The University of Alabama

Department of Chemistry

Graduate Student Seminar Series

The Discovery and Applications of Fullerenes

Jian Tang

Literature Seminar

12:45 PM October 4th, 2005

Room 151, Shelby Hall

1. Introduction

Carbon is one of the commonest substances on Earth and it is widely distributed in nature. All life is carbon-based, and this gives rise to the description of the chemistry of carbon compounds as Organic. Carbon was probably the first element that man was aware of since it is produced in the form for charcoal from burned wood. Charcoal, used in early cave painting and by the artists today, consists of very small crystals of graphite, one of two forms of carbon.[1] The other form is diamond, which is especially famous for its hardness and its high dispersion of light. These properties make diamond valuable in jewel industry as well as in other industrial applications. Carbon is the only element that gives name to two scientific journals, Carbon and Tanso.[2] Until the late twentieth century, graphite and diamond were the only known allotropes of carbon. Fullerenes were first discovered in 1985 in an apparatus designed by Prof. Rick Smalley to produce atomic clusters of the non-volatile element.[3] The discovery of this new form of pure carbon, and the insight that led to the interpretation of the magic number features in the observed mass spectra in terms of hollow carbon molecules, led to the award of the Noble Prize in Chemistry to Curl, Kroto and Smalley in 1996. This paper will review the discovery of these novel carbon-based structures and illustrate how their unique properties can be utilized in application across scientific disciplines.

2. Discovery of Fullerenes

The discovery of C_{60} has a long and very interesting history.[4] The structure of truncated icosahedron was already known in about more than 500 years. Archimedes is credited for discovering the structure and Leonardo da Vinci included it in one of his drawings. At the end of 1960’s, scientists were increasingly interested in non-planar aromatic structure, and thereafter the saucer-shaped corannulene was synthesized.[5] In 1970, Eiji Osawa realized that a molecule made up of sp^2 hybridized carbons could have the soccer structure. He therefore made the first proposal for C_{60}.[6] But this prediction turned out to be incorrect later. Then, a group of Russian scientists independently proposed the C_{60} structure, the paper published by Bochvar and Gal'pern in 1973 not only predicted some properties of C_{60}, but also of C_{20} (the smallest fullerene) as well.[7] The first spectroscopic evidence for C_{60} and other fullerenes was published in 1984 by Rohfing and coworkers.[8]

In 1985, Professor Kroto, from University of Sussex, UK, met Professor Curl, from Rice University, at a conference on molecular structure in Austin, Texas. Kroto went back to Houston with Curl, who introduced him to Smalley and showed him around the lab. They arranged to examine a special kind of carbon produced in a cluster beam apparatus of Smalley. They soon reproduced the earlier work of Rohlfing and coworkers. What is more important is that research student James Heath, now professor at Cal. Tech., found conditions whereby C_{60} was formed exclusively, showing it to be a particularly stable species. After discounting various highly improbable structures, they concluded that the molecule must be a cage, and Smalley succeeded in building it out of his paper and tape. The paper including describing this work was submitted to *Nature,* on September 12th, 1985.[3] They named C_{60} as Buckminsterfullerene, because of the similarity of the structure to be geodesic structures widely credited to R. Buckminster Fuller. Because of this work, Kroto, Smalley, and Curl were awarded the Nobel Prize in Chemistry in 1996.

However, the fullerenes would be interesting only to a small number of scientists if the major breakthrough was made by Wolfgang Kratschmer of Heidelberg University and Donald

Huffman of the University of Arizona in 1990 was not achieved.[9] These scientists discovered a really simple way to produce solid fullerenes by arc-vaporization of graphites in a helium environment. Since then, the field of fullerenes developed rapidly and made an impact in many different scientific areas.

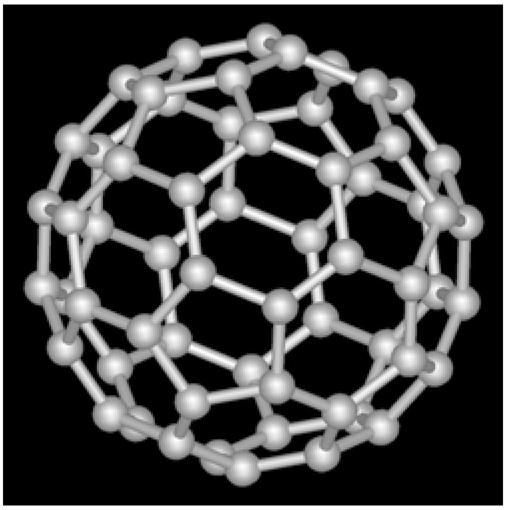

Fig.1 C_{60} (source: http://en.wikipedia.org/wiki/Fullerene)

3. Properties of Fullerenes

Unlike graphite or diamond, fullerenes are closed–cage carbon molecules, consisting of a number of five-membered rings and six-membered rings. In order to make a closed cage, all the fullerene molecules should have the formula of C_{20+m}, where m is a integer number. For example: the structure of C_{60} is a truncated icosahedron, which looks like a soccer ball with 12 pentagons and 20 hexagons (Fig.1). Some important properties of C_{60} are given below. The bonds in C_{60} are having two different kinds. The reason for this is that it would increase strain to have a double bond in a pentagon.[10] As a result, the length of a bond in a pentagon is 1.45Å, that of a bond between pentagons is 1.40Å.[11] As the size increases, the solubility of fullerene decreases. At room temperature, the solubility of C_{60} is about 2.8mg/ml in toluene.[12] As the size increases, the heat of sublimation of fullerene increases. For C_{60}, the value is 43.3

Kcal/mol.[13] The HOMO-LUMO gaps of C_{60} and C_{70} are 1.68eV and 1.76eV, respectively.[14] Because of the low-lying LUMO, fullerenes are always ready to be reduced. This makes C_{60} a good oxidizing agent. C_{60} is unstable at higher temperatures and measurable decomposition can be observed about 830K.[15] The process of decomposition is faster in the presence of oxygen.

4. Production of Fullerenes

4.1 Preparation of Fullerenes

Fullerenes can be prepared in simple processes. Graphite rods are vaporized in an atmosphere of inert gas, helium the best, by passing a high electric current through them.[9] This produces a light condensate called fullerene soot, which contains a variety of different fullerenes. The fullerenes can be extracted by a number of different solvent. Toluene is the most widely used due to its low cost, low boiling point and relatively large capacity of carrying fullerenes. Separation and purification can be achieved by column chromatography.

4.2 Endohedral Fullerenes

At the same time the C_{60} was discovered, Heath, Smalley and coworkers showed that lanthanum could be incorporated inside C_{60}.[16] This was the first formation of a member of the class of compounds known as endohedral fullerenes. So far, endohedral species with La, Y, Ce, Gd, Eu, Nd, Sm, Tb and Ho have been made. More articles describing these species can be found elsewhere.[17-18]

4.3 Nanotubes and Nanoparticles

In addition to fullerenes and endohedral fullerenes, carbon nanotubes is another kind of carbon materials that can be produced by vaporizing graphite rods under specific conditions.

These tubes can be synthesized in relatively large quantities and has been predicted for many applications. Basically, nanotubes are elongated fullerenes, they are made up by hexagons as well as pentagons in the end caps in order to close the tube. Arranging the pentagon in different ways can give different shape to the caps. The shapes of the outer caps is parallel to that of the inner ones.[2] Because nanotubes are elongated fullerens, as fullerenes can be either empty (single-wall nanotube, SWNT) or nested (multi-wall nanotube, MWNT). MWNTs are usually straight, while SWNTs are more flexible.

After Iijima reported that carbon nanotubes could be in a deposit on the cathode of a fullerene-soot generator,[19] Ebbesen and Ajayan published a paper on how to make large quantities of nanotubes.[20] They also got a particular type of carbonaceous deposit formed on the cathode of their apparatus. Under some further study, they conclude that certain interior region contained large quantities of carbon nanotubes as well as nanoparticles. The nanoparticles are normally tens of nm in diameter and consist of many concentric graphite layers. Ebbesen and coworkers have reported the separation of nanotubes form nanoparticles by heating mixture of nanotubes and nanoparticles in pure oxygen.[21] It is worth pointing out that although fullerenes, nanotubes and nanoparticles can form in the same environment and they also have similar formation process, nanotubes and nanoparticles form in significant yield under a broader range of conditions than fullerenes do.[12]

5. Applications of Fullerenes

Because of their unique structures and properties, fullerenes draw lots of attention from physicists, chemists and engineers, who are trying to find some potential applications of these new carbon structures.

Nowadays, scanning probe microscopy (SPM) is one of the most important tools in the field of surface chemistry. Carbon nanotubes, which have small diameter and high aspect ratio, is a ideal material that can used as tips in SPM, such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM). It is reported that nanotubes attached tip can be used to enhance SPM resolution to nanoscale.[22-24] In these papers, nanotubes were attached on conventional Si tips under a microscope by acrylic adhesive. However, this method is difficult to control the length of the tip, and it is always difficult to get a strong and reliable attachment. In 1999, a new method to make carbon nanotube tips for SPM was reported.[25] In this method, nanotubes were prepared by conventional arc discharge method.[20] After purification, they were aligned by electrophoresis on the knife edge of a disposable razor. Then one single nanotube was transferred onto a Si tip and it was attached onto the Si tip by the deposition of carbon. In order to compare the nanotube tip and conventional Si tip, both tips were used to image DNA molecules by AFM(see Fig.2). As a result, the image produced by nanotube tip showed a factor of two lateral resolution improvement than the image by the conventional tip.

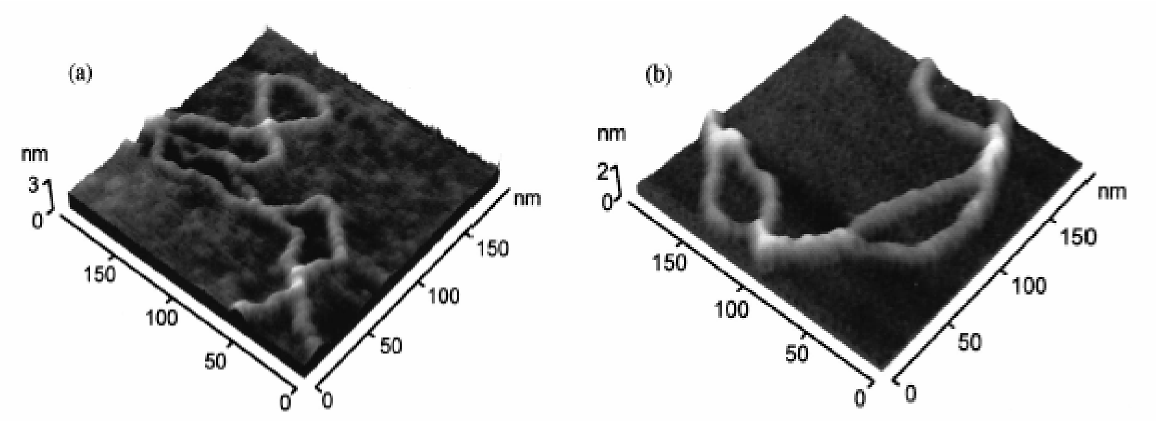

Fig.2 AFM image of DNA using (a) nanotube tip and (b) a standard Si tip.[25]

These manual methods of producing nanotube tips, though produce some good results, is very time consuming. A new method called chemical vapor deposition (CVD) was developed to make the production of nanotube tips more practical. There are several good articles on explaining the detailed fabrication process of CVD.[26-27] The fabrication of nantube tips by CVD can overcome the limitations that manual methods have. So it is a preferred method to produce nanotube tips.

Overall, the advantage of the nanotube tips over conventional Si tips is high lateral resolution due to its high aspect ratio and small diameter. It is also more mechanically flexible, so it can be elastically buckled without any damage to the tip. It has long life time because it won't be broken by an accidental contact on the surface. It can be applied to image some structure with steep sidewalls, such as silicon trenches.[22]

Fullerenes and their derivatives are also applied to coat materials on some chemical sensors, such as quartz crystal microbalance (QCM) and surface acoustic wave sensors (SAW). Both QCM and SAW have a key component called piezoelectric crystals, which are well know to be very sensitive to mass changes on their surface. Thus, they can be applied for trace quantitative analysis. Because of its affinity to organic molecules, fullerenes C_{60} and its derivatives can be coated onto piezoelectric crystal and applied as a chemical sensor for organic molecules. In studies carried out by Shih, J.S. *et al.*[28-29], they prepared a kind of fullerene derivatives called fullerene C_{60}-cryptand22 and then spin coated them onto both sides of the piezoelectric crystal of a chemical sensor. The sensor was used to detect organic molecules such as propanol, butanol, ethanol and methanol. As the organic molecules adsorbed on to the fullerene derivative film, the oscillating frequency of the piezoelectric crystal decreases, the change is proportional to the concentration to the concentration of the adsorbent. In this way, the concentration can be determined.

Molecular sensor based on semiconducting single-walled carbon nanotubes are also developed.[30] The electrical resistance of this SWNT changes dramatically when it is exposed to gas molecules such as NO_2 and NH_3. For the NO_2 case, the conductance of the SWNT increases by about three orders of magnitude when 200ppm NO_2 is introduced (Fig.3). For the NH_3 case, using the same SWNT, the conductance decreases 100-fold when it is exposed to an Argon flow with 1% NH_3 (Fig.4). Combing with their small size, room temperature operation and high sensitivity, carbon nanotube sensors should be a promising chemical sensors.

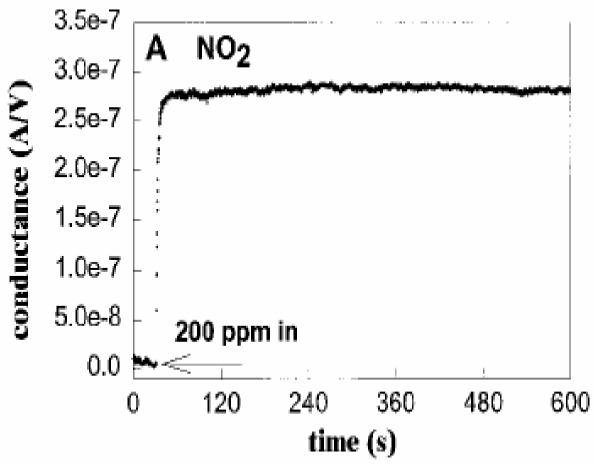

Fig.3 Conductance of SWNT vs. Time[30]

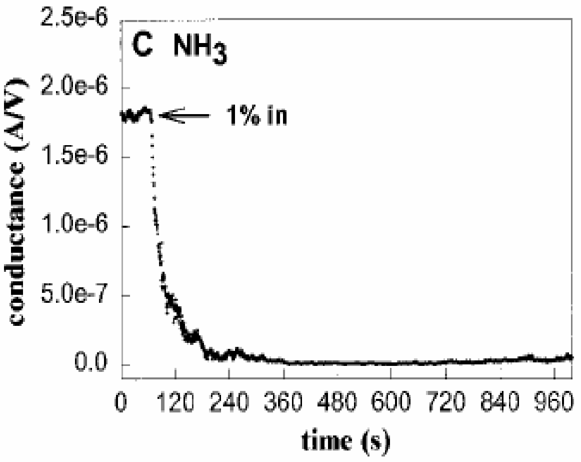

Fig.4 Conductance of SWNT vs. Time[30]

Because of their high aspect ratios, carbon nanotubes can be also used as a field emission source.[31-34] At 1995, an electron gun based on field emission for a film of aligned carbon nanotubes was made by Dr. W. A. de Heer and coworkers.[31] The schematic diagram of the electron source is showed at Fig.5. It consists of three important components. Component a is a carbon nanotube film on a polytetrafluoroethylene (PTFE) substrate. Component b is a perforated mica sheet with a thickness of 20μm and a hole of 1mm in diameter. Component c is an electron microscopy copper grid, which covers the hole in b.

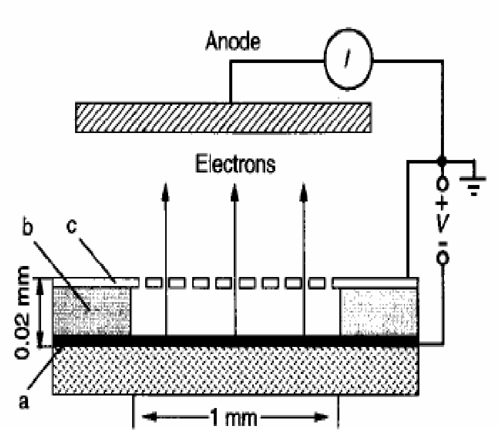

Fig.5 Schematic diagram of the CNT electron source [31]

The field emission current was measured on the anode about 1cm above the grid. According to their data, the field emission current density of 0.1mA/cm^2 can be observed when the voltage is 200V. If the voltage goes higher to 700V, current density of 100mA/cm^2 can be obtained.

Scientists are now trying to make field emission displays (FED) using carbon nanotubes as field emission electron sources.[35-36] FEDs is similar to the conventional television cathode ray tubes (CRT). But the big difference is that each pixel has its own electron source. This difference allows FEDs to be made only several millimeter thick and still have the same picture quality as conventional CRTs. Compared to other kinds of flat panel display, such as LCD and Plasma, FEDs are more power saving, cheaper to make and having wide view angles.

6. Conclusions

The discovery of fullerenes and carbon nanotubes have opened a new chapter on the physics and chemistry of carbon. So far, the physical and chemical properties of fullerenes and carbon nantotubes are still under investigation. More research are needed to be done to confirm the suitability of some important application.. Some potential applications will need more time for them to become reality.

References

(1) Taylor, R. *Lecture Notes on Fullerene Chemistry: A handbook for chemists*; Imperial College: London, 1999

(2) Pierson, H. O. *Handbook of Carbon, Graphite, Diamond and Fullerenes-Properties, Processing and Applications*; William Andrew, 1993

(3) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985,** *318*, 162-163.

(4) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerene and Carbon Nanotubes*, Academic, 1996.

(5) Barth, W. E.; Lawton, R.G. *J. Am. Chem. Soc.* **1968**, *93*, 1730.

(6) Osawa, E. *Kagaku* **1970**, *25*, 654.

(7) Bochvar, D. A.; Gal'pern, *E.G. Proc. Acad. Sci*. **1973**, *209*, 239.

(8) Rohlfing, E. A.; Cox, D. M.; Kaldor, A. *J. Chem. Phys.* **1984**, *81*,3322.

(9) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(10) Taylor, R. *Tetrahedron Lett.* **1971**,3134.

(11) David, W. I. F. et al. *Nature* **1991**, **353,** 147.

(12) Taylor, R. *The Chemistry of Fullerenes;* World Scientific: Singapore, 1995.

(13) Piacente, V.; Palchetti, C.; Gigli, G.; Scardala, P. *J. Phys. Chem.* **1997**, *101*, 4303.

(14) Andreoni, W.; Gygi, F.; Parrinello, M. *Chem. Phys. Lett*. **1992**, *189*, 241.

(15) Chen, H. S.; Kortan, A. R.; Haddon, R. C.; Fleming, D. A. *J. Phys. Chem.* **1992**, *96*, 1016.

(16) Heath, J. R. et al. *J Am. Chem. Soc.* **1985,** *107*, 7779.

(17) Gillan, E. G. et al. *J. Phys. Chem.* **1992**, *96*, 6869-6871.

(18) Bethune, D. S. et al. *Nature* **1993**, *366*, 123.

(19) Iijima, S. *Nature* **1991**, *354*, 56-58.

(20) Ebbesen, T. W.; Ajayan, P. M. *Nature* **1992**, *358*, 220-222.

(21) Ebbesen et al. *Nature* **1994**, *367*, 519.

(22) Dai, H.; Hafner, J. H.; Rinzler, A. G.; Colbert, D. T.; Smalley, R. E. *Nature* **1996**, *384*, 147.

(23) Wong, E. W.; Harper, J. D., Lansbury, P. T.; Lieber, C. M. *J. Am. Chem. Soc.* **1998**, *120*, 603

(24) Wong, E. W.; Sheehan, P. E.; Lieber, C. M. *Science* **1997**, *277*, 1971.

(25) Nishijima, H. et al. *Appl. Phys. Lett.* **1999**, *74*, 4061.

(26) Hafner, J. H. et al. *Nature* **1999**, *398*, 761

(27) Cheung, C. L. et al. *Appl. Phys. Lett.* **2000**, *76*, 3136.

(28) Shil, J. S. et al. *Sensors and Actuators B* **2001**, *76*, 347-353.

(29) Lin, H. B.; Shih, J. S. *Sensors and Actuators B* **2003**, *92*, 243-254.

(30) Dai, H. et al. *Science* **2000**, *287*, 622.

(31) de Heer, W. A.; Chatelain, A; Ugarte, D. *Science* **1995**, *270*, 1179.

(32) Collins, P. G.; Zettl, A. *Appl. Phys. Lett.* **1996**, *69*, 1969.

(33) Xu. X.; Brandes, G. R. *Appl. Phys. Lett.* **1999**, *74*, 2549.

(34) Dai, H. et al. *Science* **1999**, *283*, 512.

(35) Wang, Q. H; Yan. M.; Chang, R. P. H. *Appl. Phys. Lett.* **2001**, *78*, 1294.

(36) Amaratunga, G. *IEEE Spectrum* **2003**, *9*, 28