Carbon Nanotubes: Synthesis to Functionalization

Kathryn Guy Literature Seminar October 17, 2002

In 1990, Krätschmer, Lamb, Fostiropoulos, and Huffman disclosed the carbon arc method for preparing bulk amounts of the molecular carbon allotropes named fullerenes, which had been reported by Curl, Kroto, and Smalley in 1985.[1,2] Shortly thereafter in 1991, Iijima modified the technique to produce carbon nanotubes.[3]

Carbon nanotubes are described as sheets of graphite that have been rolled into a cylindrical shape,[3] and single-walled carbon nanotubes (SWNTs) are nanotubes that have only a single sheet. SWNTs have been observed as having armchair, chiral, or zigzag conformations depending upon the orientation of the hexagons around the circumference of the tube (fig. 1).[4] How to generate SWNTs in high yield and with control of their helicity is a question under active study.

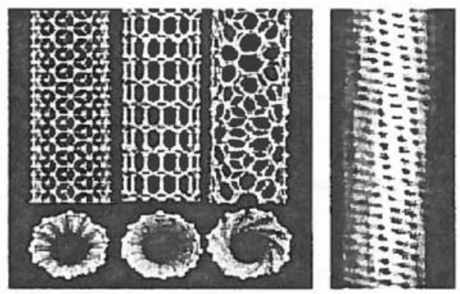

Figure 1. (left to right) Schematic illustrations of armchair, zigzag, and chiral SWNT. The image of the far right is a TEM image of a chiral single wall nanotube.[4]

The properties of single-walled carbon nanotubes are dependent on their helicity, diameter, and bundling. Mechanically, carbon nanotubes are some of the strongest fibers known.[5] They are reported as having a Young's modulus of up to 1.4TPa and a tensile strength of greater than 100 GPa. For comparison, high strength steel only has a modulus of 200 GPa and a tensile strength of 1-2GPa. Electrically, SWNT can be either metallic (armchair) or semi-conducting (chiral or zigzag). The band gap in the semi-conducting nanotubes is a function of their diameter.[4] Bundles of SWNTs held together by van der Waal interactions have been shown to exhibit characteristics different than the individual tubes themselves. For example, armchair nanotubes appear to be truly metallic only when isolated from other tubes due to pseudo energy gaps that are formed between nanotubes in bundles.[6]

With their high strength and metallic nature, there are many potential applications of nanotubes. However, practical implementation of these ideas has been hampered by low yields and impurities. Current methods of producing carbon nanotubes are laser ablation, electric arc, chemical vapor deposition, and the HiPco process.[4] These methods have common components, they all need a source of carbon (graphite, CH_4, CO, etc.) and they utilize a transition metal catalyst to promote growth. Major impurities of nanotube synthesis are carbon forms other than SWNTs and carbon coated metal catalyst. These impurities can be removed by acid treatment at the risk of adding defects to the tubes. Purification also adds considerably to the already costly nanotube price.[5]

Recent efforts have also been made to chemically modify SWNTs. For carbon nanotubes with open ends, acid treatments (such as those used for purification) often result in carboxylic acid groups lining the edges.[7] A bridging molecule can react with these acid groups to link two nanotubes or to attach a nanotube to another substrate. In 2001, Mashahito and co-workers formed ring and star structures following the functionalization of nanotube ends.[8]

The sidewalls of the carbon nanotubes have also been functionalized. Functional groups covalently bonded to the side of the tubes increase nanotube solubility, allow structural modifications, and are useful catalysts.[9,10] An early sidewall functionalization technique was the addition of elemental fluorine to nanotube sidewalls. Fluorine addition was known to occur with graphite, and offered promise for the similar aromatic structure of the nanotube walls.[10,11] STM images of fluorinated SWNTs show that the fluorine attaches in bands along the length of the nanotube (fig.2).[12] These bands may explain why pyrolysis of fluorinated nanotubes cut the nanotubes into small tubes less than 50 nm on average.[13]

Figure 2: Bands of fluorine added to the sidewalls of a SWNT.[12]

Alkylation has been suggested as a route to increasing nanotube solubility. Fluorinated nanotubes can undergo reaction with alkyl lithium and Grignard reagents to add alkyl groups to the nanotube sides.[10] In 2001, direct alkylation using nitrenes, carbenes, and radicals was reported.[14]

Over the past two years, some research groups have also examined the possibility of adding transition metals or metal complexes to nanotube surfaces.[9,15,16] Nanotubes with metal catalysts are soluble, yet can be precipitated by the addition of sodium chloride.[16] Thus, nanotube supported catalysts can be recovered easily from homogeneous solutions.

Single-walled nanotubes possess many interesting physical, chemical, and electrical properties. Over the past nine years since they were first characterized, there has been a great amount of effort dedicated to better understanding these carbon structures. As more is learned in the laboratory setting, more practical applications are likely to develop.

References:

1. Krätschmer, W.; Lamb, L.D.; Fostiropoulos, K.; Huffman, D.R. "Solid C-60 – A New Form of Carbon," Nature 1990, 347, 354-358.

2. The Royal Swedish Academy of Sciences, Press Release: 1996 Nobel Prize in Chemistry. http://www.nobel.se/chemistry/laureates/1996/press.html (accessed Oct 2002).

3. Iijima, S. "Helical Microtubules of Graphitic Carbon," *Nature* **1991**, *354*, 56-58.

4. Baughman, R.H.; Zakhidov, A.A.; de Heer, W.A. "Carbon Nanotubes- the Route Toward Applications," *Science* **2002**, *297*, 787-792.

5. Carbon Nanotechnologies Incorporated, Buckytube Properties and Uses. http://www.cnanotech.com/5-0_buckytube_properties_uses.cfm (accessed Sept. 2002).

6. Ouyang, M.; Huang, J.; Cheung, C.L.; Lieber, C.M. "Energy Gaps in 'Metallic' Single-Walled Carbon Nanotubes," *Science* **2001**, *292*, 702-705.

7. Chiu, P.W.; Duesberg, G.S.; Roth, S. "Interconnection of Carbon Nanotubes by Chemical Functionalization,"

8. Sano, M.; Kamino, A.; Okamura, J.; Shinkai, S. "Shaping Carbon Nanotubes with Chemistry," *J. Inclusion Phenom.* **2001**, *41*, 49-52.

9. Banerjee, S.; Wong, S.S. "Functionalization of Carbon Nanotubes with a Metal-Containing Molecular Complex," *Nano Lett.* **2002**, *2*, 49-53.

10. Hirsch, A. "Functionalization of Single-Walled Carbon Nanotubes," *Angew. Chem. Int. Ed.* **2002**, *41*, 1853-1859.

11. Seifert, G.; Kohler, T.; Frauenheim, T. "Molecular Wires, Solenoids, and Capacitors by Sidewall Functionalization of Carbon Nanotubes," Appl. *Phys. Lett.* **2000**, *77*, 1313-1315.

12. Kelly, K.F.; Chiang, I.W.; Mickelson, E.T.; Hauge, R.H.; Margrave, J.L.; Wang, X.; Scuseria, G.E.; Radloff, C.; Halas, N.J. "Insight into the Sidewall Functionalization of Single-walled Nanotubes: and STM Study," *Chem. Phys. Lett.* **1999**, *313*, 445-450. 14.

13. Gu, Z.; Peng, H.; Hauge, R.H.; Smalley, R.E.; Margrave, J.L. "Cutting Single-Wall Carbon Nanotubes through Fluorination," *Nano Lett.* **2002**, *2*, 1009-1013.

14. Holzinger, M.; Vostrowsky, O.; Hirsh, A.; Hennrich, F.; Kappes, M.; Weiss, R.; Jellen, F. "Sidewall Functionalization of Carbon Nanotubes," *Angrew. Int. Ed.* **2001**, *40*, 4002-4005.

15. Azamian, B.R.; Coleman, K.S.; Davis, J.J.; Hanson, N.; Green, M.L.H. "Directly Observed Covalent Coupling of Quantum Dots to Single-wall Carbon Nanotubes," *Chem. Commun.* **2002**, *4*, 366-367.

16. Banerjee, S.; Wong, S.S. "Structural Characterization, Optical Properties, and Improved Solubility of Carbon Nanotubes Functionalized with Wilkinson's Catalyst," *J. Am. Chem. Soc.* **2002**, *124*, 8940-8948.