

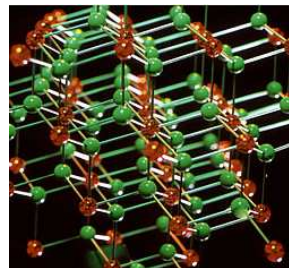
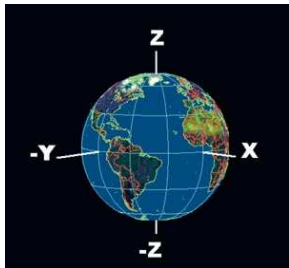
Nanoscience: A historical perspective

R. Díez Muiño and P. M. Echenique

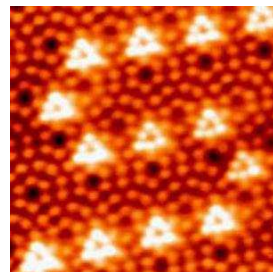
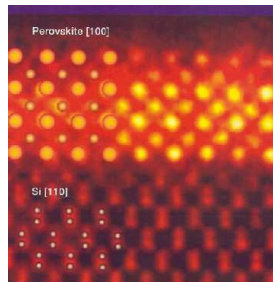
Lecture Notes
Fall 2007



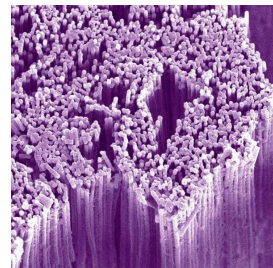
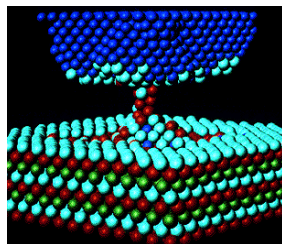
Nanoscience and reduced dimensionality



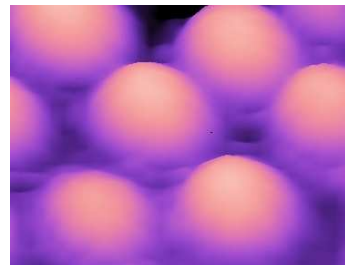
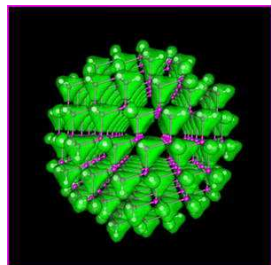
ours is a three-dimensional (3D) world



thin films and surfaces can be 2D

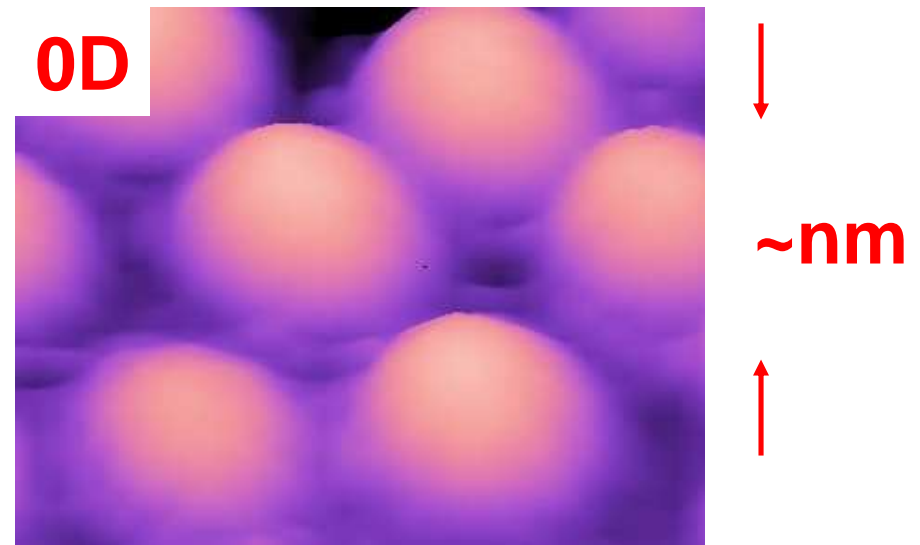
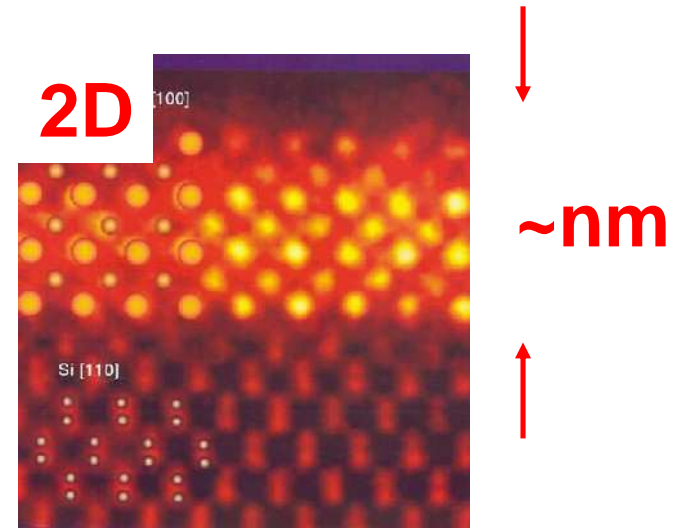
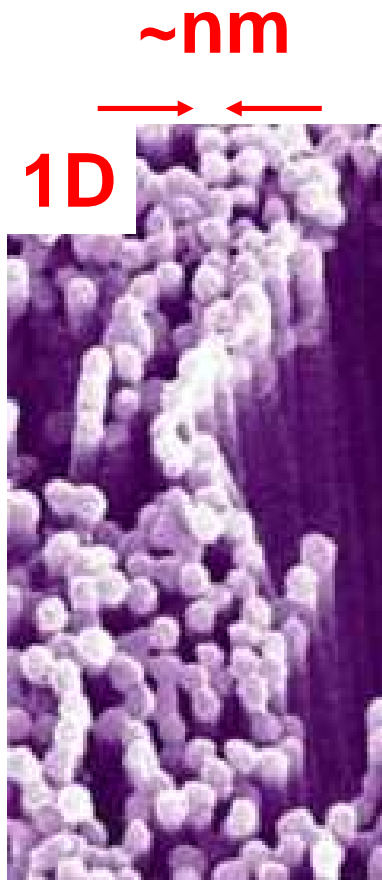


nanowires are, in practice, 1D



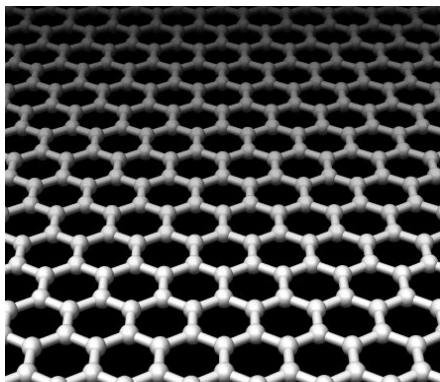
nanoscience reduces dimensionality to objects that can be considered 0D

Nanoscience: from 3D → 0D CONFINEMENT!!



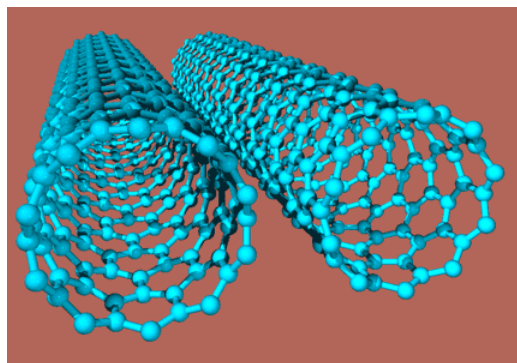
Low-dimensional Nanostructures of Carbon

2D



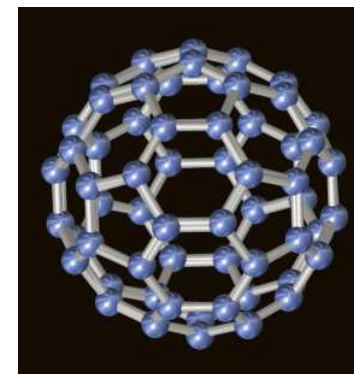
graphene

1D



nanotubes

0D



buckyballs

Periodic Table of the Elements

| | IA | IIA | III B | IV B | V B | VI B | VII B | VIII | IX | X | XI | XII | I B | II B | III A | IV A | V A | VI A | VII A | 0 | |
|---|------------------------|----------------------|-------------|---------------------|----------------------|---------------------|----------------------|---------------------|---------------------|----------------------|----------------------|---------------------|---------------------|---------------------|------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|----------------------|
| 1 | H 1.00794 | | | | | | | | | | | | | | | | | | | He 4.0026 | |
| 2 | Li 6.941 | Be 9.01218 | | | | | | | | | | | | | | B 10.811 | C 12.011 | N 14.007 | O 16.00 | F 18.9984 | Ne 20.1797 |
| 3 | Na 22.989769 | Mg 24.305 | | | | | | | | | | | | | Al 26.981538 | Si 28.086 | P 30.974 | S 32.06 | Cl 35.453 | Ar 39.948 | |
| 4 | K 39.0983 | Ca 40.078 | Sc | Ti 47.88 | V 50.942 | Cr 51.996 | Mn 54.938 | Fe 55.845 | Co 58.933 | Ni 58.69 | Cu 63.546 | Zn 65.38 | Ga 69.723 | Ge 72.64 | As 74.922 | Se 78.96 | Br 79.904 | Kr 83.80 | | | |
| 5 | Rb 85.468 | Sr 87.62 | Y | Zr 91.224 | Nb 92.906 | Mo 95.94 | Tc | Ru 101.07 | Rh 102.91 | Pd 106.42 | Ag 107.87 | Cd 112.41 | In 114.82 | Sn 118.71 | Sb 121.76 | Te 127.6 | I 126.905 | Xe 131.29 | | | |
| 6 | Cs 132.905 | Ba 137.33 | * La | Hf 178.49 | Ta 180.948 | W 183.84 | Re 186.207 | Os 190.23 | Ir 192.22 | Pt 195.084 | Au 196.967 | Hg 200.59 | Tl 204.38 | Pb 207.2 | Bi 208.98 | Po | At | Rn 222 | | | |
| 7 | Fr | Ra | + Ac | Rf | Ha | 106 | 107 | 108 | 109 | 110 | | | | | | | | | | | |

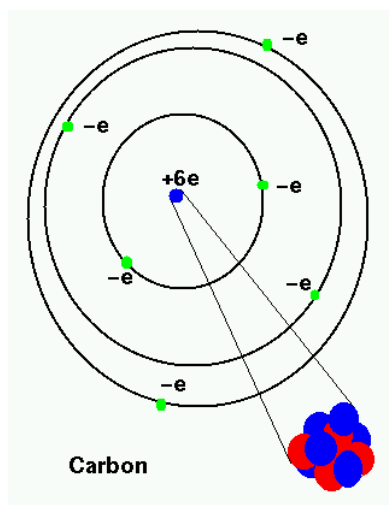
| | | | | | | | | | | | | | | |
|----|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 58 | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| 90 | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

- * Lanthanide Series
- + Actinide Series

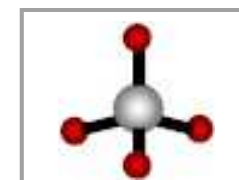
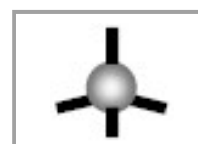
Importance of Carbon

Carbon is the sixth most abundant element on Earth
Carbon occurs in all organic life
Carbon is the basis of organic chemistry
Carbon forms flammable compounds (hydrocarbons)
Carbon is added to iron to make steel
etc.

Carbon atom



C atom
electronic structure
 $1s^2 2s^2 2p^2$
(four bonding electrons)

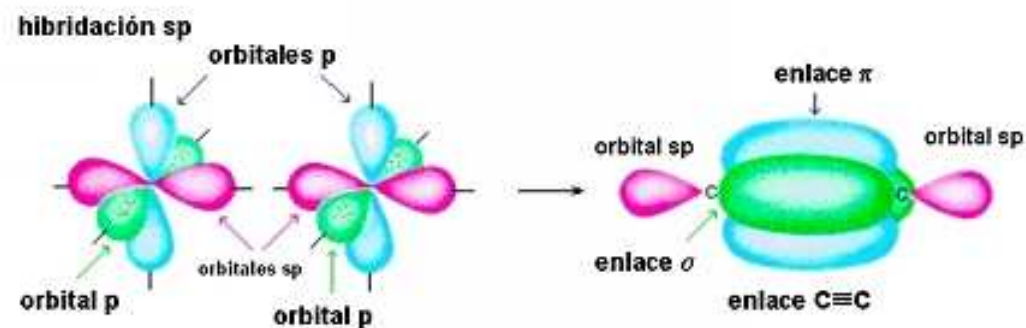


Methane: CH_4

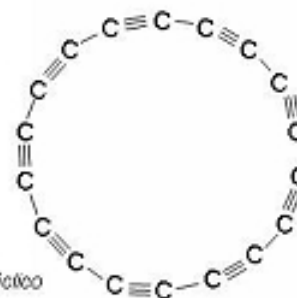
Carbon bonding orbitals

C atom: $1s^2 2s^2 2p^2$

sp hybridization



Carbino: modelo lineal

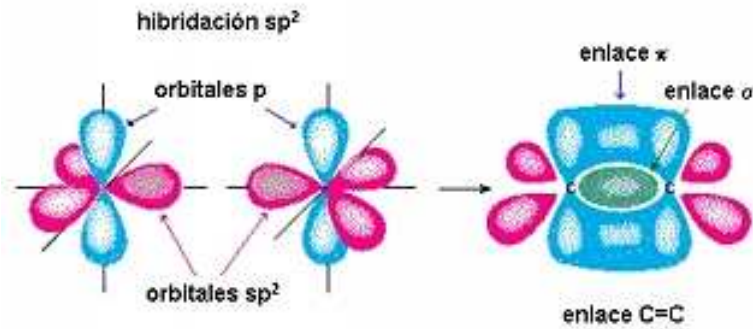


carbino (C18): modelo cíclico

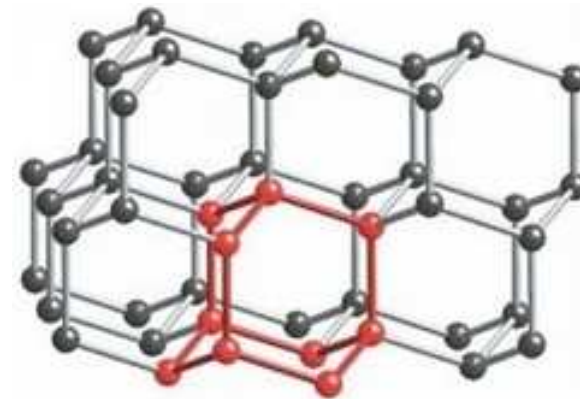
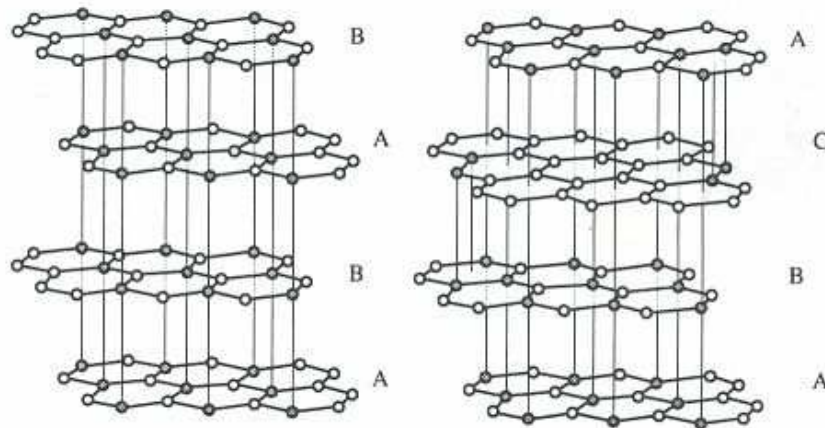
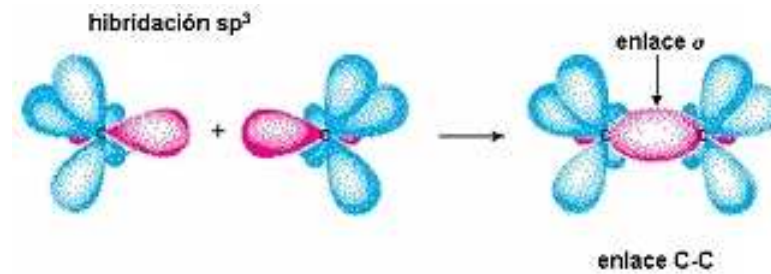
Carbon bonding orbitals

C atom: $1s^2 2s^2 2p^2$

sp^2 hybridization



sp^3 hybridization



Carbon, from the Latin word 'Carbo' = charcoal, coal



Charcoal is a blackish residue consisting of impure carbon obtained by removing water and other volatile constituents from animal and vegetation substances. Charcoal is usually produced by heating wood, sugar, bone char, or others substances in the absence of oxygen. It is **85% to 98% carbon** with the remainder consisting of volatile chemicals and ash.

olentzero



Charcoal in Art



Cave paintings made using charcoal and other materials have been dated as early as 30,000 years BC (although this one, in Rouffignac, is 'only' from ~13.000 BC)



Head of the Virgin, by Leonardo da Vinci (~1510).
Painted with charcoal and chalk.

Charcoal and Graphite in Art



charcoal drawing



pencil drawing
(started XVIth century)

Charcoal and graphite pencil properties are very different. Graphite has a layered crystal structure with very weak chemical bonds between the layers. As a result, a graphite pencil slides easily over paper leaving marks which result from the shearing away of tiny shards of graphite from the parent crystals. A graphite pencil can also be sharpened to a fine point, enabling accurate, fine lines to be drawn. Charcoal, instead, has a rough texture which does not glide smoothly over paper. Marks made with charcoal result from the deposition of tiny carbon particles into depressions in the fibrous paper surface. Graphite pencils can never achieve as dark a black as charcoal, since pure graphite is grey and metallic in appearance, rather than black.

Polymorphism (allotropy) of solid Carbon

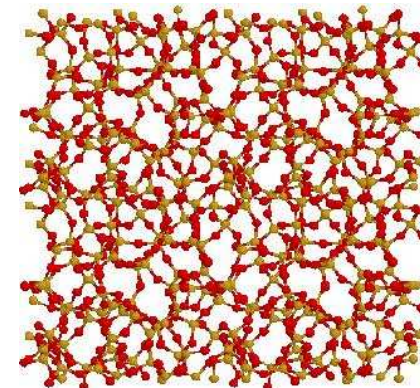
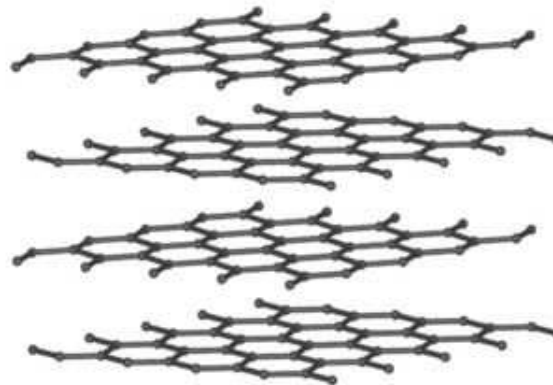
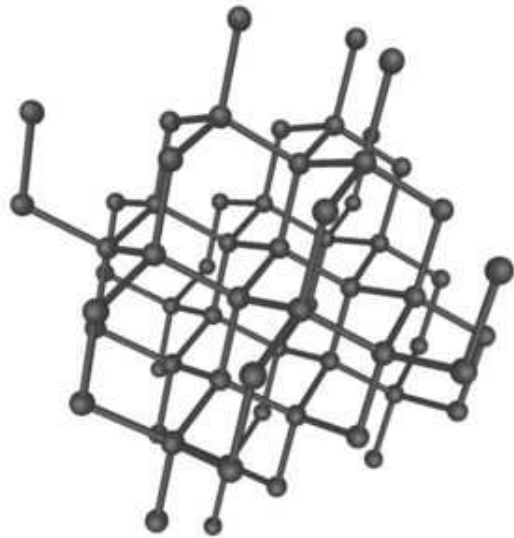
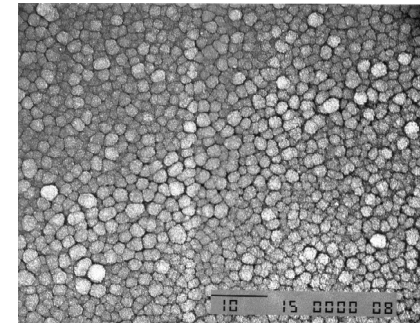
diamond



graphite



amorphous
Carbon



... + fullerenes!!!

Polymorphism (allotropy) of solid Carbon

diamond



graphite



The chemistry is the same (just C atoms), but...

- Diamond is the hardest natural mineral. Graphite one of the softest.
- Diamond is an excellent electrical insulator. Graphite is a good conductor.
- Diamond is the ultimate abrasive. Graphite is a very good lubricant.
- Diamond is usually transparent. Graphite is opaque.
- Diamond crystallizes in the Isometric system. Graphite in the hexagonal system.

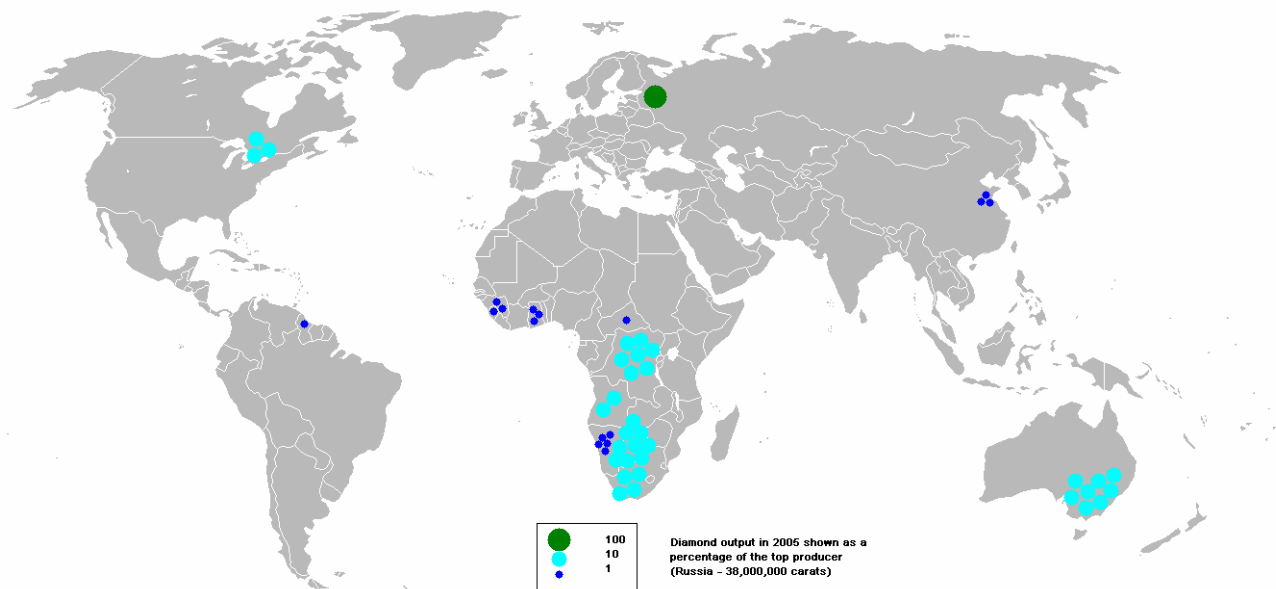
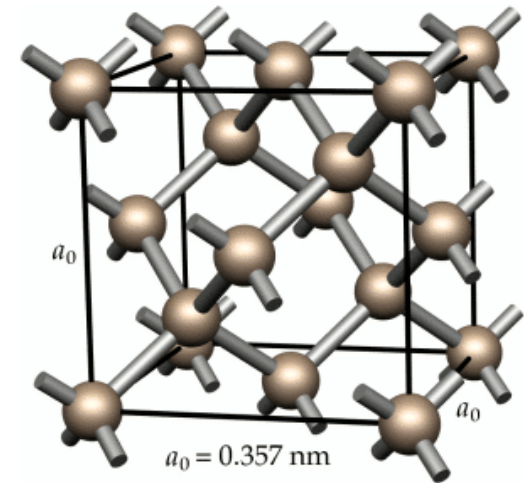
fullerenes have different physical and chemical properties as well

Polymorphism of Carbon: Diamond

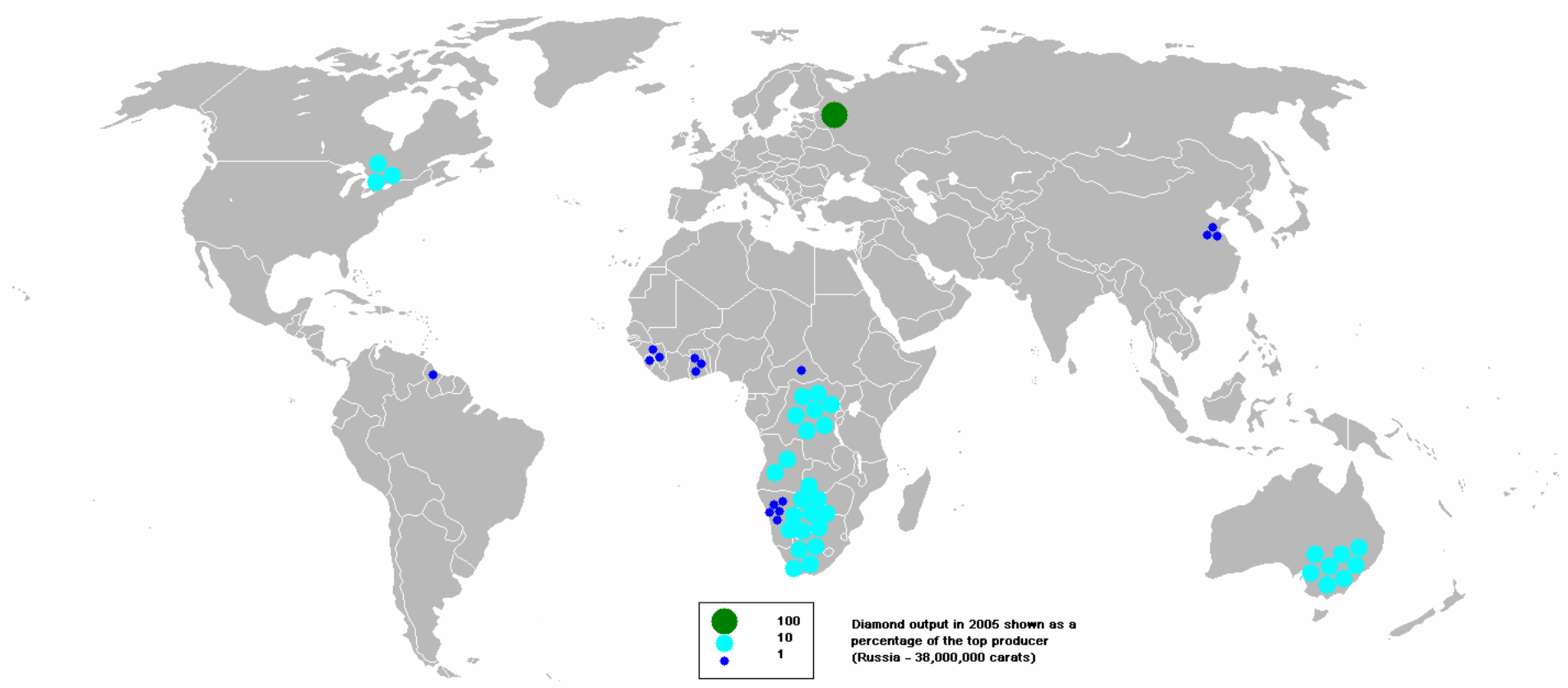


Diamond is the hardest known natural material

crystal structure:
a face-centred cubic (FCC)
lattice, with a basis of two
identical carbon atoms: one
at (0, 0, 0) and the other at
(1/4, 1/4, 1/4)



Polymorphism of Carbon: Diamond

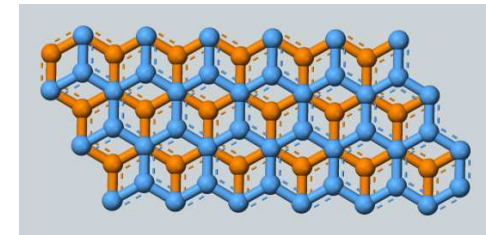
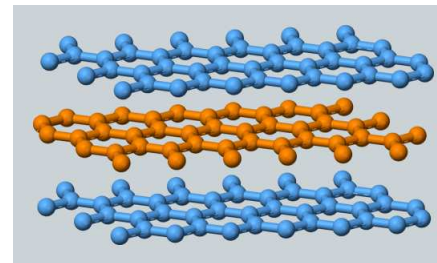
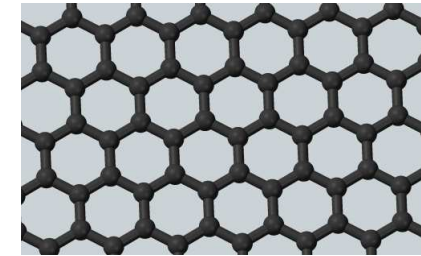


Polymorphism of Carbon: Graphite



Graphite is the most stable form of solid C. It is one of the softest minerals

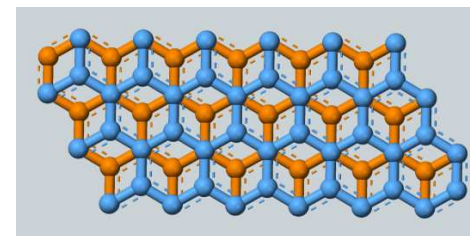
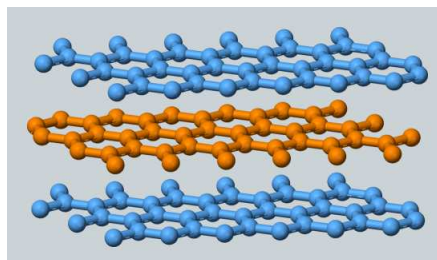
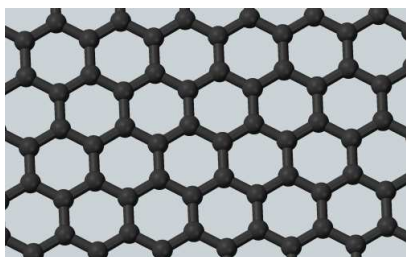
Graphite is arranged in a sheet like structure: hexagonal layers, with weak interaction among them



In the XVIth century, an enormous deposit of graphite was discovered at the site of *Seathwaite Fell* near Borrowdale, Cumbria, England. The locals found that it was very useful for marking sheep. This particular deposit of graphite was extremely pure and solid, and it could easily be sawn into sticks. This was and remains the only deposit of graphite ever found in this solid form.

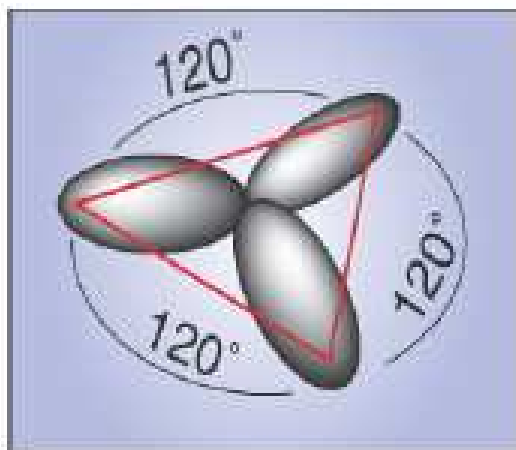


Polymorphism of Carbon: Graphite



C-C sp^2 : interatomic distance = 1.42 Å
Graphite interplanar distance = 3.35 Å

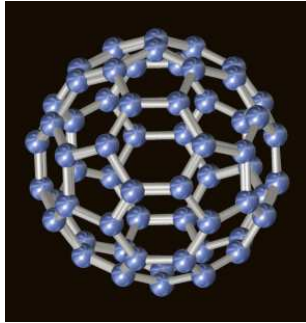
Some words on graphite electronic properties:



Each C atom is covalently bonded to three other surrounding carbon atoms.

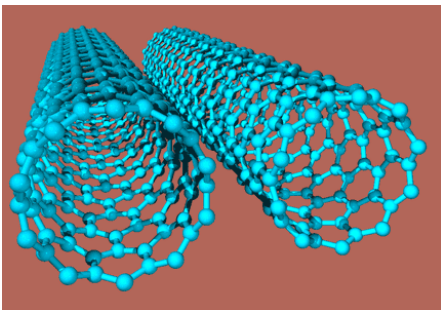
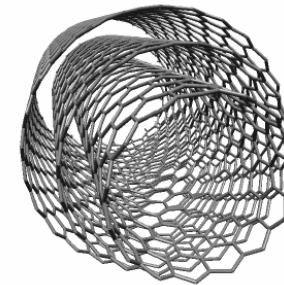
Each C atom possesses an sp^2 orbital hybridization. The π orbital electrons delocalized across the hexagonal atomic sheets of carbon contribute to the graphite's conductivity.

Polymorphism of Carbon: Fullerenes



1985: Harold Kroto, Robert Curl, and Richard Smalley discover the buckyball C_{60} (they received the 1996 Nobel Prize in Chemistry for that);
Kroto, Heath, O'Brien, Curl, and Smalley,
' C_{60} : *Buckminsterfullerene*', *Nature* **318**, 162 (1985).

1991: S. Iijima 'discovers' the MWCNTs
Helical microtubules of graphite carbon
Nature **354**, 56 (1991).



1993: First reports of SWCNTs
S. Iijima and T. Ichihashi, *Nature* **363**, 603 (1993)
D. S. Bethune *et al.*, *Nature* **363**, 605 (1993)

Previous works on Carbon low-dimensional systems

This article has appeared in
CARBON 44 (2006) 1621
(ELSEVIER)

Guest Editorial

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

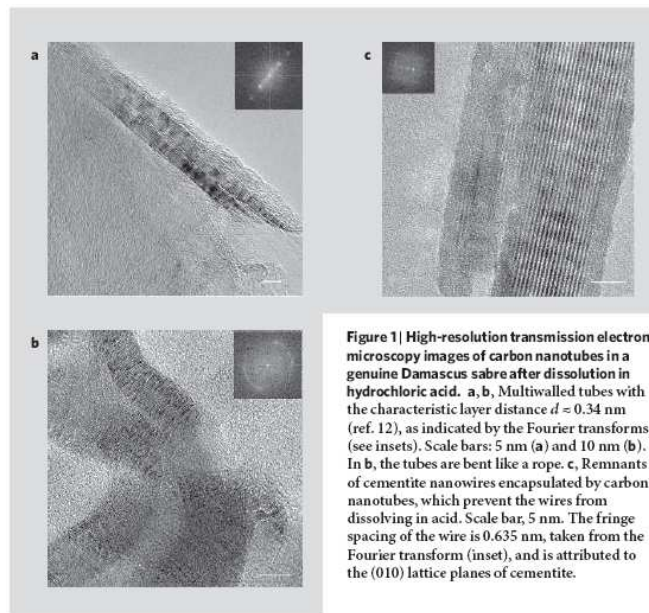
Carbon nanotubes play a large part in manuscript topics submitted to CARBON and, of course, to many other journals in almost every field of research and technology. Many of them start with referring to “the discovery of carbon nanotubes by Iijima in 1991...”. Such a recurrent sentence makes a statement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

Monthioux and Kuznetsov,
Carbon **44**, 1621 (2006).

Carbon Nanotechnology in History

In medieval times, 'Damascus blades' were extraordinarily strong, but still flexible enough to bend from hilt to tip. And they were reputedly so sharp that they could cleave a silk scarf floating to the ground, just as readily as a knight's body.

These superlative weapons gave the Muslims a great advantage, and their blacksmiths carefully guarded the secret to their manufacture. The secret eventually died out in the eighteenth century and no European smith was able to reproduce their method.

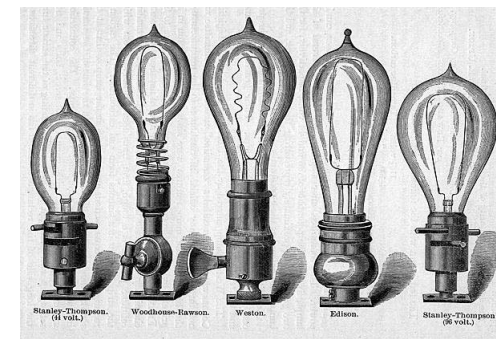
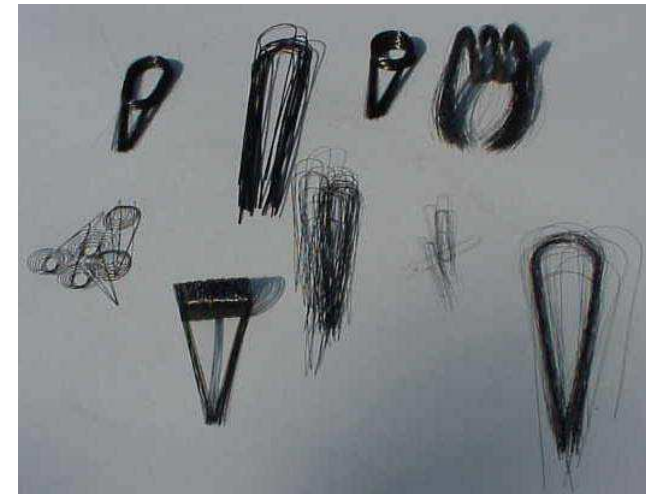


An electron microscope experimental analysis has recently shown that the steel in these blades contained carbon nanotubes, each one just slightly larger than half a nanometre.

Reibold *et al.*, Nature **444**, 286 (2006).

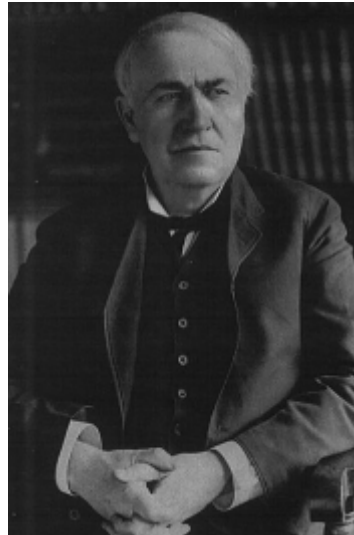
Previous works on Carbon low-dimensional systems: Carbon filaments in light bulbs

- **1809**: Sir Humphry Davy, Carbon Arc lamp
- **1841**: Frederick de Moleyns, powdered charcoal between platinum wires
- **1845**: John W. Starr, light bulb made of Carbon filaments
- **1851**: Jean Eugène Robert-Houdin publicly demonstrates incandescent light bulbs in Blois.
- **1854??**: carbonized bamboo filament by Heinrich Göbel
- **1875-80**: Joseph W. Swan, patent and commercialization of light bulbs, made of carbonized paper filaments
- **1878-80**: Thomas Edison's patents on Carbon filament based light bulbs.
- **1889**: Hugues and Chambers patent on the fabrication of Carbon filaments from vapor phase.

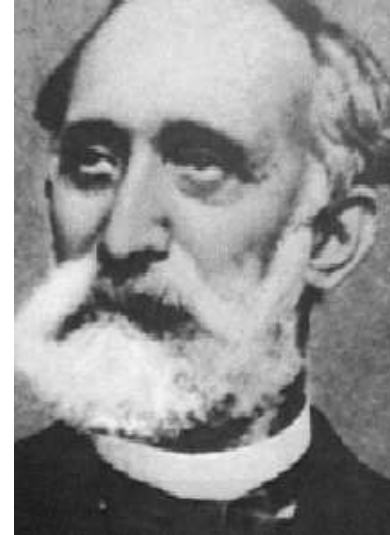


Although these filaments were macroscopic, it was thus demonstrated that thick carbon filaments could be vapour-grown

Previous works on Carbon low-dimensional systems: Carbon filaments in light bulbs



Thomas A. Edison



Heinrich Göbel

Göbel made a claim for the invention of the first practical bulb which he designed in 1854, a quarter of a century before Edison's patent.

But Lewis Latimer demonstrated that the bulbs Göbel had purportedly built in the 1850's had in fact been built much later, and actually found the glassblower who had constructed the fraudulent exhibits for Göbel.

Tomas Edison: not only bulbs

Black Maria was Thomas Edison's movie production studio in New Jersey. It was built in 1893 and is considered by many as "America's First Movie Studio."



Edison movies:

[On Frankenstein](#)

[On street dance](#)

[On female boxing](#)

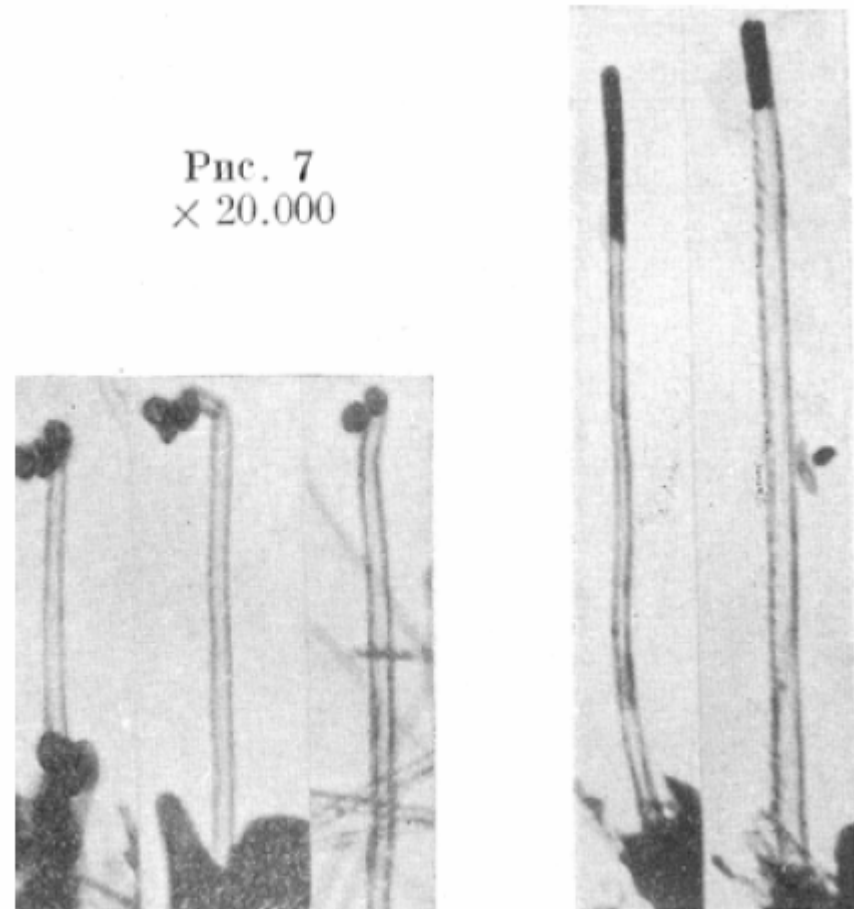


Previous works on Carbon low-dimensional systems: TEM images of C nanotubes (1952)

*electron microscopy,
necessary for nanometer
resolution, was developed
in the late 1930's*

Figures clearly show carbon filaments exhibiting a continuous inner cavity, thereby forming tubes. The indicated magnification value allows one to calculate that the diameters of the carbon tubes imaged are in the range of 50 nm.

This is consistent with their perfect electron transparency in-between the dark contrast representing the tube walls. The nanotubes imaged are obviously of MWCNT type, with walls being made up from 15-20 graphenes, assuming a concentric texture (which cannot be ascertained).



L. V. Radushkevich, V. M. Lukyanovich,
*O strukture ugleroda, obrazujucegosja pri termiceskom
razlozenii okisi ugleroda na zeleznom kontakte*
Zurn. Fisic. Chim. **26**, 88 (1952).

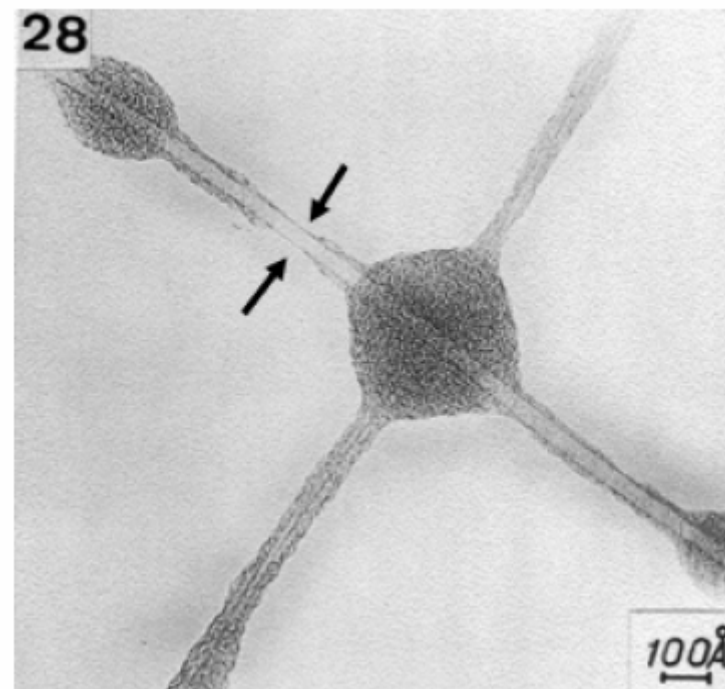
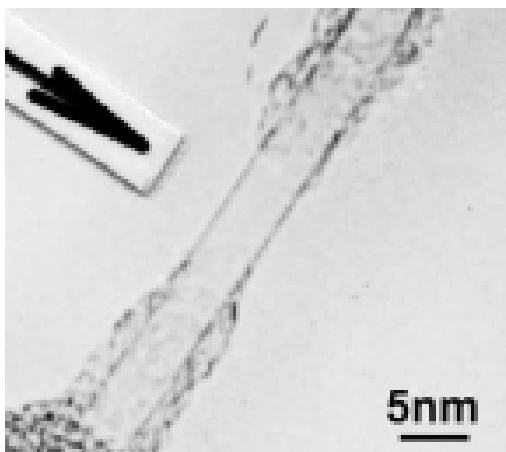
**Previous works on Carbon low-dimensional systems:
more TEM images of CNTs (1958)**

M. Hillert and N. Lange,
The structure of graphite filaments,
Zeitschr. Kristall **111**, 24 (1958)

It is quoted that
“Filamentary growth of graphite
... has recently been discovered again, ...”

Previous works on Carbon low-dimensional systems: more TEM images of CNTs (1976)

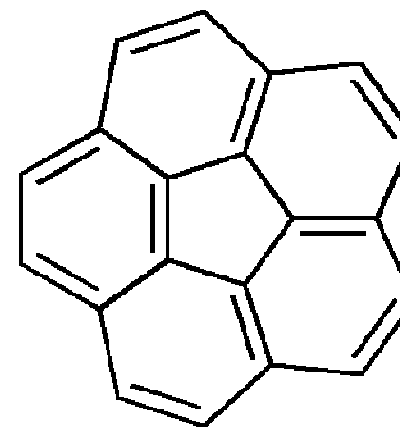
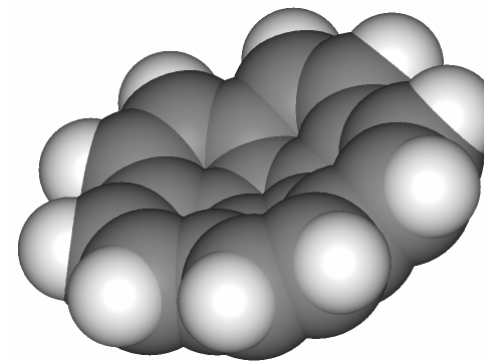
TEM image of what could be a SWCNT specifically from the bare part between arrows. However, considering the diameter of this tube (~5 nm) and what is expected from calculations of the energetic stability of a SWCNT, it is unlikely that a nanotube with such a large diameter could be single-walled.



A. Oberlin, M. Endo, T. Koyama,
*Filamentous growth of carbon
through benzene decomposition.*
J. Cryst. Growth **32** , 335 (1976).

Previous works on Carbon low-dimensional systems: prediction of C₆₀ fullerenes by Osawa (1970)

Eiji Osawa of Toyohashi University of Technology, noticed in 1970 that the structure of a corannulene molecule was a subset of a soccer-ball shape, and he made the hypothesis that a full ball shape could also exist. His idea was reported in Japanese magazines, but did not reach Europe or America.



Corannulene C₂₀H₁₀

First report of C₆₀ buckyballs (1985)

Kroto, Heath, O'Brien, Curl, and Smalley,
'C₆₀: Buckminsterfullerene', *Nature* **318**, 162 (1985).

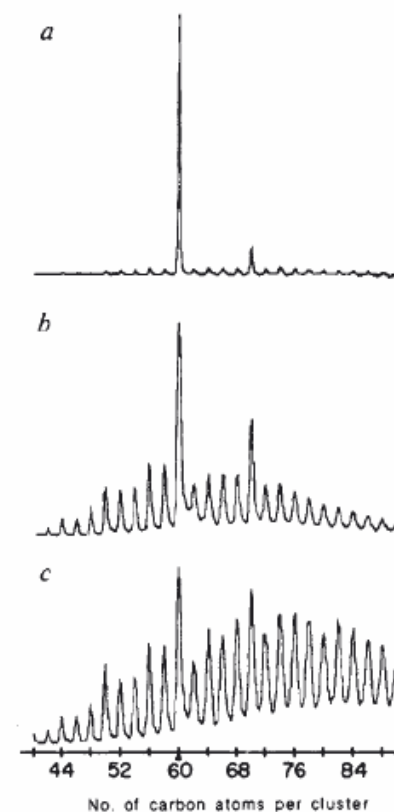
C₆₀: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl
& R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical
Engineering, Rice University, Houston, Texas 77251, USA

During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells¹, graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C₆₀ molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C₆₀ molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.



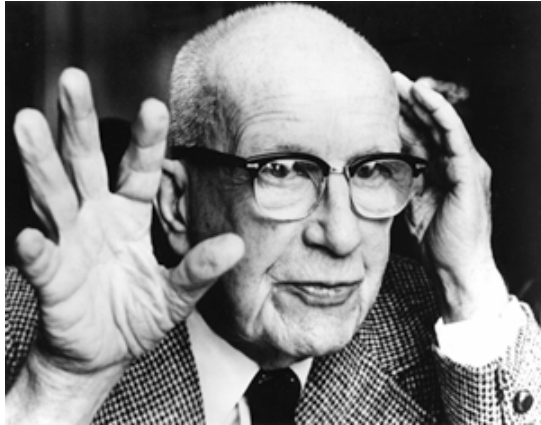
First report of C₆₀ buckyballs (1985)

Kroto, Heath, O'Brien, Curl, and Smalley,
'C₆₀: Buckminsterfullerene', Nature **318**, 162 (1985).

valences. Thus a search was made for some other plausible structure which would satisfy all sp² valences. Only a spheroidal structure appears likely to satisfy this criterion, and thus Buckminster Fuller's studies were consulted (see, for example, ref. 7). An unusually beautiful (and probably unique) choice is the truncated icosahedron depicted in Fig. 1. As mentioned above, all valences are satisfied with this structure, and the molecule appears to be aromatic. The structure has the symmetry of the icosahedral group. The inner and outer surfaces are covered with a sea of π electrons. The diameter of this C₆₀ molecule is ~ 7 Å, providing an inner cavity which appears to be capable of holding a variety of atoms⁸.

We are disturbed at the number of letters and syllables in the rather fanciful but highly appropriate name we have chosen in the title to refer to this C₆₀ species. For such a unique and centrally important molecular structure, a more concise name would be useful. A number of alternatives come to mind (for example, ballene, spherene, soccerene, carbosoccer), but we prefer to let this issue of nomenclature be settled by consensus.

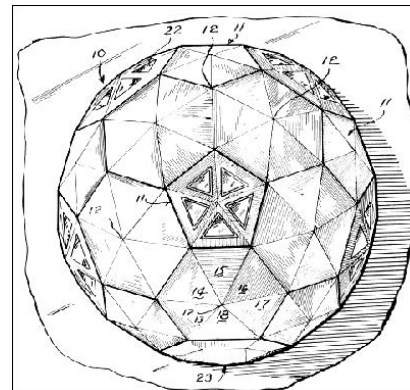
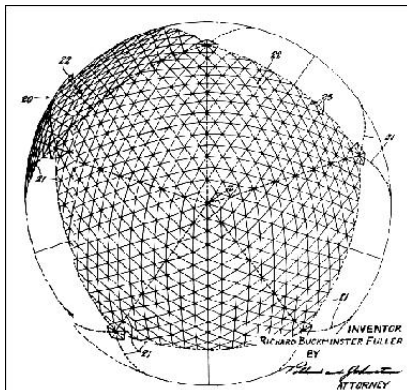
Naming buckyballs and fullerenes: Richard Buckminster Fuller



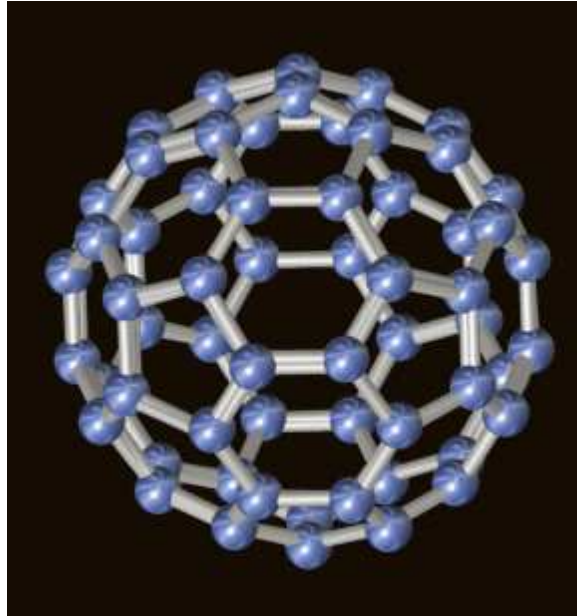
Richard Buckminster Fuller (1895-1983)
American inventor, architect, engineer,
mathematician, poet and cosmologist
(according to the Buckminster-Fuller Institute).
And theorist of Geodesic Domes

A sphere encloses the most volume with the least surface. Thus, any dome that is a portion of a sphere has the least surface through which to lose heat or intercept potentially damaging winds.

A geodesic dome uses a pattern of self-bracing triangles in a pattern that gives maximum structural advantage, thus theoretically using the least material possible. (A "geodesic" line on a sphere is the shortest distance between any two points.)



Physical and chemical properties of C_{60}



- Buckyballs are very stable (indeed this is one of the reasons why Smalley, Curl, and Kroto initially considered its spherical-like geodesical shape).
- They are resilient to impact and deformation.
- They are very inert, and are not as prone to reactions as other carbon molecules.
- Since they have cyclo-hexanes in abundance, they are very aromatic (delocalized electrons)

'First' report of multi-walled Carbon nanotubes (1991)

S. Iijima,
Helical microtubules of graphite carbon
 Nature **354**, 56 (1991).

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 fullerenes¹ 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 appears that this helical structure may aid the growth process. The formation of these needles, ranging from a few to a few tens of nanometres in diameter, suggests that engineering of carbon structures should be possible on scales considerably greater than those relevant to the fullerenes.

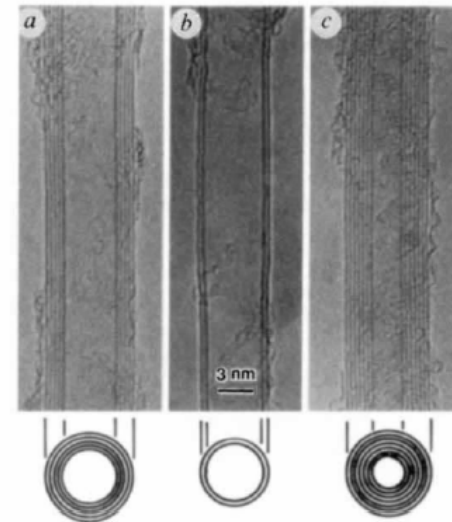


FIG. 1 Electron micrographs of microtubules of graphitic carbon. Parallel dark lines correspond to the (002) lattice images of graphite. A cross-section of each tubule is illustrated. a, Tube consisting of five graphitic sheets, diameter 6.7 nm. b, Two-sheet tube, diameter 5.5 nm. c, Seven-sheet tube, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm).

this article is the first unambiguous evidence for the possibility of growing nano-sized carbon nanotubes without the need of any catalyst

'First' report of multi-walled Carbon nanotubes (1991)

S. Iijima,
Helical microtubules of graphite carbon
 Nature **354**, 56 (1991).

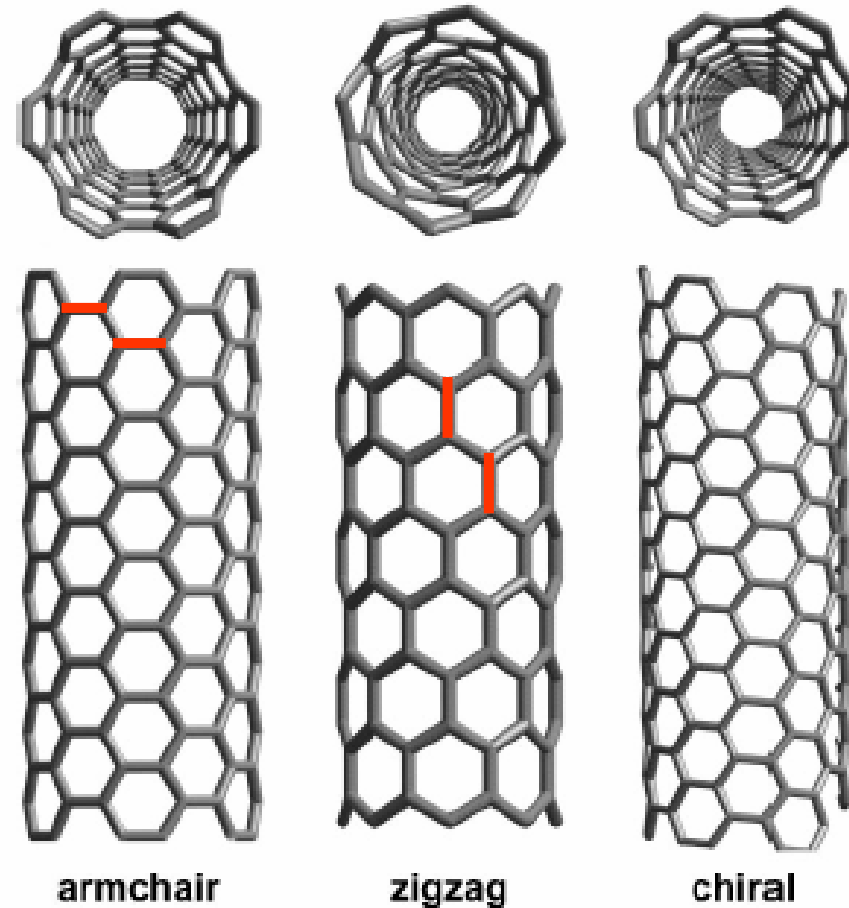
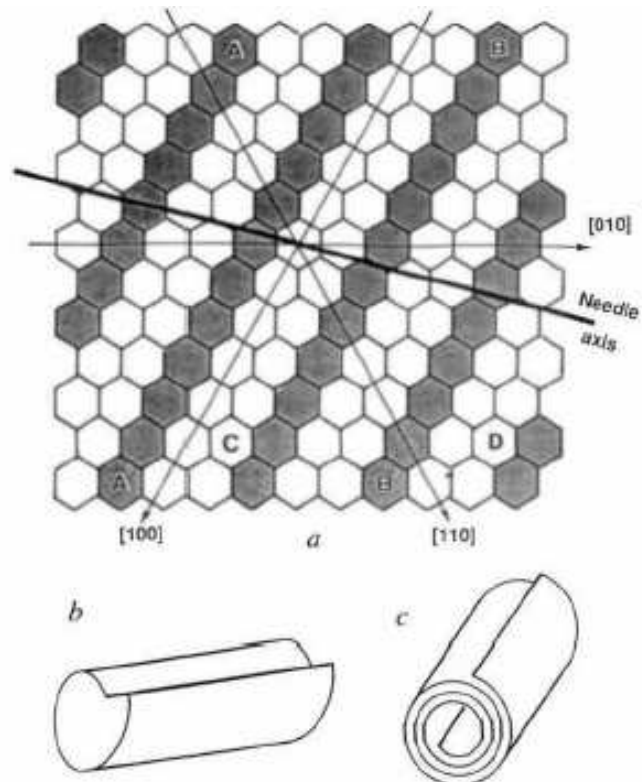


FIG. 4 a, Schematic diagram showing a helical arrangement of a graphitic carbon tubule, which is unrolled for the purposes of explanation. The tube axis is indicated by the heavy line and the hexagons labelled A and B, and A' and B', are superimposed to form the tube (for the significance of C and D, see text). b, The row of hatched hexagons forms a helix on the tube. The number of hexagons does not represent a real tube size, but the orientation is correct. c, A model of a scroll-type filament.

First reports of single-walled Carbon nanotubes (1993)

S. Iijima and T. Ichihashi, Nature **363**, 603 (1993)

D. S. Bethune, C. H. Klang, M. S. De Vries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers, Nature **363**, 605 (1993)

Single-shell carbon nanotubes of 1-nm diameter

Sumio Iijima & Toshinari Ichihashi

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



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



First reports of single-walled Carbon nanotubes (1993)

Single-shell carbon nanotubes of 1-nm diameter

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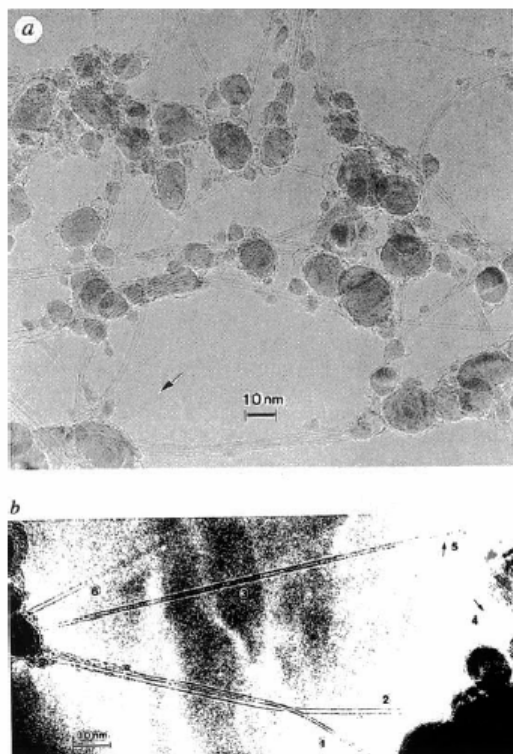


FIG. 1a. Electron micrograph showing bundles of single-shell carbon nanotubes which are curved and entangled. Dark blobs are cementite particles which assist in tubule growth. A terminated tubule is indicated by an arrow. *b*. Electron micrograph showing individual single-shell nanotubes. The tubule labelled 1 is 0.75 nm in diameter and tubule 2 is 1.37 nm in diameter. A straight tubule (3) and two terminated ones (4 and 5) can also be seen.

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

D. S. Bethune, C.H. Kiang*, 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

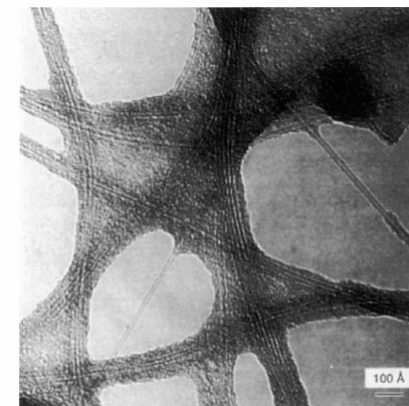


FIG. 2 TEM image at higher magnification showing details of the web-like material. Running through the deposited non-graphitic carbon are single-walled nanotubes about 1.2 nm in diameter. Bare portions of these nanotubes are also evident. The dark spot in the upper-right corner is a cobalt cluster.

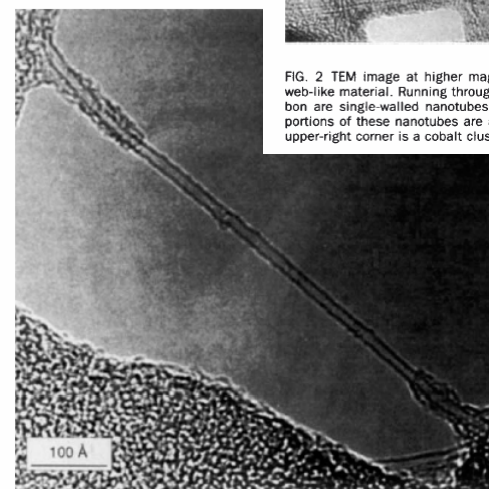


FIG. 3 TEM image of a bare section of a single-walled nanotube. The round objects adhering to the tube have diameters corresponding to fullerenes with 60–100 carbons.

Electronic properties of single-walled Carbon nanotubes

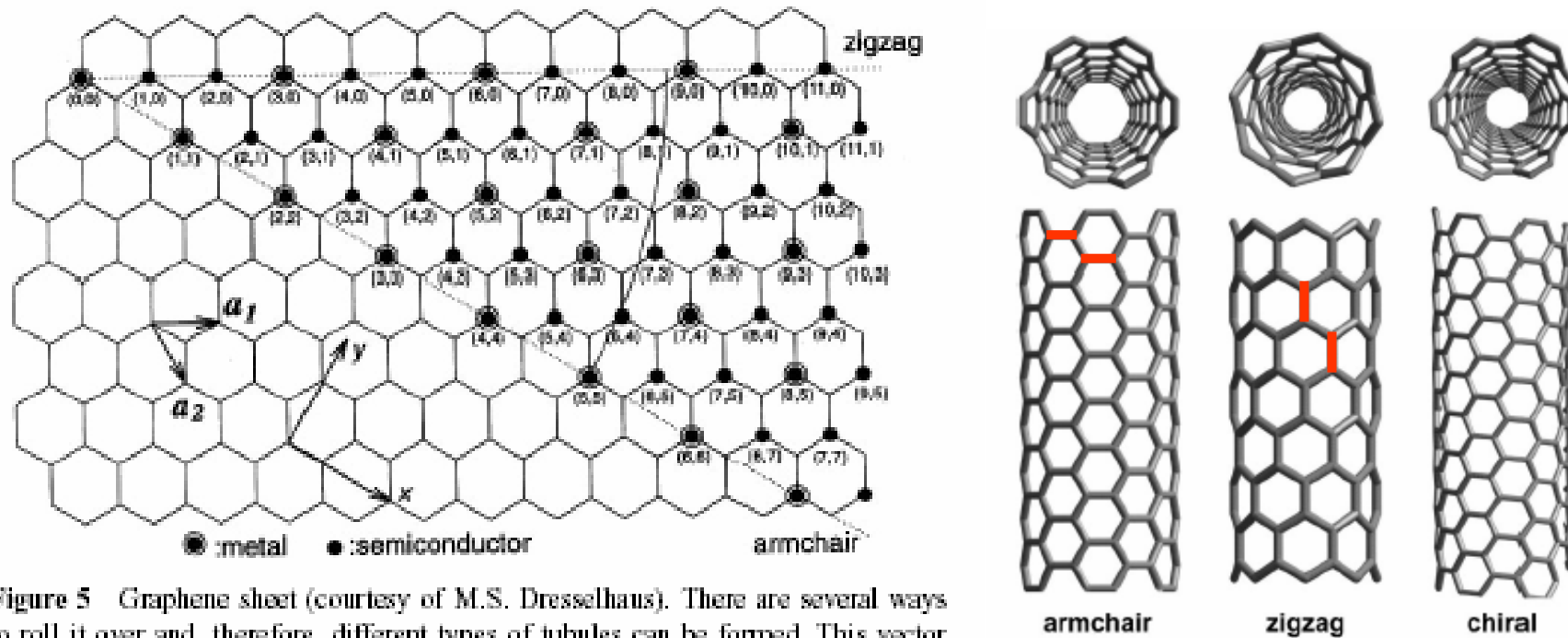
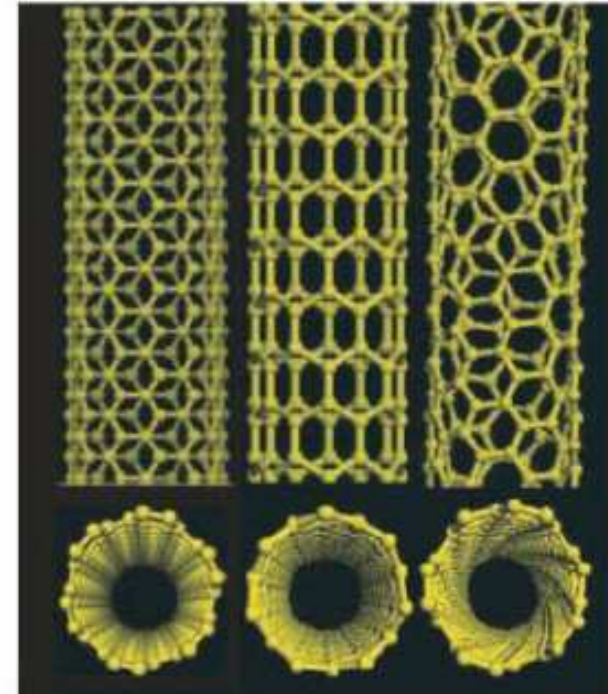
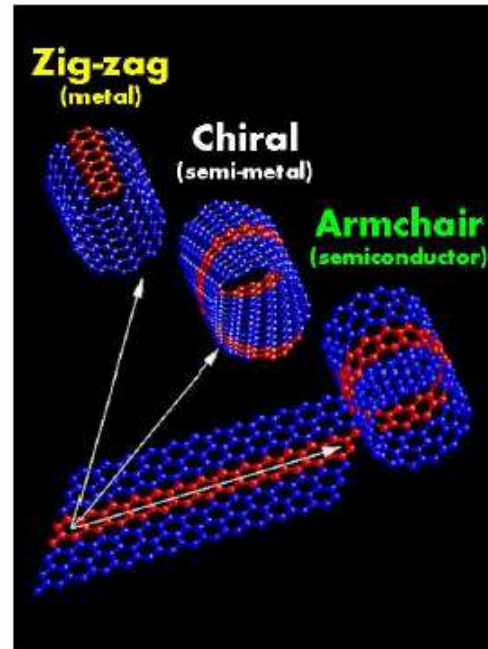
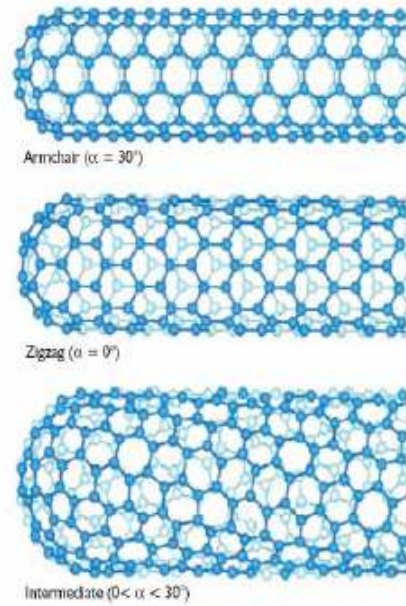


Figure 5 Graphene sheet (courtesy of M.S. Dresselhaus). There are several ways to roll it over and, therefore, different types of tubules can be formed. This vector convention is used to define each point on the lattice. Unitary vectors a_1 and a_2 are necessary to determine the rolling direction expressed by vector C_n . Note that all armchair tubes are metallic, as well as tubes with indices $(m - n = 3)$.

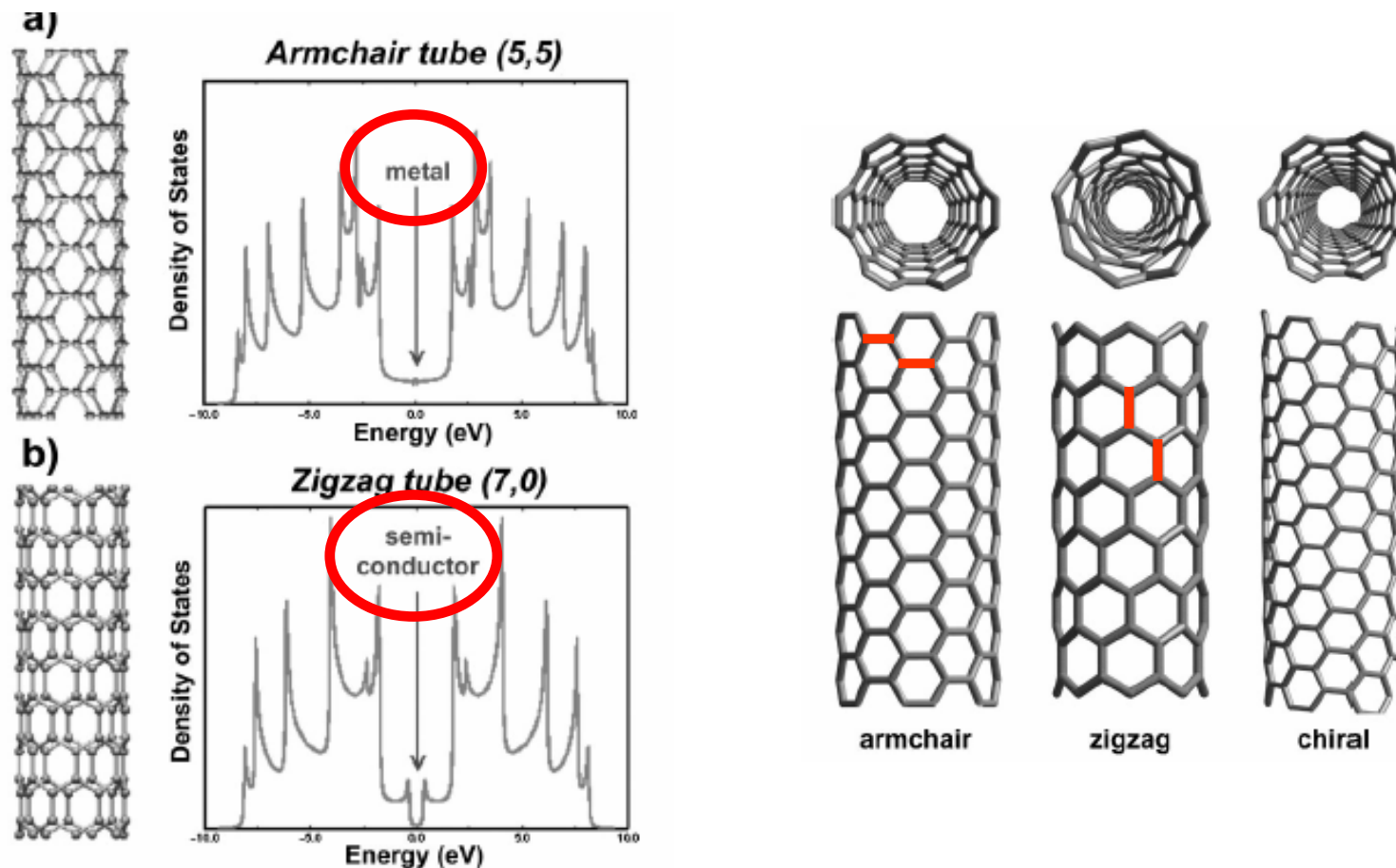
Electronic properties of single-walled Carbon nanotubes



Source: Baughman, R. H., Zakhidov, A. A., Heer, W. A.
Carbon Nanotubes-the Route Toward Applications.
Science's Compass Review. Science, 297, 787-792
(2002).

Electronic properties of single-walled Carbon nanotubes

Carbon nanotubes are cylindrical carbon molecules with novel properties that make them potentially useful in a wide variety of applications. Nanotubes are composed entirely of sp^2 bonds, similar to graphite.

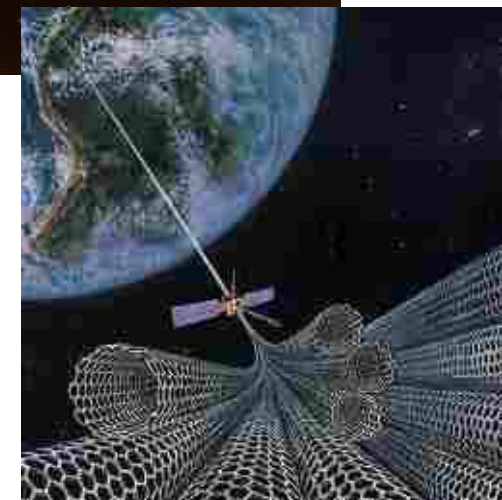
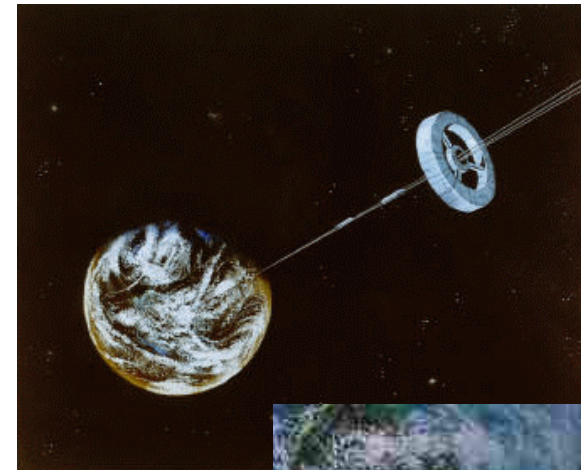


Further properties of single-walled Carbon nanotubes

Single-wall carbon nanotubes can behave like metals or semiconductors, can conduct electricity better than copper, can transmit heat better than diamond, and rank among **the strongest** materials known.

the space elevator

One end of the elevator would be attached to a satellite or a space station and the other end would be anchored someplace on Earth. When you want to go up into space or put something into orbit, all you would have to do would be to press a button. Impossible? What would it take? First of all, it would take a very very strong cable. A cable so strong that it could lift thousands of pounds. It would also take a very very long cable, probably about 100 miles long. One way to build a light and strong cable could be to use carbon nanotubes.



The space elevator

Lanka/Taprobane: he moved the island 800
Sri Lanka lies between 6 and 10 degrees north

From NASA web site:

http://science.nasa.gov/headlines/y2000/ast07sep_1.htm

According to Smitherman, construction is not feasible today but it could be toward the end of the 21st century. "First we'll develop the technology," said Smitherman. "In 50 years or so, we'll be there. Then, if the need is there, we'll be able to do this. That's the gist of the report."

Smitherman's paper credits Arthur C. Clarke with introducing the concept to a broader audience. In his 1978 novel, *Fountains of Paradise*, engineers construct a space elevator on top of a mountain peak in the mythical island of Taprobane (closely based on Sri Lanka, the country where Clarke now resides). The builders use advanced materials such as the carbon nanofibers now in laboratory study.

"His book brought the idea to the general public through the science fiction community," said Smitherman. But Clarke wasn't the first.



As early as 1895, a Russian scientist named Konstantin Tsiolkovsky suggested a fanciful "Celestial Castle" in geosynchronous Earth orbit attached to a tower on the ground, not unlike Paris's Eiffel tower. Another Russian, a Leningrad engineer by the name of Yuri Artsutanov, wrote some of the first modern ideas about space elevators in 1960. Published as a non-technical story in *Pravda*, his story never caught the attention of the West. *Science* magazine ran a short article in 1966 by John Isaacs, an American oceanographer, about a pair of whisker-thin wires extending to a geostationary satellite. The article ran basically unnoticed. The concept finally came to the attention of the space flight engineering community through a technical paper written in 1975 by Jerome Pearson of the Air Force Research Laboratory. This paper was the inspiration

for Clarke's novel.

The space elevator

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Konstantin Tsiolkovsky

From Wikipedia, the free encyclopedia

(Redirected from [Konstantin Eduardovich Tsiolkovsky](#))

Konstantin Eduardovich Tsiolkovsky (Russian: Константи́н Эдуа́рдович Циолко́вский; Polish: *Konstanty Ciołkowski*) (September 17 [o.s. September 5] 1857 – September 19, 1935) was an Imperial Russian and Soviet rocket scientist and pioneer of astronautic theory who spent most of his life in a log house on the outskirts of Kaluga, about 200 km (125 miles) southwest of Moscow.

Contents [hide]

1 Biography

2 Work

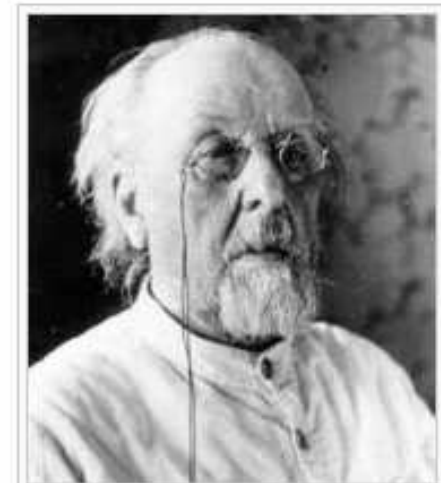
3 Quotes

4 Tributes

5 See also

6 Works

7 Notes



Konstantin Eduardovich 

[\[edit\]](#)

Biography

He was born in [Izhevskoye](#) (now in [Spassky District](#), [Ryazan Oblast](#)), in the [Russian Empire](#), to a middle-class family. His father, Edward Ciołkowski, was [Polish](#); his mother, Maria Yumasheva, was an educated [Russian](#) woman. As a child, Konstantin caught [scarlet fever](#) and became hard of hearing. He was not accepted at elementary schools because of his hearing problem, so he was [home schooled](#) until the age of sixteen.

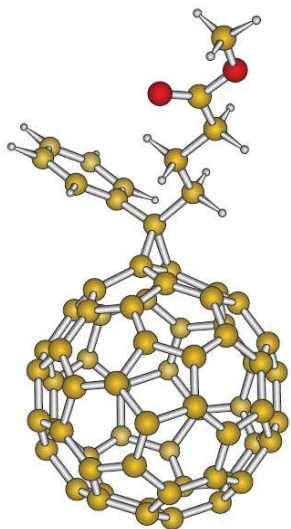
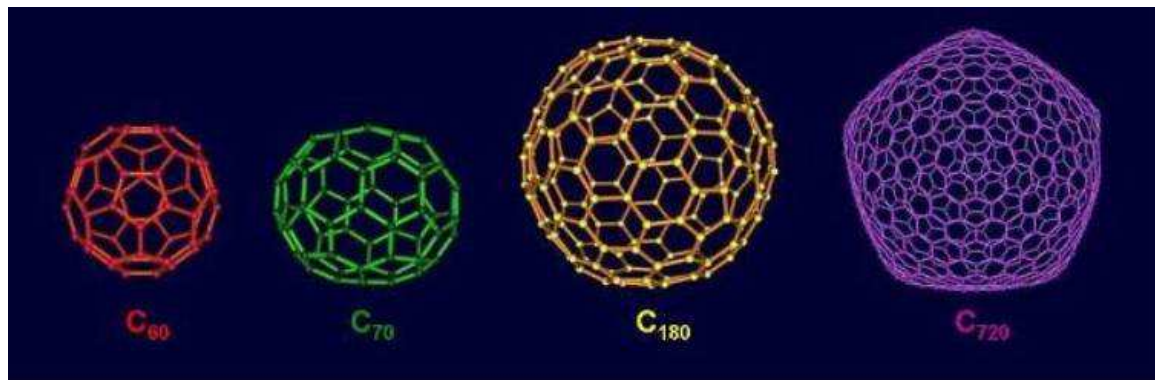
Tsiolkovsky theorized many aspects of [space travel](#) and [rocket propulsion](#). He is considered the father of human space flight and the first man to conceive the [space elevator](#), becoming inspired in 1895 by the newly-constructed [Eiffel Tower](#) in [Paris](#).

He was also an adherent of philosopher [Nikolai Fyodorov](#), and believed that colonizing space would lead to the perfection of the human race, with immortality and a carefree existence.

[\[edit\]](#)

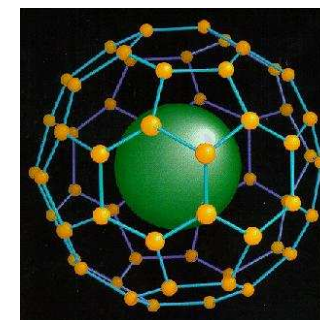
Further types of fullerenes

other sizes

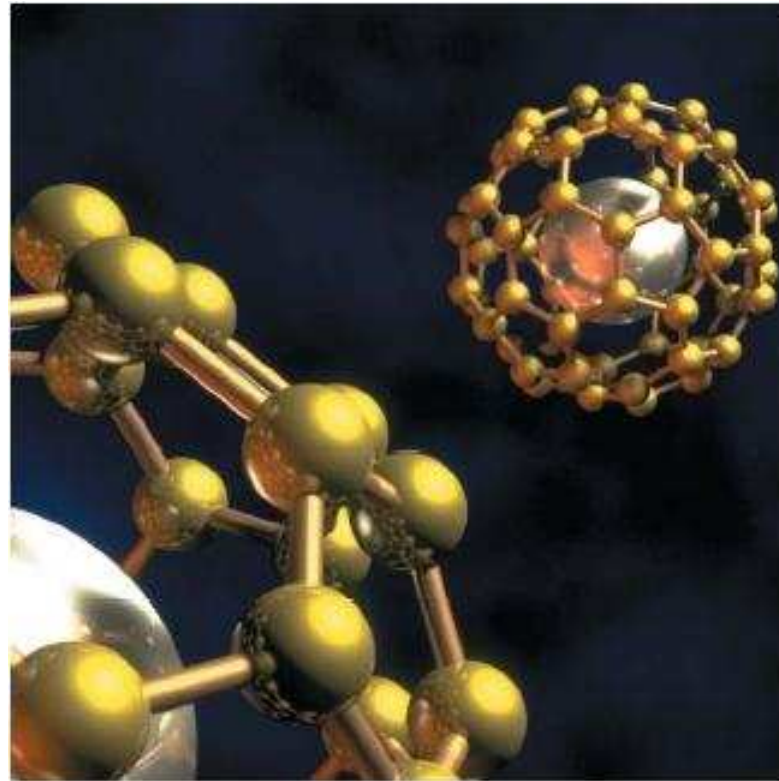


functionalized fullerenes, e. g.
PCBM= Phenyl-C₆₁-Butyric acid Methyl ester

endohedral fullerenes (containing metal atoms)

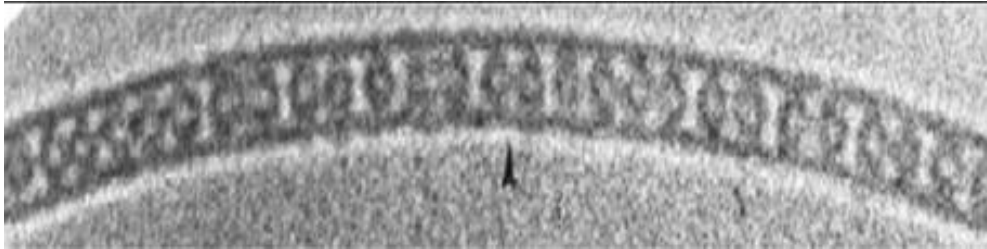


fullerenes as cages

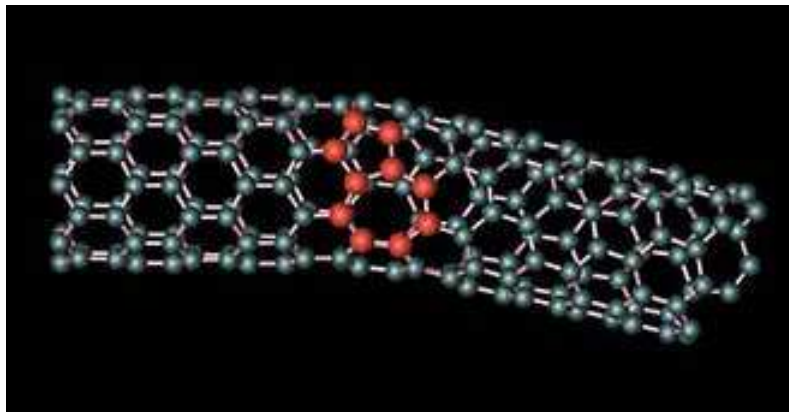


Computer-generated model of a 60-carbon molecule enclosing a potassium ion.

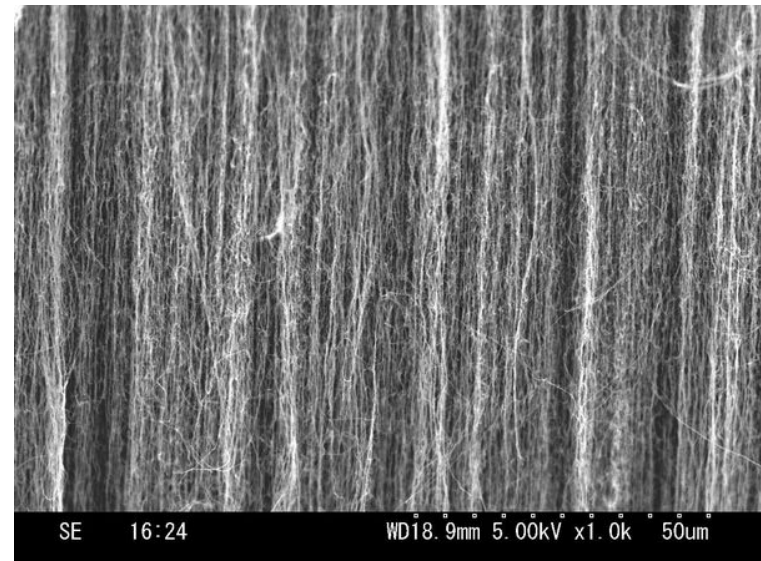
More CNTs



Peapods:
CNTs filled with C60 molecules

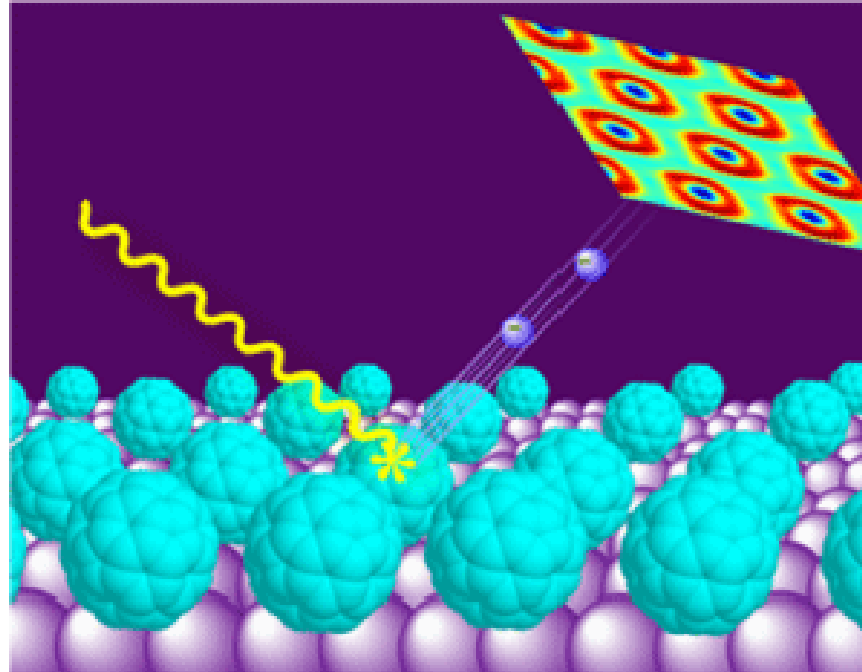


The joining of two carbon
nanotubes with different
electrical properties can form
a diode



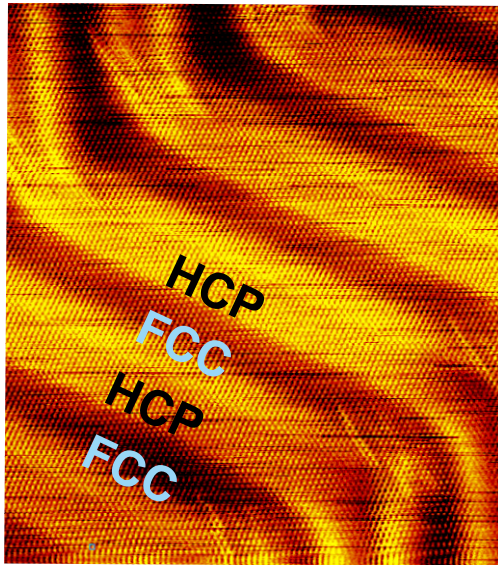
arrays of CNTs

layers of fullerenes

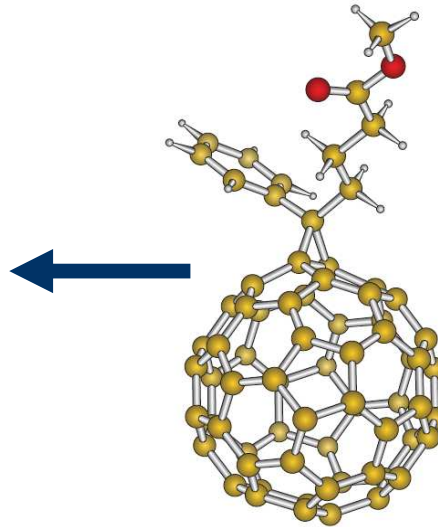


Angle-resolved photoemission of a buckyball monolayer (K₃C₆₀) on a silver substrate yields features of the electronic structure, including the two-dimensional intensity map in reciprocal (momentum or k) space of electrons with energy around the Fermi energy (Fermi surface).

Yang *et al.*, Science **300**, 303 (2003)



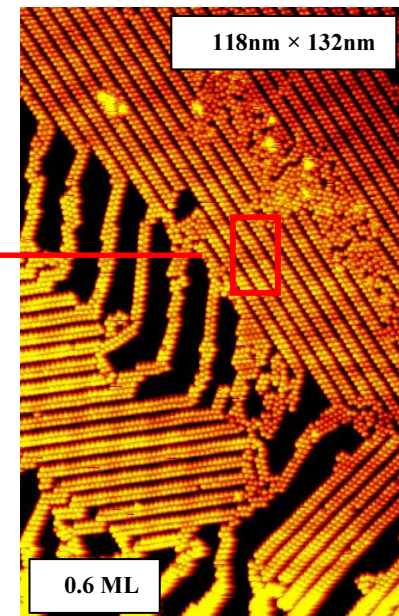
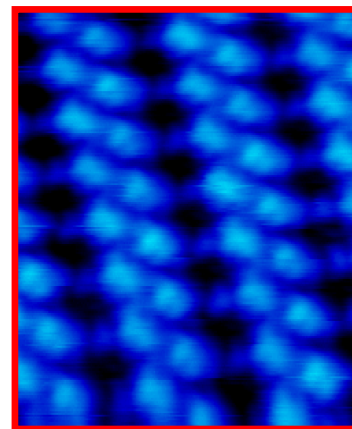
herringbone reconstruction of Au(111) surface



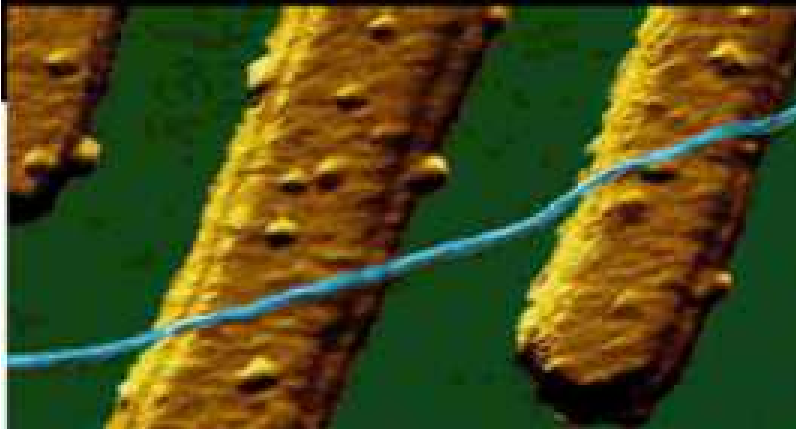
PCBM on Au(111)

PCBM=
Phenyl-C₆₁-Butyric acid
Methyl ester

parallel twin chains are connected laterally to form a well-ordered 2D arrangement

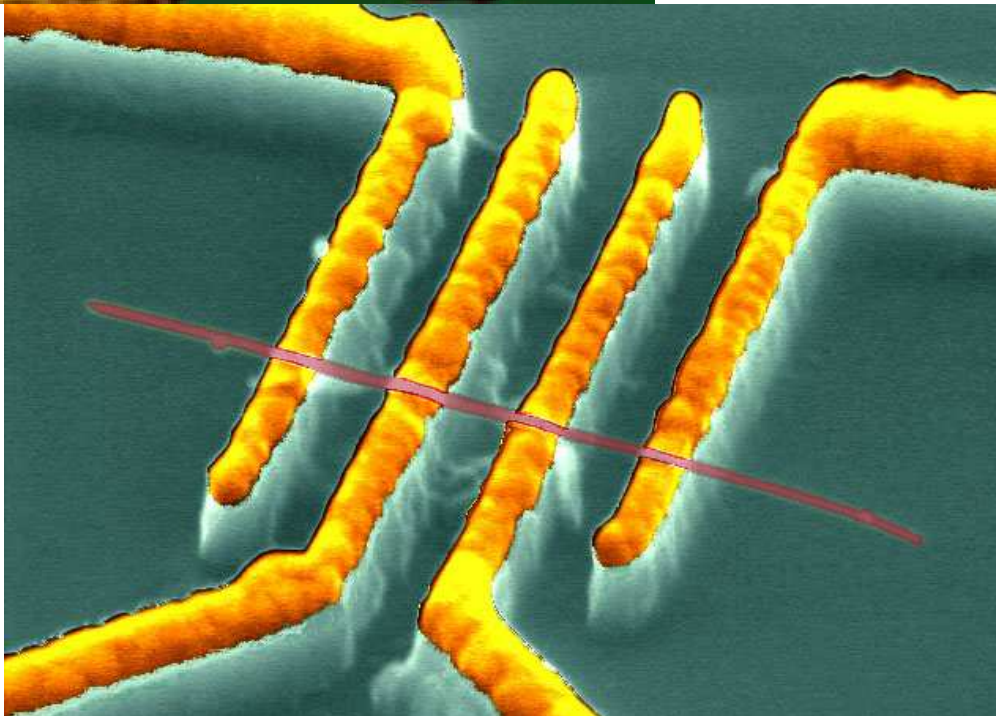


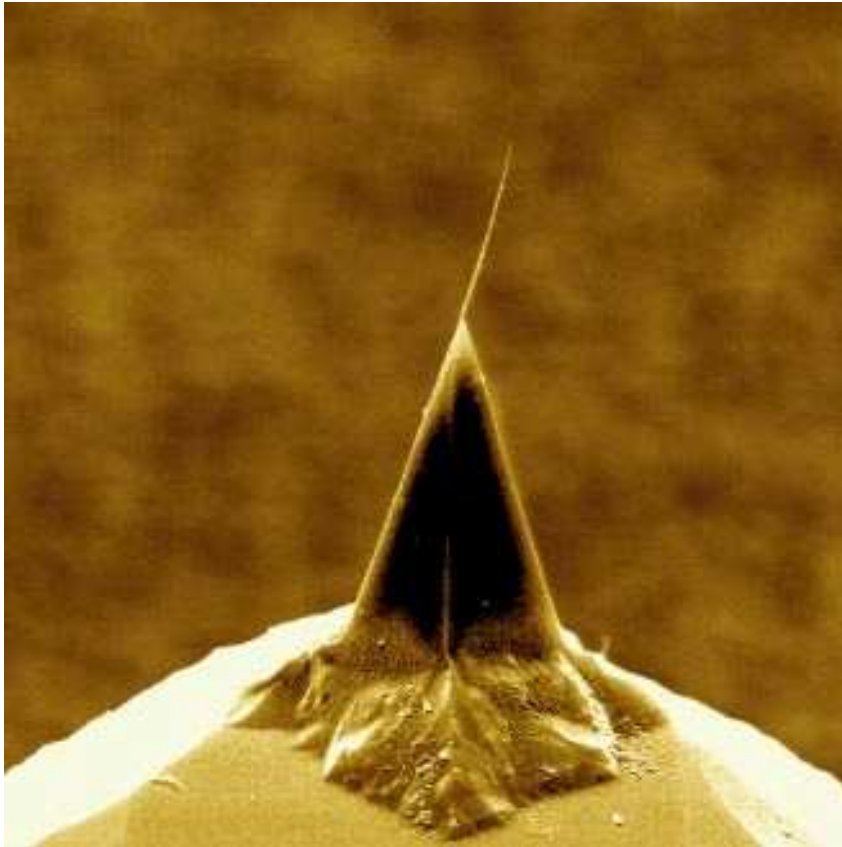
molecular electronics



Molecular Electronics combines Nanoelectronics with Synthetic Supramolecular Chemistry. Nanotubes are good candidates to act as 'conducting wires' because

- their length can be of the order of micrometer,
- they can act as ideal one dimensional conductors,
- they are among the strongest materials in nature





**Scanning electron-microscopy (SEM)
image of a carbon nanotube
attached to a cantilever tip
(Swiss Nanoscience Institute SNI)**

See for instance

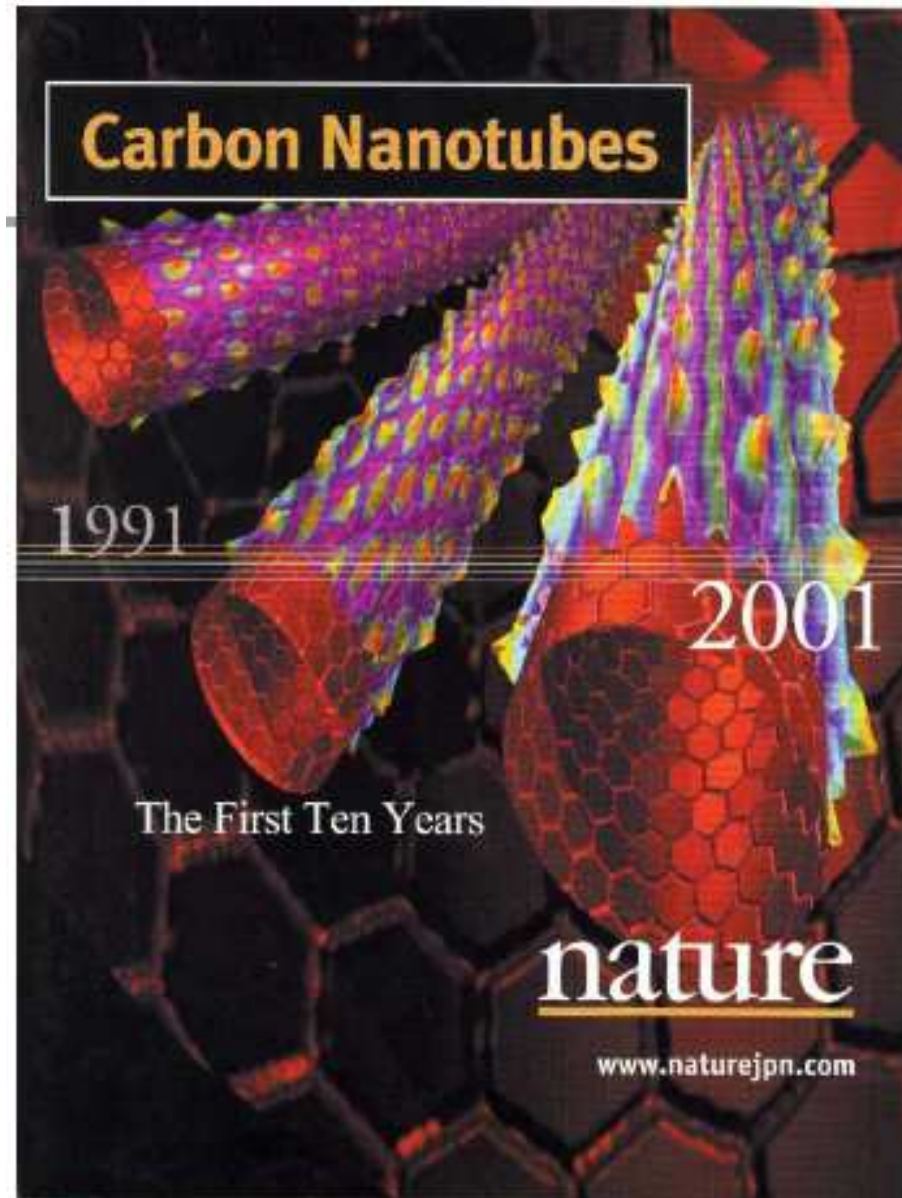
Using an electroconductive carbon nanotube probe tip in scanning nonlinear dielectric microscopy
by K. Ishikawa and Y. Cho, *Rev. Sci. Instrum.* **77**, 103708 (2006)

Large scale use of Carbon Nanotubes



Nanotubes have become the stars of scientific graphic design, the icons of Nanotechnology.

Two-dimensional imaging of electronic wavefunctions in carbon nanotubes
S.G.Lemay *et al.*,
Nature **412**, 617 (2001)





NANOTECHNOLOGY:
Logic circuits with
Carbon Nanotubes –
Toward Nanocomputers

Image TU Delft/Gripp
Science 294 (2001)

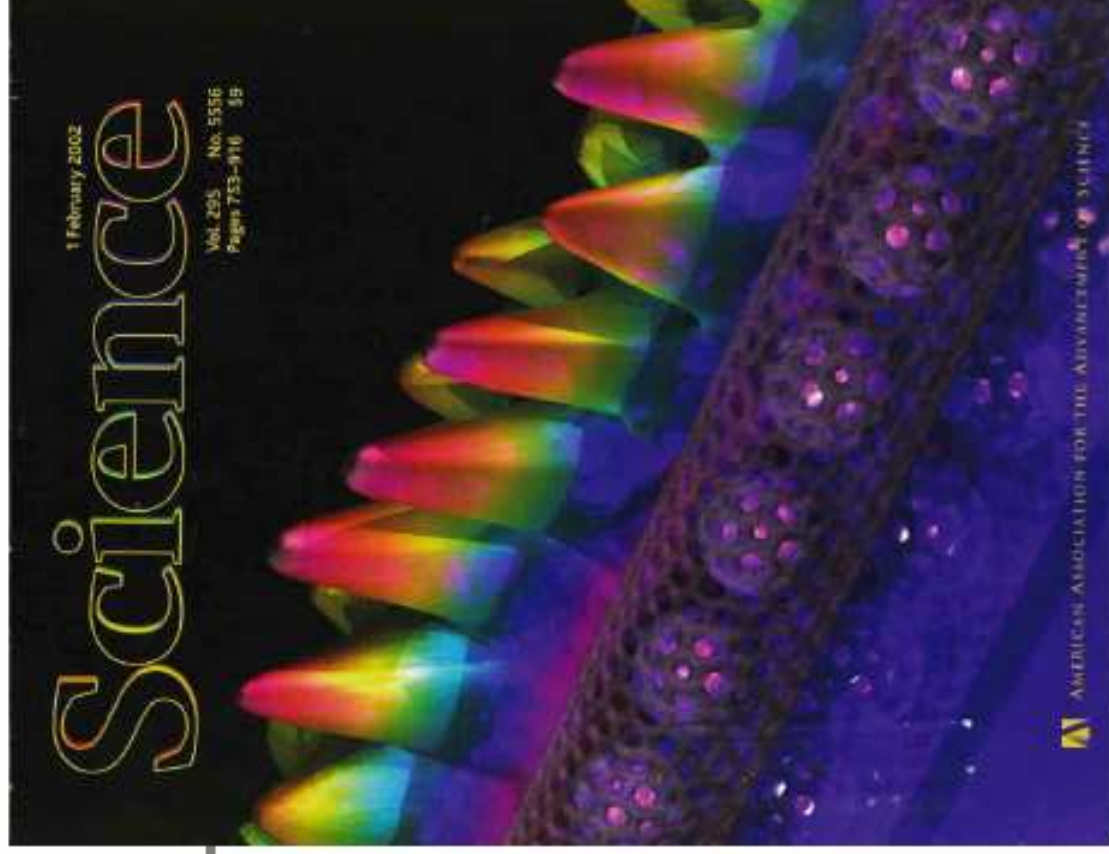




Electronic States of Nanotube Peapod Structures

D.J. Hornbaker, S.-J. Kahng,
S. Misra, B. W. Smith, A.T. Johnson,
E.J. Mele, D.E. Luzzi, A. Yazdani
Science 295, 828 (2002)

Image: D.J. Hornbaker and
A. Yazdani, *Science* **295** (2002)





Nanocircuits: “Breakthrough of the Year”

-Science Dec. 2001

What was designated “molecule
of the year” in 1991?

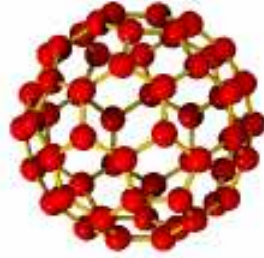
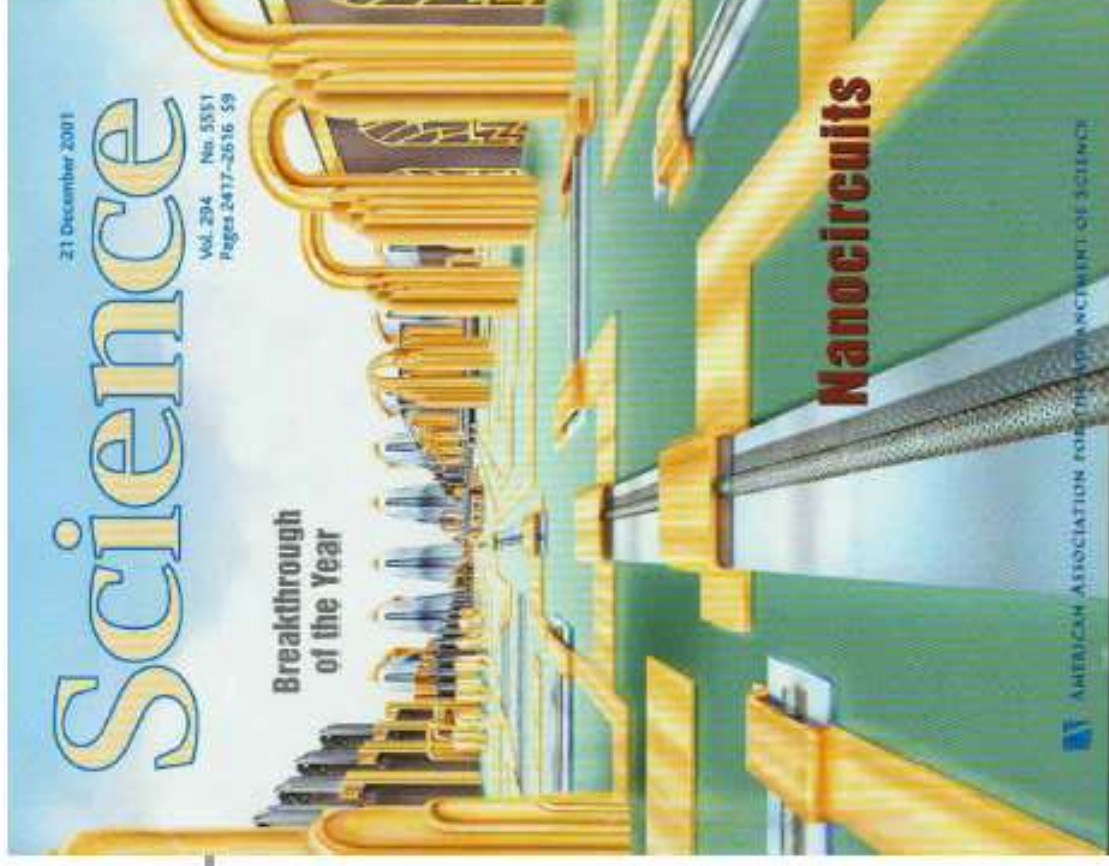
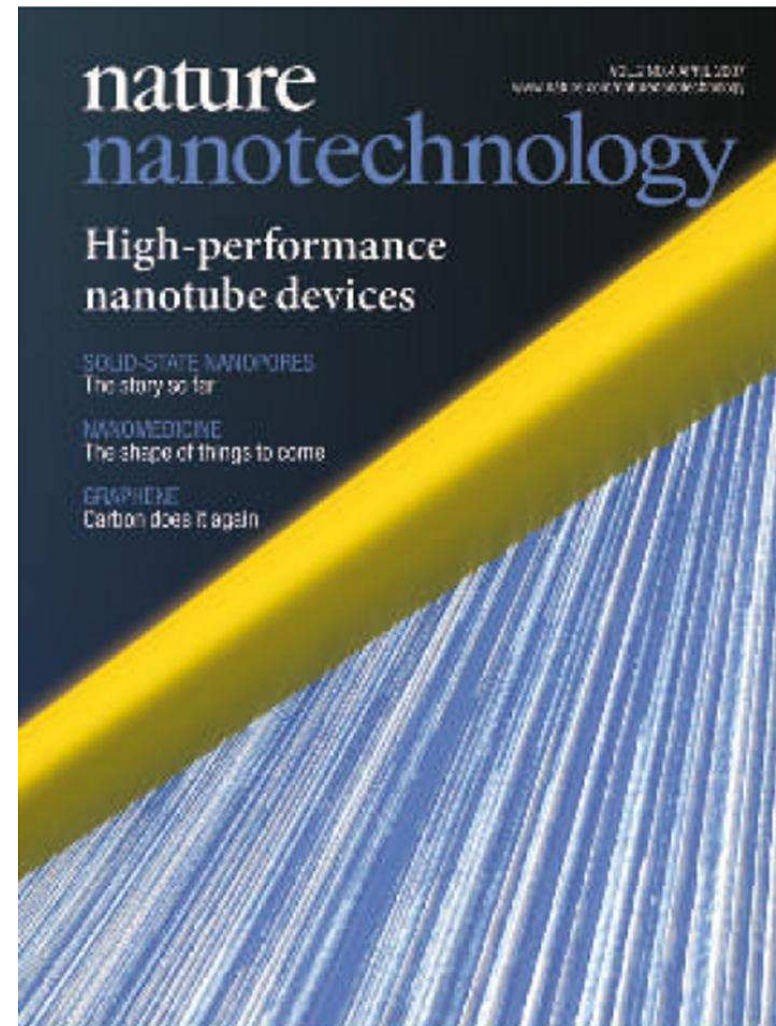


Illustration: C. Slayden,
Science **294** (2001)



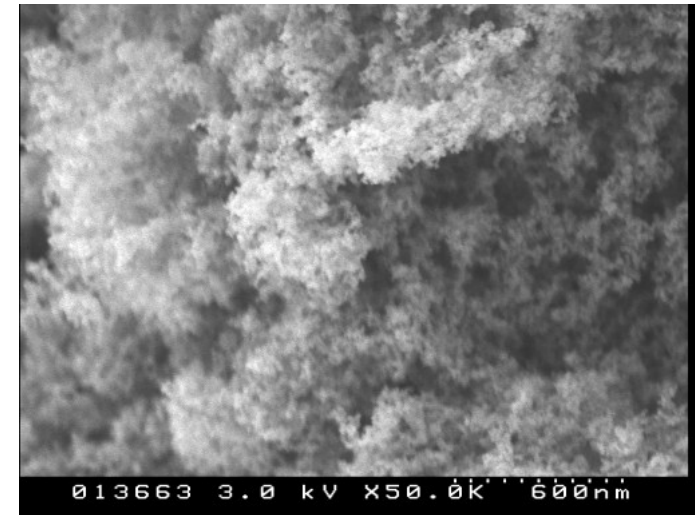
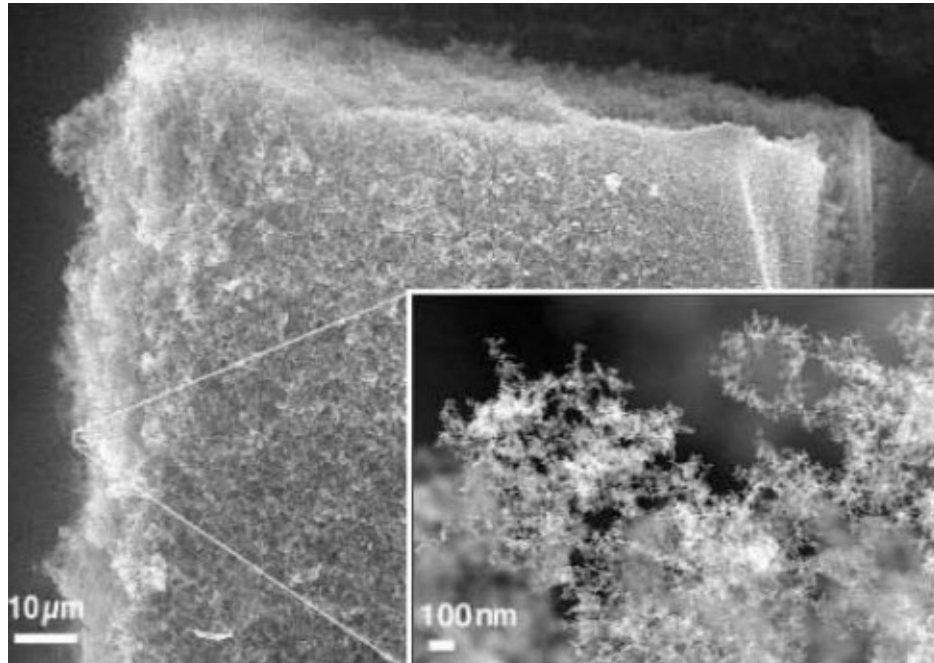
High-performance nanotube devices
Nature Nanotechnology
April 2007





"Quantum Reality (Large Buckyball Around Trees), 2006. Steel and Maple trees. Diameter 30' (9 m).
Location: Tryon Creek State Park, Portland, Oregon, USA,
By Julian Voss-Andreae

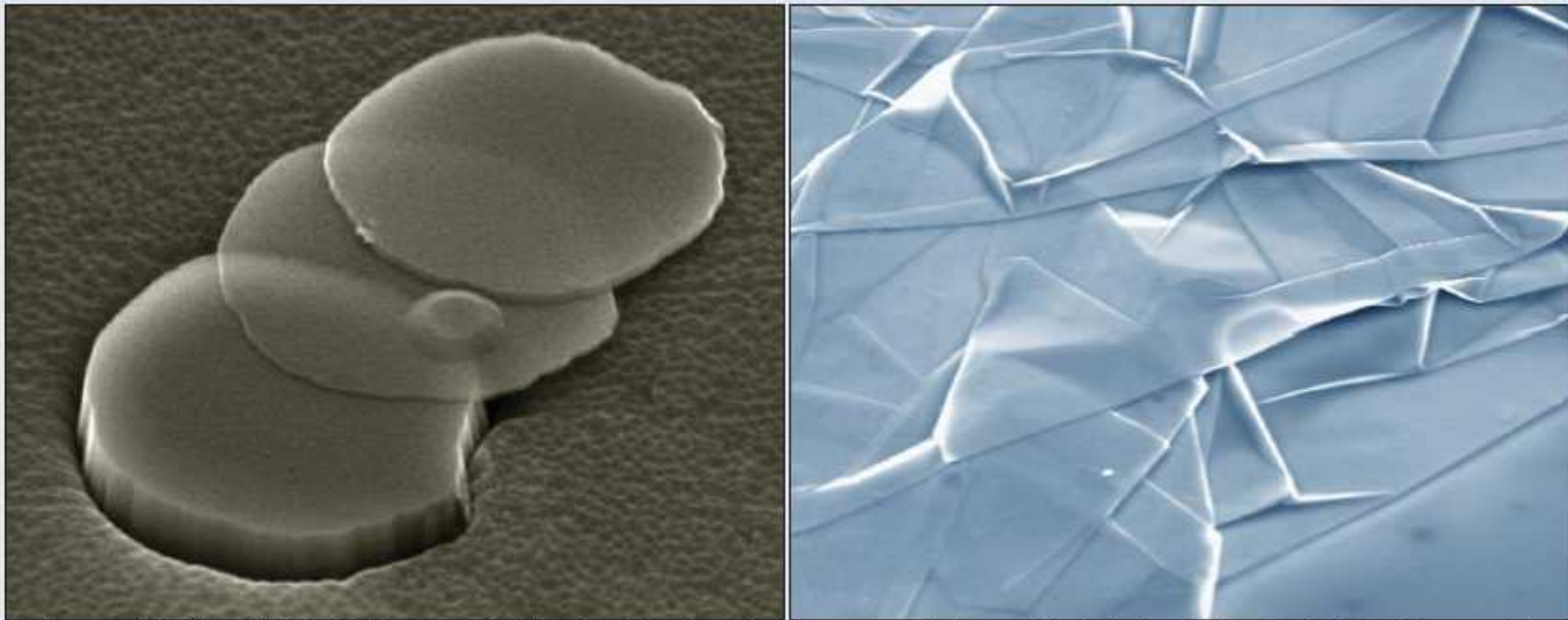
Carbon nanofoams



Nanofoam is the most recently discovered allotrope of carbon. It is constructed of groups of carbon atoms, which come together forming a loose three-dimensional web. Each of these groups are formed up of 4000 carbon atoms linked in a crystal lattice similar to that of the graphite allotrope. Unlike fullerenes these are made up of heptagons, which give it a negative curvature, making it opposite, in shape, to the fullerenes. The most unusual physical property of the nanofoam allotrope is it becomes magnetic at -138°C . It is also the lightest known solid (density = 0.002 g/cm^3),

Graphene: the next big thing?

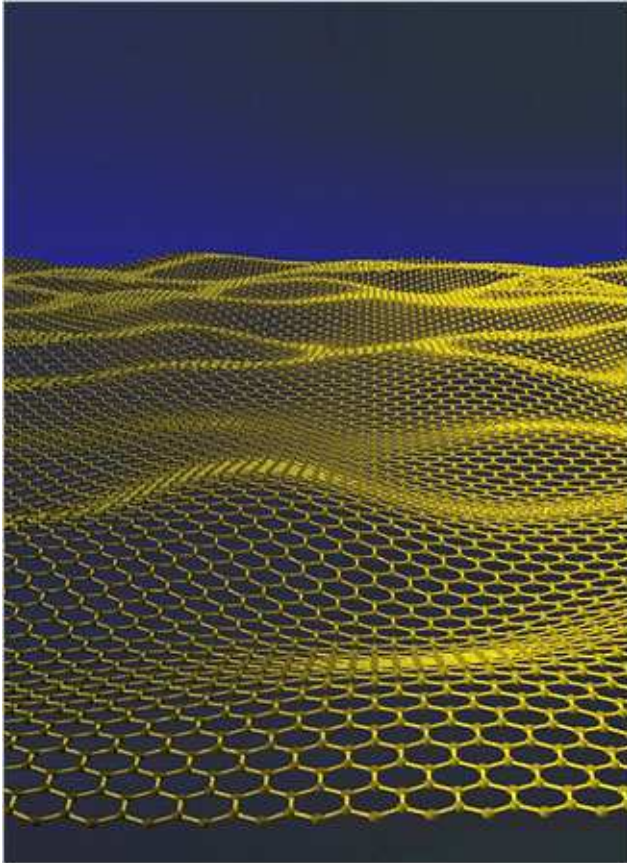
1 A sticky success



Graphene was first isolated by Andre Geim's team at the University of Manchester just two years ago using the surprisingly simple technique of ripping layers from a graphite surface using adhesive tape. By repeatedly peeling away thinner layers (left), single-atom-thick sheets were obtained (right), as shown in these scanning electron micrographs.

(as appears in Physics World, November 2006)

Graphene: the next big thing?



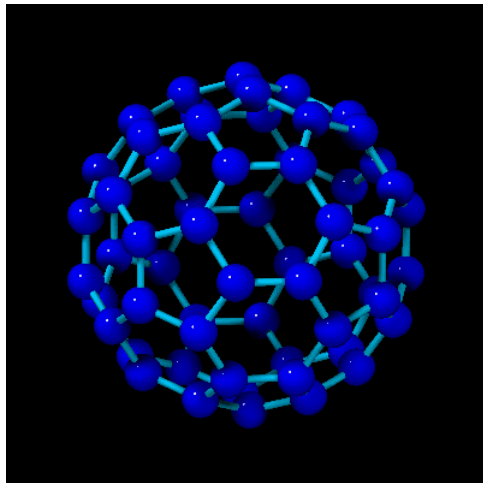
See review in
Geim and Novoselov,
Nature Materials **6**, 183 (2007)

A pure 2D material, first obtained in 2004 [Science 306, 666 (2004)], in which exotic physics and high-tech potential are combined.

- Graphene is a one-atom-thick sheet of carbon that was isolated for the first time in 2004 – a feat long thought to be impossible.
- Graphene's 2D nature and honeycomb atomic structure cause electrons moving in the material to behave as if they have no mass.
- Electrons in graphene move at an effective speed 300 times less than the speed of light in a vacuum, allowing relativistic effects to be observed without using particle accelerators.
- A key experimental signature of graphene is the way it modifies the quantum Hall effect seen in metals and semiconductors.
- The electrons in graphene can travel large distances without being scattered, making it a promising material for very fast electronic components.

clusters

 **clusters as crossroads**

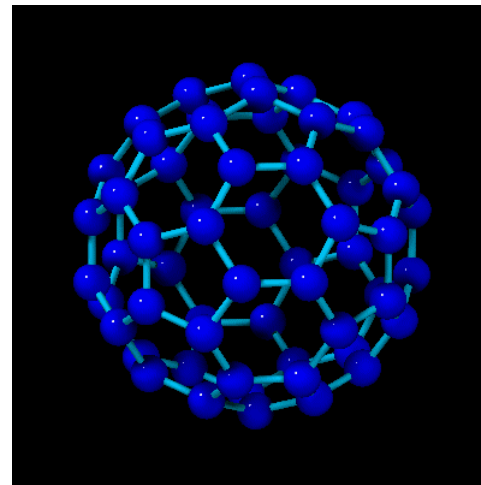


cluster = a group of atoms or molecules

clusters → nanoparticles

➔ **clusters as crossroads**

atoms and
molecules



solid state

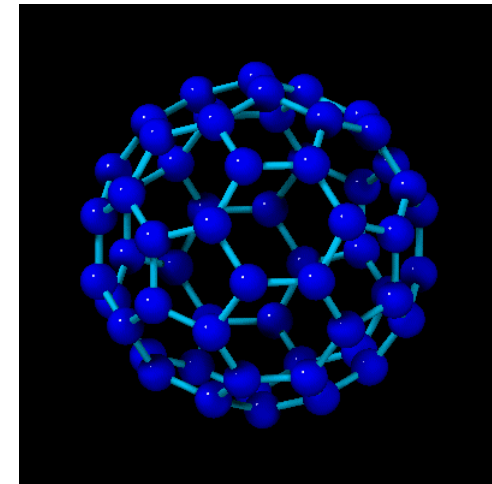
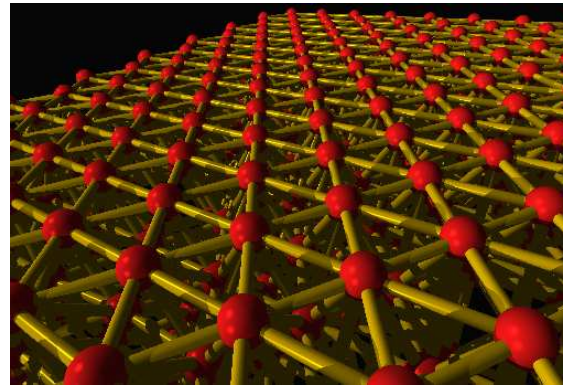
physics



chemistry

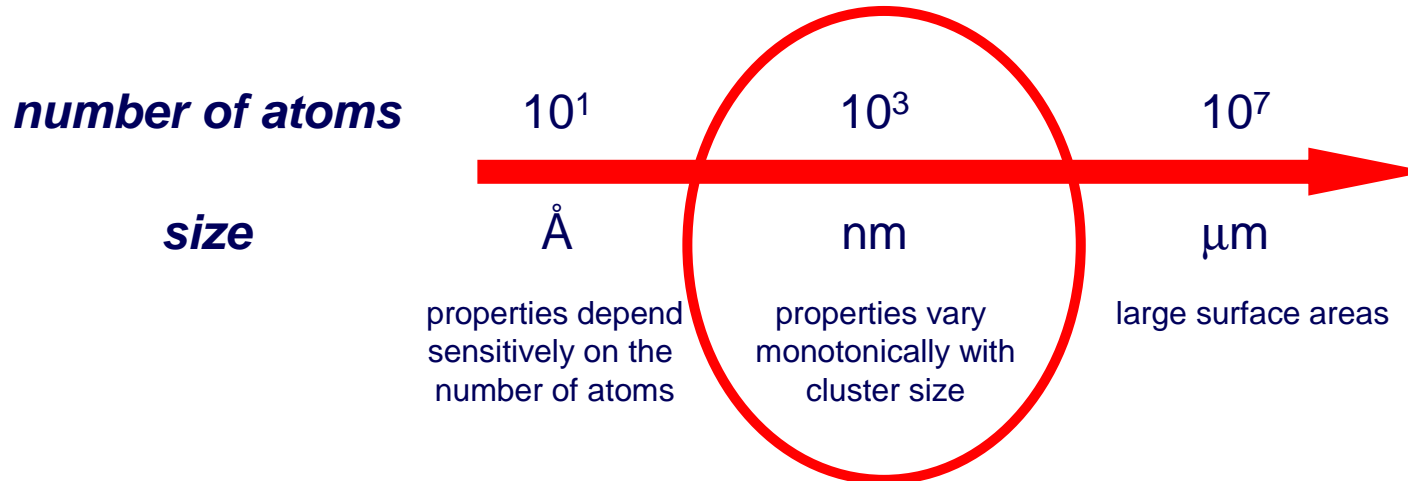


➔ clusters vs. bulk



| | metal single crystals | metal clusters |
|----------------------|-----------------------|-------------------------|
| geometric structure | simple | complex |
| electronic structure | electron bands | discrete spectrum |
| chemical properties | fixed | tunable |
| optical properties | continous behavior | Mie: resonance behavior |

size of clusters



types of clusters

van der Waals clusters (Ar, Ne)

metal clusters (Al, Ag)

ionic clusters (NaCl)

environment

gas phase

supported on surfaces

embedded in solids

the concept of superatoms

SUPERATOMS:

Atomic clusters: Building blocks for a class of solids

S. N. Khanna and P. Jena

Phys. Rev. B 51, 13705 - 13716 (1995)

Atomic clusters with suitable size and composition can be designed to mimic the chemistry of atoms in the Periodic Table. These clusters which can be viewed as “super atoms” could then form the building blocks for a class of solids with unique structural, electronic, optical, magnetic, and thermodynamic properties.



the concept of superatoms

Periodic Table of the Elements

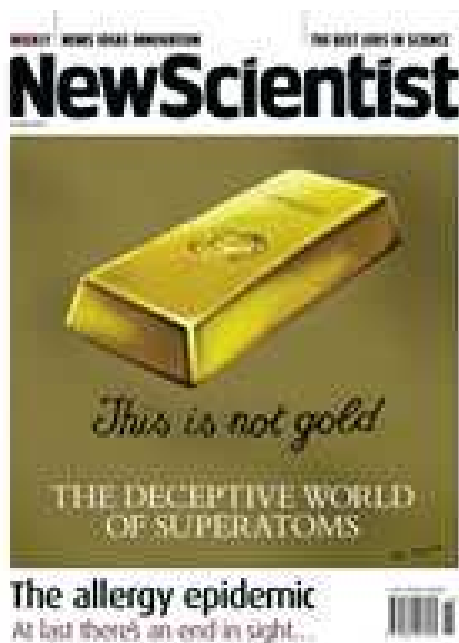
| | | | | | | | | | | | | | | | | | | | |
|---|-----|----|------|----|----|-----|-----|-----|-----|-----|-----|----|----|----|----|----|----|----|----|
| 1 | IA | | | | | | | | | | | | | | | | 2 | | |
| 1 | H | | | | | | | | | | | | | | | | | He | |
| 2 | IIA | | | | | | | | | | | | | | | | | | Ne |
| 3 | Li | Be | | | | | | | | | | | B | C | N | O | F | Ne | |
| 4 | Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar | |
| 5 | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| 6 | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| 7 | Cs | Ba | * La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| 8 | Fr | Ra | + Ac | Rf | Ha | 106 | 107 | 108 | 109 | 110 | 111 | | | | | | | | |

* Lanthanide Series
 Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
 * Actinide Series
 Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

According to Mendeleev's roll call, an element's chemistry can be deduced from where it sits in the periodic table. Reactive metals like sodium and calcium occupy the two columns on the left. The inert "noble" gases make up the column on the far right, flanked by typical non-metals such as chlorine and sulphur.

Now this neat picture is being disrupted by superatoms - clusters of atoms of a particular chemical element that can take on the properties of entirely different elements. The chemical behaviour can be altered, sometimes drastically, by the addition of just one extra atom.

Philip Ball,
 New Scientist 2495, 30
 (16 April 2005)



the concept of superatoms

Periodic Table of the Elements

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|-------------------|---------------|------------------|---------------|----------------|------------|--------------|--------------|-----|-----|----|----|-------------|-------------|--------------|------------|--------------|----------------|--------------|--------------|----|----|---|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 1 | | | | | | | | | | | | | | | | | 2 | | | | | | | | | | | | | | | | | | | |
| 1 | H 1.00794 | | | | | | | | | | | | | | | | | He 4.002602 | | | | | | | | | | | | | | | | | | |
| 2 | 3 | 4 | | | | | | | | | | | 10 | 11 | 12 | | | | | | | | | | | | | | | | | | | | | |
| | Li 6.941 | Be 9.01218 | | | | | | | | | | | B 10.811 | C 12.011 | N 14.0067 | O 16.00 | F 18.9984 | Ne 20.1797 | | | | | | | | | | | | | | | | | | |
| 3 | 5 | 6 | 7 | 8 | 9 | | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 18 | | | | | | | | | | | | | | | |
| | Na 22.98976928 | Mg 24.304 | Al 26.9815385 | Si 28.0855 | P 30.973762 | S 32.06 | Cl 35.453 | Ar 39.948 | | | | | | | | | | | K 39.0983 | Ca 40.078 | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 4 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | | | | | | | | | | | | | | | | | | |
| | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | | | | | | | | | | | | | | | | | | |
| 5 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | | | | | | | | | | | | | | | | | | |
| | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | | | | | | | | | | | | | | | | | | |
| 6 | 55 | 56 | 57 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | | | | | | | | | | | | | | | | | | |
| | Cs | Ba | * La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | | | | | | | | | | | | | | | | | | |
| 7 | 87 | 88 | 89 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | Fr | Ra | + Ac | Rf | Ha | 106 | 107 | 108 | 109 | 110 | | | | | | | | | | | | | | | | | | | | | | | | | | |

* Lanthanide Series

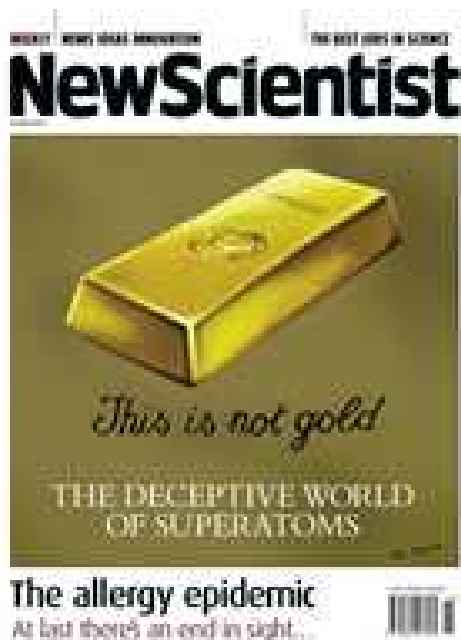
| | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 |
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |

* Actinide Series

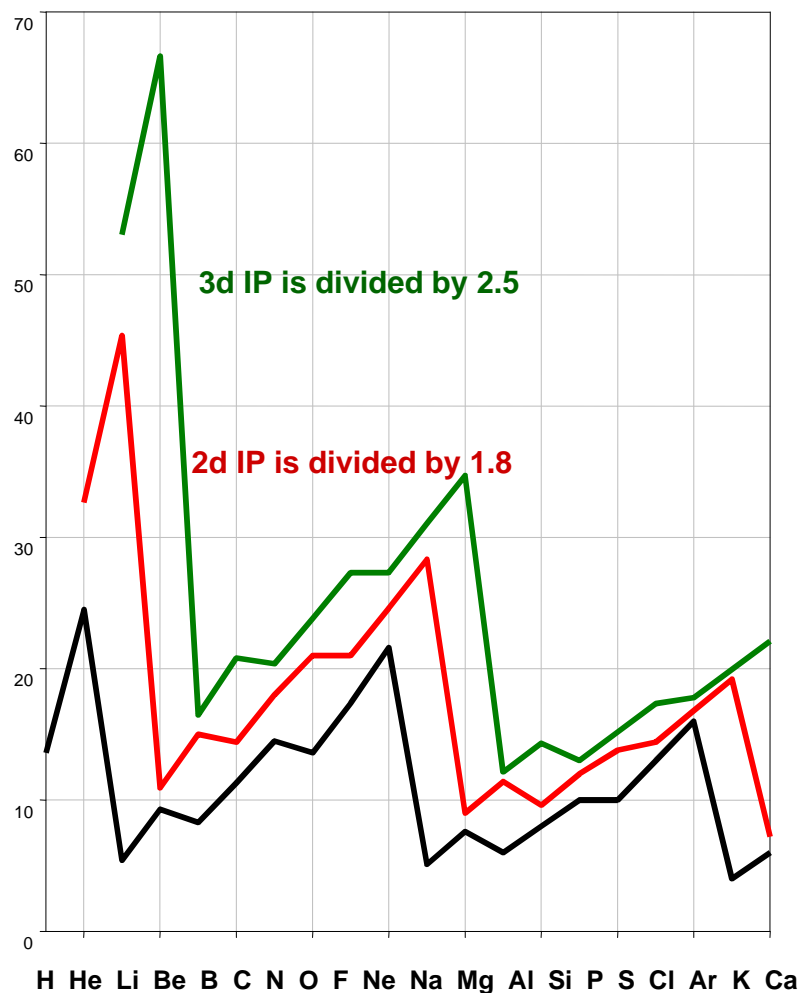
| | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|-----|-----|-----|-----|
| 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 | 103 |
| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

TWO SIDES OF SUPERATOMS:

- Chemical properties of clusters can be very different from those of their constituents.
- Chemical properties of clusters can change drastically when adding just a single atom



superatoms



First, second, and third ionization potentials (in eV's) of the first 20 elements in the periodic table (Jim Heath, UCLA).

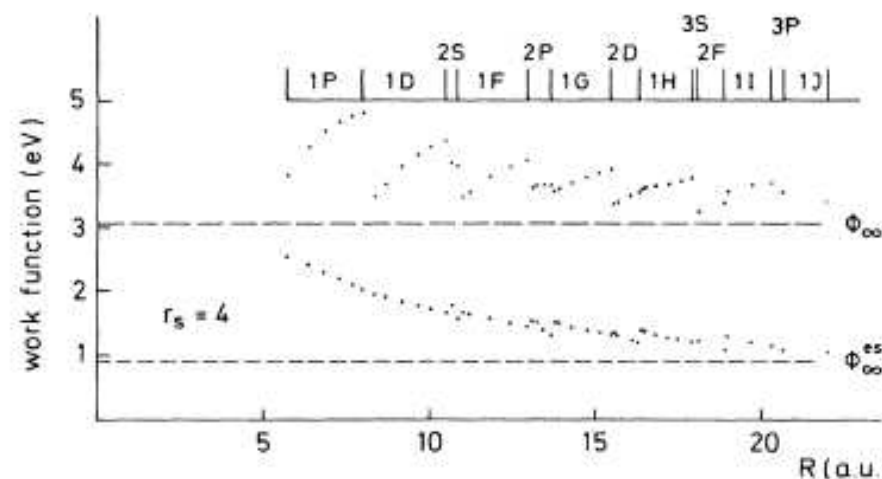


FIG. 1. Work function of small metal particles as calculated in the self-consistent SJBM. R is the particle radius, $R = r_s N^{1/3}$ with N the number of particles. ϕ_{∞} is the work function of the infinite, flat surface. ϕ_{∞}^{es} is the electrostatic part of ϕ_{∞} , sometimes called χ , the electrostatic surface barrier. $1p$, $1d$, $2s$, etc., are the quantum numbers of the spherical potential hole. $1p$ is the lowest state with $l=1$, and $2s$ is the second state with $l=0$, etc. The results for the $1s$ shell are not shown. The cluster with a completely filled $1j$ shell contains 168 electrons. $r_s=4$ is the mean bulk density of Na. Whereas the total work function shows pronounced shell effects, the electrostatic part of it behaves rather smoothly.

Ekardt, PRB 29, 1558 (1984)

the same origin: filling of electronic shells!

magic numbers

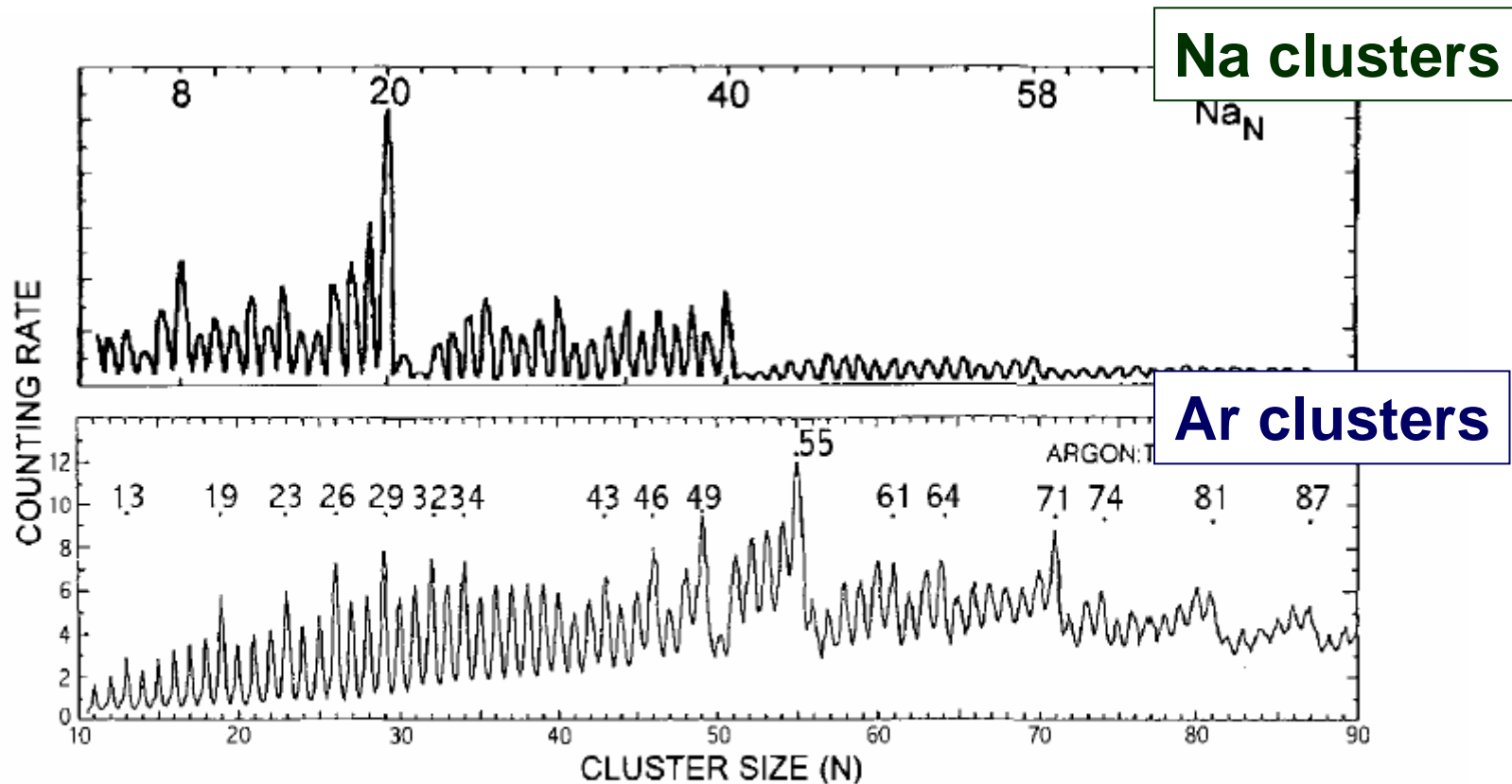


Fig. 2. Mass spectra measured for Ar and Na clusters (see Refs. 10,12,15 and references therein). The intense peaks indicate enhanced stability.

The van der Waals forces lead to enhanced stability of cluster geometries based on the most dense icosahedral packing. The most prominent peaks in mass spectra of argon clusters correspond to completed icosahedral shells of 13, 55, 147, 309 etc. atoms. The origin of these magic numbers can be understood on the basis of the classical equations.

Magic numbers in clusters

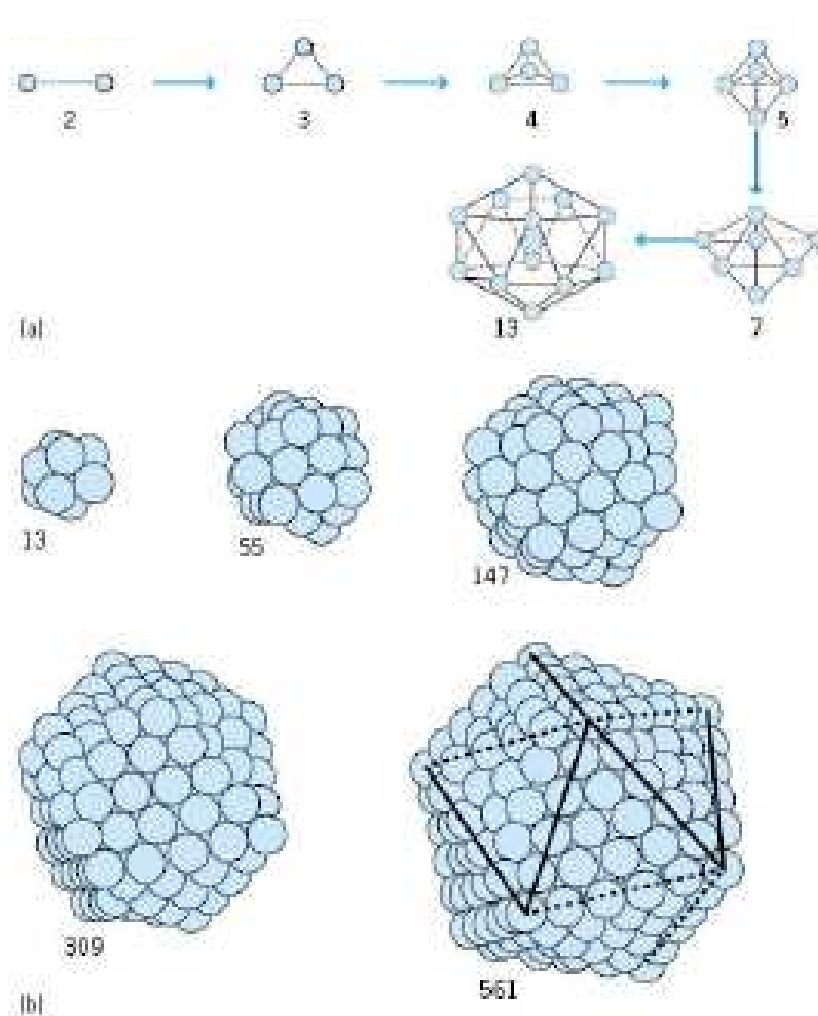
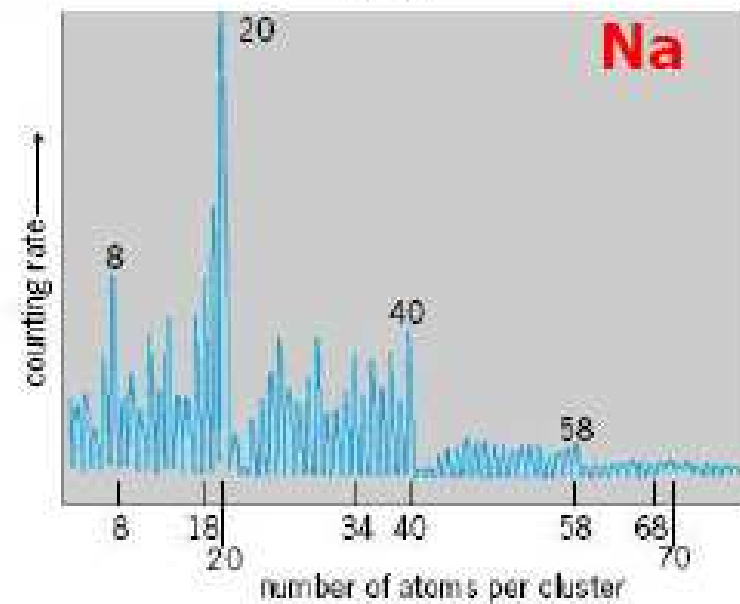
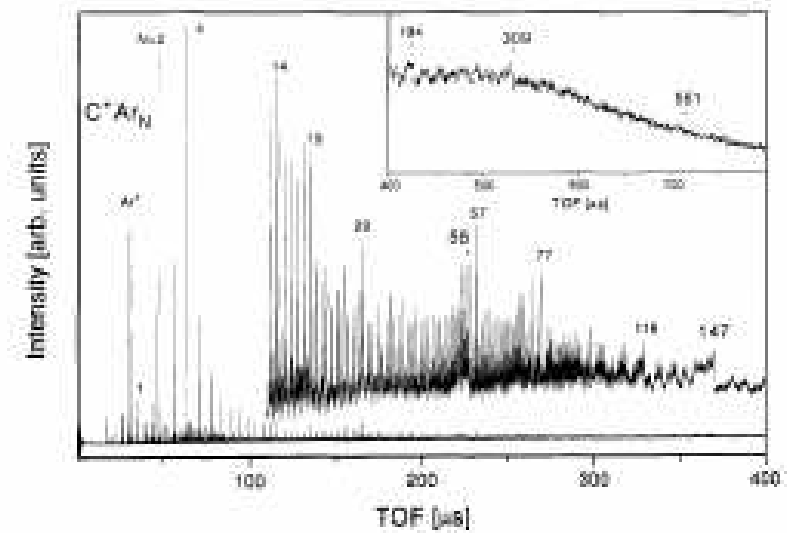


Fig. 1. Growth sequence of neutral rare-gas clusters. Number of atoms in cluster, N , is indicated for each cluster. (a) Microclusters, (b) small and large clusters, all of which are icosahedra with threefold symmetry. (After H. Haberland, ed., *Clusters of Atoms and Molecules*, vol. 1, Springer-Verlag, 1994)



magic numbers

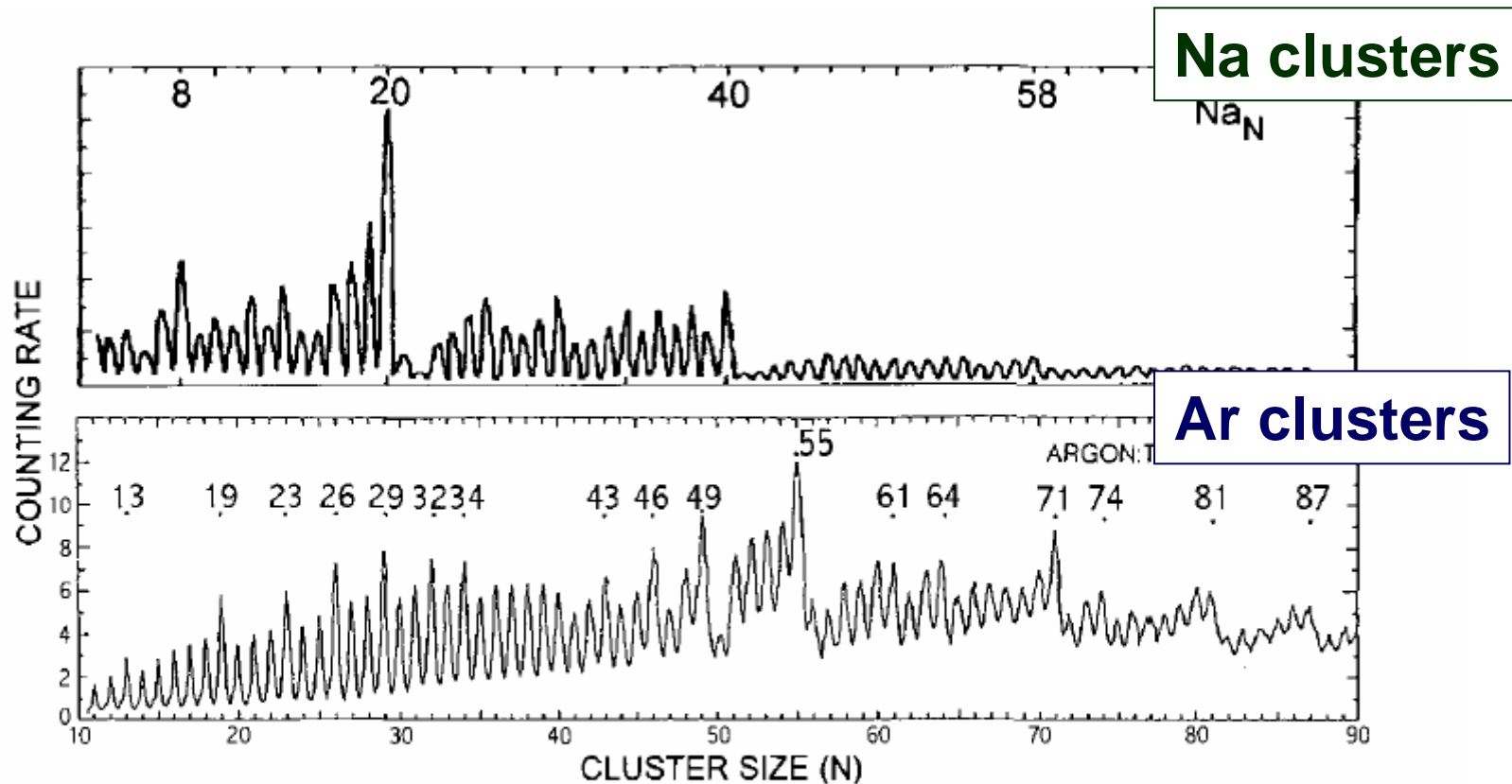


Fig. 2. Mass spectra measured for Ar and Na clusters (see Refs. 10,12,15 and references therein). The intense peaks indicate enhanced stability.

Understanding the magic numbers of metal clusters is pretty well equivalent to understanding its electronic and ionic structure. A good example of this kind occurs for Na clusters. In this case, the magic numbers arise from the formation of closed shells of delocalised electrons, one from each atom.

magic numbers

Na clusters carrying a single positive charge (hence a cation) were predicted to exhibit magic numbers that are shifted by 1, namely at sizes containing 3, 9, 21, 41, etc. atoms as they respectively contain 2, 8, 20, 40, etc. valence electrons,

Rao *et al.*, PRL **58**, 1188 (1987).

This prediction was indeed later verified experimentally and suggested that the stability of metal clusters can be altered by manipulating their number of valence electrons,

Bhaskar *et al.* PRB **36**, 4418 (1987).

Rb clusters

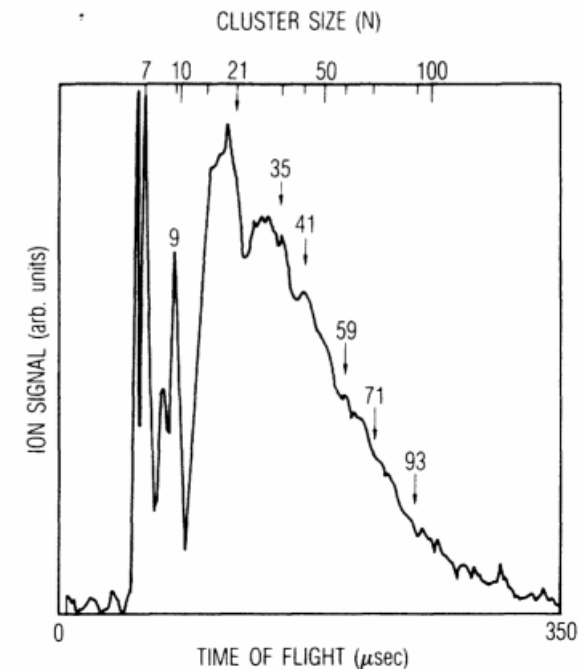
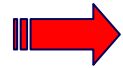
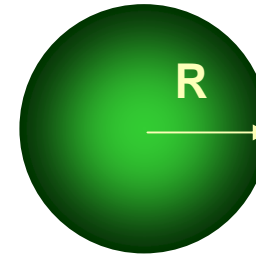


FIG. 3. Mass spectra of ions extracted from the source operating at high emission current ($\sim 150 \mu\text{A}$). Cluster sizes where steps in the relative abundances appear are also indicated.



DFT calculation of a jellium cluster

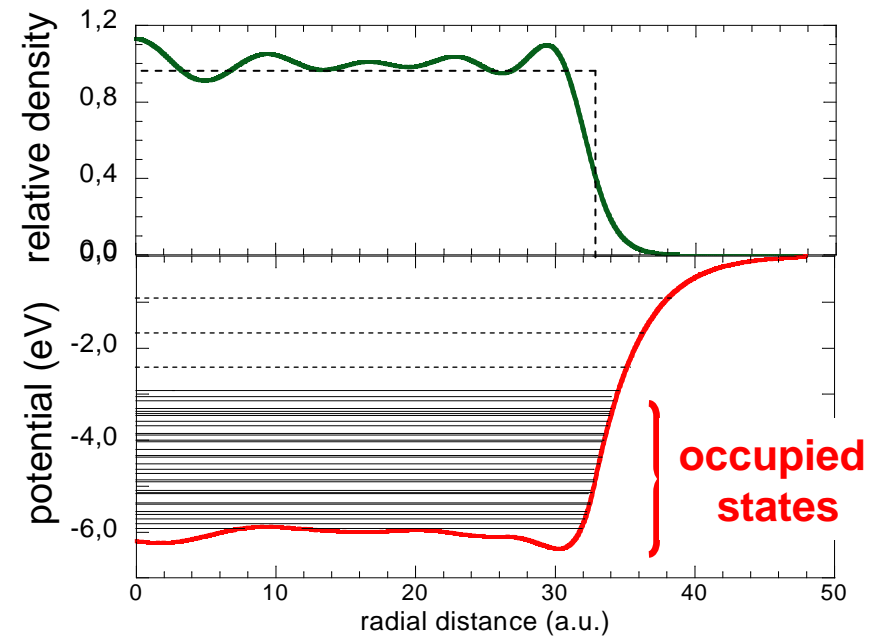
cluster is described in the jellium model (a background of constant positive charge)

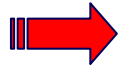


Kohn-Sham equations
 solved self-consistently

$$\left\{ -\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right\} \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

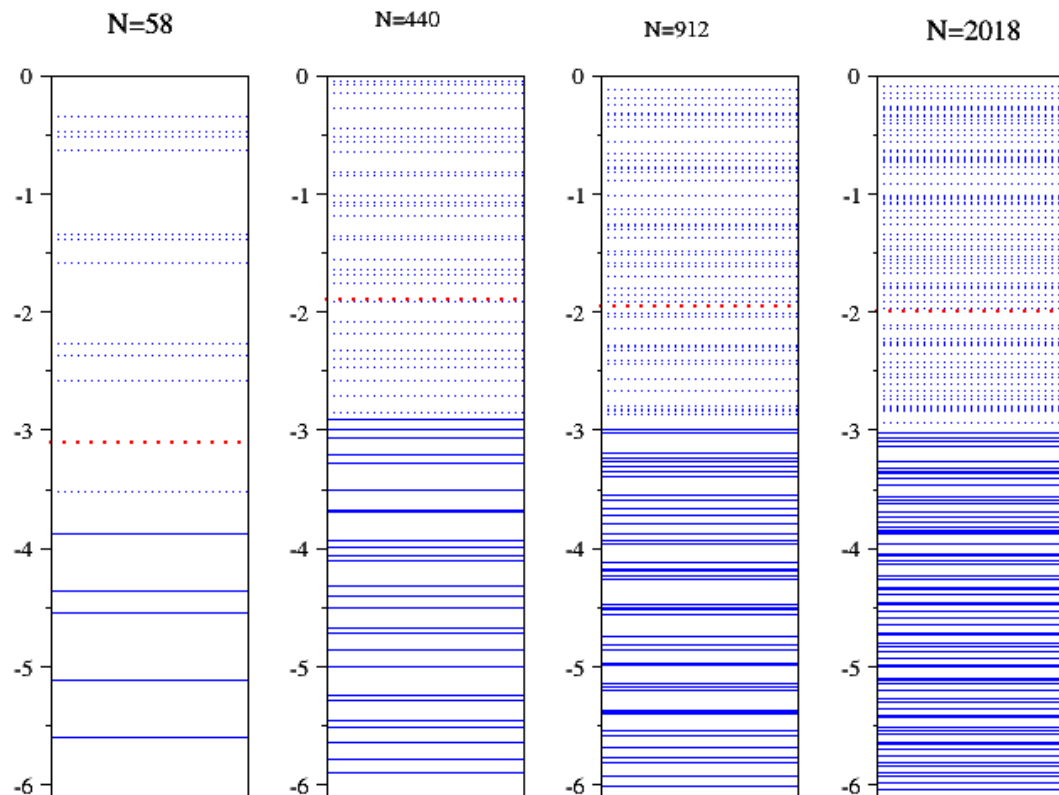
$$v_{\text{eff}}(\mathbf{r}) = v_{\text{jellium}}(\mathbf{r}) + v_{\text{Hartree}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$$





evolution of the density of states as a function of size

DFT calculation of the density of states in a
jellium cluster of $r_s=4$



First report of C₆₀ buckyballs (1985)

Kroto, Heath, O'Brien, Curl, and Smalley,
'C₆₀: Buckminsterfullerene', Nature **318**, 162 (1985).

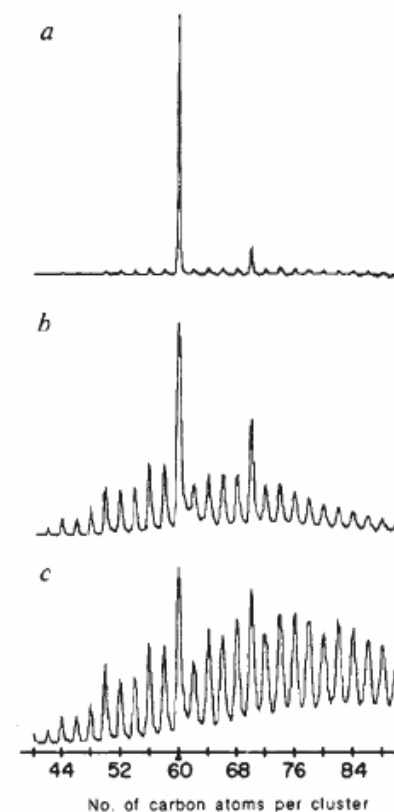
C₆₀: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl
& R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical
Engineering, Rice University, Houston, Texas 77251, USA

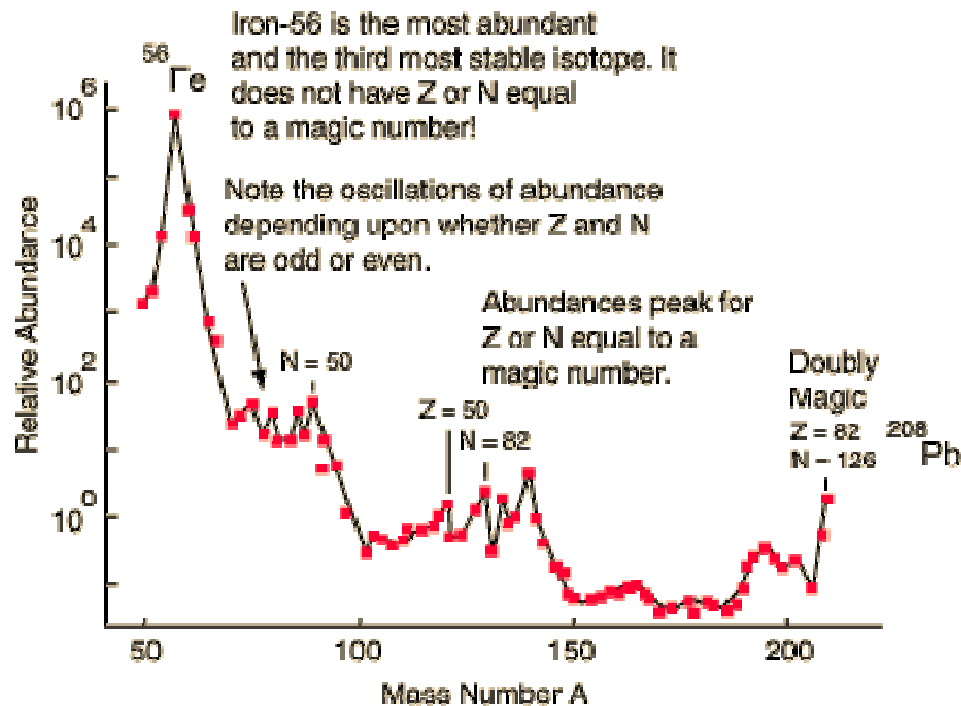
During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells¹, graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C₆₀ molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C₆₀ molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.



magic numbers

Therefore, there are sizes of clusters with exceptional stability. This is analogous to the exceptional stability of the **atoms of the inert gases** helium, neon, argon, krypton, and xenon and of the so-called **magic number nuclei**—i.e., the sequence of unusually stable atomic nuclei beginning with the α -particle,

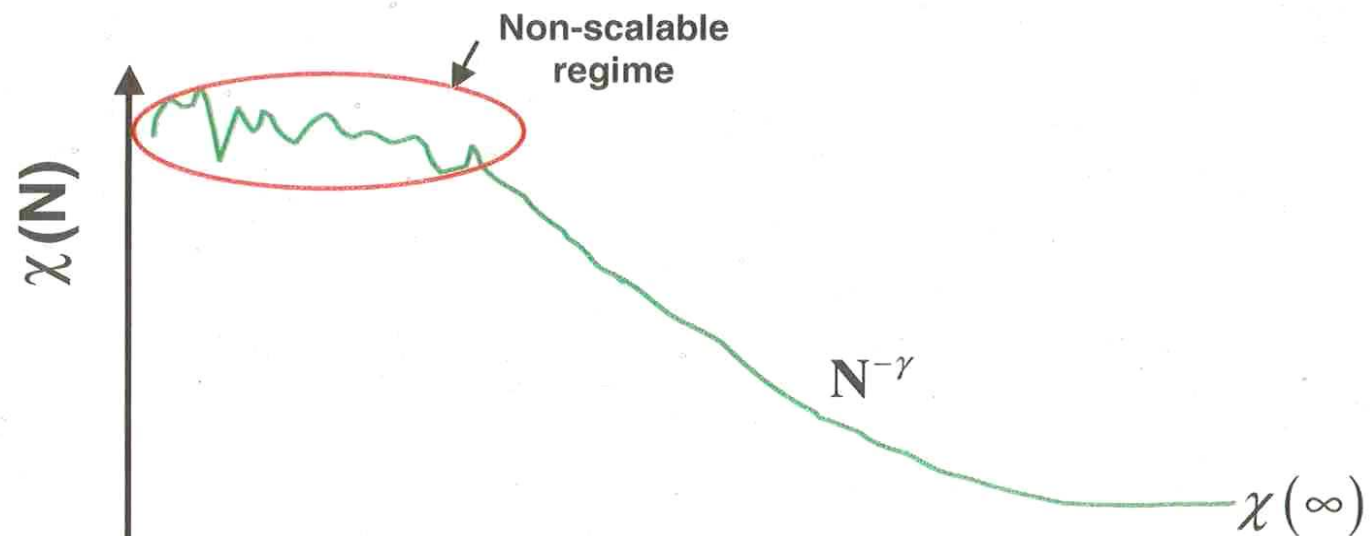


link to atomic physics

link to nuclear physics
(shell model)

Small is Different

The non-scalable regime



properties can be tuned at wish!!!

size dependent properties: magnetic moment of Fe clusters

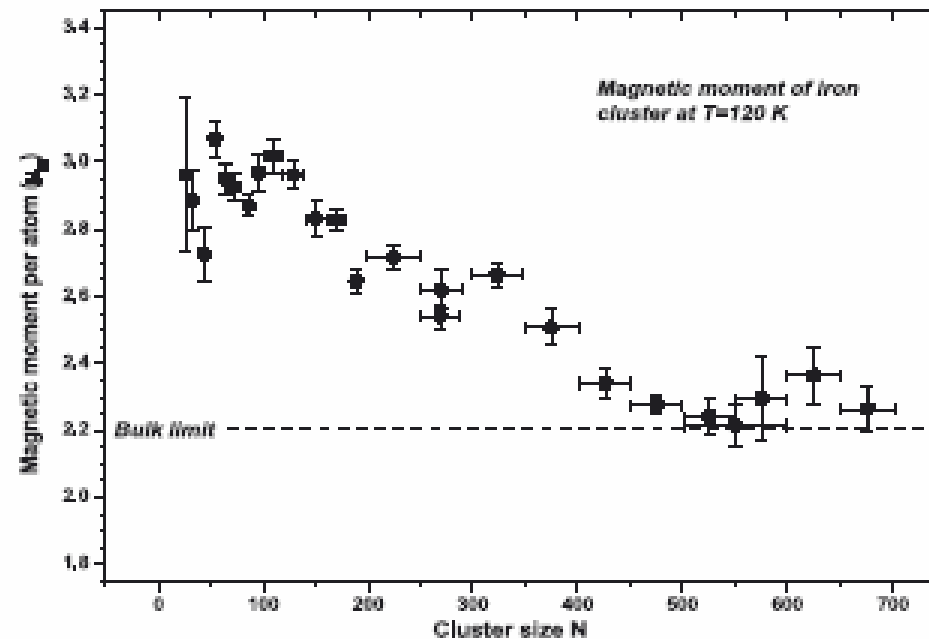


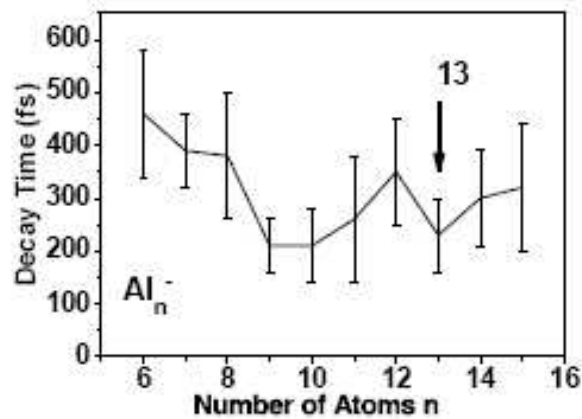
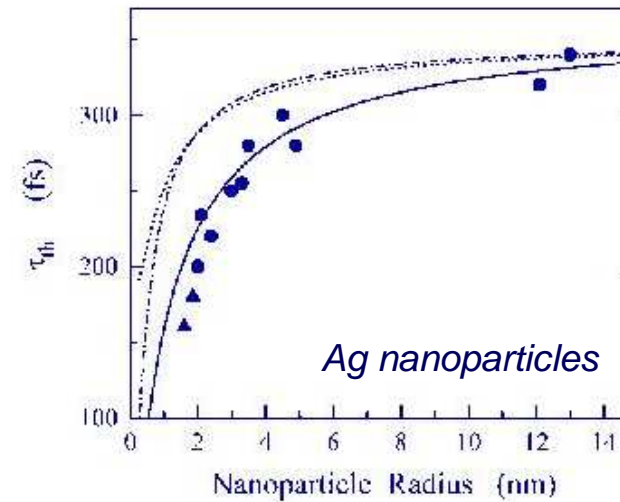
Fig. 6. Magnetic moments of Fe clusters (69). [Reprinted with permission from ref. 69 (Copyright 1993, American Physical Society).]

Billas, I. M., L., Becker, J. A., Chatlain, A. & de Heer W. A.
(1993) Phys. Rev. Lett. 71, 4067–4070.

➔ experimental measurements of size-dependent electron dynamics

A sharp increase of the electron energy exchange rate is demonstrated for nanoparticles smaller than 5 nm. ... due to surface induced reduction of the Coulomb interaction screening.

Voisin *et al.*,
 Size-dependent electron-electron interactions in metal nanoparticles
PRL **85**, 2200 (2000)



... very effective relaxation mechanism, independent on the electronic structure (phonons?)

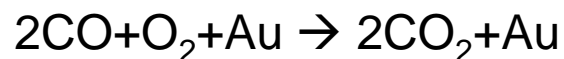
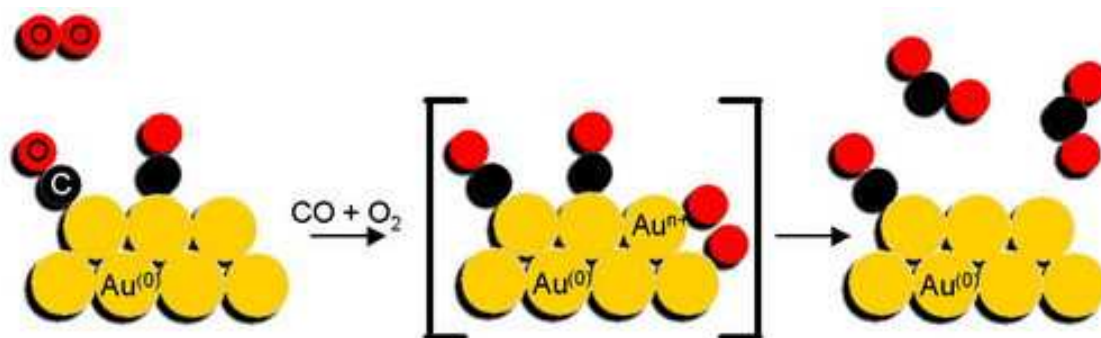
Gerhardt *et al.*,
 Fast electron dynamics in small Al clusters
CPL **382**, 454 (2003)

emergence of new properties

Clusters are not atoms any more but not yet solids. Their properties can differ substantially from those of the two extremes and new physics can be derived.

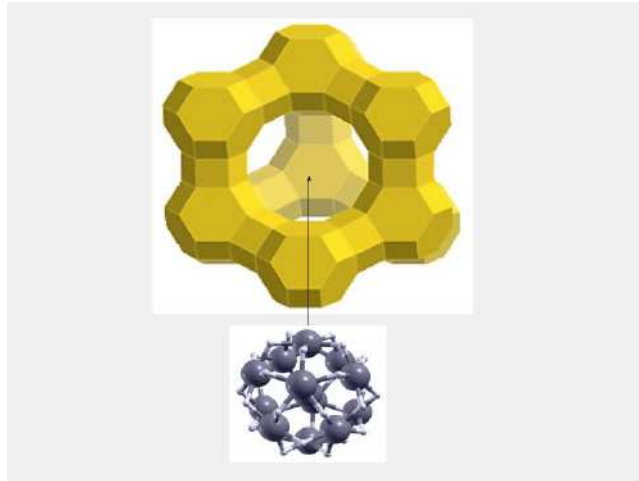
Cluster properties provide a better understanding of the transition from the single atom or molecule to the solid state limit. Modern experimental techniques have made it possible to study this transition. By increasing the cluster size, one can observe the emergence of the physical features in the system, such as plasmon excitations, electron conduction band formation, superconductivity and superfluidity, phase transitions, fission and many more. Most of these many-body phenomena exist in solid state but are absent for single atoms.

**emergence of new properties:
Au clusters are not noble anymore**



Au bulk hardly reacts with molecular atmospheric oxygen or water and is therefore very much used, for instance, in jewelry. But small gold clusters, however, do react with oxidation. Thereby, the reactivity largely depends on the number of atoms forming the cluster. The extraordinary properties of gold cluster and gold nanoparticles regarding to chemisorption, not only of CO and O₂ but also other adsorbents such as N₂ and H₂, suggest gold nanoparticles as possible nanocatalysts.

emergence of new properties: Pt small clusters become magnetic



Magnetization measurements of well-characterized monodisperse Pt clusters consisting of 13 ± 2 atoms in a zeolite confirm the predicted extraordinary magnetic polarization with up to 8 unpaired electrons on a cluster, corresponding to a magnetic moment of $0.65(5)\mu\text{B}$ per atom.

Liu *et al.*,
Phys. Rev. Lett. **97**, 253401 (2006)

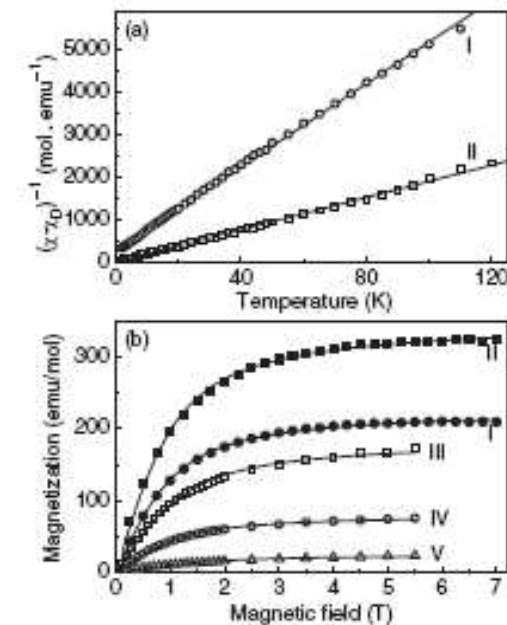


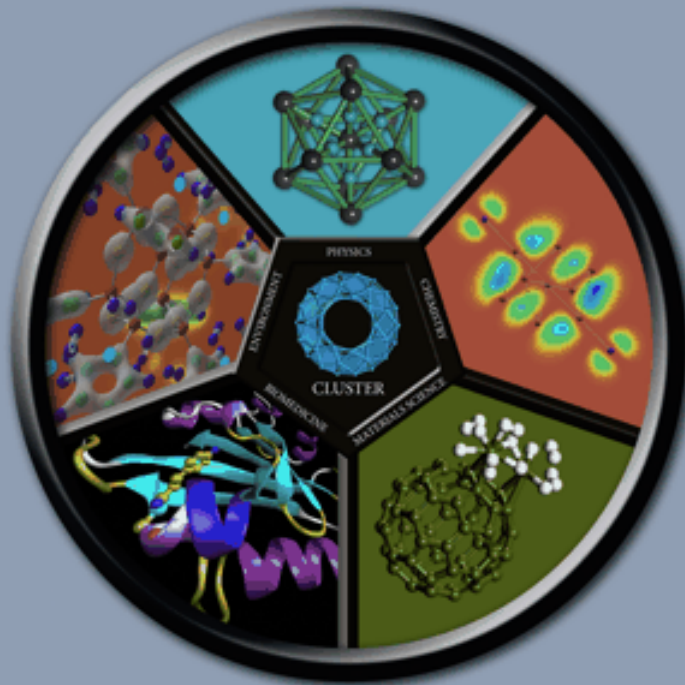
FIG. 3. (a) Inverse magnetic susceptibility (magnetization divided by field) per mol of Pt atoms on NaY in the range of 1.8–120 K in an external field of 0.2 T before (I) and after hydrogen desorption (II); (b) Molar magnetization at 1.8 K of Pt/NaY before and after hydrogen desorption, compared with literature data for analogous measurements of Pt nanoparticles embedded in a poly-*N*-vinyl-2-pyrrolidone (PVP) polymer [5]. The particles have diameters of 2.3 nm (ca. 420 atoms, III), 3.0 nm (940 atoms, IV) and 3.8 nm (V, 1900 atoms).

Some history on cluster research

The phrase *cluster* was coined by F.A. Cotton, a reputed chemist well known for his work on the chemistry of transition metals. Cotton used the term cluster for the first time in the early 1960s when referring to compounds containing metal-metal bonds.



But cluster science, as we currently understand it, as the science of size-dependent properties, blossomed in the early 80's



Multidisciplinary cluster dynamics
PNAS, July 11, 2006

Although reference to the formation of aggregates and related nucleation phenomena can be found in literature dating from the 1930s and earlier, studies of clusters in mass spectrometer ion sources and later in molecular beams (1) began to emerge in the 1950s and developed rapidly as a subject of considerable interest in the 1970s and 1980s. The **advent of the laser vaporization technique** enabled researchers to produce clusters of virtually any element in the periodic table and spawned wide-ranging interest in the studies of clusters of various compositions, beyond systems of volatile materials, which had been the focus in the beginning. For this community, in the past 30 years clusters have come to symbolize a new embryonic form of matter that is intermediate between atoms and their bulk counterpart. Clusters bridge phases as well as disciplines.

A. W. Castleman, Jr. and Puru Jena,
PNAS **103**, 10552 (2006)

Enormous Yield of Photoelectrons from Small Particles

A. Schmidt-Ott

Laboratory for Atmospheric Physics^(a) and Laboratory for Solid State Physics, Eidgenössische Technische Hochschule, CH-8093 Zürich, Switzerland

and

P. Schurtenberger and H. C. Siegmann

Laboratory for Solid State Physics, Eidgenössische Technische Hochschule, CH-8093 Zürich, Switzerland

(Received 7 July 1980)

A new ac bridge technique allows detailed photoelectric studies on very small particles suspended in gases. The photoelectric yield Y near threshold Φ still follows the Fowler-Nordheim law $Y = c(\hbar\nu - \Phi)^2$; yet c is generally much larger compared to surfaces of extended solids. For Ag particles of radius 20 Å in an airlike mixture of N_2 and O_2 , $c \approx 100c_0$, where c_0 applies to a macroscopic Ag surface in the same environment.

The purpose of this Letter is to report on a large enhancement of the yield Y of photoelectrons per incident photon if ultrafine particles with radii $R \leq 50$ Å are chosen as photoemitters. The results were obtained with Ag and WO_3 by use of a novel technique in which the density Z of the particles does not have to be known.

The particles are suspended in an N_2 - O_2 mixture similar to air. The photoelectric size effect to be reported here has wide implications including photoemission from interstellar dust grains by starlight,¹ atmospheric electricity,² nucleation,³ and smog photochemistry,^{3,4} simply because pho-

size effect!!

TABLE I. Radius R , photoelectric threshold φ , and photoemission constant c [Eq. (7)] of Ag particles and macroscopic surface.

| | R (Å) | φ (eV) | c |
|---------------------|----------|----------------|----------------------|
| Particle | 30 | 4.55 | 1.8×10^{-3} |
| | 27 | 4.57 | 3.9×10^{-3} |
| | 20 | 4.65 | 8.9×10^{-3} |
| Macroscopic surface | ∞ | 4.90 | 7.3×10^{-5} |

Assembling Crystals from Clusters

S. N. Khanna and P. Jena

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000
(Received 14 April 1992)

It is shown that the stability of a cluster can be substantially enhanced by changing its size and/or composition so as to take advantage of the electronic shell filling as well as close atomic packing. The interaction between two such clusters is found to be weak and can form the basis for synthesizing a new class of cluster-assembled crystals with uncommon properties.

PACS numbers: 61.50.Cj, 36.40.+d, 68.65.+g

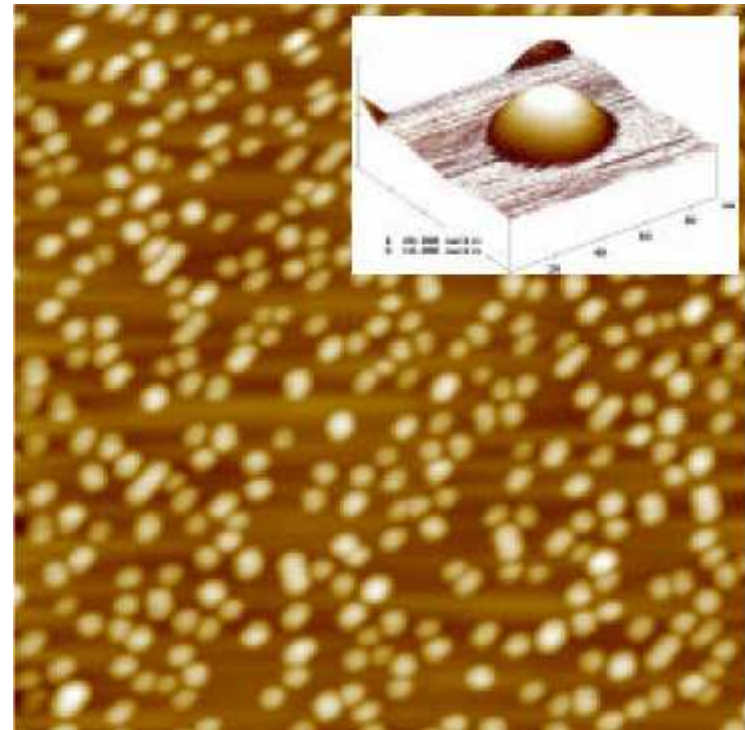
Atomic clusters have become one of the most exciting areas of research in the last decade not only because their study can bridge our understanding between molecular and condensed matter physics [1], but also because they can serve as a source of new materials with uncommon properties [2]. The electronic, optical, magnetic, and structural properties of clusters are size specific and the possibility that materials with desired properties can be custom made by changing the size and composition of cluster aggregates is limitless. However, there are some

quantum dots

Quantum Dots

Quantum Dots (QDs) are made from semiconductor nanostructures that confine the motion of conduction band electrons, valence band holes, or excitons in all three spatial directions.

- A quantum dot has a discrete quantized energy spectrum.
- The corresponding wave functions are spatially localized within the quantum dot, but extend over many periods of the crystal lattice.
- A quantum dot contains a small finite number (of the order of 1-100) of elementary electric charges.

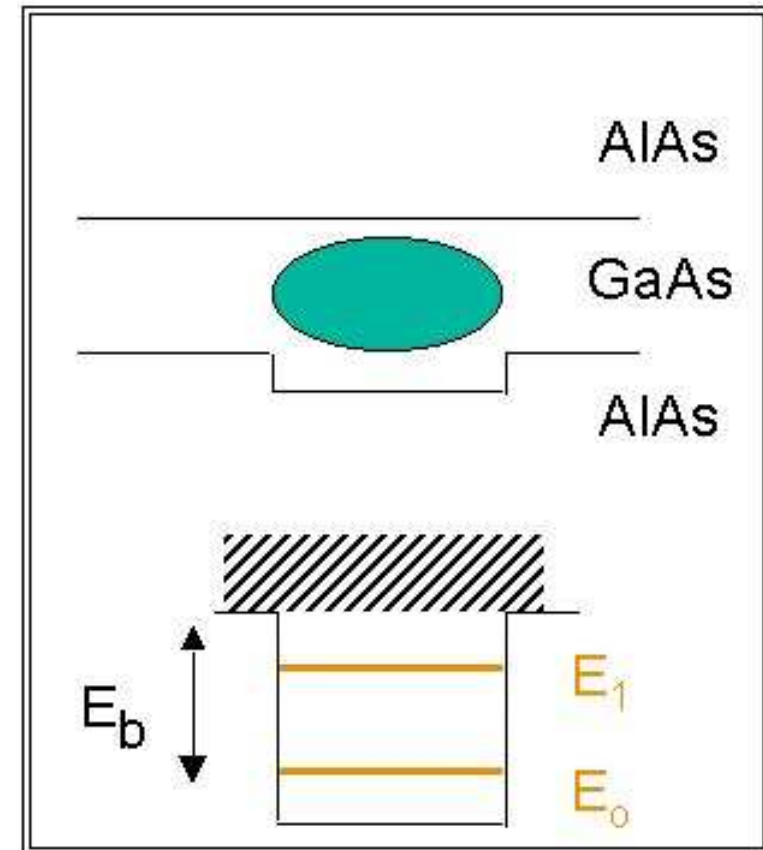


(CQD, Northwestern University)

Quantum Dots

Quantum Dots (QDs) are made from semiconductor nanostructures that confine the motion of conduction band electrons, valence band holes, or excitons in all three spatial directions.

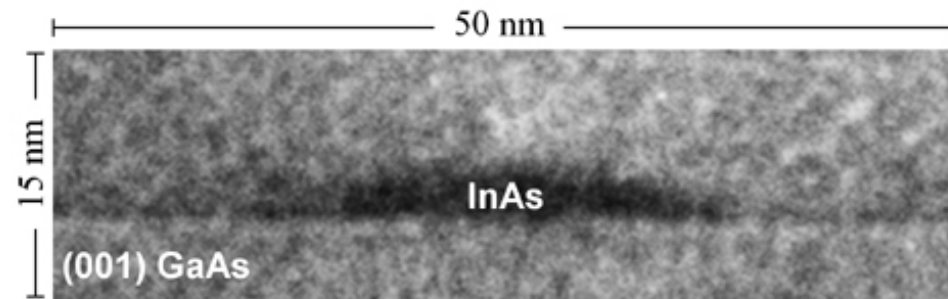
- A quantum dot has a discrete quantized energy spectrum.
- The corresponding wave functions are spatially localized within the quantum dot, but extend over many periods of the crystal lattice.
- A quantum dot contains a small finite number (of the order of 1-100) of elementary electric charges (active electrons and/or holes).



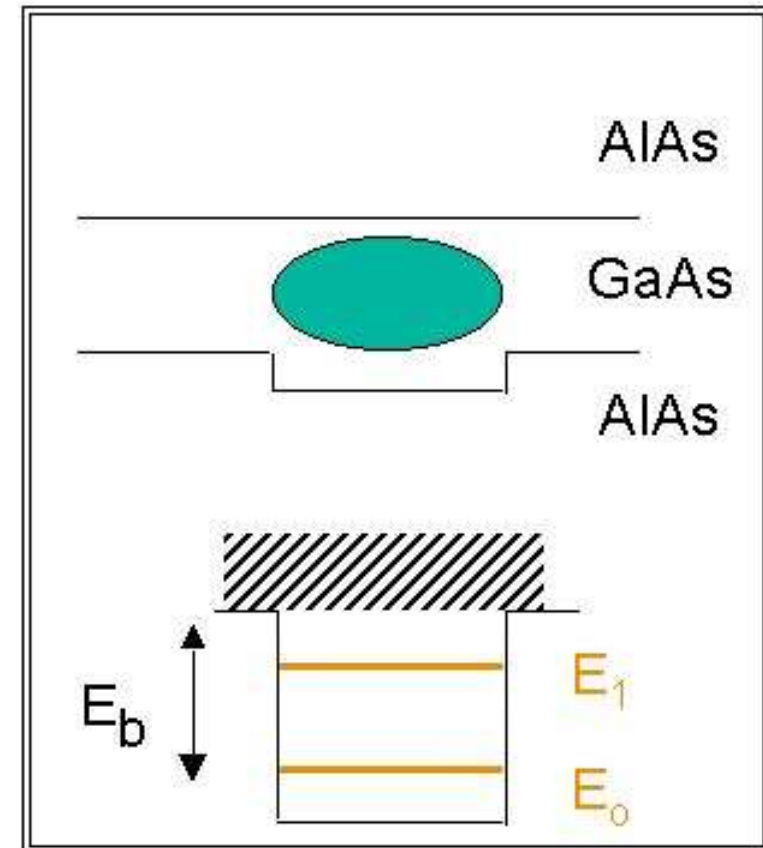
Self-Organized QDots



Quantum Dots



Cross section image of an InAs quantum dot imbedded into a GaAs matrix obtained by Transmission Electron Microscopy (Gilles Patriarche, LPN, CNRS, Marcoussis, France).

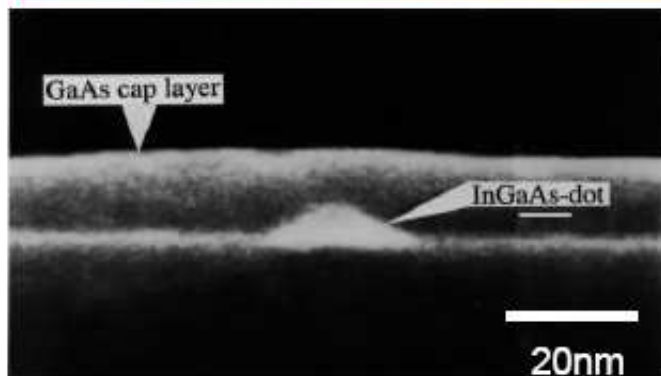


Self-Organized QDots

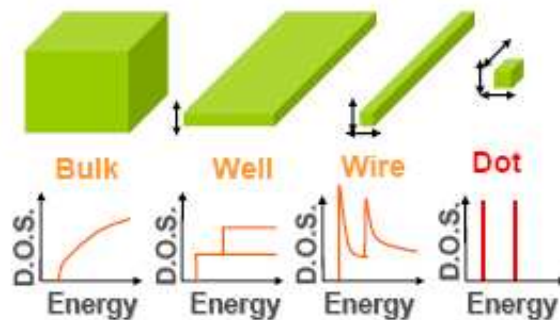
Quantum Dots: artificial atoms

It was 1982 that the concept of the "quantum dots" was proposed as artificial atoms for semiconductor laser applications by Arakawa and Sakaki.
(Appl. Phys. Lett. 40, 939 (1982).)

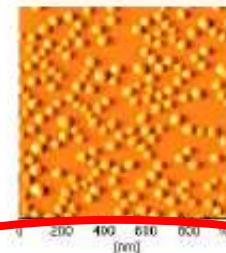
Quantum Dots



Quantum dot was proposed as a nanostructure for full confinement of electrons. Arakawa and Sakaki 1982



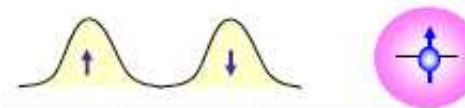
• Many electrons can take the same energy through spatial separation. Electrons are free from the Fermi-particle nature \rightarrow δ -function like DOS



• Individual control of electrons



• Quantum control of entanglement states with spin effects



Methods of fabrication: Synthesis of colloidal Quantum Dots



Synthesis of CdSe nanocrystals by injection of cadmium and selenium precursors into a high boiling point coordinating solvent at 360 degrees C. ~3nm particles of CdSe are initially generated. The intense color results from the quantum confinement effect on the electron as a result of the nanocrystal size being less than the Bohr radius of the electron. Thus, as the particles grow larger, they become redder in color. A size series was generated by allowing the crystals to grow at 280C over a period of ~2 minutes. The visible spectrum from 515nm (green) to 650nm (red) was covered.

Methods of fabrication: Synthesis of colloidal Quantum Dots

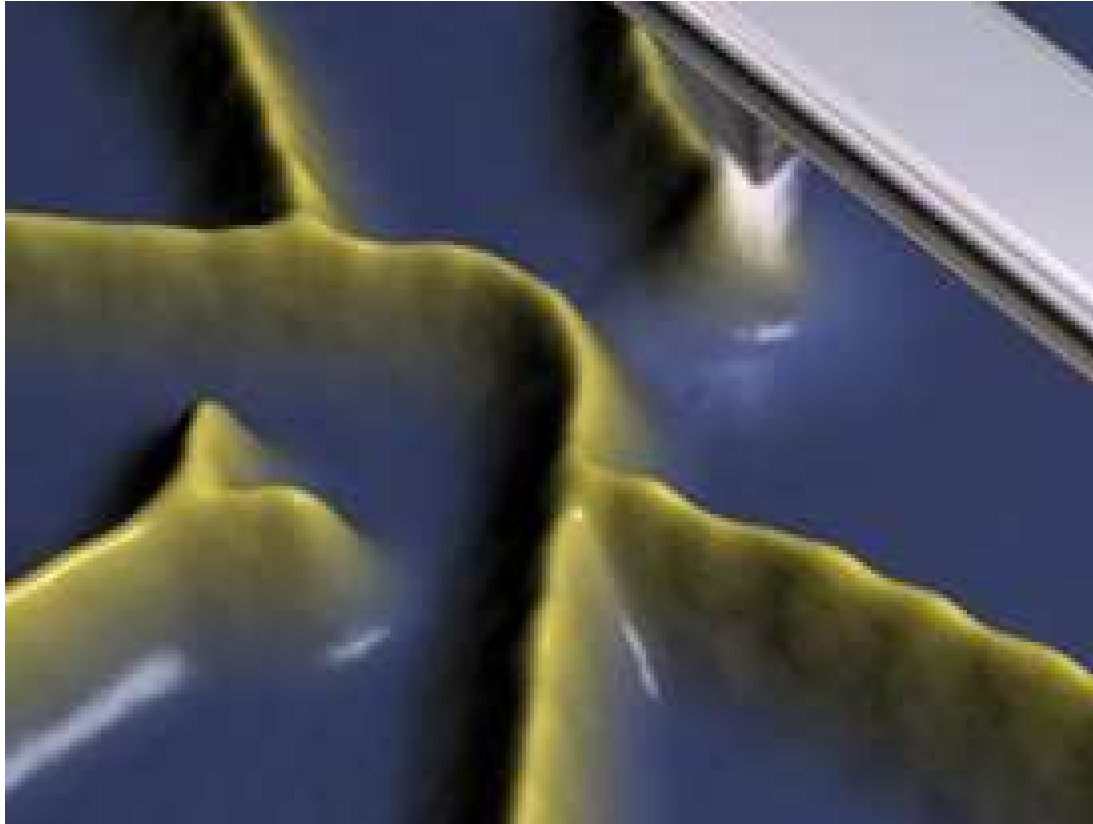
Quantum confinement in semiconductors occurs in volumes roughly 100 angstroms across. The optical absorption threshold for nanocrystallites of this size shifts to higher energies, away from the red end of the spectrum, as the crystallite becomes smaller. This effect appears most elegantly in CdSe clusters; the progression from deep red to orange to yellow as the diameter of the cluster declines can be clearly seen by the naked eye.

(Reed, Scientific American 1993)



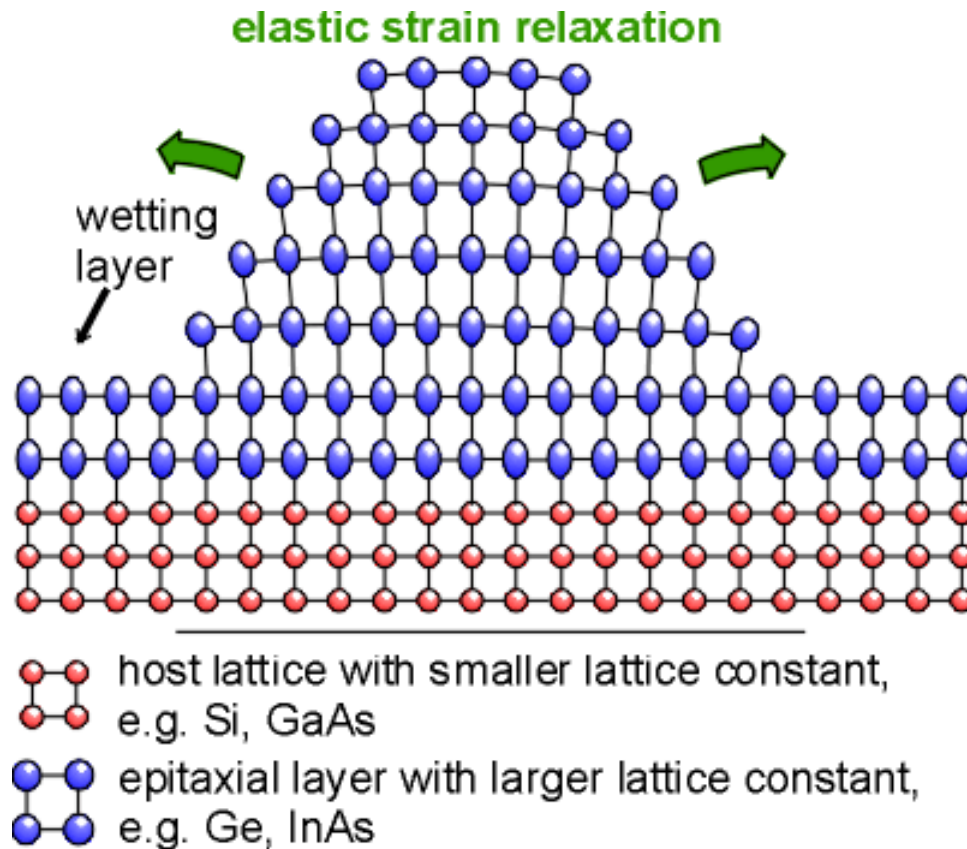
Image: Michael L. Steigerwald of AT&T Bell Laboratories.

Methods of fabrication: lithography



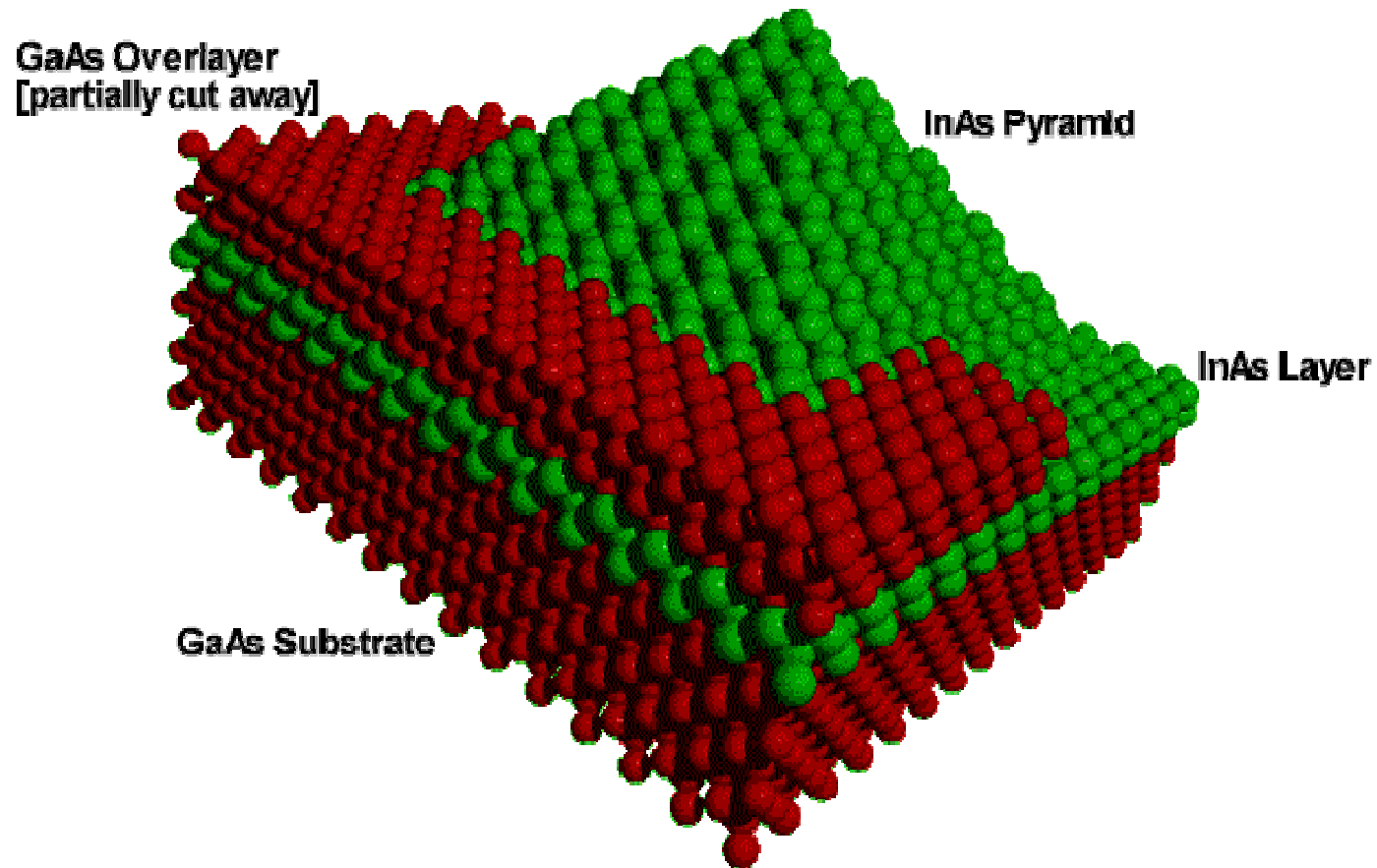
The samples can be created by oxidizing lines on the surface of a semiconductor heterostructure with a cantilever tip. The regions below the oxide lines become insulating, and in this way we are able to confine electrons to a small region in space.

Methods of fabrication: self-assembling (Molecular Beam Epitaxy)



Self-assembled quantum dots nucleate spontaneously under certain conditions during molecular beam epitaxy (MBE) and metallorganic vapor phase epitaxy (MOVPE), when a material is grown on a substrate to which it is not lattice matched. The resulting strain produces coherently strained islands on top of a two-dimensional "wetting-layer". This growth mode is known as Stranski-Krastanov growth. The islands can be subsequently buried to form the quantum dot.

Methods of fabrication: self-assembling (Molecular Beam Epitaxy)



<http://dipc.ehu.es/ricardo/master/nanohistory.htm>

