Lecture 8. Carbon Nanotube Purification. CNT Functionalization

The purpose of the lecture: to familiarize students carbon nanotube purification and functionalization.

Expected results: students getting information about carbon nanotube purification and functionalization.

As synthetized, CNTs contain substantial impurities that can change their electronic and chemical properties. Crude nanotubes are not suitable for biomedical applications. Therefore, the newly synthetized CNTs must be purified for further applications.

Use of strong acid and hydrogen peroxide is a problem in the purification of CNTs because the reagents may damage the structural integrity of the tubes. However, acid induced defects in the nanotubes are often utilized in their functionalization.

Structural Defects and Reactivity

Pristine CNTs are homogenous hexagonal honeycomb structures that are chemically inert. However, when a graphene sheet is folded into CNTs, the curvature induces a band gap that confers CNTs either metallic or semiconductor properties. CNTs also have inherent structural defects that (1) modulate their mechanical, topological, and electronic properties and (2) have significant beneficial and/or toxicological consequences. In general, there are four types of defects reported in CNTs:

• Vacancy or point defects: Vacancy involves a missing or extra atom, resulting in dangling bonds capable of rehybridizing with another atom within the CNT or with an atom outside in the environment. Although vacancies occur in both graphene and CNTs, the defects are more complicated in CNTs because of circumferential and/or curvature-induced strain. The defect stabilities depend on their position within the CNT's lattice, diameter, and helicity.

• Interstitials: This defect is usually transient and occurs when a carbon atom is rendered free due to knockout damage. The reactive group may form a bond with other carbon atoms or environmental chemicals.

• Bond rotation: This defect may cause topological changes by replacing two hexagons with other forms, such as a pentagon and a heptagon. Because the bond angle strain in a pentagon is greater than that in a hexagon, replacement of two hexagons with a pentagon and a heptagon may increase overall molecular strain and ensuing changes in electronic properties and chemical reactivity. The electronic perturbations occurring due to a defect are not local but are spatially localized.

• Stone-Wales defects (SWDs): This defect represents rotation of a C-C bond in hexagonal CNTs. SWDs can adsorb hydrogen and other foreign atoms; hence, CNTs containing this defect have a potential usage for energy storage.

Taken together, these observations suggest that the structural defects increase chemical reactivity and ensuing biological activity/toxicity of CNTs. Structurally defective CNTs can be used for (1) hydrogen storage, (2) miniature electron sources for e-beam and X-ray instruments and display applications, (3) detection of intracellular pH, and (4) screening of NO2, NH3, and CO.

Since pristine SWCNTa are chemically inert, addition-based covalent binding of functional groups to nanotubes' surface is difficult. SWCNTs have three main sources of reactivity: (1) the curvature-induced strain arising from sp2 carbons, (2) the misalignment of the p orbitals, and (3) structural defects. The most reactive place in any CNT is in the cap of the thinnest tube. Derivatization of the side wall required direct attachment of functional groups using either 1,3-dipolar cycloaddition or reactions with nitrenes, radicals, and carbenes.

CNT Functionalization

The medicinal application of CNTs has been severely limited due to their poor interfacial reactivity and aggregation due to VDW interactions. The commercial CNTs are heavily entangled and poorly dispersed bundles. Reactivity of fullerene molecules is strongly dependent on the curvature of the carbon framework. Their outer surface reactivity increases with an increase in curvature. The moderately curved CNTs are relatively less reactive than fullerene molecules. Structural defects increase their reactivity to organic molecules. Therefore, selective structural defects may be generated for further functionalization. In general, two basic approaches are commonly used to functionalize CNTs or fullerenes: covalent (chemical) and noncovalent (physical) functionalization.

COVALENT FUNCTIONALIZATION

Two important addition reactions of the CNT sidewall are fluoridation and aryl diazonium addition. Fluoridation improves solubility and further functionalization. Diazonium reacts only with metallic CNTs; thus, this reaction can be used to separate metallic and semiconductor CNTs. In addition to fluoridation or diazonium addition, CNTs can also be functionalized using cycloaddition such as Dielse Alder reaction, carbene and nitrene addition, chlorination, bromination, hydrogenation, and azomethineylidation. Many of these reactions require induction of defects in CNTs to generate free reactive functional groups such as carboxylic acid, ketone, alcohol, and ester groups that can be further functionalized via silanation, polymer grafting, esterification, thiolation, and biomolecule-addition.

A significant disadvantage of covalent functionalization is that it leads to drastic changes in the CNT's electronic states that may extend beyond the vicinity of the addendum site. Monofunctionalization (eF, eNH2, eCOOH, etc.) distorts the Fermi level electronic state, while bi-functionalization (]NH,]O,]CCl2, etc.) moves the distortion away from the Fermi level. Thus, mono-functionalization is more potent than bi-functionalization in distorting the metallic properties of the CNTs. Unlike covalent functionalization, noncovalent functionalization does not alter the electronic state of CNTs.

NONCOVALENT FUNCTIONALIZATION

The procedures for noncovalent functionalization of CNTs have been described earlier in the metal nanoparticle section. However, some of the procedures unique for noncovalent functionalization of CNTs are listed here.

SURFACE STABILIZATION

As described above, commercial CNTs exist in a highly aggregated form that cannot be integrated in biological and medicinal applications. Therefore, it is essential to disaggregate and disperse CNTs uniformly in appropriate media. One of the key approaches commonly used to decrease the nanotube agglomeration is ultrasonication of surfactant-stabilized CNT. Ultrasonication provides high shear that separates the CNT monomers that are stabilized by the surfactants. However, excessive sonication may fragment the CNT into smaller particles.

NANOPARTICLE SOLUBILIZATION

Qin et al. (2004) have described a twostep procedure using grafted poly(sodium 4-styrenesulfonate) that allows soft dissociation of aggregated CNTs. Islam et al. (2003) compared several different forms of surfactants and found that those containing a benzene ring are better dispersants than those lacking it.

ENDOHEDRAL FUNCTIONALIZATION

One of the unique aspects of CNT's noncovalent functionalization is endohedral (inner side of the tube) functionalization or filling in which particles are enclosed inside the CNTs for biomedical use. Unlike the graphite surfaces that have comparable reactivity, the external surface of CNTs is more reactive than the internal surface. This may be because the exterior CeC p-electrons may be more distorted than the interior surface; however, an increase in nanotube diameter reduces the distortion. This relatively inert interior allows CNTs to store large quantities of particles without much CNT-particle interaction. CNTs could be filled with particles suspended in either gas or liquid (organic or aqueous). Gases, in a pressure and temperature-dependent

manner, preferred endohedral filling as opposed to surface binding. Aqueous and polar-organic liquids (such as methanol) entered CNTs more effectively than nonpolar organic liquids. Joseph and Aluru (2008) and Mattia and Gogotsi (2008) have shown that despite the hydrophobic nature of nonfunctionalized CNTs, water can enter the nanotube at a very high rate that is optimal at 10 nm diameter, but decreased as (1) the nanotube diameter increased and (2) the meniscus angle decreased.