

CARBON NANOTUBES

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ABSTRACT: Carbon nanotubes are among the most extensively researched materials today, Research in this area is throwing up numerous surprises. This is the most versatile materials, with the properties ranging from optical absorption and emission on one hand to the mechanical properties of bulk materials such as young's modulus, on the other. The various aspects of science such as chemistry, physics, biology and material science are creating numerous possibilities for application. An overview of carbon nanotubes and their applications is presented here.

INTRODUCTION:

Carbon is responsible for creating the most diverse variety of compounds. It has more allows tropes than any other element. A single sheet of graphite is called graphene. A carbon nanotube is produced by curling a graphene sheet. The structure of a cylindrical tube is best described in terms of a tubule diameter d and a chiral angle θ . The chiral vector $C = na_1 + na_2$ along with the two para meters d and θ define the tube. The unit vectors a_1 and a_2 define the graphene sheet. The vector C connects two crystallo graphically equivalent points. The angle θ is with respect to the zigzag axis and it is 30° for the armchair tube. If we roll over from one end of the tube to the other end, we obtain a cylinder. The properties of the tube get modified depending on the chiral angle θ and the diameter d . While the $(n,0)$ tubes are called 'zigzag tubes' Where θ is zero, the (n,n) tubes are called 'armchair tubes' where θ is 30° . These two types of tubes of tubes have high symmetry and a plane of symmetry perpendicular to the tube axis. The tubes will be optically active to circularly polarized light, circulating along the tube axis.

SYNTHESIS AND PURIFICATION:

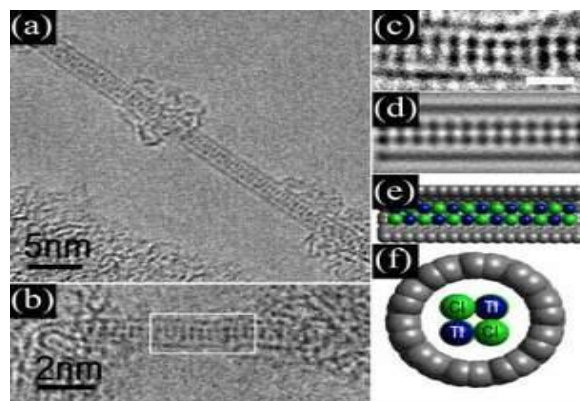


Carbon nanotubes were first noticed in the graphitic soot deposited on the negatively charged electrode used in

the arc-discharge synthesis of fullerene. Nanotubes are mostly found with closed ends on either side, through open tubes are also seen. Thus these are three-dimensional closed-cage objects and may be considered as elongated fullerenes. In order to make a closed-cage structure, There must be at least 12 pentagons according to the Euler's theorem, considering only pentagons and hexagons. The hexagons make the elongated body of the tube and the ends contain both hexagons and pentagons, with a minimum of six pentagons on each face. However, the tube body and the ends can have effects. While pentagons result in positive curvature, heptagonal defects result in negative curvature.

Chemical vapour deposition is another useful way in which the synthesis of SWNTs and MWNTs can be achieved. Here, an organometallic precursor is mixed with a carbon containing feed gas, it is pyrolyzed in a quartz tube and the nanotubes are collected from the cooler end of the reaction vessel. The feed gas may contain several species and is often mixed with an inert gas. Both, MWNTs and SWNTs are formed with significant quantities of carbonaceous materials. One way of separating the tubes from the carbon mass is to heart-treat the product. Although all the carbon forms react with oxygen, they do so at different rates. All the amorphous carbon materials can be burnt off by heating the soot at 750°C for half an hour. At the end of this process, only less than 1 percent of the original material is left, but the product thus optioned is essentially a mixture of nanotubes. The existence of a large number of defects in amorphous carbon make it react at a higher rate, in comparison to nanotubes. Acid-based cleaning procedures can also be used.

FILLING OF NANOTUBES:



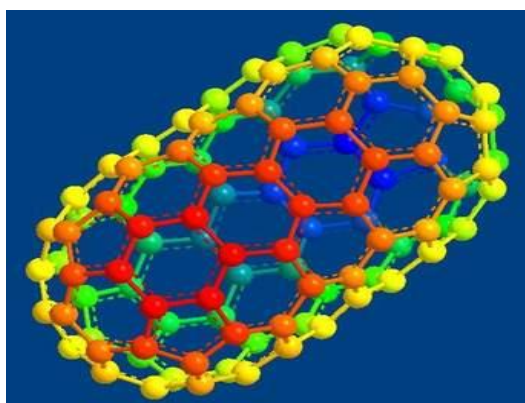
The nanotubes obtained directly from the synthetic processes are closed on both the ends. The

ends can be opened by suitable chemistry. One of the methods used in acid treatment which oxidizes the ends and leaves behind the oxide containing functionalities. The common functional groups are -COOH and -OH. These may be removed by heating the tubes at 600°C in following Ar. Other methods such as treating with liquid bromine followed by heat treatment are also used. There are several ways to fill the open tubes with materials. In one, the nanotubes are soaked in a concentrated solution of the desired metal salt, dried and fired in a reducing atmosphere at high temperature to form metal in the Nano form. This has been done with metals such as Au and Ag. Filling can also be done from the melt of the filling materials, If the surface tension is less than 100-200 nN/m. This leads to long crystals of the filled materials, filling uniformly inside the tube. A number of different materials are found to be stuck into the nanotube cavity. Nanotubes may be used as templates to fill materials. In such strategies, the tubes are fired after filling so as to burn off the carbon and obtain nanorods or tubes of the required materials.

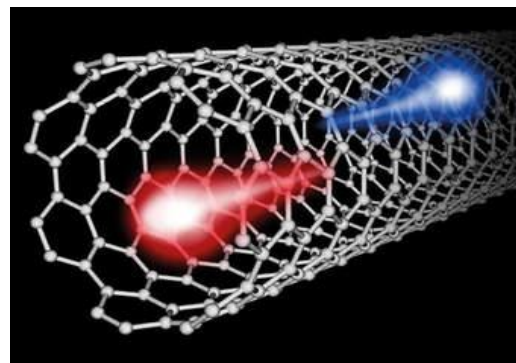
MECHANICS OF GROWTH:

The process of nanotube growth has still not been fully understand. The presence of MWNTs and SWNTs in uncatalyzed and catalysed conditions, respectively, indicate that two different growth mechanisms may be operative. In an open-end mechanism, in which atoms are continuously added to the growing end, the dangling bond energy is stabilized by interaction between the adjacent layers. The bond may be breaking and forming at the periphery of an open-ended tube. In the case of SWNTs, catalysts are important and it appears that catalysts atoms decorate the growing end, which absorb and incorporate the incoming carbon atoms into the nanotube structure. The most recent suggestion pertaining to this mechanism is that carbon fibres grow on nickel nanocrystals through reaction induced reshaping of the particles. The nucleation and growth of the graphene layers occur along with the dynamic formation and restructuring of Nano- atomic step edges at the nickel surface. The surface atoms takes place during the growth of the nanotubes.

ELECTRONIC STRUCTURE:



Nanotubes can have distinctly different electronic properties depending on the chirality. Early calculation predicted that they can be semiconducting or metallic depending on the type of structure. While armchair tubes are always metallic, others can be semi conducting or metallic. The curling of the graphite layers and a decrease in the number of layers cause changes in the electronic structure of the metallic tubes, as compared to these of graphite. The presence of defects on the body of the tube can alter the electronic structure and can make nanoscopic device structure within one tube itself. During one such attempt, a single tube was seen to possess, a Y-junction. Each arm of this tube can have different electrical transport properties, thereby making a transistor possible within one tube. Early theoretical studies predicted drastic change in the properties with change in the tube indices. The electronic density of states of (12,8) and (10,10) tubes are presented. The density of states shows a distinct gap in the (10,0) tube, while no gap exists in the (12,8) tube. Gapless conduction is thus possible in this tube making it metallic. The (10,10) tube is semi-conducting and in general, the band gap varies depending on the tube indices. In a synthesis both metallic and semi-conducting SWNTs are formed simultaneously. It has been shown recently that chemical processes can be used to separate metallic SWNTs from the others.



TRANSPORT PROPERTIES:

Scanning tunnelling spectroscopy has shown that the band gaps of the nanotubes vary from 0.2 to 1.2 eV. The gap varies along the tube body and reaches a minimum value at the tube ends. This is due to the presence of localized defects at the ends due to the extra states. The measurements on SWNTs show the helicity and size-dependent changes in the electronic structure.

The transport properties of MWNTs and NWNTs have been measured. However, the principal problem in these measurements relates to the need for making proper contacts. Due to large contact resistances, it is not possible to obtain meaningful information without four probe measurement. The conductive behaviour of MWNTs was consistent with the weak two-

dimensional localization of the carriers. The inelastic scattering of carrier-phonon scattering. In SWNTs conduction occurs through discrete electronic contacts. This means that nanotubes can be treated as quantum wires, at least at very low temperatures.

MECHANICAL PROPERTIES:

The strength of the carbon-carbon bond is among the highest and as a result, any structure based on aligned carbon-carbon bonds will have the ultimate strength. Nanotubes are therefore the ultimate high strength carbon fibres. The measurement of young's modulus gave a value of $1.8 T_{p_a}$. The theoretical prediction is in the range of 1-5 T_{p_a} , which may be compared to the in-plane graphite value of 1 T_{p_a} . It is difficult to carry out measurements on individual nanotubes. The problem with MWNTs is that the individual SWNTs slip from a bundle, thereby again reducing the experimentally measured young's modulus. Measurements based on vibration spectroscopy, AFM and transmission electron microscopy can be used in determining estimates and all of them come up with nearly the same numbers.

One of the important properties of nanotubes is their ability to withstand extreme strain in tension. The tubes can recover from severe structural distortions. The resilience of a graphite sheet is manifested in the property, which is due to the ability of carbon atoms to rehybridize. Any distraction of a tube will change the bonding of the nearby carbon atoms and in order to come back to the planar structure, the atoms have to reverse to SP^2 hybridization. If the tube is subjected to elastic stretching beyond a limit, some bonds are broken. The defect is then redistributed along the tube surface.

PHYSICAL PROPERTIES:

Nanotubes have a high strength -to- weight ratio. This is indeed useful for lightweight applications. This value is about 100 times that of steel and over twice that of conventional carbon fibres. Nanotubes are highly resistant to chemical attack. It is difficult to oxidize them and the onset of oxidation is higher than that of carbon fibres. As a result, temperature is not a limitation in practical application of nanotubes. The surface area of nanotubes is of the order of 10-20 m^2/g , which is higher than that of graphite but lower than that of mesoporous carbon used as catalytic supports where the value is of the order of 1000 m^2/g .

Nanotubes are expected to have a high thermal conductivity and the value increases with decrease in diameter. The thermal conductivity of single nanotubes were shown to be comparable to diamond and in-plane graphite.

APPLICATIONS:

The use of nanotubes as electrical conductors is an exciting possibility. A nanotube-based single molecule field effect transistor has already been built. The performance of this device is comparable to that of semiconductor-based devices, but the integration of this into circuits will require a lot of effort. One of the problems associated with such devices is the need to make contacts and adopt newer kinds of approaches. It has been seen that it is possible to fabricate nanotube based connectors. Such interconnectors between structures patterned on substrates have also been made.

Nanotubes tips can be used as nanoprobes. The possibility using AFM and STM tips has been demonstrated. The functionalization of tips can be used in chemical force microscopy wherein a chemical functionality interacts with an appropriate one on the substrate. Such studies help one deduce information such as strength of a chemical bond. Being flexible, the probes are not susceptible to frequent crashes, unlike in the case of normal STM tips. The tubes can also penetrate into crevices, which facilitates sub-surface imaging.

Nanotubes based filters have also been demonstrated. Here a liquid containing a mixture of molecules such as petroleum is separated into the components by filtration. Such an approach makes it possible to filter out bacteria, viruses and chemicals from water. The most important aspect in the development of such a filter is the fabrication of a mechanically stable filter with aligned carbon nanotubes.

CONCLUSION:

In principle, any planar structure should be able to curl and make a tubular structure. Certain clays such as chrysolite and imogolite are found in tubular structure characteristics of CNTs such as helicity and rotational disorder, are found in these clays too. The first nanotube structure found with inorganics has been reported with WS_2 and MoS_2 . These structure consists of alternating layers of w/Mo and S . They have an excellent lubricating property and they roll on the substrate. Nanotubes have been made with BN and BCN as well as with $B_xC_yN_z$.

A variety of polyhedral and tubular structures of WS_2 have been obtained by heating a thin tungsten film in H_2S . The tubes observed are hollow and are closed at ends. The curling of a graphite-like sheet of WS_2 leads to the creation of defects. Such defects can be nucleated by high temperature treatment. Structures other than tubes, such as onions, have also been made in this way. These are, in general, called inorganic fullerenes. The properties of inorganic nanotubes have been thoroughly researched. Analogous to carbon nanotubes, several properties of these systems have also been studied.

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