Lecture 7. Structure of CNTs and Fullerenes. Synthesis of CNTs and Fullerenes.

The purpose of the lecture: to familiarize students with structure and synthesis of CNTs and fullerenes.

Expected results: students getting information about structure and synthesis of CNTs and fullerenes.

CNTs and fullerenes are allotropes of carbon. Fullerenes are closed-caged structures consisting of hexagonal and pentagonal rings. In C60 fullerene, each carbon is connected to three other carbon atoms by one double bond and two single bonds. Electronically, this arrangement is referred to as sp2-carbons because the three adjacent carbons are hybrids of the 2s orbital and the two 2p orbitals (2px and 2py). The remaining 2p orbital (2pz) is responsible for the p-bond. CNTs have diameters ranging from <1 to 4 nm and length-to-diameter aspect ratios up to 132,000,000:1. CNTs are one of the most massively manufactured nanoparticles (approximately 270 tons/year) worldwide. CNTs exhibit chemical and physical properties not found in the bulk allotropes of carbon: diamond, graphite, or amorphous carbon. CNTs have 100 times the tensile strength of steel, thermal conductivity comparable to diamond, and electrical conductivity greater than copper.

These unique characteristics make CNTs a promising candidate for applications in microelectronics, medicine, hydrogen fuel cell technology, etc. However, consistent with earlier incidences of industrial pollutants including, but not limited to, freon, methyl-t-butyl ether flame retardants, and surfactants, there is high probability that unregulated production of nanoparticles, including CNTs, may lead to serious environmental problem and ensuing health issues.

There are three basic types of CNTs currently being produced: single-walled carbon nanotubes (SWCNTs), multiwalled carbon nanotubes (MWCNTs), and carbon nanowires. SWCNTs are rolled-up graphene sheets having an electronic makeup closely related to graphite (three-coordinated carbons in which three electrons are in sp2 hybridization and one is delocalized) than to diamond (four-coordinated carbons with sp3 hybridization). The intrinsic strength of the sp2 carbone carbon bonds may result in high mechanical strength and a very large Young's modulus, 50 times higher than that of steel.

The properties of SWCNTs are determined by the graphene sheet's folding patterns. The graphene sheet folding is represented by a pair of indices (n, m) that denote the number of unit vectors along the two directions in the honeycomb lattice of graphene. If m j 0 (11, 0), the nanotubes are called zigzag nanotubes. If n j m, the nanotubes are called armchair nanotubes. The rest are called chiral nanotubes. The zigzag and armchair CNTs have q values of 0_ and 30_, respectively. The chiral CNTs have q values greater than 0_ but less than 30_. The CNT properties are determined by the chiral vector (Ch), charily angle (q), structural defects, topology, diameter, surface area, and length. The armchair SWCNTs are always metallic. The zigzag and chiral CNTs, depending on whether or not they satisfy n e m j 3I (where I is an integer), are metallic or semimetallic.

The MWNTs are a group of concentric SWNTs separated by 0.35e0.40 nm and held together by VDW forces. The outer diameter of MWCNTs may range from several nanometers up to 100 nm. Unlike SWCNTs, MWCNTs may be metallice metallic (inner-outer), metallic-semiconducting, semiconducting-metallic, or semiconducting-semiconducting.

Carbon nanowires consist of stacked cones defined by a finite cone angle. CNTs exhibit significantly higher surface-to-volume ratio (SA/V) that increases exponentially as particles get smaller without changing their shape. Since more surface area provides more reaction sites for the same volume, nanoparticles less than 100 nm react much faster than bulk particles.

This suggests that chemical reactivity of structurally identical CNTs may depend on their diameter; a decrease in diameter increases their reactivity exponentially.

CNT Synthesis

ARC-DISCHARGE METHOD

In an arc-discharge method, the graphite anode and cathode terminals are placed in an inert environment (He or Ar at 500 Torr) and a current of 100 A is delivered. Generation of arc-induced plasma evaporates the carbon atoms in the graphite. The nanotubes grow from the surface of these terminals.

SWNTs are formed with the use of a metal catalyst such as iron or cobalt, while MWNTs can be formed without a catalyst.

LASER ABLATION METHOD

In this method, a laser beam evaporates carbon from graphite at high temperatures (approximately 1200 _C) under pure argon at 500 Torr. The nanotubes, mixed with undesired amorphous carbon, are collected on a cooled substrate at the end of the chamber. Arc-discharge and laser ablation methods have limited potential for scale-up. The nanotubes produced are in an entangled form, and extensive purification is required to remove the amorphous carbon and fullerenes that are naturally produced in the process.

CHEMICAL VAPOR DEPOSITION

Chemical vapor deposition (CVD) is capable of mass producing defect-free CNTs at relatively low temperatures. A porous substrate, such as alumina or quartz, is subjected to electrochemical etching in hydrofluoric acid/methanol mixture. Nanotubes grow at a higher rate on a porous substrate. A catalyst (e.g., iron, nickel) is deposited onto the substrate by thermal evaporation. An acid treatment followed by sonification removes the impurities. Catalyst (iron nanoparticles)-supported formation of CNTs occurs either by extrusion, in which CNTs grow upward from the nanoparticles that remain attached to the substrate, or by lifting of the catalyst nanoparticles by growing CNT. The catalyst particle diameter plays an important role in defining the synthesized carbon nanostructure.

Catalyst particles of the order of 1e15 nm diameter predominantly form SWCNTs, while particles with 20e50 nm diameter form MWCNTs; particles greater than 50 nm form a complex onion-like structure.

HYDROCARBON FLAMES

Hydrocarbon flames provide a unique combination of the chemical and catalytic factors that are conducive to initiation and growth of CNTs. Growth mechanisms similar to those observed in the CVD process govern the growth of nanotubes in flames. The choice of catalysts determines the structural properties of the carbon nanotubes.

CNT SYNTHESIS USING TWISTED GRAPHENE RIBBONS (NANO-TEST TUBE CHEMISTRY)

Although the seed-mediated synthesis of CNTs is commonly used in commercial applications, these methods result in considerable impurities and are not suitable for selective CNT synthesis, such as 5.0, 5.5, 11.5 (and so on) CNTs. To address the deficiencies, a nano-test tube chemistry method has been proposed in which molecules and atoms confined inside CNTs are used to synthesize selective CNTs via synthesis of nanoribbons. Jiang et al. (2011) showed that the graphene nanoribbons residing inside a CNT would impose geometric constraints, resulting in transformation of the nanoribbons into helical conformations with restricted chirality of the newly synthesized CNTs. Lim et al. (2013) showed that the chirality of CNTs can be controlled by carefully choosing the polycyclic aromatic hydrocarbon precursors. Miyata et al. (2010) developed the inner-shell extraction technique for extraction of inner CNTs from double walled CNTs.

Synthesis of Fullerenes

In 1985, Kroto, Smalley, and Curl discovered fullerenes in carbon vapor from the laser ablation of graphite, although the method resulted in microscopic quantities of fullerenes. Large

quantities of fullerenes were produced by striking an electric arc between two graphite electrodes and then evaporating the graphite in low pressure (<100 Torr) under helium.

However, the method also generated carbonaceous soot impurities. A graphite arc vaporization method is suitable for commercial formation of fullerenes.

Other methods of fullerene synthesis include ion sputtering and electron beam evaporation of graphite, vaporization of graphite using highly concentrated solar heating, resistive heating of graphite, laser ablation of graphite, inductive heating of graphite, and carbon particle evaporation in a hybrid thermal plasma. A pyrolysis method uses naphthalene, a nongraphitic raw material, in an argon atmosphere at approximately 1000 _C to make fullerene.