Chapter 4: Carbon nanotubes

1- General information on carbon nanotubes

Carbon, which comes from the Latin **carbo** meaning: coal in the form of soot and charcoal, is a very abundant chemical element in the earth's crust. Carbon is tetravalent and its ground state electronic configuration is $1s^2 2s^2\ 2p^2$. It owes its importance to the fact that it forms more compounds on its own than all the other elements combined because it can bond with other carbon atoms to form complex chains and cycles of great stability. It exists in nature in two allotropic forms: graphite and diamond and it was until 1985 that fullerenes, the third allotropic form of carbon, was discovered. Since then, many other forms of carbon structure have been observed such as nanotubes or graphene sheets. The figure below summarizes the main allotropic forms of carbon.

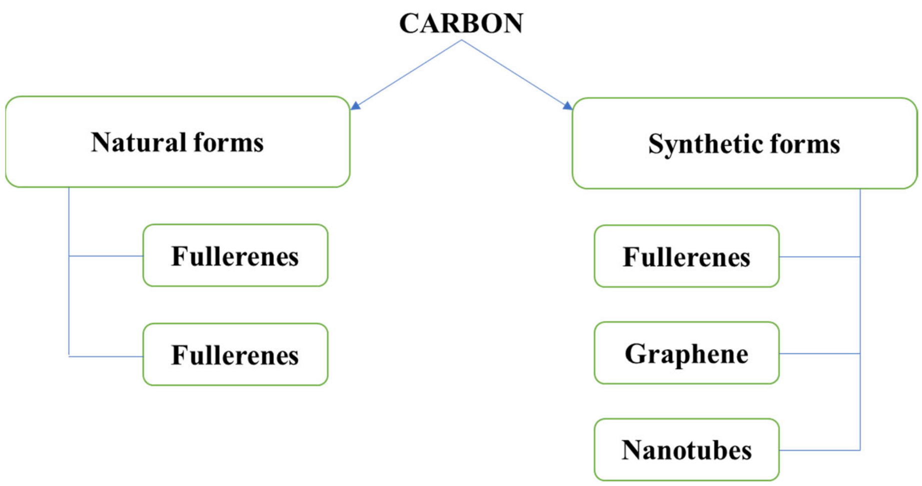


Figure 1: The different allotropic forms of carbon

2. The allotropic forms of carbon

2.1. Natural forms

- **Diamond**

Diamond is one of the compact allotropic forms of carbon. The carbon atoms are in a state of sp^3 hybridization. Their spatial arrangement is made according to a tetrahedral geometry (three-dimensional cubic structure) and the distance between 2 carbon atoms is 0.154 nm. Diamond is the hardest material available. It is also a good electrical insulator and has the highest thermal conductivity. Diamond is a metastable form of carbon under normal conditions of temperature and pressure unlike graphite.

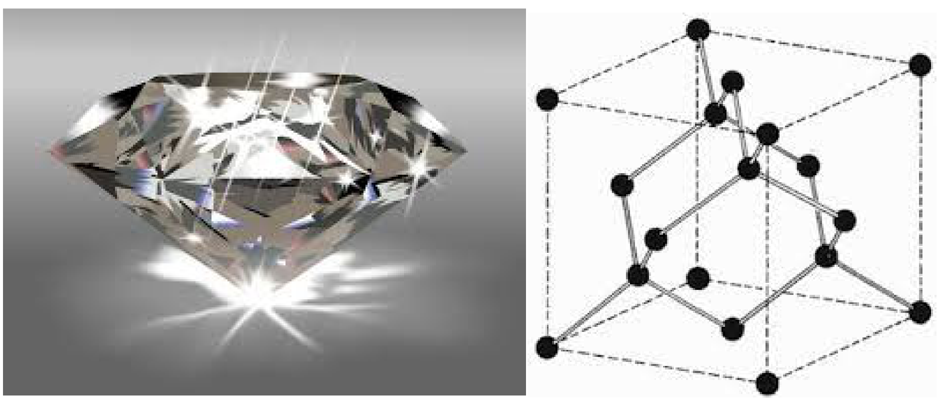


Figure 2: Face-centered cubic structure of the diamond.

- **Graphite**

Graphite (hexagonal and mono-plane crystal structure and gray in color) is the stable form of carbon (Figure 3). It has long been used in particular for writing where it is present in Indian ink and used for pencil leads. It corresponds to a stack of monosheet (graphite monoplane) called graphene, 0.34 nm apart and linked together by weak p bonds which give it a relative fragility, which is why graphite is easy to leaf. Each graphene sheet corresponds to a hexagonal, honeycomb-shaped arrangement of carbon atoms 0.142 nm apart.

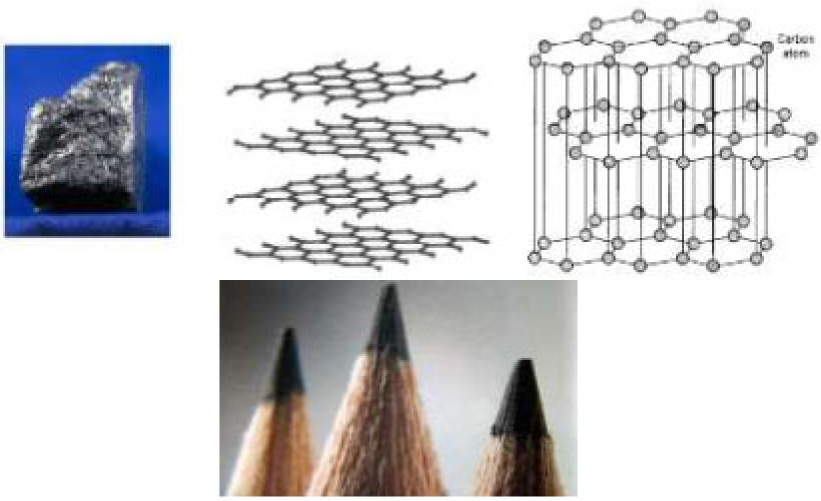


Figure 3: Structure of graphite.

2.2. Synthetic forms

- **Fullerene**

The third known form of carbon to which the nanotube belongs is called fullerene. In 1985, H. Kroto et. Smalley have discovered a new stable structure of 60 carbon atoms, the fullerenes (C_{60}), and have proposed a structural model comparable to that of a soccer ball while respecting the valence of carbon, where the vertices are replaced by atoms of carbon, i.e. a polygon composed of 32 faces, 12 pentagons and 20 hexagons, The C_{60} fullerene is the best known representative of the fullerene family, cage molecules of more than 60 carbon atoms. Best-known fullerene are the C_{60} and C_{70} but there are also the C_{76}, C_{82}, C_{84}…

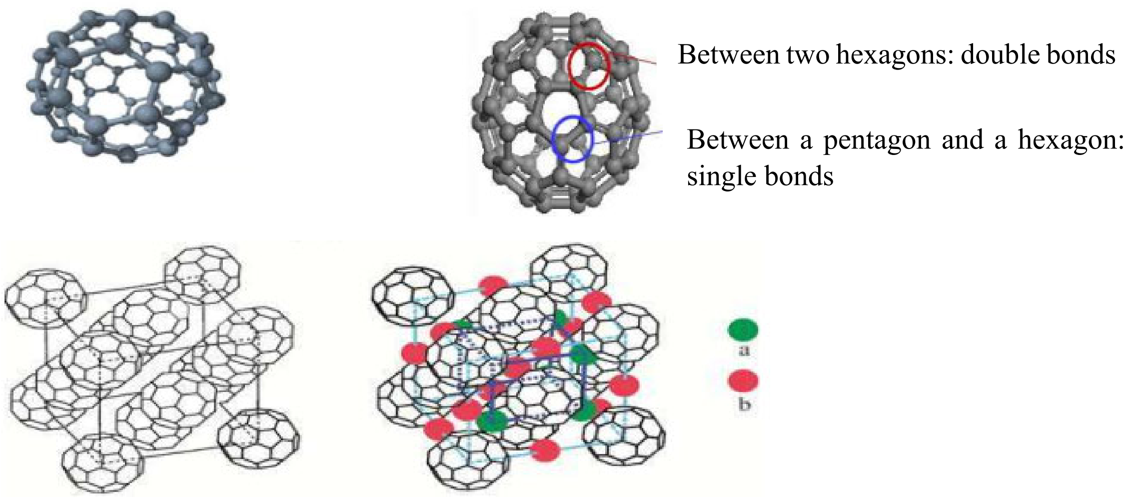


Figure 4: Fullerene C60

- **Graphene**

Graphene corresponds to a plane of carbon atoms assembled in 2 dimensions (2D) according to a honeycomb structure as illustrated in figure.5. It has a hexagonal structure with sp^2 type bonds. It was for a long time a simple theoretical object making it possible to model the properties of carbon nanotubes.

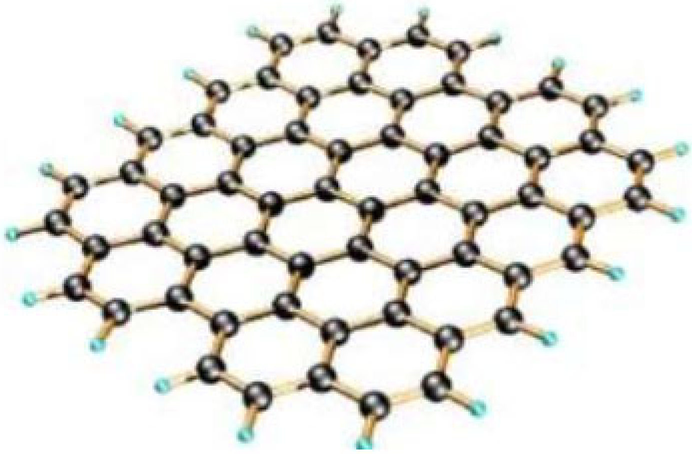


Figure 5: Graphene sheet

- **Carbon nanotubes**

Carbon nanotubes (CNTs) were discovered in 1991 by the Japanese researcher S. Lijima when he was interested in the synthesis of fullerenes. It has been observed in soot deposits obtained by the discharge of an electric arc between two carbon electrodes. These carbon nanotubes can be defined as one or more sheets of graphene rolled up on themselves to form a hollow graphitic cylinder 0.5 to 10 nm in diameter and no longer than a few microns. They consist only of sp2 hybridized carbon atoms thus forming a network of hexagons. Their one-dimensional character associated with the strength of the bonds between carbon atoms gives them, on a theoretical level, exceptional mechanical properties.

Carbon nanotubes continue to surprise and amaze with their mechanical and electrical properties. They are perfect conductors capable of making perfect electrical interconnections and very intense electron sources for televisions. For their mechanical properties, we can make ropes whose robustness will be matched only by their lightness. Finally on the surface, they constitute an exceptional hydrophobic coating.

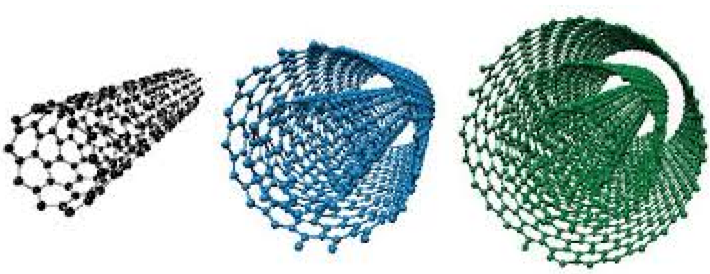


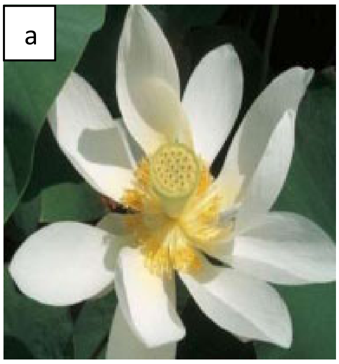
Figure 6: Carbon Nanotube

3. Properties of carbon nanotubes

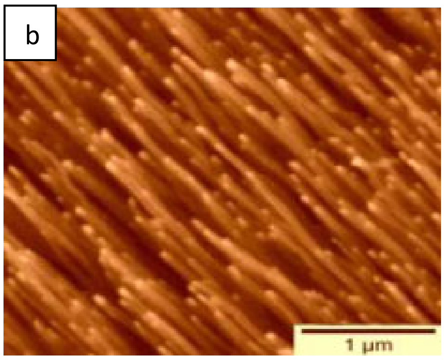
Carbon nanotubes arouse enormous interest in the world of both basic and applied research because their properties are exceptional in many respects. From a mechanical point of view, they have both excellent rigidity (measured by Young's modulus), comparable to that of steel, while being extremely light. From the electrical and optical points of view, single-sheet nanotubes have the quite exceptional particularity of being able to be either metallic or semi-conducting depending on their geometry (rolling angle of the graphene sheet). Carbon nanotubes have very high thermal conductivity.

- **The lotus effect**

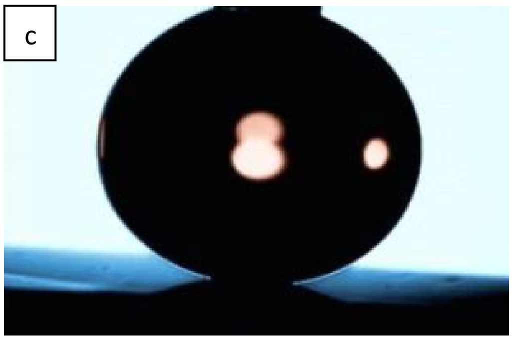
In Asian cultures and religions, the lotus symbolizes purity. Indeed, this plant emerges of the most brackish and troubled waters while remaining immaculate. This flower comes out of the water without wet, because its leaves have an exceptional self-cleaning mechanism. Nanocrystalloids cover the surface of the leaves and transform the rain into drops which bead on its surface carrying with them the dirt particles. By controlling the growth conditions or using other techniques, we know how to organize nanotubes into a “brush carpet”: these are all nanoscopic points similar to the crystalloids of lotus flowers. In this form, one can achieve a self-cleaning surface in the manner of the lotus. Such a self-cleaning coating is very attractive (glass, clothes...). As it is known to prepare transparent nanotube films, the potential for their "lotus effect" is very promising.



Lotus flower



Carbon Nanotube Brush Mat



Drop floating on a carpet of nanotubes

Figure 7: (a) Lotus flower; (b) Carbon Nanotube Brush Mat; (c) Drop floating on a carpet of nanotubes.

A rigid and light rope (a space elevator): The diamond is the most emblematic crystalline form of carbon. In this form, the carbon is very strong (due to the CC covalent bond). Diamond is used to cut glass, very rigid steels, sapphire etc. In many ways, carbon nanotubes are even stiffer, despite their hollow structures. By way of comparison, they are 20 times more rigid in tension than steels while being ten times lighter. By controlling growth, nanotubes can be self-organized into ropes or bundles. For this rope to have the same rigidity as the nanotubes that compose it, the nanotubes must be woven together to prevent them from sliding on each other. With very reactive gases, we know how to build very rigid covalent bonds between the nanotubes giving the whole an incomparable rigidity. Nanotubes are materials with very high porosity. This property allows it to adsorb many gases including hydrogen. In carbon nanotubes these planes grow directly into tubes. We can have either single plane, which in general are between 1 to 3 nm, or several concentric layers closed in a tube (multi-walled nanotube). The thicknesses can be quite numerous (up to 50 thicknesses) and the properties of the nanotube result from the sum of the properties of all the layers which constitute it.

Single-walled nanotube   Single wall nanotube rope   Multi-walled nanotube

Figure 8: (a) Single-walled nanotube; (b) Single wall nanotube rope; (c) Multi-walled nanotube.

4. Applications of carbon nanotubes in electronics

The first applications envisaged relate to ultra-thin film conductivity to make, for example, conductive blankets providing electrostatic protection. This type of conductive film can be used on the carcass of an aircraft in order to prevent that when lightning strikes the aircraft, it is transmitted to travelers. Carbon nanotubes have also been studied for transistor applications. Hundreds of single nanotube transistors have been produced, for which it has been shown that the intrinsic electronic qualities are excellent and that they can reach or even exceed in some cases the qualities of the best silicon transistors. Carbon nanotubes can be prepared in a mixture with organic dopants which consist of carbon, nitrogen, which are plastics. Very different applications are therefore envisaged for carbon nanotubes. In thin film, their transparent character, to make, for example, flexible electronics, integration in fabric, on flexible plastic, on paper... This electronics also has the advantage of being inexpensive.

Fig 9: Flexible screen made using nanoparticles

Fig 10: Some applications of nanomaterials