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A Review of Structures and Properties of Carbon Nanotubes

Upendra Sharan Gupta[1], Kantesh Kumar[2]
Kratika Sohale[3] , Mayank Bansal[4]
[1] Reader Dept. of Mech. Engineering, SVITS, Indore, (India)
[2,3,4]UG Scholar Dept. of Mech. Engineering ,SVITS, Indore, (India)

ABSTRACT

Engineered nanomaterials, like carbon nanotubes(CNTs), hold a great promise for a variety of industrial, consumer and biomedical applications, due to their structures and properties. Over the last two decades many different types of CNTs have been produced at the industrial scale. Carbon nanotubes are unique tabular structures of nanometer diameter and large length/diameter ratio. Moreover, CNTs have high physical durability, high electrical and thermal conductivity and are light and flexible. On the basis of such excellent characteristics, CNTs can be used in electron emission sources, optical communication switches, high strength composites and thermal devices. This paper intends to highlight the properties of CNT and describes the strength and the remarkable chemical and physical properties of these structures enable a broad range of promising applications.

Keywords: Carbon Nanotubes, Properties, Nanostructure.

I. INTRODUCTION

The discovery of carbon nanotubes (CNT) in 1991 opened up a new era in materials science. These incredible structures have an array of fascinating electronic, magnetic and mechanical properties. CNT are at least 100 times stronger than steel, but only one-sixth as heavy, so nanotube fibers could strengthen almost any material. Nanotubes can conduct heat and electricity far better than copper. CNT are already being used in polymers to control or enhance conductivity and are added to anti-static packaging. Owing to the material's exceptional strength and stiffness, nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000:1, significantly larger than for any other material. Nanotubes are members of the fullerene structural family. Their name is derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon, called graphene. Carbon nanotubes have many structures, differing in length, thickness, and number of layers. The characteristics of nanotubes can be different depending on how the graphene sheet has rolled up to form the tube causin.

II. APPLICATION OF CARBON NANO TUBES

CNTs has used for applications in energy storage, automotive parts, boat hulls, sporting goods, water filters, thin-film electronics, coatings, actuators and electromagnetic shields.

Recently, several studies have highlighted the prospect of using carbon nanotubes as building blocks to fabricate three-dimensional macroscopic (>1mm in all three dimensions) all-carbon devices. These 3D all-carbon architectures may be used for the fabrication of the next generation of energy storage, supercapacitors, field emission transistors, high-performance catalysis, photovoltaic, and biomedical devices and implants.

Due to low weight % of carbon nanotubes can lead to significant improvements in the mechanical properties of biodegradable polymeric nano-composites for applications in tissue engineering including bone, cartilage, muscle and nerve tissue. Dispersion of low weight % of graphene (~0.02 wt.%) results in significant increases in compressive and flexural mechanical properties of polymeric nanocomposites.

IV. BONDING OF CARBON ATOM

A CNT can be viewed as a hollow cylinder formed by rolling graphite sheets. Bonding in nanotubes is essentially *sp*2. However, the circular curvature will cause quantum confinement and σ-π re-hybridization in which three σ bonds are slightly out of plane; for compensation, the orbital is more delocalized outside the tube.

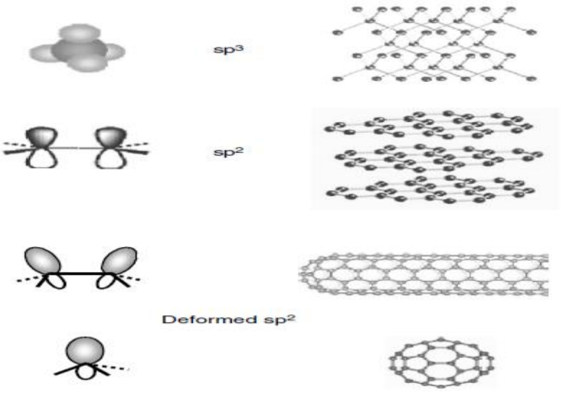

FIGURE 1 *Bonding structures of diamond, graphite, nanotubes, and fullerenes: when a graphite sheet is rolled over to form a nanotube, the sp2 hybrid orbital is deformed for re-hybridization of sp2 toward sp3 orbital or σ-πbond mixing. This re-hybridization structural feature, together with electron confinement, gives nanotubes unique, extraordinary electronic, mechanical, chemical, thermal, magnetic, and optical properties*.

This makes nanotubes mechanically stronger, electrically and thermally more conductive, and chemically and biologically more active than graphite. In addition, they allow topological defects such as pentagons and heptagons to be incorporated into the hexagonal network to form capped, bent, toroidal and helical nanotubes whereas electrons will be localized in pentagons and heptagons because of redistribution of π electrons. For convention, we call a nanotube defect free if it is of only hexagonal network and defective if it also contains topological defects such as pentagon and heptagon or other chemical and structural defects. Fullerenes are made of 20 hexagons and 12 pentagons. The bonding is also *sp*2, although once again mixed with *sp*3 character because of high curvature. The special bonded structures in fullerene molecules have provided several surprises such as metal–insulator transition, unusual magnetic correlations, very rich electronic and optical band structures and properties, chemical functions, and molecular packing. Because of these properties, fullerenes have been widely exploited for electronic, magnetic, optical, chemical, biological, and medical applications.

V. DEFECT-FREE NANOTUBE

There has been a tremendous amount of work studying defect-free nanotubes, including single or Multi-walled nanotubes (SWNTs or MWNTs). A SWNT is a hollow cylinder of a graphite sheet whereas a MWNT is a group of coaxial SWNTs. SWNT was discovered in 1993, 2 years after the discovery of MWNT. They are often seen as straight or elastic bending structures individually or in ropes by transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), and scanning tunneling microscopy (STM). In addition, electron diffraction (EDR), x-ray diffraction (XRD), Raman, and other optical spectroscopy can be also used to study structural features of nanotubes.

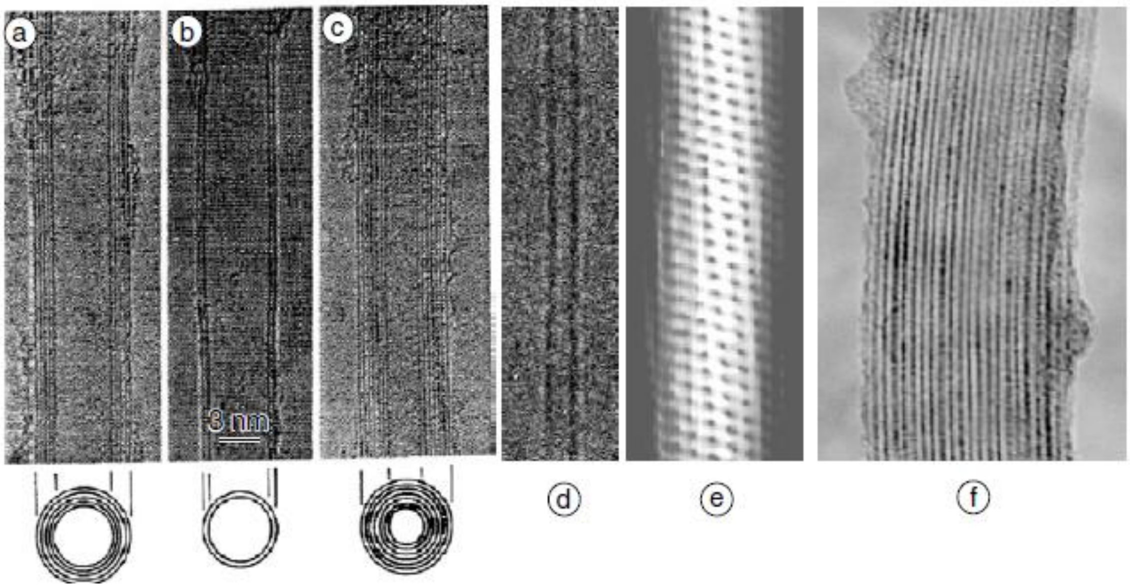

FIGURE 2 Homogeneous nanotubes of hexagonal network: TEM images (a), (b), and (c) for three multi-walled nanotubes (MWNTs)

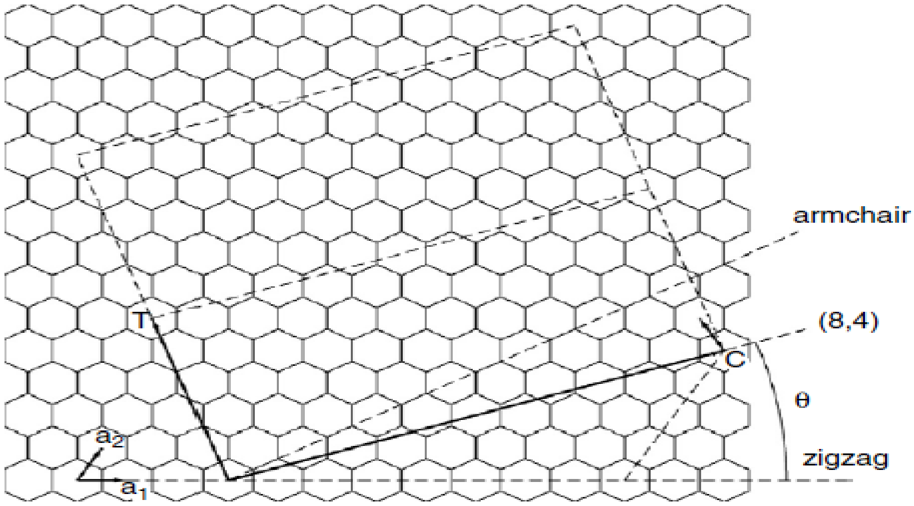

FIGURE 3 An STM image with atomic resolution of a single SWNT from which one can see the hexagonal structural feature and TEM images of a SWNT rope and a few MWNTs

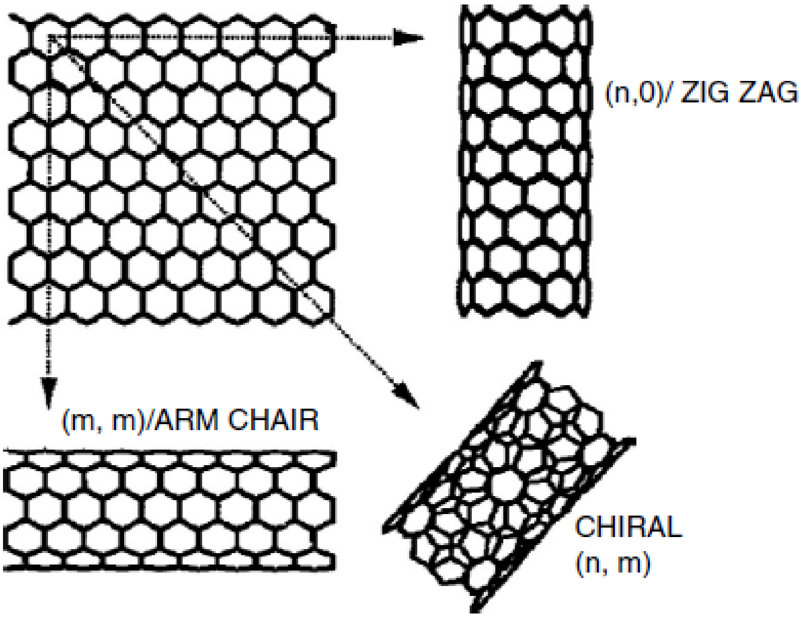

FIGURE 3 By rolling a graphite sheet in different directions, two typical nanotubes can be obtained: zigzag (n, 0), armchair (m, m) and chiral (n, m) where n>m>0

A nanotube (n, m) is formed by rolling a graphite sheet along the chiral vector **C** = n**a**1 + m**a**2 on the graphite where **a**1 and **a**2 are graphite lattice vector. The nanotube can also be characterized by the diameter |**C**| and the chiral angle θ is with respect to the zigzag axis, θ = 0°.

A SWNT can be visualized as a hollow cylinder, formed by rolling over a graphite sheet. It can be uniquely characterized by a vector **C** in terms of a set of two integers (n, m) corresponding to graphite vectors **a**1 and **a**2 (Figure 3)

C = *n***a**1+ *m***a**2 (Figure 1)

Thus, the SWNT is constructed by rolling up the sheet such that the two end-points of the vector **C,** are superimposed. This tube is denoted as (*n*,*m*) tube with diameter given by

$D = |C|/\pi = a\,(n2 + nm + m2)^{1/2}/\pi$

Where,

$\boldsymbol{a}$ = |**a**1| = |**a**2| is lattice constant of graphite. The tubes with *m* = *n* are commonly referred to as armchair tubes and *m* = 0 as zigzag tubes. Others are called chiral tubes in general with the chiral angle, θ defined as that between the vector **C** and the zigzag direction **a1**,

$\theta = \tan{-1}\,[3^{1/2}\, m/(m + 2n)]$ “θ” ranges from 0 for zigzag (*m* = 0) and 30° for armchair (*m* = *n*) tubes.

VI. DEFECTIVE NANOTUBES

In addition to defect-free nanotubes, experimentally observed structures also include the capped and bent, branched (L, Y, and T), and helical MWNTs, and the bent, capped, and Toroidal SWNTs. Figure 1.5 shows TEM images of some of these structures. Most of these structures are believed to have topological defects such as pentagons and heptagons incorporated in the nanotube of hexagonal network. In addition, the reported

MWNTs also include nontubular structures such as multi-walled carbon nano-fibers and bamboo structures, as illustrated in Fig.1.5. A bamboo structure can be viewed as many capped short nanotubes. In general, most SWNTs are defect-free whereas MWNTs are relatively more defective, containing either topological defects (pentagon-heptagon) or structural defects (discontinuous or cone-shaped walls or bamboo structure).

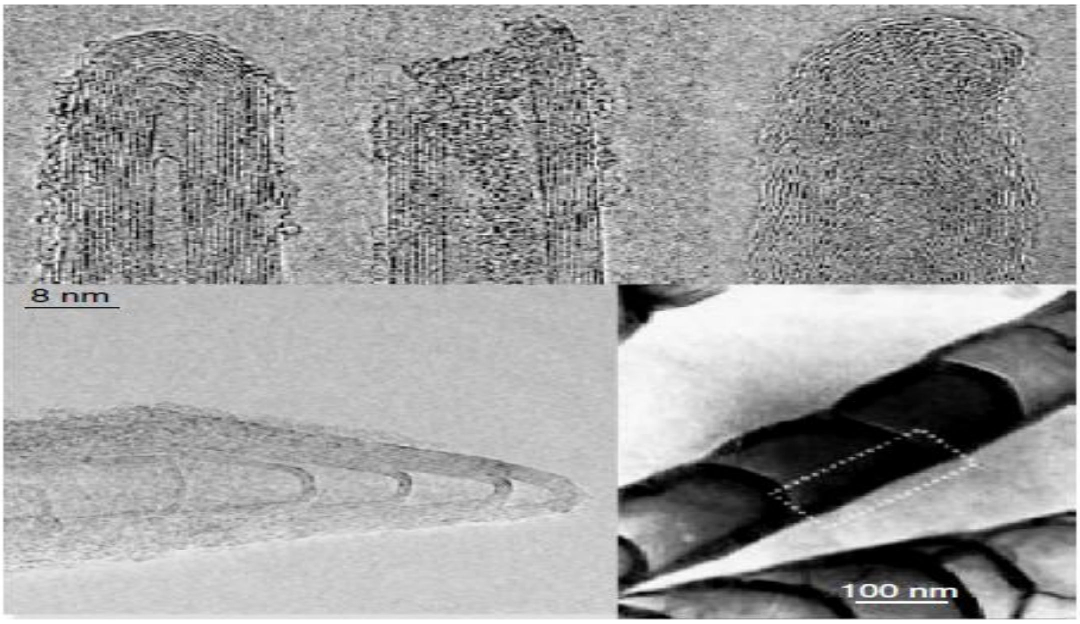

FIGURE 5 Capped MWNTs and MWNT variations including carbon fibers (CNF) and bamboo structures 8 nm.

VII. ELECTRONIC PROPERTIES

Electronic properties of nanotubes have received the greatest attention in nanotube research and applications. Extremely small size and the highly symmetric structure allow for remarkable quantum effects and electronic, magnetic, and lattice properties of the nanotubes.

In the simplest model, the electronic properties of a nanotube derived from the dispersion relation of a graphite sheet with the wave vectors (*kx*, *ky*).

$$E(k_x , k_y) = \pm\gamma\{1 + 4\cos(\sqrt{3}k_x a/2)\cos(k_y a/2) + 4\cos^2(k_y a/2)\}^{1/2}$$

Where, E is the nearest neighbor-hopping parameter and "*a"* is lattice constant.

$\gamma = 2.5 – 3.2$ eV from different sources and $a = 0.246$ nm.

VIII. OPTICAL AND OPTOELECTRONIC PROPERTIES

Defect-free nanotubes, especially SWNTs, offer direct band gap and well-defined band and sub-band structure, which is ideal for optical and optoelectronic applications. Optical spectra have been established for individual SWNTs and ropes using resonant Raman, fluorescence, and ultraviolet to the near infrared (UV-VIS-NIR) spectroscopies. In addition, electrically induced optical emission and photoconductivity have been studied for individual SNWTs. A typical optical spectrum measured for a SWNT rope is shown in Figure 1.10 with that for a graphite sample for comparison. Three peaks for the SWNT ropes cannot be observed for the graphite and attributed to symmetric transitions between the lowest sub-bands in semiconducting (A and B) and metallic (C) tubes. Usually, as-grown nanotube samples are a mixture of semiconducting and metallic tubes, as mentioned before. The measured peak position and intensity are correlated with electronic structures or tube chirality (*n*, *m*) or (*D*, θ).

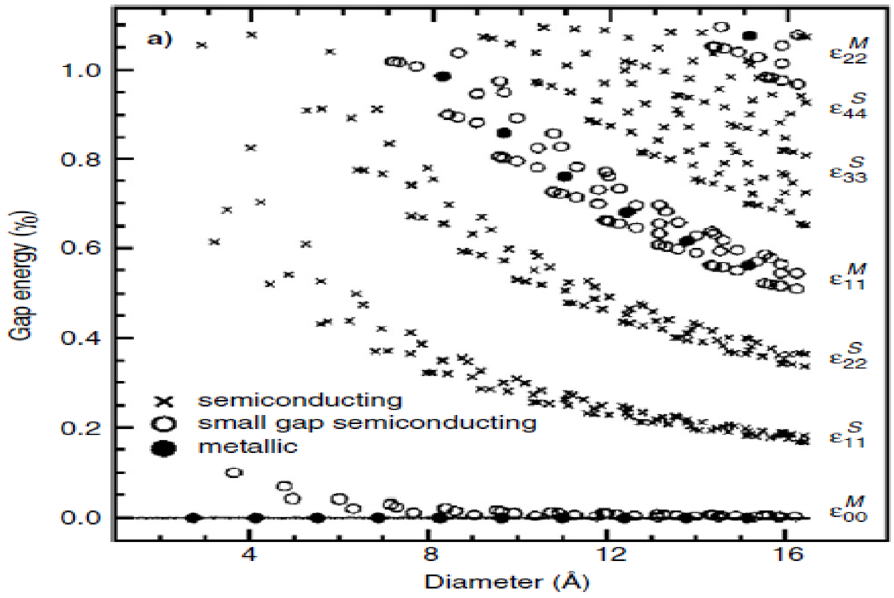

FIGURE 6 Energies for symmetric inter-band transitions in SWNTs as a function of their diameter.

IX. MECHANICAL AND ELECTROMECHANICAL PROPERTIES

σ bonding is the strongest in nature, and thus a nanotube that is structured with all σ bonding is regarded as the ultimate fiber with the strength in its tube axis. Both experimental measurements and theoretical calculations agree that a nanotube is as stiff as or stiffer than diamond with the highest Young's modulus and tensile strength. Most theoretical calculations are carried out for perfect structures and give very consistent results. Table 1 summarizes calculated Young's modulus (tube axis elastic constant) and tensile strength for SWNT and bundle and MWNT with comparison with other materials. In general, various types of defect-free nanotubes are stronger than graphite. This is mainly because the axial component of σ bonding is greatly increased when a graphite sheet is rolled over to form a seamless cylindrical structure or a SWNT. Young's modulus is independent of tube chirality, but dependent on tube diameter. The highest value is from tube diameter between 1 and 2 nm, about 1 TPa. Large tube is approaching graphite and smaller one is less mechanically stable. When different diameters of SWNTs consist in a coaxial MWNT, the Young's modulus will take the highest value of a SWNT plus contributions from coaxial inter-tube coupling or van der Waals force. Thus, the Young's modulus for MWNT is higher than a SWNT, typically 1.1 to 1.3 TPa, as determined both experimentally and theoretically. On the other hand, when many SWNTs are held together in a bundle or a rope, the weak van-der Waal force induces a strong shearing among the packed SWNTs. This does not increase but decreases the

Young's modulus. It is shown experimentally that the Young's modulus decreases from 1 TPa to 100 GPa when the diameter of a SWNT bundle increases from 3 nm (about 7 (10, 10) SWNTs) to 20 nm. The elastic response of a nanotube to deformation is also very remarkable. Most hard materials fail with a strain of 1% or less due to propagation of dislocations and defects. Both theory and experiment show that CNTs can sustain up to 15% tensile strain before fracture. Thus the tensile strength of individual nanotube can be as high as 150 GPa, assuming 1 TPa for Young's modulus. Such a high strain is attributed to an elastic buckling through which high stress is released. Elastic buckling also exists in twisting and bending deformation of nanotubes. All elastic deformation including tensile (stretching and compression), twisting, and bending in a nanotube is nonlinear, featured by elastic buckling up to ~15% or even higher strain. This is another unique property of nanotubes, and such a high elastic strain for several deformation modes is originated from *sp*2 re-hybridization in nanotubes through which the high strain gets released.

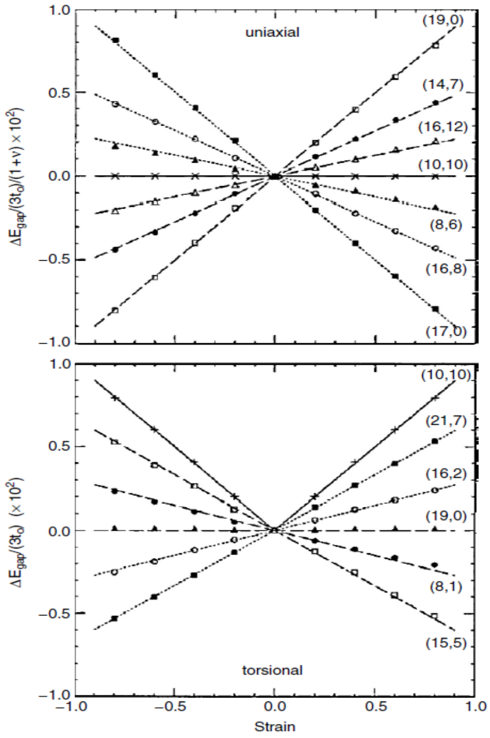

FIGURE 7 Band gap change of SWNTs under uniaxial strain (>0 for tension and <0 for compression) and torsional strain (>0) for net bond stretching and <0 for net bond compression),

	Young's Modulus (GPa)	**Tensile Strength (GPa)**	**Density (g/cm^3)**
MWNT	1200	≈150	2.6
SWNT	1054	75	1.3
SWNT Bundle	563	≈150	1.3
Graphite (in-plane)	350	2.5	2.6
Steel	208	0.4	7.8

Mechanical properties of Carbon Nanotubes

Magnetic and Electromagnetic Properties

Magnetic properties such as anisotropic g-factor and susceptibility of nanotubes are expected to be similar to those for graphite while some unusual properties may exist for nanotubes. Indeed, it is found from ESR that the average observed g-value of 2.012 and spin susceptibility of

$7\text{-}10^{-9}$ emu/g in MWNTs are only slightly lower than 2.018 and $2\text{-}10^{-8}$ emu/g in graphite. Some interesting properties are also found from ESR studies of Pauli behavior. For example, aligned MWNTs are metallic or semi-metallic. The measured susceptibility gives the density of state at the Fermi level of $1.5\text{-}10^{-3}$ states/eV/atom, also comparable with that for in-plane graphite. The carrier concentration is about 1019cm–3, as compared with an upper limit of 1019 cm–3 from Hall measurement.

Chemical and Electrochemical Properties

Small radius, large specific surfaces and σ-π re-hybridization make CNTs very attractive in chemical and biological applications because of their strong sensitivity to chemical or environmental interactions. These, however, also present challenges in characterization and understanding of other properties. The chemical properties of interest include opening, wetting, filling, adsorption, charge transfer, doping, intercalation, etc. Applications include chemical and biological separation, purification, sensing and detection, energy storage, and electronics.

Opening

The nanotube end is more reactive than the sidewall because of the presence of pentagons or metallic catalysts sitting on the opened ends and greater curvature. Many approaches have been used to open nanotube ends, including, for example, vapor phase oxidation, plasma etching, and chemical reaction using acids such as HNO3. The opened end is terminated with different functional groups such as carboxyl etc. The opening is required for many applications as described below.

Wetting and Filling

Nanotubes are hydrophobic and do not show wetting behavior for most aqueous solvents. It is reported that various organic solvents, HNO3, S, Cs, Rb, Se, and various oxides such as Pb and Bi_2O_2 can wet nanotubes. A nanotube provides a capillary pressure proportional to $(1/D)$. Therefore, these wetting agents can be driven to fill inside the nanotube by the capillary pressure. It is also likely to fill non-wetting agents inside a nanotube by applying a pressure that is higher than the capillary pressure. An effective alternative is to use wetting agents such as HNO3 to assist filling of non-wetting agents inside the nanotube.

Adsorption and Charge Transfer

Enhanced molecular adsorption and charge transfer can be expected for nanotubes. Strong adsorption and charge transfer of oxygen to CNTs have been experimentally observed at room temperature. Extensive calculations have been carried out for various gas molecules using first principles approaches. The gas adsorption and charge transfer capability are functions of sites and gas molecules. The site on which a gas molecule can adsorb includes interstitial in tube bundles, groove above the gap between two neighboring tubes, nanopore inside a tube, and surface of a single tube. The adsorption and charge transfer capability is found to follow a decreasing order.

Chemical Doping, Intercalation, and Modification

The substitutional doping with B and N dopants was pursued to make nanotubes p- and n-types.

However, molecular adsorption as discussed above provides a simple, non-covalent doping approach to turn nanotubes into p-type with oxygen or water adsorption or n-type with, for example, C_6H_{12}. On the other hand, intercalation of the alkali metals with nanotubes is used for enhanced metallic conductivity or halogens with nanotubes for charge- or energy-storage applications. Experimental observation and theoretical calculations show that these intercalating agents mainly enter intertube spaces or defects on nanotubes for enhanced electrochemical capability for charge transfer and storage.

Indeed, nanotubes as electrode materials show enhanced electrochemical capability. The reduction and oxidation reactions that occur at the electrodes produce a flow of electrons that generate and store energy. In battery applications, conventional graphite, or other electrodes can reversibly store one lithium ion for every six carbon atoms. Experiments reveal an electrical storage capacity approximately double that of graphite. Theoretical studies show that the tubes' open ends facilitate the diffusion of lithium atoms into interstitial sites.

Thermal and Thermoelectric Properties

Graphite and diamond show extraordinary heat capacity and thermal conductivity. It can be expected that nanotubes have similar thermal properties at room and elevated temperatures but unusual behavior at low temperatures because of the effects of phonon quantization. Both theory and experiment show that intertube coupling in SWNT bundles and MWNTs is weak in temperature region of >100 K. The specific heat of MWNTs has not been examined theoretically in detail. Experimental results on MWNTs show a temperature-dependent specific heat, which is consistent with weak interlayer coupling, although different measurements show slightly different temperature dependencies.

Summary

Both theory and experiment show extraordinary structures and properties of carbon nanotubes. Thesmall dimensions, strength and the remarkable chemical and physical properties of these structures enablea broad range of promising applications. A SWNT can be metallic and semiconducting, dependent on its chirality. Semiconducting SWNTs have been used to fabricate transistors, memory and logic devices, and optoelectronic devices. SWNT nanoelectronics can be further used for chemical and biological sensors, optical and optoelectronic devices, energy storage, and filed emissions. However, it is currently not possible to selectively control the tube chirality or obtain either metallic or semiconducting SNWTs. These constraints in addition to problems of nanoscale contacts and interconnects stand in the way of large-scale fabrications and integration and applications of CNT electronics. A MWNT basically behaves like a metal or semimetal because of the dominating larger outermost tube. Therefore, MWNTs are suitable for nanoelectrodes, field emission, and energy storage applications. In these applications, the tube chirality control is not critical. But MWNTs allow incorporation of diverse defects, which significantly affect electrical and mechanic properties.

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