Why are we so excited about carbon nanostructures?

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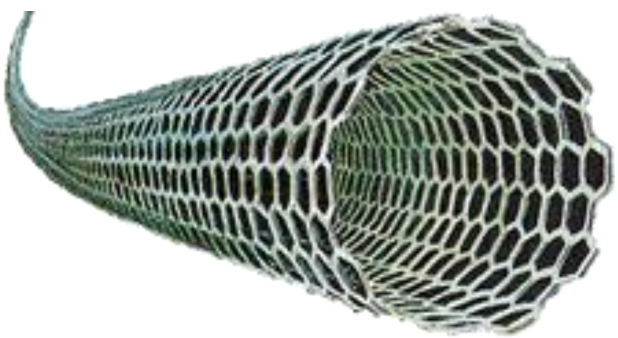
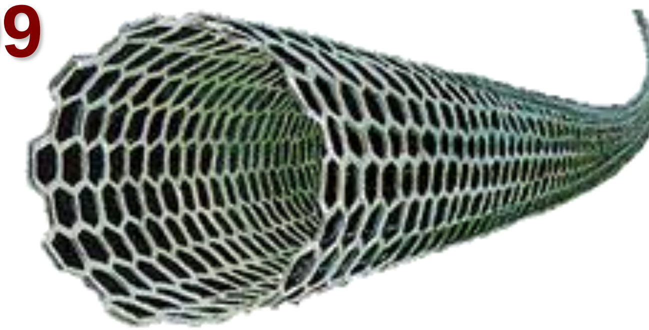
Conference for Undergraduate Women in Physics at Yale
January 18, 2009

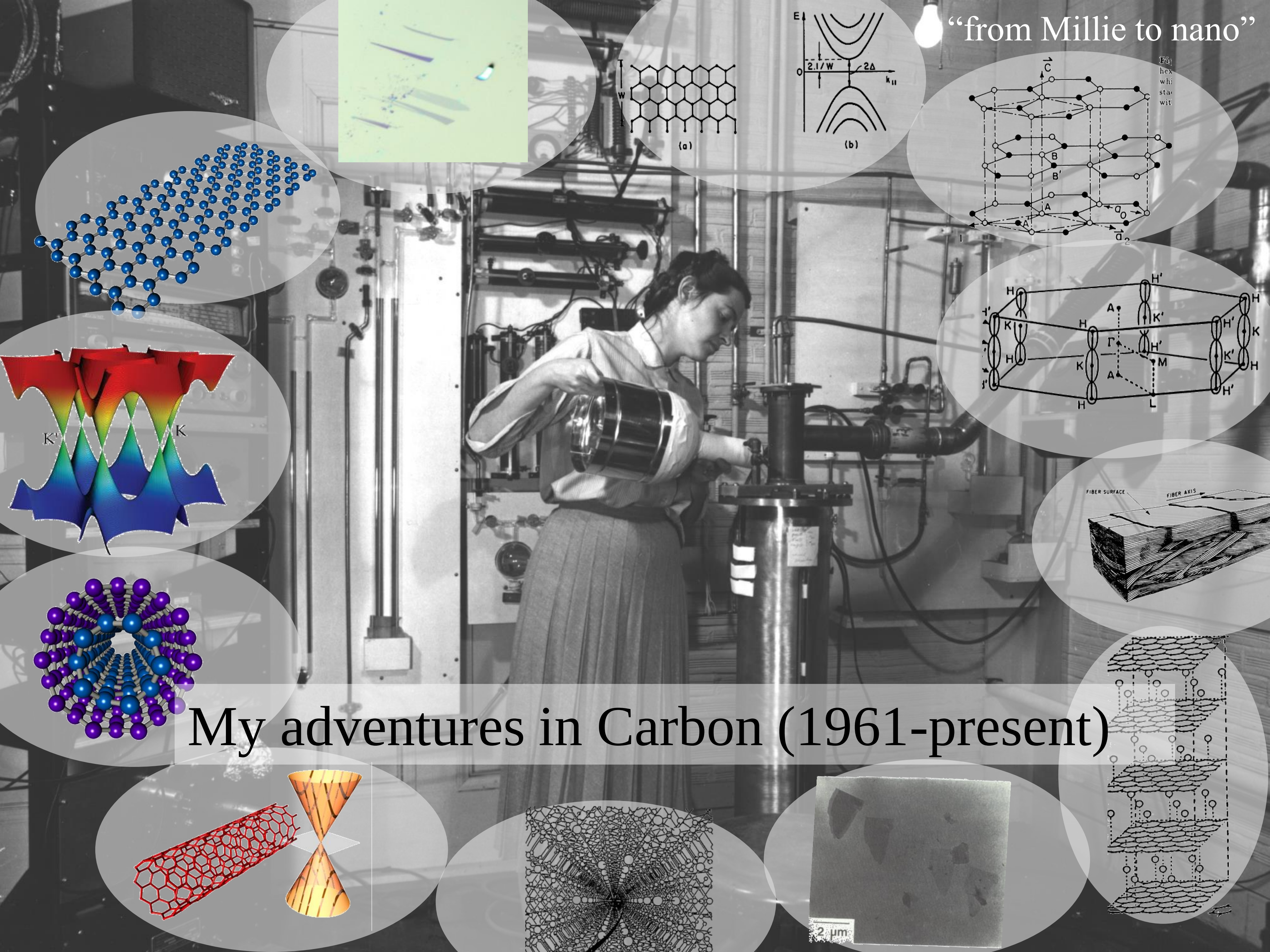




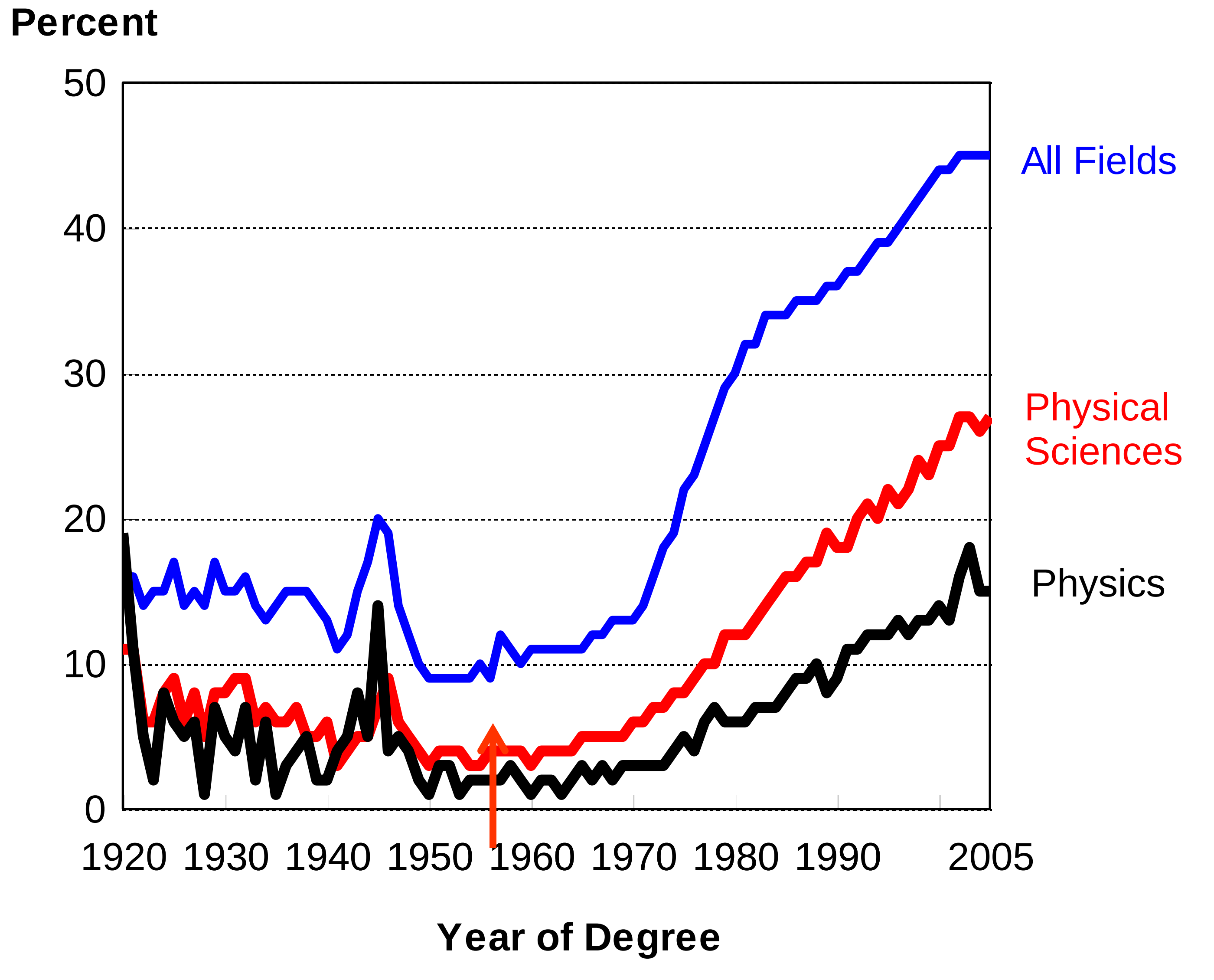
Why are we so excited about carbon nanostructures?

outline

- Early adventures with graphene, graphite and related nanostructures
- Adventures with Carbon Nanotubes
- Graphene and Graphene Ribbons
- Looking to the Future of Carbon Nanostructures


"from Millie to nano"
My adventures in Carbon (1961-present)
(a)
(b)
2.1/W
2Δ
K'
K
FIBER SURFACE
FIBER AXIS
2 µm

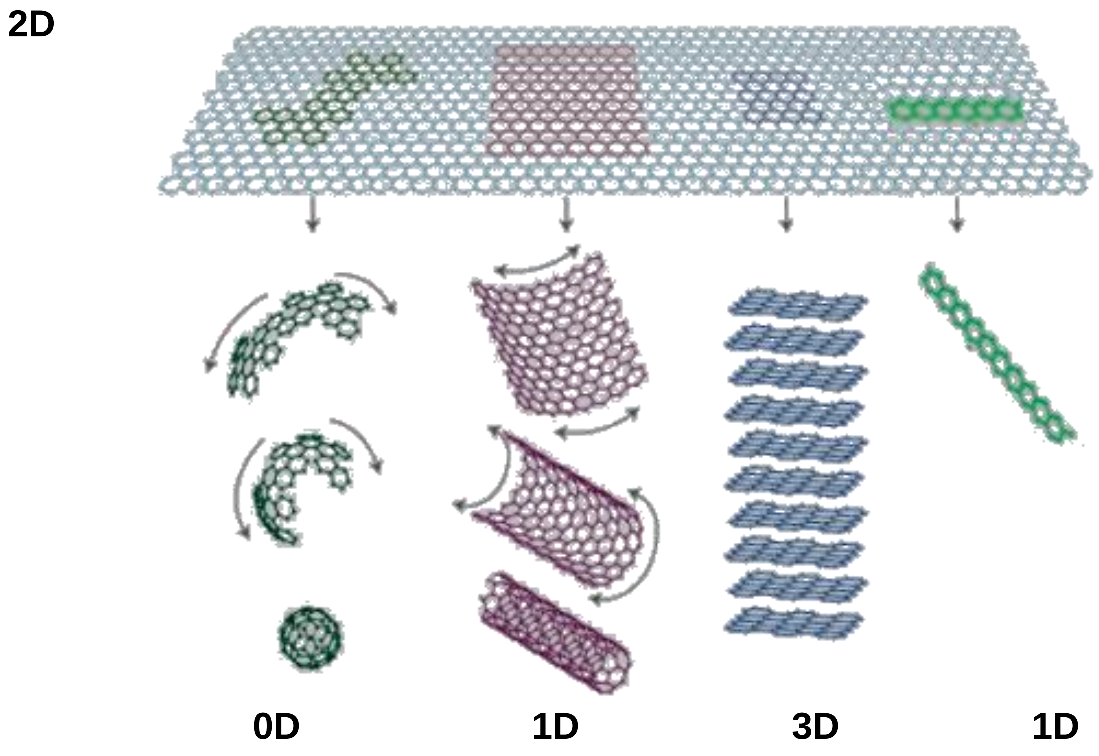
Percent of PhDs awarded to women in selected fields, 1920-2005.



National Research Council, National Opinion Research Center , and National Science Foundation. Data compiled by AIP Statistical Research Center.

Graphene

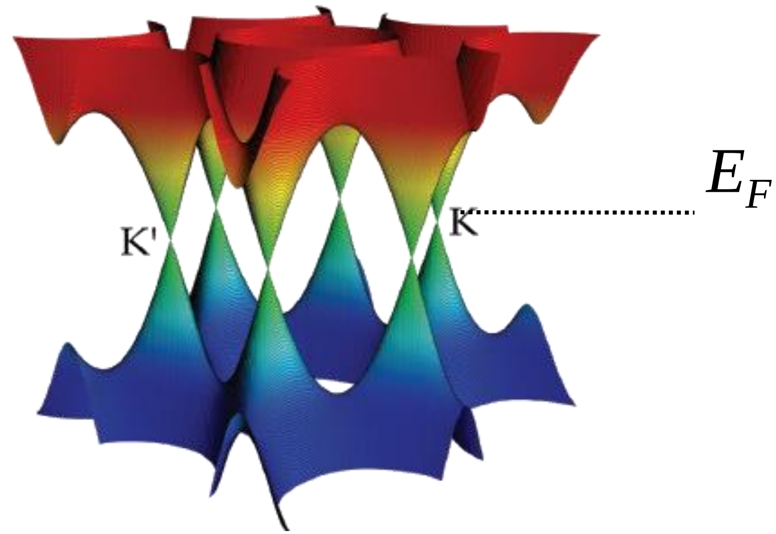
-the Mother of all nano-Graphitic forms



- **A graphene sheet is one million times thinner (10^{-6}) than a sheet of paper.**
- **Graphene is a 2D building block material for other sp^2 bonded carbon materials. It can be wrapped up into 0D fullerenes, rolled into 1D nanotubes, cut into 1D graphene ribbons or stacked into 3D graphite**

(After A. Geim)

The Novel Electronic Structure of Graphene



P.R. Wallace, Phys. Rev. **71**, 622 (1947)

Near the K point

$E(\kappa) = \pm\hbar v_F |\kappa|$ linear κ relation

where $v_F = \frac{\sqrt{3}\gamma_0 a}{2\hbar}$

and $a = \sqrt{3} \cdot a_{C-C}$

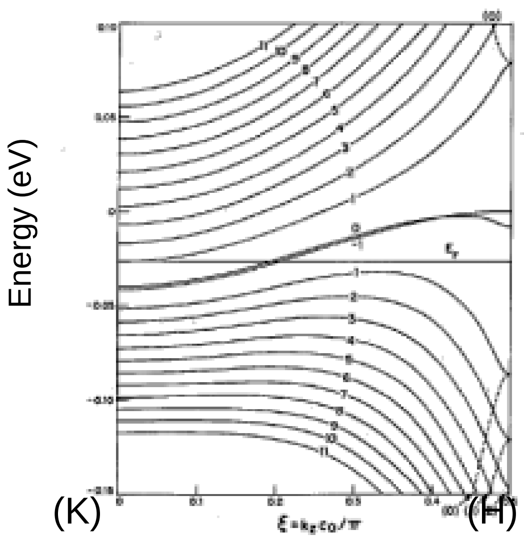
and γ_0 is the overlap integral between nearest neighbor π-orbitals (γ_0 values are from 2.9 to 3.1eV).

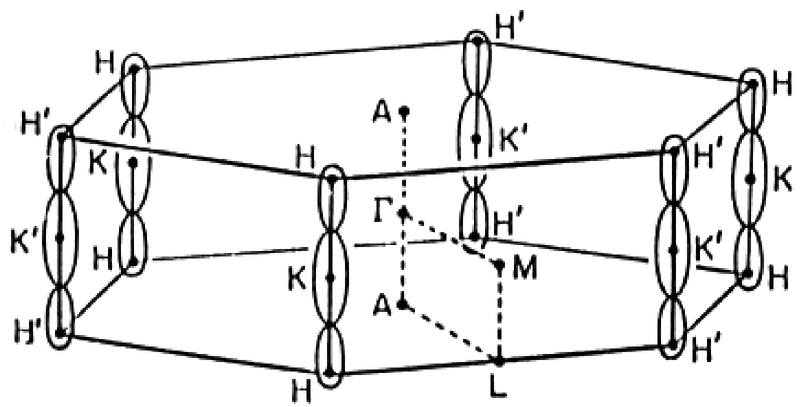
In 1957-1960 McClure extended the 2D graphene electronic structure to 3D graphite

J.W. McClure, Phys. Rev, **108**, 612 (1957); **119**, 606 (1960)

Magnetoreflection in Graphite

First magneto-optical experiment to measure energy bands at several regions of the Brillouin zone (near K and H)





M.S. Dresselhaus and J.G. Mavroides. IBM Journal of Research and Development **8**, 262 (1964)

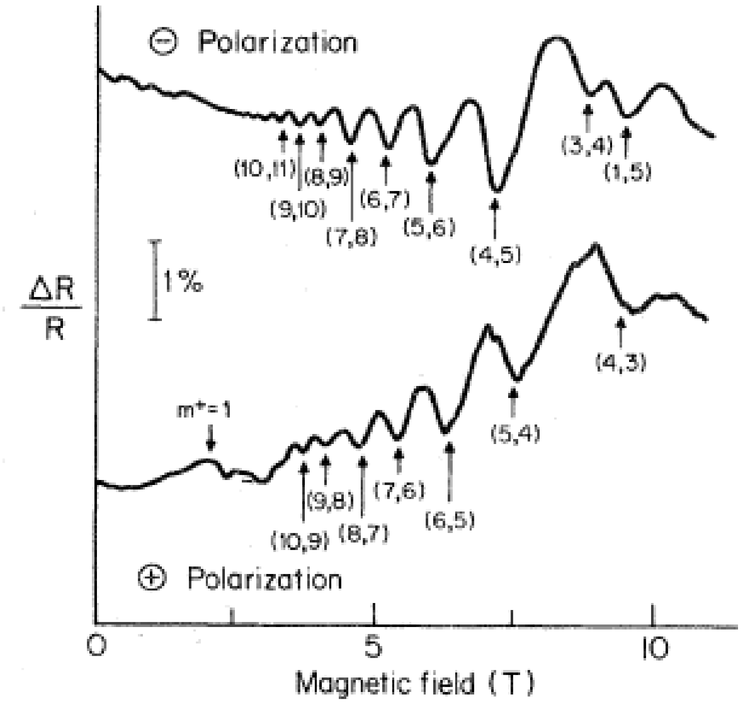
This experiment (1961) was enabled by the availability of a new material, highly oriented pyrolytic graphite (HOPG) Ubbelohde (1960)

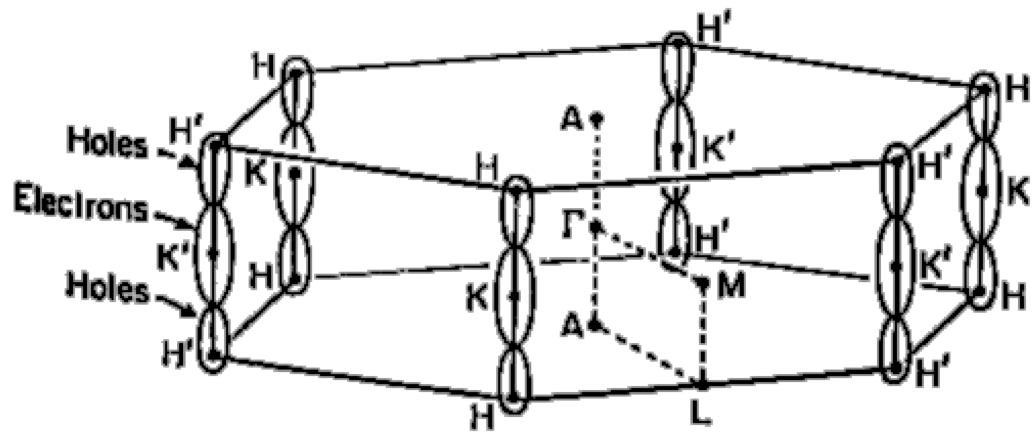
Using the McClure-Slonczewski-Weiss symmetry-based E(k) model, the band parameters for the electronic structure of graphite were deduced.

J.W. McClure, Phys. Rev, **108**, 612 (1957); **119**, 606 (1960)

Identification of Electrons and Holes in Graphite

Using circularly polarized radiation in the first magneto-optical experiment to use a laser, the locations of electrons and holes in the Brillouin zone for graphite were identified





P.R.Schroeder, M.S. Dresselhaus and A.Javan, Phys.Rev. Lett 20,1292 (1968)

This experiment established the location for electrons and holes in graphite that we use today

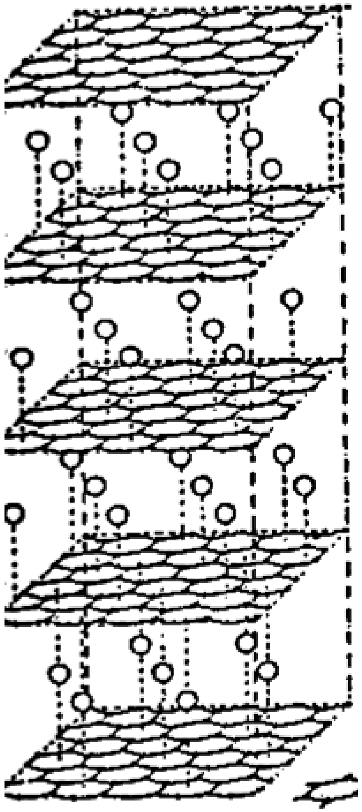
My entry into the Nanoworld (1973)

- Observation of superconductivity in stage 1 graphite intercalation compounds (C_8K)

  Hannay et al, Phys.Rev.Lett. 14, 225 (1965)

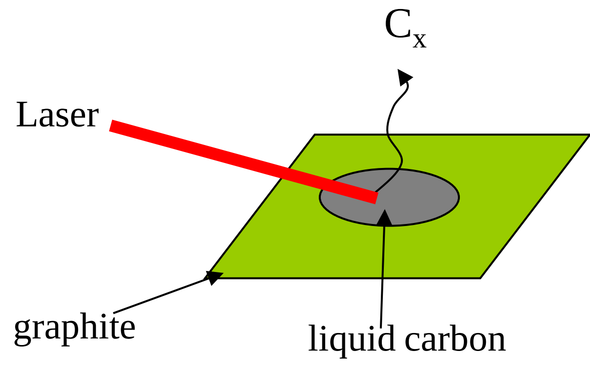
  aroused much interest in nanocarbons since neither potassium nor carbon is superconducting

- Intercalation compounds allowed early studies to be made of individual or few graphene layers in the environment of the intercalant species.



C_8K

Concurrent Studies on Forerunners of Fullerenes

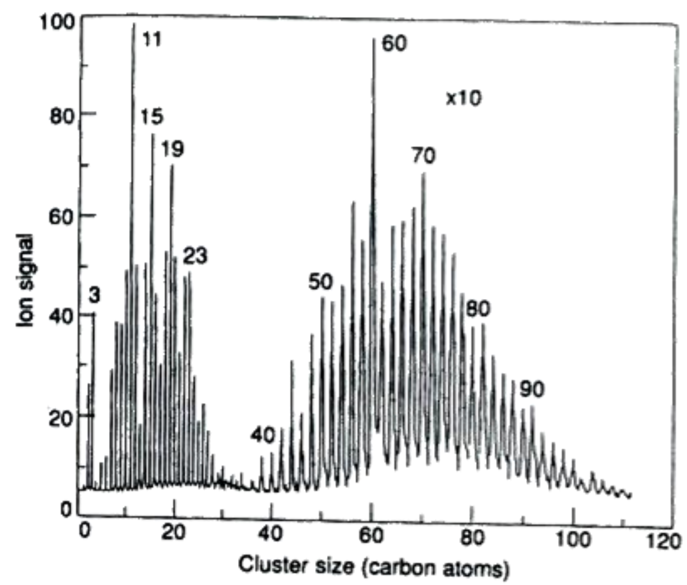


- Intercalation led to studies of ion implantation and photon irradiation and to liquid carbon studies (1983).

  Liquid carbon was found to be metallic

  T. Venkatesan et al, Phys. Rev. Lett. 53, 360 (1984)

- The Laser ablation process used to make liquid carbon caused the emission of large carbon clusters (like C_{100}) rather than C_2 and C_3 with relatively low laser energy input

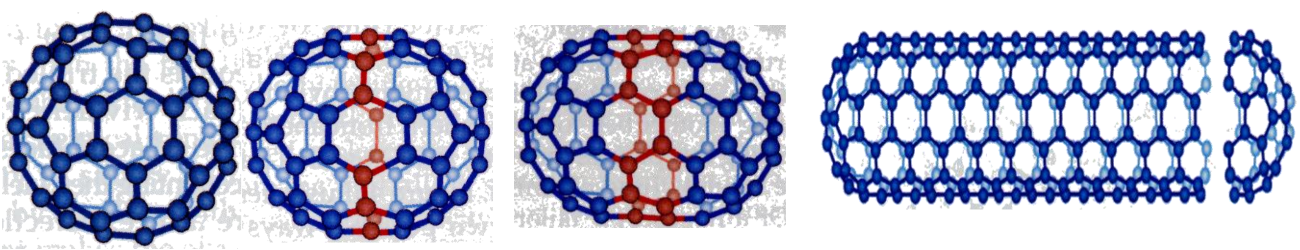


- A trip was made to Exxon Research Lab to discuss results.
- Soon (1984) Exxon published the famous result for the mass spectra. In 1985 fullerenes were discovered by Kroto, Smalley, and Curl

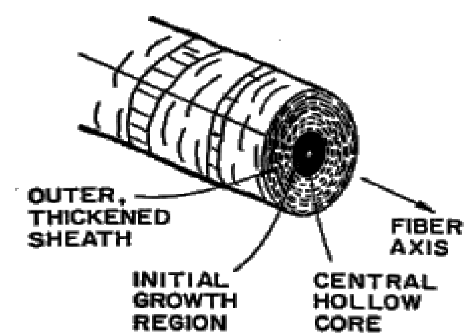
E.A.Rohlfing, D.M. Cox and A.Kaldor. J. Chem.Phys., **81**, 332 (1984)

Forerunners of Carbon Nanotubes

- In 1980, Morinobu Endo showed me vapor grown carbon fibers. At the center of carbon fibers is a multiwall carbon nanotube
- The nanotube-fullerene connection was made by going from $C_{60} \rightarrow C_{70} \rightarrow C_{80} \rightarrow$CNT in a public discussion (Dec. 1990) with Richard Smalley
- This idea suggested that a single wall Carbon nanotube would be interesting (August 1991) and led to calculating the electronic structure of SWNTs before they were ever seen



C_{60} C_{70} C_{80} CNT

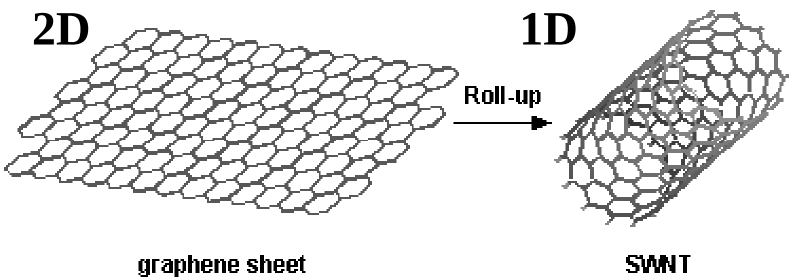


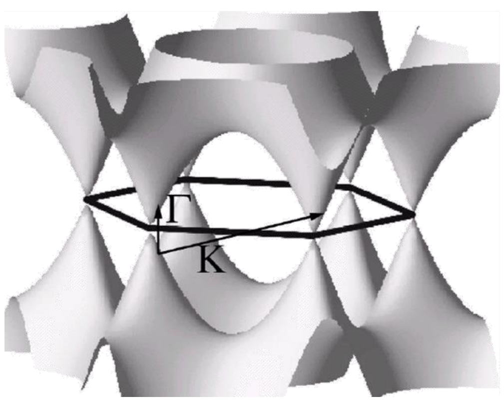
M.S.Dresselhaus et al., Graphite Fibers and Filaments, Springer (1988)

Saito, Fujita, Dresselhaus^2, Electronic structure of carbon fibers based on C_{60}, PRB 46, 1804 (1992)

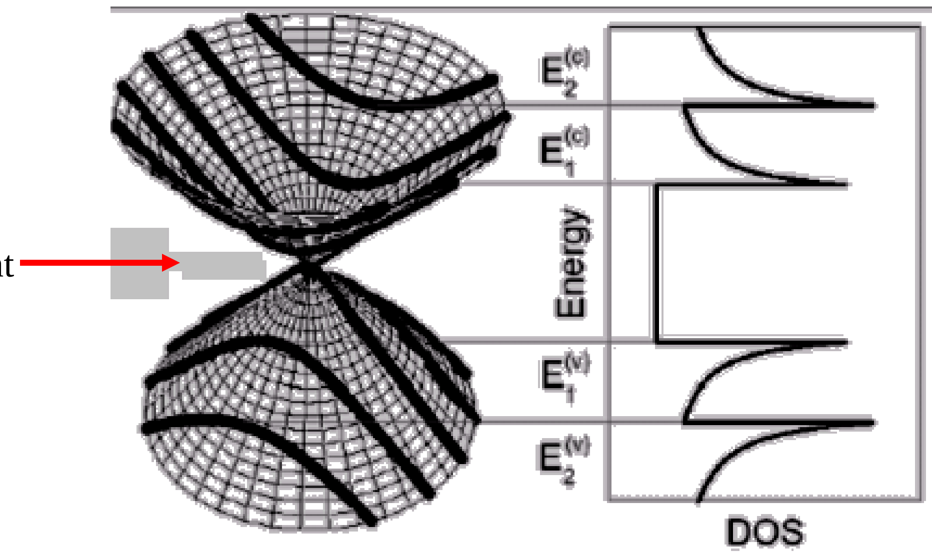
General Relations between 1D and 2D Systems shown in terms of carbon nanotubes

Rolling up a 2D sheet





Confinement of 1D electronic states on **cutting lines**

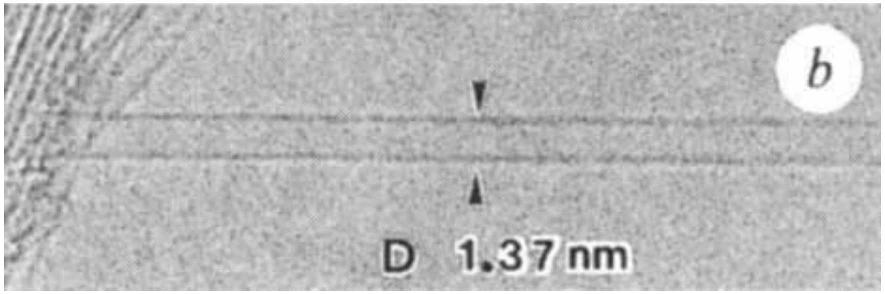


1D van Hove singularities give a high density of electronic states (DOS) at well defined energies

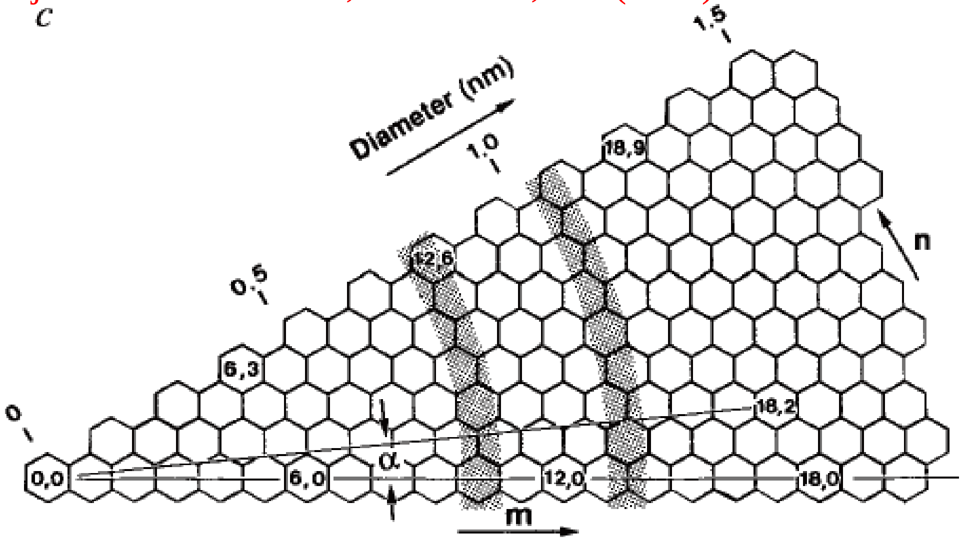
Carbon nanotubes are metallic if a cutting line passes through the K point; otherwise they are semiconducting

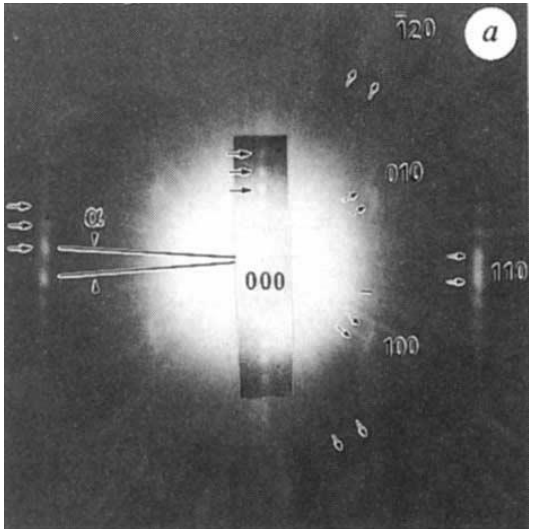
Discovery of Single Wall Carbon Nanotubes

- First synthesis and (n,m) characterization of Single Wall Carbon Nanotubes (1993)



D. Bethune et al Nature 363, 605 (1993)
S. Iijima and T. Ichihashi, Nature 363, 603 (1993)





Identified (*n*,*m*) chirality of the nanotube by TEM

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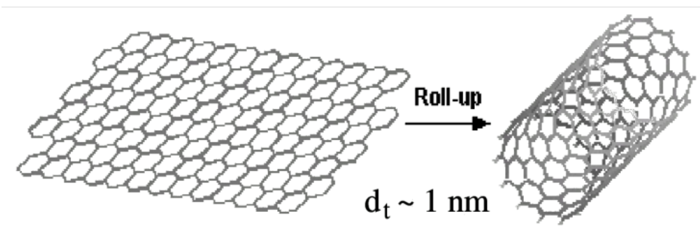
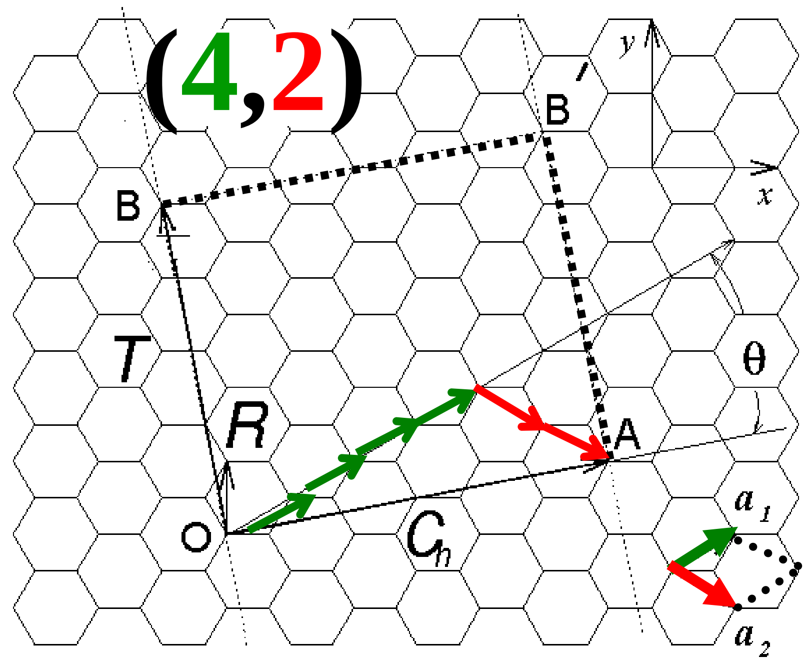
Nanotube Structure in a Nutshell



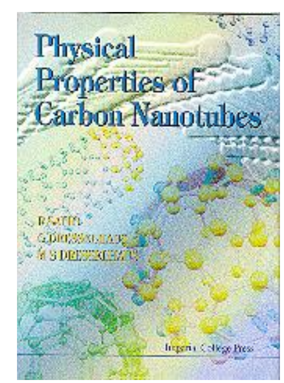
Graphene Sheet **SWNT**



Rolled-up graphene layer
Large unit cell.

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \equiv (n,m)$$

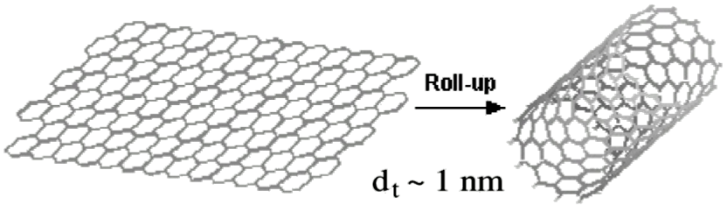
$$\begin{cases} d_t = \dfrac{L}{\pi} = \dfrac{a}{\pi}\sqrt{n^2 + nm + m^2} \\ \theta = \tan^{-1}\dfrac{\sqrt{3}m}{2n+m} \end{cases}$$



Each (*n*,*m*) nanotube is a unique molecule

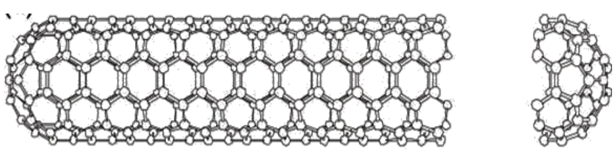
R.Saito, MS Dresselhaus, G. Dresselhaus,,
Imperial College Press, 1998

Unique Properties of Carbon Nanotubes within the Nanoworld

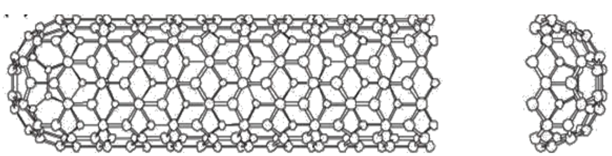


graphene ribbon **SWNT**

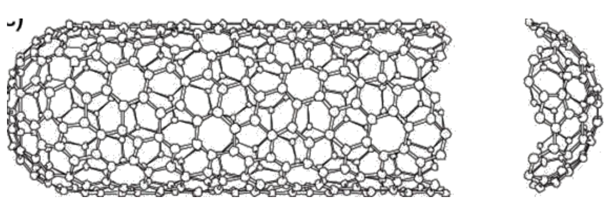
armchair



zigzag

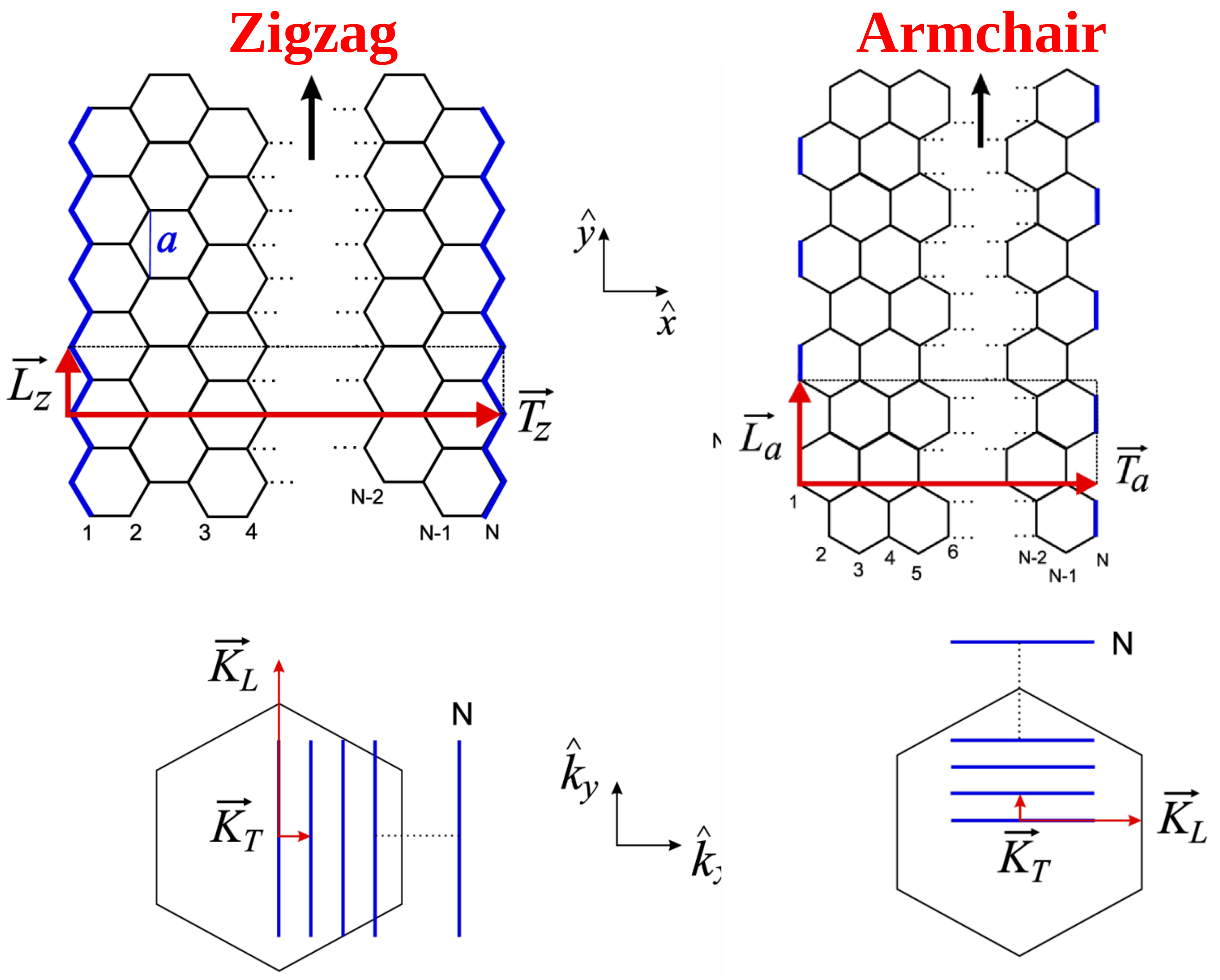


chiral



- Small size: ~1 nm diameter (down to ~10 atoms around the circumference)
- Electronic Properties: can be either metallic or semiconducting depending on diameter and orientation of the hexagons
- Mechanical: Very high strength, modulus, and resiliency.
- Physics: model system for 1D density of electronic states.
- Single molecule Raman spectroscopy, luminescence and transport properties.

Graphene Ribbons

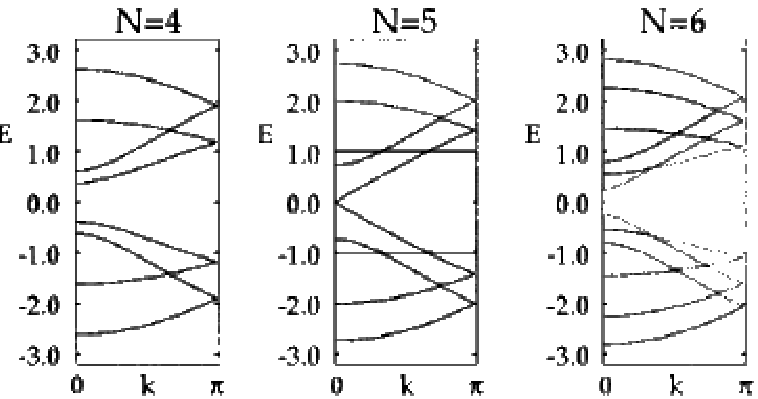


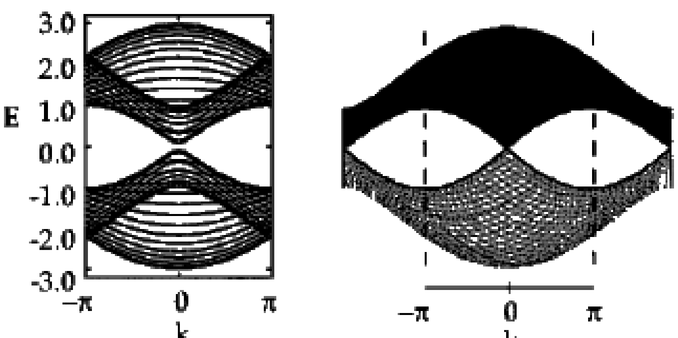
Direction of cutting lines

- Special feature of graphene ribbons is that they have edges and few columns of carbon atoms along the width.

Electronic structure of graphene ribbons

Armchair

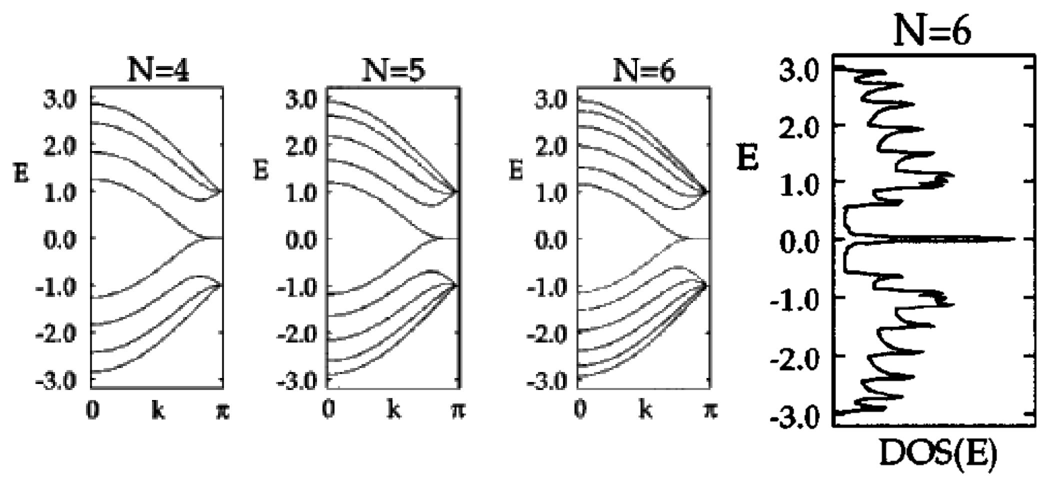


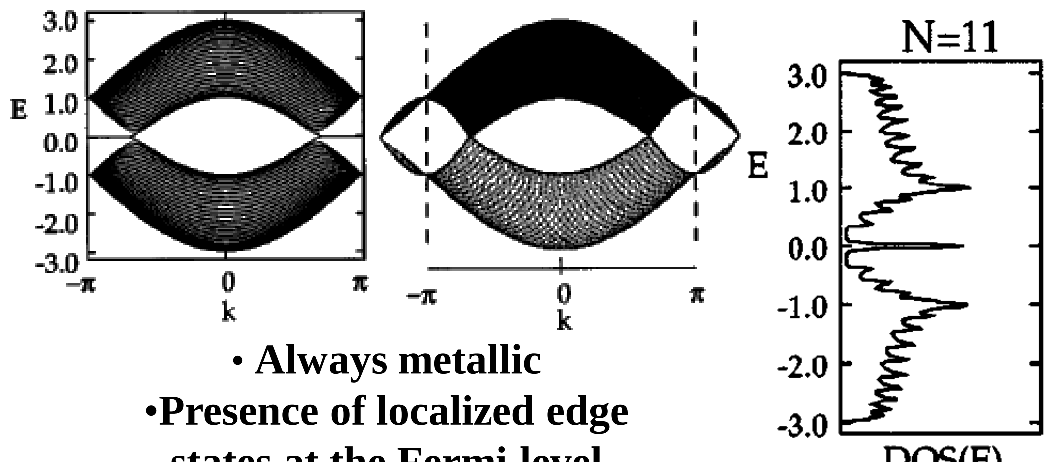


Metallic for N=3M-1 (M integer)
Semiconducting for N=3M and 3M-2
Examples: ***Metallic for N=5***
and Semiconducting for N=4, 6

Zigzag

Van Hove singularities in the DOS

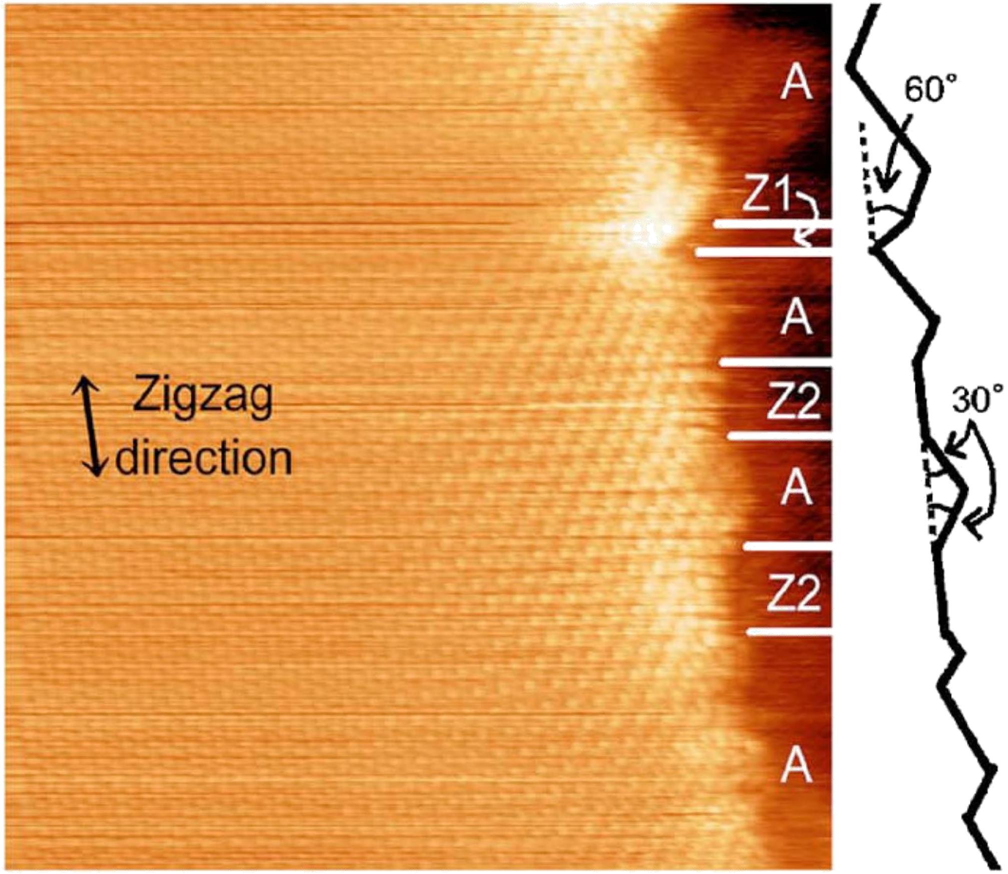




- **Always metallic**
- **Presence of localized edge states at the Fermi level**

Nakada *et al.*, Phys. Rev. B **54**, 17954 (1996).

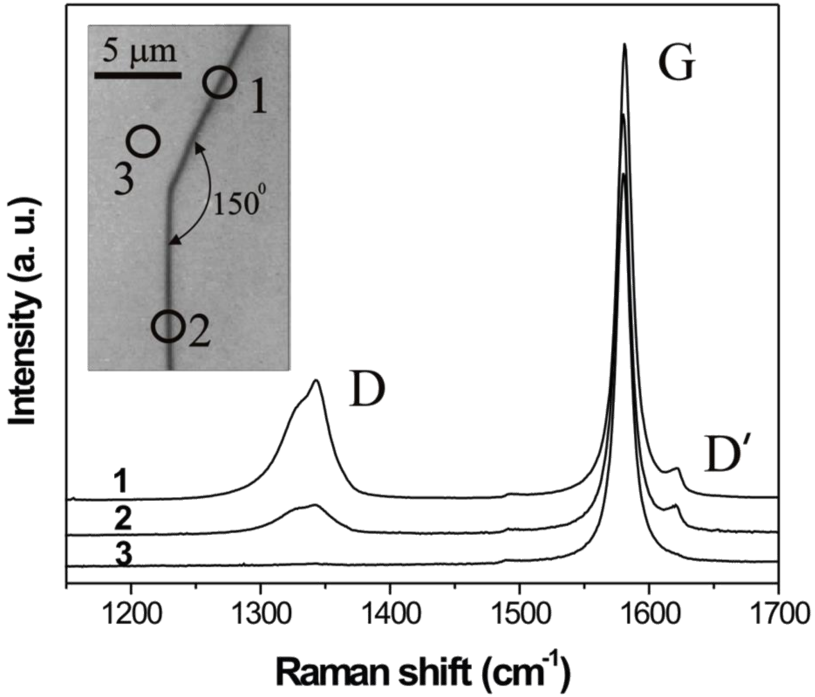
Graphene ribbon edges favor armchair and zigzag edge segments

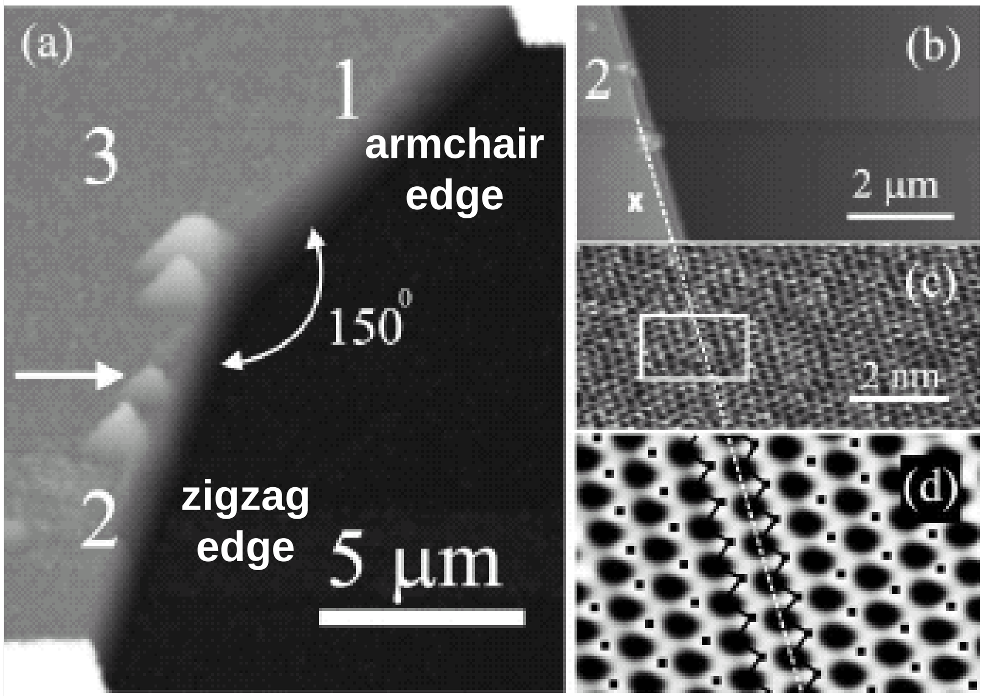


- Armchair edges are the most favored (more stable), chiral edges are least favored
- Higher intensity AFM signal along zigzag edge Z1 supports a high electron density of states along zigzag edge

Enoki *et al.*, Int. Rev. Phys. Chem. **26**, 609 (2007).

Raman studies on graphene ribbon edges



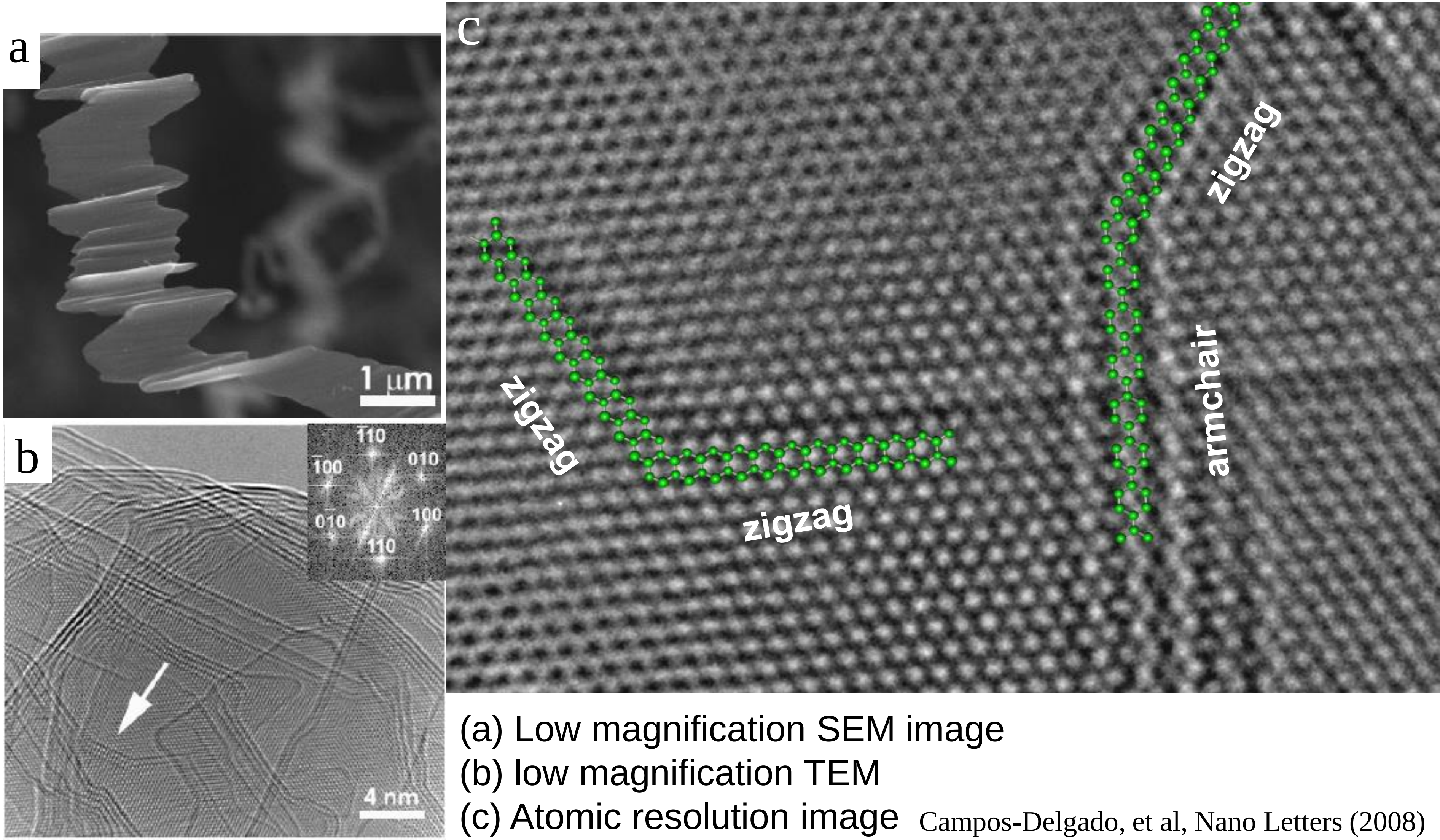


- The intervalley (K→K') D-band intensity depends on the edge type: large for armchair edge, smaller for zigzag edge.
- But the intravalley (K→K) D'-band intensity is similar for zigzag and armchair edges

L. G. Cançado, et al. Phys. Rev. Letters, 93, 247401 (2004)

Images of Graphene Ribbons and Edges

Zigzag and Armchair edges are clearly seen



(a) Low magnification SEM image
(b) low magnification TEM
(c) Atomic resolution image

Campos-Delgado, et al, Nano Letters (2008)

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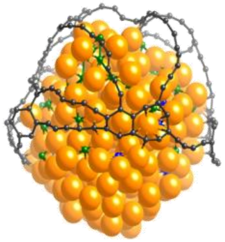
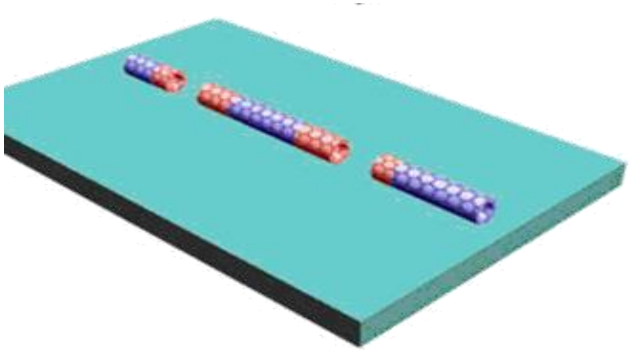
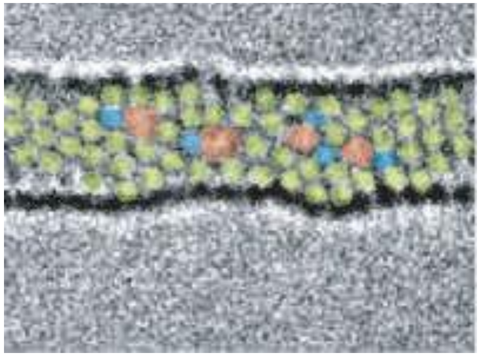
Looking to the Future of Carbon Nanostructures

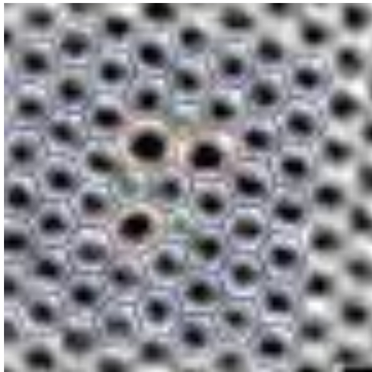




- **Synthesis**
  - Remains a main focus
  - Control and understanding of synthesis process
  - Control of (n,m) during synthesis, cloning etc
  - Control of number of graphene layers and sample size
  - Control of graphene ribbon synthesis
  - Better samples will reveal new science



- **Characterization and properties**
  - New techniques such as aberration corrected HRTEM allow detailed studies of defects, dopants and structures
  - Raman studies will provide complementary technique to study nanocarbons – also HRTEM and Raman
  - Unique studies such as separation of charge and spin transport



Thank you

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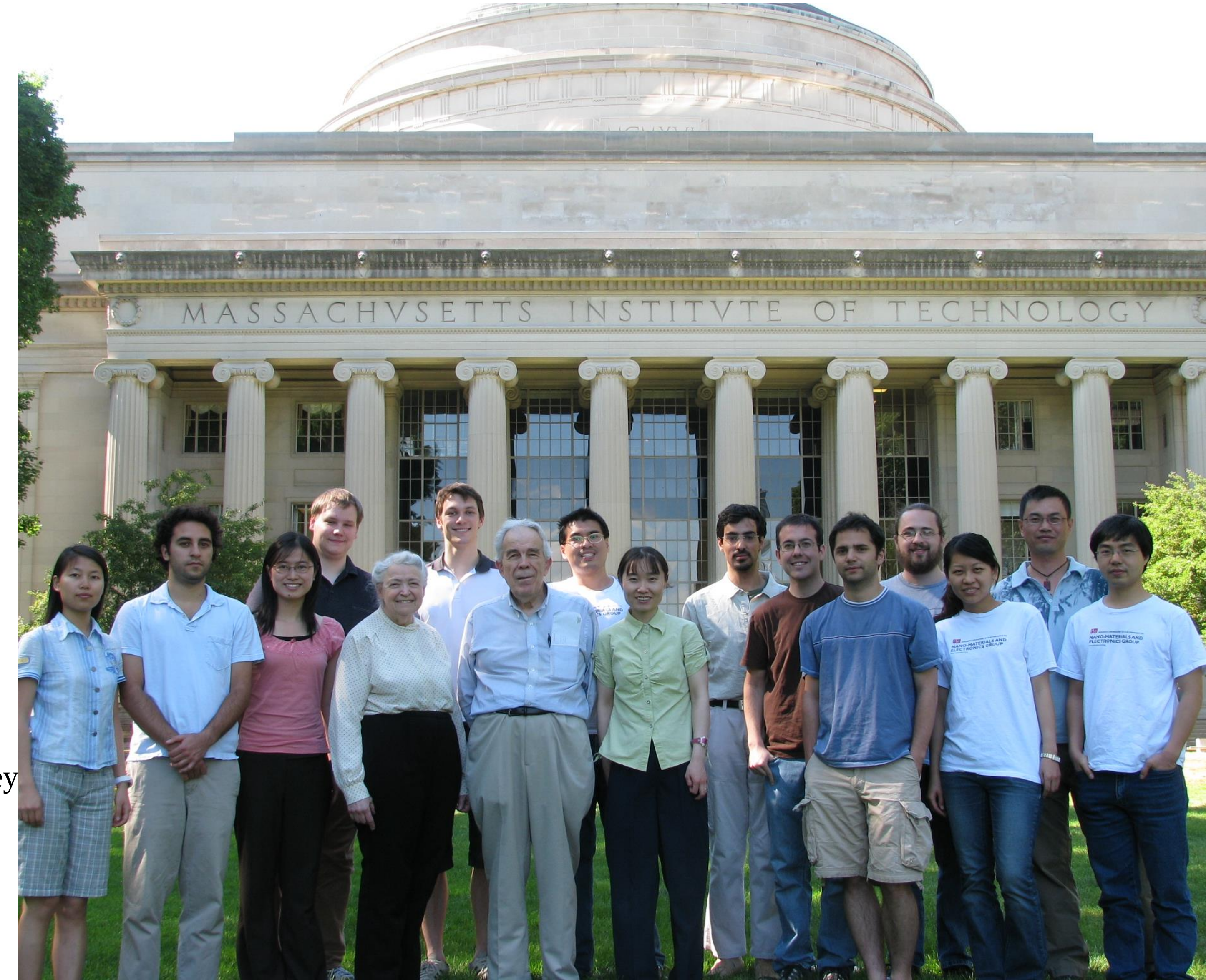

Various Presidents

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