Provencio, "Synthesis of Large Arrays of Well-Aligned Carbon Nanotubes on Glass," *Science*, 282, 1105-1107 (1998).

# Applications

• **CARBON IMAGING**



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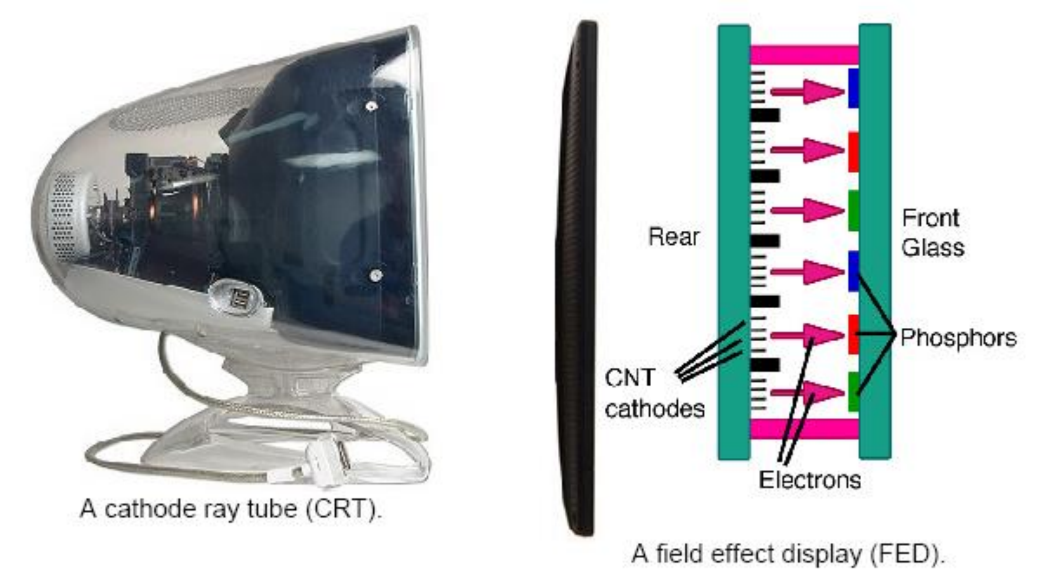
• **CARBON NANOTUBE DISPLAYS**




A cathode ray tube (CRT).

A field effect display (FED).

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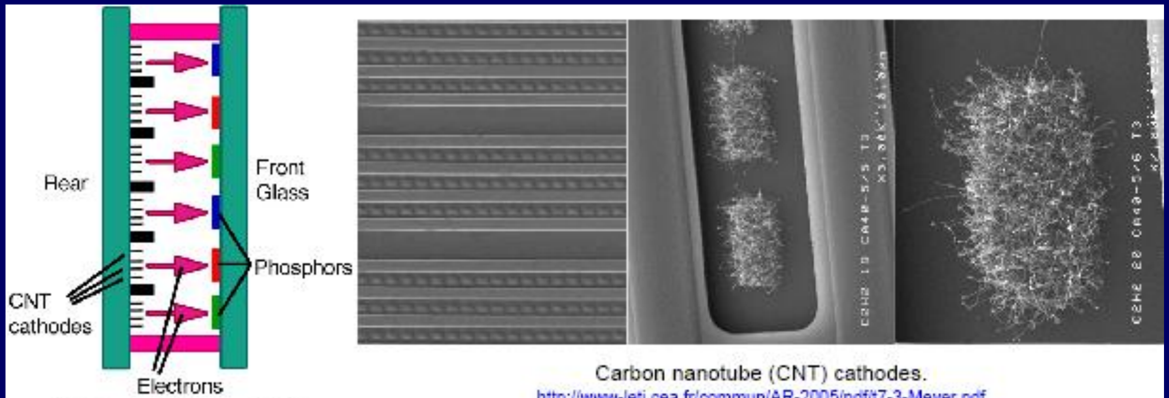


A field effect display (FED).

Carbon nanotube (CNT) cathodes.
http://www-leti.cea.fr/commun/AR-2005/pdf/t7-3-Meyer.pdf

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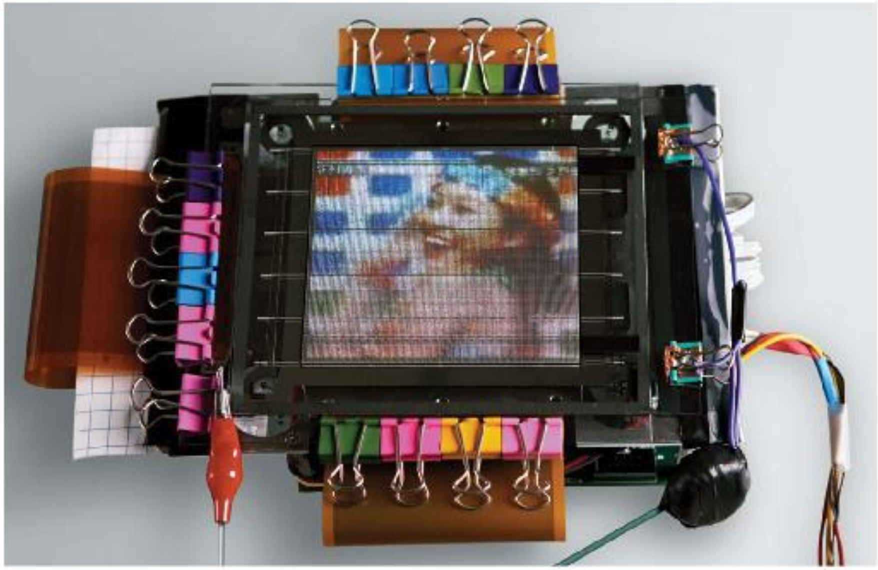
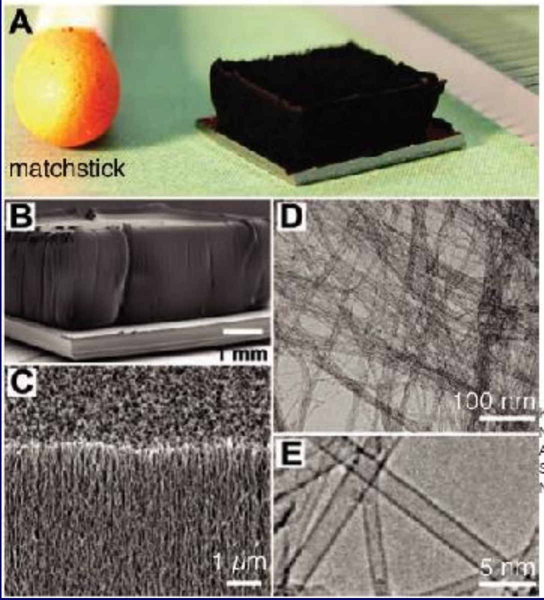


Samsung prototype field emission display using carbon nanotubes.
Technology Review, November 2004, May 2005

# Applications

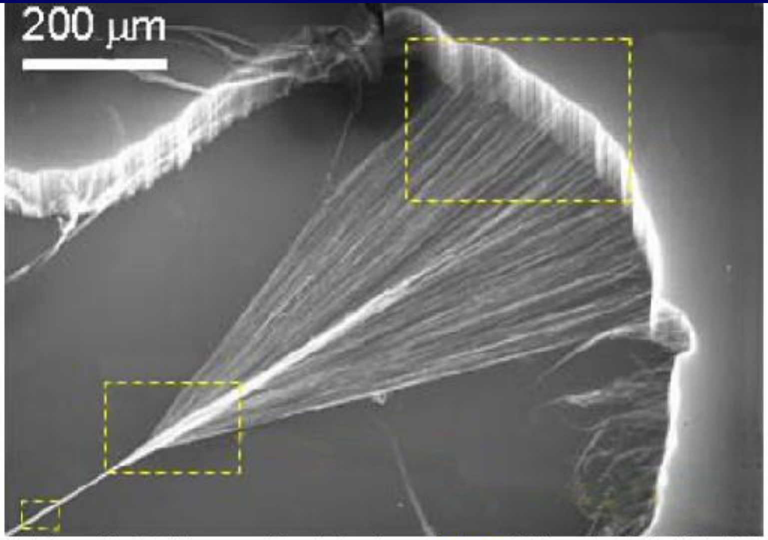
• **CARBON NANOTUBE**




Kenji Hata, Don N. Futaba, Kohei Mizuno, Tatsunori Namai, Motoo Yumura, and Sumio Iijima, "Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes," *Science*, 19 November 2004, 1362-1364.

# Applications

• **CARBON NANOTUBE SPINNING**




Mei Zhang, Ken R. Atkinson, and Ray H. Baughman, *Science*, 19 November 2004, 1358-1361.

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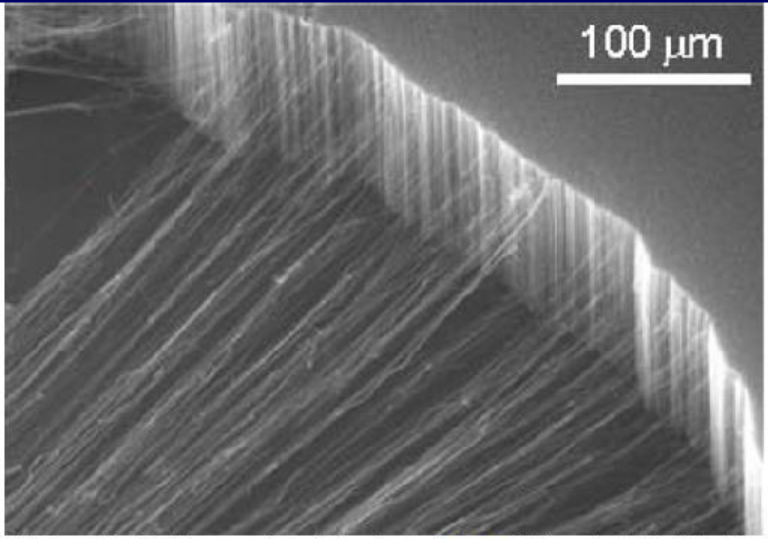
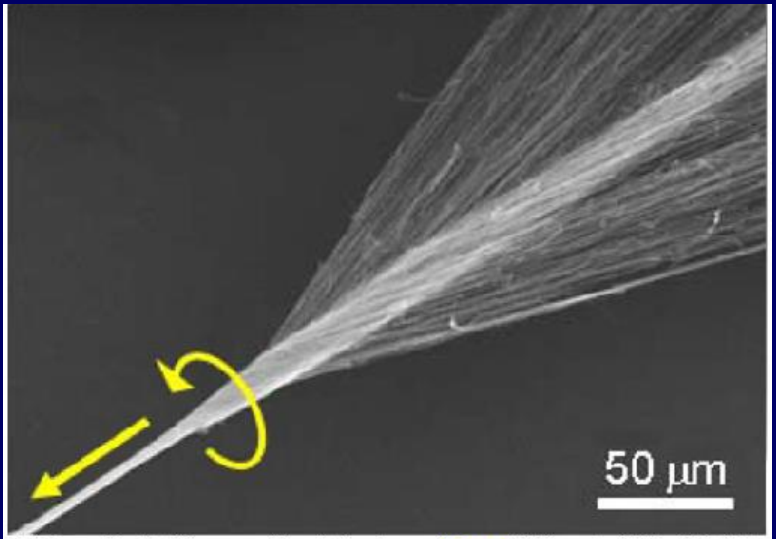



Mei Zhang, Ken R. Atkinson, and Ray H. Baughman, *Science*, 19 November 2004, 1358-1361.

# Applications

• **CARBON NANOTUBE SPINNING**




Mei Zhang, Ken R. Atkinson, and Ray H. Baughman, *Science*, 19 November 2004, 1358-1361.

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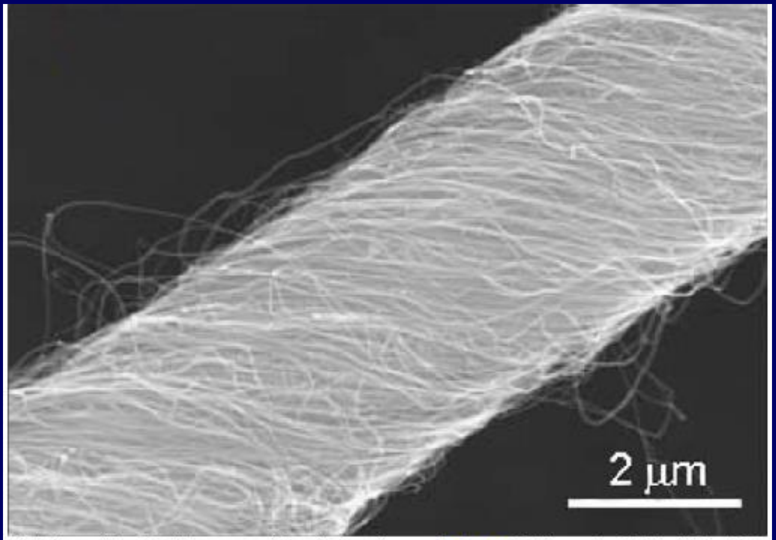


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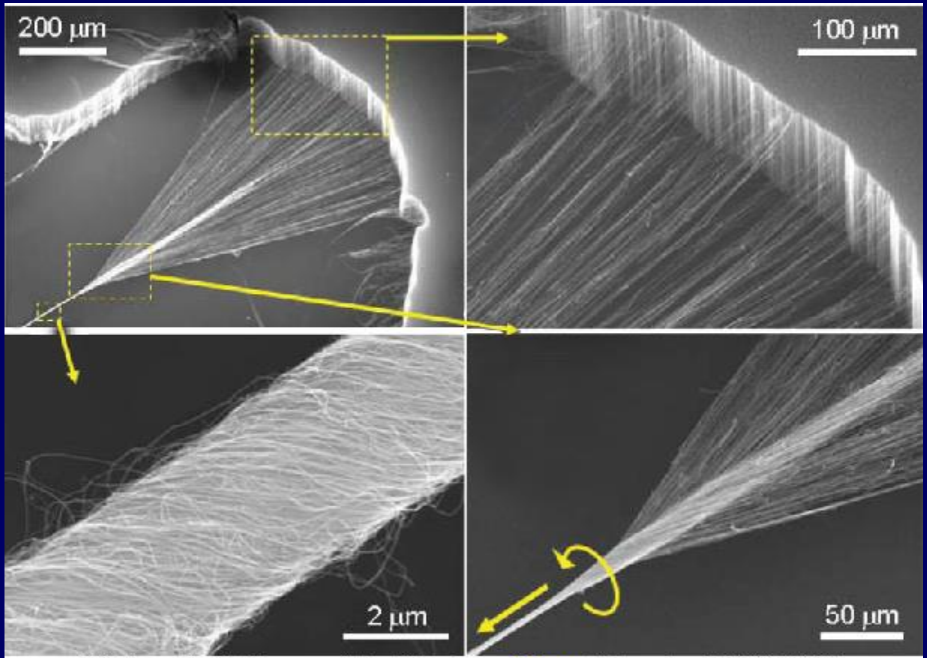


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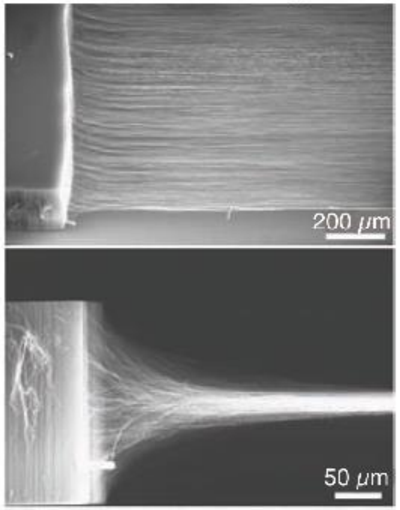
# Applications

## • CARBON NANOTUBE SPINNING

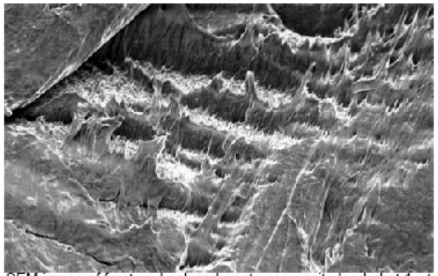
Synthesize MWNT forest by catalytic CVD of acetylene
Attach adhesive strip (Post-it) to sidewall
Draw 5 cm x 1 meter-long MWNT transparent sheets at 1 m/min




Mei Zhang, Shaoli Fang, Anvar A. Zakhidov, Sergey B. Lee, Ali E. Aliev, Christopher D. Williams, Ken R. Atkinson, Ray H. Baughman, "Strong, Transparent, Multifunctional, Carbon Nanotube Sheets," *Science*, 19 August 2005, 1215-1219.

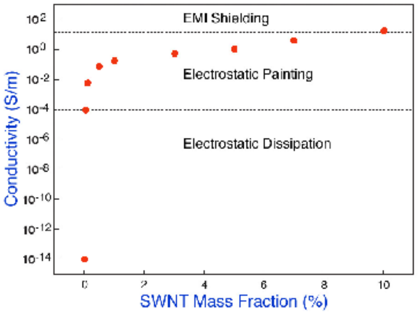
# Applications

## • POLIMER NANOTUBE COMPOSITE



SEM image of fractured polycarbonate composite loaded at 1 wt % with Zyvex processed SWNTs. The nanotubes remain embedded in the matrix even after fracture.

Electrical conductivity of polystyrene/SWNTs.




Zyvex Application Note 9709 http://www.zyvex.com/Products/CNAE_001b.html

With a tensile strength eight times that of stainless steel and with a thermal conductivity five times that of copper, CNTs are obvious choices for creating a new class of composite materials. Their inclusion in a polymer or ceramic matrix holds the potential to boost the host material's electrical, mechanical, or thermal values by orders of magnitude if poor dispersion and poor adhesion to the host can be overcome.

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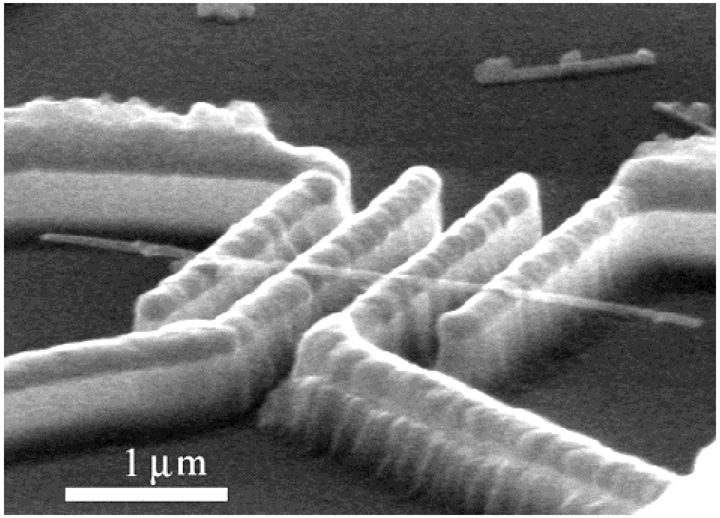
MATERIAIS NANOESTRUTURADOS E NANOTECNOLOGIAS

• **POLIMER NANOTUBE COMPOSITE**




Appl. Phys. Lett. 73, 274 (1998).

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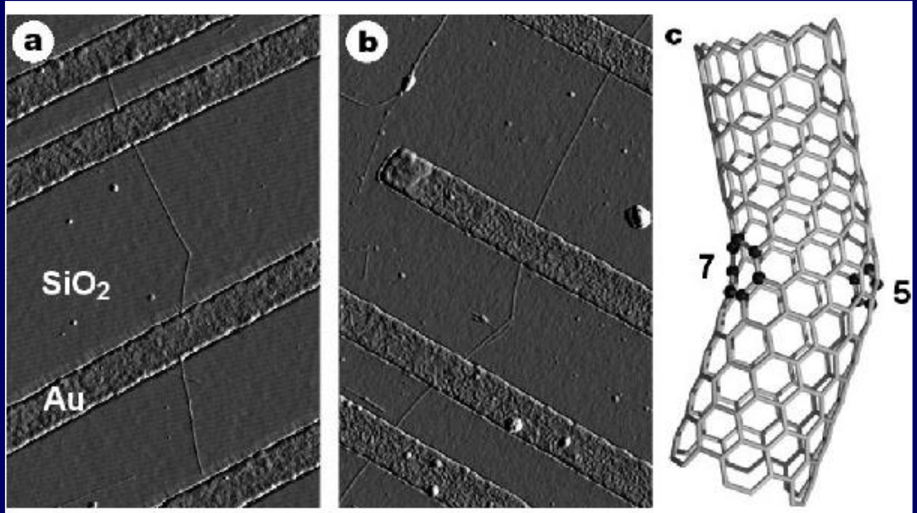
• **POLIMER NANOTUBE COMPOSITE**




(a, b) Atomic force microscope images of nanotube junction devices with a single kink of 36° and 41° respectively. The gold electrodes are 250-nm wide. Nanotubes are deposited on top of the electrodes by spin coating of a drop of SWNT suspension in dichloroethane. (c) A kink junction constructed between an 'armchair' tube and a 'zigzag' tube using pentagon and heptagon defects.

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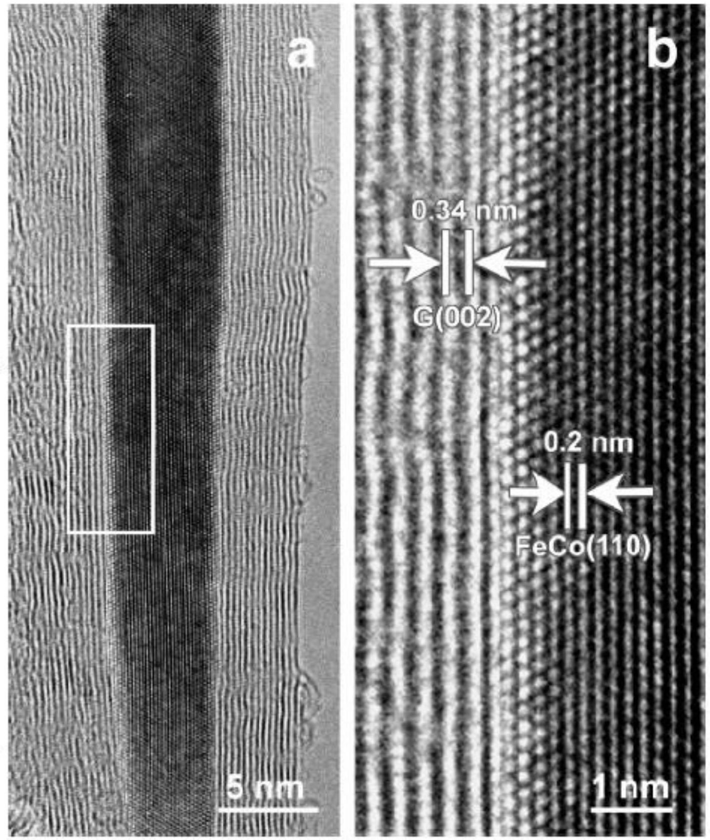
**• Fe-Co FILLED CARBON NANOTUBES**

- Carbon nanotubes may be used as templates to form single crystal wires coated by perfect graphene cylinders.
- Aerosol thermolysis of Fe $(C_5H_5)_2$ Co $(C_5H_5)_2$ $C_6H_5CH_3$ solutions at 700° C in an Ar atmosphere.
- Periodic arrays of ferromagnetic nanostructures could be used in the fabrication of high-density magnetic storage devices.




HRTEM image of FeCo-filled MWCNTs produced at 700 °C.

A. L. Elias, J. A. Rodriguez-Manzo, M. R. McCartney, D. Golberg, A. Zamudio, S. E. Baltazar, F. Lopez-Urias, E. Munoz-Sandoval, L. Gu, C. C. Tang, D. J. Smith, Y. Bando, H. Terrones, and M. Terrones, "Production and Characterization of Single-Crystal FeCo Nanowires Inside Carbon Nanotubes," *Nanoletters*, 5, 467-472 (2005).

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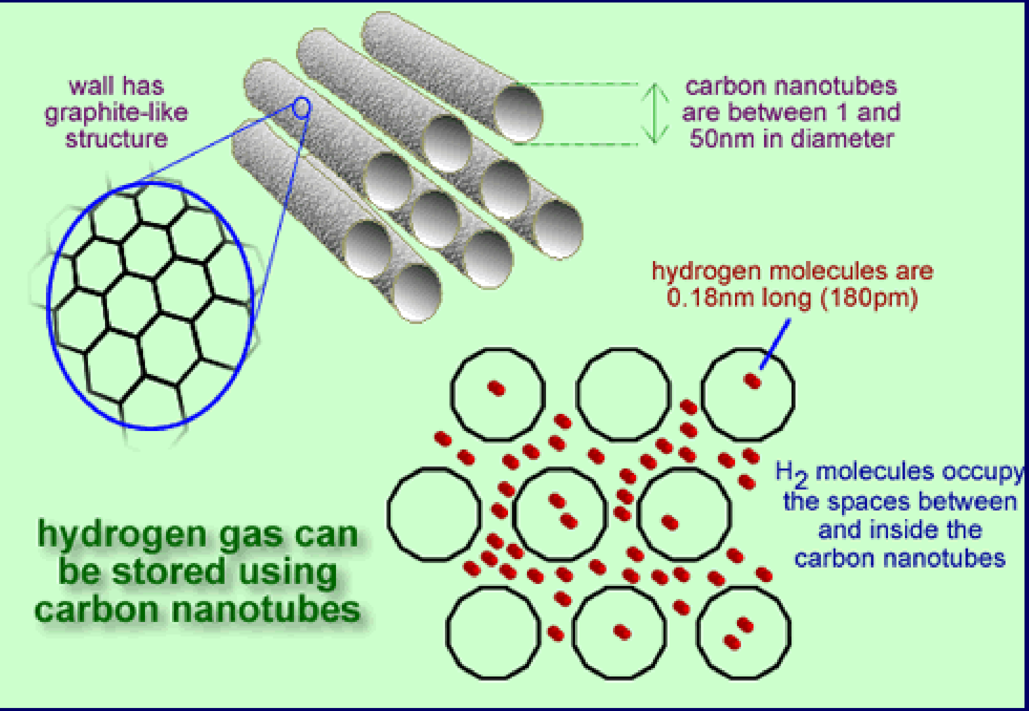
• **HYDROGEN STORAGE**



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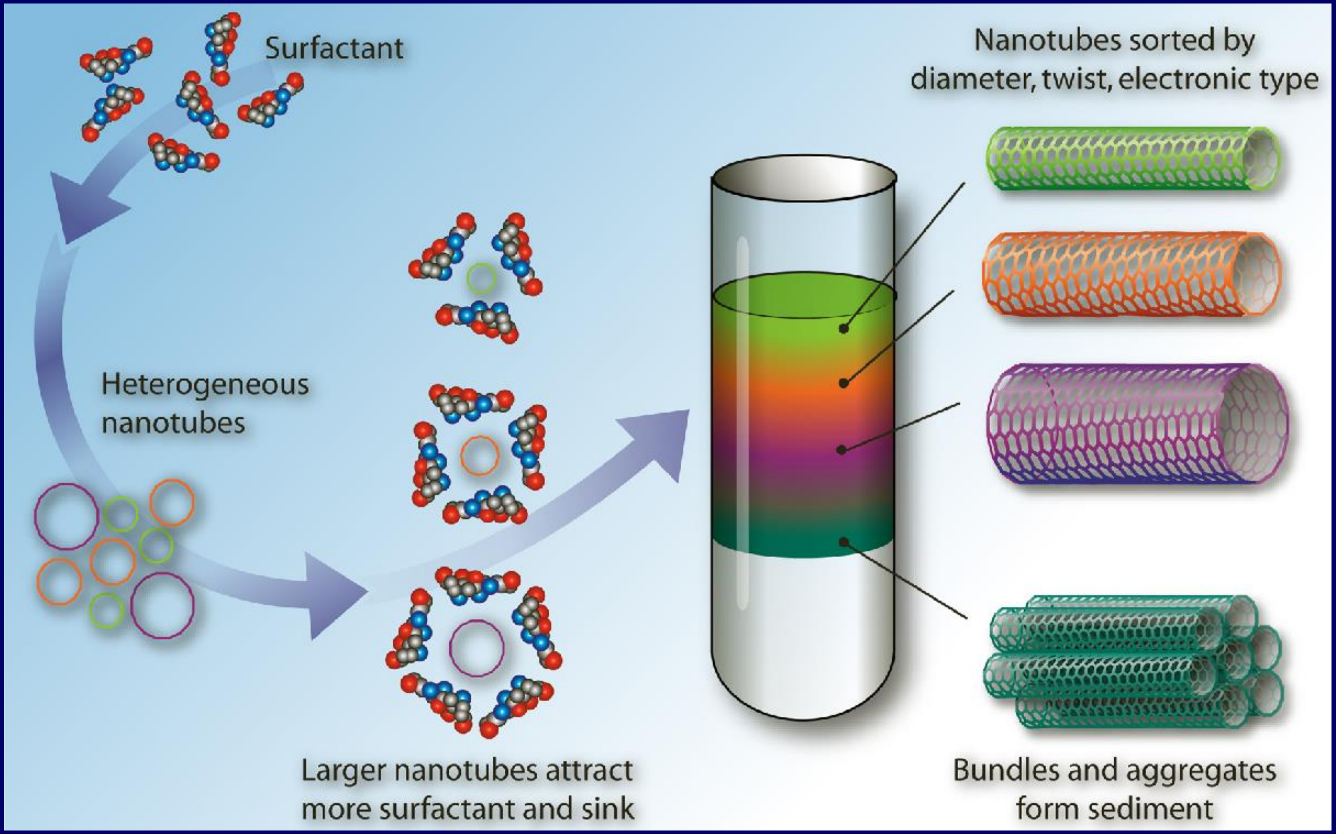
MATERIAIS NANOESTRUTURADOS E NANOTECNOLOGIAS

• **SURFACTANT STORAGE**



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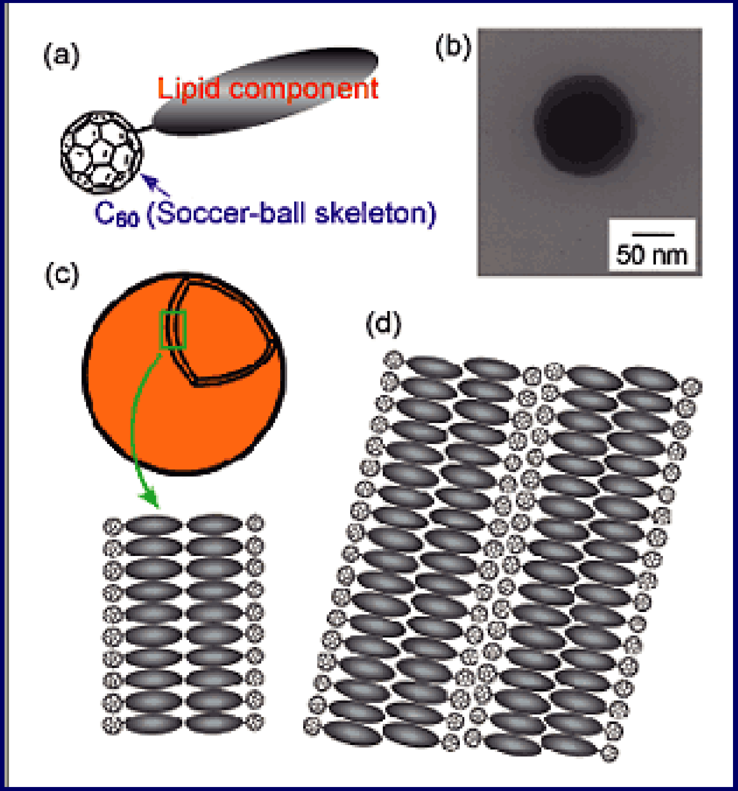
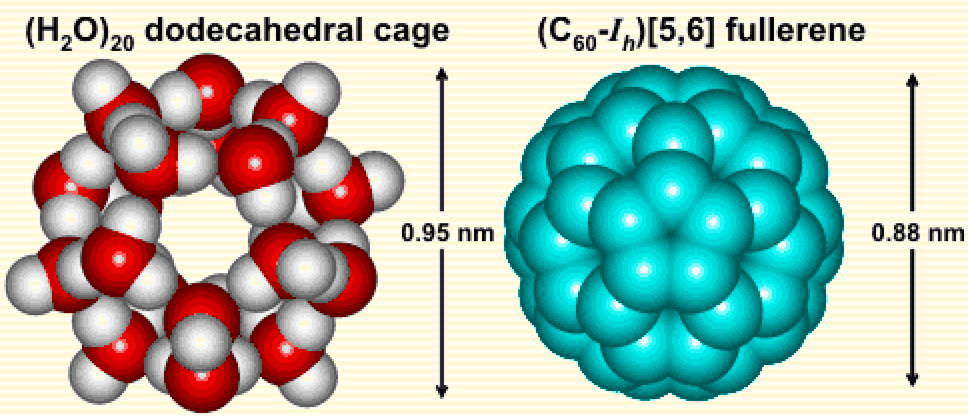
**• LIPIDS STORAGE**



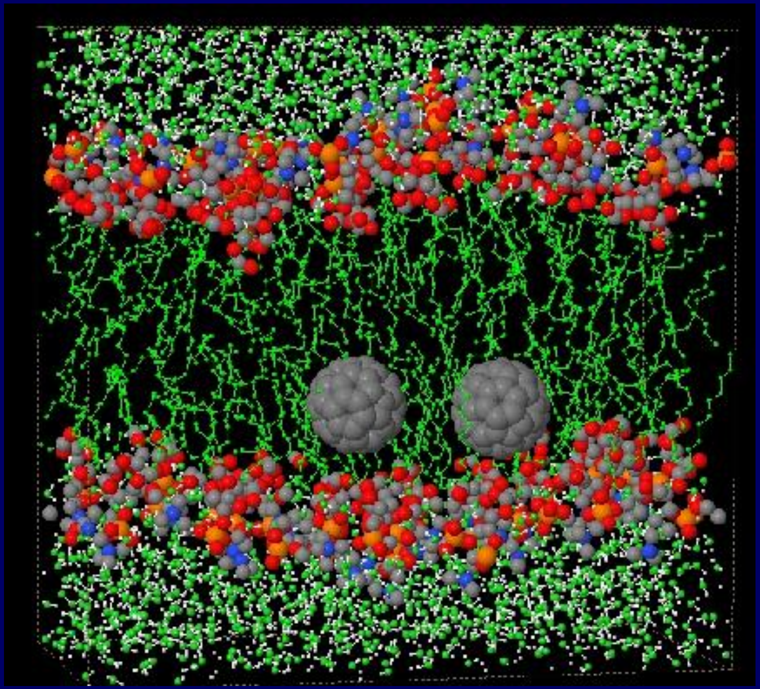
# • FULLERENE SOLUBILITY

The solubility of single $C_{60}$ molecules may be explained if the fullerene may sit (ideally) in an icosahedral water cluster (ES) missing its inner water dodecahedron. The size of the C60 molecule and the ceenral aqueous dodecahedron are similar (see opposite).

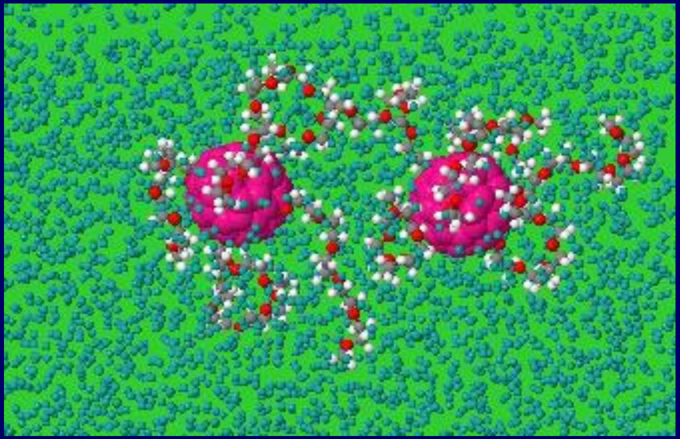


# Applications

• **FULLERENE SOLUBILITY**



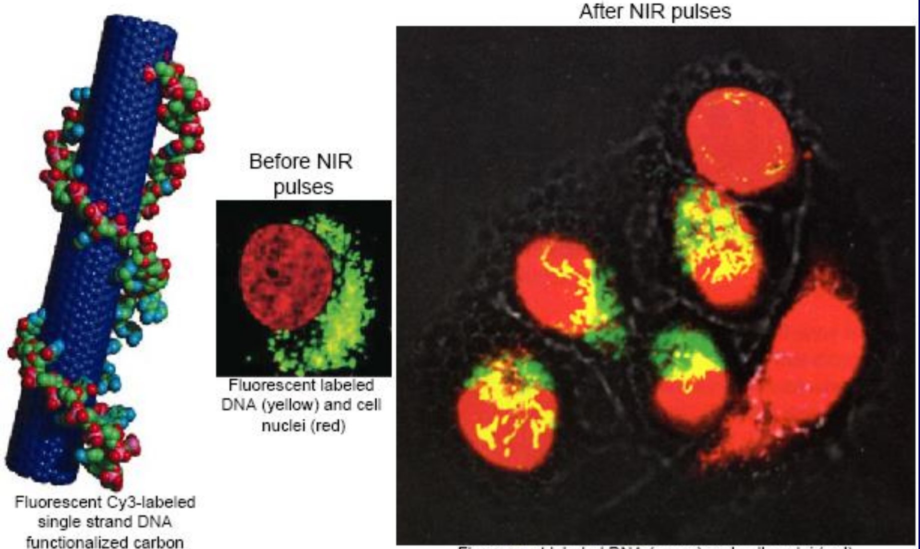
FULLERENES INSIDE A LIPID BILAYER



FULLERENES IN WATER

# Applications

**• NANOTUBES FOR MOLECULAR TRANSPORT**




Fluorescent Cy3-labeled single strand DNA functionalized carbon nanotube.

Fluorescent labeled DNA (yellow) and cell nuclei (red)

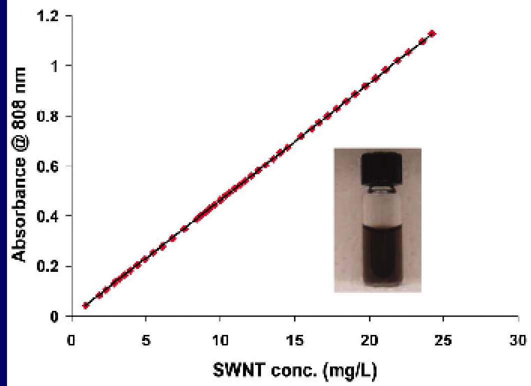
Fluorescent labeled DNA (green) and cell nuclei (red)
Discover Magazine, November 2005

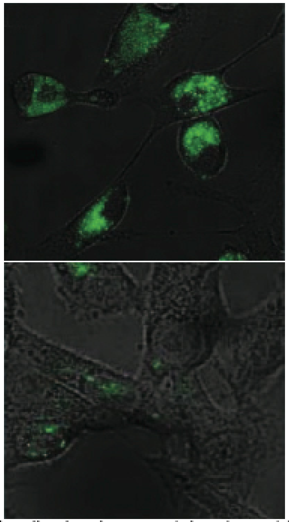
- Nanotubes with non-covalently bound DNA (left) taken into cell by endocytosis.
- Cargo stays on carrier and outside the nucleus (center).
- Pulsed excitation with 808 nm NIR light releases cargo inside cell.
- Released DNA is taken up by nucleus (right).

Nadine Wong Shi Kam, Michael O'Connell, Jeffrey A. Wisdom, and Hongjie Dai, "Carbon nanotubes as multifunctional biological transporters and near-infrared agents for selective cancer cell destruction," PNAS, 102, 11600-11605, (2005)

# Applications

## • KILLING CANCER



Functionalized carbon nanotubes (green) taken up by cancer cells with folate receptors (top) and normal cells (bottom). Magnification 20x.

- Biological systems are highly transparent to 700-1100 nm near-infrared (NIR) light.
- Single-walled carbon nanotubes (SWNTs) strongly absorb NIR light.
- Folate (vitamin B9) phospholipid functionalized SWNTs taken up by tumors with folate receptors.
- Selective cancer cell destruction can occur by NIR local heating, without harming receptor-free normal cells.

Nadine Wong Shi Kam, Michael O'Connell, Jeffrey A. Wisdom, and Hongjie Dai, "Carbon nanotubes as multifunctional biological transporters and near-infrared agents for selective cancer cell destruction," PNAS, 102, 11600-11605, (2005) and Discover Magazine, November 2005.

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# Further Reading


- Nanostructures and Nanomaterials. Synthesis, Properties & Applications, G. Cao, ICP Imperial College Press, 2007 (ISBN 1-86094-480-9).

- Nanotechnology. Basic Science and Emerging Technologies. M. Wilson, K. Kannagara, G. Smith, M. Simmons, B. Raguse, Chapman & Hall/CRC, 2002 (ISBN 1-58488-339-1).