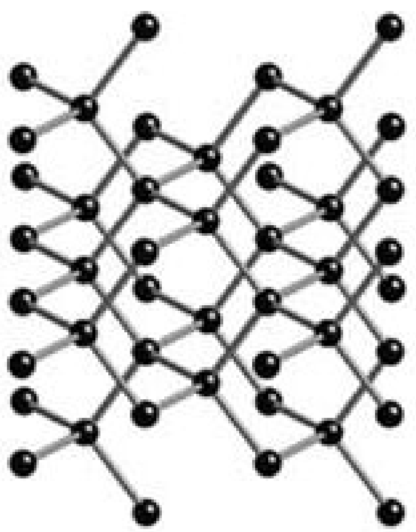
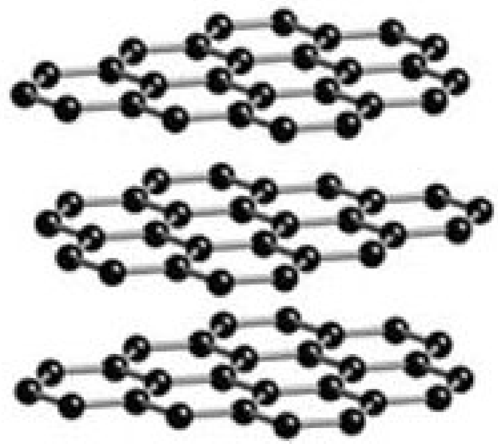
The Discovery, Development, and Applications of Fullerenes

-Dr. M. Baby Mariyatra

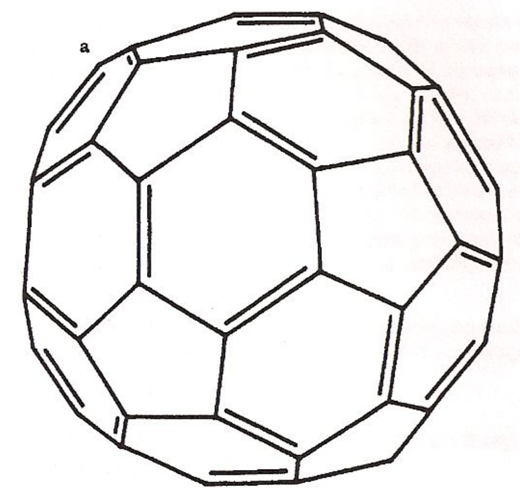
A New Form of Carbon



Diamond



Graphite



C_{60} Buckyball

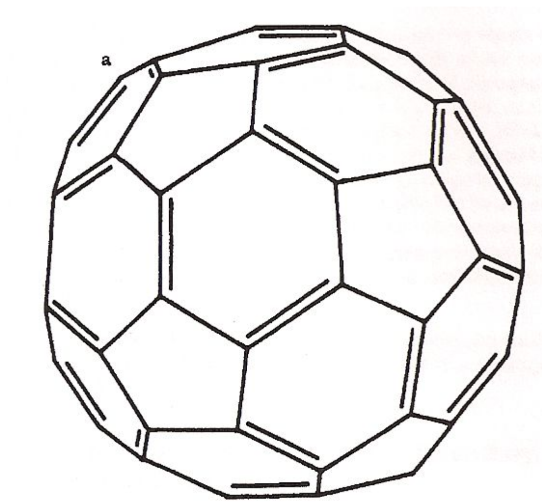
Diamond, graphite images: "Buckyballs." Australian Academy of Science. Nov. 1999. 22 Mar. 2007 <www.science.org.au/nova/024/024key.htm>.
Buckyball image: Haymet, A. D. J. "Footballene: a Theoretical Prediction for the Stable, Truncated Icosahedral Molecule C60."
Journal of the American Chemical Society 108 (1986): 319-321.

Buckyball Discovery

- 1985: British chemist Harry Kroto studied molecules with exactly sixty carbon atoms found near red giant stars
- Kroto collaborated with Richard Smalley and Robert Curl to recreate the conditions in the laboratory and form C_{60} molecules by laser vaporization of graphite
- The scientists hypothesized that the molecules were made of hexagonal carbon rings blasted apart from the graphite structure, and that the molecule must be spheroid to satisfy valence requirements

Determining the C_{60} Structure

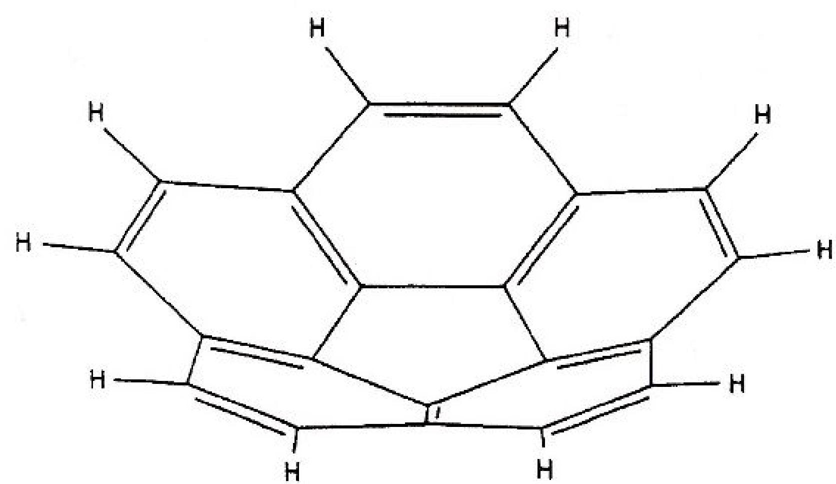
- After considerable work, Kroto, Smalley, and Curl determined that the structure of the C_{60} buckyball was a combination of 12 pentagonal and 20 hexagonal rings, forming a spheroid shape with 60 vertices for the 60 carbons.
- The pentagonal rings sit at the vertices of an icosahedron such that no 2 pentagonal rings are next to each other
- Curl, Kroto, and Smalley received the Nobel Prize in 1996 for their work.
- The architect R. Buckminster Fuller designed a geodesic dome for the 1967 Montreal World Exhibition with the same structure; the scientists thus named the new molecule Buckminsterfullerene, which was shortened to fullerene when referring to the family of molecules.



Haymet, A. D. J. "Footballene: a Theoretical Prediction for the Stable, Truncated Icosahedral Molecule C60." Journal of the American Chemical Society 108 (1986): 319-321.

Haymet's Prediction

- Independently, near the same time, Tony Haymet of the University of California at Berkeley published a paper predicting the existence of a compound of this kind, which he called "footballene."
- The molecule corannulene, with a similar nonplanar assembly of carbons in pentagonal and hexagonal rings, led Haymet to predict the existence of a similar spheroid molecule, with sixty carbons in twelve pentagons and twenty hexagons.



Haymet, A. D. J. "Footballene: a Theoretical Prediction for the Stable, Truncated Icosahedral Molecule C60."
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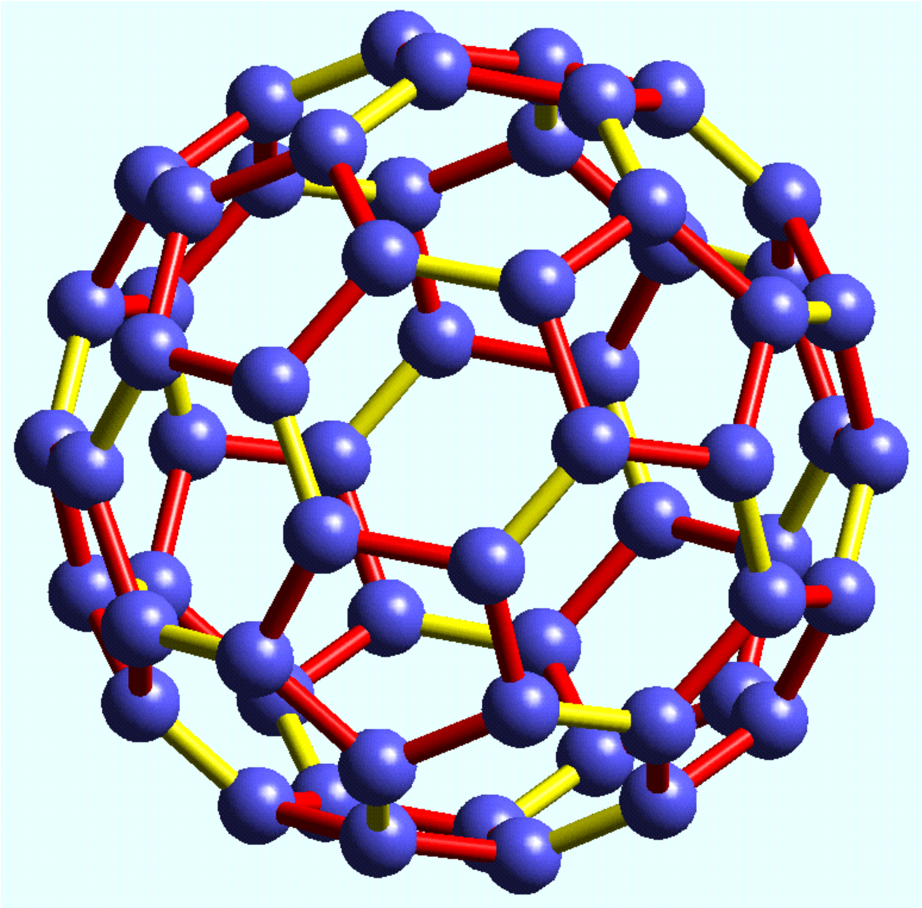
Bond Structure and Reactivity

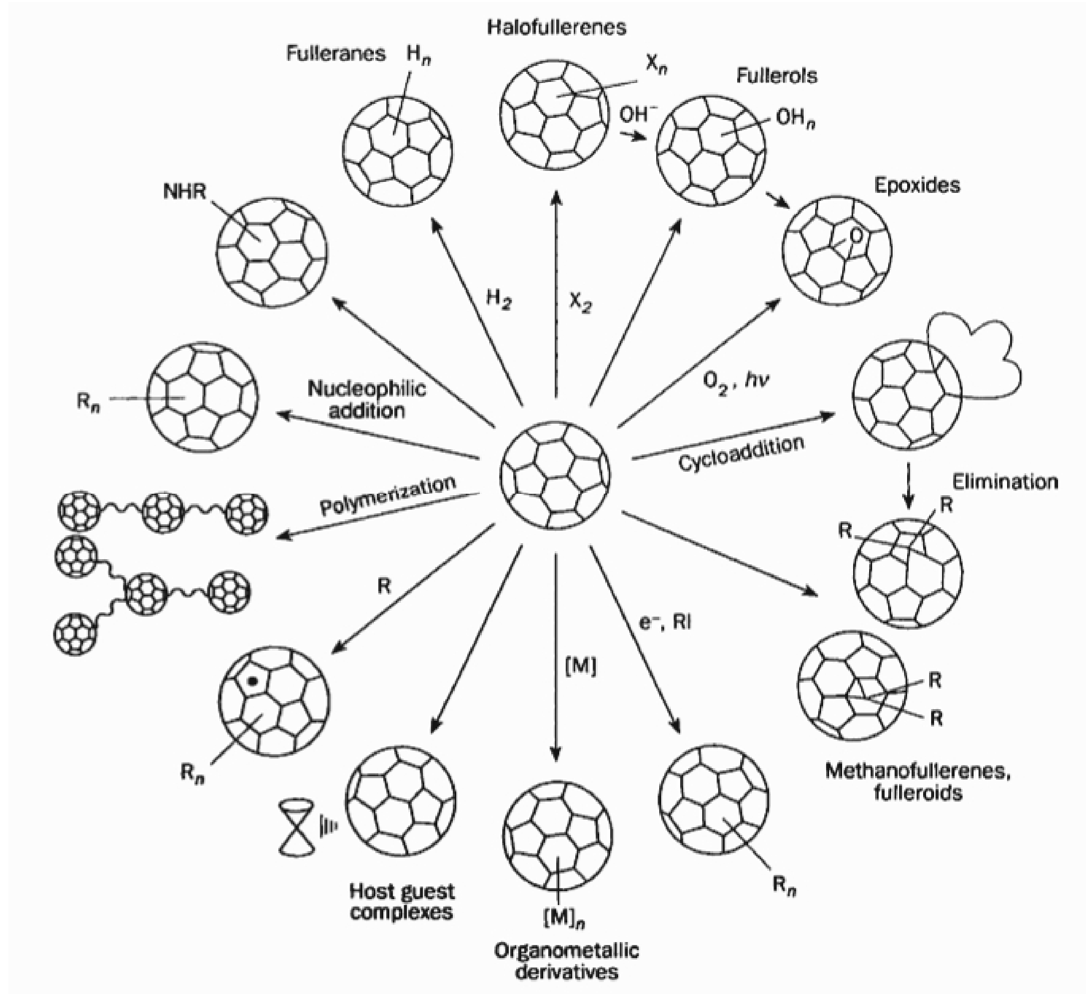
- The bonding pattern of the C_{60} fullerene is shown here, with yellow bonds representing double bonds and red bonds representing single bonds.
- The pentagonal rings contain only single bonds; double bonds have a shorter bond length and lead to instability in the pentagonal ring.
- The limitations on double bond locations lead to poor delocalization of electrons, increasing the molecule's reactivity.



http://www.godunov.com/Bucky/buckyball-3.gif

Fullerene Reactions

- Possible reactions C_{60} and C_{70} (to a lesser extent) may undergo
  - Additions
  - Polymerization
  - Substitutions also possible (doping with boron)



Taylor, Roger, and David R. Walton. "The Chemistry of Fullerenes." Nature 363 (1993): 685-693. 23 Mar. 2007

Conventional Synthesis

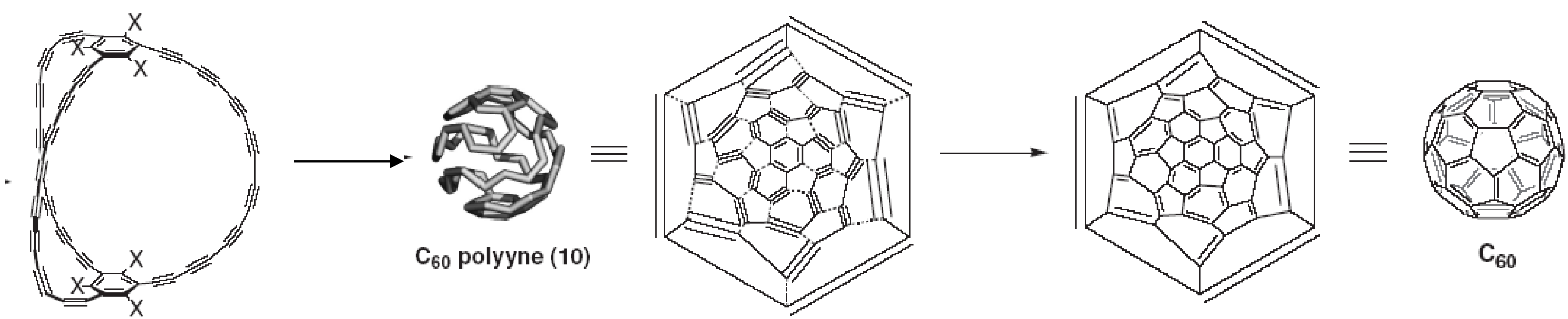
- Kroto, Smalley, and Curl used laser vaporization of graphite to produce the carbon soot from which the fullerenes could be isolated in microscopic quantities
- Krätschmer and colleagues developed a contact arc discharge method for macroscopic production, known as the Krätschmer-Huffman method.
  - Graphite electrodes kept in gentle contact are arc passing alternating current through them in an atmosphere of helium
  - The evaporated graphite takes the form of soot, which is dissolved in a nonpolar solvent. The solvent is dried away and the C_{60} and C_{70} fullerenes can be separated from the residue.
  - Optimizing current and helium pressure and flow rate leads to yields of up to 15% with this method.

Selective-Size Synthesis

- There is a desire to control the size of the fullerenes for various applications.
  - Example: to increase the size of molecules to encage in fullerenes creates the need for a larger cage
  - Currently the mechanism by which fullerenes form is unknown
  - In conventional fullerene formation only C_{60} and C_{70} are produced due to their stability
- Two groups (Rubin and Tobe) independently investigated cyclic polyynes as precursors to fullerenes.
  - Neither group were able to produce C_{60} by flash vacuum pyrolysis (FVP) of the cyclic polyyne
  - They still believe this synthesis will work

Proposed Mechanism

- Cyclic polyyne folds onto itself so tightly the new carbon bonds can form (dotted lines)



Umeda, Rui, Motohiro Sonoda, Tomonari Wakabayashi, and Yoshito Tobe. "Approaches to Size-Selective Formation of Fullerenes by Cyclization of Highly Reactive Polyyne Chains." *Chemistry Letters* 34 (2005). J-Stage. University of Rochester. 22 Mar. 2007.

Fullerene Engineering

- Exohedral Fullerenes
  - Atoms, molecules, and complexes are attached to the exterior of the cage
- Endohedral Fullerenes
  - Molecules are enclosed within the cage
- Nanopeapods
  - Fullerene molecules contained in carbon nanotubes

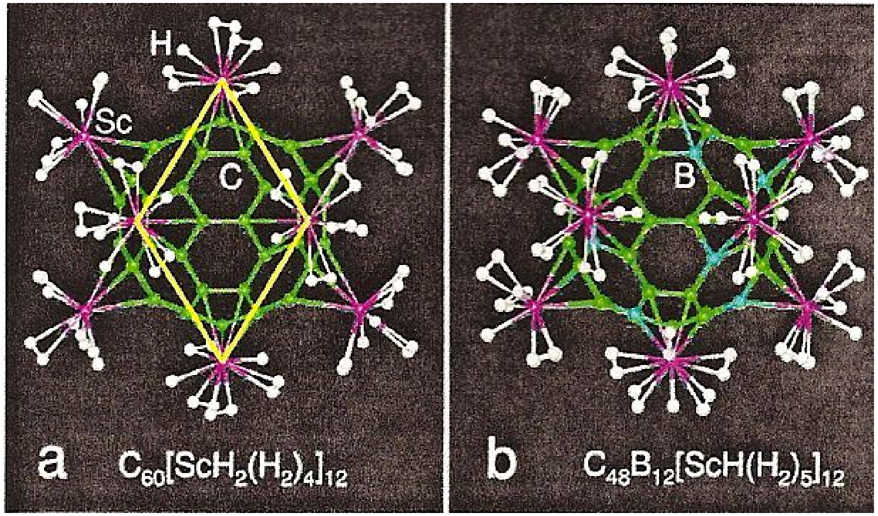
Exohedral Fullerenes--Application for Hydrogen Storage

Examples and applications:

- Organometallic molecules based upon C_{60} and boron-doped $C_{48}B_{12}$
- Complexes of transition metals with hydrogen on pentadiene rings can store up to six dihydrogen species
  - May polymerize when the hydrogen is removed, rendering the process irreversible.
- Arranging the complexes on buckyballs, such as $C_{60}[ScH_2]_{12}$ and $C_{48}B_{12}[ScH]_{12}$, leads to stable species which can reversibly absorb additional hydrogen.

Hydrogen Storage

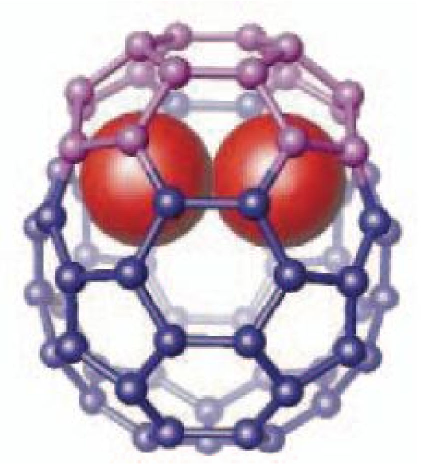
- Nearly 9 wt% can be retrieved reversibly and room temperature and near ambient pressure.
- Doping with boron
  - Reduces the fullerene weight
  - Enhances the complex's stability by increasing the binding energy
  - Allows the binding of an additional H_2 molecule per Sc, increasing the amount of retrievable H_2



Zhao, Yufeng, Yong-Hyun Kim, A. C. Dillon, M. J. Heben, and S. B. Zhang. "Hydrogen Storage in Novel Organnometallic Buckyballs." Physical Review Letters 94 (2005). University of Rochester. 22 Mar. 2007.

Endohedral Fullerenes

- Fullerene cages with encapsulated molecule have many potential applications. For example scientists believe they will be able to encage a radioactive tracer and inject that safely into the human body.
- Currently various molecules can be encaged in the fullerene cage.
  - Metal ($La@C_{82}$), noble gas ($He@C_{60}$), multimetallofullerene ($Sc_2@C_{66}$)
  - Product yields are less than 2% in all cases
- Endohedral fullerenes have presented a lot of new information to researchers.
  - For metallofullerenes there is a charge transfer between the cage and enclosed metal, $Sc_2@C_{66}$ stabilizing what may not be a stable cage alone



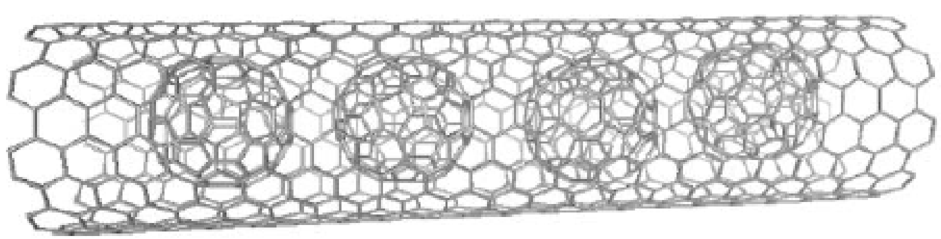
Dunsch, Lothar, and Shangfeng Yang. "The Recent State of Endohedral Fullerene Research." *The Electrochemical Society Interface* (2006).

TNT Synthesis

- Improved synthesis of endohedral formation came in 1999 by introducing nitrogen to conventional Krätschmer-Huffman generator
    - $Sc_3N@C_{80}$ – trimetal nitride fullerene
    - Increased yields to ~5%
- This new process was named trimetal nitride template (TNT) and applied to form a variety of products.
    - M3N@C80 where M=Sc, Y, Tb, Ho, and Er
- Dunsch and co-workers enhanced the synthesis by using NH_3 as the reactive gas in the generator. Endohedral fullerenes were formed as the major product for the first time.
- C_{80} and Sc_3N are not stable individually.
- Very restricting, it can only apply to trimetal nitrides.

Nanopeapods

- Single-walled carbon nanotubes (SWNTs) encapsulating C_{60}
- Conventional synthesis of nanopeapods had a lot of challenges. Reactions had to be run under very difficult conditions and were very restricting.
  - Vaporization of thermally stable fullerene molecules
  - At least 350° C in high vacuum
- Theoretical studies showed the activation barrier for this reaction to be only ~0.37eV.
  - The reaction should proceed at room temperature

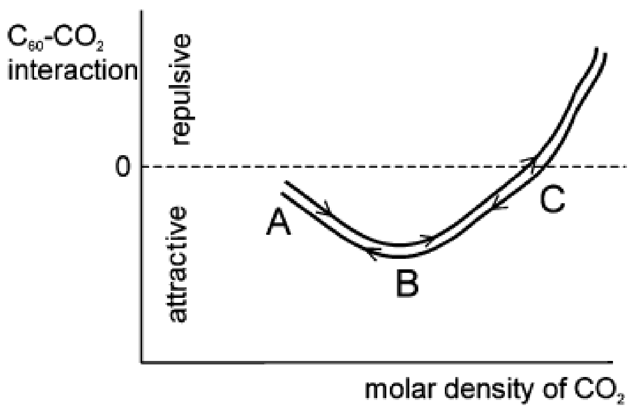


Khlobystov, Andrei N., David A. Britz, Jiawei Wang, S. Adam O'neil, Martyn Poliakoff, and G. Andrew D. Briggs. "Low Temperature Assembly of Fullerene Arrays in Single-Walled Carbon Nanotubes Using Supercritical Fluids." *Journal of Materials Chemistry* 14 (2004): 2852-2857. Royal Society of Chemistry Archive. University of Rochester. 22 Mar. 2007

Various Nanopeapod Syntheses

- Khlobystov and group attempted numerous synthesis methods at or near room temperature (30-50° C) with a yield <1%
  - Mechanical mixing
  - Adding SWNTs to concentrated solution of fullerenes
  - Adding fullerenes to SWNTs solution
- Supercritical fluids, most important scCO_2, was the next used in the process
  - SWNTs and fullerenes mixed in solvent, evaporated solvent, put in supercritical CO_2 under high pressure for 10 days
  - Produced yields ~30%

$scCO_2$ Properties



Solvent	Solubility of C_{60}/g L^{-1}	Molar fraction of C_{60} in solution	Critical diameter of solvent/Å
o-Dichlorobenzene	27	5.3×10^{-3}	7.8
Toluene	2.8	4.0×10^{-4}	6.7
Ethanol	0.001	1×10^{-7}	4.4
Ethene	unknown	unknown	4.0
Carbon disulfide	7.9	6.6×10^{-4}	3.6
Carbon dioxide	unknown	unknown	2.8

- Investigating why $scCO_2$ increases product yield compared to other solvents
  - The interaction with carbon 60 can vary between favorable and repulsive by changing the molar density of CO_2, a function of temp and pressure
  - Carbon dioxide has the smallest critical diameter

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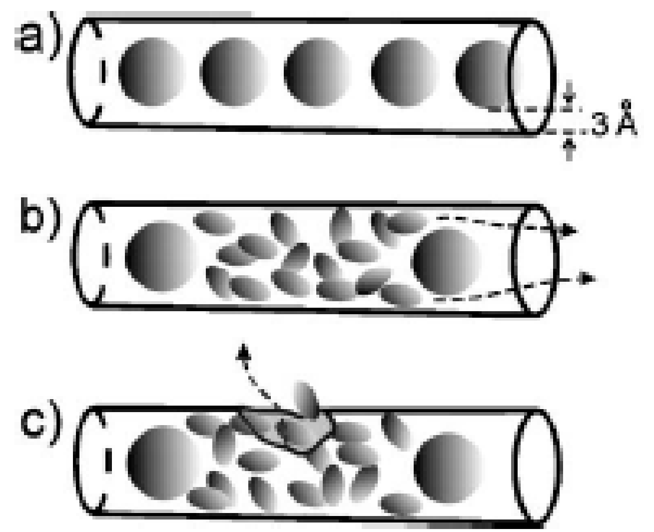
Mechanism for Nanopeapod Formation

- $scCO_2$ can carry the fullerene into the SWNT because of the attraction between the molecules
- Varying temperature and pressure can create a repulsive interaction encouraging the solvent molecule to diffuse out of the SWNT



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Summary

- C_{60}, buckyball, was the first fullerene discovered
    - It is the third form of pure carbon (graphite, diamond, buckyballs)
- Variations of fullerenes include exohedral, endohedral and nanopeapods
- Synthesis challenges still exist for all variations of fullerenes because the mechanism of formation is still unknown
- Potential applications in medicine, nanoelectronics, and energy

Thank you

Acknowledgements:

Internet Sources