Quantum Chemistry Investigation of Carbon Nanotube Sidewall Defects

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It is well known that sonication of nanotubes in strong acid solutions results in their being cut into shorter lengths and their capped ends being opened. Under these conditions, carbon atoms with exposed dangling bonds are subject to oxidation by the acid solution or air, resulting in the formation of attached hydroxyl, carbonyl and carboxyl groups at the nanotube ends. The reactivity of the carboxyl groups has been exploited in the functionalization of carbon nanotube probes. It is presumed that similar chemistry occurs around holes in nanotube sidewalls that result from missing carbon atoms. Some nanotubes, such as the hydrothermal multiwall nanotubes produced by Gogotsi and coworkers[1], exhibit large numbers of internal and external defect sites that cause their surfaces to display hydrophilic interactions with encapsulated water.

Not much is known about the structure and chemistry of the sidewall defect sites that result from the removal of individual carbon atoms. In this presentation, the results of quantum chemistry calculations are used to characterize possible defects in the sidewalls of single-walled nanotubes and to model the ensuing oxidation that occurs.

Several different defects are generated by removing one or two carbon atoms from the sidewall of a pristine zigzag nanotube. The nanotube is modeled by a representative polycyclic aromatic hydrocarbon (PAH) molecule with its edge atoms constrained to maintain the curvature found in a (16,0) nanotube. This procedure has been used in previous studies of nanotube sidewall functionalization [2]. When one carbon atom is removed from the nanotube sidewall, three carbons with dangling bonds are formed. A new C-C bond can form between two of these, generating a pentagon. The remaining carbon has two unsatisfied valences, making it a carbene intermediate that is likely to scavenge a hydrogen atom or hydroxyl group from the solution. The figures show two possible intermediates that can form after the loss of one carbon atom. If two adjacent carbon atoms are removed, the result can be formation of two pentagons and an octagon with no dangling bonds.

In this presentation, the structures and energetics of several possible defect models will be studied with the goal of identifying the ones most likely to form during the growth and processing of carbon nanotubes.

References
[1] Y. Gogotsi, J. A. Libera, A. Guvenc-Yazicioglu and C. M. Megaridis, Appl. Phys. Lett. 2001, **79**, 1021.
[2] R. L. Jaffe, "Quantum chemistry studies of chemical functionalization reactions of fullerenes and carbon nanotubes", in "Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials", P. V. Kamat, D. M. Guldi and K. M. Kadish, eds, Electrochemical Society, Pennington, NJ, 1999, 153.

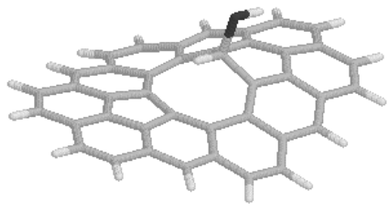

Figure 1: Model for a carbon nanotube defect formed by removal of one carbon atom. Unsatisfied valences are eliminated by formation of a pentagon and bonding of -H and –OH (dark atom is oxygen) to the carbene site.

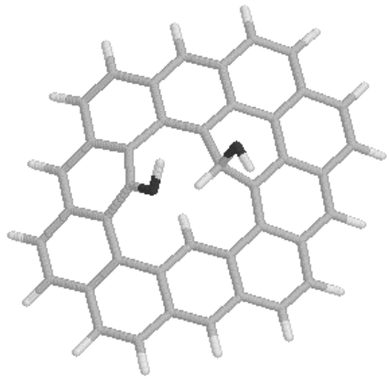

Figure 2: Two views of a model for a carbon nanotube defect formed by removal of one carbon atom. Unsatisfied valences are eliminated by bonding of -H and –OH (dark atom is oxygen) moieties to the carbon atoms with dangling bonds.