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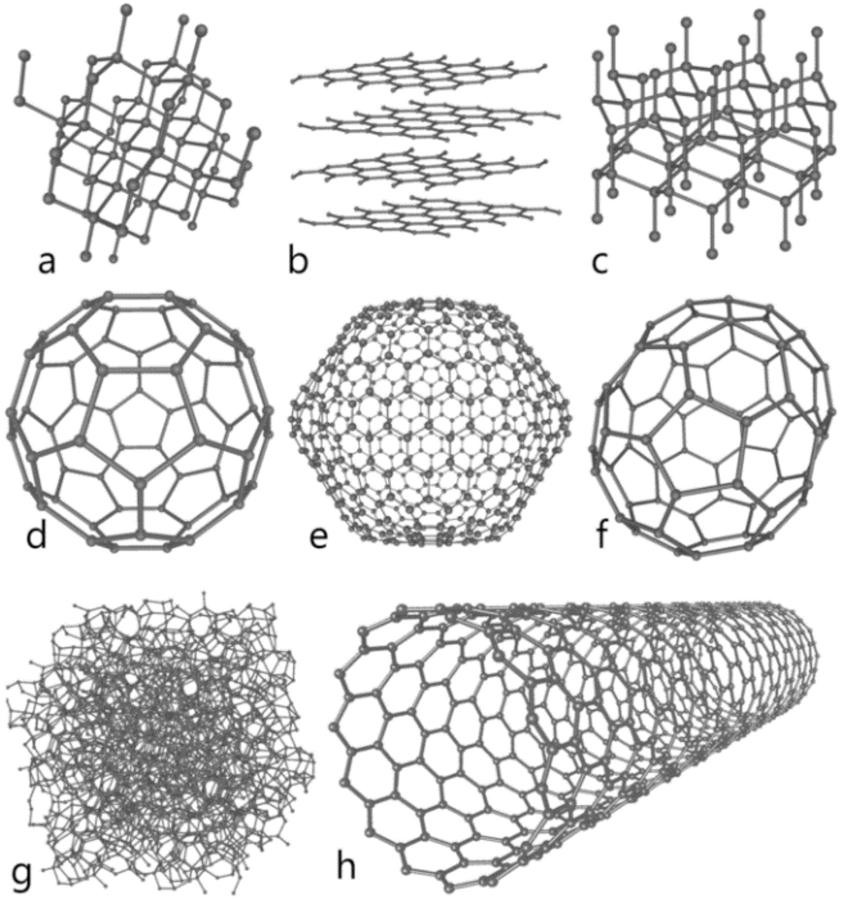
CARBON ALLOTROPES: FULLERENES AND NANOTUBES

IoT Team of
Valahia University of Targoviste, ROMANIA


a
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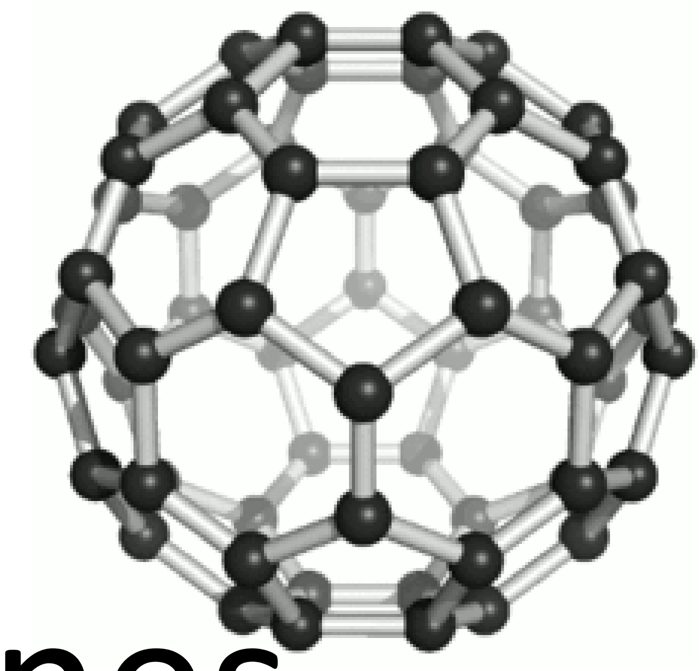
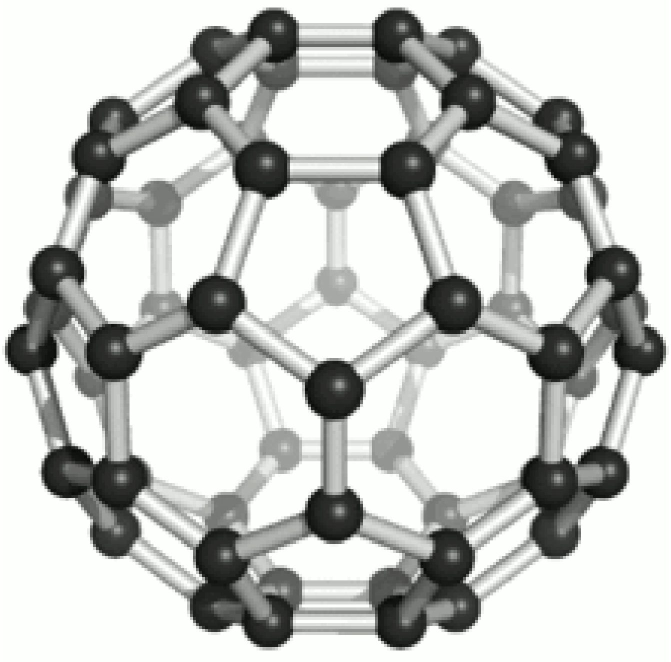
Carbon-based nanomaterials

From ^{12}C *to*



Fullerenes

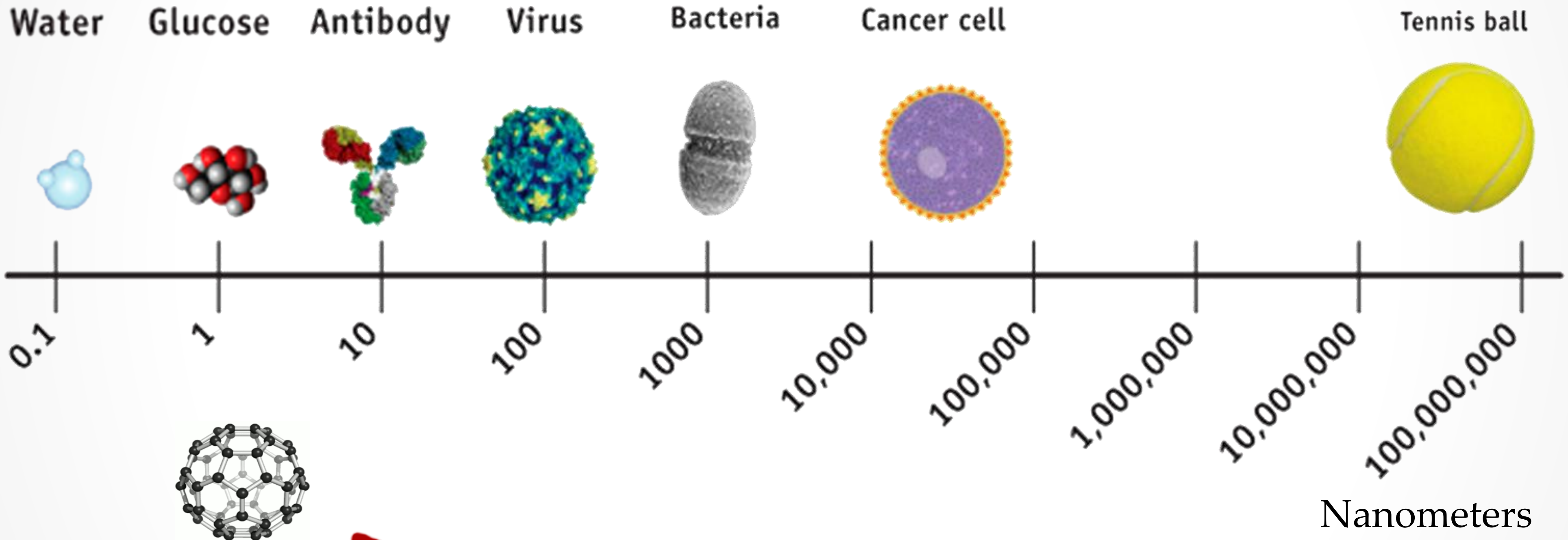
What are fullerenes?

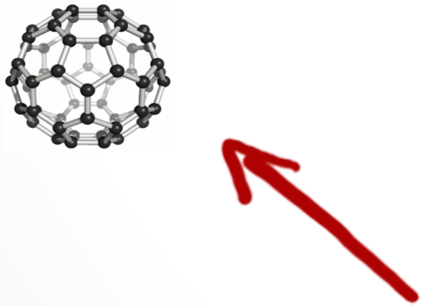


- Molecular compounds composed of carbon, an allotropic form of carbon, that looks like a soccer ball.

Dimension of fullerenes

Fullerenes are some fairly small molecules. In size fullerene C60 would be a little bigger than glucose and slightly smaller than an antibody.

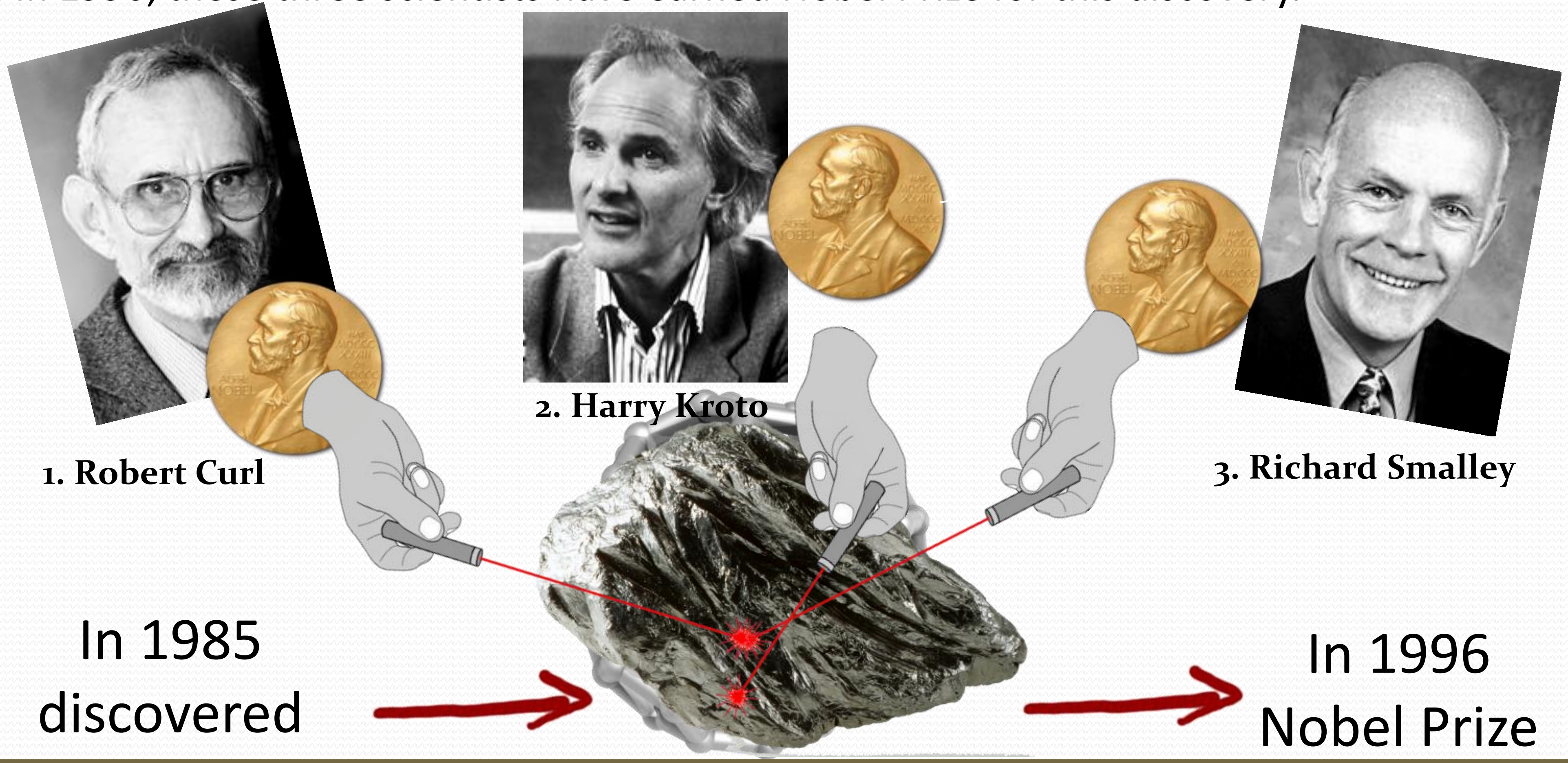




Diameter of fullerene C_{60} = 1,1 nm

The history of fullerenes

The discovery of fullerenes has been accidental. Three scientists Robert Curl, Harry Kroto and Richard Smalley in 1985 have acted with the laser on graphite. In obtained material according to analyzes were discovered fullerenes. In 1996, these three scientists have earned Nobel Prize for this discovery.



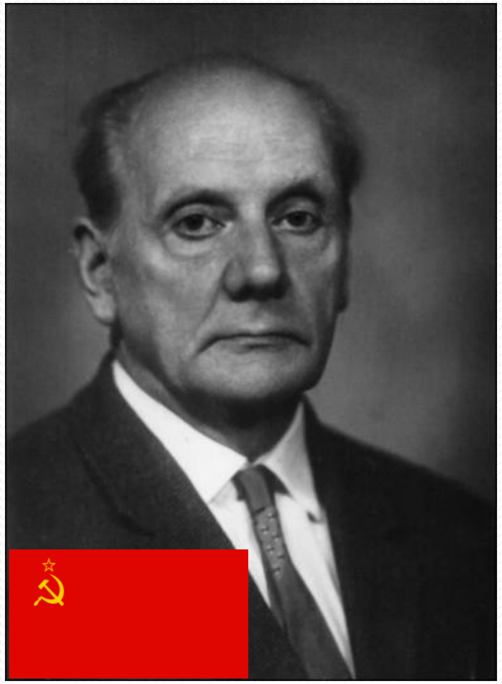
The first research on fullerenes

Even though in 1985 th fullerenes were discovered, related research began much earlier, in the 1970s.

E. Osawa

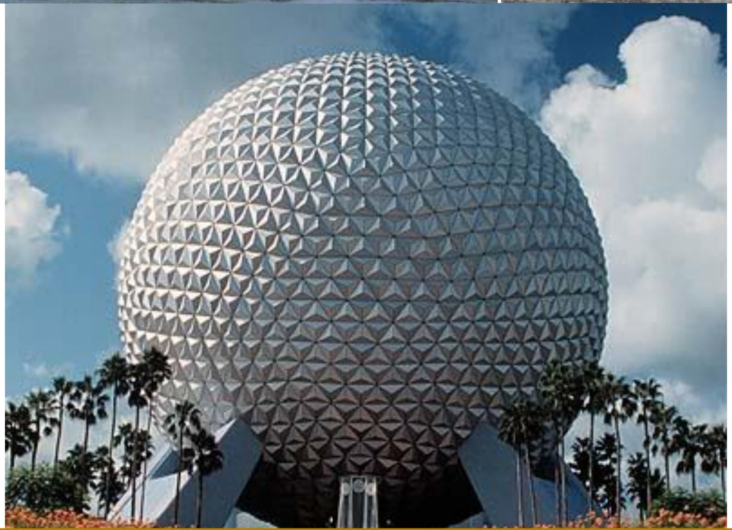
1971 – Predicting the occurrence of fullerenes

D.A. Bochvar



1973 – mathematical model of fullerenes

Whence it cometh name of fullerene?



Richard Buckminster "Bucky" Fuller

American architect, systems theorist,
author, designer, inventor, and futurist who has worked on futuristic ball-shaped projects. So, in honor of Fuller have been named these molecules - fullerenes.

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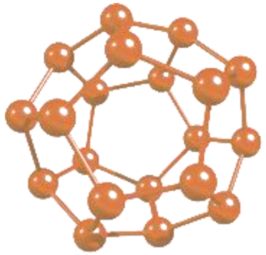
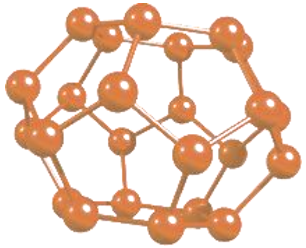
Types of fullerenes

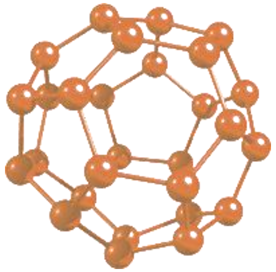
Now we know several types of fullerenes. Some have 20 carbon atoms in the molecule, while others reach up to 540 atoms!



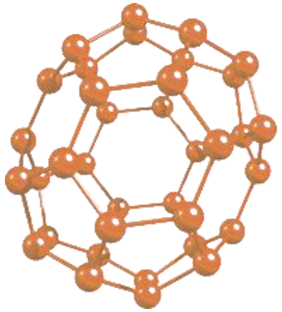
C_{20}



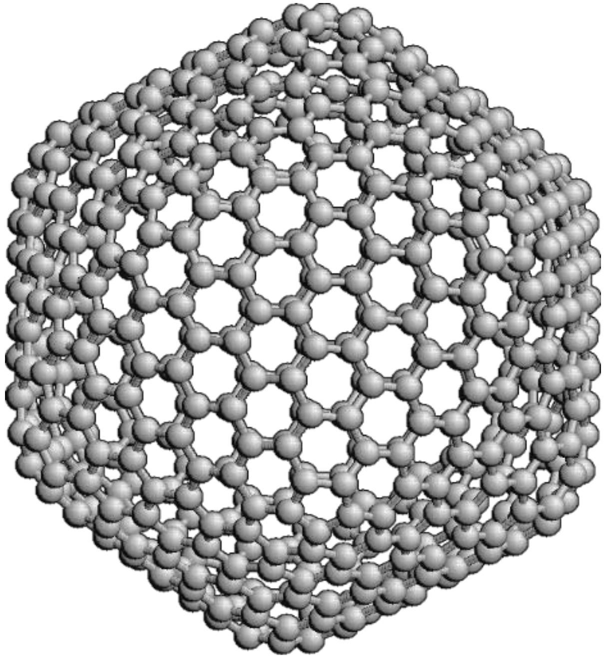
C_{24}



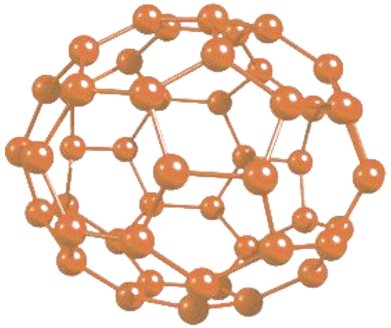
C_{28}



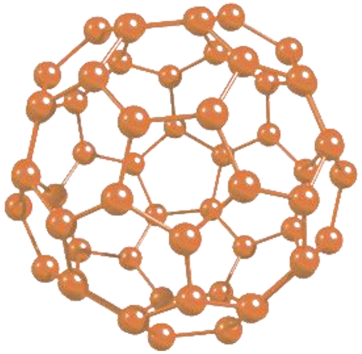
C_{36}



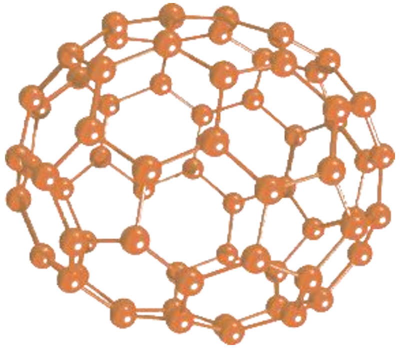
C_{540}



C_{50}

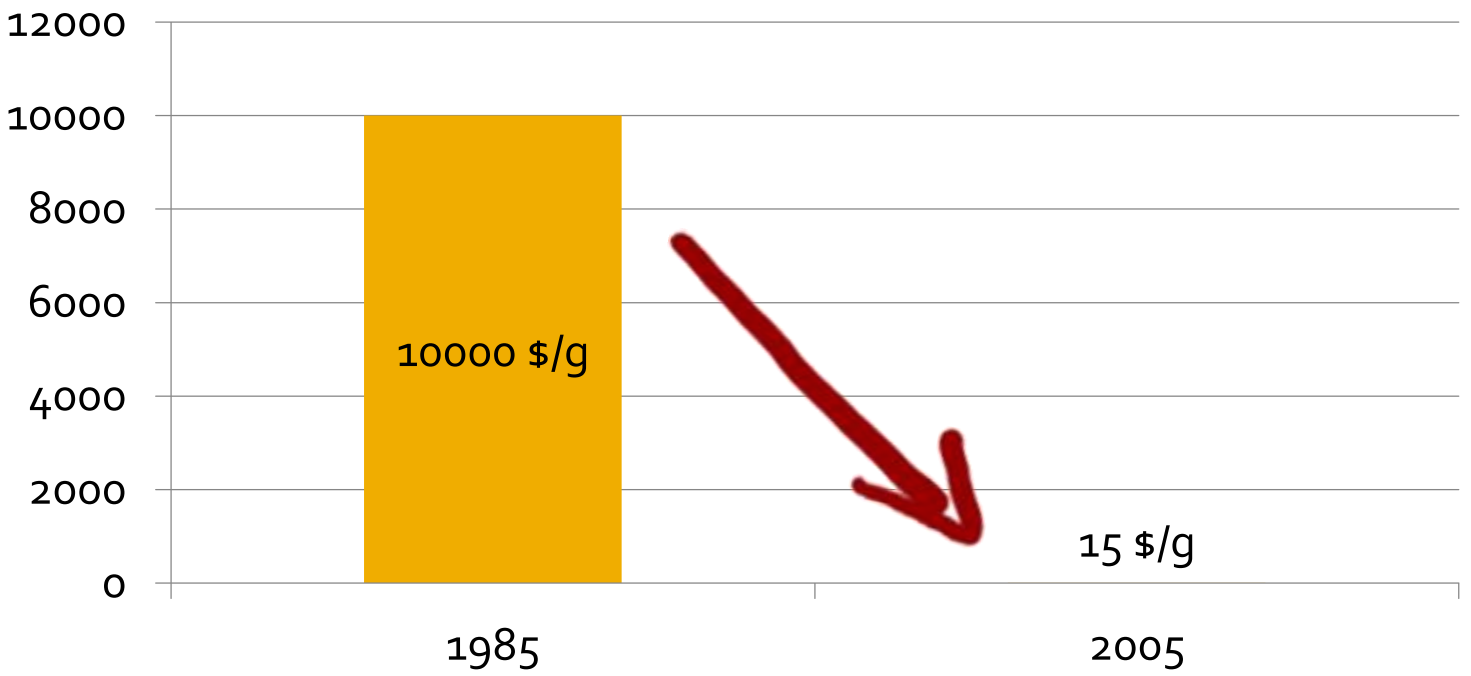


C_{60}



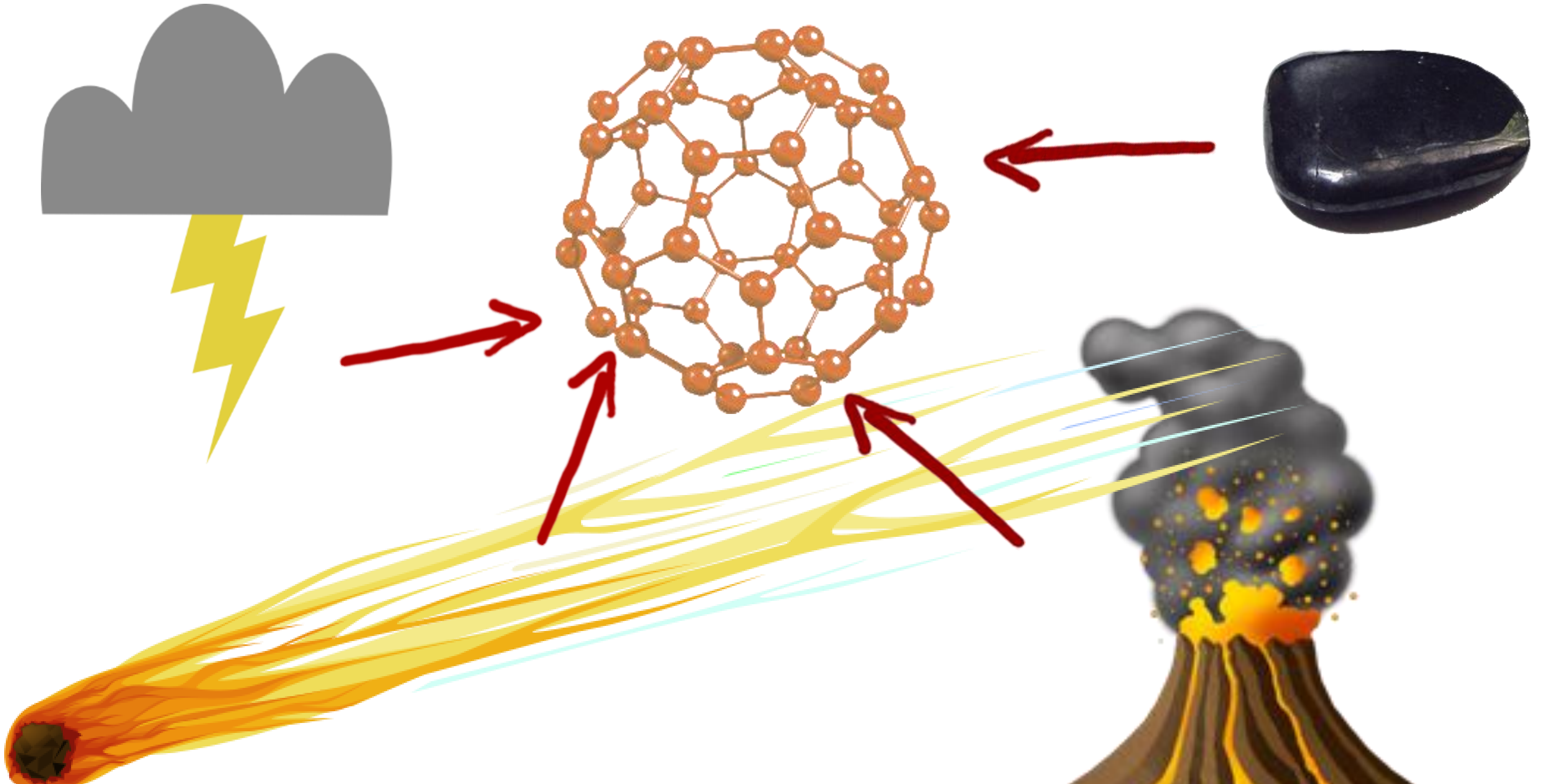
C_{70}

The cost of fullerenes



The first time then were discovered fullerenes, the cost of a gram of these compounds was $ 10,000, while in 2005 due to the improvement of obtaining methods, the cost are dropped to $ 15 per gram.

Fullerenes in nature

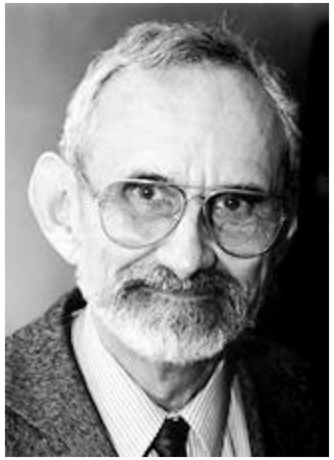


Nature can produce fullerenes without LASER. Volcanoes, meteors, lightnings and some minerals can produce or content fullerenes.

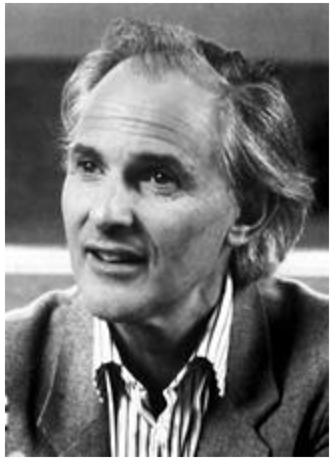
Synthesis of fullerenes

LASER evaporation of graphite

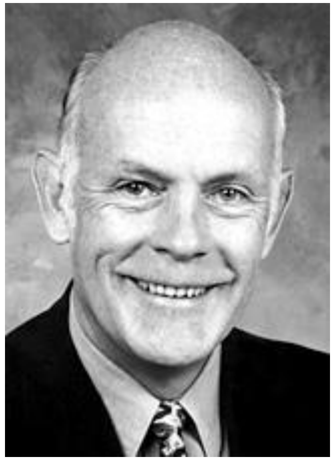
1985



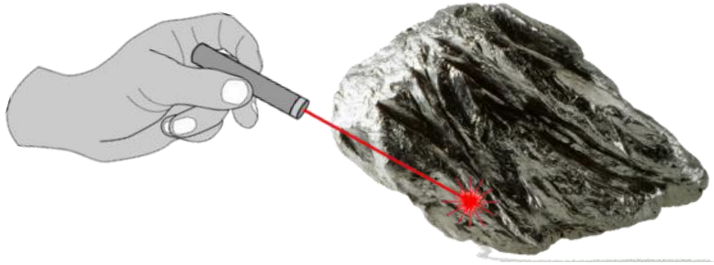
Robert Curl



Harry Kroto



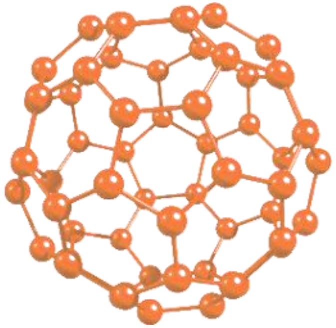
Richard Smalley



LASER

Graphite

traces of



C60

The first fullerenes synthesis method is based on LASER action on graphite. The result was not very good, because it produce only traces of fullerenes.

Thermal evaporation of graphite

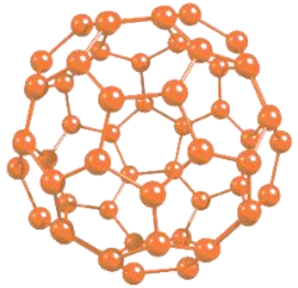
1990

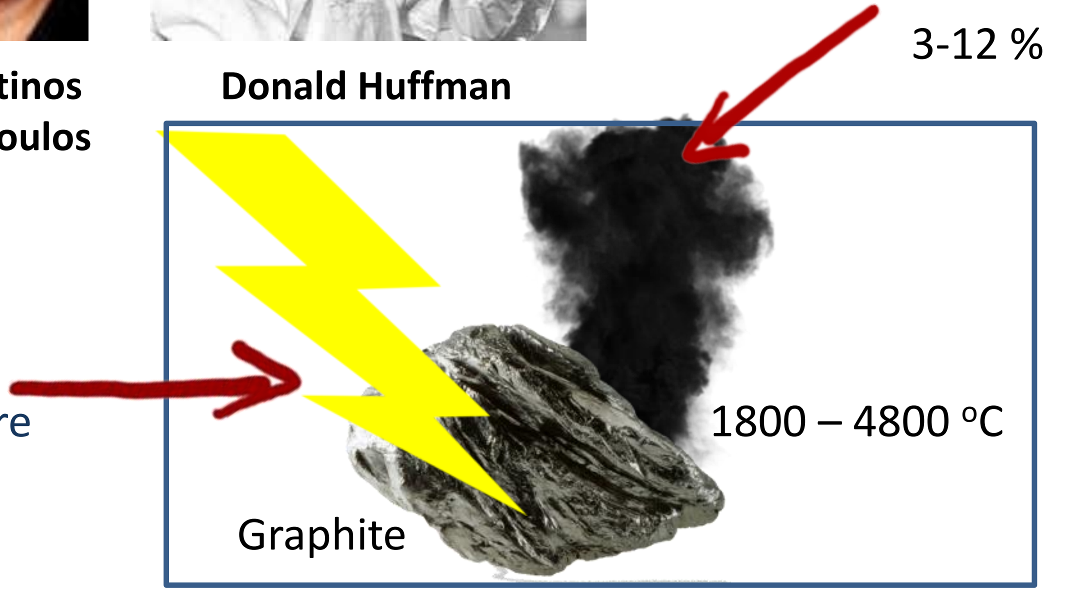
Wolfgang Krätschmer

Lowell D. Lamb

Konstantinos Fostiropoulos

Donald Huffman



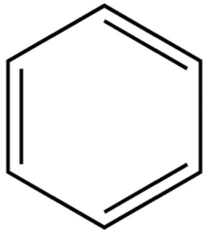


In the 1990s, a research team led by W. Kratschmer and D. Huffman found a better method for the fullerenes synthesis. They put graphite in a helium atmosphere and led to high temperatures this material using electricity. 3-12% of the formed soot containing fullerenes.

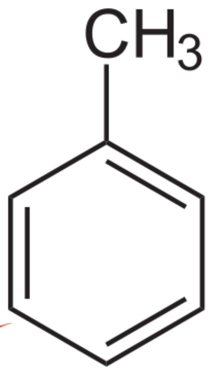
Burning and pyrolysis of carbonaceous compounds

1999

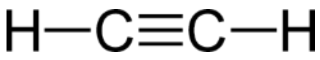
Eiji Osawa



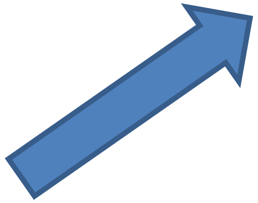
Benzene



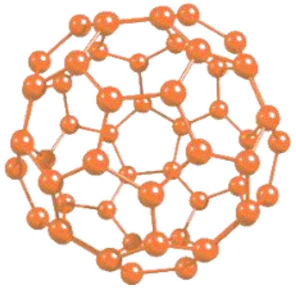
Toluene



Acetilene



6 %



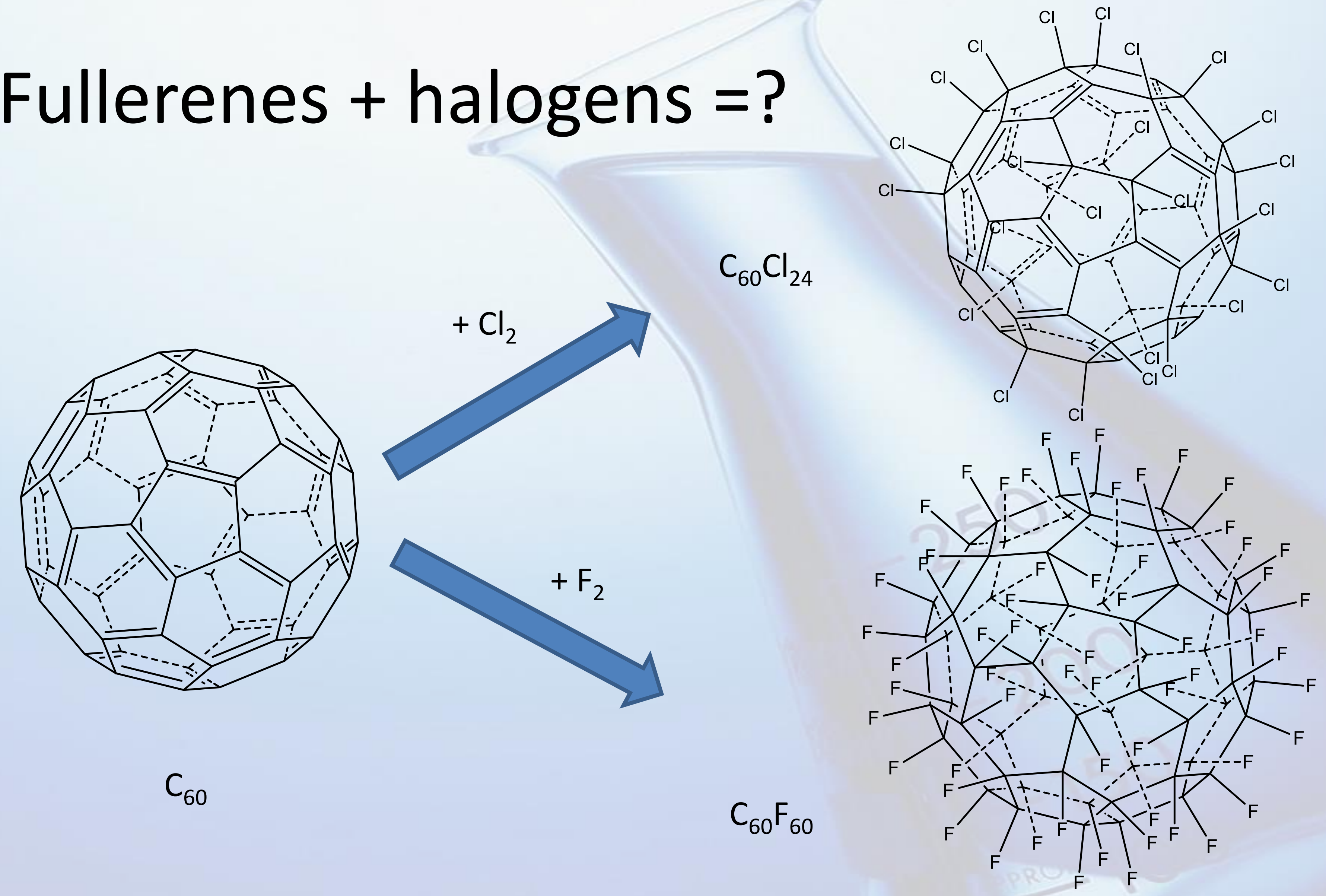
1600 – 4600 ^{o}C

Scientists have looked for alternative ways to produce fullerenes. E. Osawa found that by controlled burning of compounds such as benzene, toluene and acetylene may result fullerenes.

Fullerenes

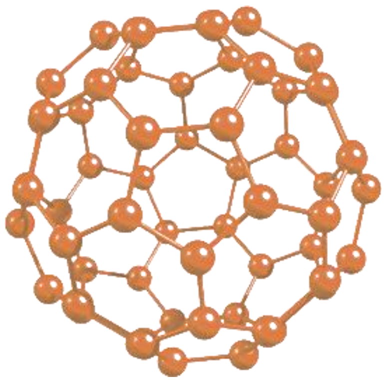
Reactions, properties, interesting facts about …

Fullerenes + halogens =?



Although fullerenes seem very bizarre compounds, they can enter into reactions with various compounds. With halogens such as chlorine and fluorine react very well resulting some related compounds with hedgehogs.

Chemical properties of fullerenes



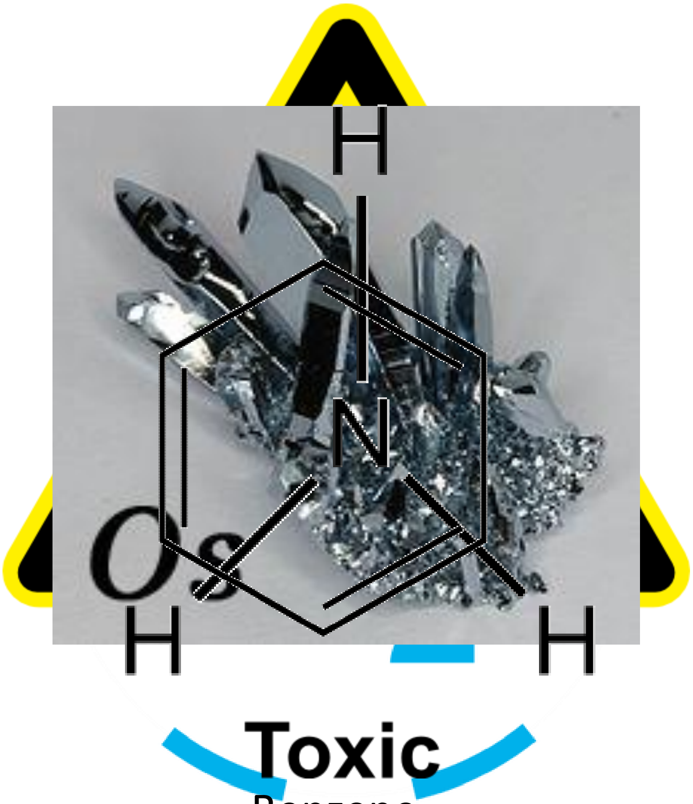
$+\ O_2$

$+\ KCN$

$+\ OsO_4$

$+\ NH_3\ /\ Na$

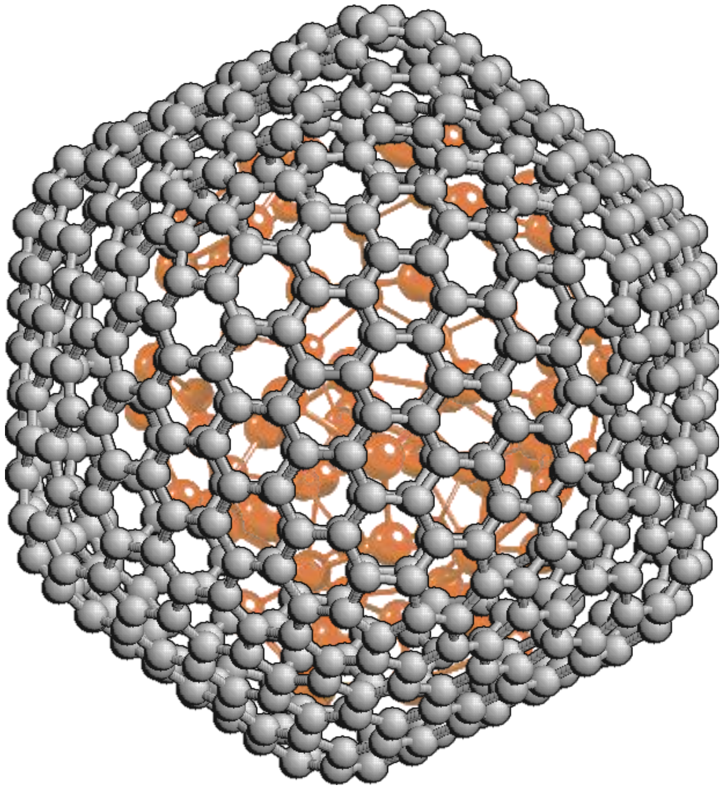
$+\ C_6H_6$



Benzene
Osmium tetroxide
Oxygen
Ammonia
Potassium cyanide

Fullerenes can react with various compounds such as oxygen, toxic potassium cyanide, osmium tetraoxide, ammonia, benzene.

Fullerenes in fullerenes



Scientists have proposed to create fullerenes in fullerenes which may have special properties. Until this time, it was not able to obtain such structures.

Fullerenes in space

Bernard H. Foing

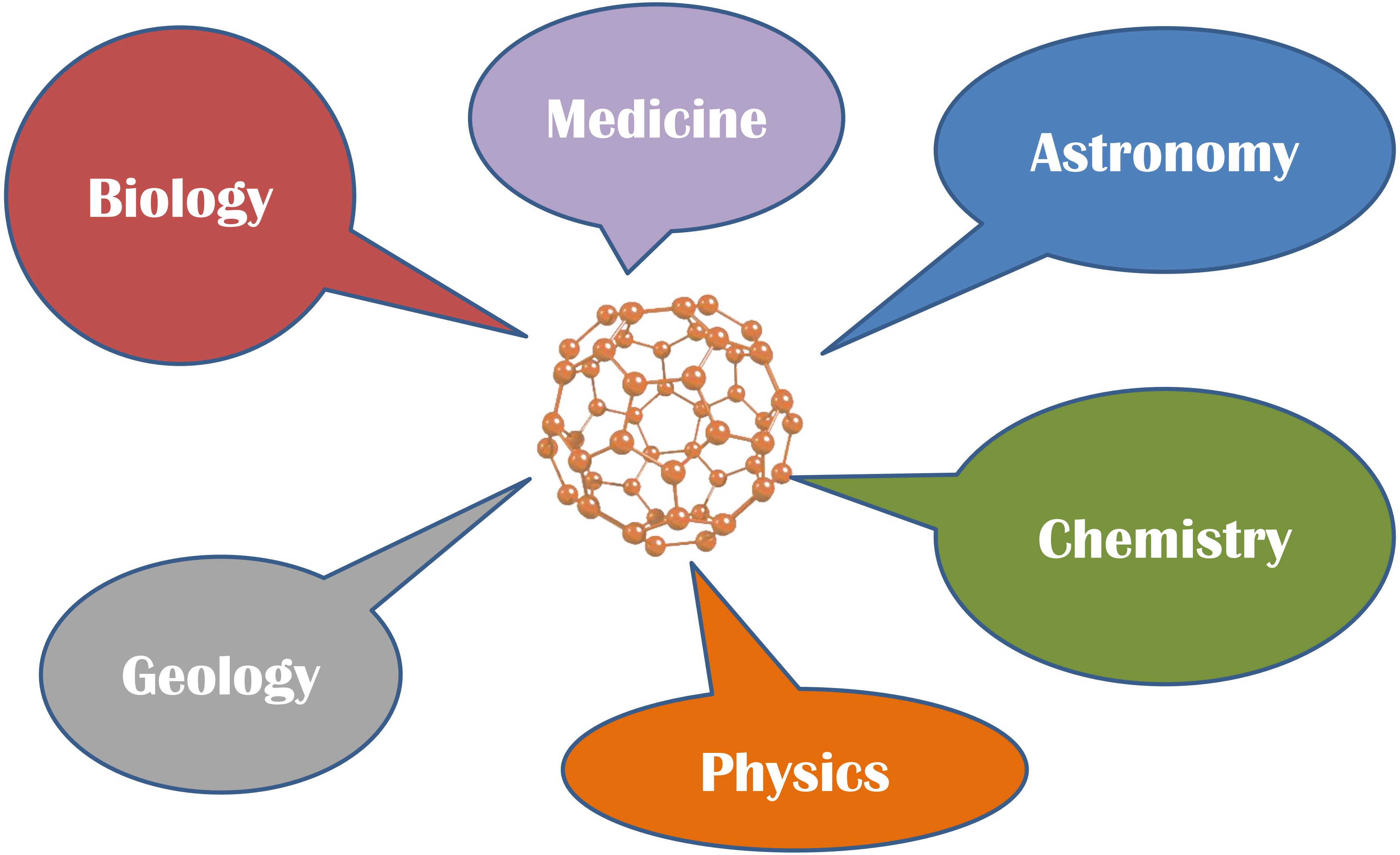
Pascale Ehrenfreund

Nebula Tc1

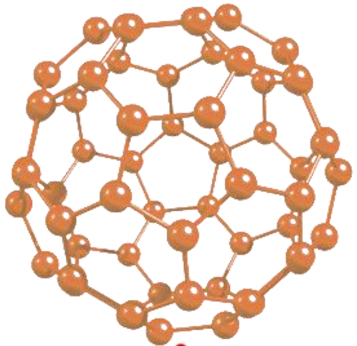
Scientists Bernard Foing and Pascale Ehrenfreund with Spitzer telescope (NASA) did an unexpected discovery for many of us: fullerenes exist in space!

Related fields of fullerenes

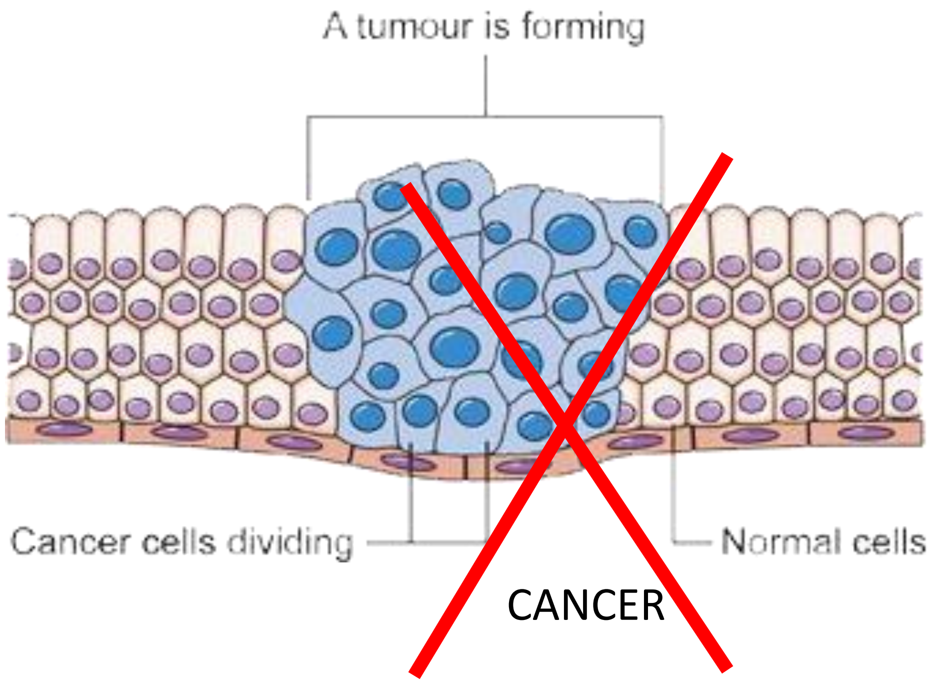
Although fullerenes are known very little time compared to other chemical structures, they had entered in different areas:

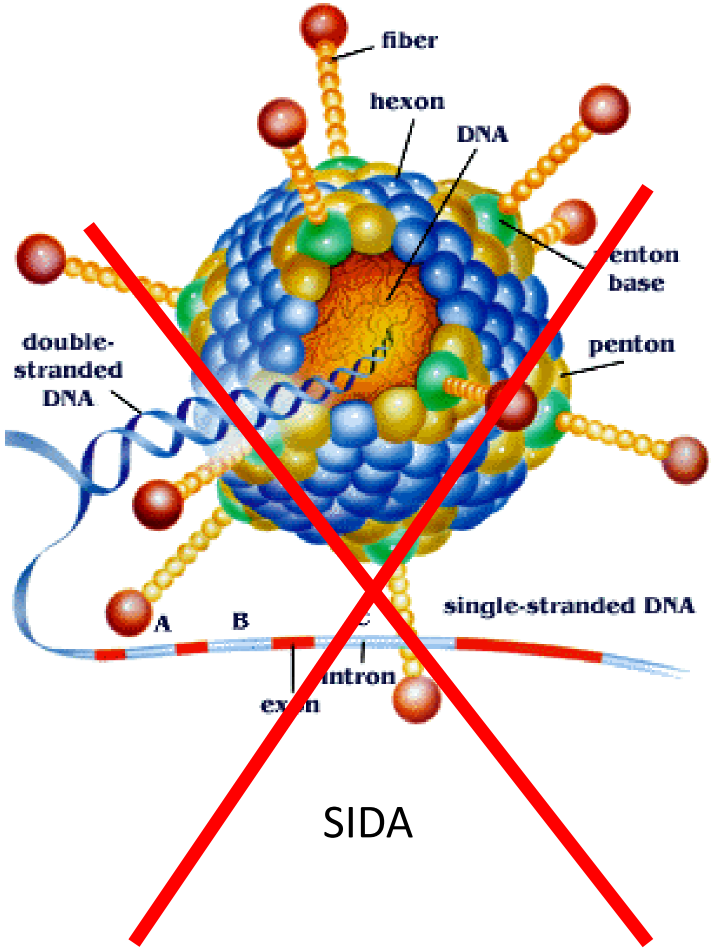


Fullerenes in medicine



C_{60}

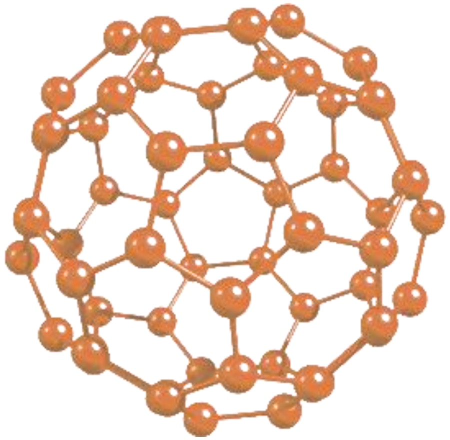




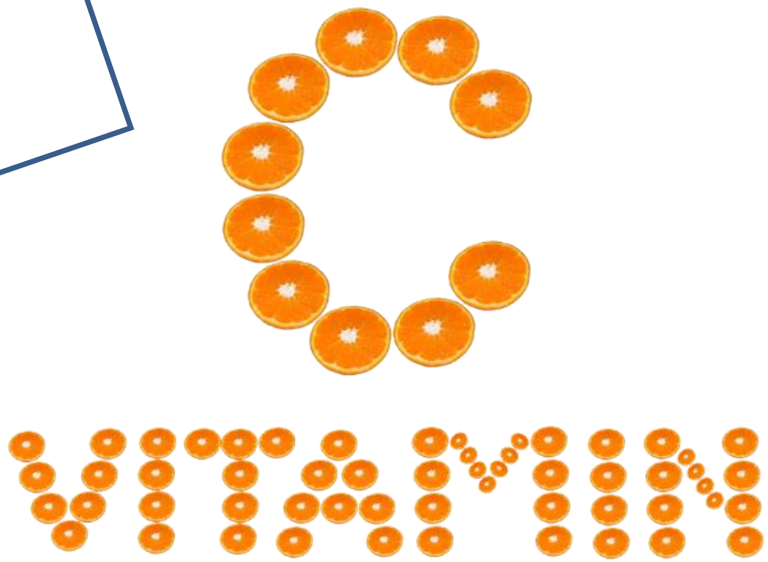
The studies on fullerenes not stop. Recently, researchers found that fullerenes can help cure cancer and AIDS patients. Since tests are in progress and in the future it is possible that these molecules wonderful enable mankind to forget these serious diseases.

Fullerenes - antioxidants

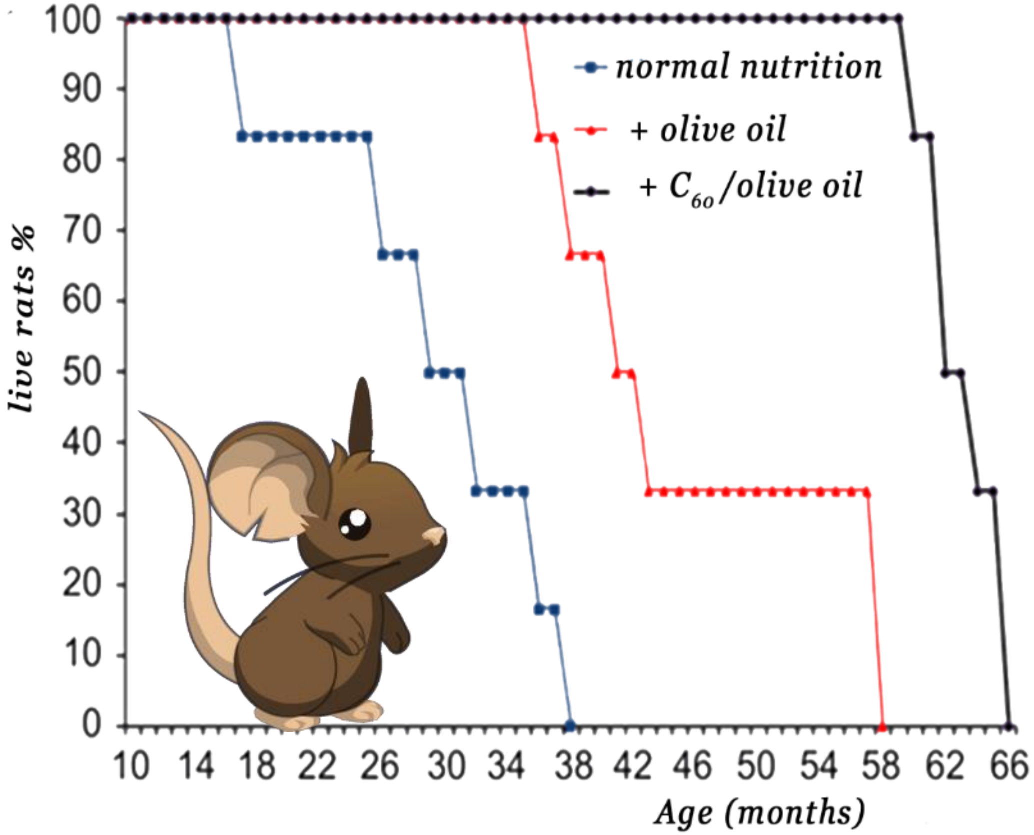
Studies of fullerenes compared with various needed compounds for organism, such as vitamins, show that fullerenes have an antioxidant action 125 times stronger than vitamin C.

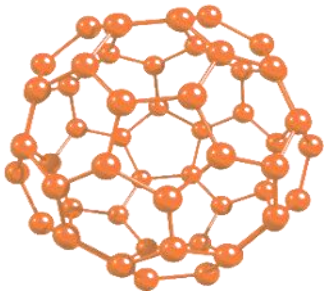


125 times more powerful



Fullerenes lengthen life

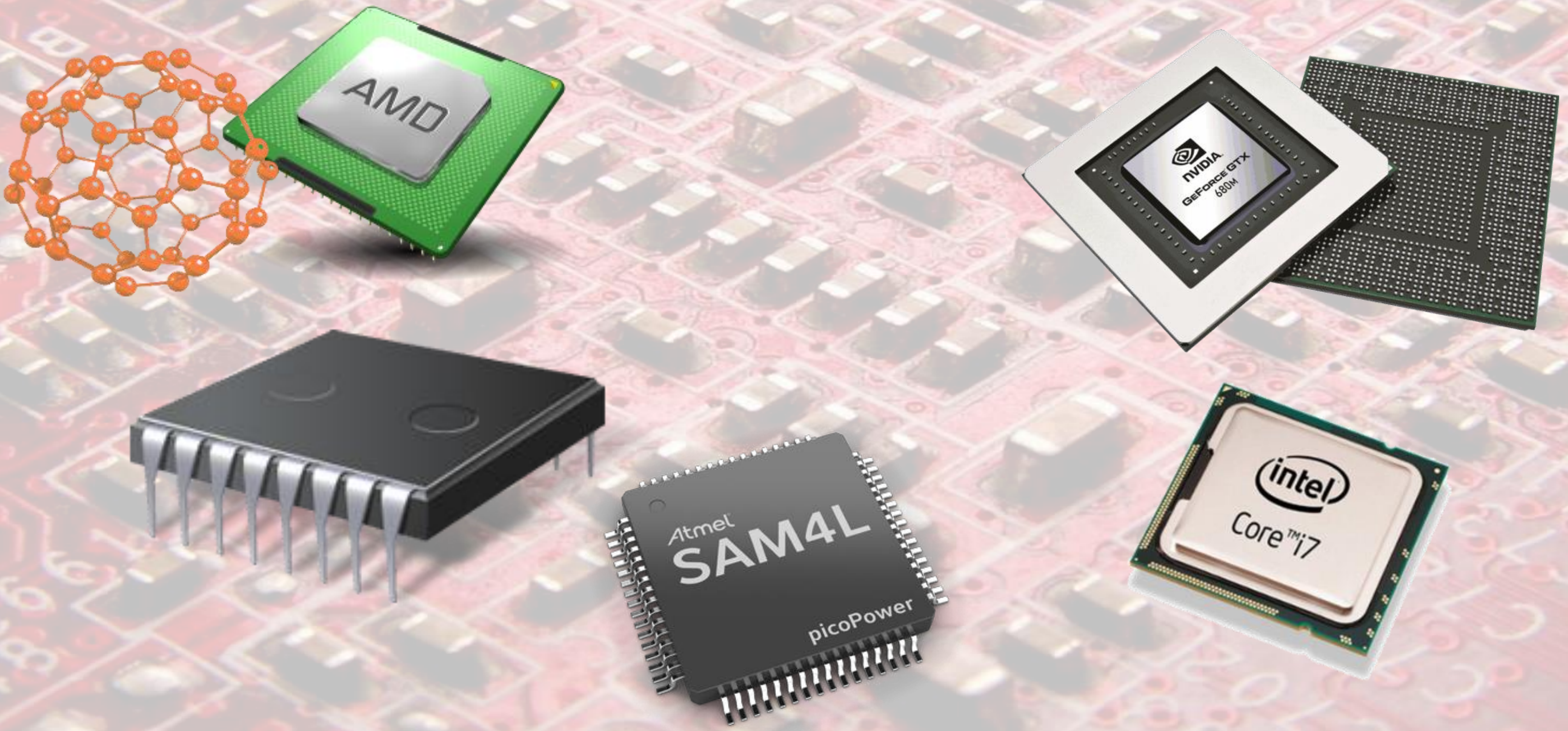




Vitamin A?

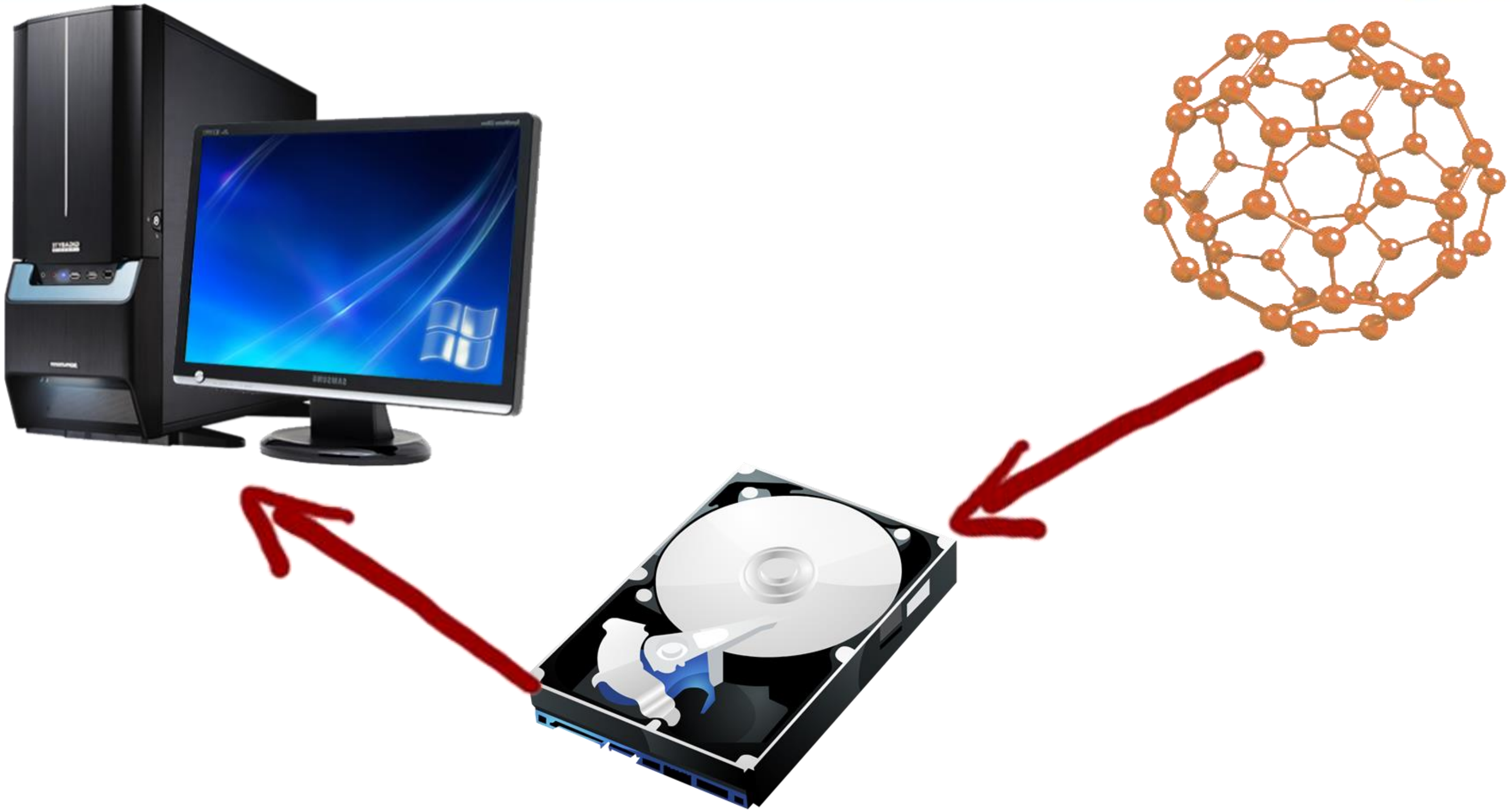
The fullerenes can extend life. Experiments on mice have shown that mice that had in food added olive oil and fullerenes have lived almost 2 times longer than mice that ate normally. Scientists believe that it is possible that fullerenes can activated vitamin A in an unusual way.

Fullerenes in nanotechnology



Nanotechnology use fullerenes in the manufacture of various chips and microcircuits. Large companies would use them to create new generation equipment.

The creation of large and better storage devices of information

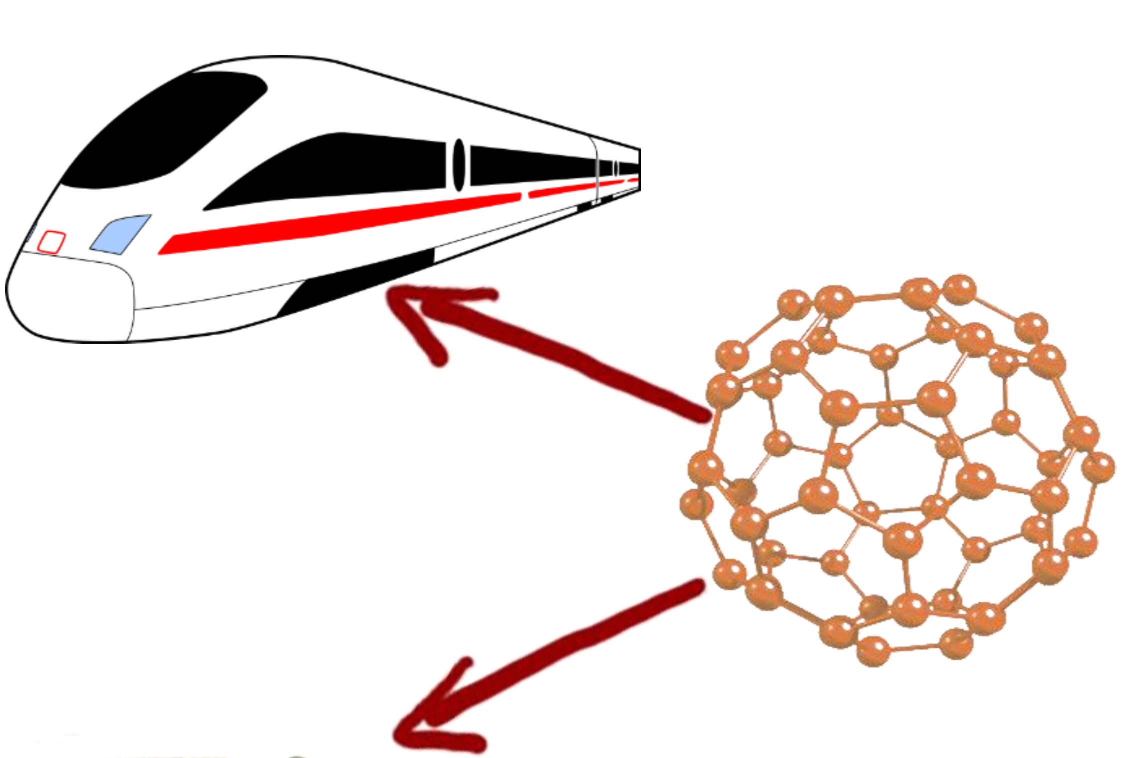


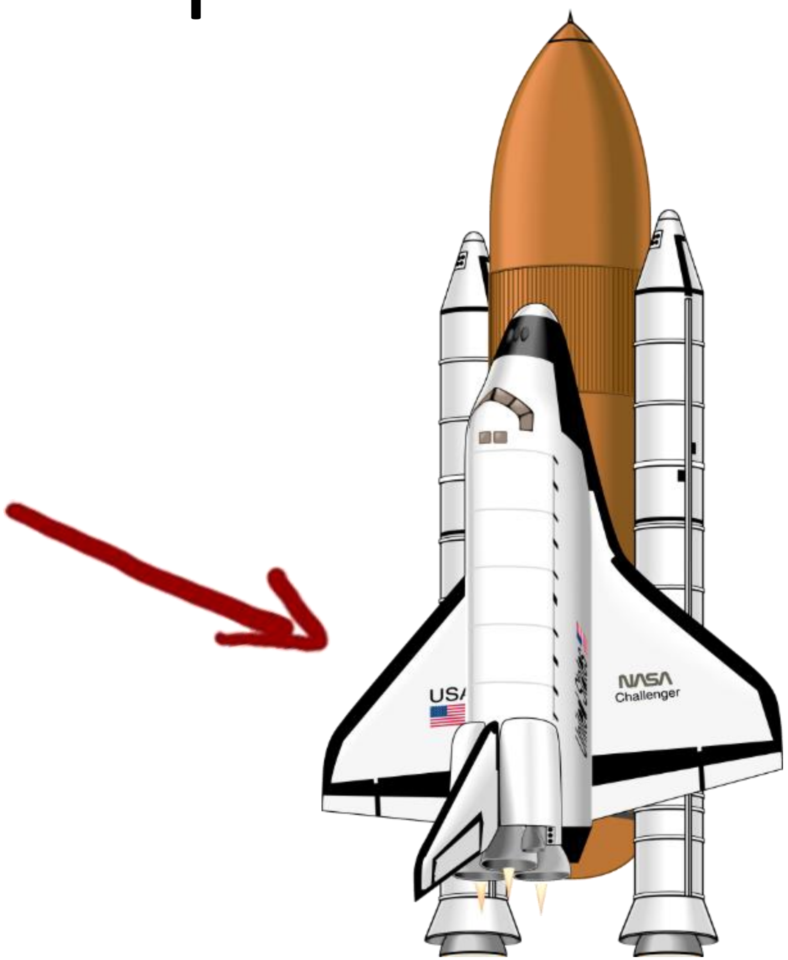
Fullerenes have entered in the field of informational technology. It is expected that by using fullerenes in creation of hard disks, it will be large computer storage space.

Changed materials by fullerenes

Fullerenes have found applications in construction. Created new materials based on the addition of fullerenes will increase the durability of buildings over time.

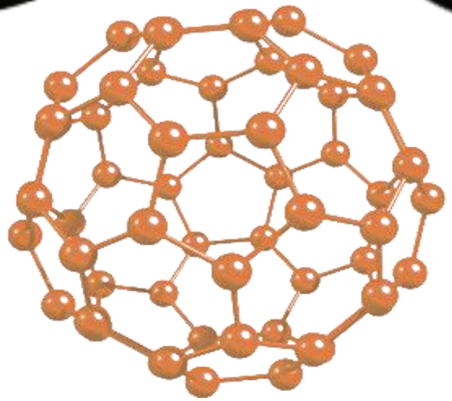
Fullerenes and transport





Transport shows interest for fullerenes. The application of these molecules in various alloys, could decrease the degradation processes of materials.

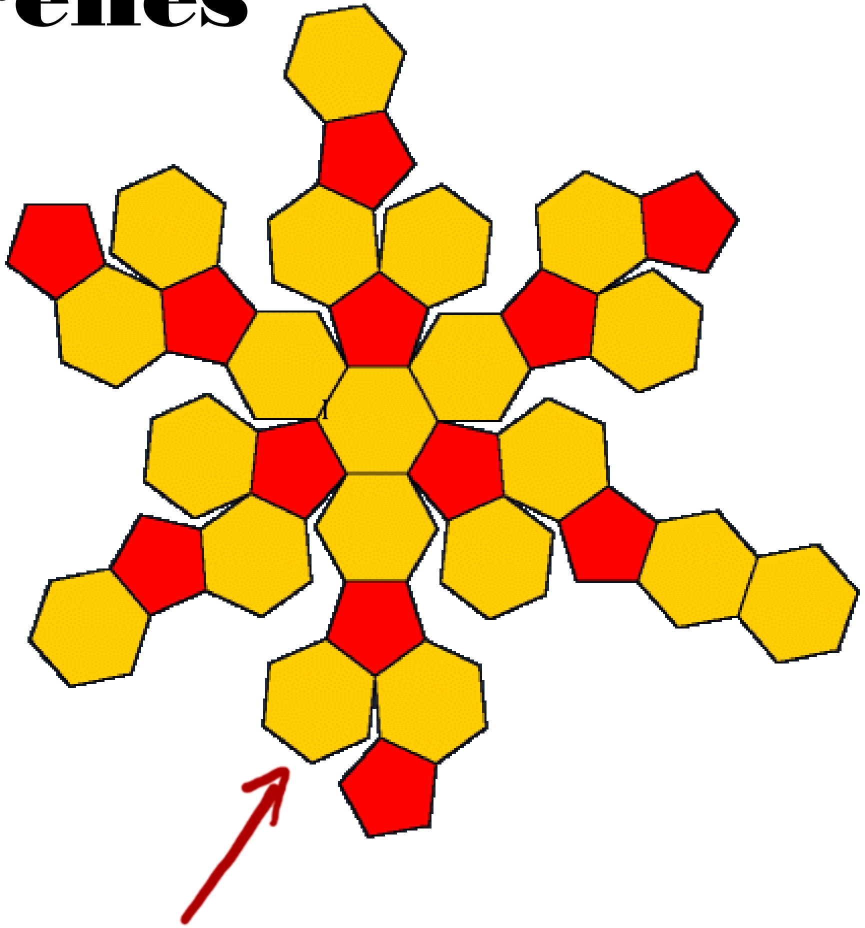
Optical materials



If you have sunglasses or telescope is possible that they contents fullerenes. In the case of sunglasses, fullerenes serve to protect the eyes.

Fullerenes

- Try to model for 3d printing the unit structure of the C60 fullerene buckyball, in respect with what you learn about its structure, till now.
- The C_{60} fullerene structure contains 20 hexagons and 12 pentagons of carbon linked together in coordination. Each pentagon of carbon is connected to five hexagon of carbon. The unfolded structure is shown in the right.
- If you can't print it in 3d, print it in 2d on the glossy paper and then make the 3d structure by paper folding.

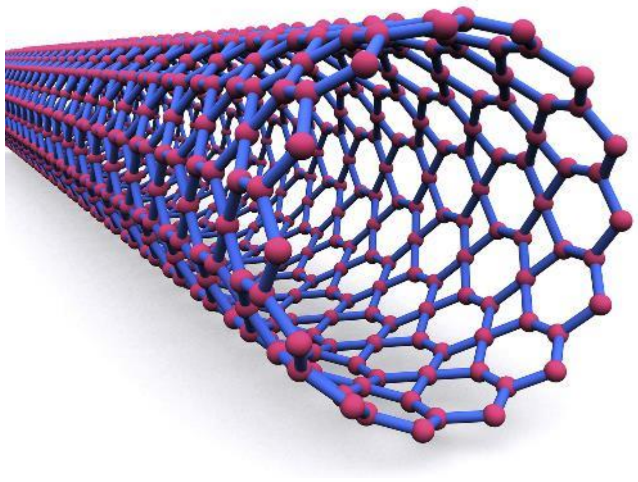


Structure unit of fullerene C_{60}

- After printing and obtaining the 3d model of the C_{60} fullerene structure, analyse the angles and the lengths of the bonds and try to observe the rigidity/flexibility given by the structure of the fullerene.

Carbon-based nanomaterials

From ^{12}C *to*



Nanotubes

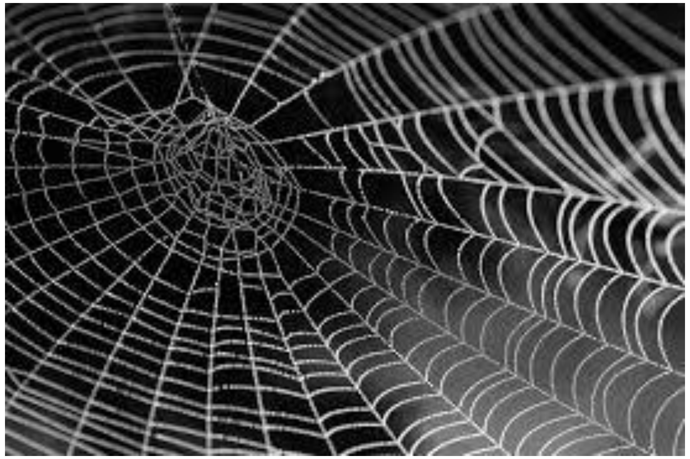
From spider silk to nanotubes?

Most of us don’t like insects like spiders. But, we all know that they have an amazing talent: to produce spiders’ web.

Spiders build their web via extruding a proteinaceous spider silk out of their spinnerets.

The tensile strength of spider silk is greater than the same weight of steel and has much greater elasticity. Spider silk is five times as strong as steel! Isn’t that amazing?

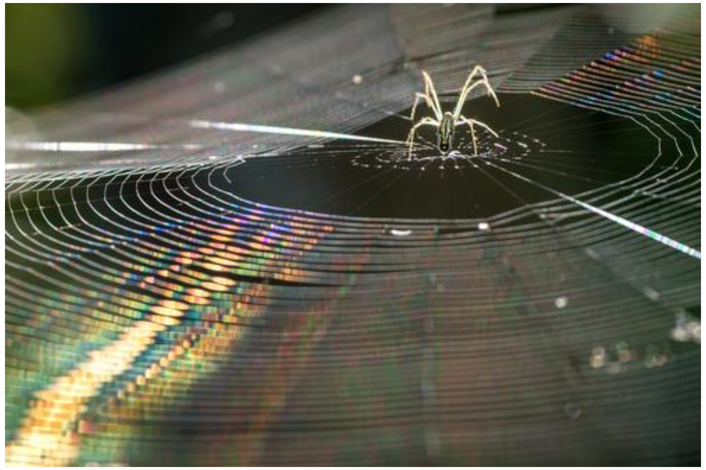
Some spider webs can even withstand hurricane-force winds!



Spider Web.

Dew on Spiders’ Web

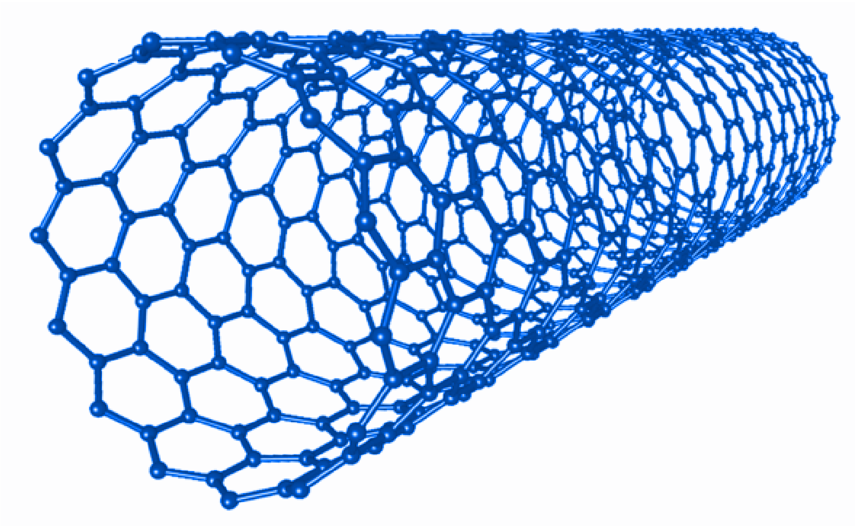
From Spider silk to nanotubes?

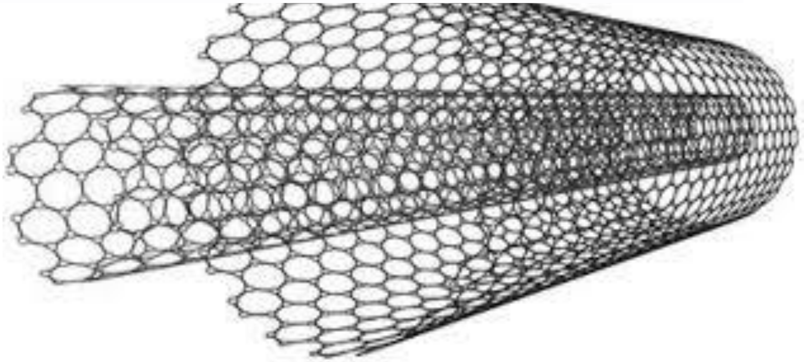


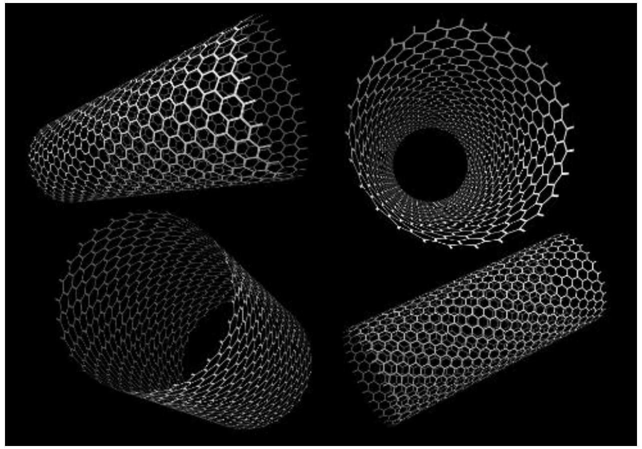
As well as movie producers, the amazing properties of spider silk and web has also been a wonder for scientists.

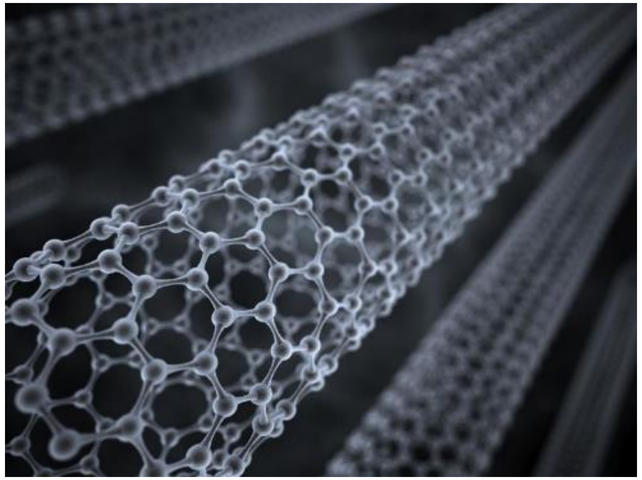
Scientists first investigated the properties of spider silk and web. Then, as usual they decided to mimic the spiders' silk. And, found out that the most suitable material to mimic spiders' silk is the "Carbon Nanotubes".

What are the nanotubes?



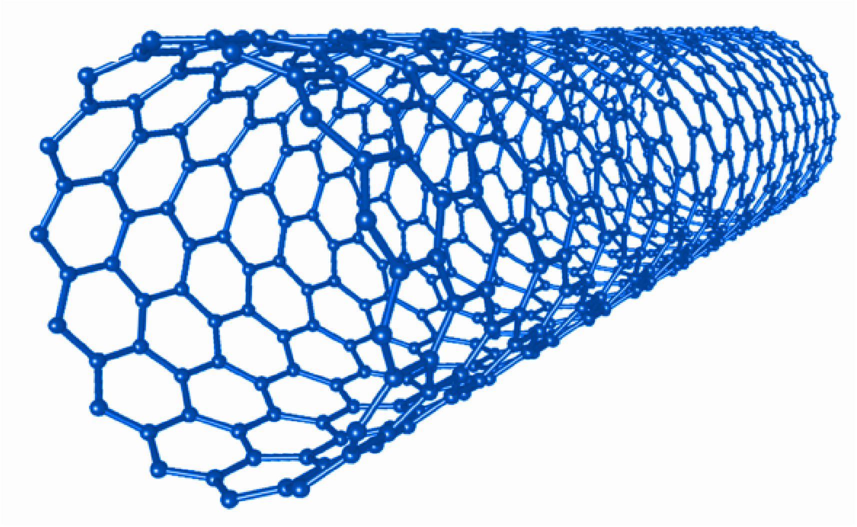






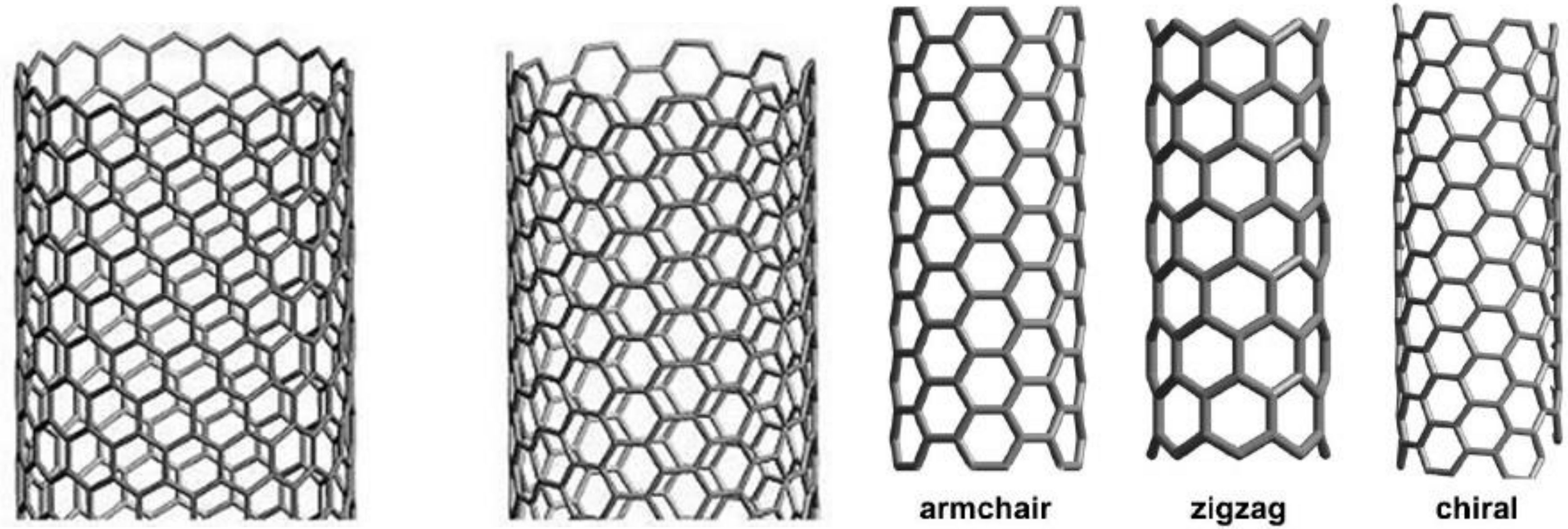
Carbon nanotubes are alternate forms or "allotropes" of carbon, just like diamond and graphene (pencil lead), which are shaped like cylinders

What are the nanotubes?



They were discovered by Japanese scientist Sumio Iijima in 1991.

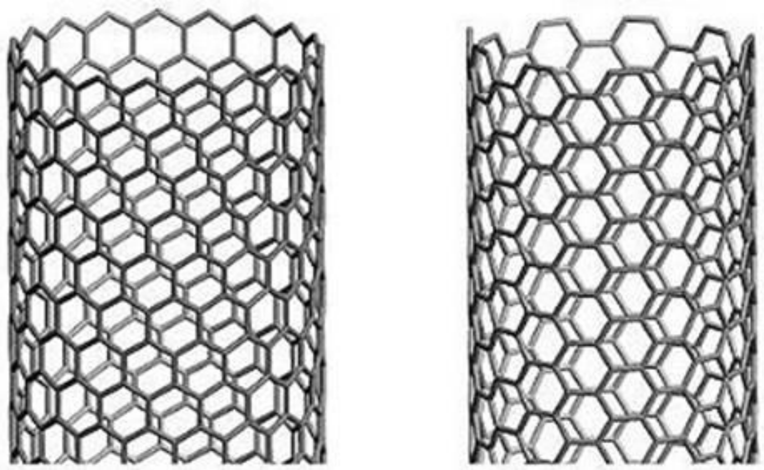
Nanotubes structure



- The special nature of carbon combines with the molecular perfection of buckytubes (single-wall carbon nanotubes) to endow them with exceptionally high material properties such as electrical and thermal conductivity, strength, stiffness, and toughness.
- No other element in the periodic table bonds to itself in an extended network with the strength of the carbon-carbon bond.
- The delocalised pi-electron donated by each atom is free to move about the entire structure, rather than stay home with its donor atom, giving rise to the first molecule with metallic-type electrical conductivity.
- The high-frequency carbon-carbon bond vibrations provide an intrinsic thermal conductivity higher than even diamond.

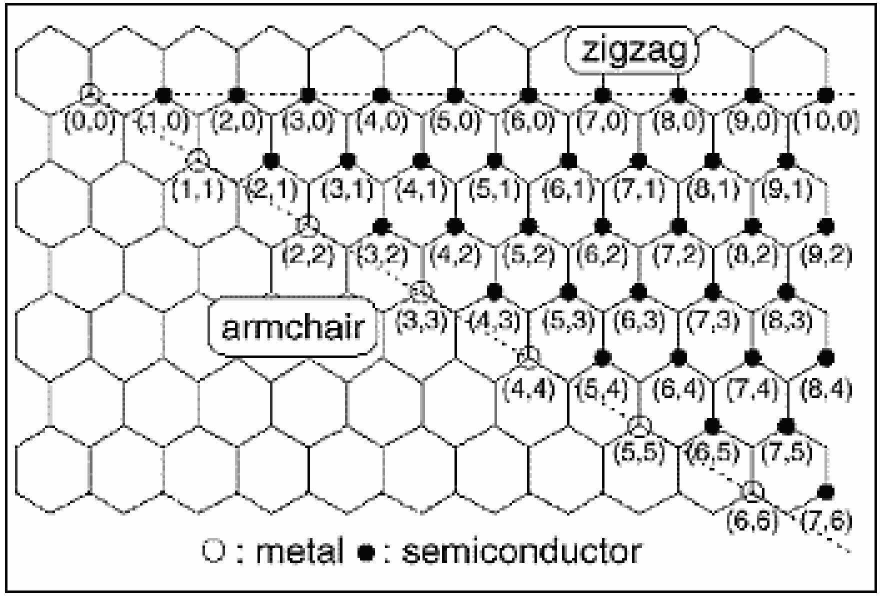
Buckytube structures

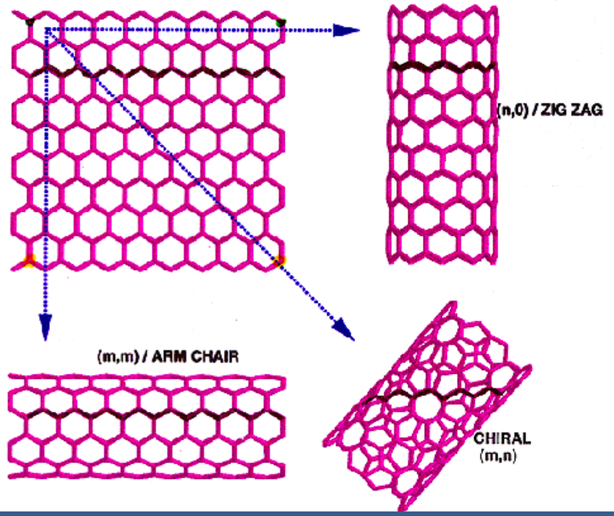
- Buckytubes are single-wall carbon nanotubes, in which a single layer of graphite - graphene - is rolled up into a seamless tube.
- Graphene consists of a hexagonal structure like chicken wire. If you imagine rolling up graphene or chicken wire into a seamless tube, this can be accomplished in various ways.
- For example, carbon-carbon bonds (the wires in chicken wire) can be parallel or perpendicular to the tube axis, resulting in a tube where the hexagons circle the tube like a belt, but are oriented differently.
- Alternatively, the carbon-carbon bonds need not be either parallel or perpendicular, in which case the hexagons will spiral around the tube with a pitch depending on how the tube is wrapped. The bellow figure illustrates these points:



Naming Convention

- There is a straightforward labelling convention to distinguish differently wrapped tubes from one another.
- The mapping specifies the number of unit vectors required to connect two atoms in the planar hexagonal lattice to form a seamless tube.
- These numbers specify a "vector" for the mapping, commonly expressed as (m,n), where m and n are integers.
- These numbers constitute a unique "name" for a tube. Any tube "named" (n,0) has carbon-carbon bonds that are parallel to the tube axis, and form, at an open end, a **"zig-zag"** pattern; these tubes are referred to as **"zig-zag"** tubes.





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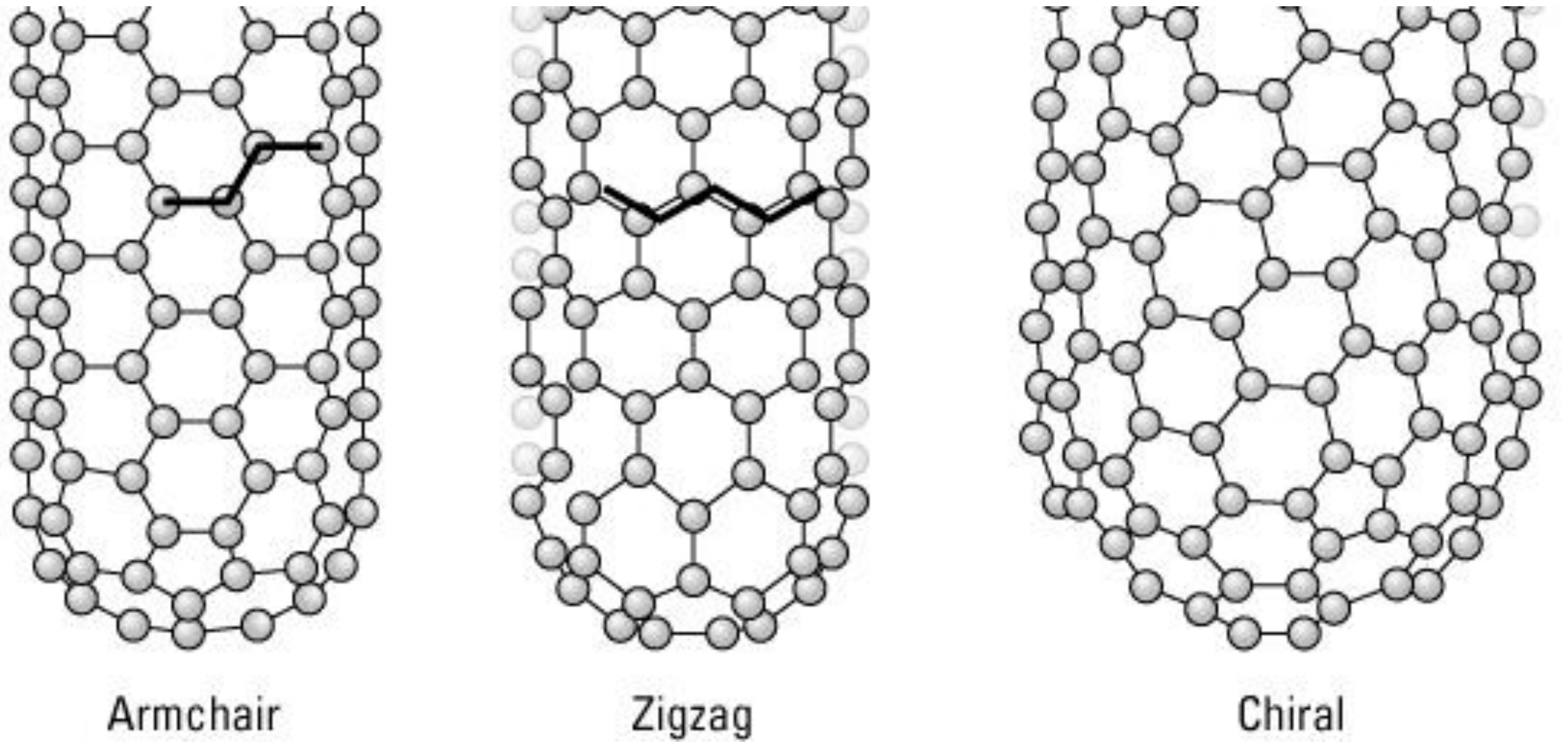
Naming Convention

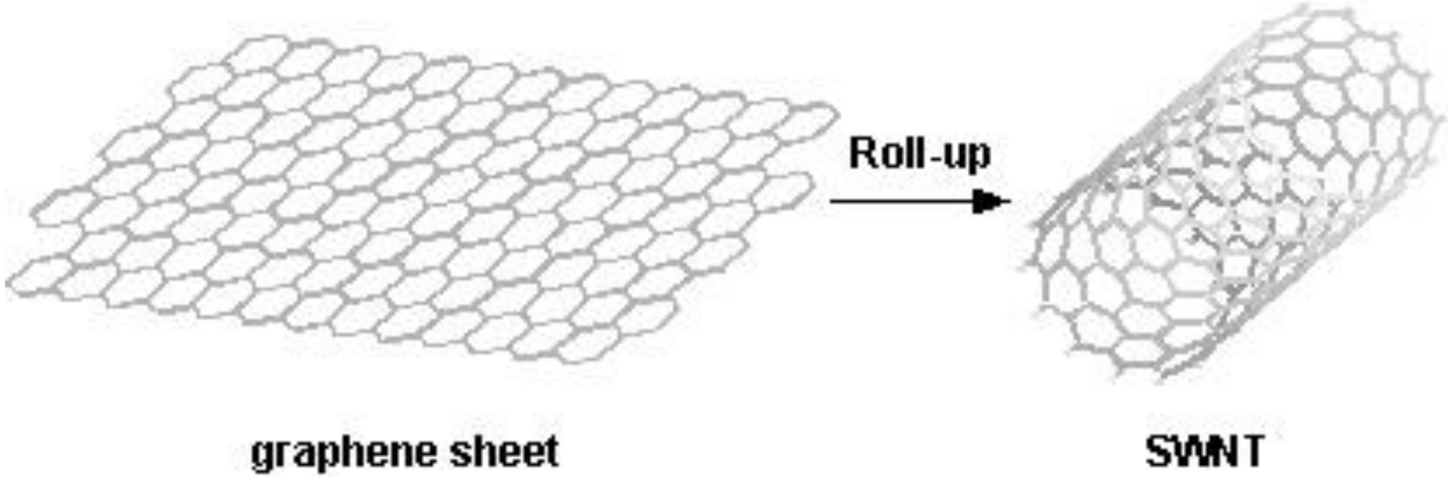
- The tubes named (n,n), where the two integers are equal, have carbon-carbon bonds that are perpendicular to the tube axis, and are often called **"armchair"** tubes. These two basic types are ***achiral***, meaning they do not have a distinct mirror-image, like left and right hands.
- All the other tubes, named **(m,n)**, where m does not equal n, and neither is 0, are **chiral**, and have left- and right-handed variants.



Carbon Nanotubes structures

- CNTs are categorized as Single Walled Nanotubes (SWCNTs) and Multi Walled Nanotubes (MWCNTs).

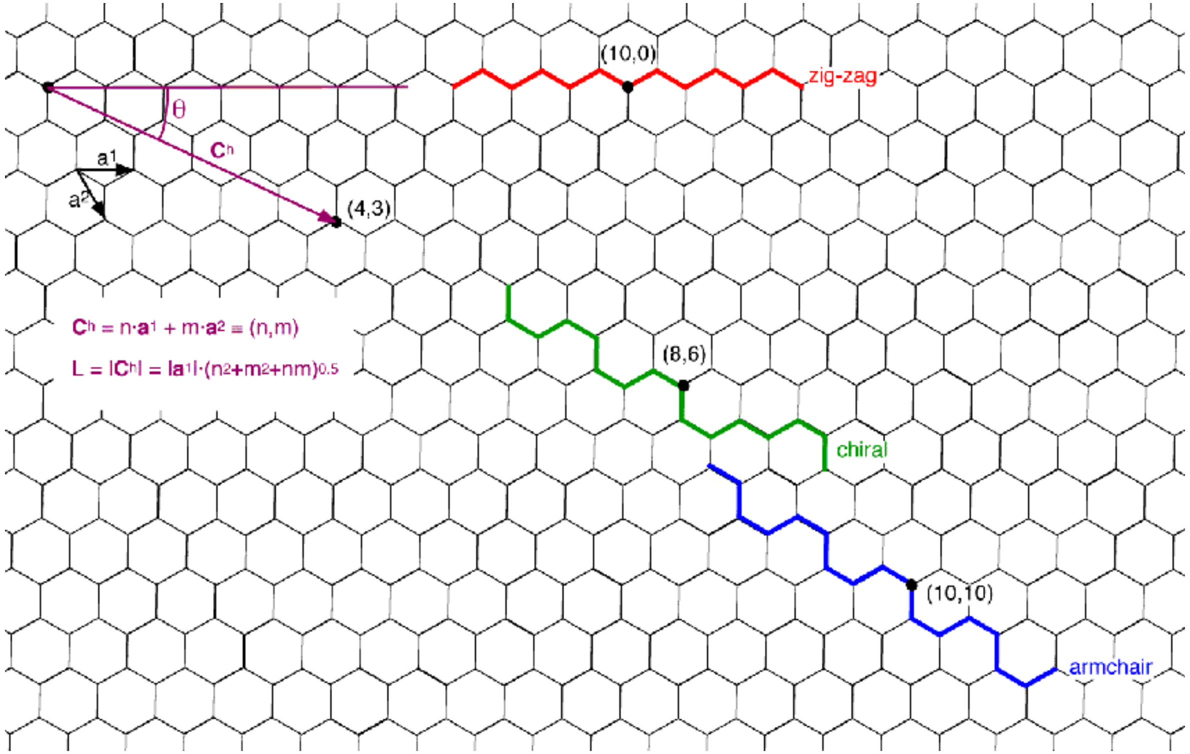
Single Walled Carbon Nanotubes (SWCNTs):
When a graphene sheet is rolled up, a single walled CNT is formed.



Single walled nanotube.[3] (Copyright Professor Charles M. Lieber Group)
The graphene sheets are rolled at specific and discrete angles. The combination of the rolling angle and the radius determines the properties of CNTs. The products are grouped as “Armchair”, “Zigzag”, and “Chiral”.

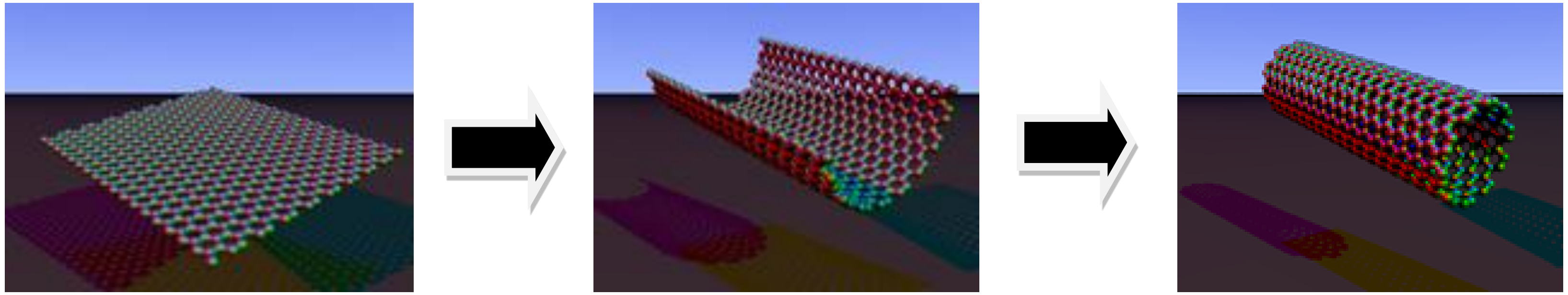
Carbon Nanotubes structures

Armchair and Zigzag SWCNT:
As the graphene sheet is rolled up along one symetry axis, this could end up with either armchair or zigzag CNTs.



Axis to roll up the graphene sheet.(4)

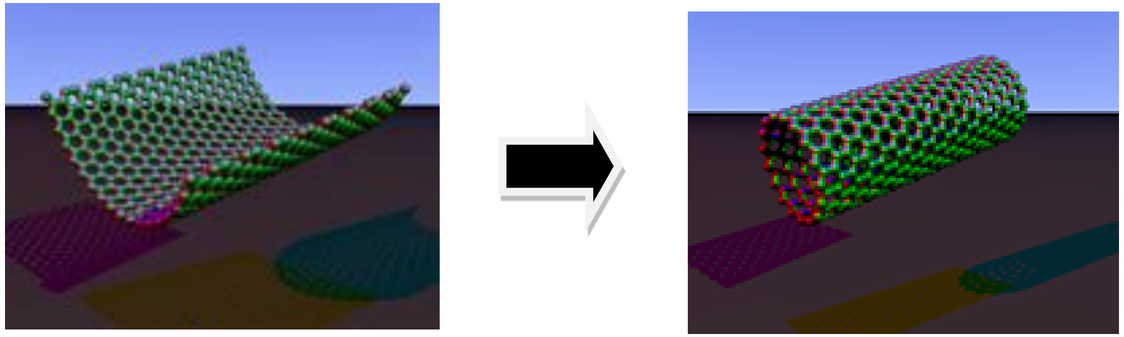
Carbon Nanotubes structures



Graphene nanoribbon

Armchair

Armchair SWCNTs.[5]



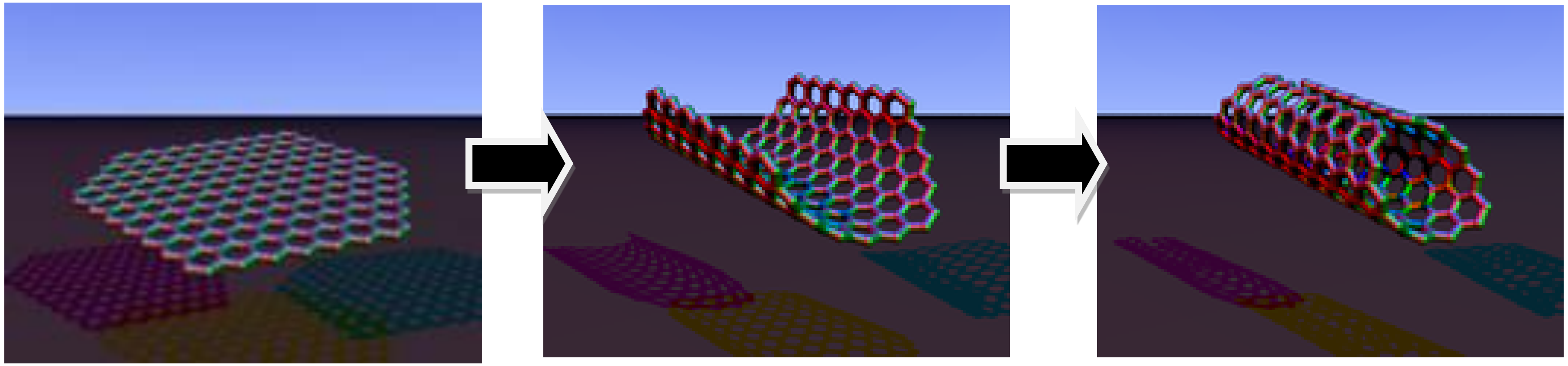
Zigzag

Zigzag SWCNTs[5]

Carbon Nanotubes structures

Chiral SWCNTs:

It is also possible to roll up the sheet in a direction that differs from a symmetry axis: one obtains a chiral nanotube, in which the equivalent atoms of each unit cell are aligned on a spiral.



Graphene nanoribbon

Chiral

Chiral SWCNTs.[5]

Carbon Nanotubes structures

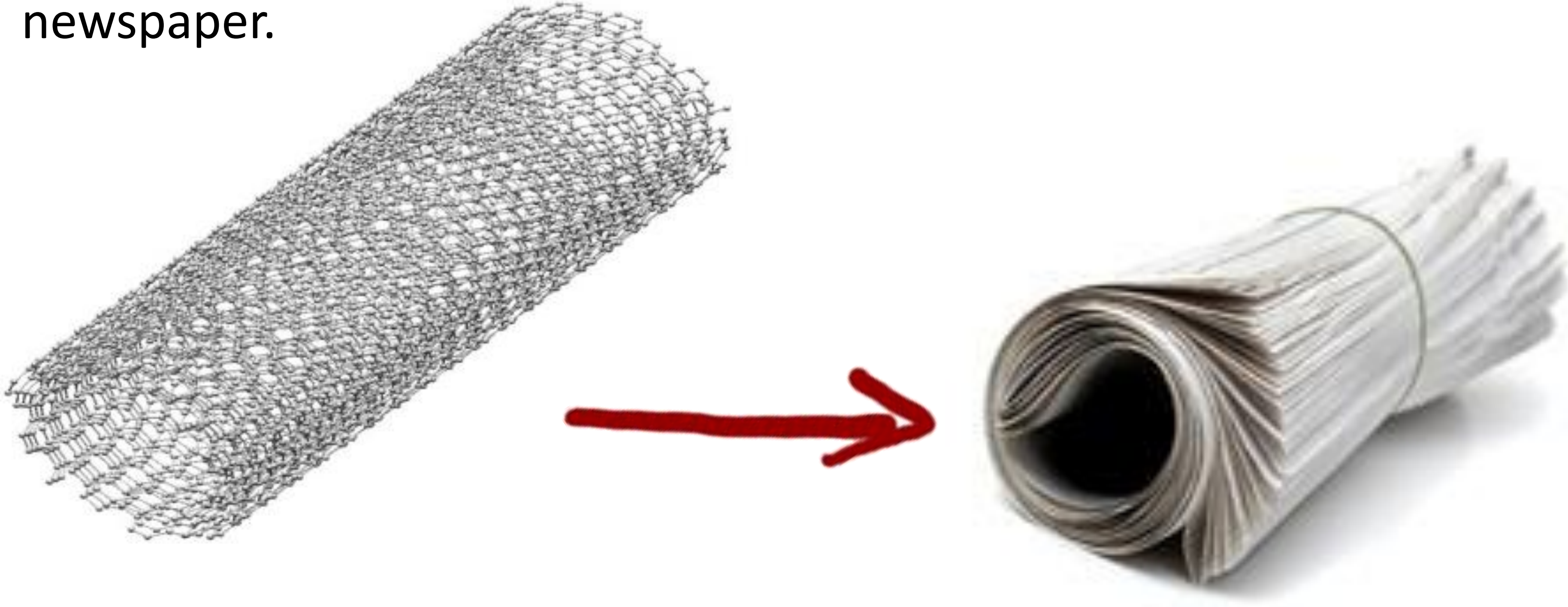
Multi Walled CNTs:

Multi-walled nanotubes (MWNT) consist of multiple rolled layers (concentric tubes) of graphene. There are two models that can be used to describe the structures of multi-walled nanotubes. In the *Russian Doll* model, sheets of graphite are arranged in concentric cylinders.

Multi walled Carbon Nanotubes – Russian Doll Model (MWCNTs)[6]

Carbon Nanotubes structures

In the *Parchment* model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled newspaper.



Multi walled Carbon Nanotubes – Parchment Model.

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Properties of Different Tube Types

The strength of bonding between carbon atoms, gives carbon nanotubes amazing mechanical properties.

According to Young Modulus (a measurement scale of stiffness), the stiffness of CNTs is 5 times higher than steel.

Nanotubes can be either electrically conductive or semiconductive, depending on their helicity, leading to nanoscale wires and electrical components. These one-dimensional fibers exhibit electrical conductivity as high as copper, thermal conductivity as high as diamond, strength 100 times greater than steel at one sixth the weight, and high strain to failure. All armchair CNTs exhibit metallic properties and they are semiconductors of electricity.

Properties of Different Tube Types

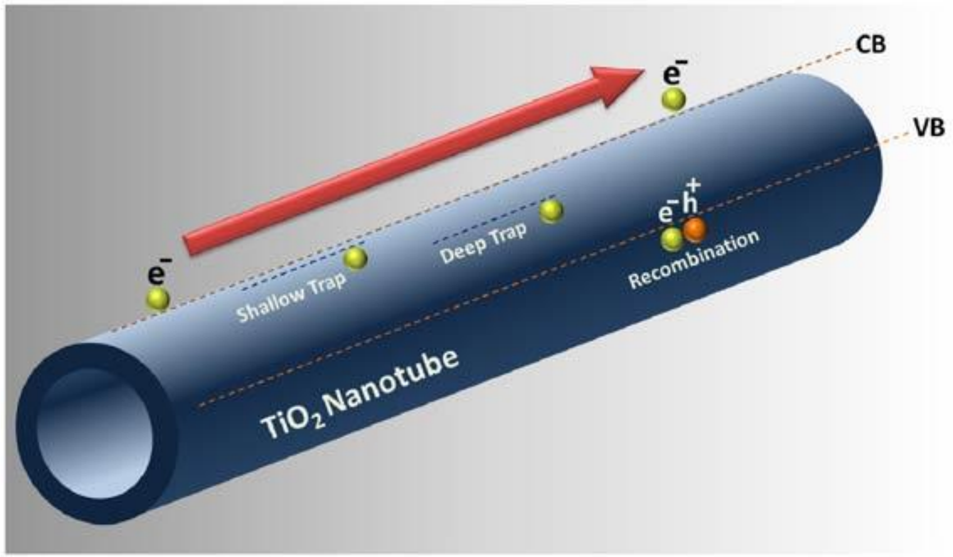
Carbon nanotubes feature a number of extraordinary properties, amongst which are:
high electric conductivity, high thermal conductivity, mechanical strength, thermal resistivity / stability

Size	• Diameter SWNT 0.6-1.8 nm
Heat conductivity	• 6000 W/m K at room temperature
Thermal stability	• In vacuum up to 28000C, in air up to 10000C, in dependence of purity
Density	• 1,33 – 1,4 g/cm3
Tensile strength	• 45 Milliarden Pa
Flexibility	• Can be widely distorted without damage and returns back to the previous shape. The electrical properties changes.
Field- emission	• Light emission materials can be already activated at 1-3 V if the electrode distance is 1 mm

Properties of Different Tube Types

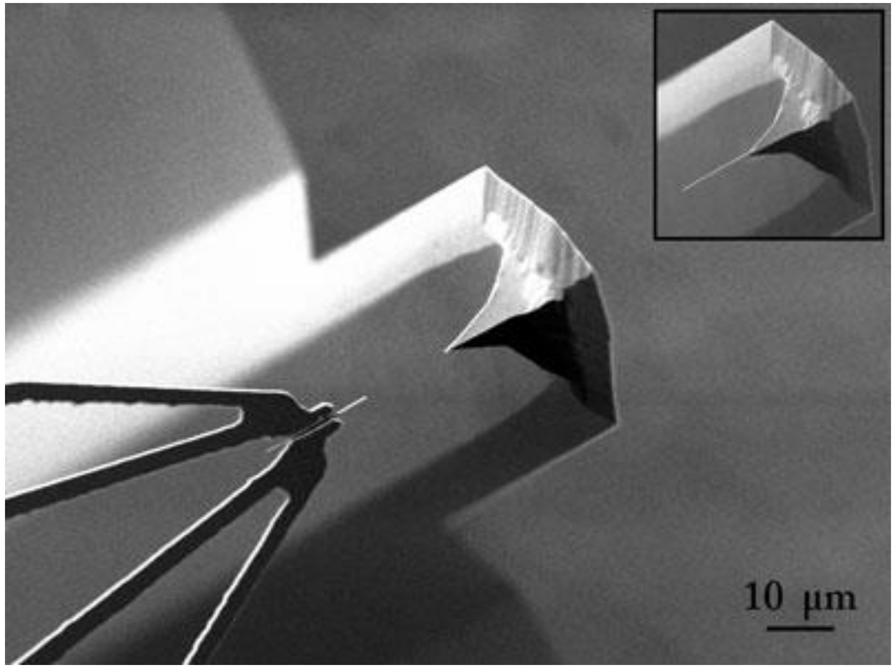
In most respects, the properties of tubes of different types are essentially the same. The exception to this is in their electrical conductivity, where these subtle structural differences can have profound effects. For example, all armchair tubes - i.e., where m=n - have truly metallic electrical conductivity.

They transport electrons along the tube axis just as metals do, without a single atom of metal in their structure! This behaviour in a molecule is unprecedented. In contrast, the other tubes are intrinsically semiconducting, either with a very small band gap of a few meV, or with moderate band gaps on the order of 1 eV. The rule here is that those tubes where (n-m) is a multiple of 3 are the small-gap type, while the others have medium gaps.

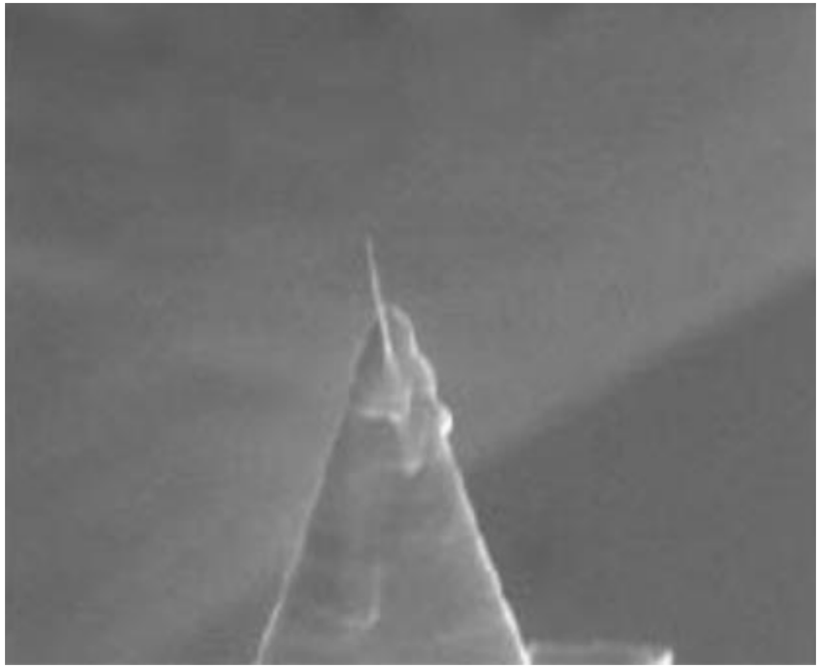


Application areas of CNTs:

Carbon nanotubes possess many unique properties which make them ideal AFM probes. Their high aspect ratio provides faithful imaging of deep trenches, while good resolution is retained due to their nanometer-scale diameter.



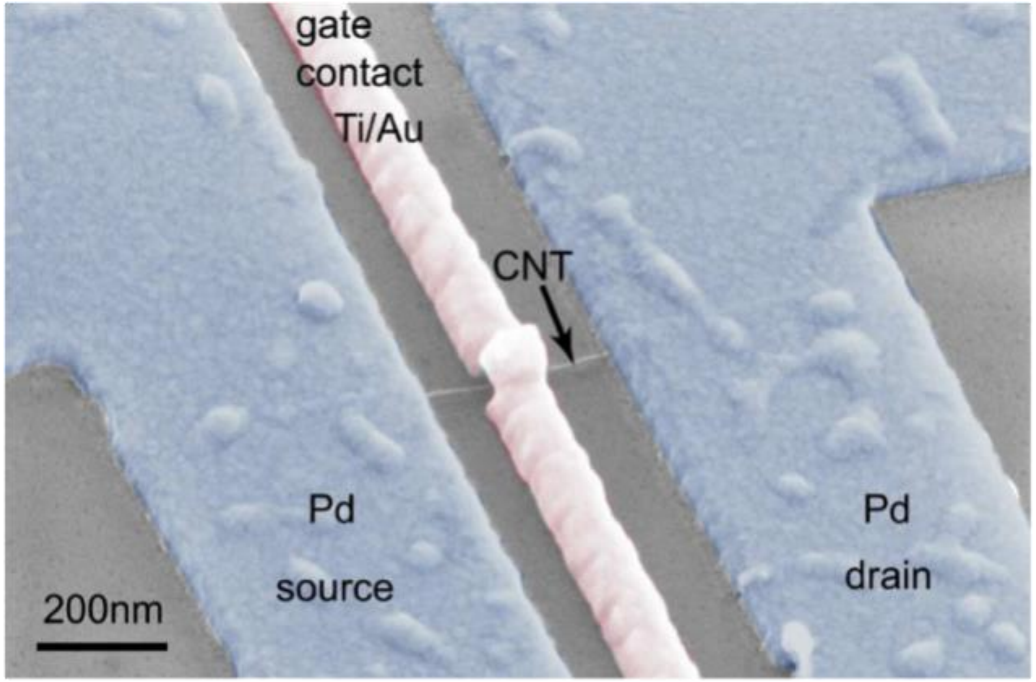
CNT-enhanced AFM super-tips (Image: ÖzlemSardan, DTU).[7]



AFM Probe Tip.[8]

Application areas of CNTs:

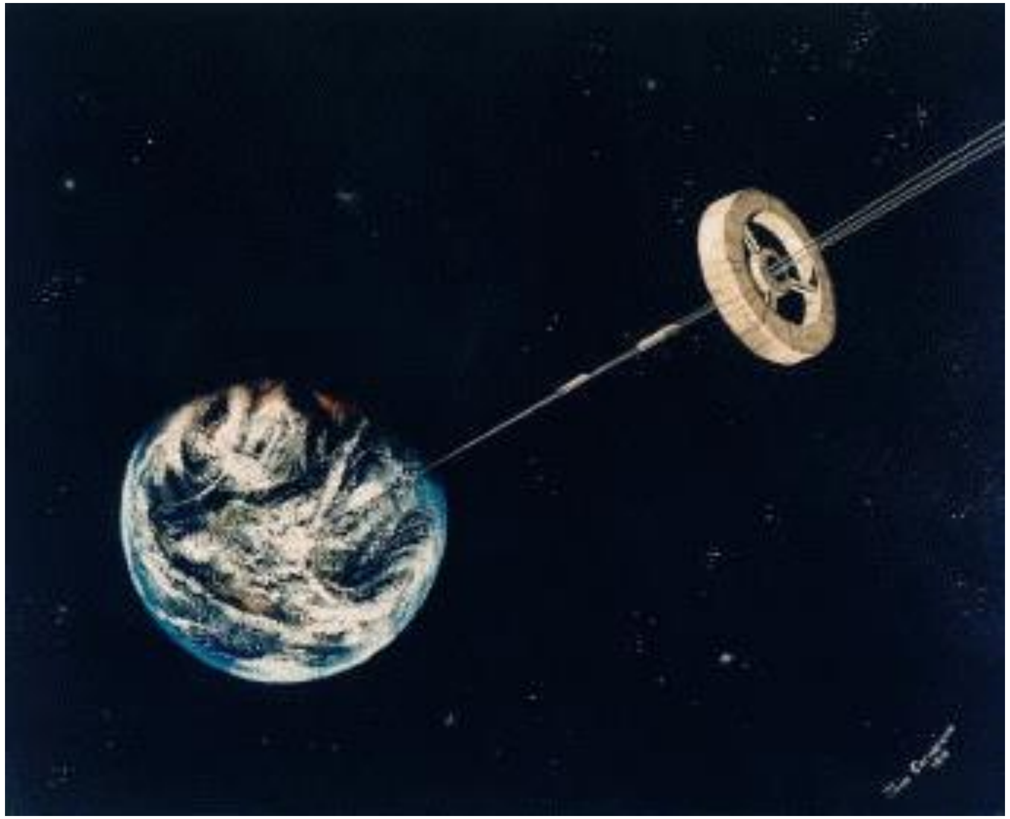
Carbon Nanotube Transistors exploit the fact that nm- scale nanotubes (NT) are ready-made molecular wires and can be rendered into a conducting, semiconducting, or insulating state, which make them valuable for future nanocomputer design.



CNTs used in circuits.[9]

Application areas of CNTs:

Carbon nanotubes are quite popular now for their prospective electrical, thermal, and even selective-chemistry applications. CNTs are thought to be used in Space Elevators and as a protection package material to be used around the pipe line going deep under the sea.



Space Elevator[10]

Application areas of CNTs:

The fascinating mechanical and electrical properties of carbon nanotubes can be exploited in many applications, which might include lightweight and strong vehicle or aircraft body with in situ health monitoring and self healing properties, superior aircraft or car brake carbon-carbon composite discs that could dissipate a heat more efficiently, strong and interactive windscreens with de-icing properties.

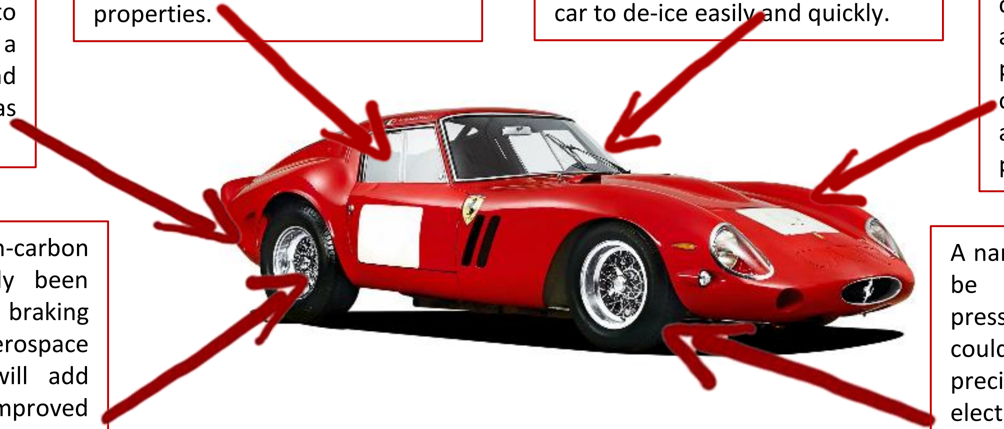
Even a few percent loading of carbon nanotubes in polymer matrix could make non conductive polymers to conduct electricity and solve many problems with static electricity that could be a spark of fire within a vehicle.

The smart carbon fibre / carbon nanotube body will decreased the car's weight and will also improve performance. The body could also be infused with carbon nanotube epoxy and this will give the body stronger structural and sensing properties.

Carbon nanotube composite materials could be used for the windows, windscreens etc. This will add good electrical conductivity properties and allow the windscreen and windows to be connected to a heater and the car to de-ice easily and quickly.

Carbon nanotubes are produced using hydrocarbon gases and catalysts in a similar conditions that exist in a vehicle exhaust systems. It might be possible to produce carbon nanotubes in a vehicle exhaust using catalyst and reducing green house gas emission.

Carbon nanotubes used in MMC could make an engine weigh less and will also improve structural properties. Carbon nanomaterials could be also used in fuel cells and butteries in hybrid and cars powered by alternative energy.



Carbon nanotube carbon-carbon composites have already been developed for braking applications in aerospace industry. This brakes will add further weigh loss and improved performance.

A nanotube pressure gauge could be installed to measure air pressure in the tyres. The gauge could be very accurate and precise due to the unique electrical and mechanical properties of the nanomaterials.

Transport Applications of Carbon Nanomaterials

Application areas of CNTs:

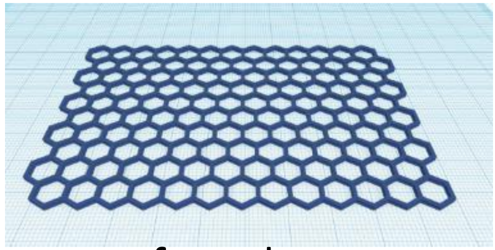
In an aircraft wing carbon nanotubes conductivity could provide de-icing and lighting strike protection with reduction of weight. They could improve strength of a body in an aircraft or a vehicle, decrease weight and make army vehicle or military aeroplane electromagnetically invisible. Carbon nanotubes and nanofibers could be added to metals in order to improve properties and make lighter engines, they could be used in tyres instead of carbon black to improve wear properties and provide in sity pressure sensing.

Transport Applications of Carbon Nanomaterials

Obtaining your own model of Nanotubes:

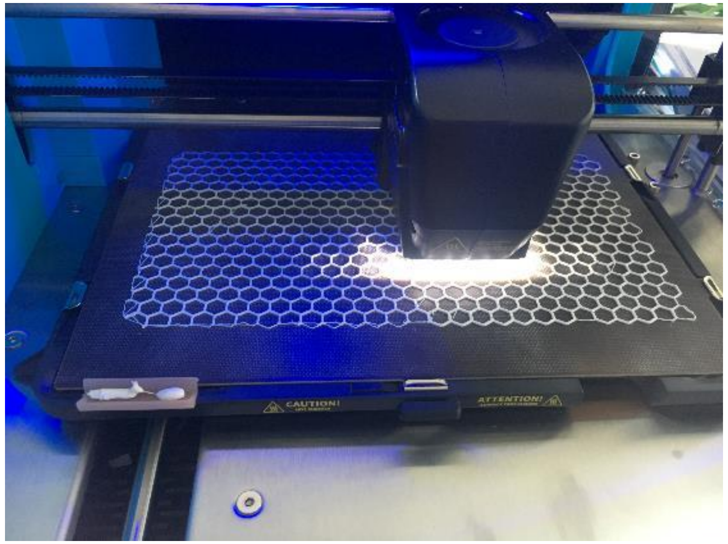
- Starting from the hexagonal unit, try to model for 3d printing the unit structure of the graphene, in respect with what you learn about the angles between the atoms and bond lengths it till now.

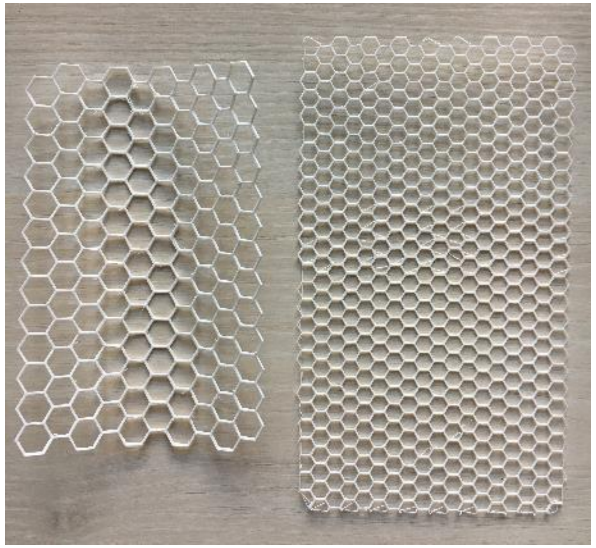
Hexagon unit



Structure of graphene

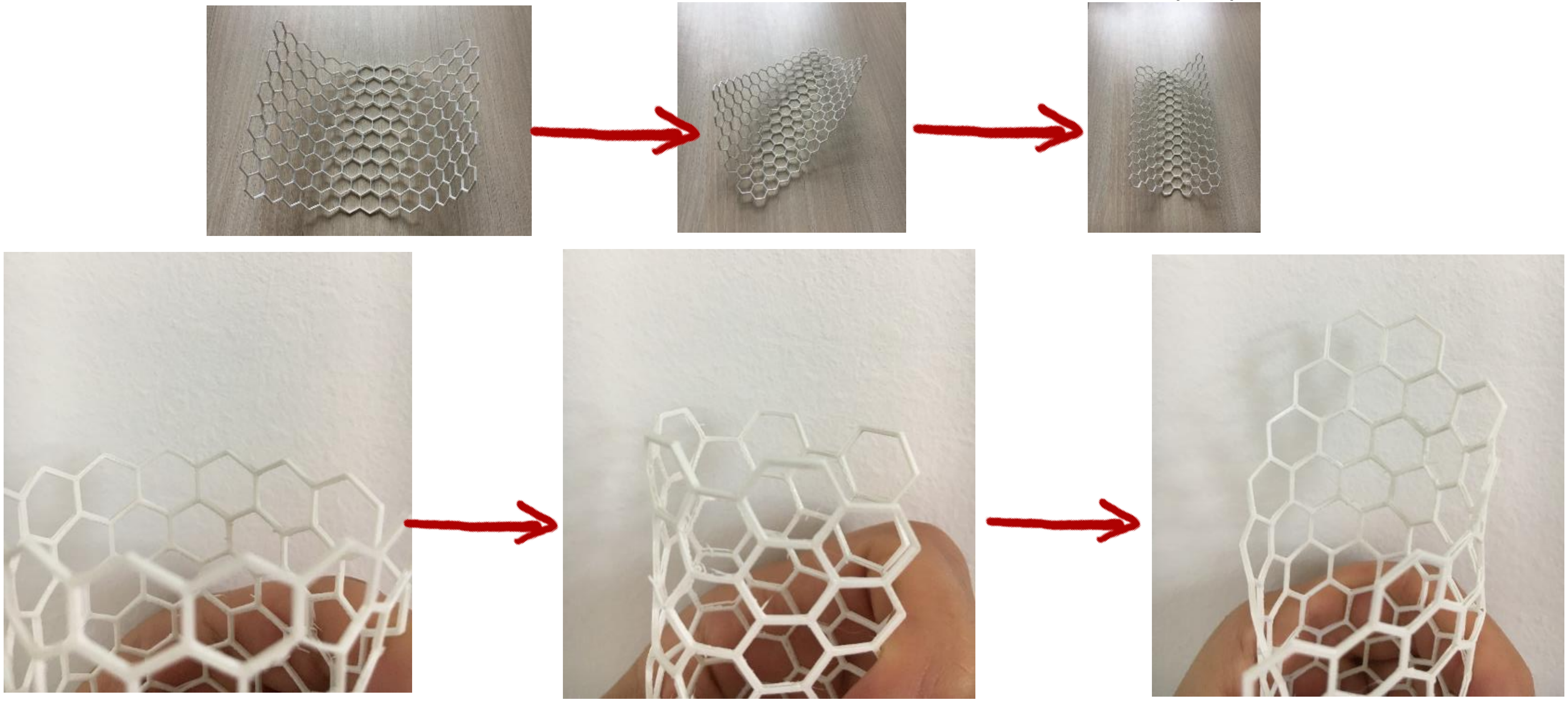
- Print your model of graphene by using the 3d printer. You should obtain objects like those in the bellow figures:





Obtaining your own model of Nanotubes:

- After printing, try to check the flexibility of the structure. Observe the big difference between this structure and the diamond one? Think about connections between the structure and the properties!



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