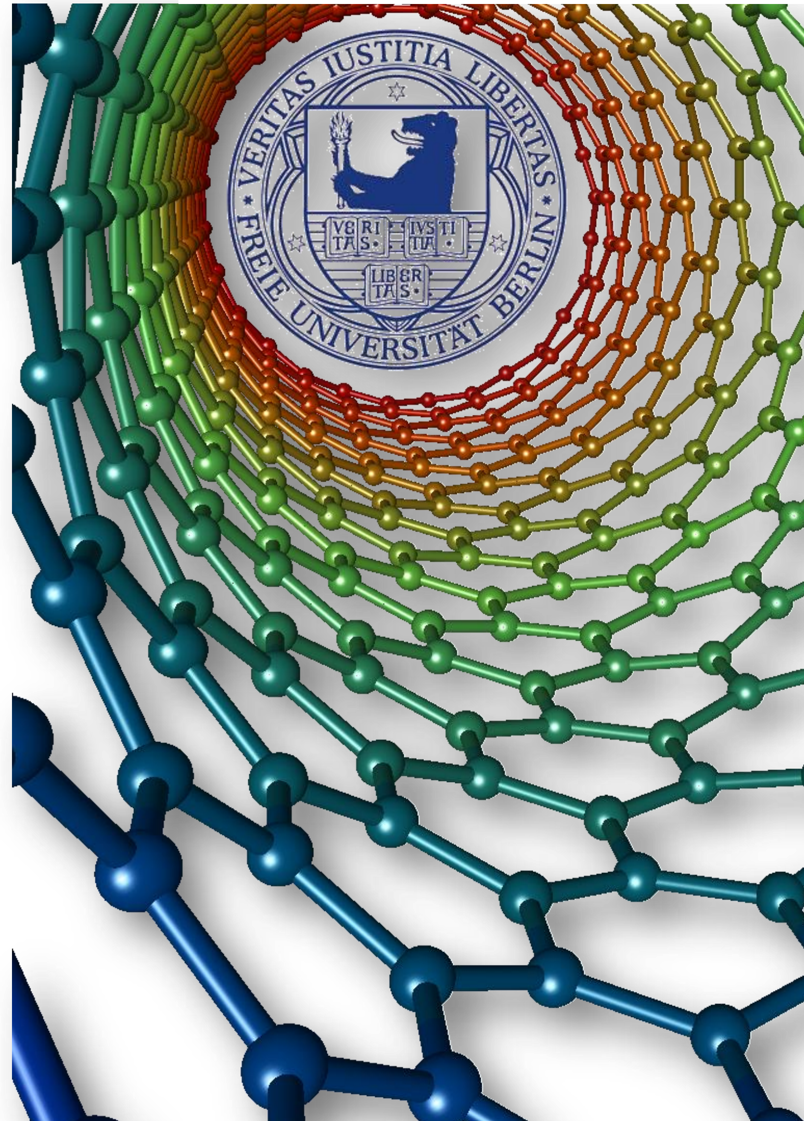
Carbon

From Graphite to Nanotubes



Michael Kleinert

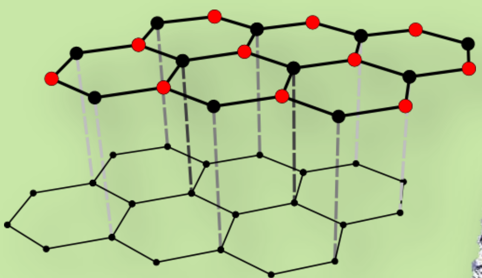
http://en.wikipedia.org/wiki/File:FlyingThroughNanotube.png

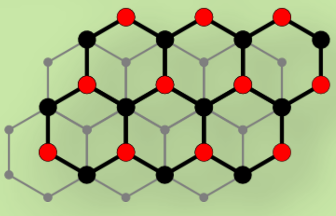
28th April 2011

Content – Timeline

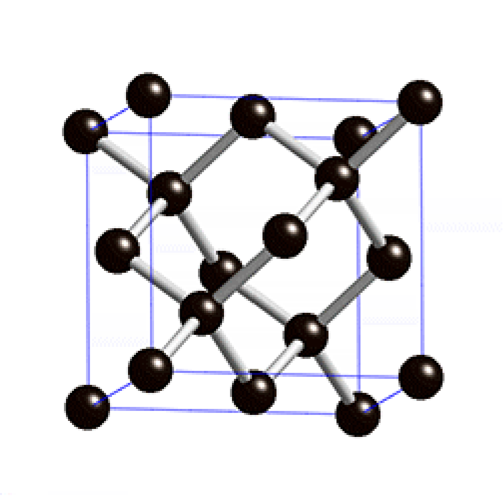
Freie Universität Berlin

Graphite





Diamond



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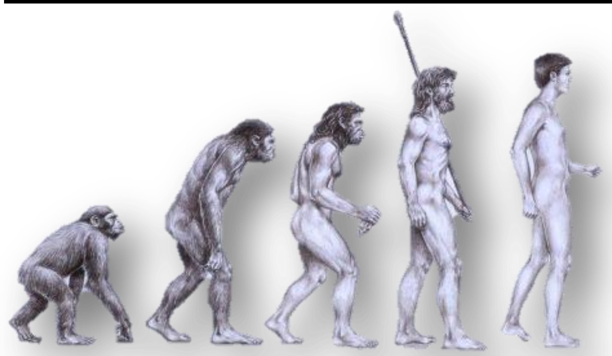
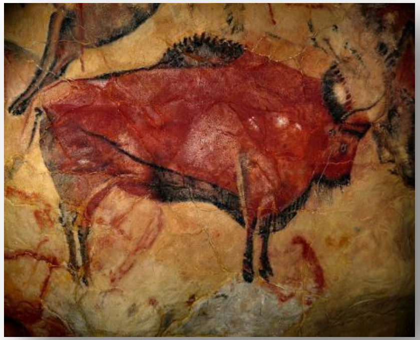
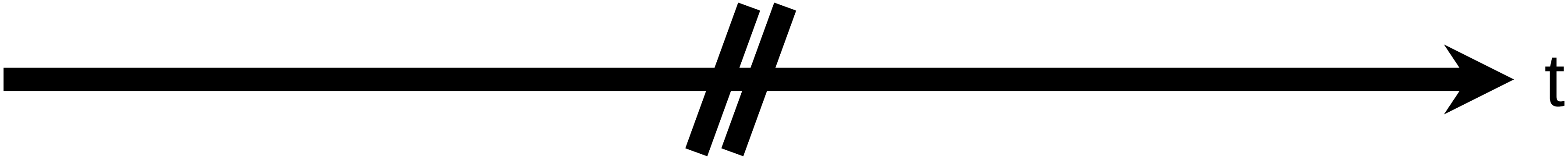




30,000 BC

Rob Lavinsky, iRocks.com
http://en.wikipedia.org/wiki/File:Apollo_synthetic_diamond.jpg
http://de.wikipedia.org/w/index.php?title=Datei:GraphitGitter4.png&filetimestamp=20101021113501
http://www.jesus.ch/www/lfiles/img/38293.jpg

Content – Timeline



Content – Timeline

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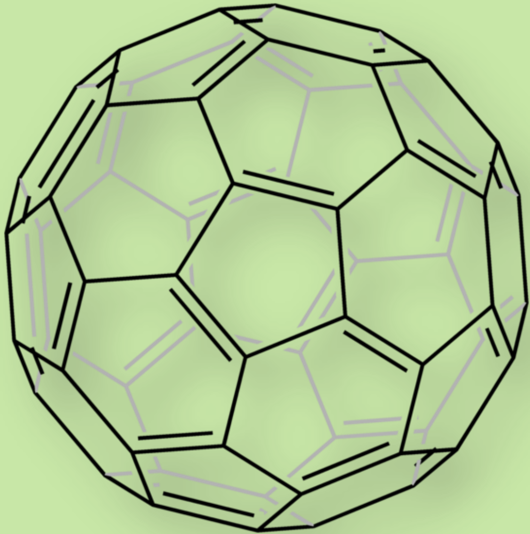
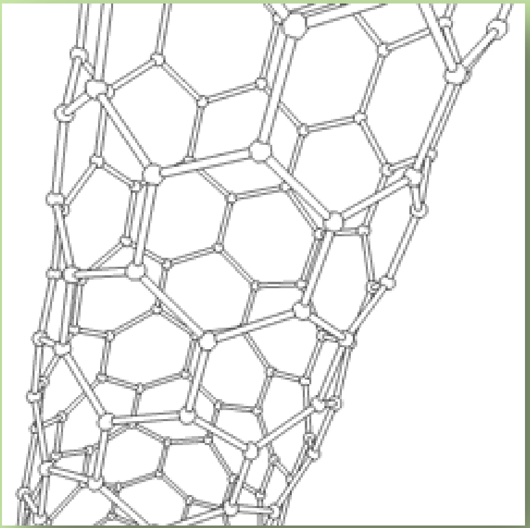
Fullerenes



Nanotubes



t

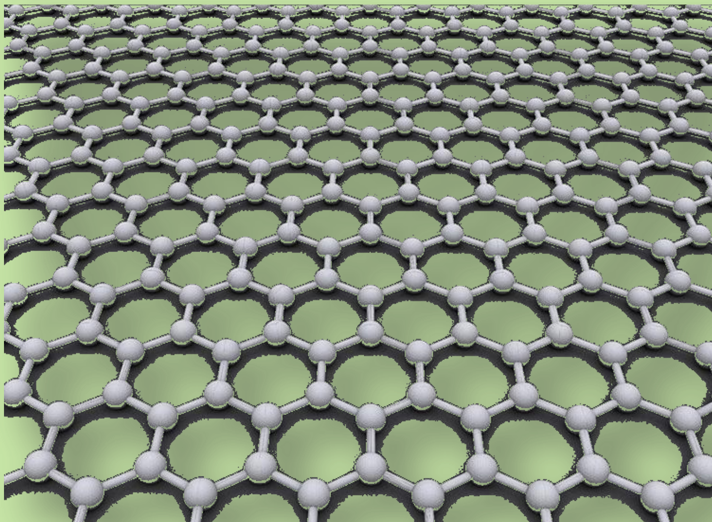
1985

1990s - Today

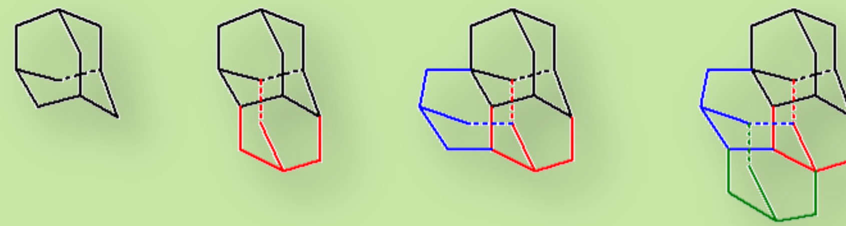
http://en.wikipedia.org/wiki/File:Kohlenstoffnanoroehre_Animation.gif

Freie Universität Berlin

Graphenes



Diamondoids



t

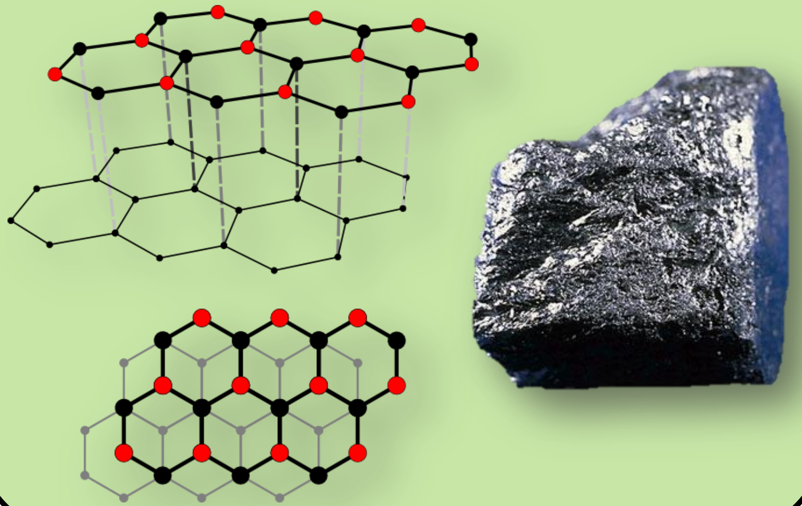
2004 - Today

http://en.wikipedia.org/wiki/File:Diamondoids.png
http://de.wikipedia.org/w/index.php?title=Datei:Graphen.jpg&filetimestamp=20100826054350

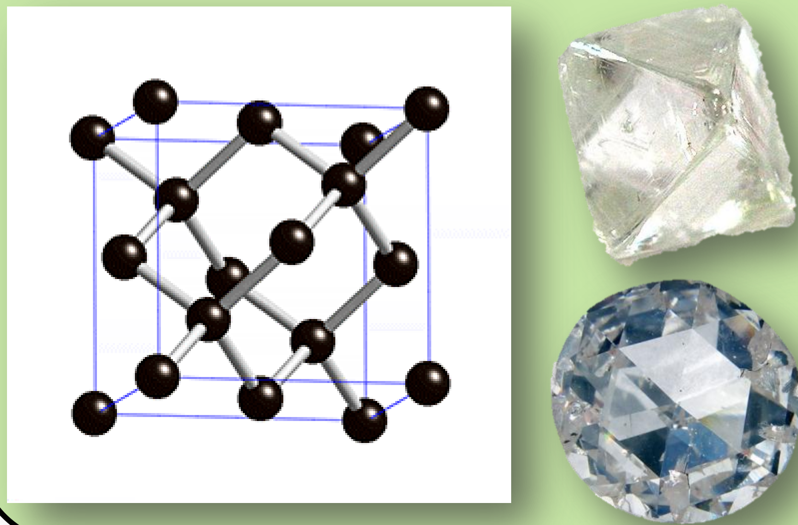
Content – Timeline

Freie Universität Berlin

Graphite



Diamond



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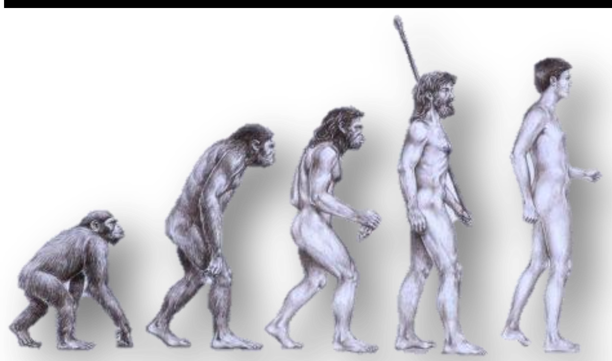
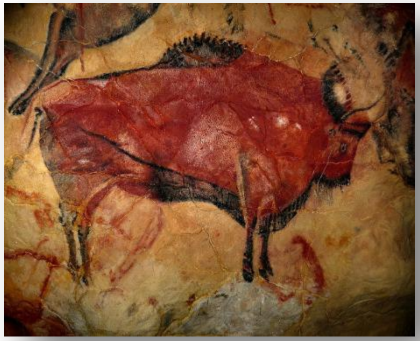


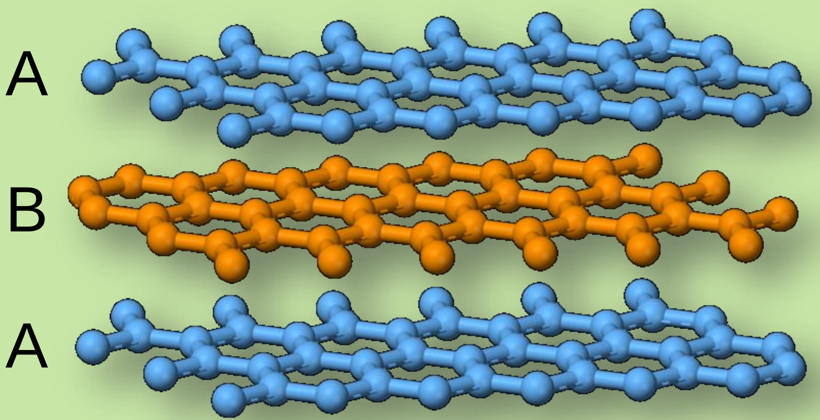


30,000 BC

Rob Lavinsky, iRocks.com
http://en.wikipedia.org/wiki/File:Apollo_synthetic_diamond.jpg
http://de.wikipedia.org/w/index.php?title=Datei:GraphitGitter4.png&filetimestamp=20101021113501
http://www.jesus.ch/www/lfiles/img/38293.jpg

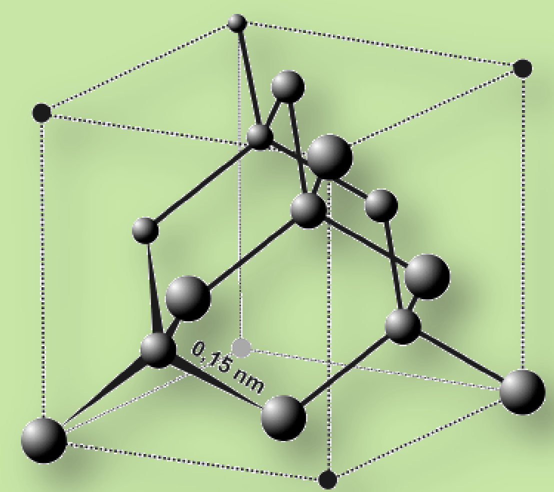
Graphite

- hexagonal lattice
- 1-2 on Mohs scale
- tunable



Diamond

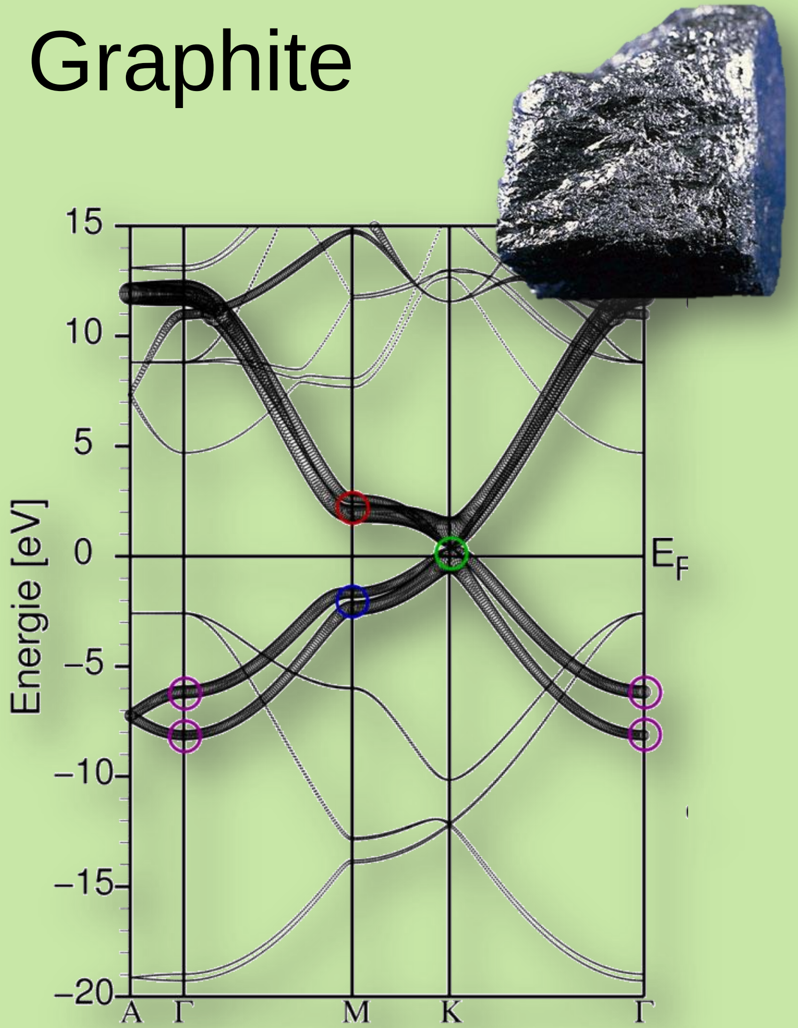
- cubic lattice
- 10 on Mohs scale
- thermal conductor



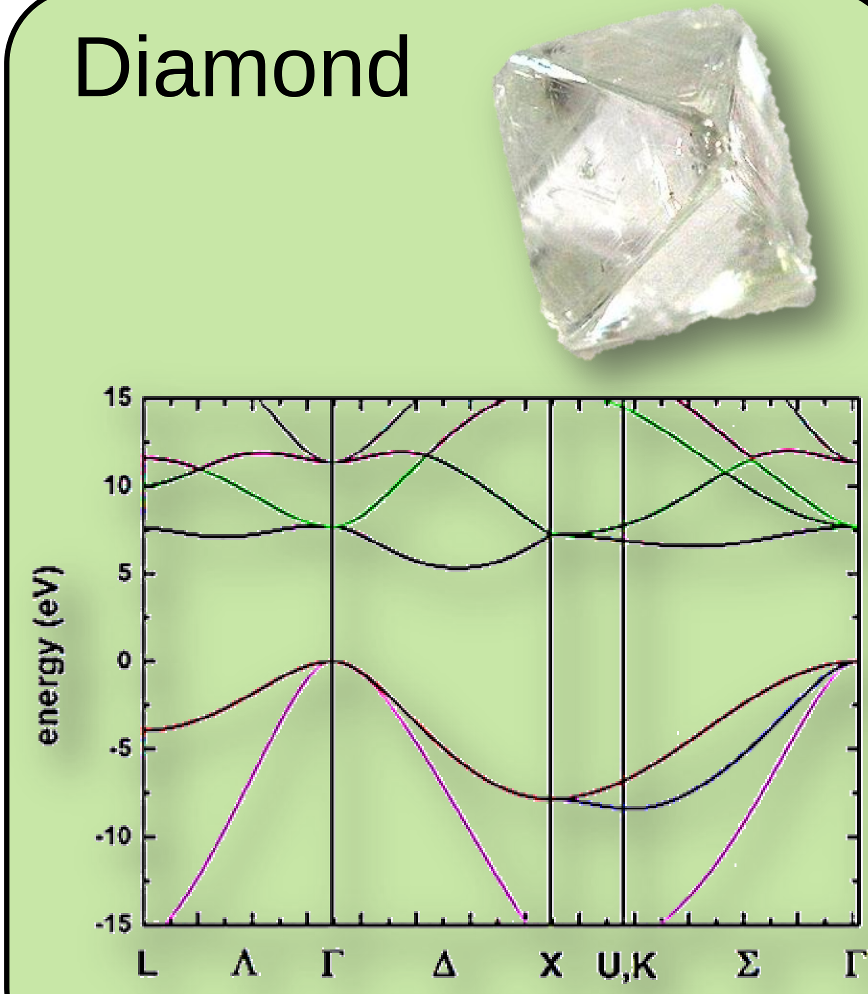
http://commons.wikimedia.org/wiki/File:Diamonds_glitter.png

Variability of Carbon

Graphite



Diamond



http://www.nextnano.de/nextnano3/images/tutorial/1DTightBinding_bulk_GaAs_GaP/BandStructureC_Vogl.jpg
http://ruby.chemie.uni-freiburg.de/Vorlesung/Gif_bilder/Strukturchemie/c_graphit_bw.png
Rob Lavinsky, iRocks.com

Diamond is beautiful

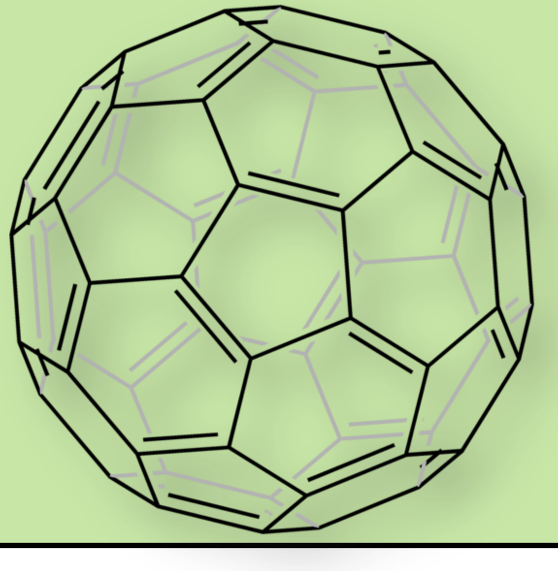
but

Graphite / Graphene
is fascinating !

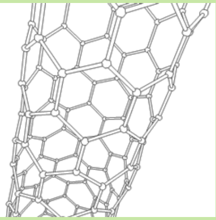
Content – Timeline

Freie Universität Berlin

Fullerenes



Nanotubes



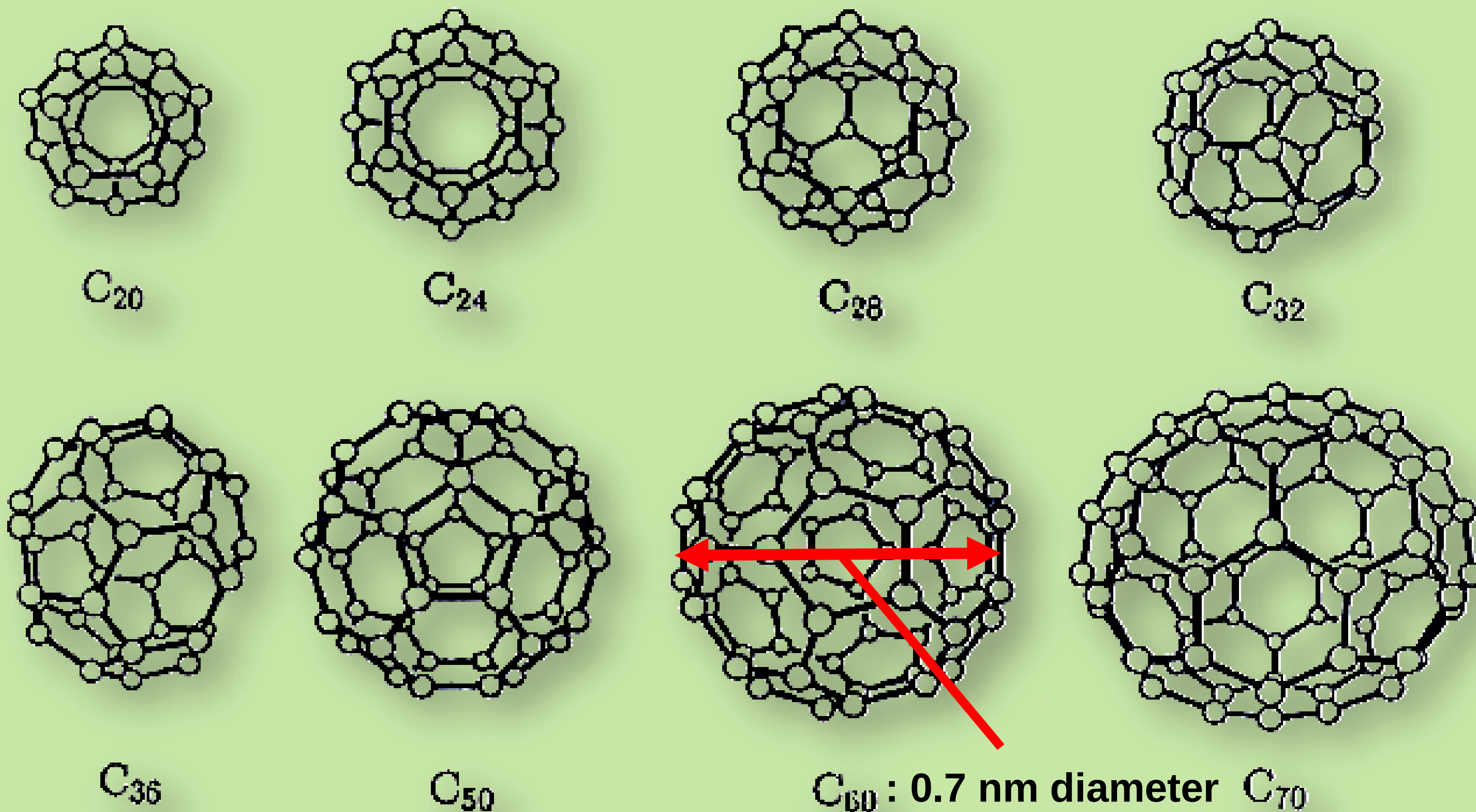
t

1985

1990s - Today

Fullerenes

Freie Universität Berlin



Nobel Lectures, Chemistry 1996-2000, Editor Ingmar Grenthe, World Scientific Publishing Co., Singapore, 2003

Robert Curl & Harold Kroto & Richard Smalley

"for their discovery of fullerenes"

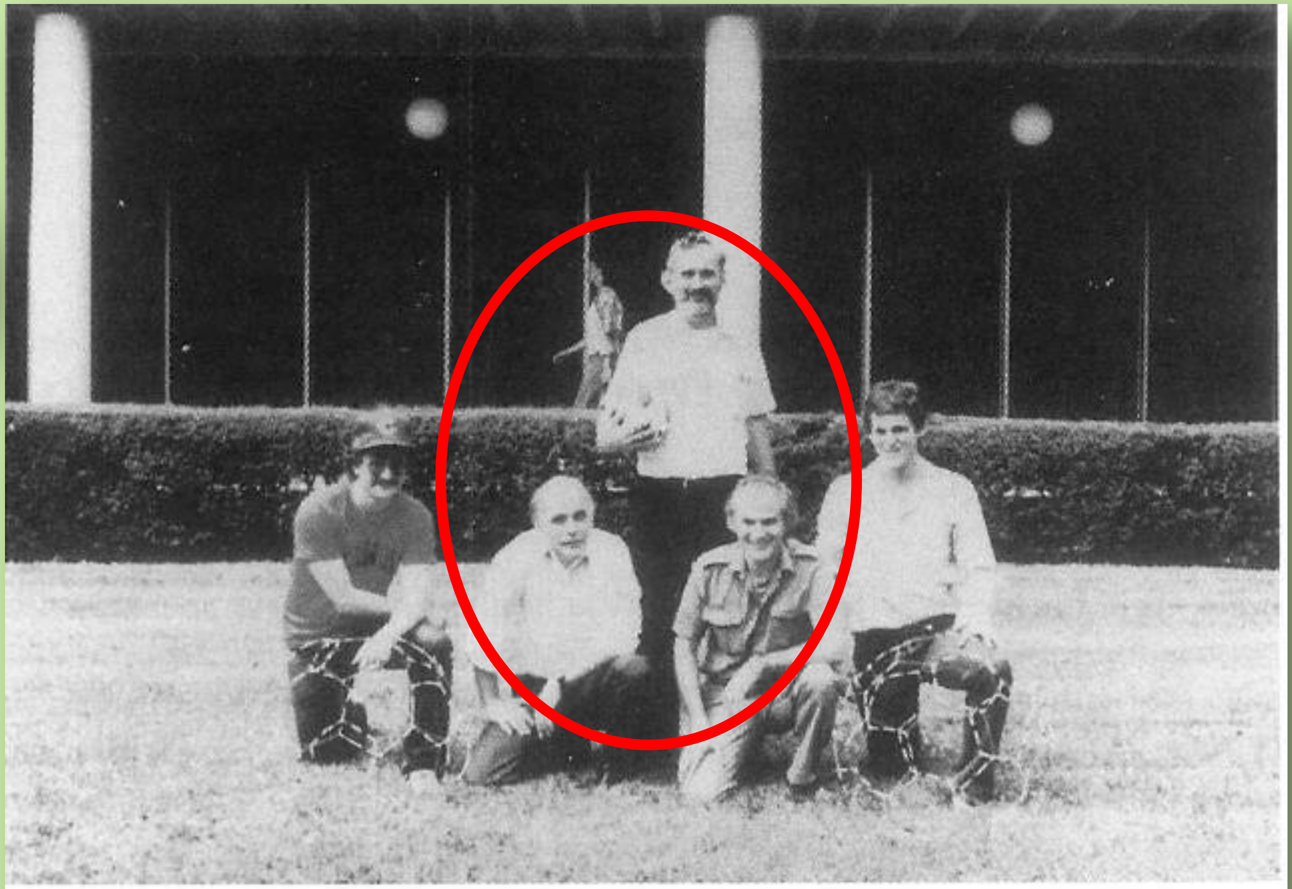


Figure 1. Photograph of the research group that discovered the fullerenes at Rice University in September of 1985. Standing: Curl. Kneeling in front, left to right: O'Brien, Smalley, Kroto, and Heath.

Nobel Lectures, Chemistry 1996-2000, Editor Ingmar Grenthe, World Scientific Publishing Co., Singapore, 2003

Freie Universität Berlin

- But why did THEY got the Nobel Prize?

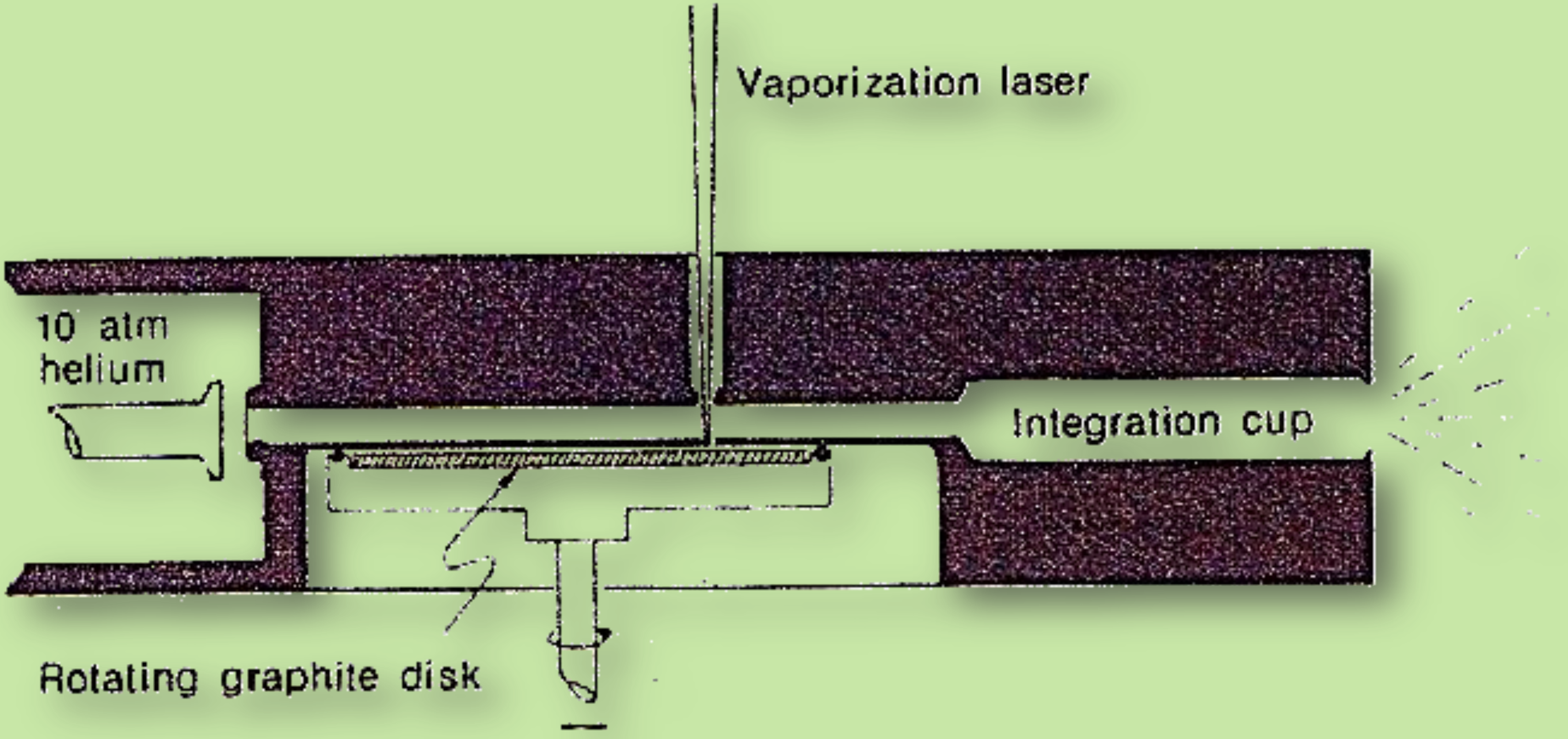
- Smalley:

the discovery that garnered the Nobel Prize was the realization that carbon makes the truncated icosahedral molecule, and larger geodesic cages, all by itself.

Nobel Lectures, Chemistry 1996-2000, Editor Ingmar Grenthe, World Scientific Publishing Co., Singapore, 2003

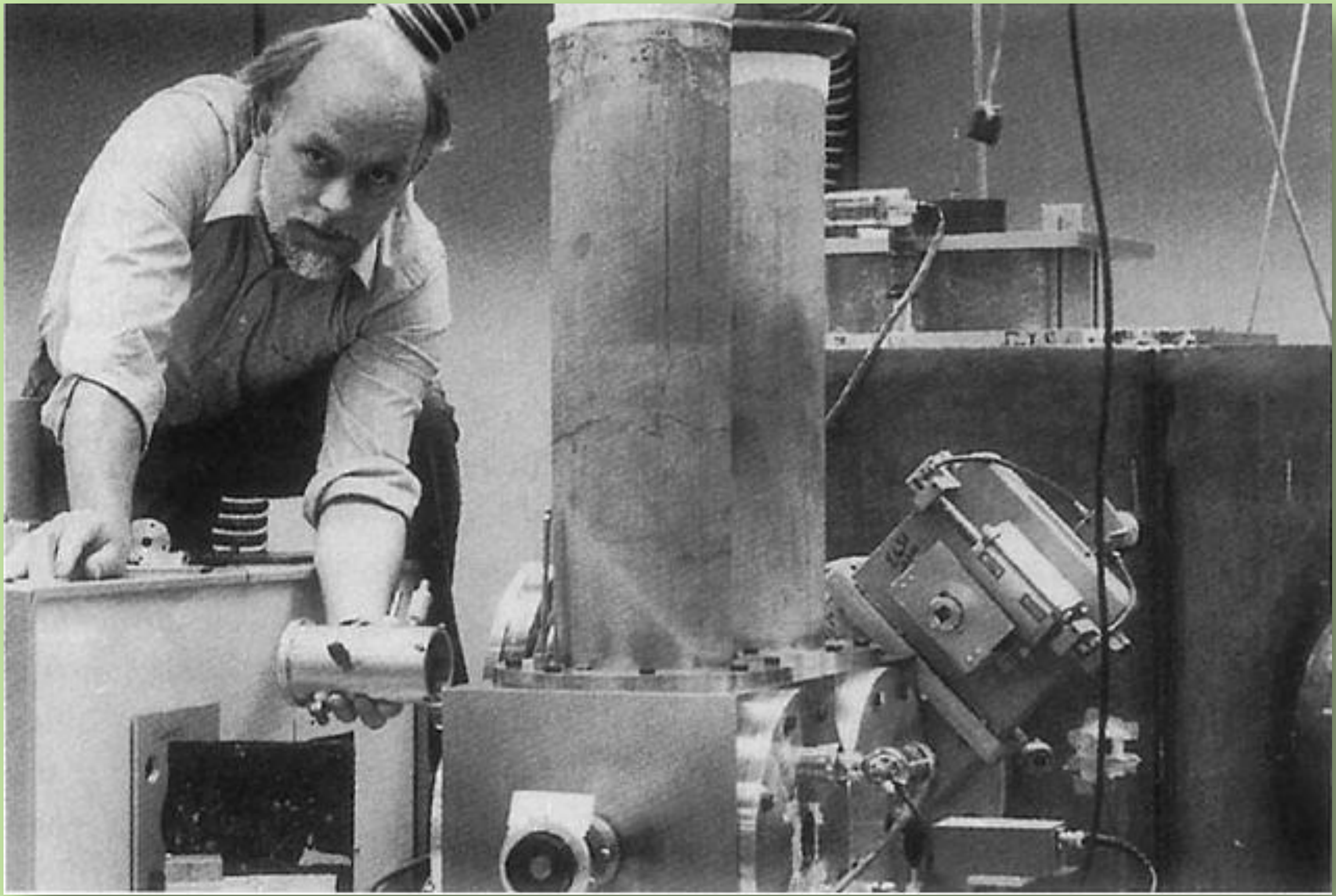
Synthesis of Fullerenes

Freie Universität Berlin



Supersonic laser-vaporization nozzle source

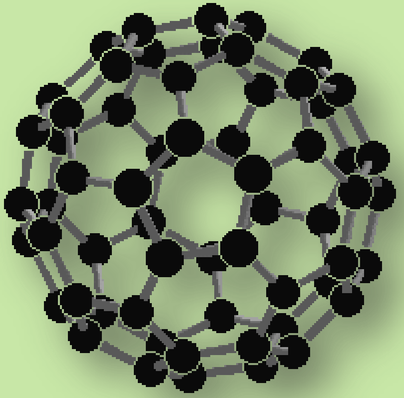
Synthesis of Fullerenes



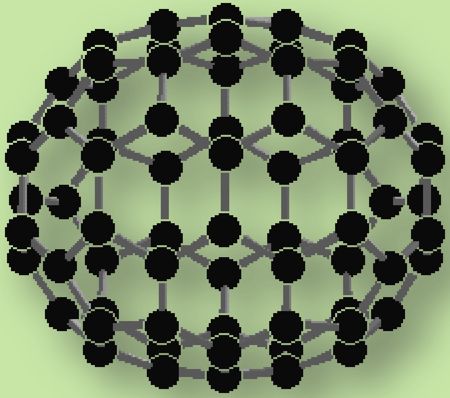
Nobel Lectures, Chemistry 1996-2000, Editor Ingmar Grenthe, World Scientific Publishing Co., Singapore, 2003

Synthesis of Fullerenes

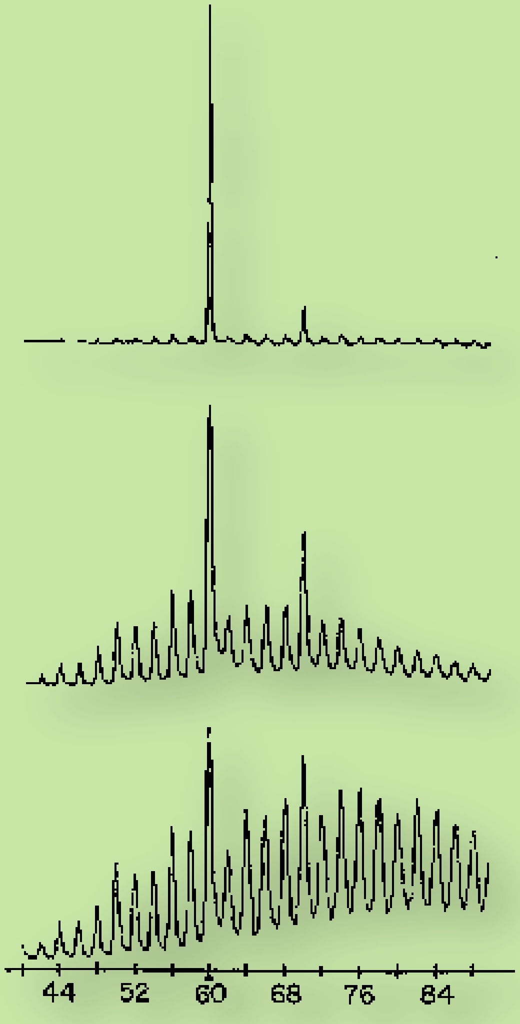
- C_{60} intensity unaffected by the boiling temperature
- “magic numbers“ are stable (60, 70)



C_{60}



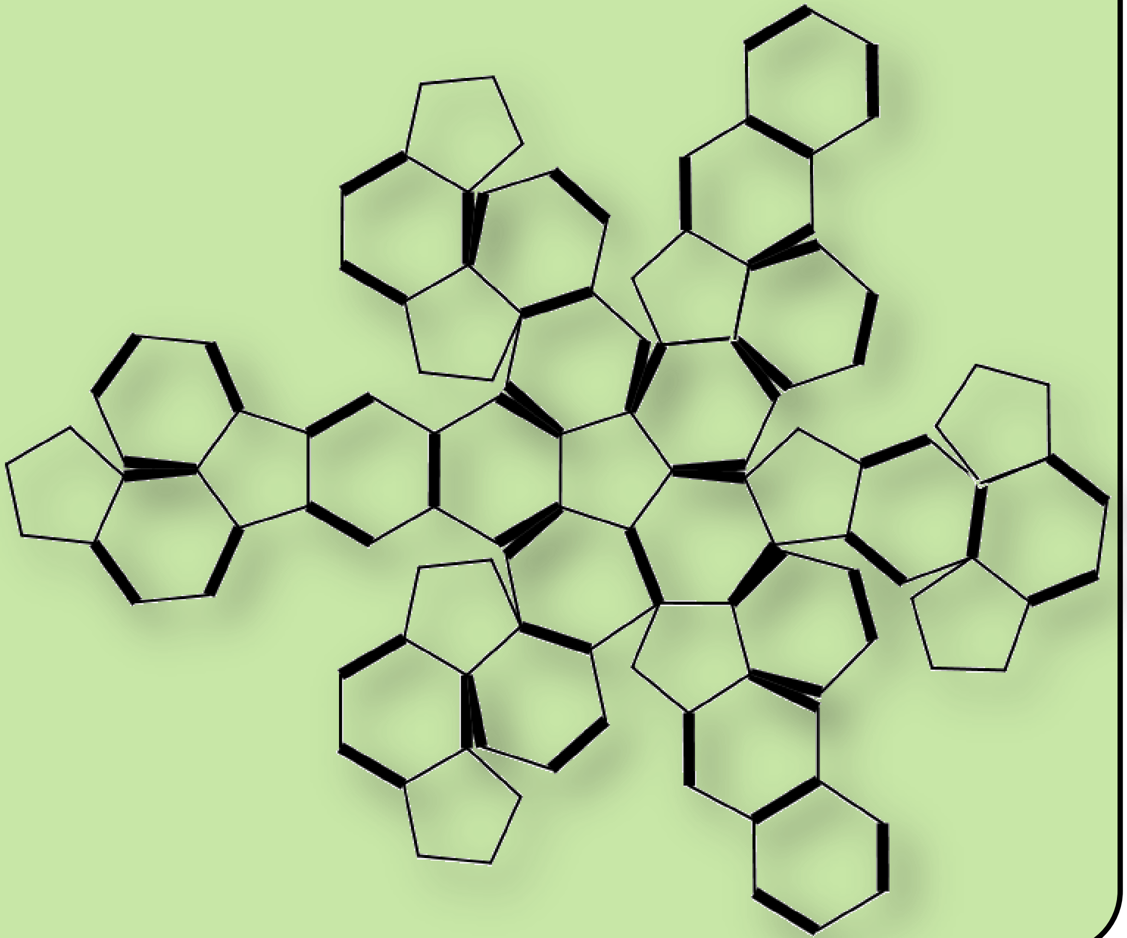
C_{70}



http://www.cumschmidt.de/sm_fullerene.htm
Acc. Chem. Res., Vol. 25, No. 3, 1992

Properties of Fullerenes

- Euler's "12 pentagon closure principle"

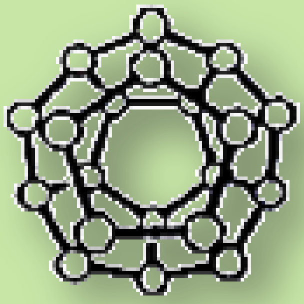


http://de.wikipedia.org/w/index.php?title=Datei:Fulleren_C60_Netzwerk.svg&filetimestamp=20100531203719

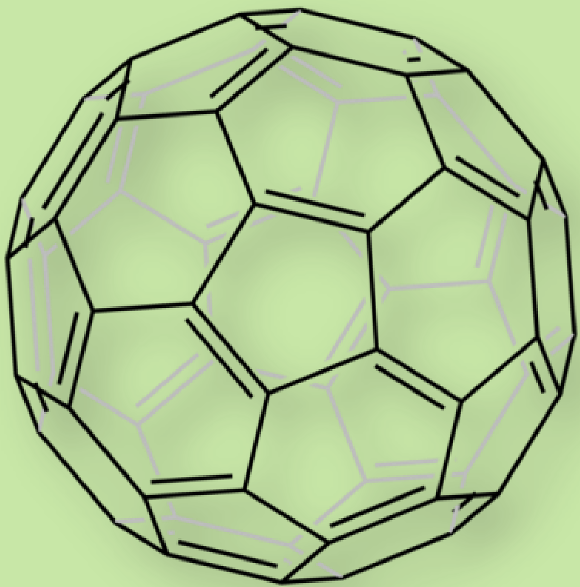
Properties of Fullerenes

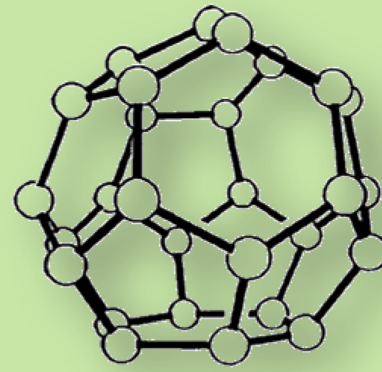
Freie Universität Berlin

- Smallest fullerene:

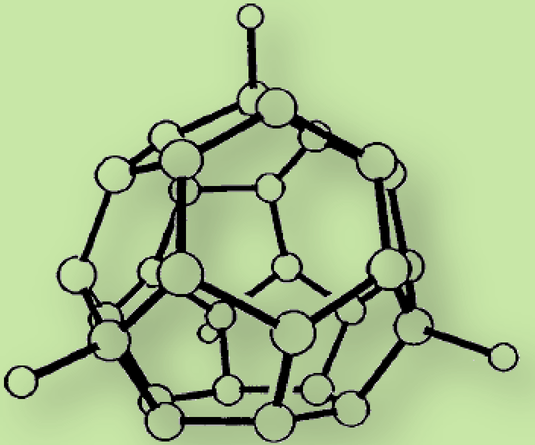


- Stability:





C_{28}



$C_{28}H_4$

Nobel Lectures, Chemistry 1996-2000, Editor Ingmar Grenthe, World Scientific Publishing Co., Singapore, 2003

Buckminster Fullerene

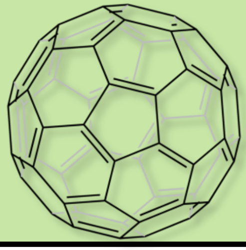
Freie Universität Berlin

Montréal, CA: 1967

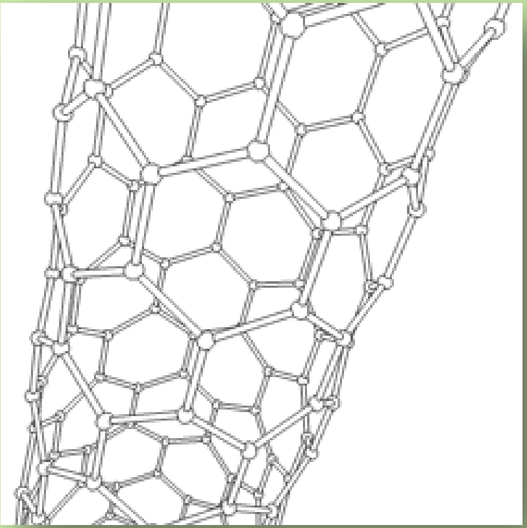
The Way to Nanotubes

Freie Universität Berlin

Fullerenes



Nanotubes



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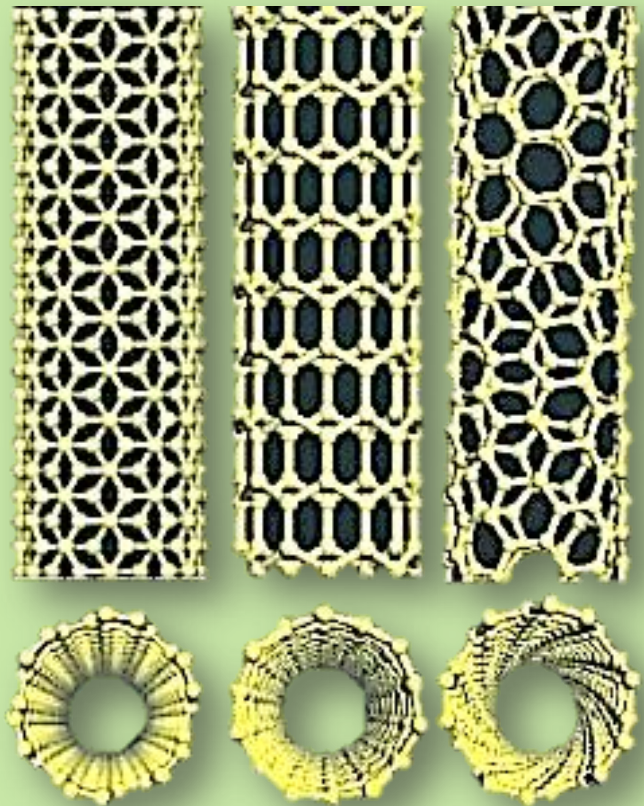
1985

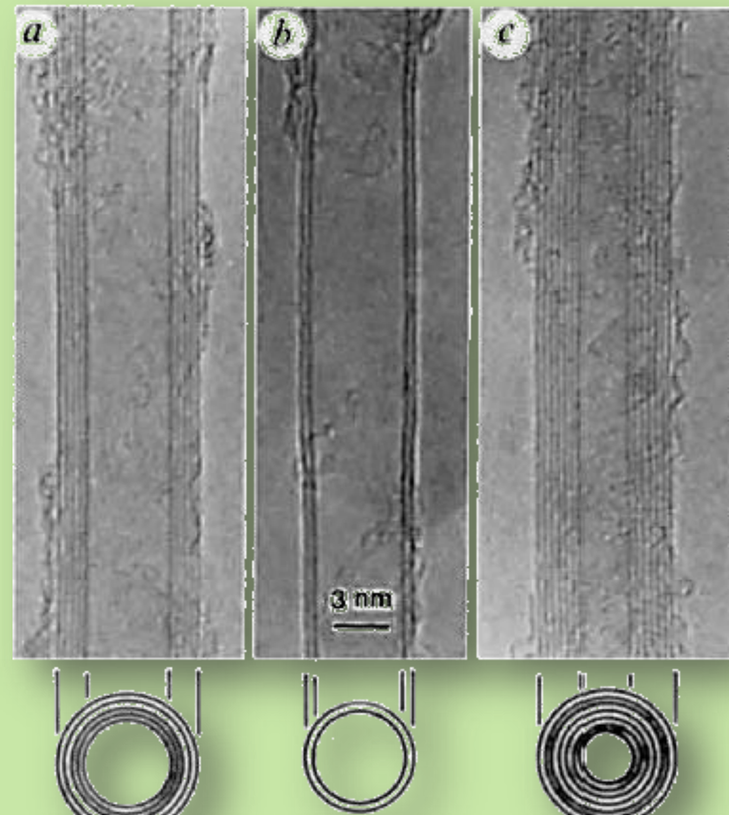
1990s - Today

http://en.wikipedia.org/wiki/File:Kohlenstoffnanoroehre_Animation.gif

Single-Wall-Nanotubes (SWNT)



Multi-Wall-Nanotubes (MWNT)



Science **297**, 787 – 792 (02 August 2002)
Nature **354**, 56 - 58 (07 November 1991); doi:10.1038/354056a0

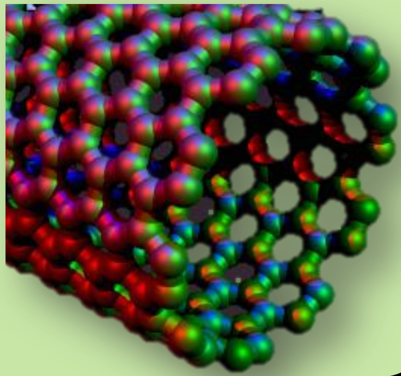
- single rolled graphite sheet
- rolling-dependent electronic structure:
  - semiconductor
  - metallic
- structure description: “chiral vector” (*n*,*m*)
- tube diameter:

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

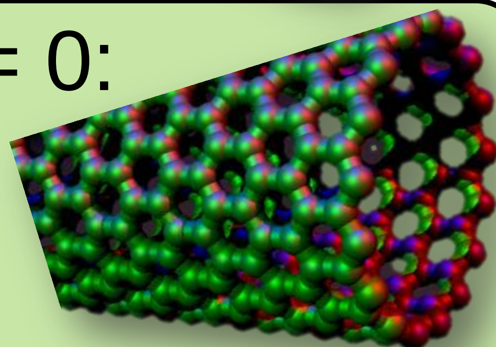
a = 0.246 nm

SWNT - Characterization

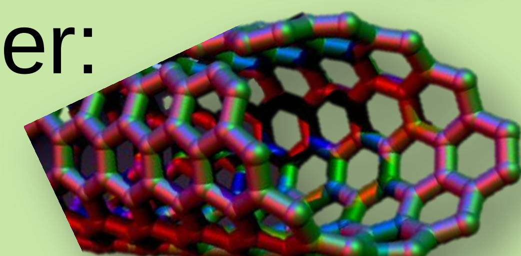
n = m:
armchair
- metallic

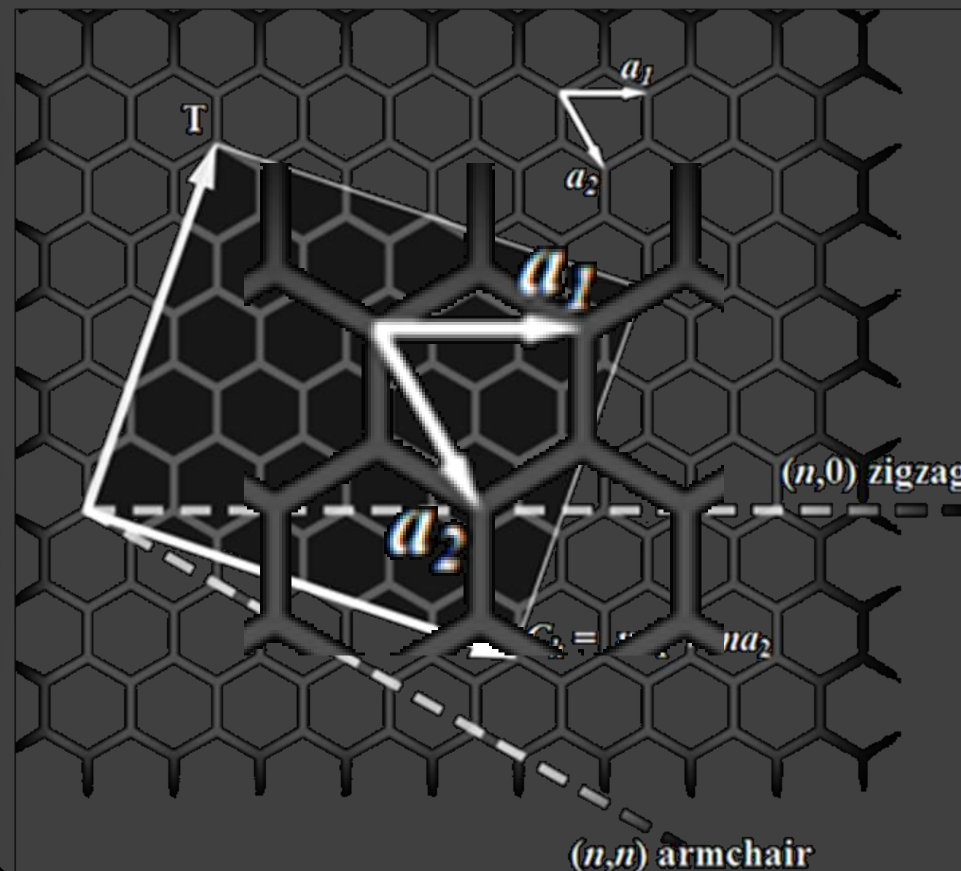


n or m = 0:
zigzag



any other:
chiral



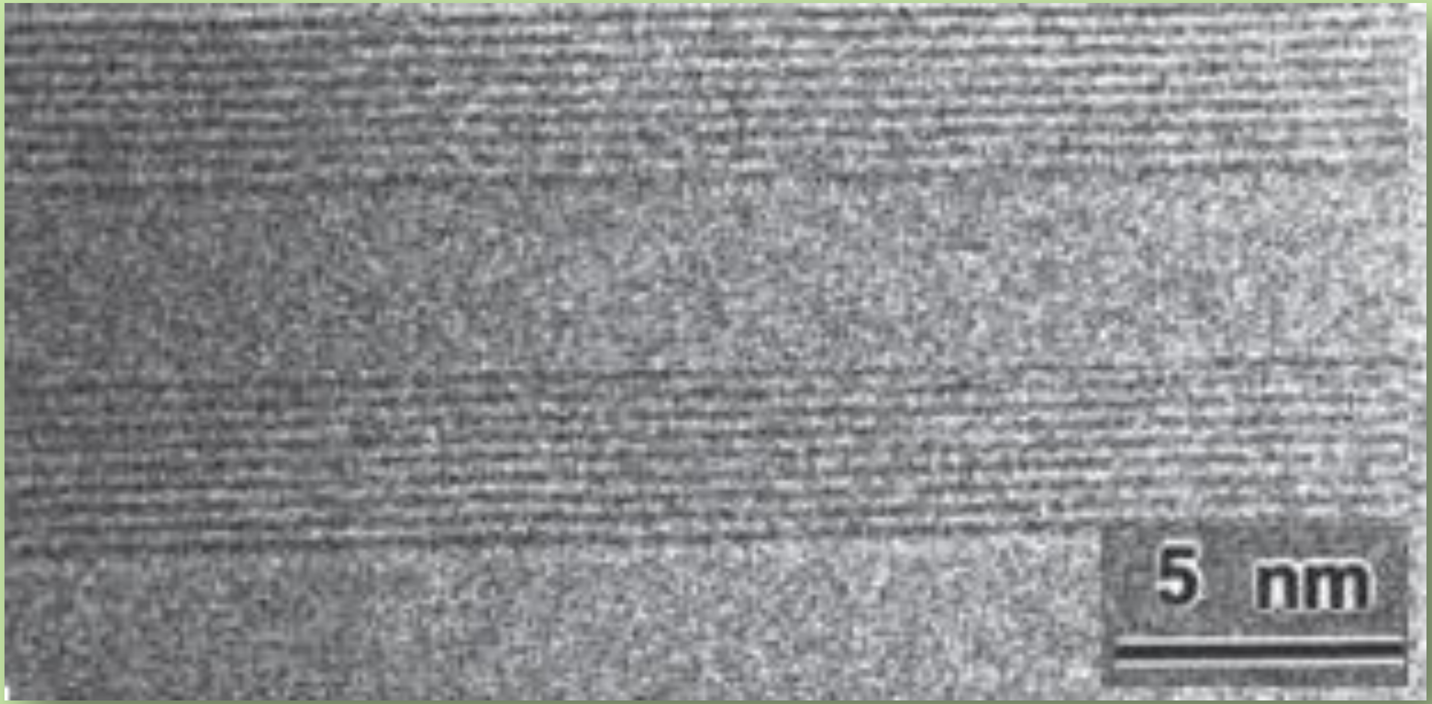


metallic $$\frac{n-m}{3} = k;\ k \neq 0$$

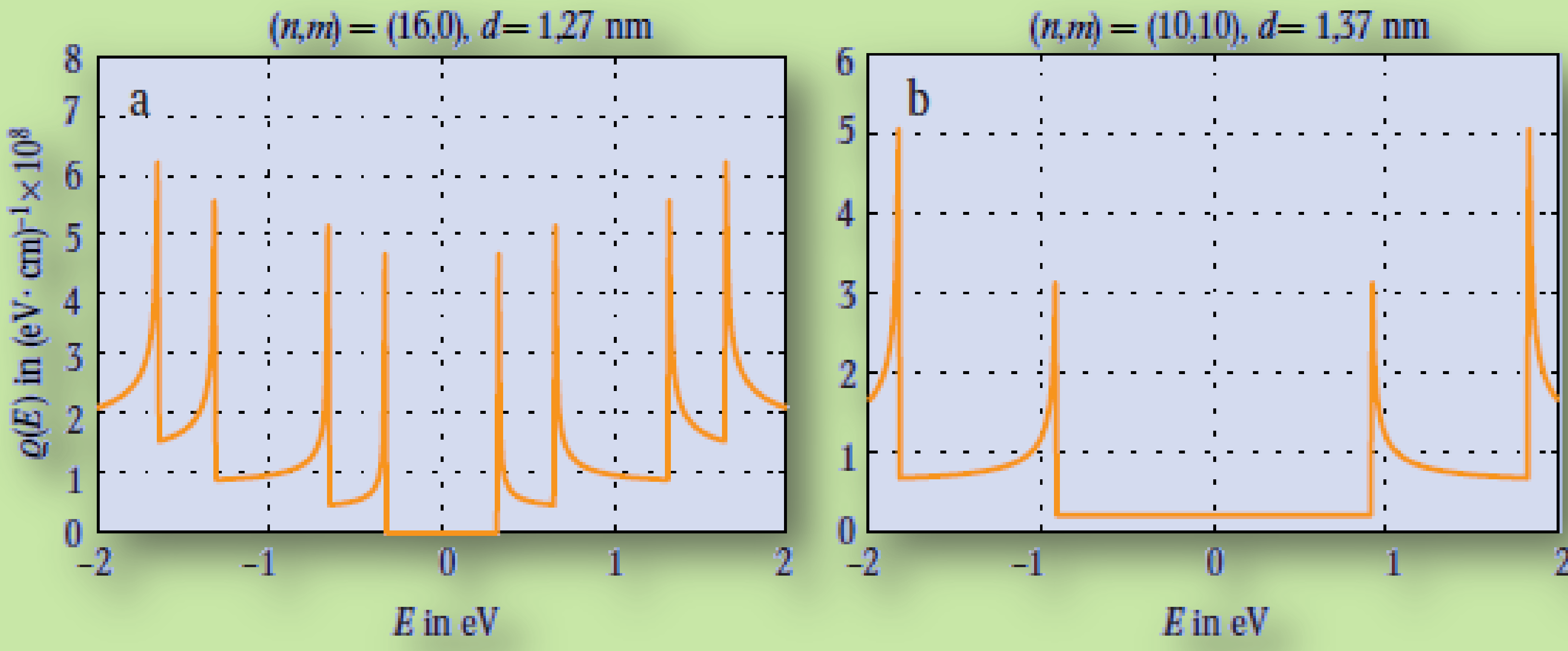
http://de.wikipedia.org/w/index.php?title=Datei:Types_of_Carbon_Nanotubes.png&filetimestamp=20090124143631

MWNT - Characterization

- MWNT: similar to SWNTs
  - between tubes: Van-der-Waals forces



Properties



- periodic b.c. along tube
  → discrete states → like potential well
- 1D electron gas → ballistic transport

Properties

- high currents, no heating:

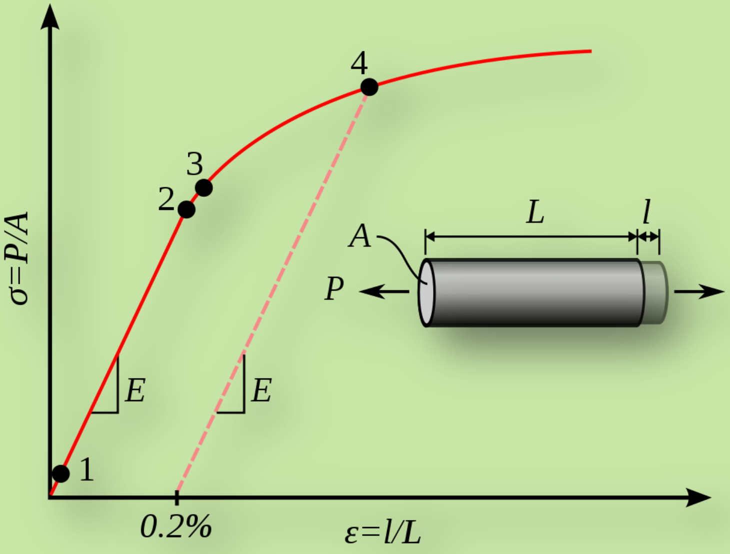
  4×10^9 A/cm^2 > 1000 x copper

- strength: high Young's modulus
  - SWNT(10,10): 0.64 TPa

    Steel: 0.2 TPa

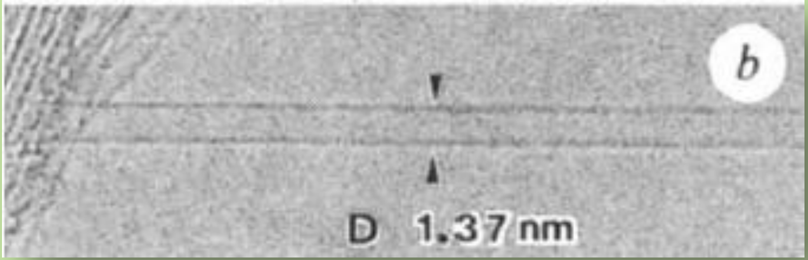
- tensile strength:
  - SWNT: 37 GPa

    e.g. 3700 kg at 1 mm^2 cable



Properties

- diameters:
  - SWNT: 0.4 – > 3 nm
  - MWNT: 1.4 – 100 nm



- price for SWNT:
  - dropped form 1500 $/g in 2000
    to 50 $/g in 2010

Nature **363**, 603 - 607 (17 June 1993); doi:10.1038/363605a0
Science **297**, 787 – 792 (02 August 2002)

INSTITUTE OF PHYSICS PUBLISHING — MEASUREMENT SCIENCE AND TECHNOLOGY

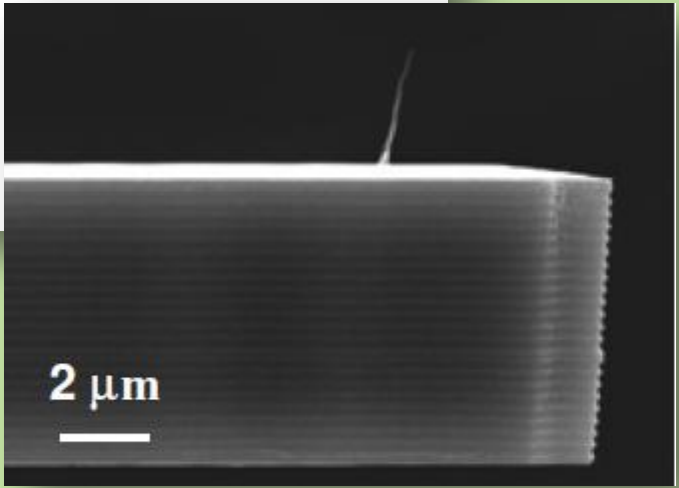
Meas. Sci. Technol. **16** (2005) 2138–2146 — doi:10.1088/0957-0233/16/11/003

Carbon nanotube tips for scanning probe microscopy: fabrication and high aspect ratio nanometrology

Cattien V Nguyen, Qi Ye and M Meyyappan

Center for Nanotechnology, NASA Ames Research Center, Moffett Field, CA 94035, USA

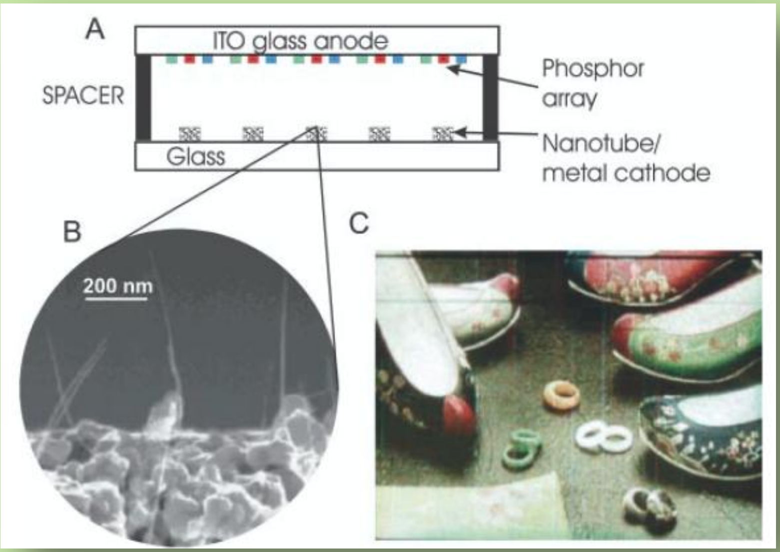
- improved resolution
- imaging of narrow deep structures



Applications

- Field Emission Devices
  - sharp tip → high electric field

- e.g. Flat Panels
  - high brightness
  - wide viewing angle
  - wide operating temp
  - contacting problems!

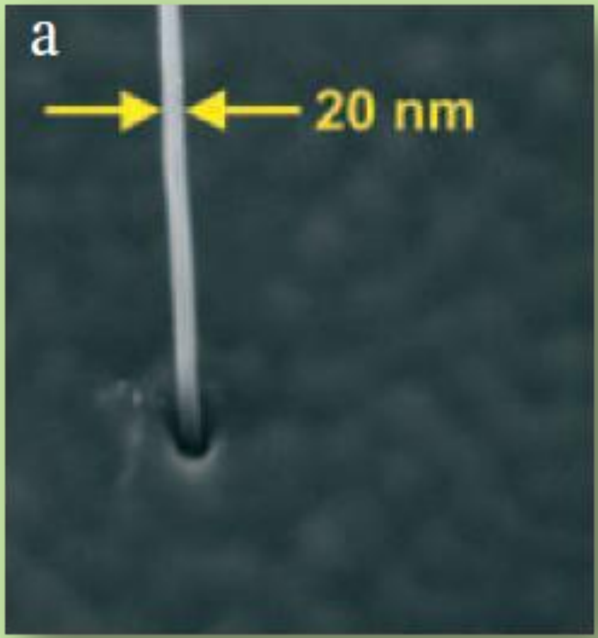


Science **297**, 787 – 792 (02 August 2002)

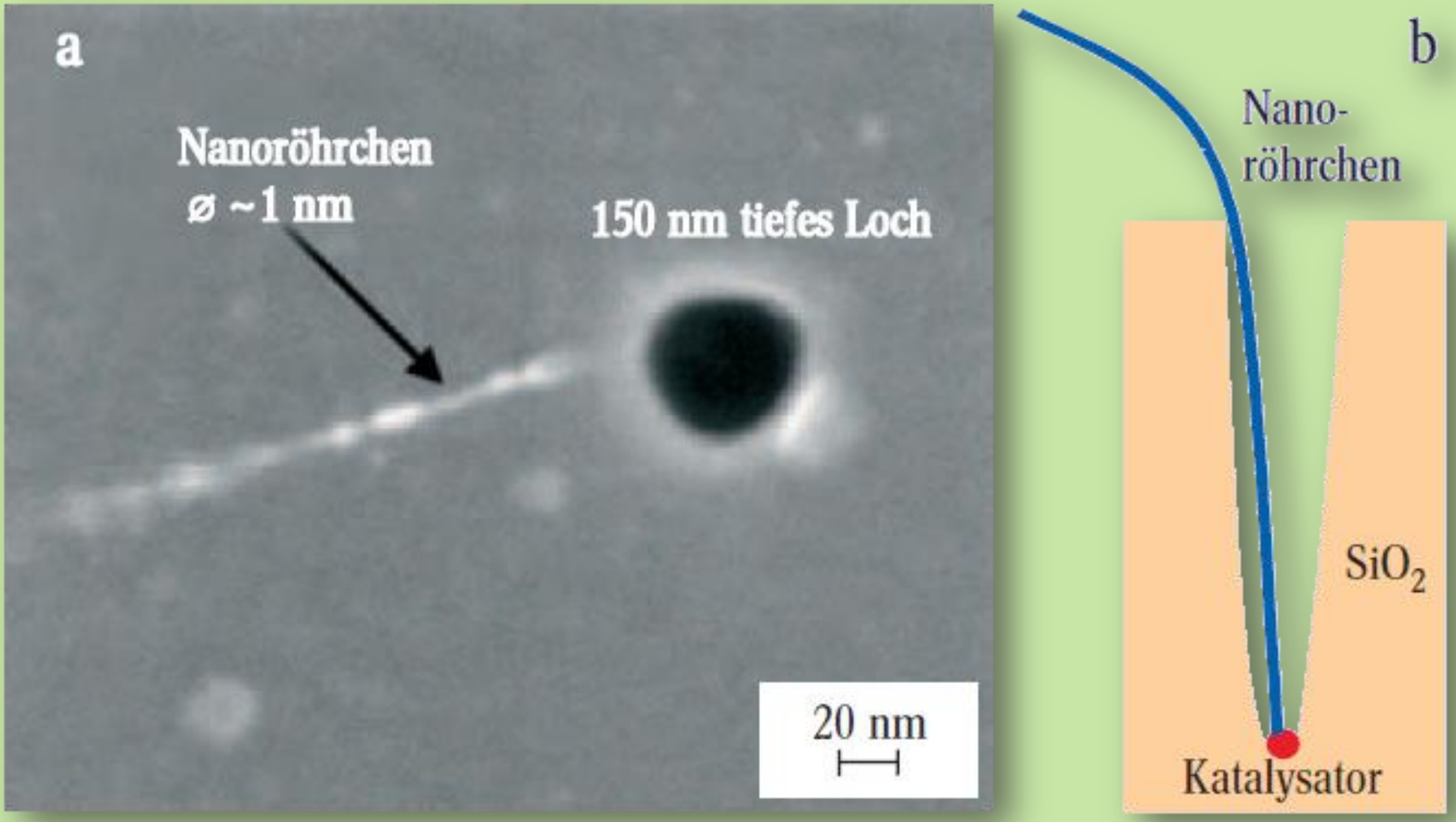
Freie Universität Berlin

- Electronic Devices
  - bottom-up creation

- e.g. nanowires
  - small diameter
    → metal wires breakdown
  - growing through holes
  - problem: large contact resistances



Applications



Physik Journal **10**, 39 – 44 (2004)

length-to-diameter ratio: > 132,000,000:1

NANO LETTERS

2009
Vol. 9, No. 9
3137-3141

Fabrication of Ultralong and Electrically Uniform Single-Walled Carbon Nanotubes on Clean Substrates

Xueshen Wang,[†] Qunqing Li,[*,†] Jing Xie,[†] Zhong Jin,[‡] Jinyong Wang,[‡] Yan Li,[‡] Kaili Jiang,[†] and Shoushan Fan[†]

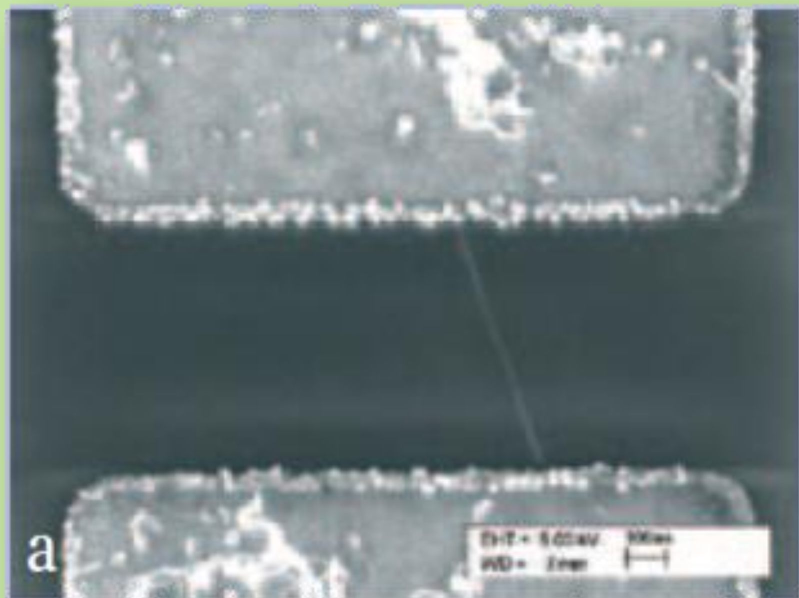
Department of Physics and Tsinghua-Foxconn Nanotechnology Research Center, Tsinghua University, Beijing 100084, People's Republic of China, and College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

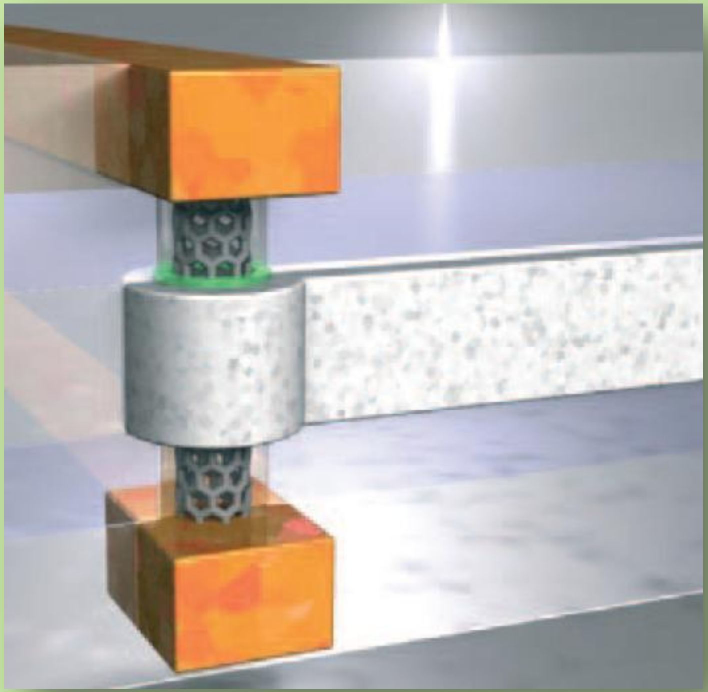
Received April 20, 2009; Revised Manuscript Received June 12, 2009

ABSTRACT

We report the controlled growth of ultralong single-wall carbon nanotube (SWNT) arrays using an improved chemical vapor deposition strategy. Using ethanol or methane as the feed gas, monodispersed Fe—Mo as the catalyst, and a superaligned carbon nanotube (CNT) film as the catalyst supporting frame, ultralong CNTs over 18.5 cm long were grown on Si substrates. The growth rate of the CNTs was more than 40 μm/s. No catalyst-related residual material was found on the substrates due to the use of a CNT film as the catalyst supporting frame, facilitating any subsequent fabrication of SWNT-based devices. Electrical transport measurements indicated that the electrical characteristics along a single ultralong SWNT were uniform. We also found that maintaining a spatially homogeneous temperature during the growth process was a critical factor for obtaining constant electrical characteristics along the length of the ultralong SWNTs.

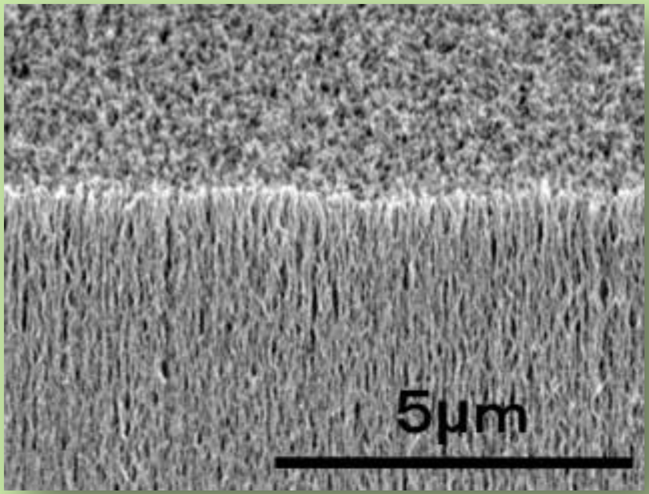
- NT-Field Effect Transistors:





Applications

- capacitors
  - capacity: $C \propto A/d$
  - nanotubes: d = 1 nm
  - capacitances: 200 F/g



- actuators (artificial muscles):
  - just small voltage compared to piezos (100 V)
  - > 26 MPa

Who were the Discoverer?

Freie Universität Berlin

Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Carbon 44 (2006) 1621–1623

CARBON

www.elsevier.com/locate/carbon

Guest Editorial

Who should be given the credit for the discovery of carbon nanotubes?

Carbon nanotubes play a large part in manuscript topics submitted to CARBON and, of course, to many other journals in almost every field of research and technology. Many of them start with referring to "*the discovery of carbon nanotubes by Iijima in 1991...*". Such a recurrent sentence makes a statement which is misleading, often wrong, and neglectful of the scientists who preceded this citation on the path to understanding carbon materials. A former Edi-

SWCNT, though not claimed to be so by the authors (Fig. 1, between the arrows).

Unfortunately, the magnification used did not allow graphene fringes to be resolved so that the number of walls cannot be determined. However, considering the diameter of this tube (~5 nm) and what is expected from calculations of the energetic stability of a SWCNT [5], it is unlikely that a nanotube with such a large diameter be

Multi Wall Nanotubes

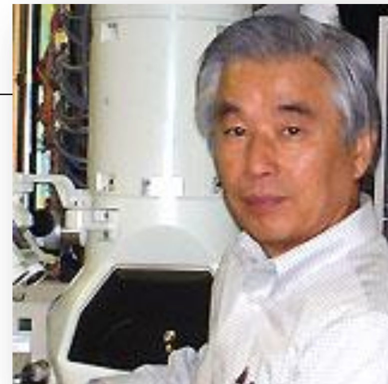
Freie Universität Berlin

LETTERS TO NATURE

Helical microtubules of graphitic carbon

Sumio Iijima

NEC Corporation, Fundamental Research Laboratories, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan



THE synthesis of molecular carbon structures in the form of C_{60} and other fullerenes[1] has stimulated intense interest in the structures accessible to graphitic carbon sheets. Here I report the preparation of a new type of finite carbon structure consisting of needle-like tubes. Produced using an arc-discharge evaporation method similar to that used for fullerene synthesis, the needles grow at the negative end of the electrode used for the arc discharge. Electron microscopy reveals that each needle comprises coaxial tubes of graphitic sheets, ranging in number from 2 up to about 50. On each tube the carbon-atom hexagons are arranged in a helical fashion about the needle axis. The helical pitch varies from needle to needle and from tube to tube within a single needle. It

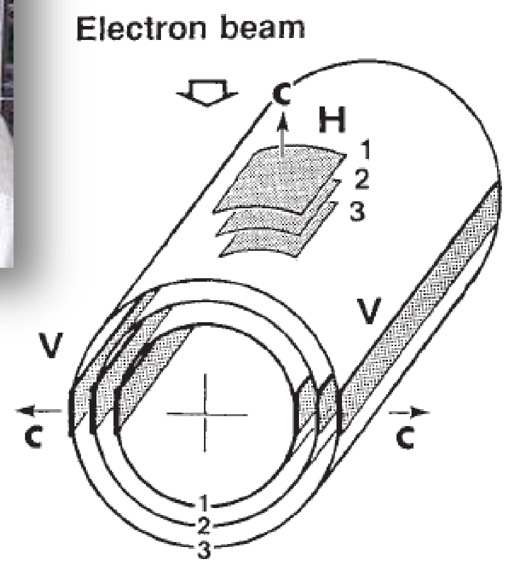


FIG. 2 Clinographic view of a possible structural model for a graphitic tubule. Each cylinder represents a coaxial closed layer of carbon hexagons. The meaning of the labels V and H is explained in the text.

http://de.wikipedia.org/w/index.php?title=Datei:Iijima.jpg&filetimestamp=20081013235958

Nature **354**, 56 - 58 (07 November 1991); doi:10.1038/354056a0

First Traces of Nanotubes

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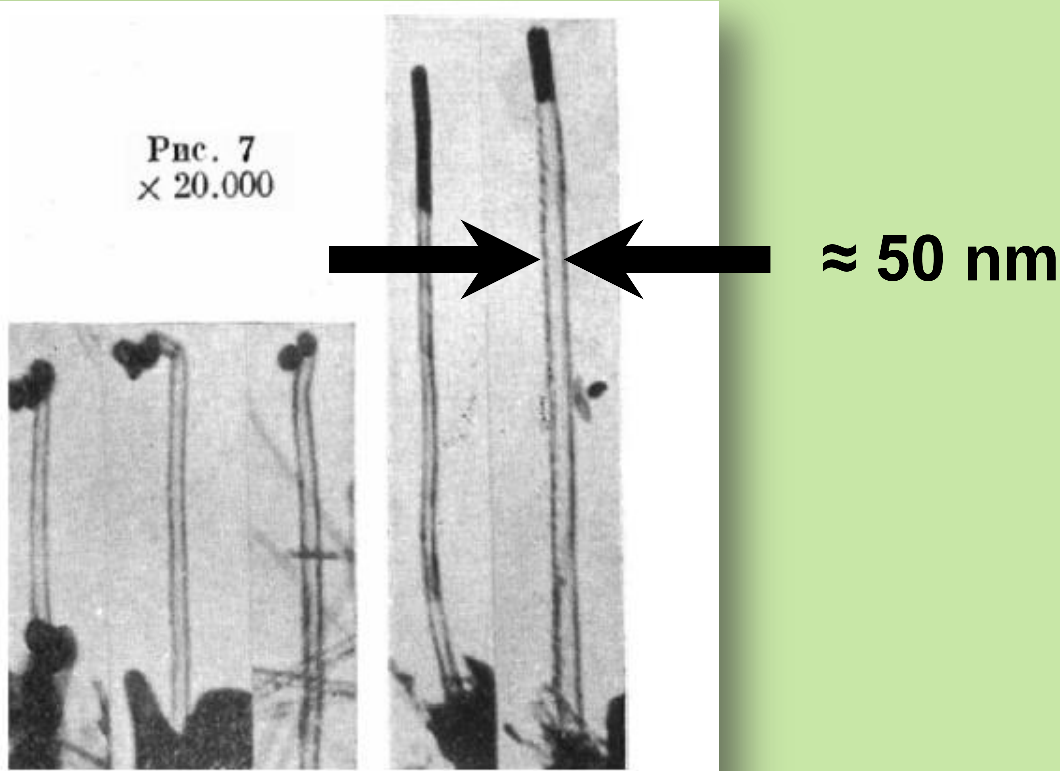


Fig. 2. Examples of TEM images of carbon nanotubes published in [12] (*reprinted by permission of Nauka Publishers*).

[12] Radushkevich LV, Lukyanovich VM. O strukture ugleroda, obrazujucegosja pri termiceskom razlozenii okisi ugleroda na zeleznom kontakte. Zurn Fisic Chim 1952;26:88–95.

Single Wall Nanotubes

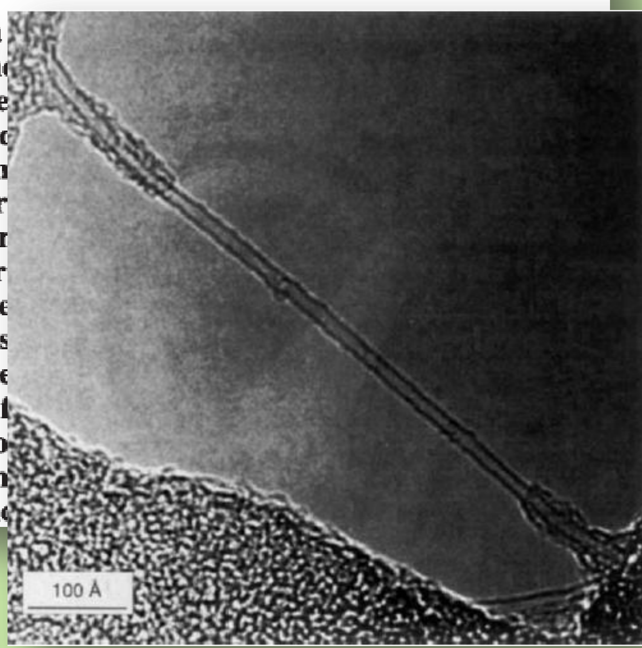
Freie Universität Berlin

Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls

D. S. Bethune, C.H. Klang*, M. S. de Vries, G. Gorman, R. Savoy, J. Vazquez & R. Beyers

IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099, USA

CARBON exhibits a
structures. In an in
spheroidal fullerene
cathode of the arc-
synthesis will form
particles[5–8]. Electr
polyhedra transfor
'onions'[9]. We now r
an arc generator le
which all have very s
a single atomic laye
woven through the
texture. The unifo
nanotubes should m
theoretical predicti



Single-shell carbon nanotubes of 1-nm diameter

Sumio Iijima & Toshinari Ichihashi

Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan

CARBON nanotubes[1] are expected to have a wide variety of interesting properties. Capillarity in open tubes has already been
demonstrated[2–
structure[6–8] an
examine the pr
well defined m
concentric shell
a range of tube
concerned with
esis produces a
the synthesis o
about one nan
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confirm the he
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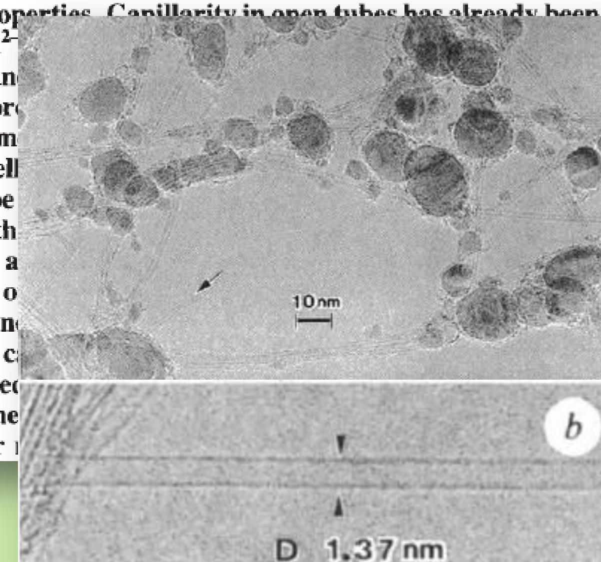
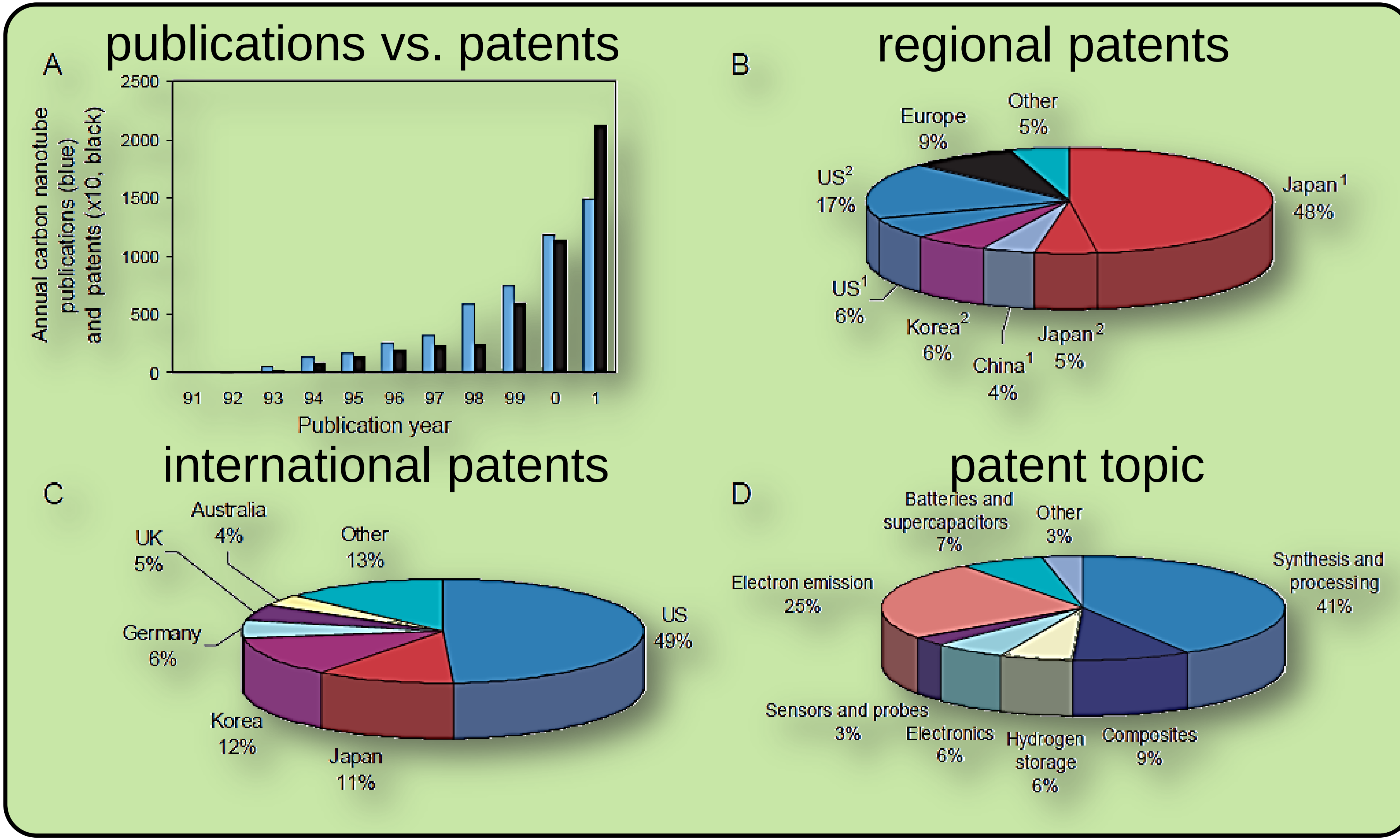


Nature **363**, 603 - 607 (17 June 1993); doi:10.1038/363605a0

Research and Developement

Freie Universität Berlin



Science **297**, 787 – 792 (02 August 2002)

Content – Timeline

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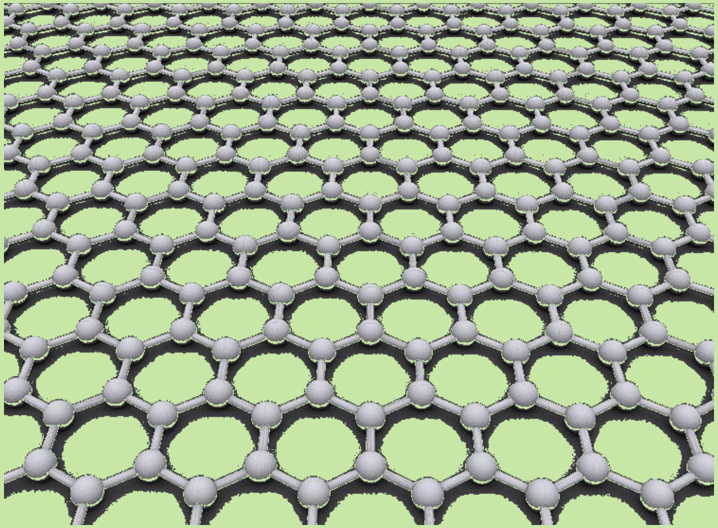
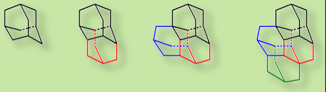
Graphenes



Diamondoids



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2004 - Today

http://en.wikipedia.org/wiki/File:Diamondoids.png
http://de.wikipedia.org/w/index.php?title=Datei:Graphen.jpg&filetimestamp=20100826054350

Andre Geim & Konstantin Novoselov

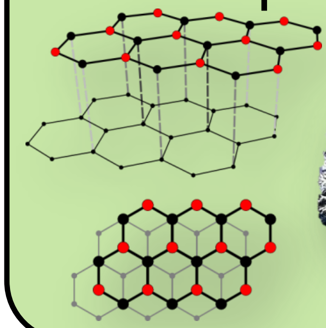
University of Manchester

"for groundbreaking experiments regarding the two-dimensional material graphene"

Space-Time Conversion

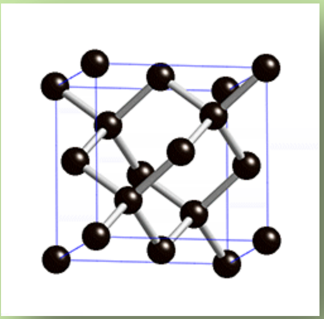
Freie Universität Berlin

Graphite



3D

Diamond



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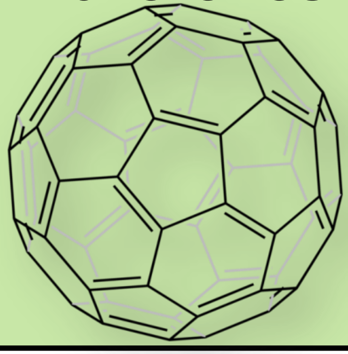
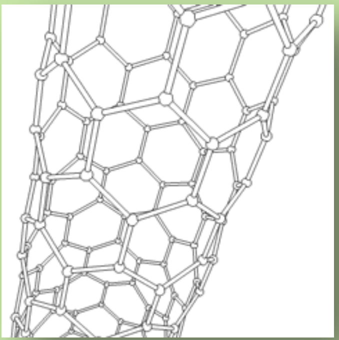
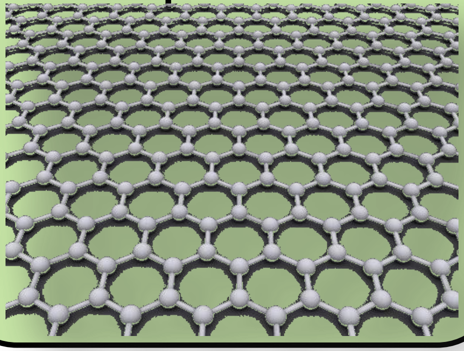
Fullerenes



Nanotubes



Graphenes



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0D 1D 2D

http://en.wikipedia.org/wiki/File:Kohlenstoffnanoroehre_Animation.gif

Importance on Graphene

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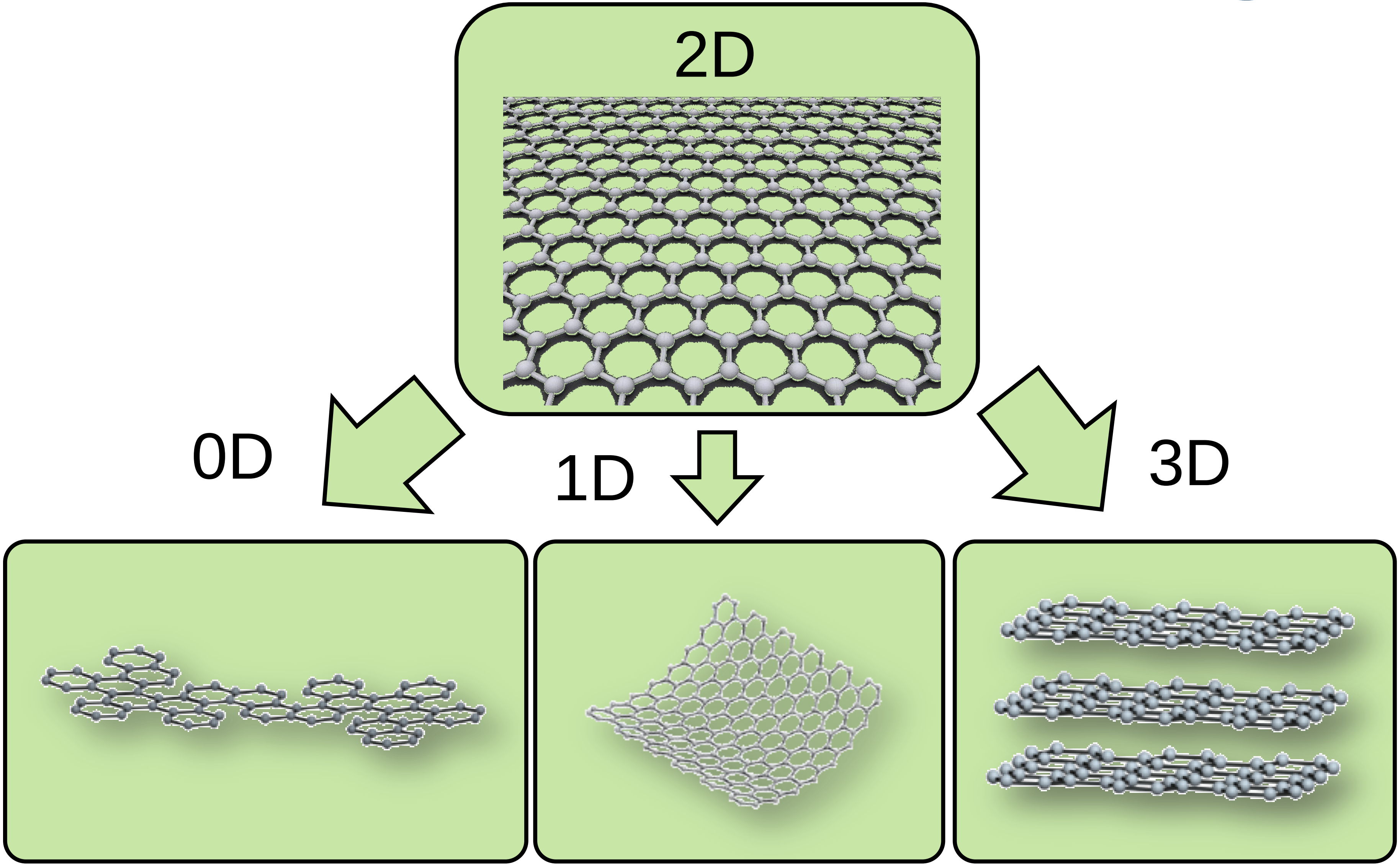


"graphene is an 'academic' material"

- theoretic calculations predict properties

PHYSICAL REVIEW VOLUME 71, NUMBER 9 MAY 1, 1947

The Band Theory of Graphite

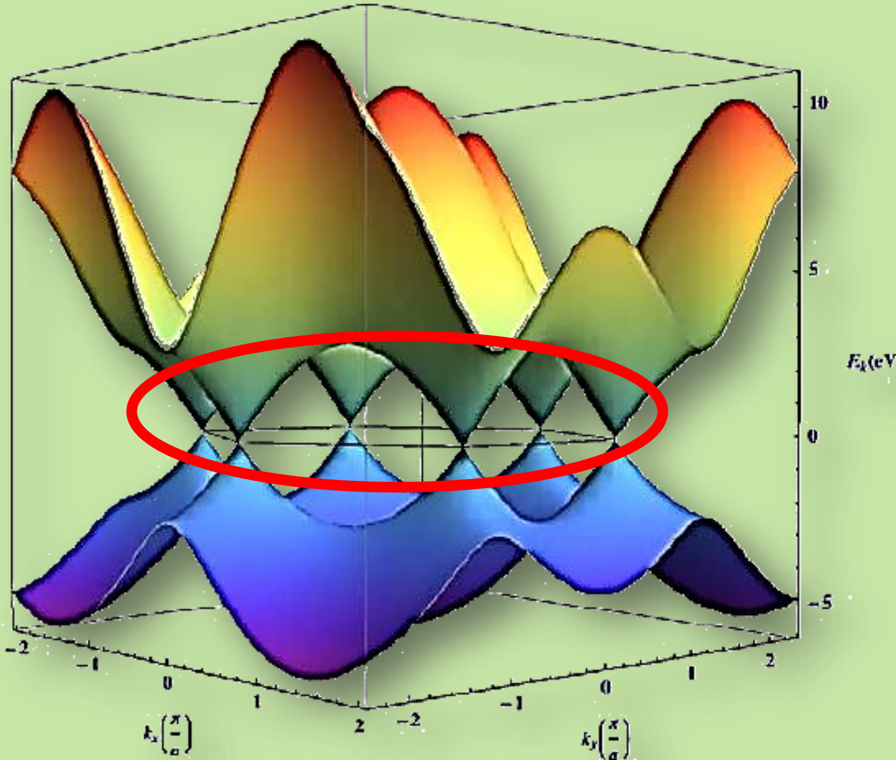
P. R. Wallace*
National Research Council of Canada, Chalk River Laboratory, Chalk River, Ontario
(Received December 19, 1946)

$$E = \pm\gamma_0 \sqrt{1 + 4\cos^2\frac{k_y a}{2} + 4\cos\frac{k_y a}{2}\cdot\cos\frac{k_x\sqrt{3}a}{2}}$$

$$\gamma_0 = 2.8\text{ eV}; \text{a} = 2.46\text{ Å}$$

Electronic Structure

- linear behavior at Fermi level
- effective mass = 0
- relativistic behavior
- description by Dirac equation



→ "Dirac electrons/holes"

- earlier attempts:
  - bulk graphite planes separated by atoms
    - large molecules → large separation
  - growth of single sheets

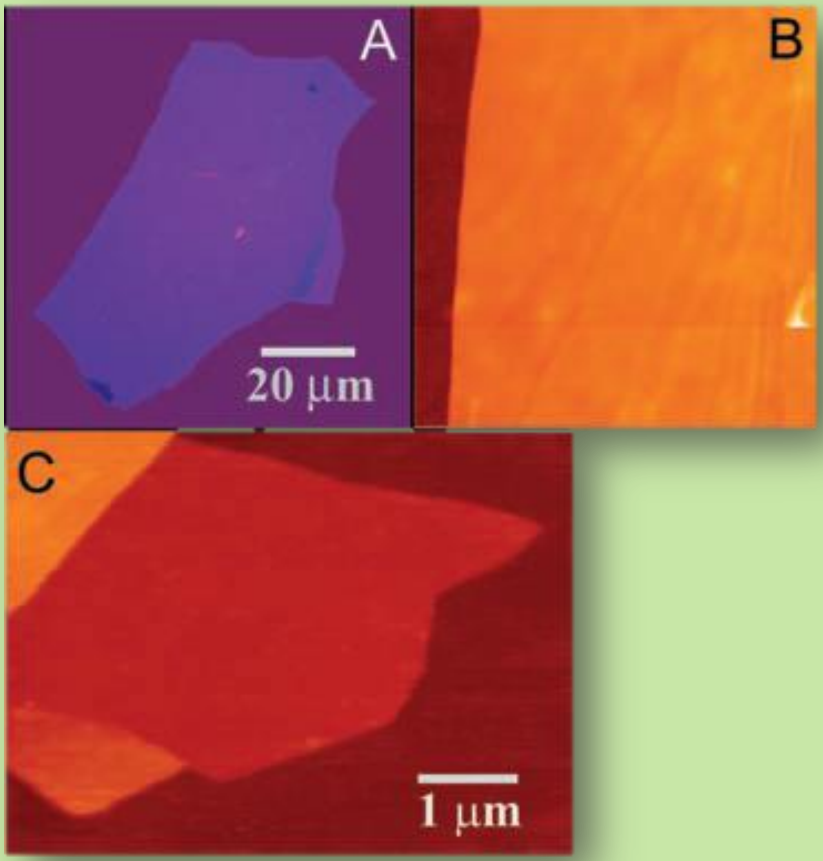
ALL FAILED

What have Geim and Novolesov done different?

Single Graphene Layers

- repeated exfoliation of Highly Oriented Pyrolytic Graphite:

1. cohesive tape splits up graphite layers
2. tape fixed on SiO_2
3. tape is dissolved



Science 22 October 2004: Vol. 306 no. 5696 pp. 666-669 DOI: 10.1126/science.1102896

Why did this simple method succeeded?

- New recognition method!
  - – SPM is too slow,
  - – SEM hides layer thickness
- Discovery: Visible in an optic microscope!
  - – on thickness tuned SiO_2 layer

Freie Universität Berlin

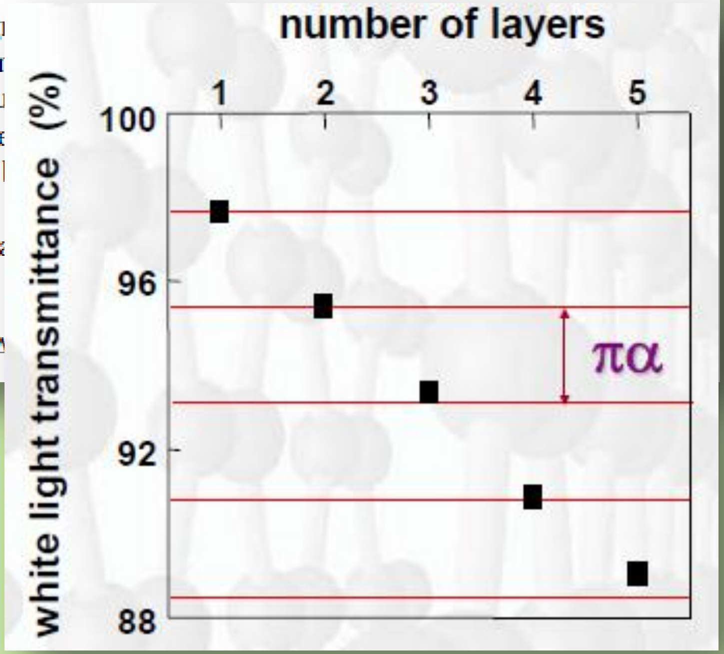
PRL 100, 117401 (2008) PHYSICAL REVIEW LETTERS week ending 21 MARCH 2008

Universal Optical Conductance of Graphite

A. B. Kuzmenko, E. van Heumen, F. Carbone,* and D. van der Marel
DPMC, University of Geneva, 1211 Geneva 4, Switzerland
(Received 5 December 2007; published 20 March 2008)

We find experimentally that the optical sheet conductance of gr
$(\pi/2)e^2/h$, which is the theoretically expected value of dynam
graphene. Our calculations within the Slonczewski-Weiss-McClu
hopping leaves the conductance of graphene sheets in graphite
between 0.1 and 0.6 eV, even though it significantly affects the
The f-sum rule analysis shows that the large increase of the
temperature is at the expense of the removed low-energy optica
hole and electron bands.

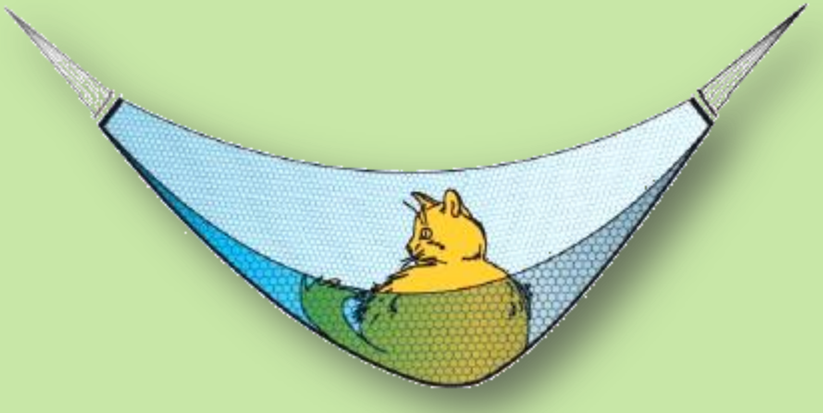
DOI: 10.1103/PhysRevLett.100.117401 PA



→ direct observation of the fine structure constant

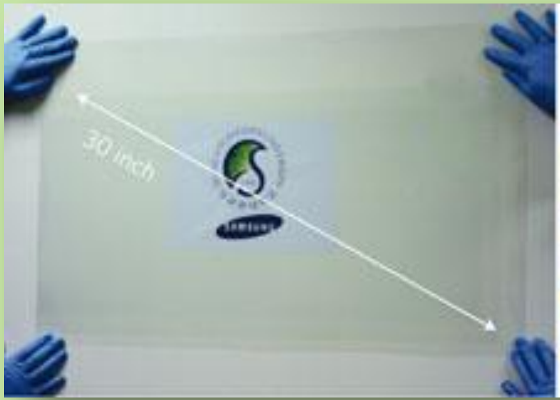
Example

- If we build a hammock out of graphene:
  - size: 1 m^2
  - weight: 0.77 mg
  - can hold: 4 kg
  - resistance: 31 Ω
  - nearly transparent



Applications

- e.g. touch-screens:
  - – cheaper, more transparent, flexible



- weak spin-orbit coupling, no hyperfine:
  - – ideal for spin qubits → quantum computing

Content – Timeline

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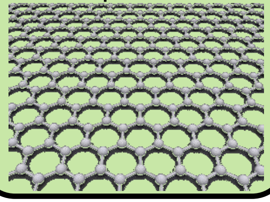
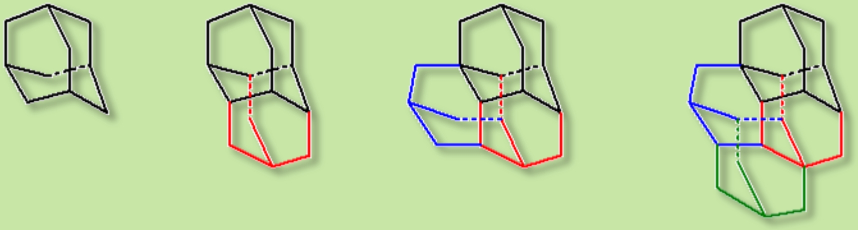
Graphenes



Diamondoids



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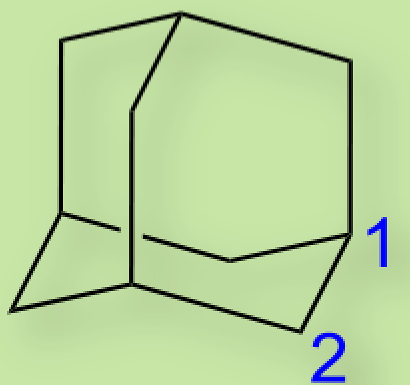
2004 - Today

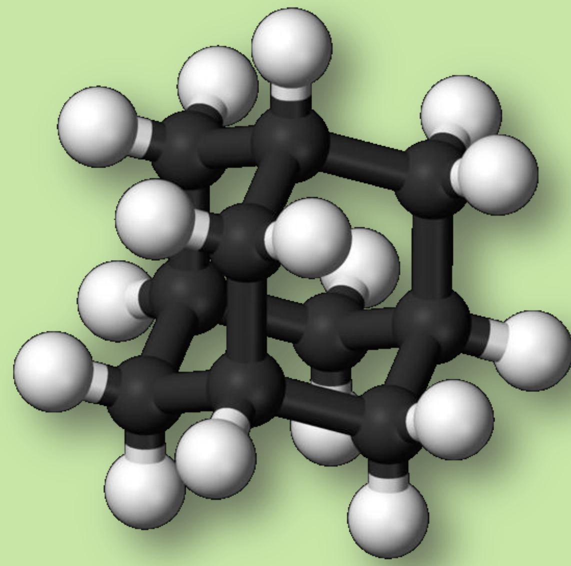
http://en.wikipedia.org/wiki/File:Diamondoids.png
http://de.wikipedia.org/w/index.php?title=Datei:Graphen.jpg&filetimestamp=20100826054350

What is a Diamondoid?

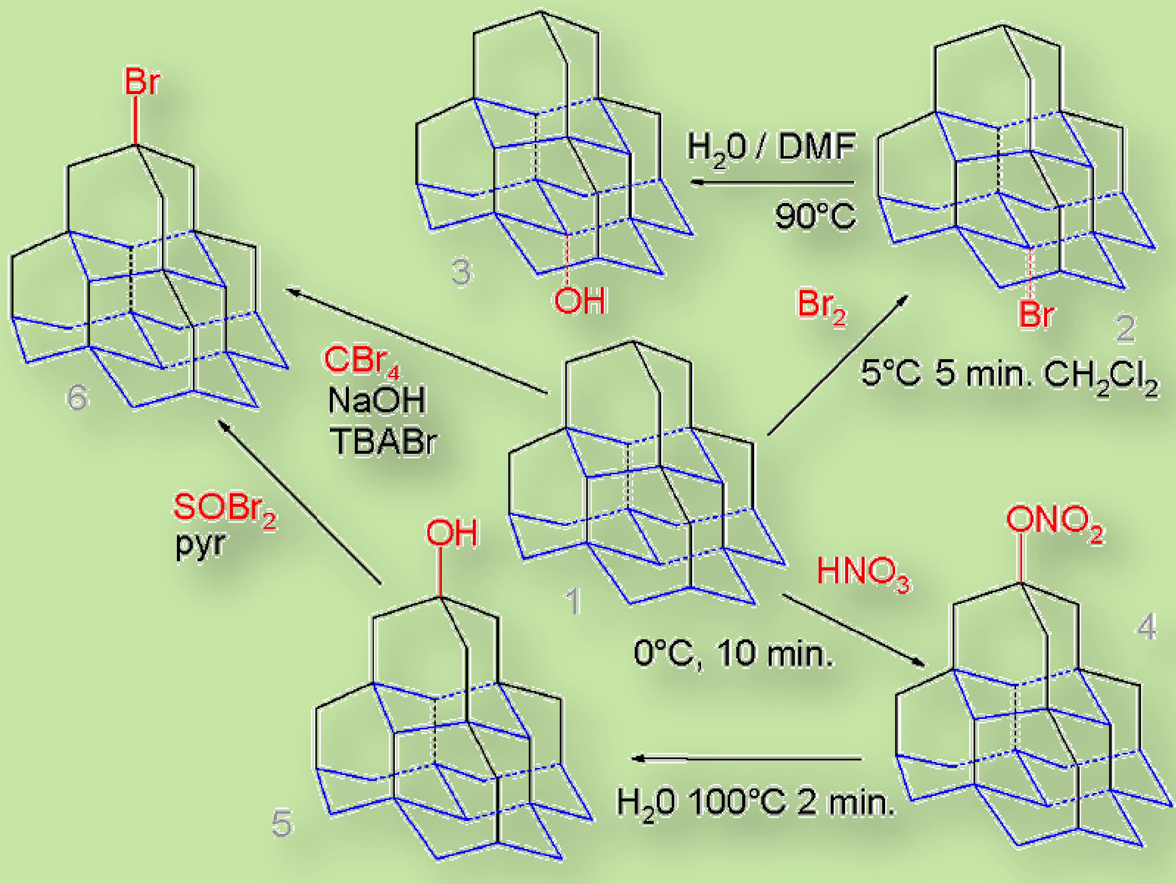
- diamondoid = diamond-like-structures:
  - 3D covalent bonds
  - stiffness and stability

- smallest structure: adamantane ($C_{10}H_{16}$)





- size-dependent electronic properties



http://en.wikipedia.org/wiki/File:PentamaneChemistry.png

Conclusion

- Nanocarbons are fascinating!
- extreme variety of properties
  - best conducting material
    - electric
    - thermal
  - allows research at real 1D and 2D electrons
  - allows research at relativistic electrons
  - strongest material
  - stiffest
  - great variety of applications

Conclusion

- They also entertain us!

Thank you for your attention!