Nanotubes: Stiff, Elastic, and Electronically Diverse

| Robert Ellenwood | Literature Seminar | November 2, 2000 |
|------------------|--------------------|------------------|
| | | |

A nanotube is an arrangement of atoms in a single tube or set of concentric tubes enclosed upon each other. These tubes typically have a radial diameter of nanometers and lengths ranging from nanometers to greater than micrometers. One of the first reports of C nanotubes was published in 1991 by Iijima,¹ and in 1992 Tenne described the discovery of WS₂ nanotubes.² Since then, the synthesis and properties of these materials have been extensively studied.

The main advances in the synthesis of C nanotubes have centered on the development of methods to make long, single-walled nanotubes in large quantities. These methods include arc discharge,³ laser ablation,⁴ and metal-catalyzed chemical vapour deposition.⁵ One of the current models for the mechanism of nanotube growth is the base growth mechanism.6

Other long nanotubes, including BN,7 WS2, and MoS2, have also been grown recently. Multi-walled MoS₂ nanotubes have been synthesized by heat treatment of MoS₂ powder,8 template growth,9 and the reductive sulfidization of MoO₃ particles.10 Multiwalled WS₂ nanotubes have been produced by the reductive sulfidization of WO₃ particles using H₂S and H₂.¹¹ The sulfidization process is proposed to proceed from the outside of the particle in, as H₂S diffuses radially inward and H₂O diffuses outward. This process results in the formation of a multi-walled nanotube structure.

The electronic properties of single walled C nanotubes were theorized to be highly dependent on their wrapping topology.¹² This wrapping is depicted below in figure 1. Tubes are indexed by a wrapping vector, (n,m), with n and m representing integer multiples of the unit cell vectors. There are three types of tubes: armchair (n=m), zig-zag (n,0), and 'chiral' (any other index). Scanning tunneling microscopy studies showed that the topology of the nanotubes was related to their electronic properties: all armchair single wall nanotubes are zero band gap materials, whereas zigzag or chiral



Figure 1¹⁶

tubes with integer values of (n-m)/3 are either small or zero band gap materials.¹³⁻¹⁵ Nanotubes with other topologies behave as semiconductors, with a typical band gap greater than 0.6eV.¹³⁻¹⁵

Nanotubes have been theoretically predicted to have impressive mechanical properties, with a Young's modulus of 1.1-5.5 TPa.^{16,17} Recently, the Young's modulus was directly measured using amplitude modulation,¹⁸ beam deflection,¹⁹ and anchored measurements.²⁰ The values of the Young's modulus of multi-walled nanotubes measured using these techniques ranged from 0.8-1.9 TPa, is similar to the experimental in-plane graphite value of 1.06 TPa, one of the stiffest materials known. The mechanical properties of both C and WS₂ nanotubes make them useful in SFM experiments.^{20,21} For example, figure 2 shows a nanotube bundle mounted on a SFM tip, which was used to image a trench that the original pyramidal tip could not image.

References

- 1. Iijima, H. "Helical Microtubules of Graphitic Carbon" Nature 1991, 354, 56-58.
- 2. Tenne, R.; Margulis, M.; Genut, M.; Hodes, G. "Polyhedral and Cylindrical Structures of Tungsten Disulphide" *Nature* **1992**, *360*, 444-446.
- Journet, C.; Maser, W. K.; Bernier, P.; Loiseau, A.; Delachapelle, M. L.; Lefrant, S.; Deniard, P.; Lee, R.; Fischer, J. "Large-Scale Production of Single-Walled Carbon Nanotubes By the Electric-Arc Technique" *Nature* 1997, 388, 756-758.
- Thess, A.; Lee, R.; Nikolaev, P.; Dai, H. J.; Petit, P.; Robert, J.; Xu, C. H.; Lee, Y. H.; Kim, S. G.; Rinzler, A. G.; Colbert, D. T.; Scuseria, G. E.; Tomanek, D.; Fischer, J. E.; Smalley, R. E. "Crystalline Ropes of Metallic Carbon Nanotubes" *Science* 1996, 273, 483-487.
- Dai, H. J.; Kong, J.; Zhou, C. W.; Franklin, N.; Tombler, T.; Cassell, A.; Fan, S. S.; Chapline, M. "Controlled Chemical Routes to Nanotube Architectures, Physics, and Devices" J. Phys. Chem. B 1999, 103, 11246-11255.
- Fan, S. S.; Chapline, M. G.; Franklin, N. R.; Tombler, T. W.; Cassell, A. M.; Dai, H. J. "Self-Oriented Regular Arrays of Carbon Nanotubes and Their Field Emission Properties" *Science* 1999, 283, 512-514.
- Lourie, O. R.; Jones, C. R.; Bartlett, B. M.; Gibbons, P. C.; Ruoff, R. S.; Buhro, W. E. "CVD Growth of Boron Nitride Nanotubes" *Chem. Mater.* 2000, 12, 1808-1810.
- Hsu, W. K.; Chang, B. H.; Zhu, Y. Q.; Han, W. Q.; Terrones, H.; Terrones, M.; Grobert, N.; Cheetham, A. K.; Kroto, H. W.; Walton, D. R. M. "An Alternative Route to Molybdenum Disulfide Nanotubes" J. Amer. Chem. Soc. 2000, 122, 10155-10158.

- Zelenski, C. M.; Dorhout, P. K. "Template Synthesis of Near-Monodisperse Microscale Nanofibers and Nanotubules of MoS₂" J. Amer. Chem. Soc. 1998, 120, 734-742.
- Feldman, Y.; Wasserman, E.; Srolovitz, D. J.; Tenne, R. "High-Rate, Gas-Phase Growth of MoS₂ Nested Inorganic Fullerenes and Nanotubes" *Science* 1995, 267, 222-225.
- Rothschild, A.; Sloan, J.; Tenne, R. "Growth of WS₂ Nanotubes Phases" J. Amer. Chem. Soc. 2000, 122, 5169-5179.
- Odom, T. W.; Huang, J. L.; Kim, P.; Lieber, C. M. "Atomic Structure and Electronic Properties of Single-Walled Carbon" *Nature* 1998, 391, 62-64.
- Wildoer, J. W. G.; Venema, L. C.; Rinzler, A. G.; Smalley, R. E.; Dekker, C. "Electronic Structure of Atomically Resolved Carbon Nanotubes" *Nature* 1998, 391, 59-62.
- 14. Odom, T. W.; Huang, J. L.; Kim, P.; Lieber, C. M. "Structure and Electronic Properties of Carbon Nanotubes" J. Phys. Chem. B 2000, 104, 2794-2809.
- Hernandez, E.; Goze, C.; Bernier, P.; Rubio, A. "Elastic Properties of Single-Wall Nanotubes" Appl. Phys. A 1999, 68, 287-292.
- Yakobson, B. I.; Brabec, C. J.; Bernholc, J. "Nanomechanics of Carbon Tubes -Instabilities Beyond Linear Response" Phys. Rev. Lett. 1996, 76, 2511-2514.
- Krishnan, A.; Dujardin, E.; Ebbesen, T. W.; Yianilos, P. N.; Treacy, M. M. J. "Young's Modulus of Single-Walled Nanotubes" *Phys. Rev. B* 1998, 58, 14013-14019.
- Salvetat, J. P.; Kulik, A. J.; Bonard, J. M.; Briggs, G. A. D.; Stockli, T.; Metenier, K.; Bonnamy, S.; Beguin, F.; Burnham, N. A.; Forro, L. "Elastic Modulus of Ordered and Disordered Multiwalled Carbon Nanotubes" *Adv. Mater.* 1999, *11*, 161-165.
- Wong, E. W.; Sheehan, P. E.; Lieber, C. M. "Nanobeam Mechanics Elasticity, Strength, and Toughness of Nanorods and Nanotubes" *Science* 1997, 277, 1971-1975.
- Dai, H.; Hafner, J.H.; Rinzler, A.G.; Colbert, D.T.; Smalley, R.E. "Nanotubes as Nanoprobes in Scanning Probe Microscopy" *Nature* 1996, 384, 147-150.
- 21. Rothschild, A.; Cohen, S.R.; Tenne, R. "WS₂ Nanotubes as Tips in Scanning Probe Microscopy" App. Phys. Lett. **1999**, 75, 4025-4027.