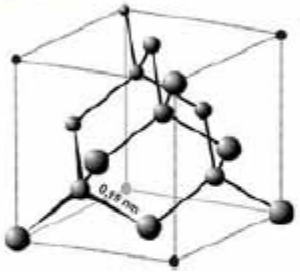
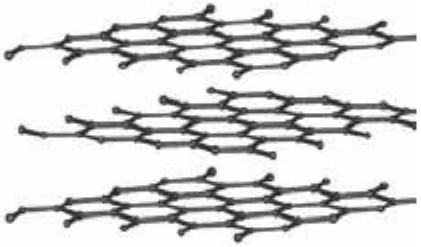
Forme allotropiche del Carbonio

FORME ALLOTROPICHE DEL CARBONIO

Forme allotropiche del carbonio

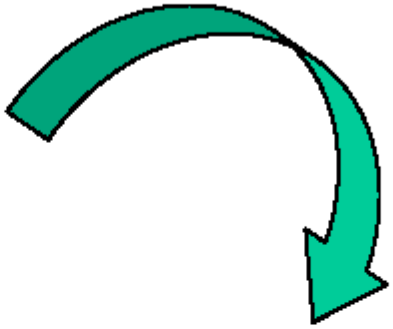


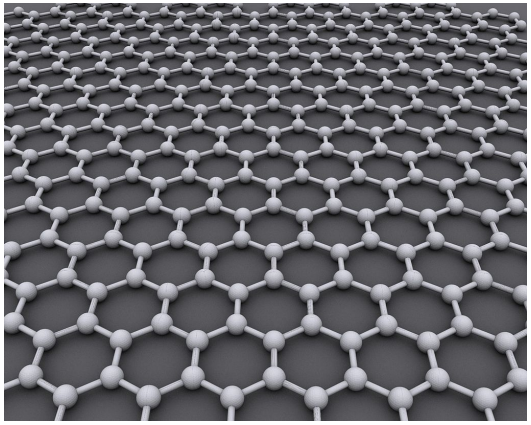


Diamante

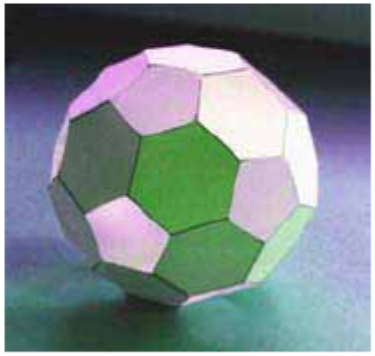
Grafite

materiale noto per
la sua durezza

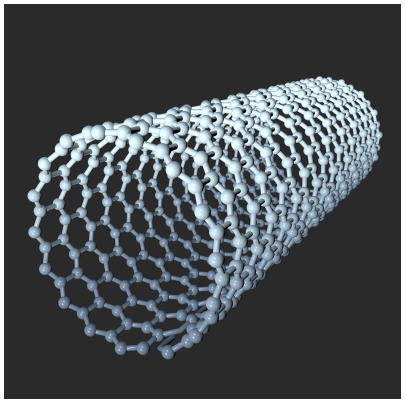




Grafene



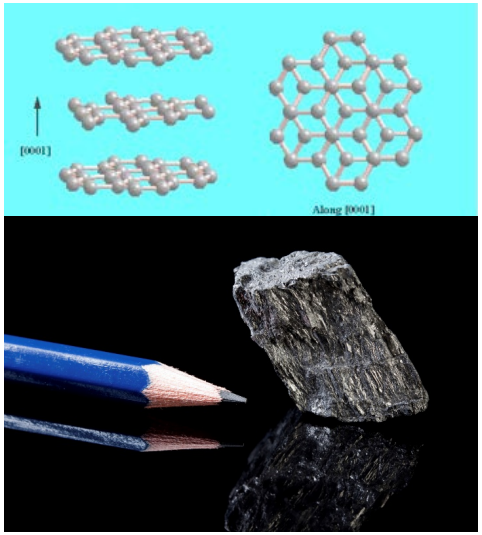
Fullerene



Nanotubi di carbonio

1970 { Eiji Osawa la teorizza
R.W.Henson la propone

GRAPHITE

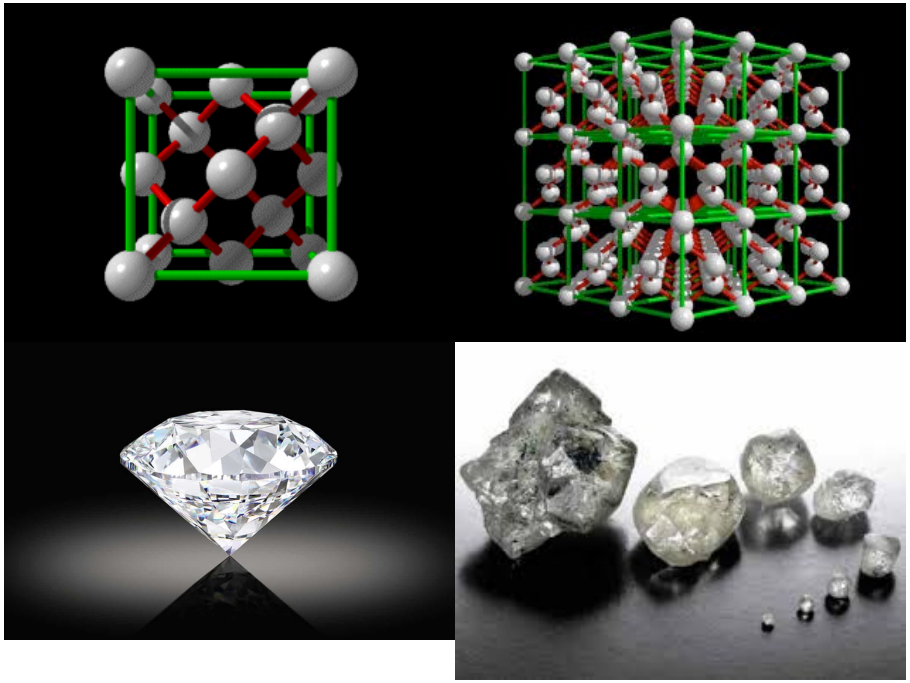


Graphite is a good electrical conductor, is greasy and finds wide use as lubricant; it is soI and black, with a weak metallic brightness.

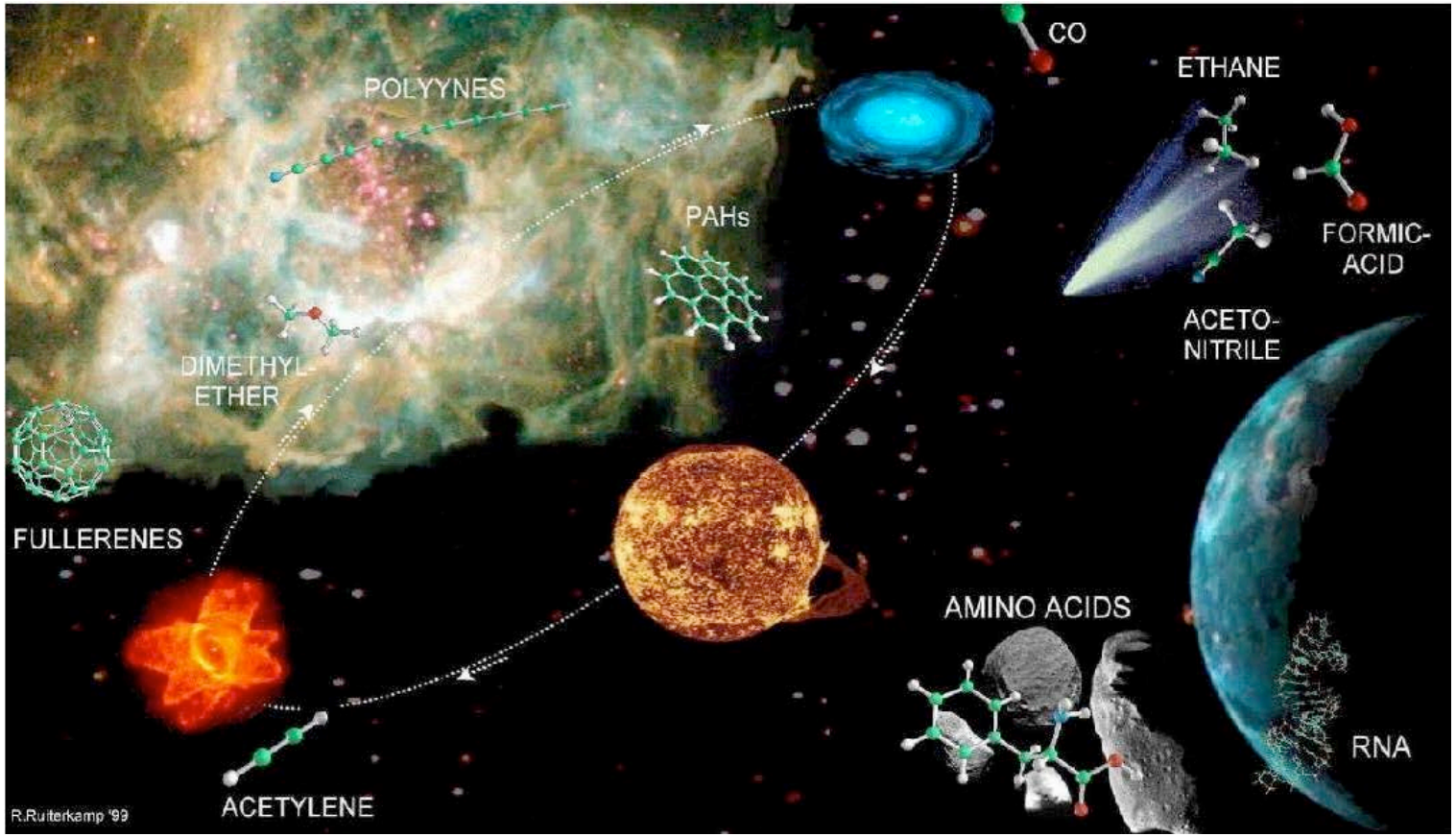
si forma alla temperatura di 1.200 ° C

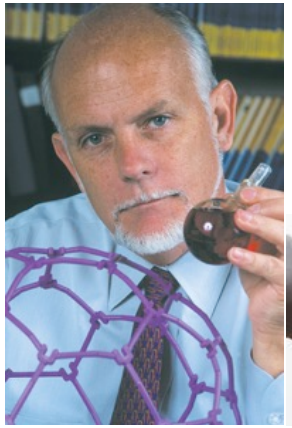
DIAMOND

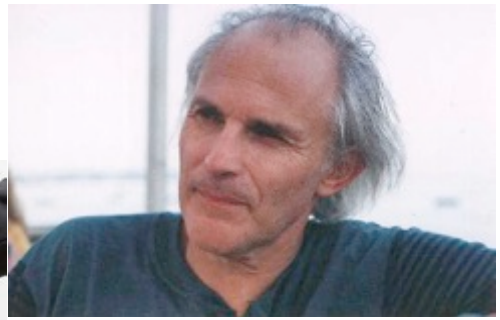
Tridimensional structure of diamond



si forma a temperature
comprese fra i 900 °C ed i 1.200 °C e pressione di circa 50 kbar

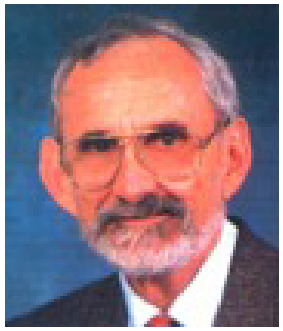

CO
ETHANE
POLYYNES
PAHs
FORMIC-
ACID
ACETO-
NITRILE
DIMETHYL-
ETHER
FULLERENES
AMINO ACIDS
RNA
ACETYLENE
R.Ruiterkamp '99





Richard E. Smalley
Rice U, USA
(1943 -2005)

Harold W. Kroto
U Sussex, UK
(1939 -2016)



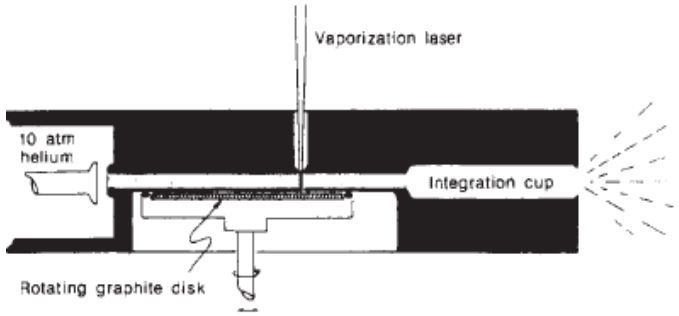
Robert F. Curl
Rice U, USA
(1933 -2022)

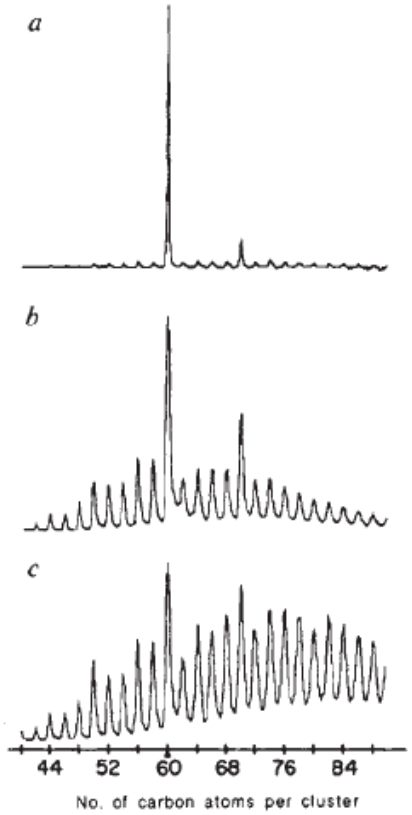
C_{60}: Buckminsterfullerene

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

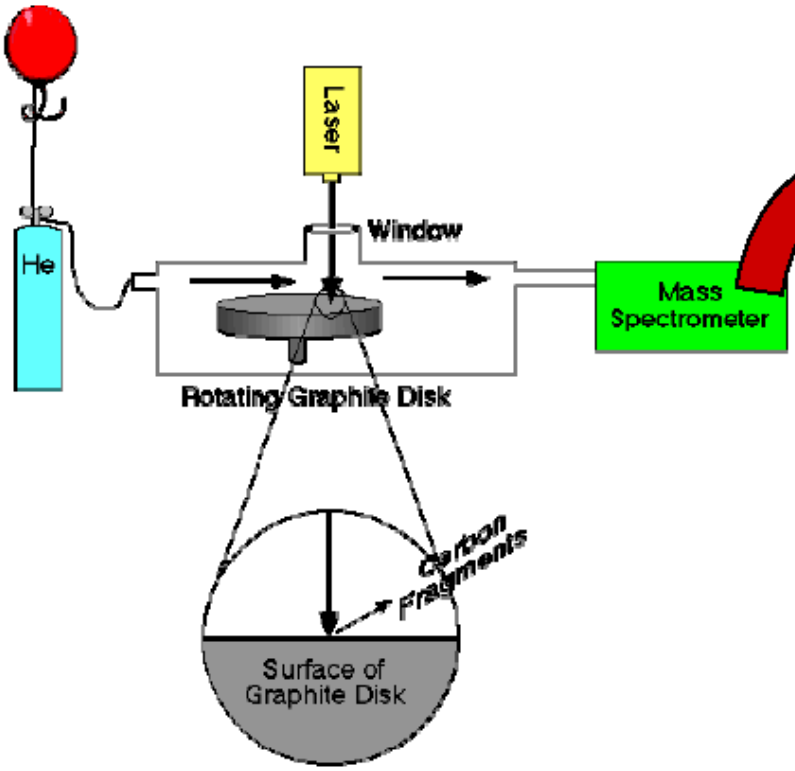
Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

NATURE VOL. 318 14 NOVEMBER 1985

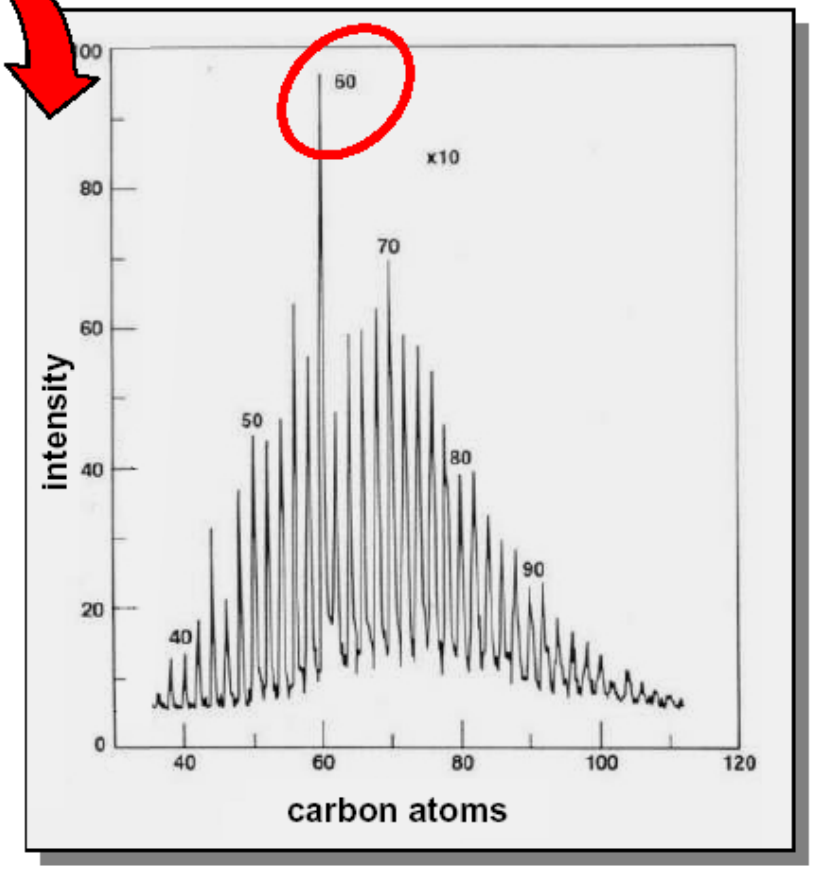




Fullerene: la scoperta

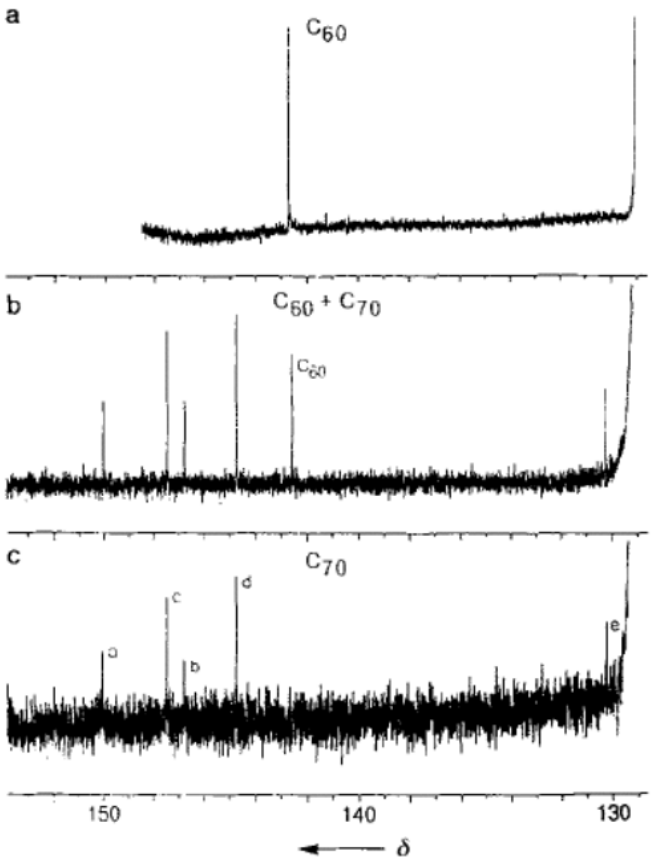


$M^+ = 720$



Nature **1985**, *318*, 162

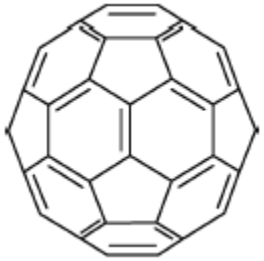
^{13}C NMR



struttura

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} 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.

FULLERENE

C_{60} 

scoperto nel 1985 da Kroto, Smalley and Curl, *Nature* **1985**, *318*, 162

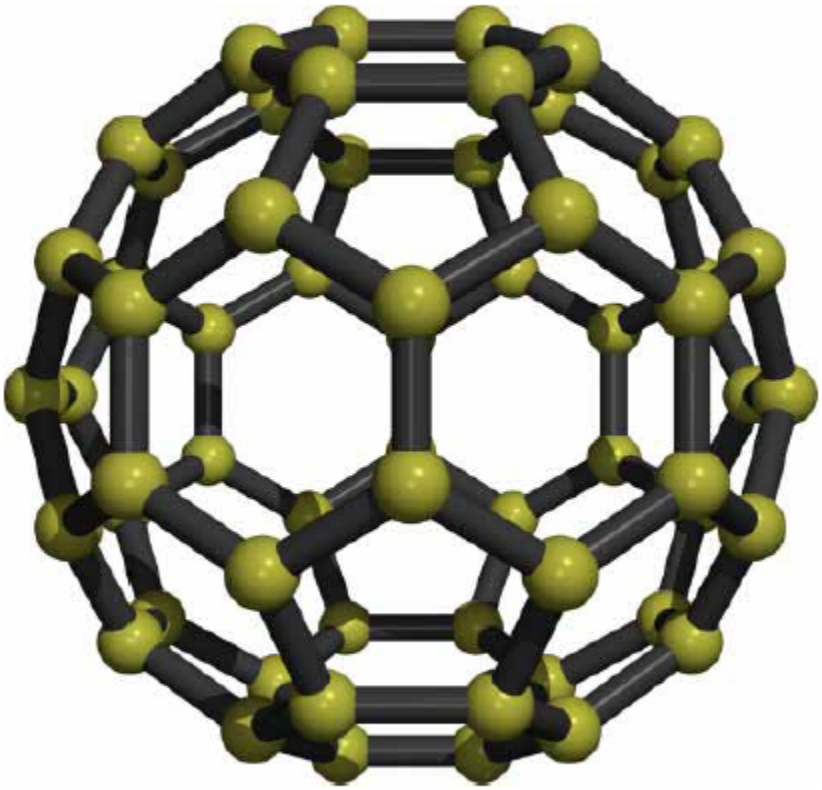
1996 Chemistry Nobel Prize

ROBERT F. CURL, Jr. , **SIR HAROLD W. KROTO** , and **RICHARD E. SMALLEY**

"for their discovery of fullerenes"

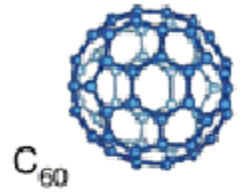
FULLERENE

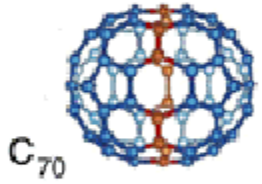
Fullereni

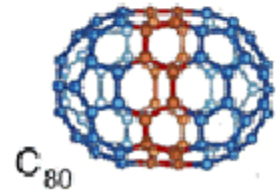


Buckminsterfullerene (C_{60})

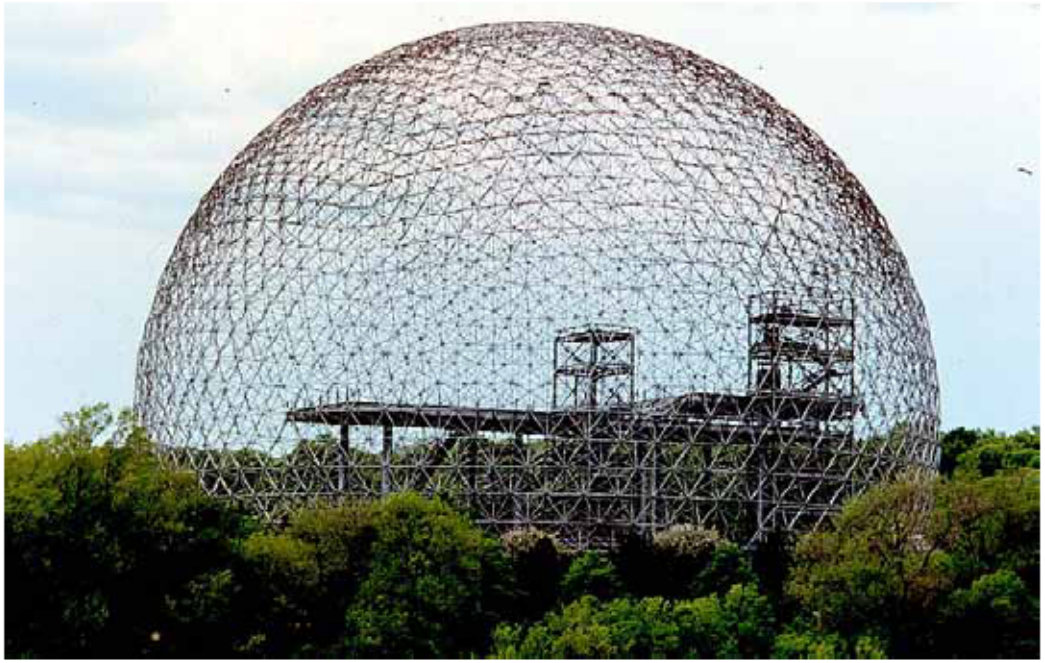
truncated icosahedron (I_h symmetry)







Buckminster Fuller



Geodesic Dome

Buckminster Fuller, US Pavilion for the 1967 International and Universal Exposition in Montreal

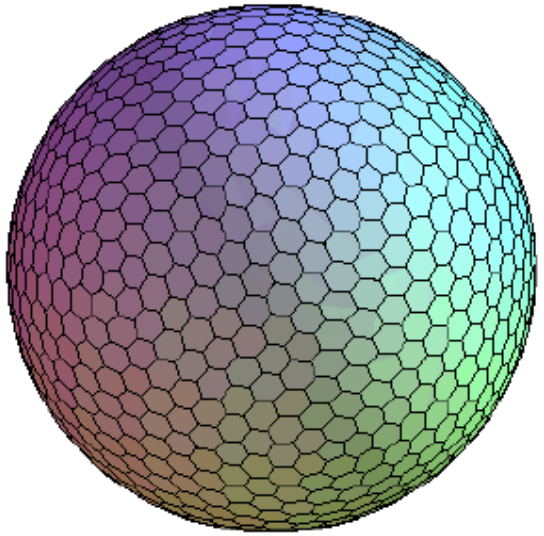
FULLERENE

Regola di Eulero

Un fullerene è un poliedro convesso con facce esagonali e pentagonali.

$$F - S + V = 2$$

Se uso solo esagoni $F - S + V = 0$. Affinché la formula di Eulero per i poliedri sia rispettata, occorre che diventi uguale a 2. In breve, occorre sostituire **12** esagoni con altrettanti **pentagoni**

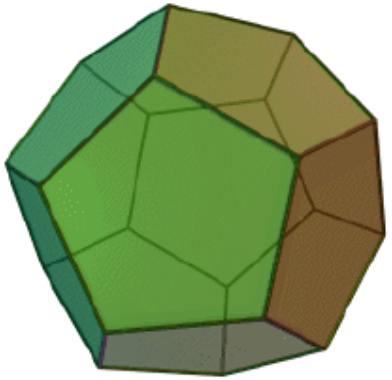


Il fullerene presenta 20 esagoni e 12 pentagoni

Facce 12

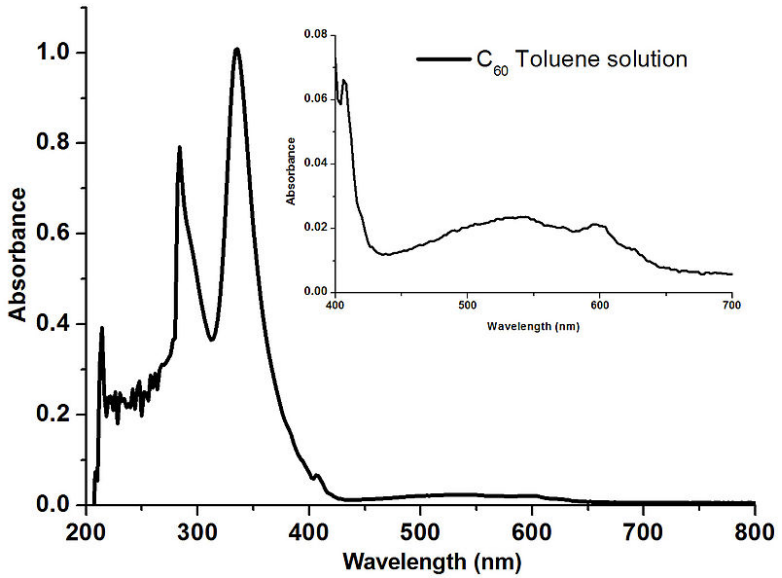
Spigoli 30

Vertici 20



C_{60} properties

Proprietà di ottica non lineare:



Spettro UV-Vis del C_{60} in toluene

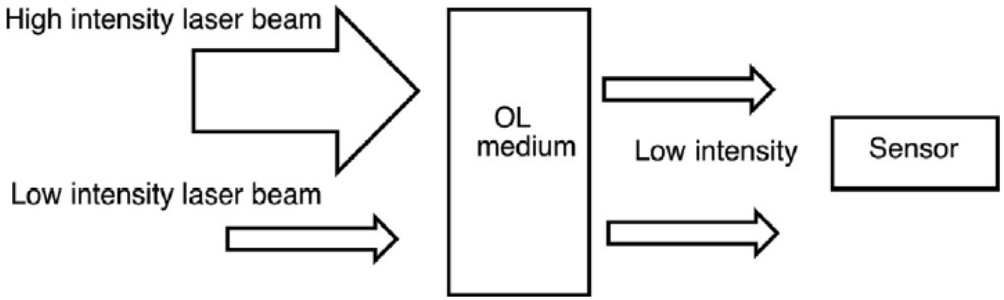
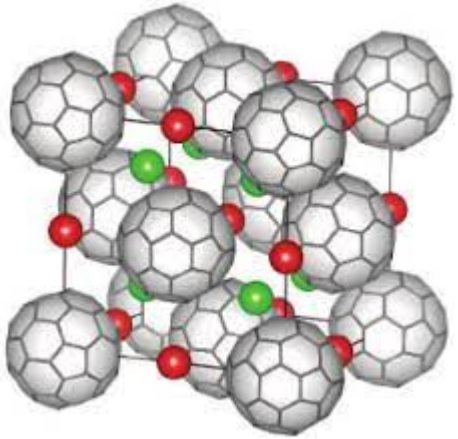


Fig. 1. Passive optical limiting for sensor protection with different laser intensities.

C_{60} properties

Superconduttore se dopato con metalli alcalini a T < 40 K



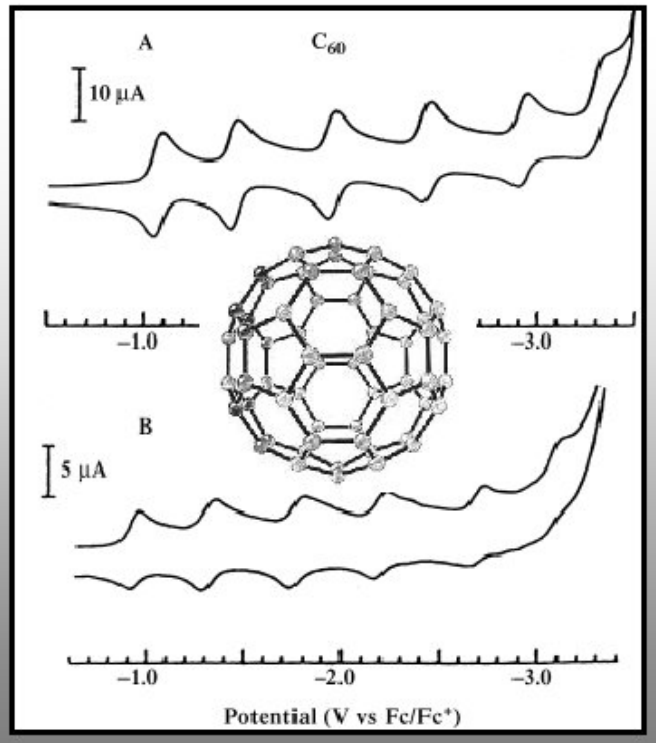
A_3C60

FULLERENE

C_{60} properties

proprietà elettrochimiche
può accettare fino a 6 elettroni

Cyclic voltammograms of C60 and C70 in a toluene solution



C_{60} properties

Organic Molecular Soft Ferromagnetism in a Fullerene C_{60}

PIERRE-MARC ALLEMAND, KISHAN C. KHEMANI, ANDREW KOCH, FRED WUDL, KAROLY HOLCZER, STEVEN DONOVAN, GEORGE GRÜNER, JOE D. THOMPSON

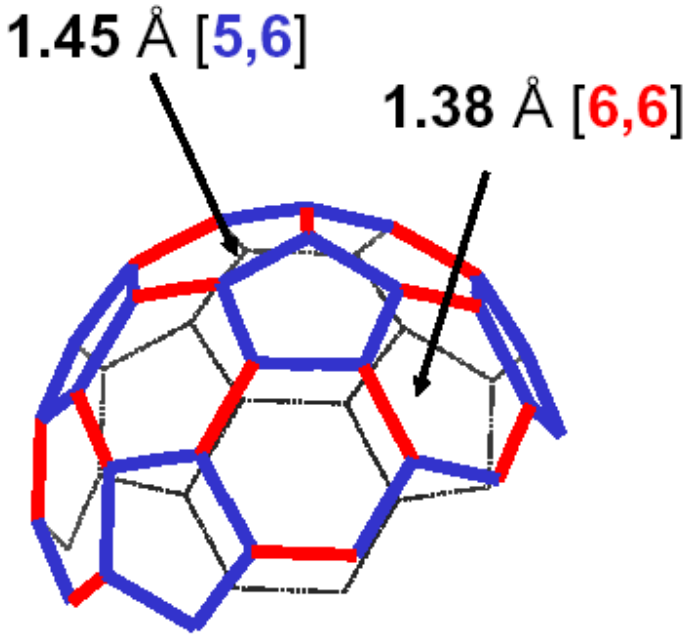
The properties of an organic molecular ferromagnet [$C_{60}TDAE_{0.86}$; TDAE is tetrakis(dimethylamino)ethylene] with a Curie temperature T_c = 16.1 kelvin are described. The ferromagnetic state shows no remanence, and the temperature dependence of the magnetization below T_c does not follow the behavior expected of a conventional ferromagnet. These results are interpreted as a reflection of a three-dimensional system leading to a soft ferromagnet.

Science, 1991

C_{60} properties

- X-Ray crystal structure determinations on C_{60} and on some of its derivatives have proved the existence of two different types of bonds: ‘short bonds’ or 6,6 junctions shared by two adjacent hexagons (ca. 1.38 A° long) and ‘long bonds’, or 5,6 junctions, fusing a pentagon and a hexagon (ca. 1.45 A° long).

Proprietà strutturali del C_{60}



ΔH_f = 10.16 Kcal/mol per C

(ΔH_f)graphite = 0 Kcal/mol

(ΔH_f)diamond = 0.4 Kcal/mol

The six-membered rings are **not aromatic** in that they contain alternating single and double bonds. 6,6-bonds are shorter than 5,6-bonds.

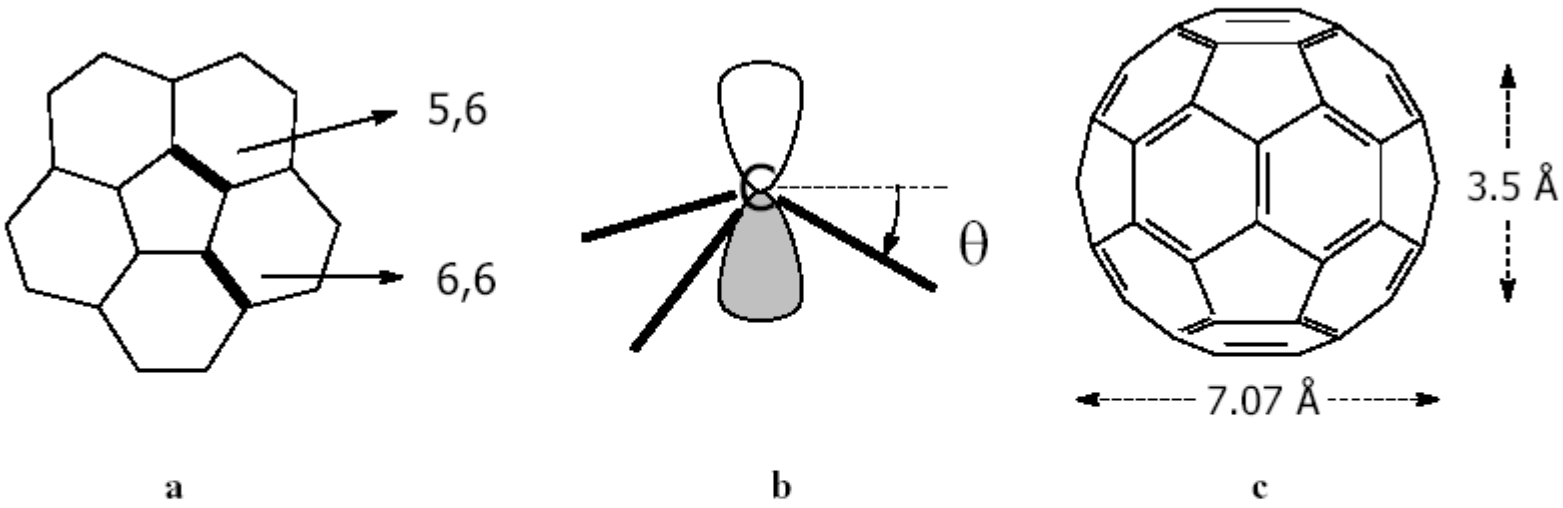
The overall buckyball structure has to be viewed as fused **1,3,5-cyclohaxatrienes** and **[5]radialenes**

spherical geometry causes **pyramidalization** of the unsaturated C-atoms. Strain Energy ≈ 80% H_f

- Haddon and Raghavachari, in *buckminsterfullerenes*, VCH, 1993
- H.D. Beckhaus et al. *Angew. Chem.* 1992, 31, 63)

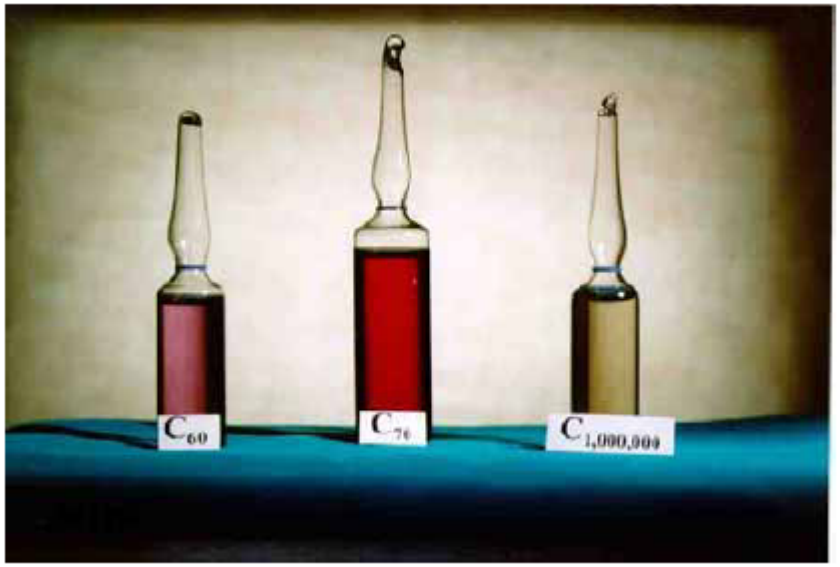
- A. Hirsch, Z. Chen, H. Jiao. *Angew. Chem.* **2000**, *39*, 3915.
- M. Bühl, A. Hirsch *Chem. Rev.* **2001**, *101*, 1119.

Proprietà strutturali del C_{60}

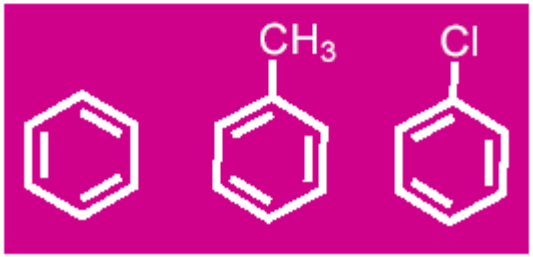


(**a**) legami 5,6 e 6,6 nel C_{60}; (**b**) angolo di piramidalizzazione θ; (**c**) diametro esterno (*edge-to-edge*) e interno del C_{60} (il diametro di Wan der Waals è circa 10.4 Å)

FULLERENE

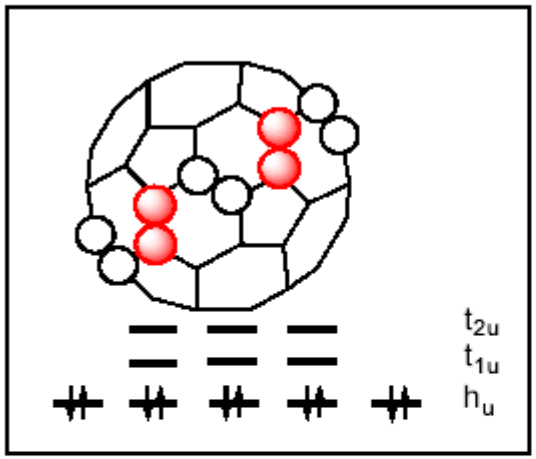


C_{60} solution in toluene



and CS_2

Reattività



C_{60} behaves essentially as a **strained electron-poor alkene**; addition chemistry is mainly driven by strain relief

fullerenes are very difficult to oxidize but are **readily reduced** (reactivity towards electron-rich reagents)

1,2-additions occur at 6,6-double bonds. In 1,2-adducts the bond- length alternation is totally preserved

the regioselectivity of addition reactions is governed by **avoidance of** products with **5,6 double bonds** in the lowest energy Kekulè structure (price tag of 8.5 kcal mol^{-1})

multiple addition to C_{60} is a complicated process governed by differences in bond order and LUMO coefficients at each site: many possible **regio-isomers**

FULLERENE

The **chemical transformations** that are possible with C60 could be classified in five main groups (figure 1.3):

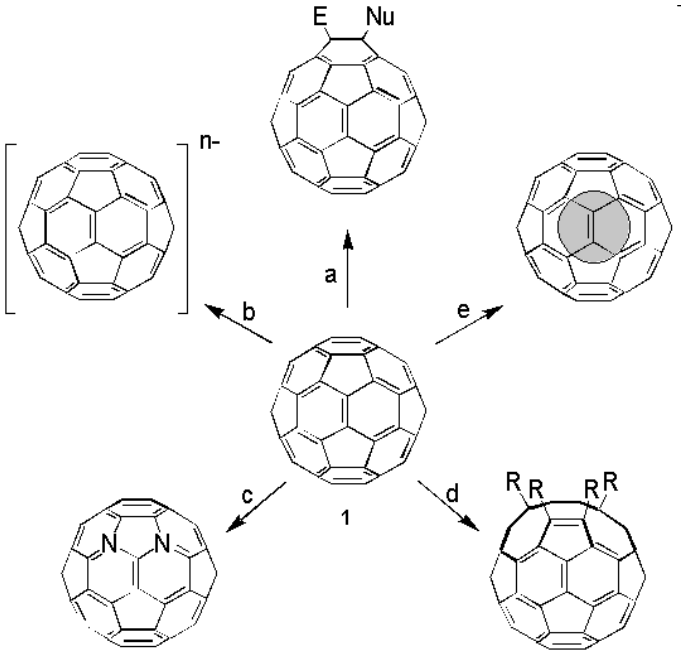
a) *Addition reactions*. Formation of exohedral compounds by addition of nucleophiles or radicals, cycloadditions, complexations with transition metals and others.

b) *Electron transfer reactions*. Chemical reduction of fullerenes can easily be achieved by reaction with electropositive alkali and alkaline earth metals or organic donor molecules.

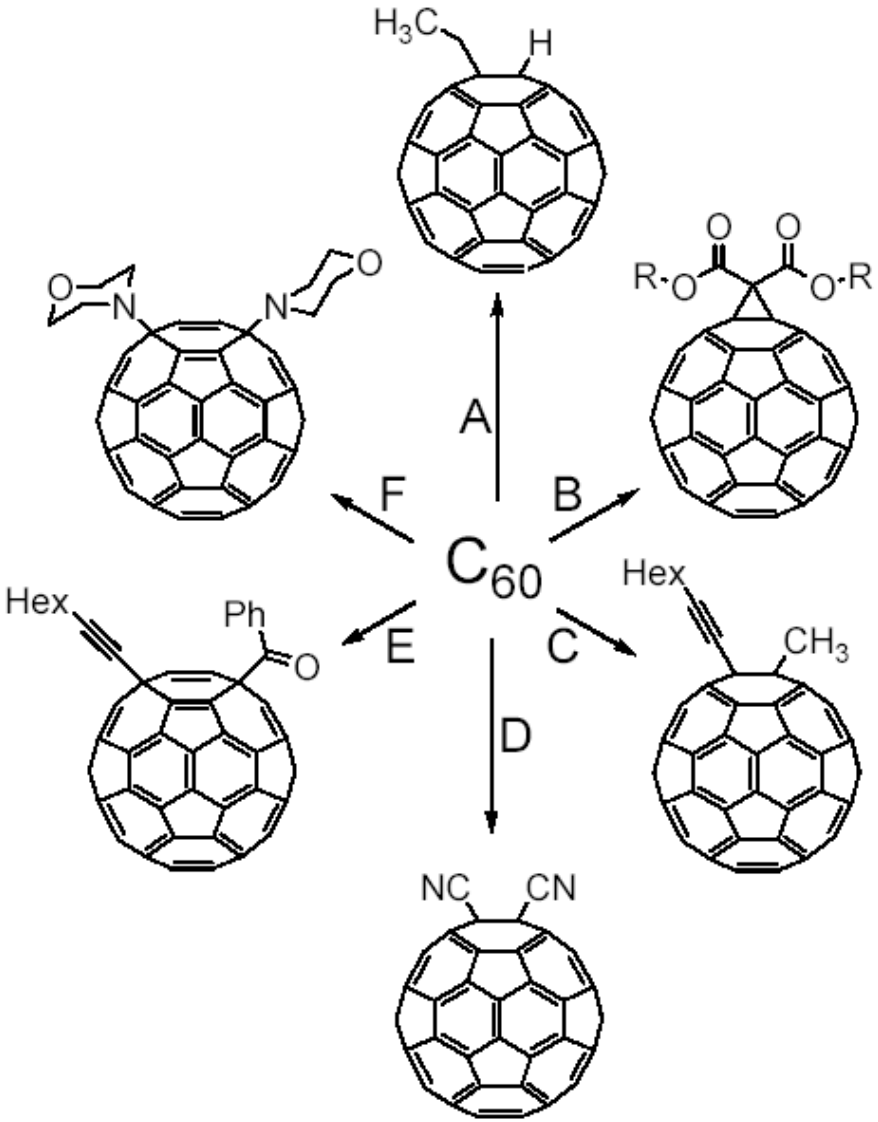
c) *Heterofullerenes*. Substitution of a carbon atom of the fullerene skeleton for a heteroatom, for example nitrogen or boron.

d) *Ring opening reactions*. Producing a hole in the C60 skeleton while breaking a discrete number of bonds.

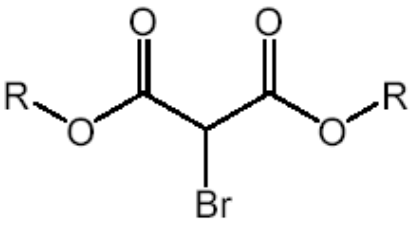
e) *Formation of endohedrals*. Introducing and trapping of atoms inside the spherical carbon cage.



Addizioni nucleofile al C_{60}



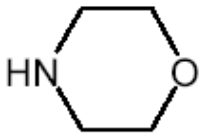
A EtMgBr, H^+

B  , NaH

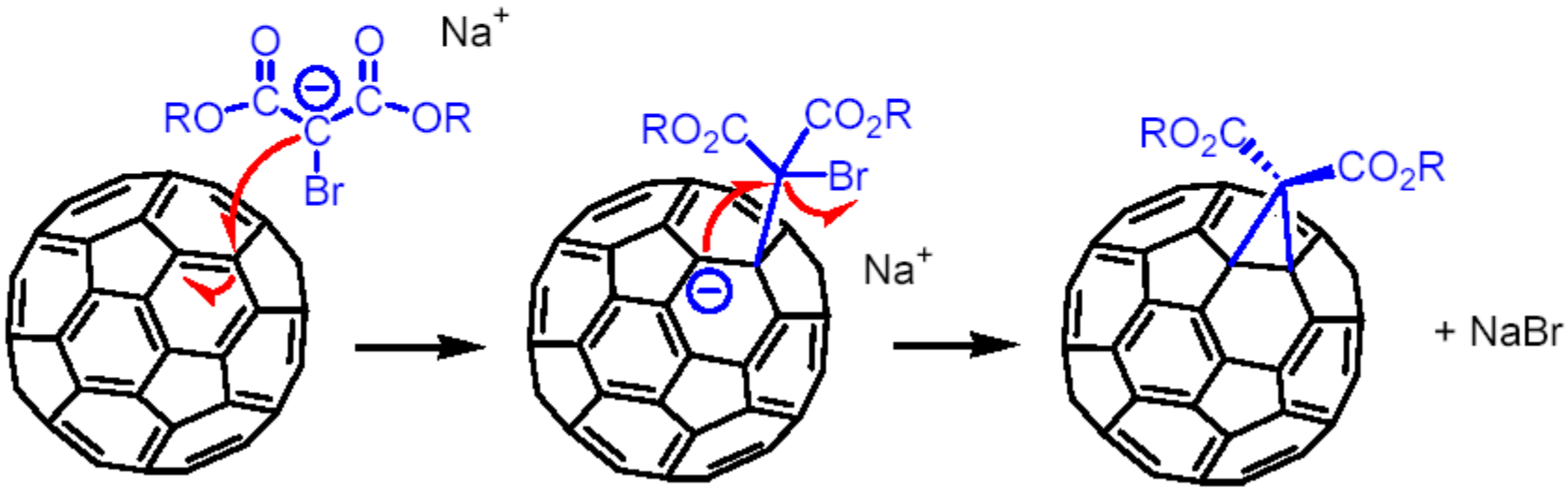
C Hex—≡—Li , MeI

D NaCN, TsCN

E Hex—≡—Li , PhCOCl

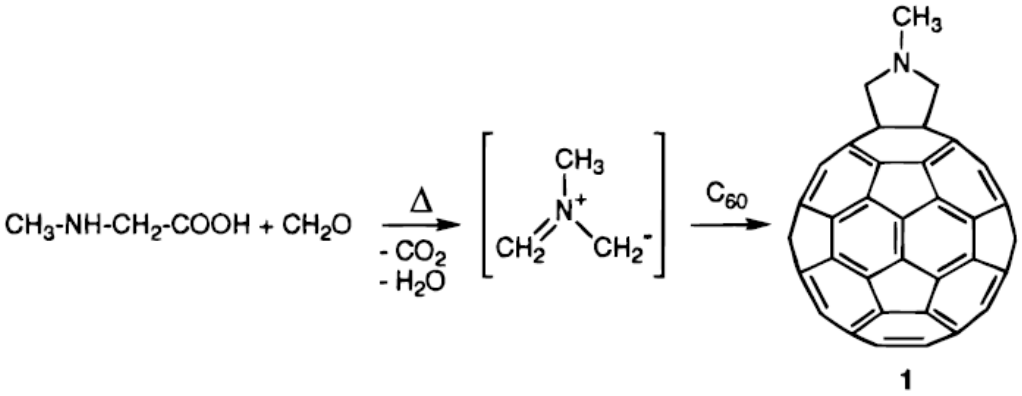
F 

Ciclopropanazione del C_{60} (metanofullereni)



1,3-dipolar cycloaddition of azomethineylides to C60

the Prato's reaction

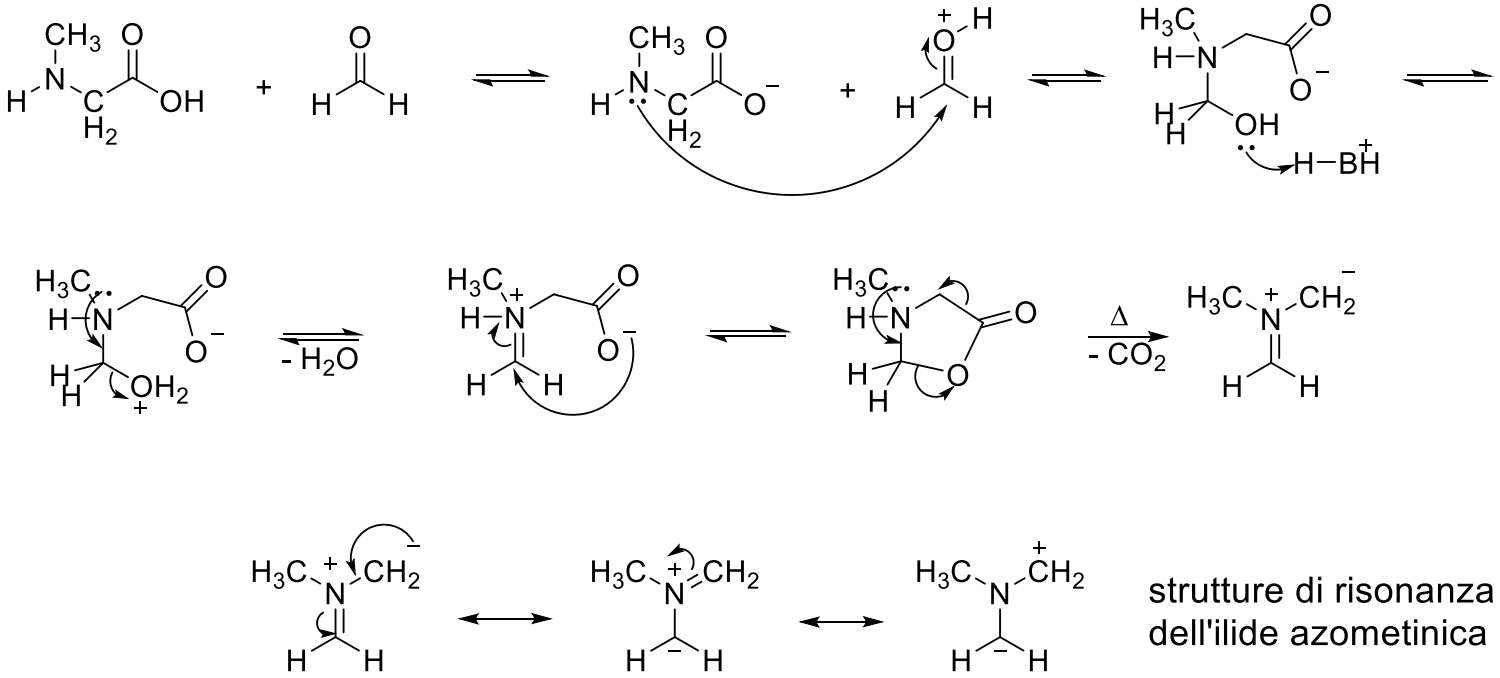


41% yield
82% on the consumed C60

the reaction is site selective in that it affords exclusively the product of cycloaddition across a 6,6 ring junction of the fullerene

Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798−9799.

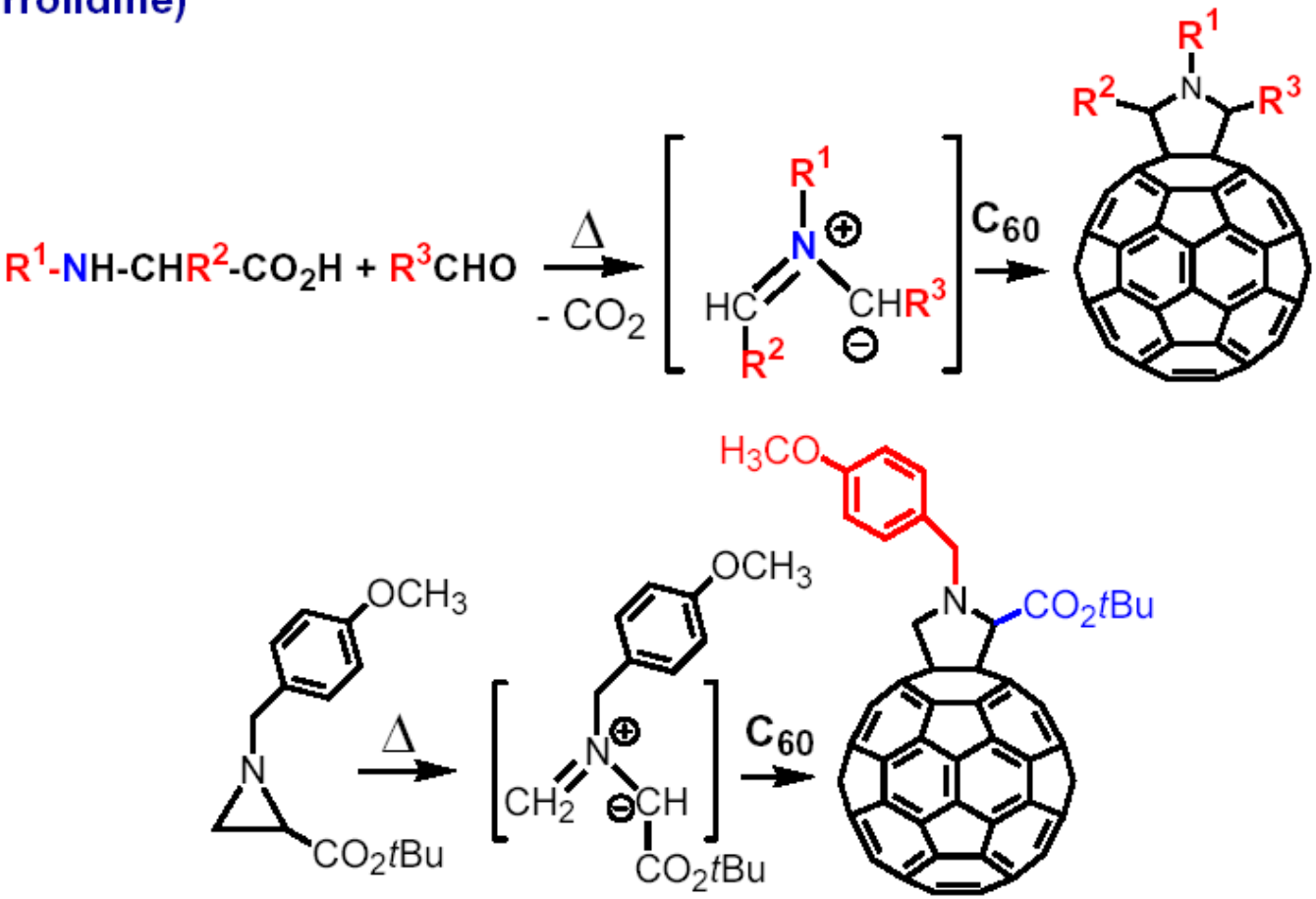
Meccanismo formazione ilide azometinica



strutture di risonanza dell'ilide azometinica

Cicloaddizione di ilidi azometiniche

(fulleropirrolidine)



M. Maggini, G. Scorrano, M Prato *J. Am. Chem. Soc.* **1993**, 9798
M. Prato, M. Maggini *Acc. Chem. Res.* **1998**, 519
X. Zhang, M. Willems, C. S. Foote *Tetrahedron Lett.* **1993**, 8187

FULLERENE

In the presence of large excesses of reagents, up to nine pyrrolidine rings can be introduced, as detected by MS analysis of the reaction crude.

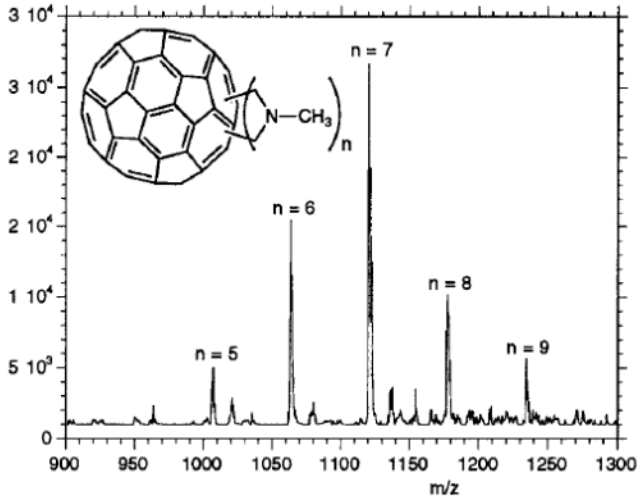
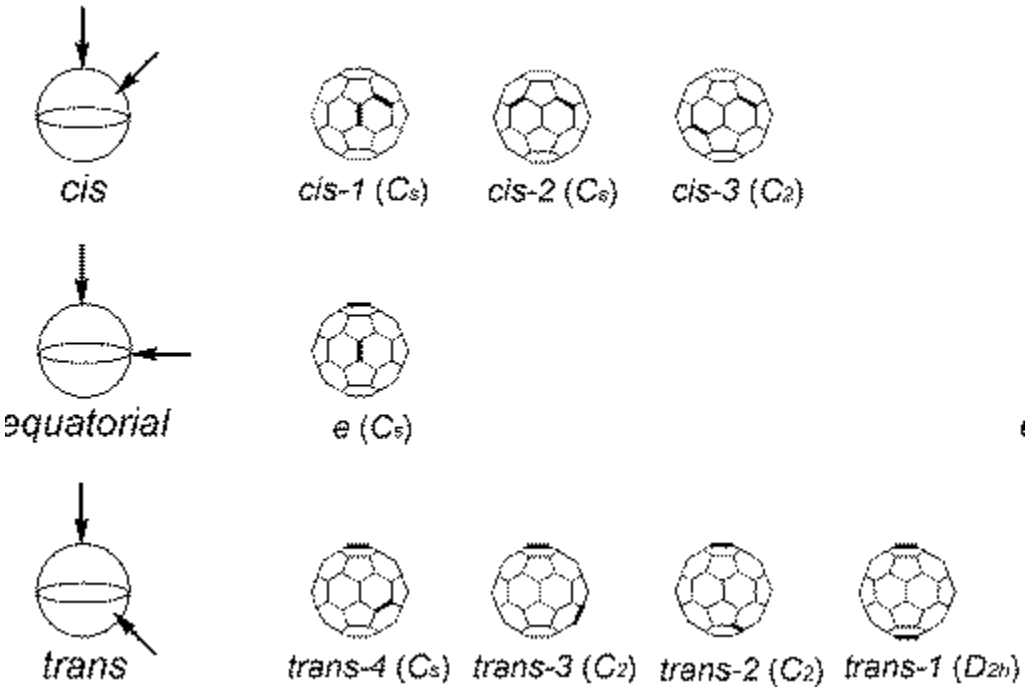


FIGURE 1. APCI-MS spectrum of the crude mixture obtained by heating a toluene solution containing C_{60}, 20 equiv of sarcosine, and 20 equiv of formaldehyde for 8 h.

Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799.

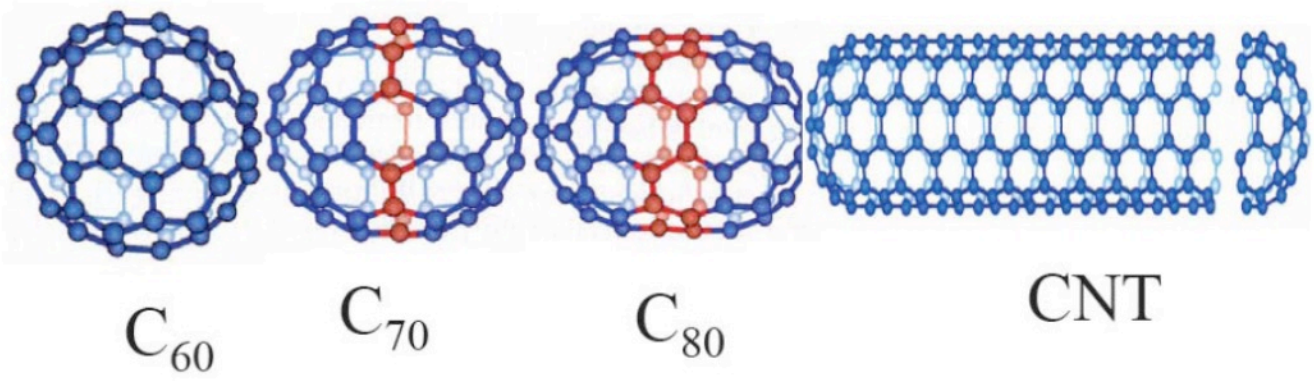
C60 bis-adducts



CNTs discover

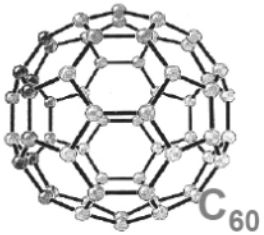
A paper by Oberlin, Endo, and Koyama published in **1976** clearly showed hollow carbon fibers with nanometer-scale diameters using a vapor-growth technique (Oberlin, A.; M. Endo, and T. Koyama, *J. Cryst. Growth* (March 1976). *Filamentous growth of carbon through benzene decomposition*. **32**. pp. 335–349.)

Iijima, Sumio (**1991**). "Helical microtubules of graphitic carbon". *Nature* **354**: 56–58.

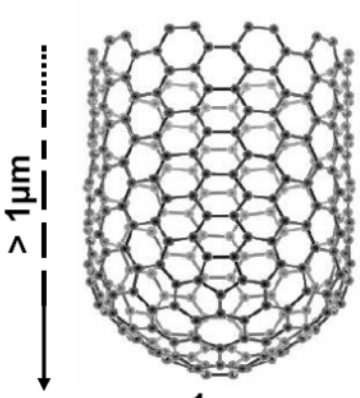


COMPOSTI AROMATICI POLICICLICI

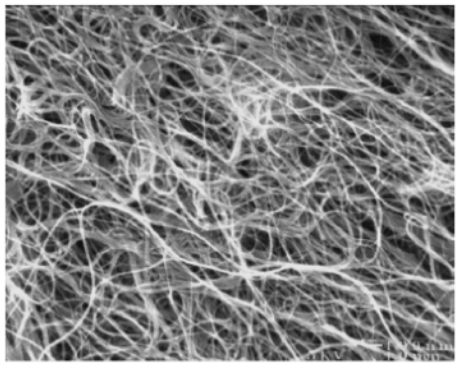
nanotubes

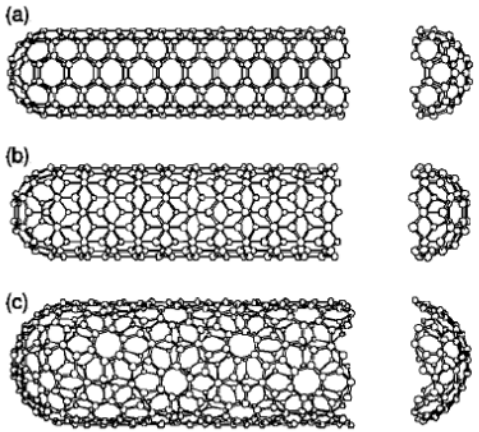


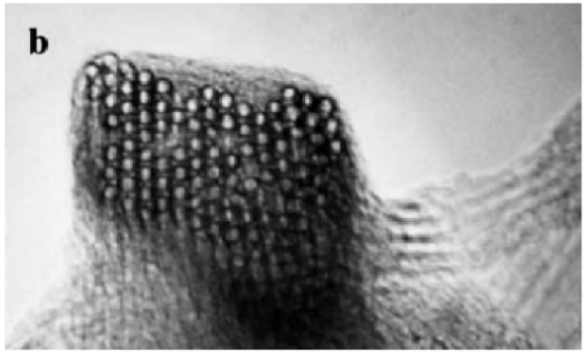
Fullerenes



Nanotubes







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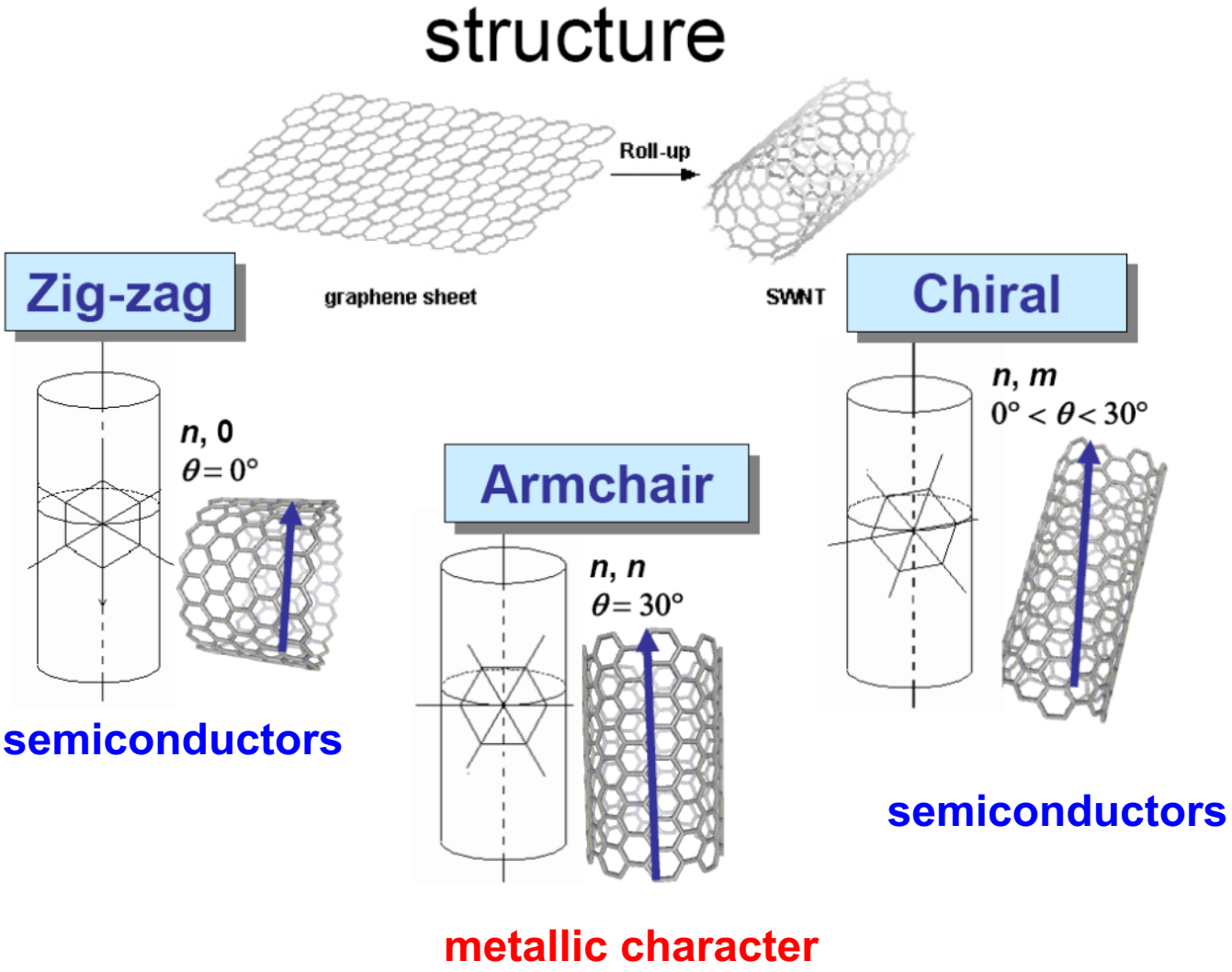

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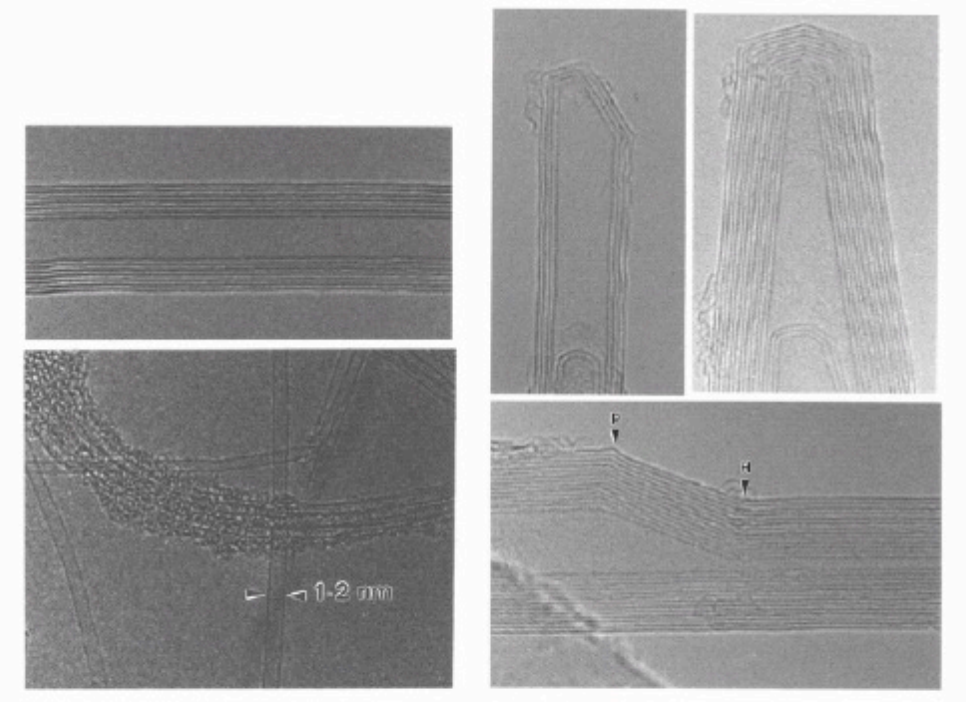


Figure 1-4: Different structures of MWNTs. Top-left: cross-section of a MWNT the different walls are obvious, they are separated by 0.34nm. Rotation around the symmetry axis gives us the MWNT. Top-right: Symmetrical or non-symmetrical cone shaped end caps of MWNTs. Bottom-left: A SWNT with a diameter of 1,2nm and a bundle of SWNTs covered with amorphous carbon. Bottom-right: A MWNT with defects. In point P a pentagon defect and in point H a heptagon defect.[6]

COMPOSTI AROMATICI POLICICLICI

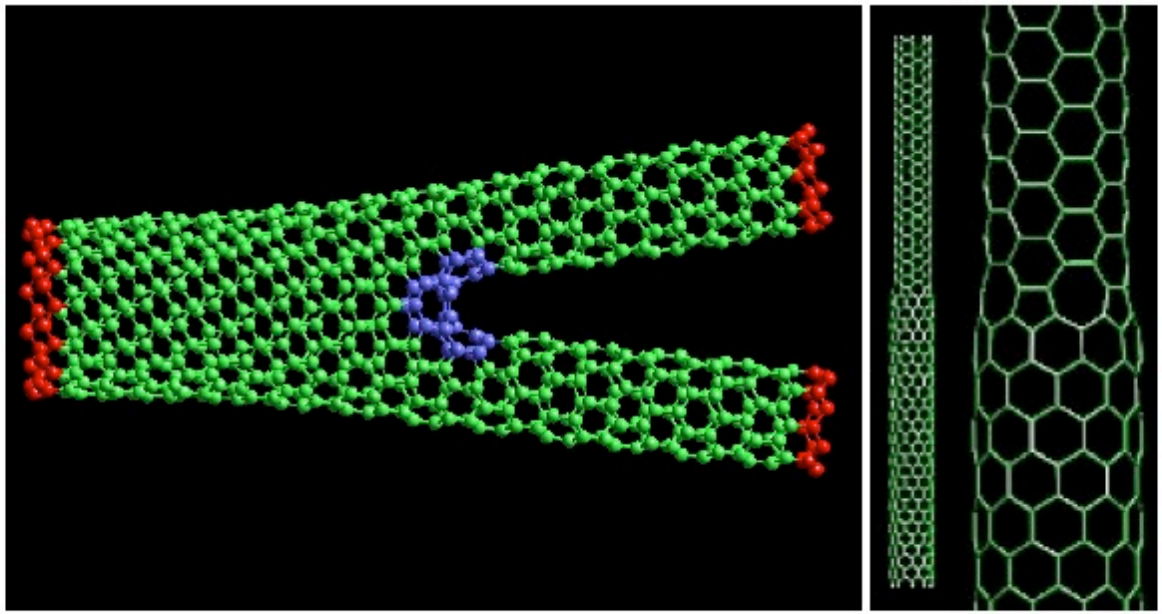


Figure 1-5: Left: A Y-branch, the defects are marked in blue. Right: A transition from a metallic to a semi-conducting SWNT. The change is made by insertion of pentagons and heptagons.

CNTs properties

SWNTs with different chiral vectors have dissimilar properties such as optical activity, mechanical, strength and electrical conductivity.

CNTs are 100 times stronger than steel

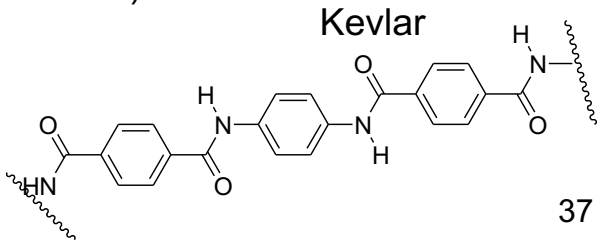
Comparison of Mechanical Properties

Material	Young's Modulus(1) (GPa)	Tensile Strength (GPa)	Elongation at Break (%)
SWNT	~1 (from 1 to 5)	13-53[E]	16
Armchair SWNT	0.94[T]	126.2[T]	23.1
Zigzag SWNT	0.94[T]	94.5[T]	15.6-17.5
Chiral SWNT	0.92		
MWNT	0.8-0.9[E]	150	
Stainless Steel	~0.2	~0.65-1	15-50
Kevlar	~0.15	~3.5	~2
Kevlar[T]	0.25	29.6	

1. misura della durezza di un materiale elastico

(The tangent modulus of the initial, linear portion of a stress-strain curve is called *Young's modulus)*

Kevlar



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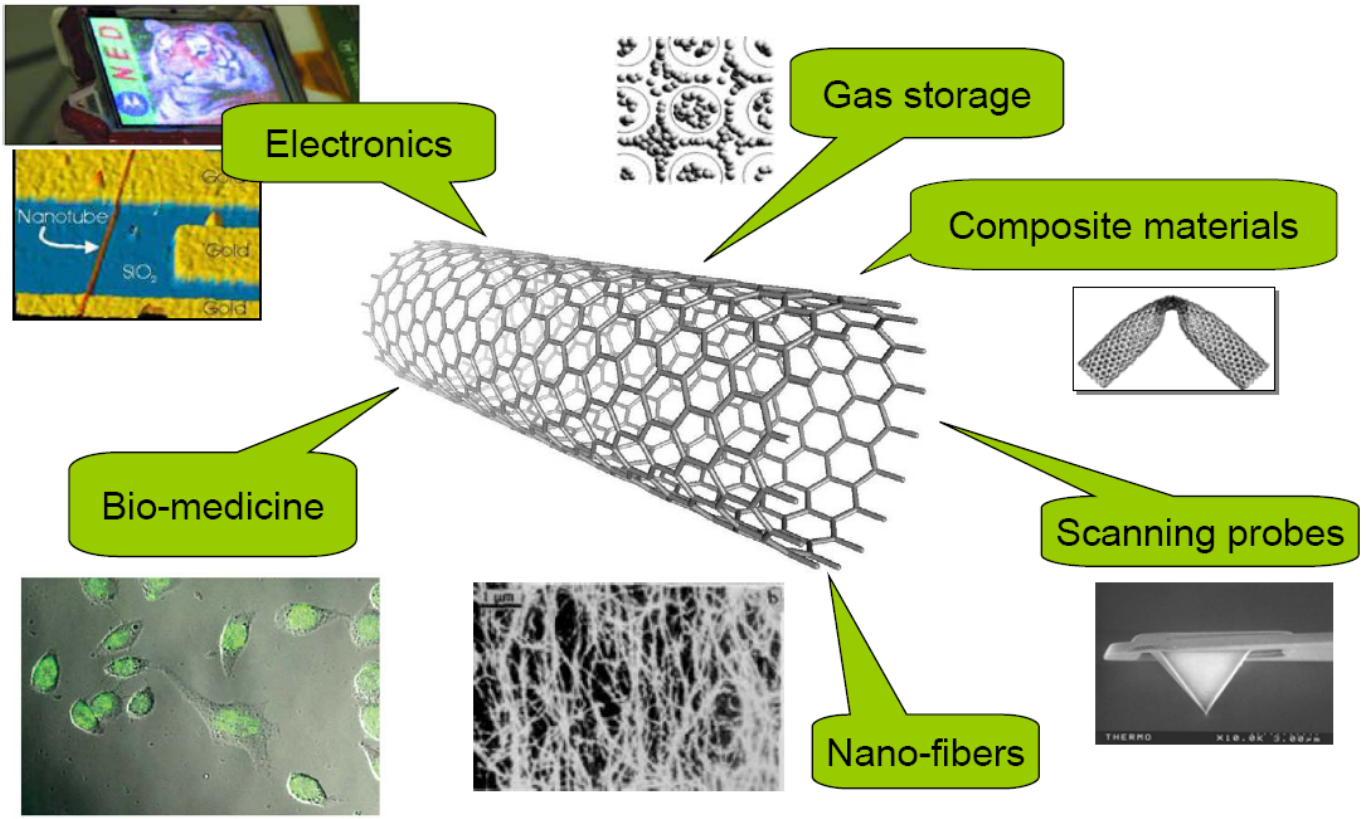


I CNT sono meccanicamente molto più resistenti delle tradizionali fibre di carbonio (sono 100 volte piú forti dell'acciaio, 2 volte piú leggeri dell'alluminio) ed eccezionalmente flessibili quando assoggettati a distorsioni (possono essere piegati a grandi angoli e poi raddrizzati senza danno).

COMPOSTI AROMATICI POLICICLICI

purification

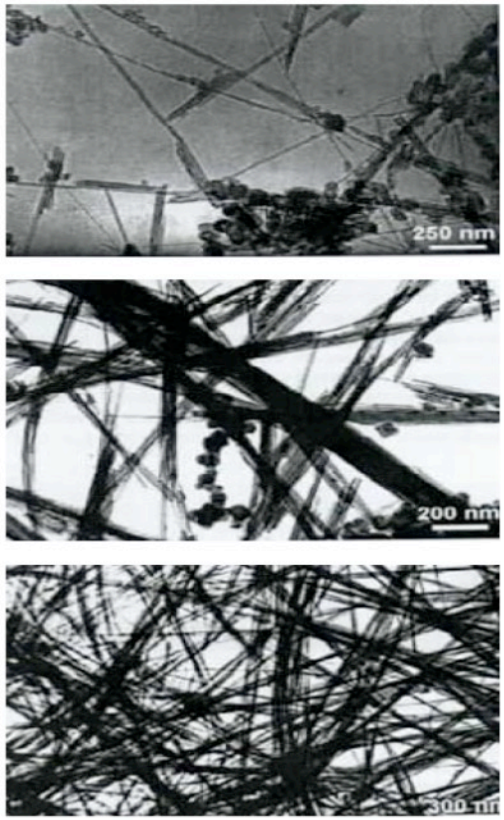
Oxidation
- acid solution
- air at high T

Separation
- surfactants
- chromatography

Annealing

10.5 %

1 %



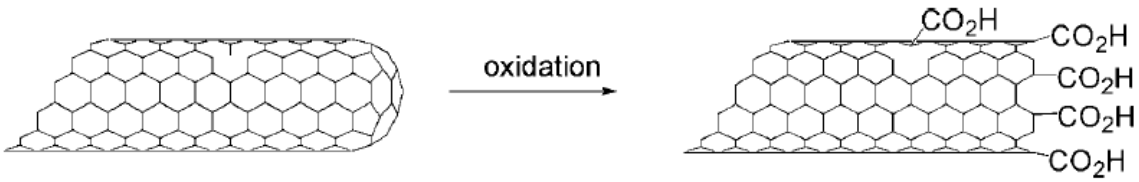
C. Furtado et al., *J. Am. Chem. Soc.* **2004**, *126*, 6095-6105

R. C. Haddon et al., *Mrs Bulletin* **2004**, *29*, 252-259.

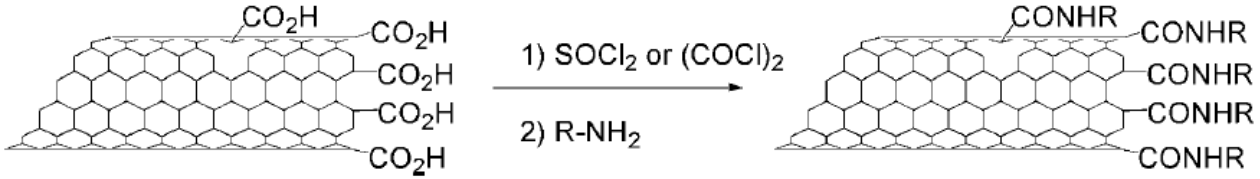
COMPOSTI AROMATICI POLICICLICI

funzionalizzazione di CNT

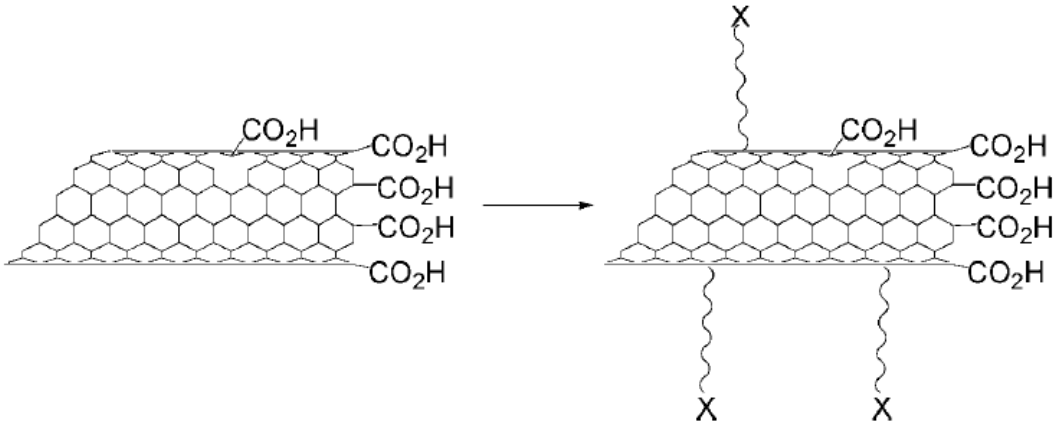
SCHEME 2. Oxidation of Carbon Nanotubes



SCHEME 3. Amidation Reaction of Oxidized Carbon Nanotubes



SCHEME 4. Functionalization of Carbon Nanotubes Using Addition Reactions (X = Functional Groups)



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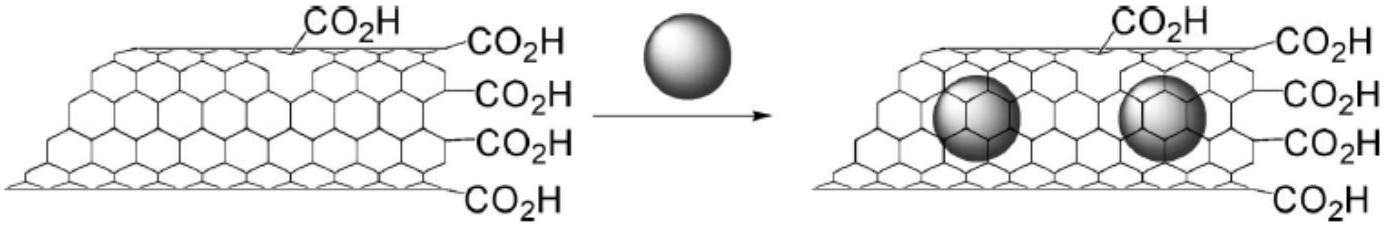
SCHEME 5. Insertion inside Carbon Nanotubes



fullerenes, porphyrins, and metals, have indeed been included
in the internal space of CNT, mostly due to hydrophobic interactions

COMPOSTI AROMATICI POLICICLICI

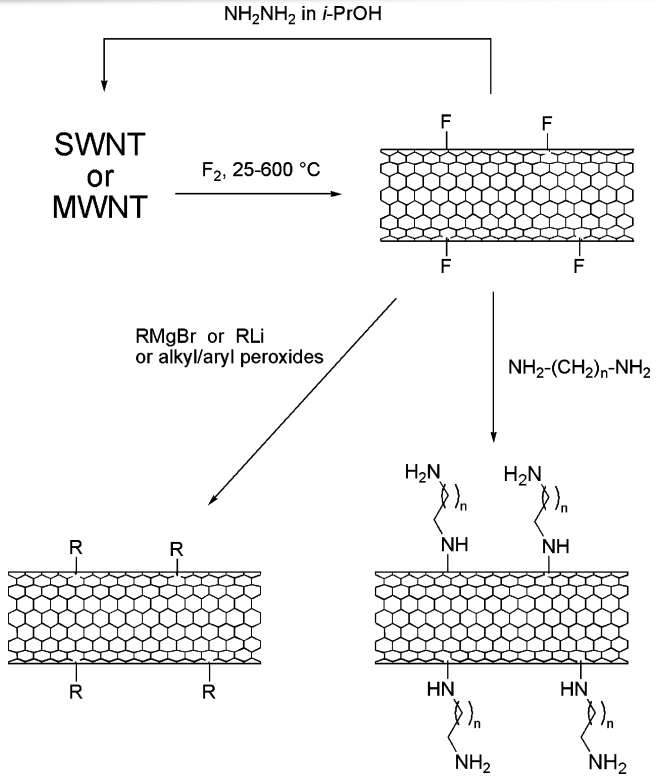


Figure 1. Reaction scheme for fluorination of nanotubes, defunctionalization, and further derivatization.

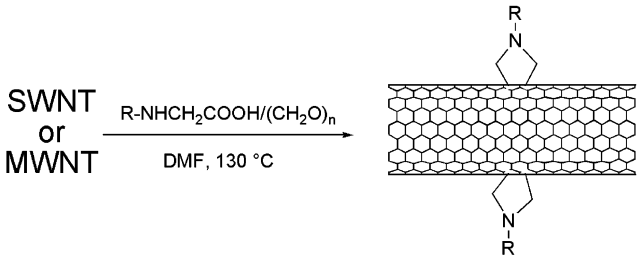


Figure 5. 1,3-Dipolar cycloaddition of azomethine ylides.

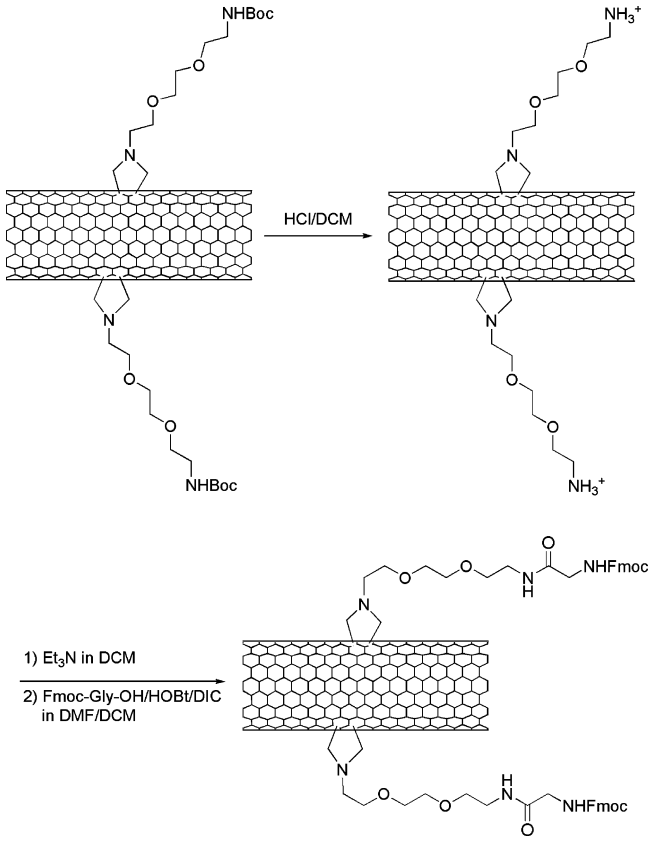


Figure 6. Reaction pathway for obtaining water-soluble ammonium-modified nanotubes. The latter can be used for the delivery of biomolecules.

COMPOSTI AROMATICI POLICICLICI

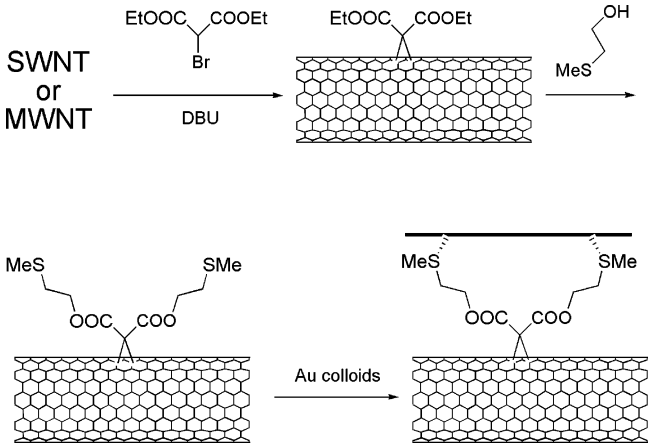


Figure 8. Bingel reaction on nanotubes and subsequent attachment to gold nanoparticles.

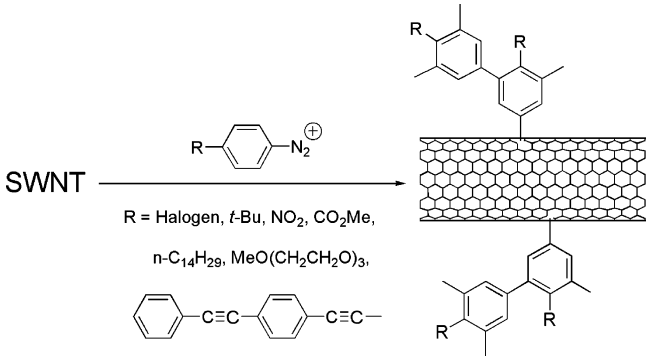


Figure 9. Derivatization scheme by reduction of aryl diazonium salts.

COMPOSTI AROMATICI POLICICLICI

funzionalizzazione via interazioni deboli

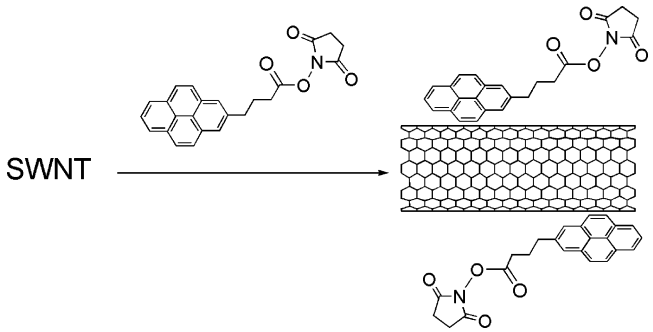


Figure 19. Interactions of nanotubes with pyrene derivatives.

nature nanotechnology

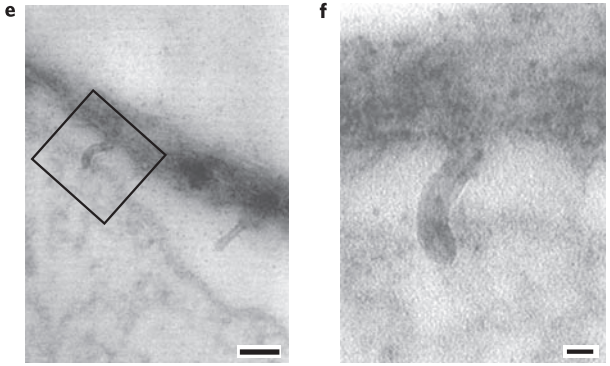
ARTICLES

PUBLISHED ONLINE: 21 DECEMBER 2008 | DOI: 10.1038/NNANO.2008.374

Carbon nanotubes might improve neuronal performance by favouring electrical shortcuts

Giada Cellot[1], Emanuele Cilia[1†], Sara Cipollone[2], Vladimir Rancic[1], Antonella Sucapane[1], Silvia Giordani[2†], Luca Gambazzi[3], Henry Markram[3], Micaela Grandolfo[4], Denis Scaini[5], Fabrizio Gelain[6], Loredana Casalis[5], Maurizio Prato[2], Michele Giugliano[3,7‡] and Laura Ballerini[1‡*]

we show, using single-cell electrophysiology techniques, electron microscopy analysis and theoretical modelling, that nanotubes improve the responsiveness of neurons by forming tight contacts with the cell membranes that might favour electrical shortcuts between the proximal and distal compartments of the neuron.



tight contact between nanotubes and membranes. The morphology of such contacts is indicative of the development of hybrid nanotubes – neuronal units .

High-magnification micrographs from a section consecutive to those of b and c. The rectangular area in e is magnified in f. Note how nanotubes are ‘pinching’ neuronal membranes.

nature chemistry

ARTICLES

PUBLISHED ONLINE: 8 AUGUST 2010 | DOI: 10.1038/NCHEM.761

Efficient water oxidation at carbon nanotube–polyoxometalate electrocatalytic interfaces

Francesca M. Toma[1,2], Andrea Sartorel[3], Matteo Iurlo[4], Mauro Carraro[3], Pietro Parisse[2,5], Chiara Maccato[3], Stefania Rapino[4], Benito Rodriguez Gonzalez[6], Heinz Amenitsch[7], Tatiana Da Ros[1], Loredana Casalis[2,5], Andrea Goldoni[5], Massimo Marcaccio[4], Gianfranco Scorrano[3], Giacinto Scoles[2], Francesco Paolucci[4], Maurizio Prato[1]* and Marcella Bonchio[3]*

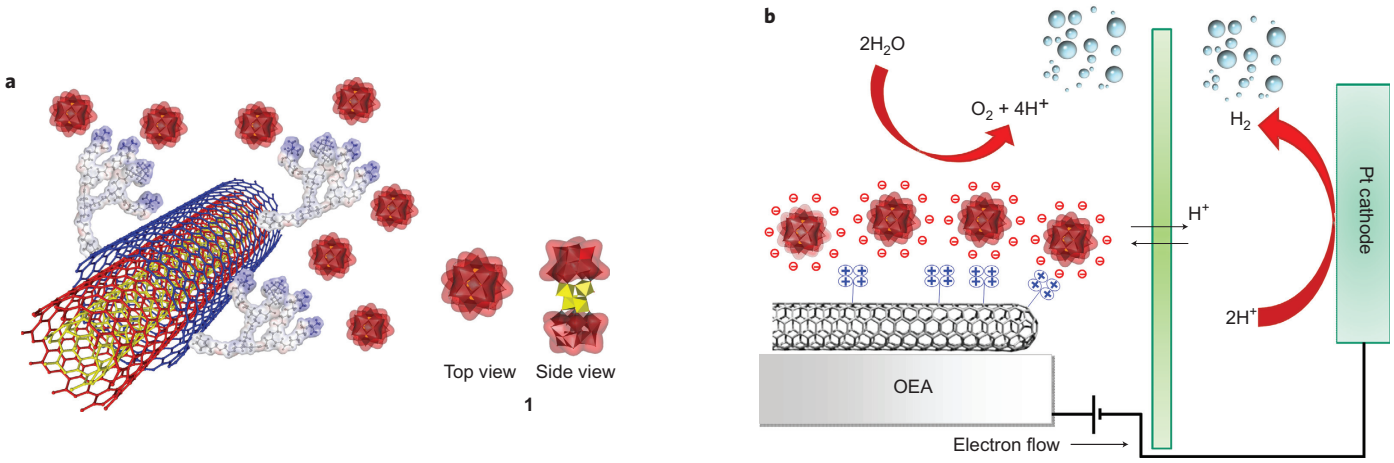
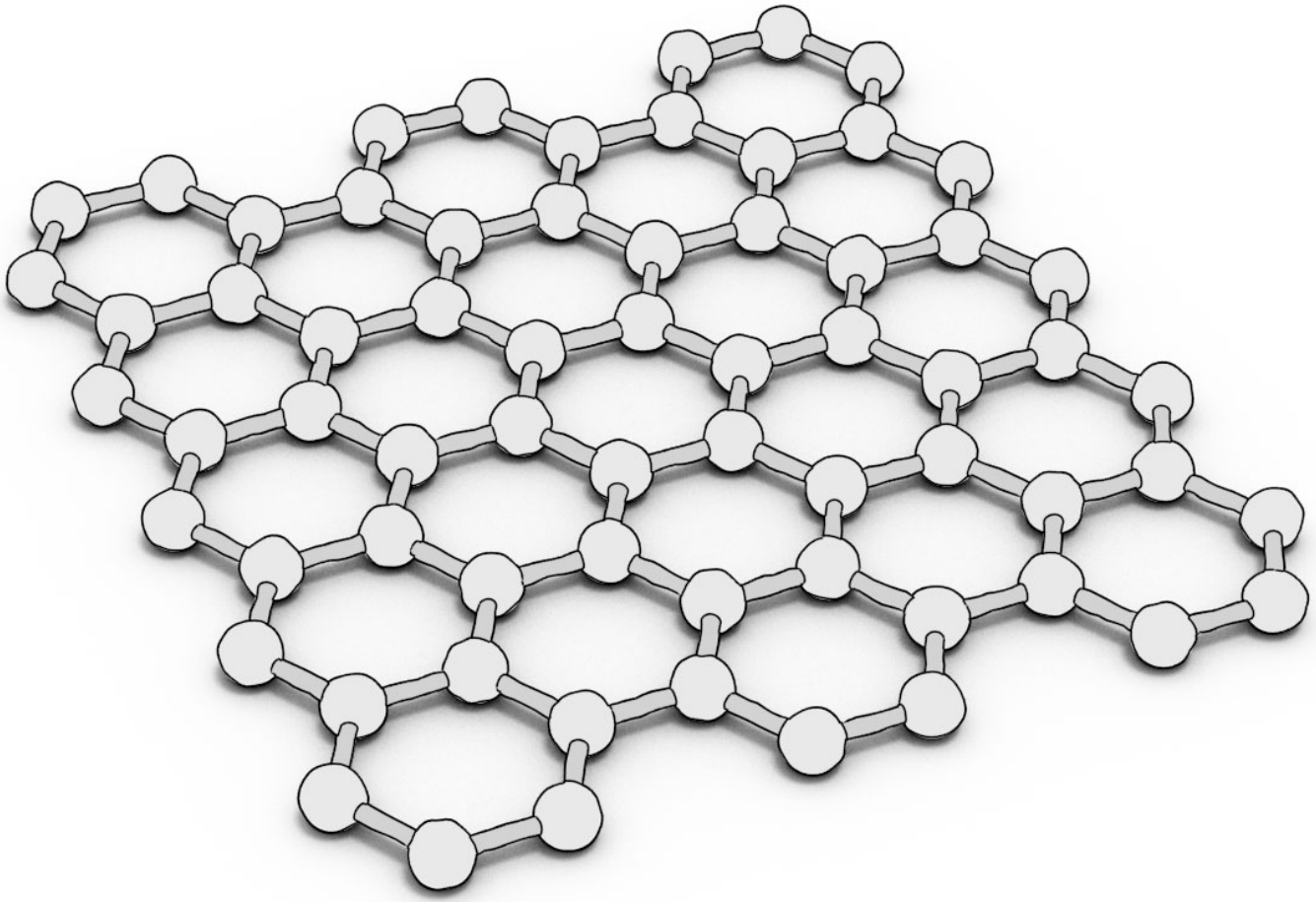


Figure 1 | Nanostructured oxygen-evolving material. a, Electrostatic capture of polyanionic ruthenium-containing clusters **1** (negatively charged, red surface) by polycationic dendrons on the MWCNT surface (positively charged, blue surface) and polyhedric structure showing the side and front view of the POM (red)-embedded tetraruthenate core of **1** (yellow). **b**, General scheme for a water-splitting electrocatalytic cell with the integrated nanostructured OEA.

Graphene



Graphene is an allotrope (form) of carbon consisting of a single layer of carbon atoms arranged in an hexagonal lattice.

It can be considered as an indefinitely large aromatic molecule, the ultimate case of the family of flat polycyclic aromatic hydrocarbons.

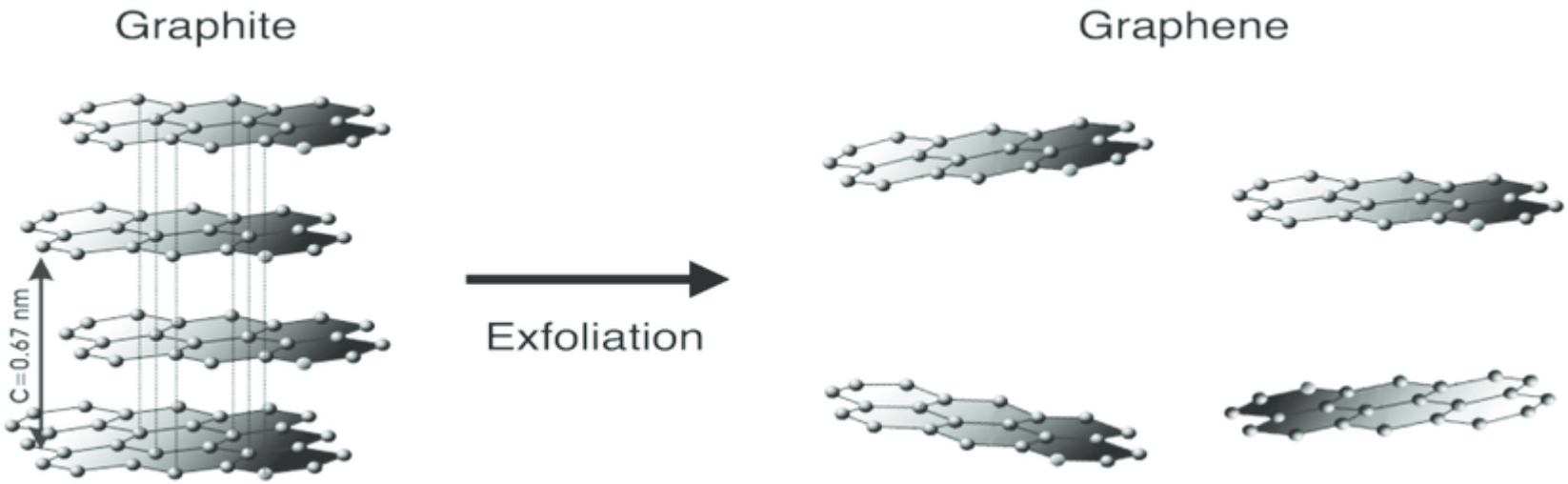
The material was rediscovered, isolated, and characterized in **2004** by **Andre Geim** and **Konstantin Novoselov** at the University of Manchester.

This work resulted in the two winning the **Nobel Prize in Physics in 2010** "for groundbreaking experiments regarding the two-dimensional material graphene".

Andre Geim

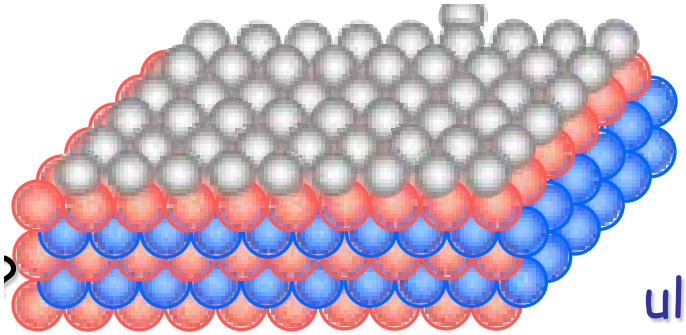
Konstantin Novoselov

exfoliation



highly oriented pyrolytic graphite (HOPG)

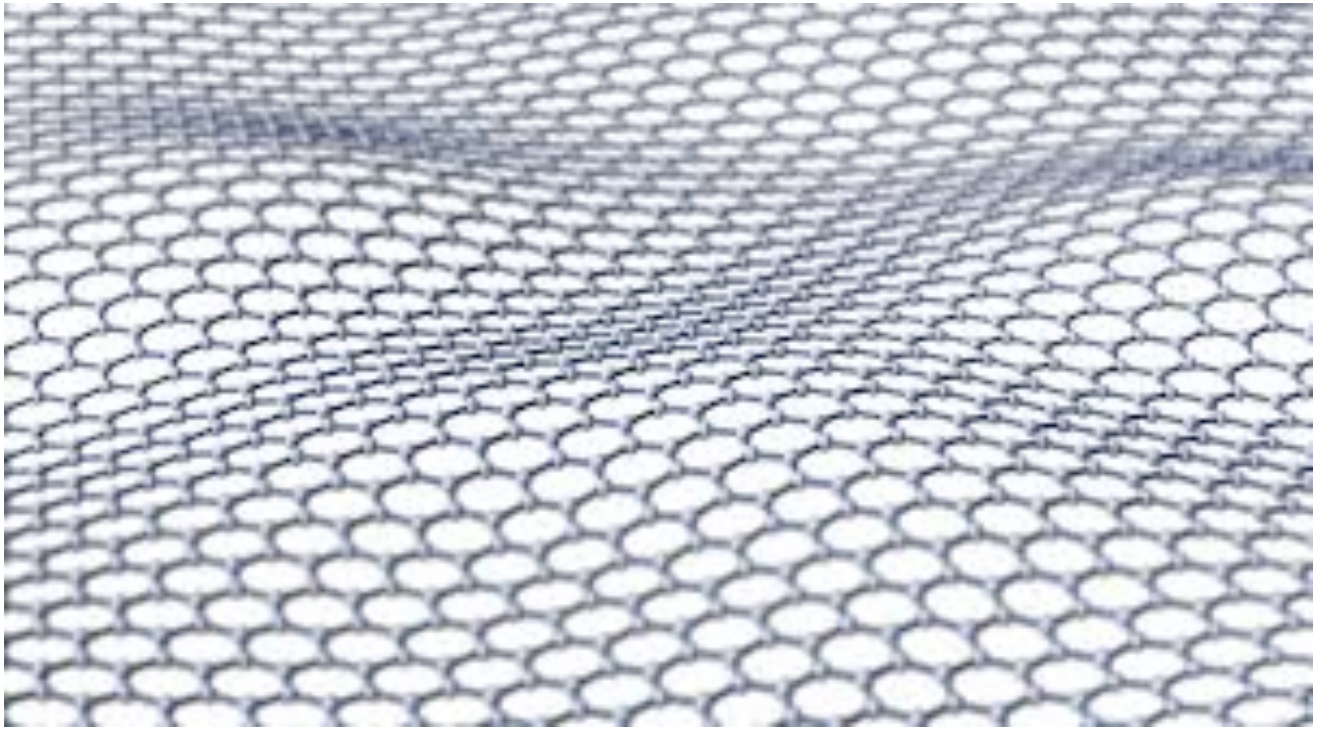
Epitaxial growth



chemically remove
the substrate
↓
ultra-thin monocrystal

"Graphene" is a combination of "graphite" and the suffix -ene, named by Hanns-Peter Boehm, who described single-layer carbon foils in 1962.

Graphene can be considered an "infinite alternant" (only six-member carbon ring) polycyclic aromatic hydrocarbon



nanoscale corrugation

Electric Field Effect in Atomically Thin Carbon Films

2 OCTOBER 2004 VOL 306 SCIENCE, p. 666

K. S. Novoselov,[1] A. K. Geim,[1]* S. V. Morozov,[2] D. Jiang,[1]
Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]

We describe monocrystalline graphitic films, which are a few atoms thick but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The films are found to be a two-dimensional semimetal with a tiny overlap between valence and conductance bands, and they exhibit a strong ambipolar electric field effect such that electrons and holes in concentrations up to 10^{13} per square centimeter and with room-temperature mobilities of ~10,000 square centimeters per volt-second can be induced by applying gate voltage.

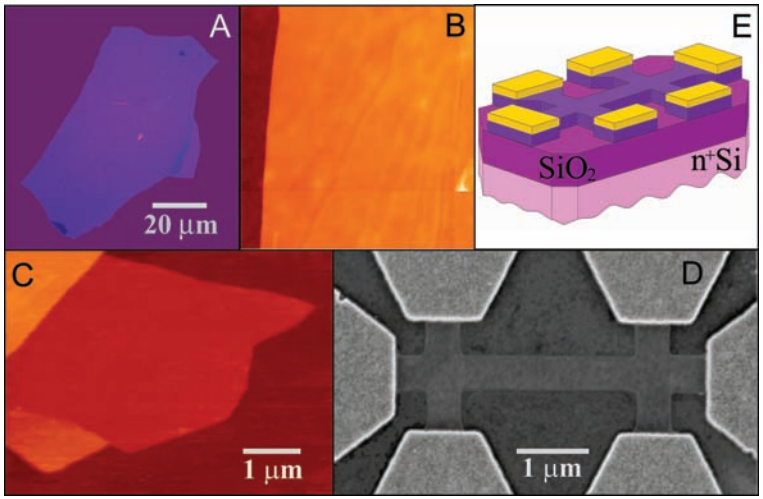


Fig. 1. Graphene films. (**A**) Photograph (in normal white light) of a relatively large multilayer graphene flake with thickness ~3 nm on top of an oxidized Si wafer. (**B**) Atomic force microscope (AFM) image of 2 μm by 2 μm area of this flake near its edge. Colors: dark brown, SiO_2 surface; orange, 3 nm height above the SiO_2 surface. (**C**) AFM image of single-layer graphene. Colors: dark brown, SiO_2 surface; brown-red (central area), 0.8 nm height; yellow-brown (bottom left), 1.2 nm; orange (top left), 2.5 nm. Notice the folded part of the film near the bottom, which exhibits a differential height of ~0.4 nm. For details of AFM imaging of single-layer graphene, see (*15*). (**D**) Scanning electron microscope image of one of our experimental devices prepared from FLG. (**E**) Schematic view of the device in (D).

Field effect

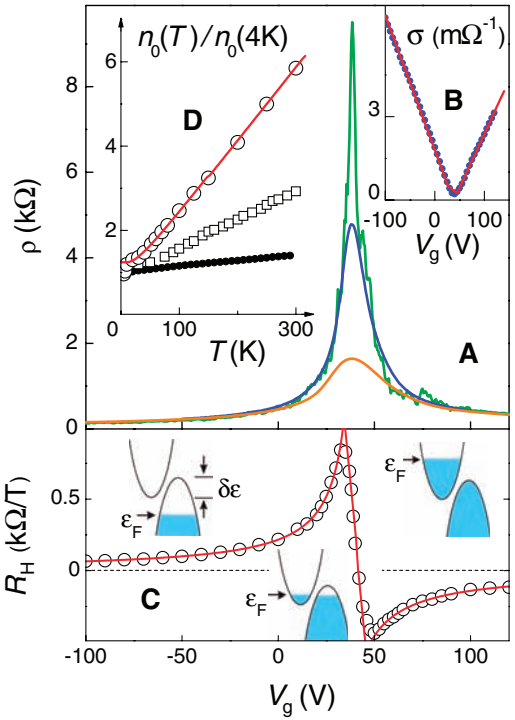
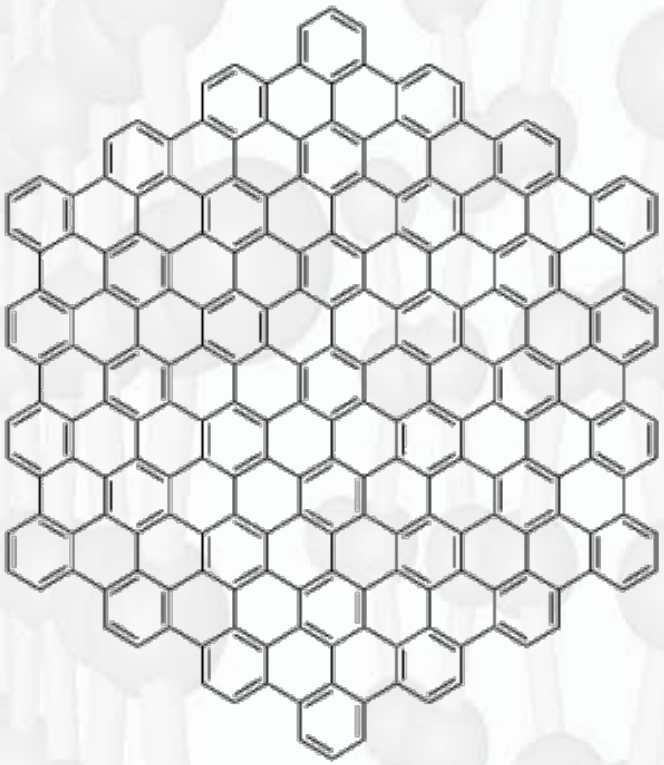


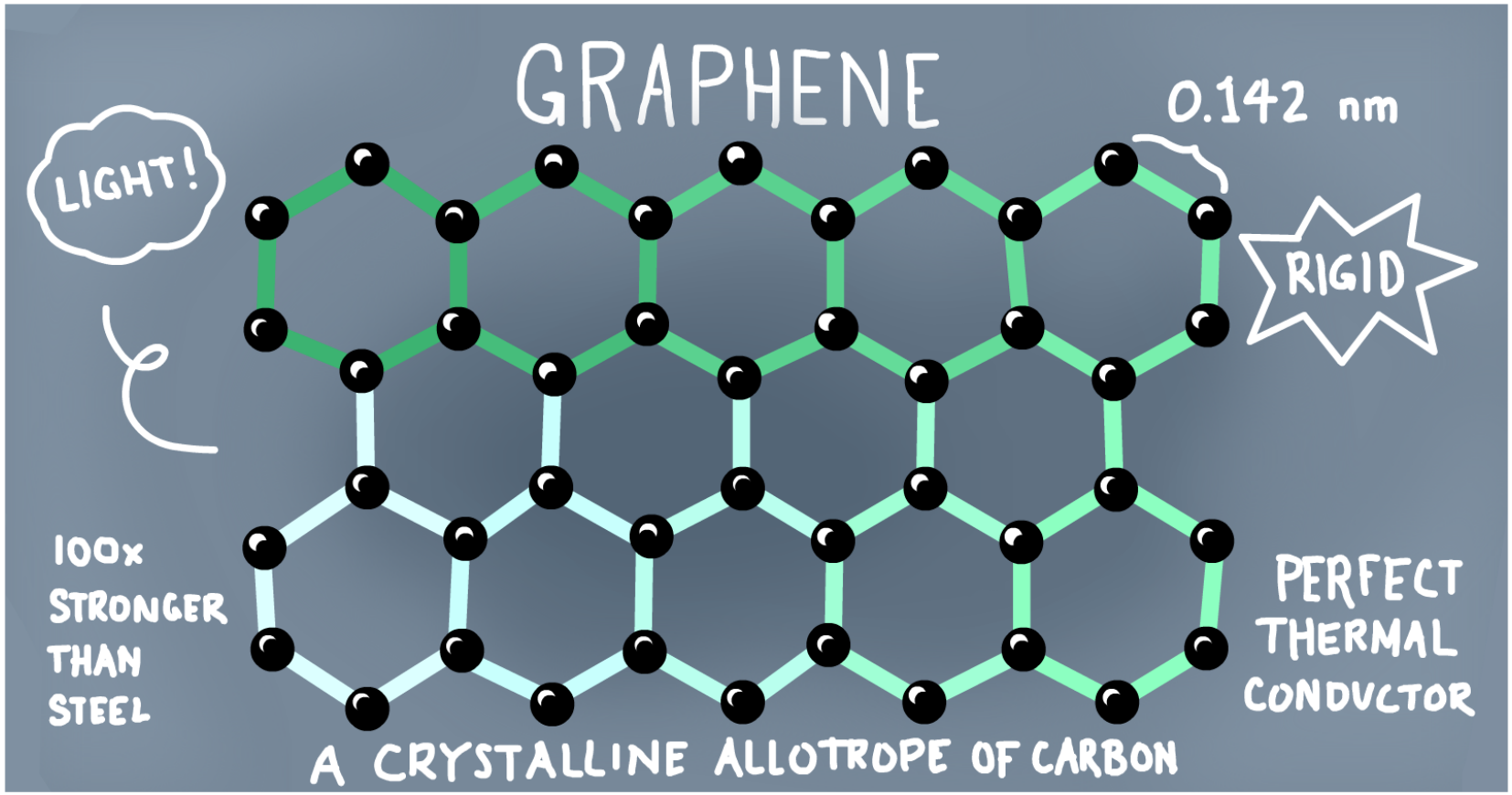
Fig. 2. Field effect in FLG. (**A**) Typical dependences of FLG's resistivity ρ on gate voltage for different temperatures (T = 5, 70, and 300 K for top to bottom curves, respectively). (**B**) Example of changes in the film's conductivity $\sigma = 1/\rho(V_g)$ obtained by inverting the 70 K curve (dots). (**C**) Hall coefficient R_H versus V_g for the same film; T = 5 K. (**D**) Temperature dependence of carrier concentration n_0 in the mixed state for the film in (A) (open circles), a thicker FLG film (squares), and multilayer graphene ($d \approx 5$ nm; solid circles). Red curves in (B) to (D) are the dependences calculated from our model of a 2D semimetal illustrated by insets in (C).



largest known flat hydrocarbon:

222 atoms or 37 benzene rings

(K. Müllen 2002)


GRAPHENE
0.142 nm
LIGHT!
RIGID
100x STRONGER THAN STEEL
PERFECT THERMAL CONDUCTOR
A CRYSTALLINE ALLOTROPE OF CARBON

Properties

Graphene has no band gap

The top five industries that target the production of graphene is in Life Sciences for medical device, electronics TV, chemical biosensors, smart phone and smart pad and desalinization membranes.

Strength and stiffness: some 200 times stronger than steel, elastic like rubber

Thinness and lightness

Heat conductivity: it has very high thermal conductivity than any other material—better by far than brilliant heat conductors such as silver and copper

Electrical conductivity carrying electricity better than even superb conductors such as copper and almost as well as superconductors

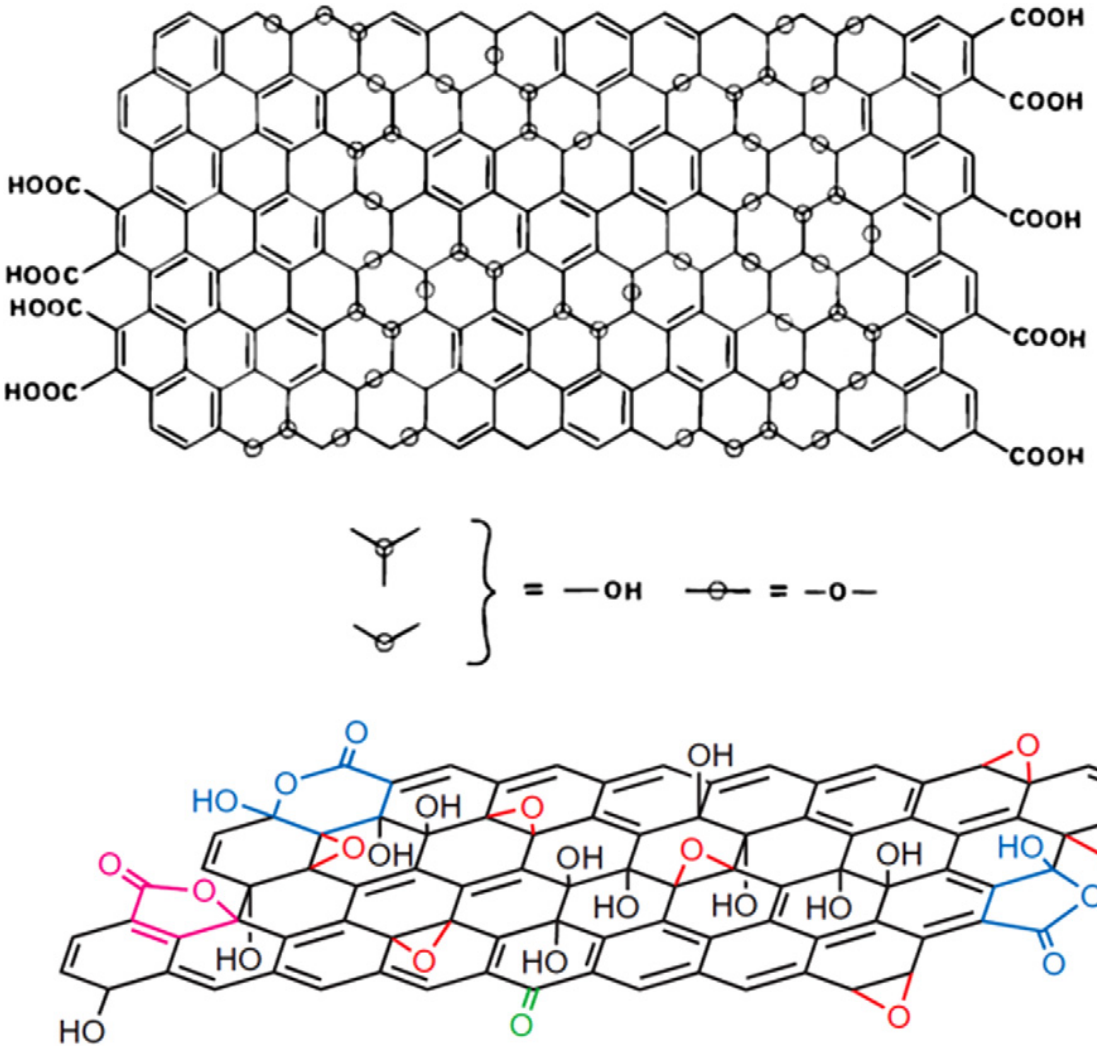
Electronic properties

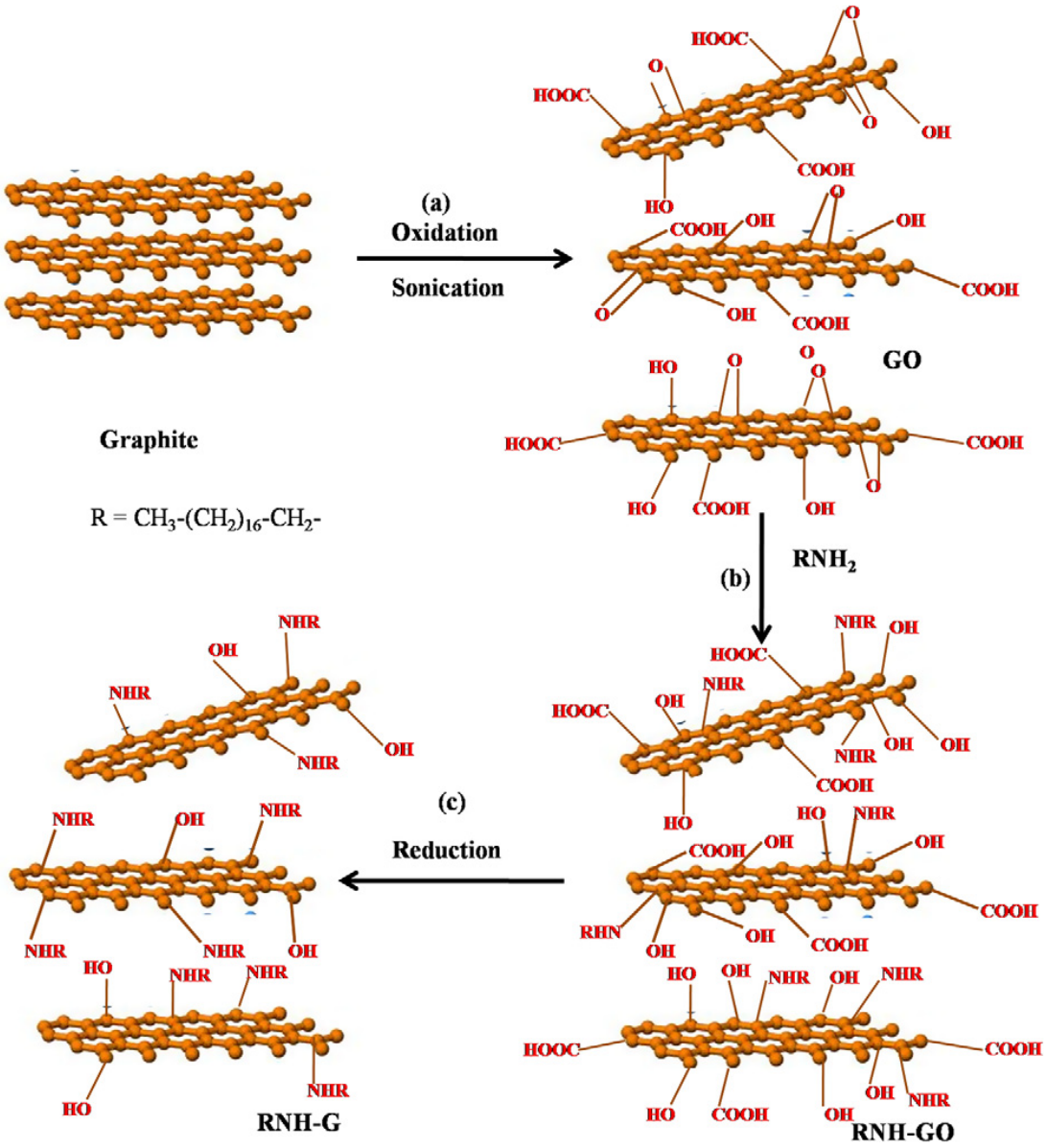
Optical properties: it is transparent

Impermeability

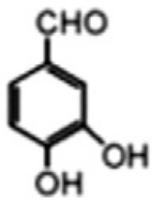
Functionalization

oxidation



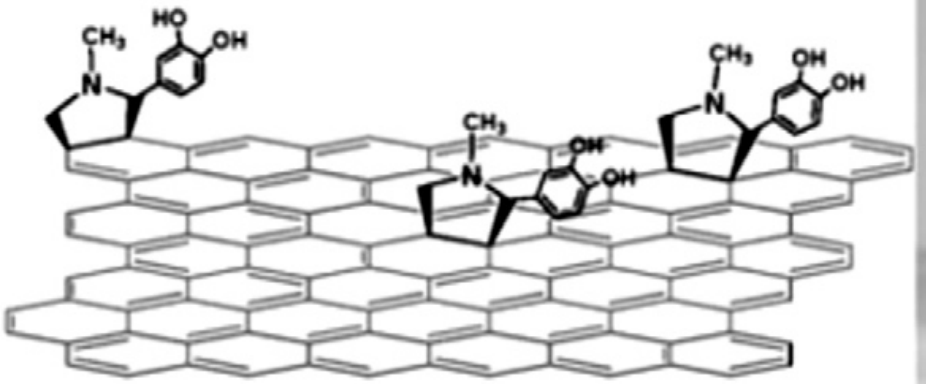

(a)
Oxidation
Sonication
Graphite
GO
R = CH_3-$(CH_2)_{16}$-CH_2-
RNH_2
(b)
(c)
Reduction
RNH-G
RNH-GO

Graphene



$CH_3NH_2CH_2COOH$

DMF, reflux 96 h



Graphene-*f*-OH