

# Introduction to Nanotechnology

- Textbook :  
Nanophysics and Nanotechnology  
by:  
Edward L. Wolf

Instructor: *H. Hosseinkhani*  
*E-mail:* hosseinkhani@yahoo.com

**Classroom: A209**  
**Time: Thursday; 13:40-16:30 PM**  
**Office hour: Thur., 10:00-11:30 AM or by appointment**

# Self-Assembled Nano-Structure in Nature and Industry

# Subjects:

1. Self-assembly Systems
2. Carbon atom
3. Nano-tube
4. Nano-wire
5. Quantum Dot
6. Nano-crystal
7. Nano-particles in Bacterial life
8. Smooth Surface

# SELF-ASSEMBLY

Other present day techniques are HOPELESSLY slow and/or expensive

So attractive alternative is SELF-ASSEMBLY

Setting things up so that Mother Nature does the fine scale work

But to ferret out where Mother Nature may give us a hand, must span:

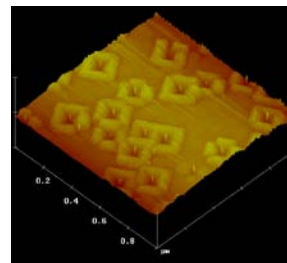
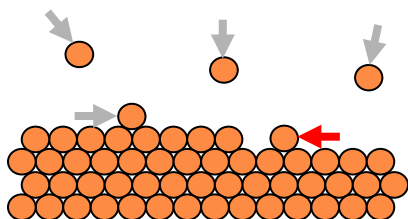
Physics, Chemistry, Biology, Materials Science . . .

So I will also put major effort into providing insights into those fields

i.e., "Opening Doors" into those subjects for you

## *Nanoscale Self-Assembly*

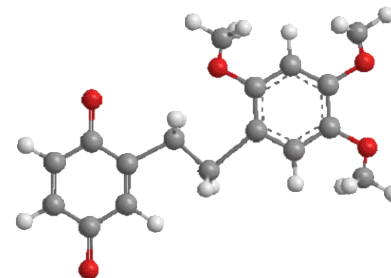
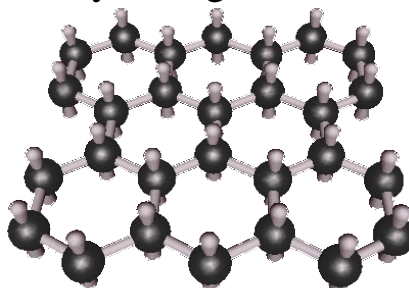
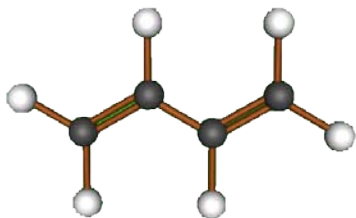
Early forms of self-assembly that man tamed (such as crystal growth)



*Leading us to the master of self-assembly: Mother Nature*

*Or what a billion years of random experimentation produced, including:*

Self-assembly of organic molecules



# 1. Self-assembly Systems

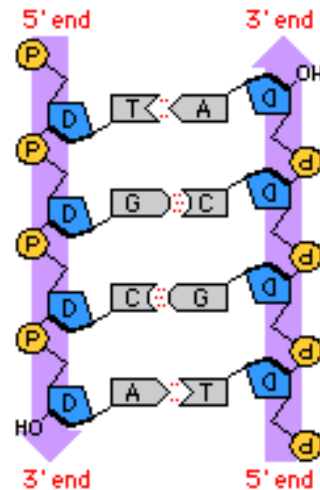
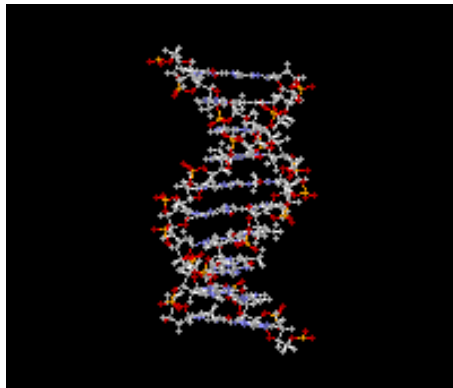
Self-assembly is definitely the preferred route to the formation of atoms.

**Molecules are mostly self-assembled and available in nature.**

**Biological Molecules:** are self-assembled.

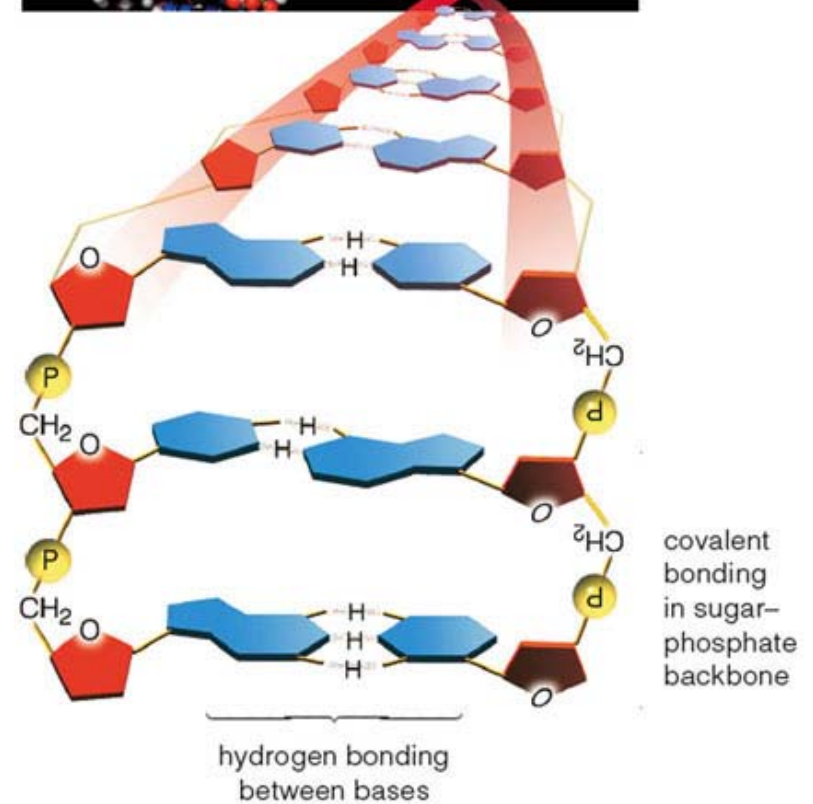
# Concept 1 Review: DNA

**DNA, made by polymerizing deoxyribonucleotides, forms a double-stranded molecule used for information storage.**

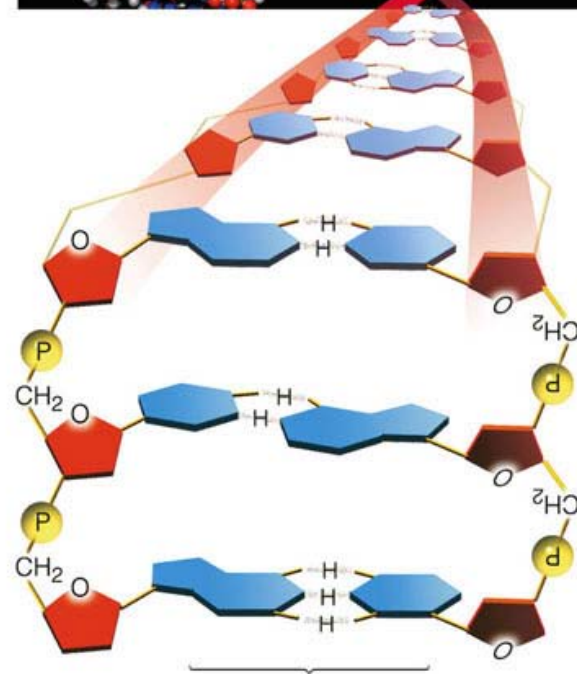


Each strand of DNA consists of a "backbone" of alternating units of phosphate and deoxyribose. Purine or pyrimidine bases are attached to the 5-C deoxyribose sugar, and form base pairs with purine or pyrimidine bases from the opposite strand. The only effective pairs are adenine with thymine (A-T pairs) and guanine with cytosine (G-C pairs).

# The DNA Molecule







**covalent  
bonding in  
sugar–  
phosphate  
backbone**

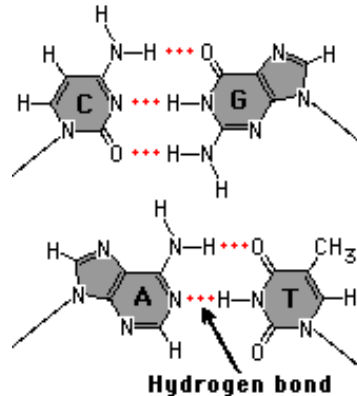
© Brooks/Cole, Cengage Learning

**hydrogen bonding  
between bases**

## Concept 1 Review: DNA Base Pairing

**A-T and G-C base pairs allow the specific interaction of nucleotides on different DNA strands.**

The purine and pyrimidine bases in DNA can associate together by forming hydrogen bonds.



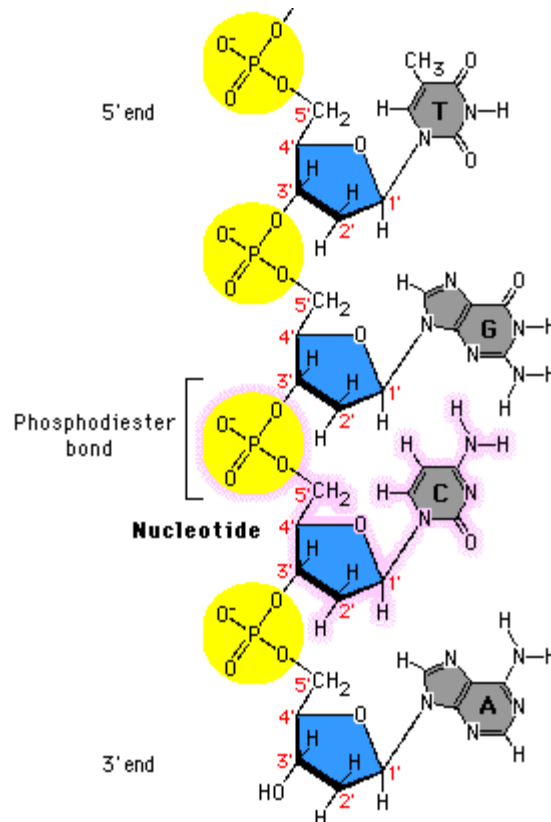
Most pairings produce only a single hydrogen bond at a time, but two types of base pairings allow for multiple hydrogen bonds. When A and T are brought into close contact, two hydrogen bonds can form simultaneously. When G and C are brought into close contact, three simultaneous hydrogen bonds can form.

The overall bond strength of many hydrogen bonds is additive. In zipper-like fashion, the presence of multiple A-T and G-C base pairs bonds the two strands of DNA tightly together.

# Concept 1 Review: The Chemistry of DNA

Atoms in each DNA nucleotide can be identified by specific numbers. The ends of a DNA molecule are called 3' and 5' ends, based on the numbering of carbon atoms in deoxyribose sugars.

Chemists identify specific atoms in a molecule by numbering the backbone atoms: C1, C2, etc. In a complex nucleotide, the atoms of the purine or pyrimidine ring are first numbered 1, 2, 3, etc. Carbon atoms in the deoxyribose sugar are then numbered 1', 2', 3', 4', and 5' (shown in red in the figure below).

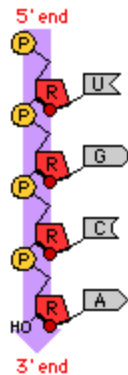
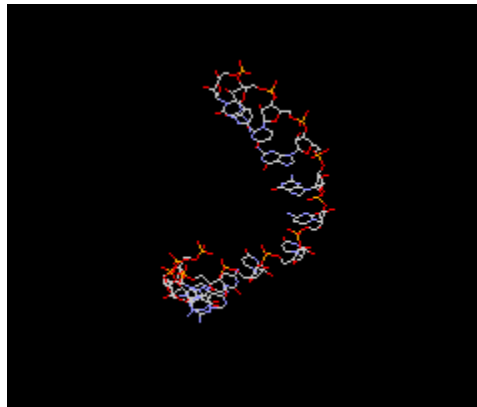


Notice that phosphate groups are attached to the 5'- and 3'-carbon atoms of each sugar to form the backbone chain of DNA. One end of the chain carries a free phosphate group attached to the 5'-carbon atom; this is called the 5' end of the molecule. The other end has a free hydroxyl (-OH) group at the 3'-carbon and is called the 3' end of the molecule.

When two DNA strands assemble in a double helix, the two strands always face in opposite directions; the 5' end of one strand is paired with the 3' end of the other strand.

## Concept 2 Review: RNA

**RNA, made by polymerizing ribonucleotides, forms single-stranded molecules used in information processing.**



An RNA consists of a "backbone" of alternating units of phosphate and ribose. Purine or pyrimidine bases are attached to the 5-C ribose sugar.

Many bases in RNA molecules, such as ribosomal RNA and transfer RNA, are chemically modified after polymerization, a process that makes these molecules more stable.

For further practice, try the exercise on Transcribing an RNA Molecule in the Transcription Lab Simulations activity.

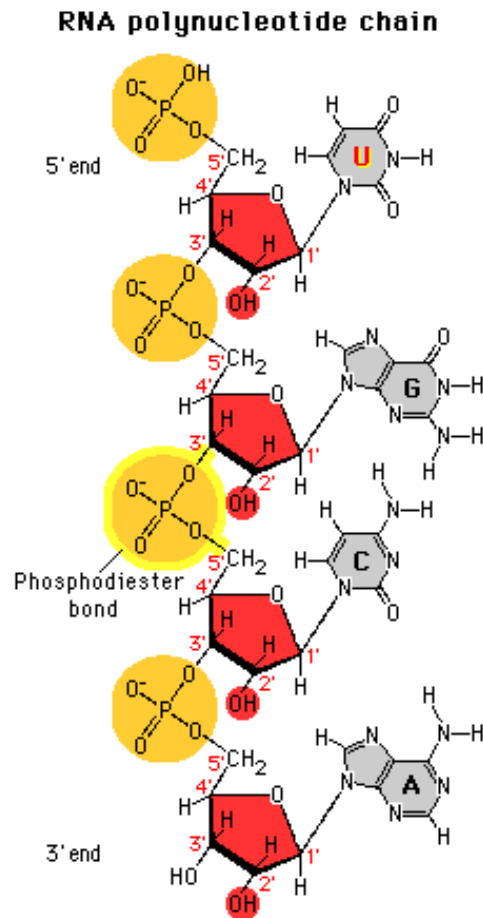
# RNA

- **RNA (ribonucleic acid)**
  - Contains four kinds of nucleotide monomers, including ATP
  - Important in protein synthesis
  - Is always at direction (and creation of) the DNA
  - Is a single helix (helix simply means curved)

# Concept 2 Review: The Chemistry of RNA

**Atoms in each RNA nucleotide can be identified by specific numbers. The ends of an RNA molecule are called 3' and 5' ends, based on the numbering of carbon atoms in ribose sugars.**

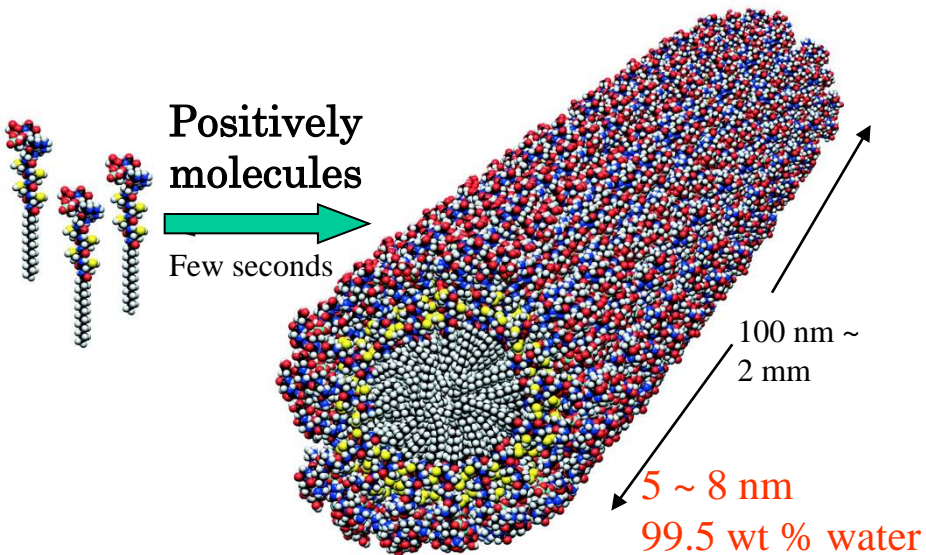
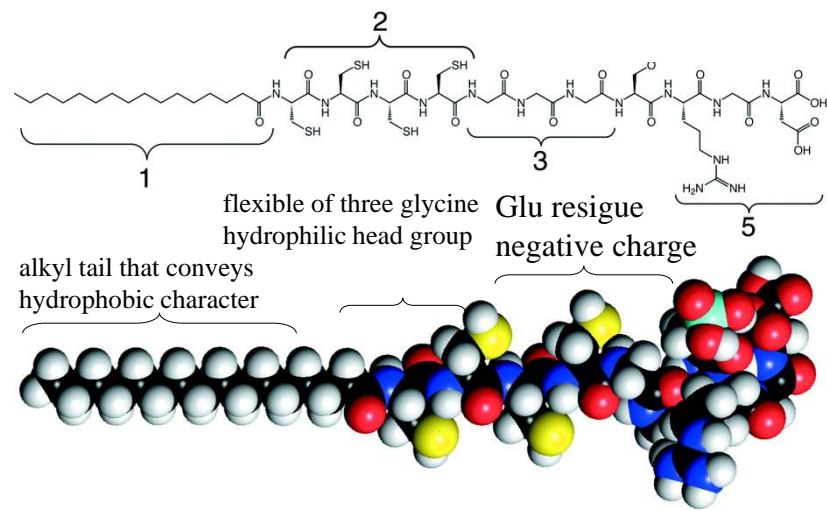
Chemists identify specific atoms in a molecule by numbering the backbone atoms: C1, C2, etc. In a complex nucleotide, the atoms of the purine or pyrimidine ring are first numbered 1, 2, 3, etc. Carbon atoms in the ribose sugar are then numbered 1', 2', 3', 4', and 5' (shown in red in the figure below).



Notice that phosphate groups are attached to the 5'- and 3'-carbon atoms of each sugar to form the backbone chain of RNA. One end of the chain carries a free phosphate group attached to the 5'-carbon atom; this is called the 5'end of the molecule. The other end has a free hydroxyl (-OH) group at the 3'-carbon and is called the 3' end of the molecule.

When new RNA molecules are synthesized, they are always made by the sequential addition of nucleotides at the 3' end of the chain. This is sometimes called 5'-to-3' synthesis. When RNA serves as a message to be translated into a polypeptide, the RNA is read starting at the 5' end and moving toward the 3' end.

Notice the presence of a hydroxyl (-OH) group at the 2' carbon of the ribose sugar. This differs from deoxyribose, where the 2' carbon lacks a hydroxyl group.



High aspect ratio  
High surface area

*Samuel I. Stupp* of Northwestern University in Chicago has discovered and considered to Peptide Amphiphile (PA) as its great capacity to form nanofibers (**Science, Vol 303, 2004**)

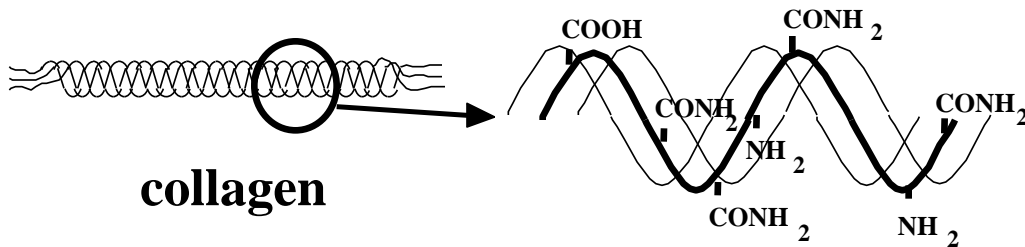
PA can self assemble into sheets, spheres, rods, disks, or channels depending on the shape, charge, and environment

Amphiphiles with a conical shape in which the hydrophilic head group is somewhat bulkier than its narrow hydrophobic tail have been shown to form cylindrical micelles.

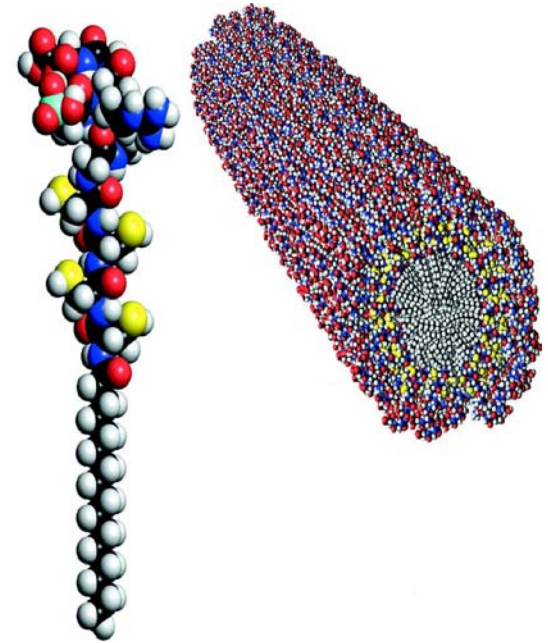
PA with mono- or di-alkyl tails were found to associate in conformations such as triple helical structures found in collagen.

Cations can screen electrostatic repulsion among Peptide, and 3-D nanofiber are driven to assemble by hydrogen bond formation and electrostatic interactions, nonspecific van der Waals interactions, hydrophobic forces, and repulsive steric forces.

**natural Collagen**      $\sim$      **self-assembled peptide amphiphile**

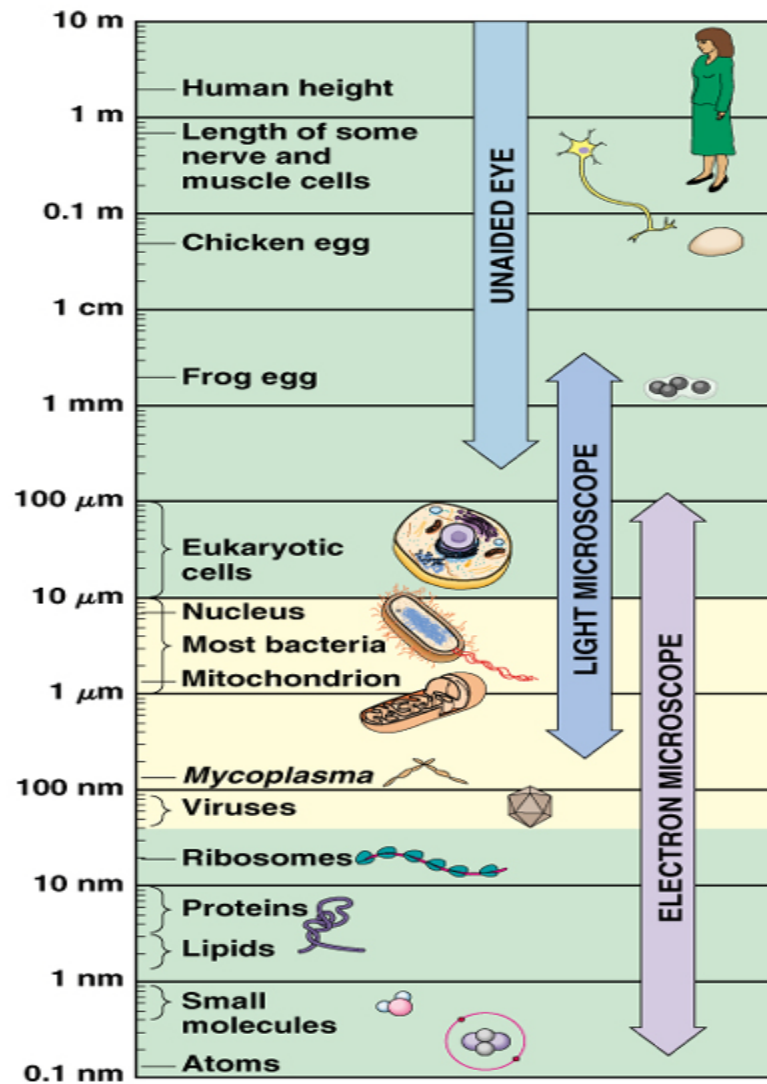


Collagen is main components of Extracellular Matrix, which make up all soft tissues consists proteins such as Collagen, Cadherins, Focal adhesion kinase, fibronectin and laminin form distinct tissue-specific networks that regulate the cell comporment.





# Scale



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# Characteristic Atomic Bonds

Bonding Energy				
Bonding Type	Substance	kJ/mol	eV/Atom, Ion, Molecule	Melting Temperature (°C)
Ionic	NaCl	640	3.3	801
	MgO	1000	5.2	2800
	Si	450	4.7	1410
Covalent	C (dia)	713	7.4	>3550
	Hg	68	0.7	-39
	Al	324	3.4	660
Metallic	Fe	406	4.2	1538
	W	849	8.8	3410
van der Waals	Ar	7.7	0.08	-189
	Cl <sub>2</sub>	31	0.32	101
Hydrogen	NH <sub>3</sub>	35	0.36	-78
	H <sub>2</sub> O	51	0.52	0

Adapted from: Fundamentals of Materials Science and Engineering / An Introduction," William D. Callister, Jr., John Wiley & Sons, NY, NY, 2001 or <http://www.scribd.com/doc/8680373/Fundamentals-of-Materials-Science-and-Engineering-Callister>

# Carbon: Molecules of Life

# Organic Molecules

- All molecules of life are built with carbon atoms
- We correctly call carbon the signature atom of life and living forms, past and present
- We can use different models to highlight different aspects of the same molecule

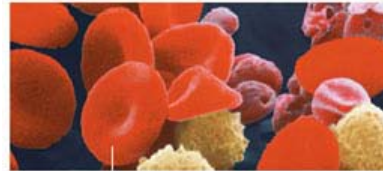
# Carbon – The Stuff of Life

- **Organic** molecules are complex molecules of life, built on a framework of carbon atoms – all the biological macromolecules below have a carbon backbone – the first two are rigid; proteins are uniquely flexible, and nucleic acids make up the DNA and RNA of heredity
  - Carbohydrates
  - Lipids
  - Proteins
  - Nucleic acids

# Carbon – The Stuff of Life

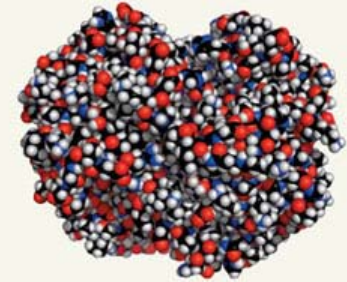
- Carbon atoms can be assembled and remodeled into many organic compounds
  - Can bond with one, two, three, or four atoms  
(only four because of electrons in outer V-shell)
  - Can form polar or nonpolar bonds
  - Can form chains or rings

# Three Models of a Hemoglobin Molecule

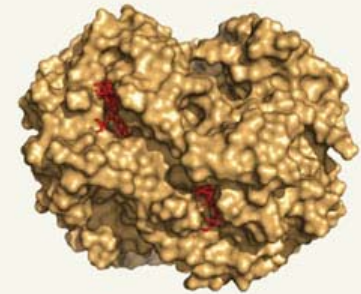


red blood cell

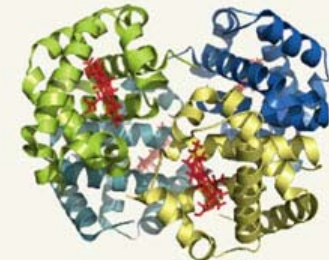
It's a protein and you can see the twists and coils and flex shapes.



**A** A space-filling model of hemoglobin shows the complexity of the molecule.



**B** A surface model of the same molecule reveals crevices and folds that are important for its function. Heme groups, in red, are cradled in pockets of the molecule.



**C** A ribbon model of hemoglobin shows all four heme groups, also in red, held in place by the molecule's coils.

# From Structure to Function

- The function of organic molecules in biological systems begins with their structure
- The building blocks of carbohydrates, lipids, proteins, and nucleic acids bond together in different arrangements to form different kinds of complex molecules



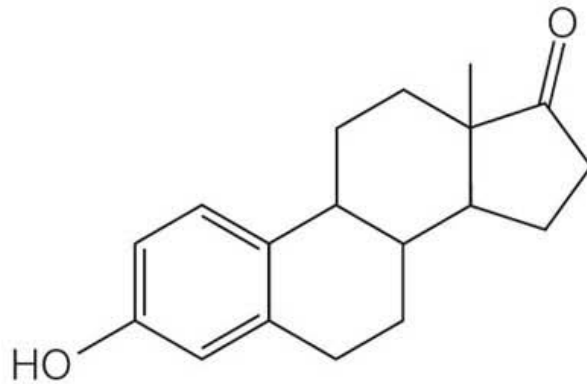
# Functional Groups

- **Hydrocarbon**
  - An organic molecule that consists only of hydrogen and carbon atoms
- Most biological molecules have at least one **functional group** (A cluster of atoms that imparts specific chemical properties to a molecule ex. polarity, acidity)

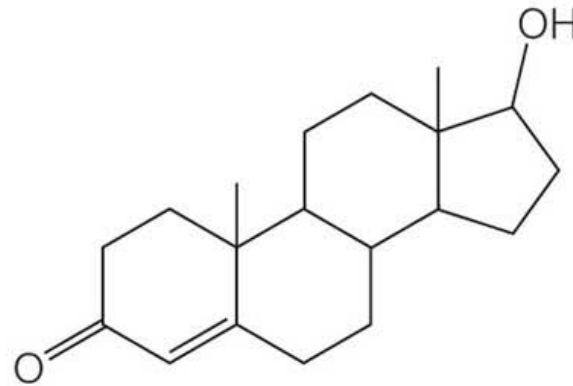
# Common Functional Groups in Biological Molecules

Group	Character	Location	Structure
hydroxyl	polar	amino acids; sugars and other alcohols	—OH
methyl	nonpolar	fatty acids, some amino acids	$\begin{array}{c} \text{H} \\   \\ -\text{C}-\text{H} \\   \\ \text{H} \end{array}$
carbonyl	polar, reactive	sugars, amino acids, nucleotides	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{H} \end{array} \quad \begin{array}{c} \text{O} \\    \\ -\text{C}- \end{array}$ (aldehyde) (ketone)
carboxyl	acidic	amino acids, fatty acids, carbohydrates	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{OH} \end{array} \quad \begin{array}{c} \text{O} \\    \\ -\text{C}-\text{O}^- \end{array}$ (ionized)
amine	basic	amino acids, some nucleotide bases	$\begin{array}{c} \text{H} \\   \\ -\text{N}-\text{H} \\   \\ \text{H} \end{array} \quad \begin{array}{c} \text{H} \\   \\ -\text{NH}^+ \\   \\ \text{H} \end{array}$ (ionized)
phosphate	high energy, polar	nucleotides (e.g., ATP); DNA and RNA; many proteins; phospholipids	$\begin{array}{c} \text{O}^- \\   \\ -\text{O}-\text{P}-\text{O}^- \\    \\ \text{O} \end{array} \quad \text{P icon}$
sulfhydryl	forms disulfide bridges	cysteine (an amino acid)	$-\text{SH} \quad -\text{S}-\text{S}-$ (disulfide bridge)

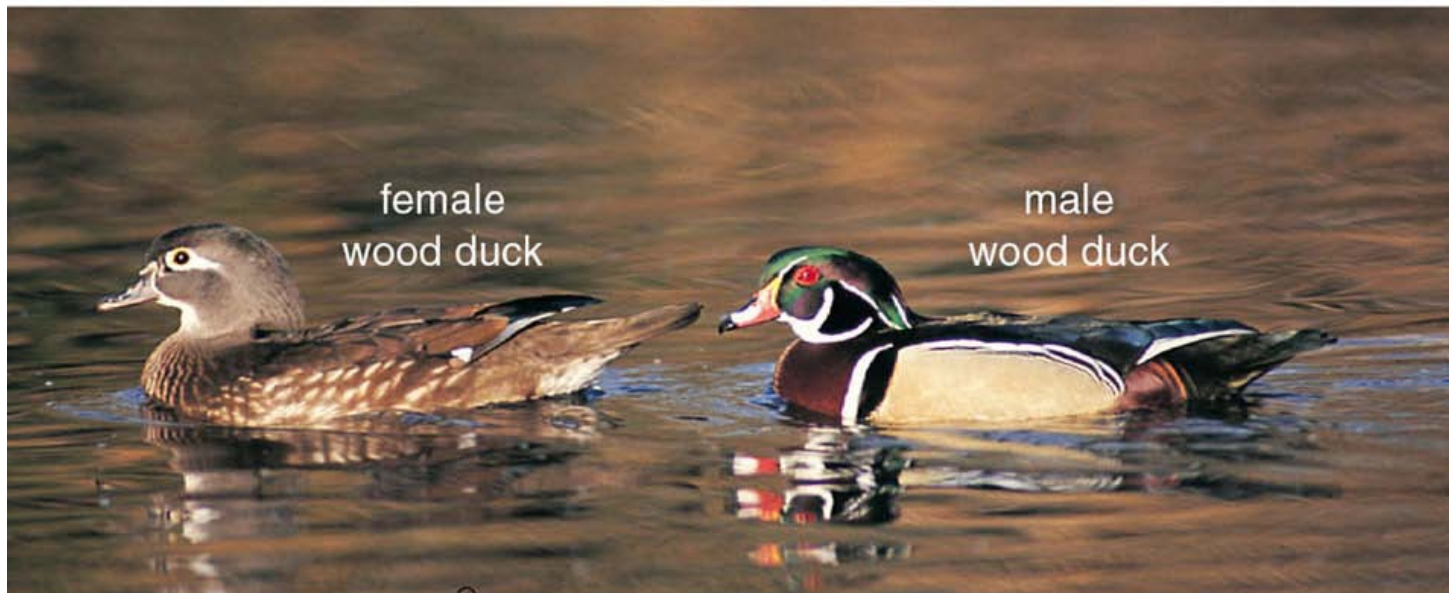
# Effects of Functional Groups: Sex Hormones



one of the estrogens



testosterone



## *Key Concepts:*

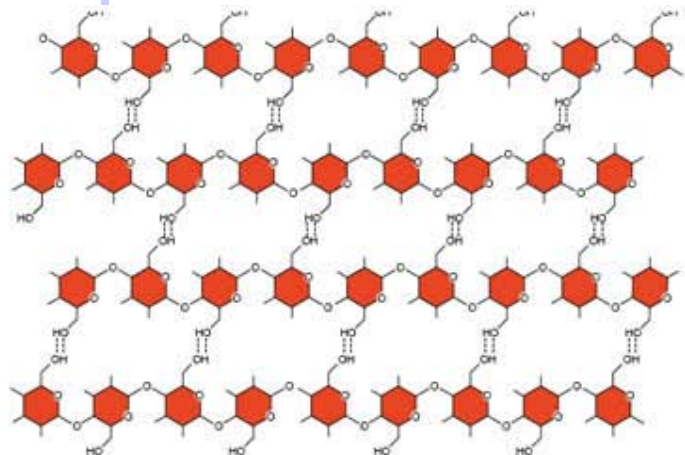
# Carbohydrates

- *Carbohydrates are the most abundant biological molecules*
- *They function as energy reservoirs and structural materials*
- *Different types of complex carbohydrates are built from the same subunits of simple sugars, bonded in different patterns*

# Complex Carbohydrates

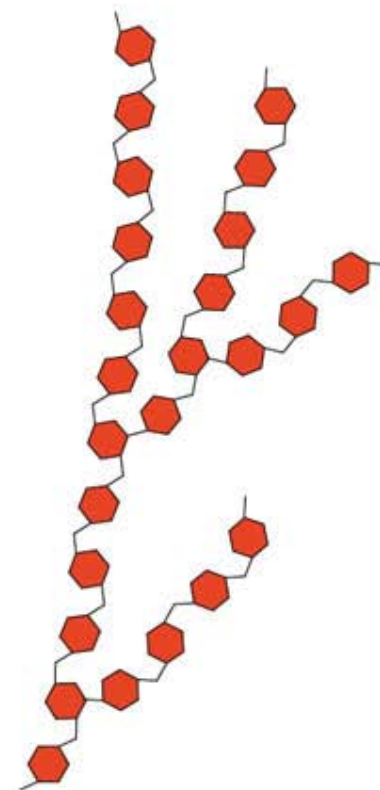
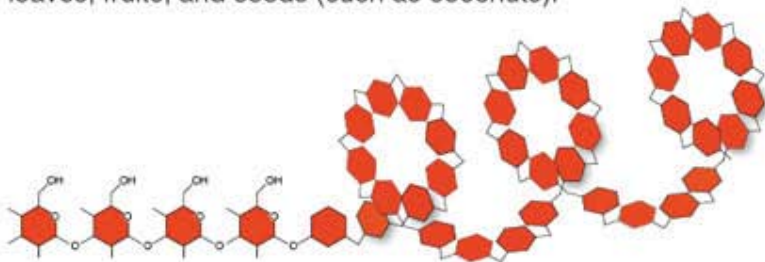
- Polysaccharides
  - Straight or branched chains of many sugar monomers
- The most common polysaccharides are cellulose, starch, and glycogen
  - All consist of glucose monomers
  - Each has a different pattern of covalent bonding, and different chemical properties

# Cellulose, Starch, and Glycogen



**a** Cellulose, a structural component of plants. Chains of glucose units stretch side by side and hydrogen bond at many —OH groups. The hydrogen bonds stabilize the chains in tight bundles that form long fibers. Very few types of organisms can digest this tough, insoluble material.

**b** In amylose, one type of starch, a series of glucose units form a chain that coils. Starch is the main energy reserve in plants, which store it in their roots, stems, leaves, fruits, and seeds (such as coconuts).



**c** Glycogen. In animals, this polysaccharide functions as an energy reservoir. It is especially abundant in the liver and muscles of active animals, including people.

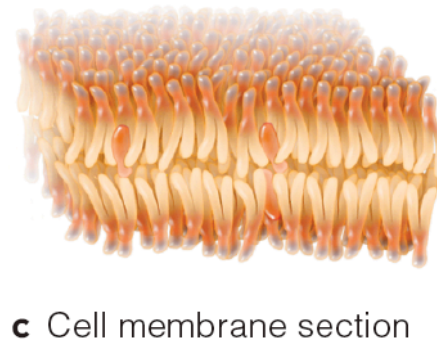
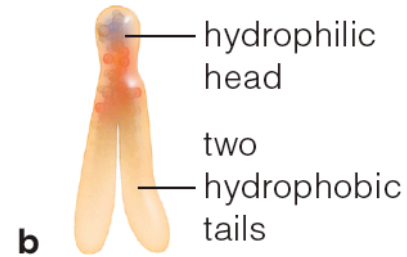
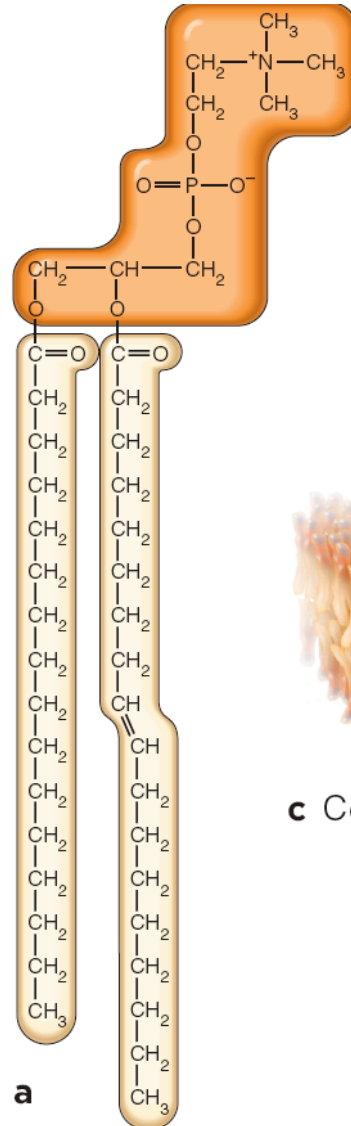


# Phospholipids

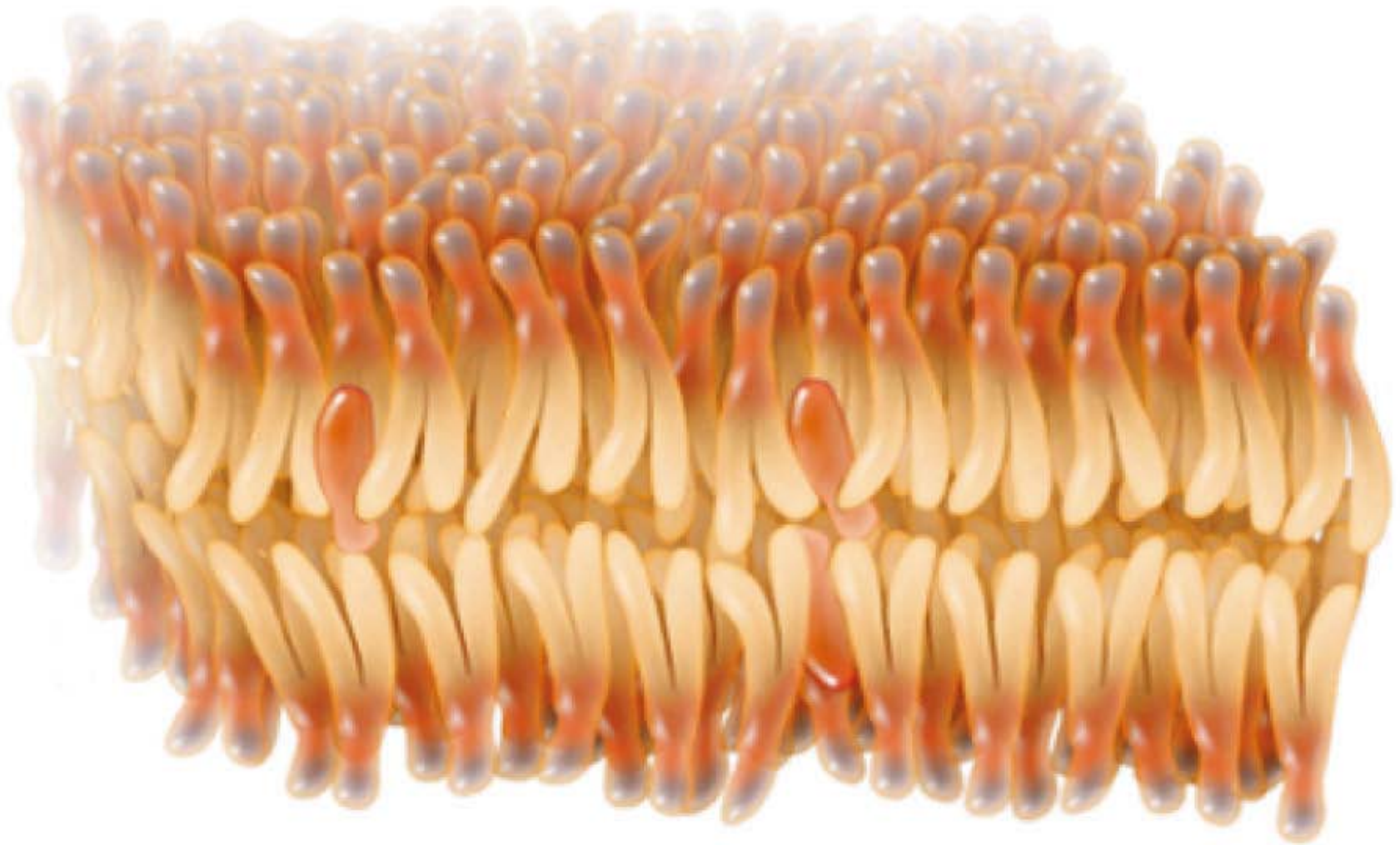
- **Phospholipids**

- Molecules with a polar head containing a phosphate and two nonpolar fatty acid tails
- Heads are hydrophilic, tails are hydrophobic
- The most abundant lipid in cell membranes
- Note that it is a double layer with the hydrophilic heads points “out” while hydrophobic tails are “in”

# Phospholipid Structure





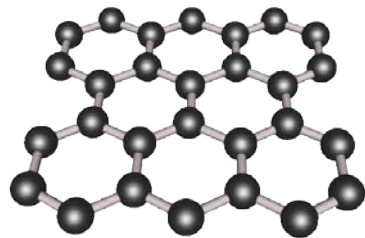


**Cell membrane section**

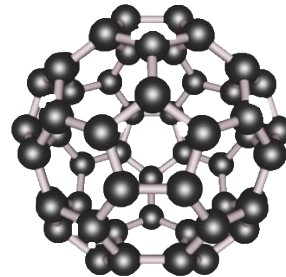
# *When people talk about Nanoscience, many start by describing **things***

Physicists and Material Scientists point to **things** like new nanocarbon materials:

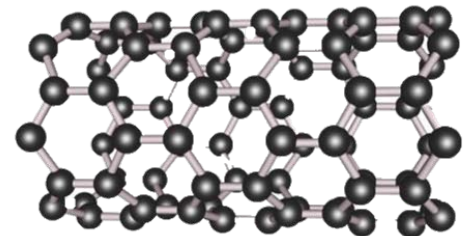
They effuse about nanocarbon's strength and electrical properties



Graphene

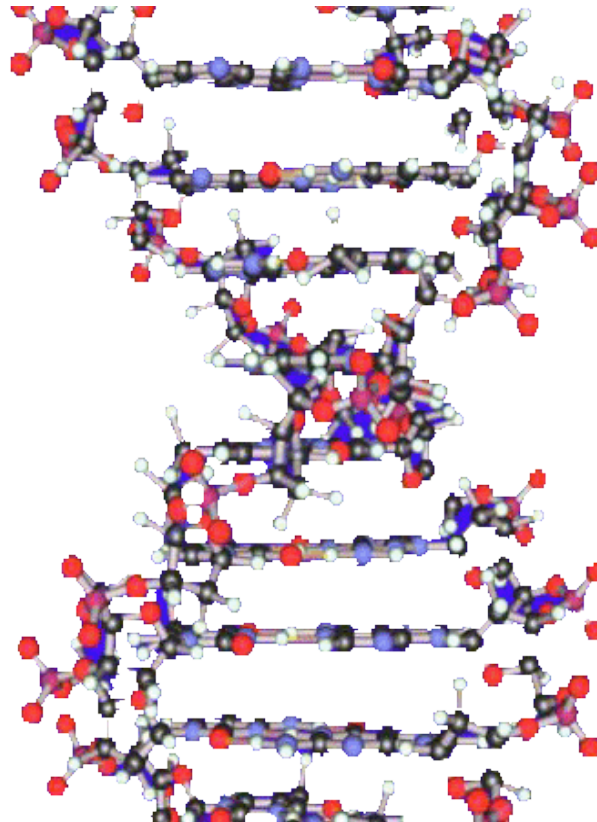


C60 Buckminster Fullerene

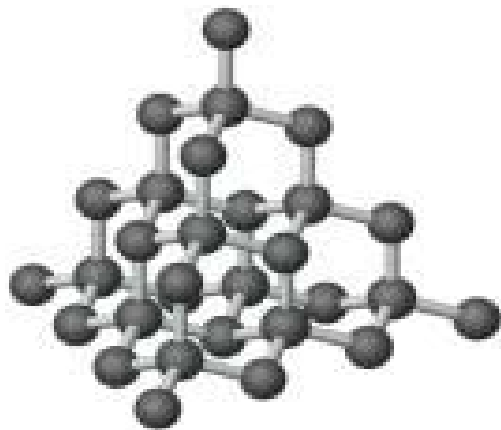


Carbon Nanotube

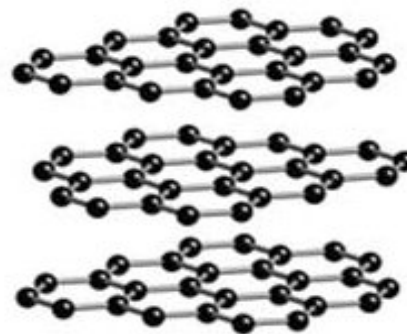
Biologists counter that nanocarbon is a recent discovery  
THEY'VE been studying DNA and RNA for *much* longer  
(And are *already* using it to transform our world)



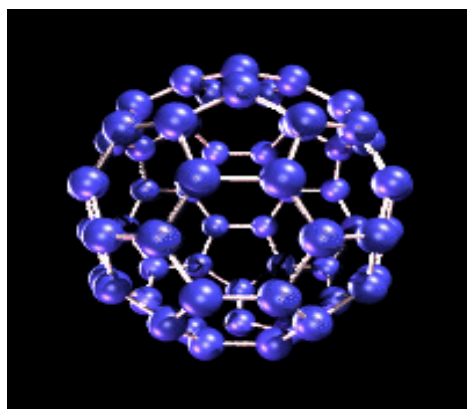
# Different forms of elemental carbon: from diamond to graphite to *buckyballs*!



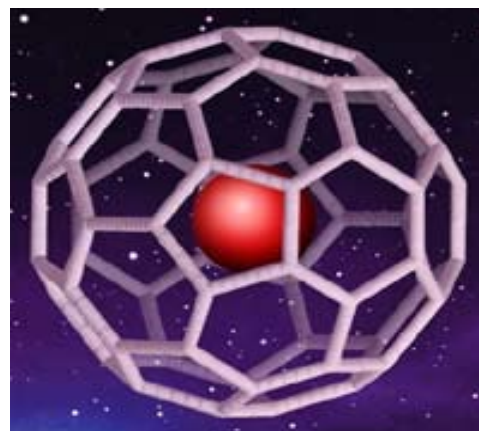
Diamond



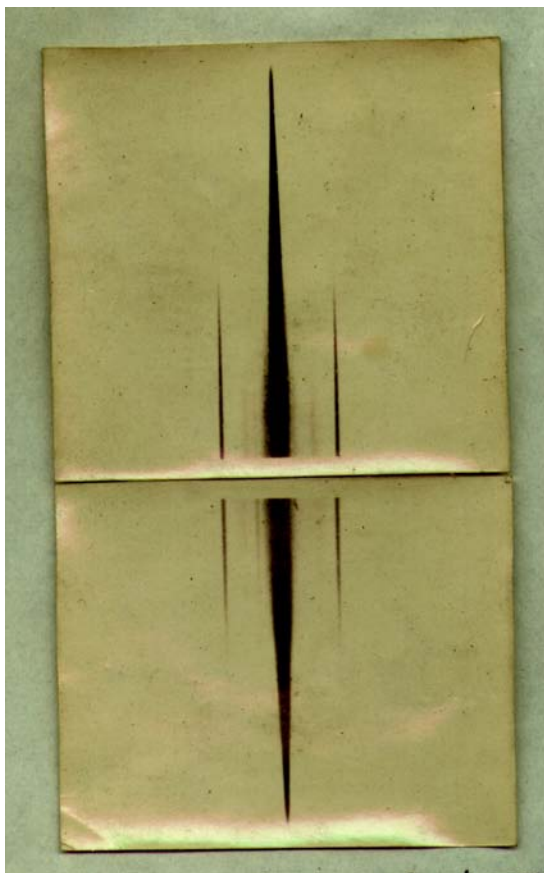
Graphite



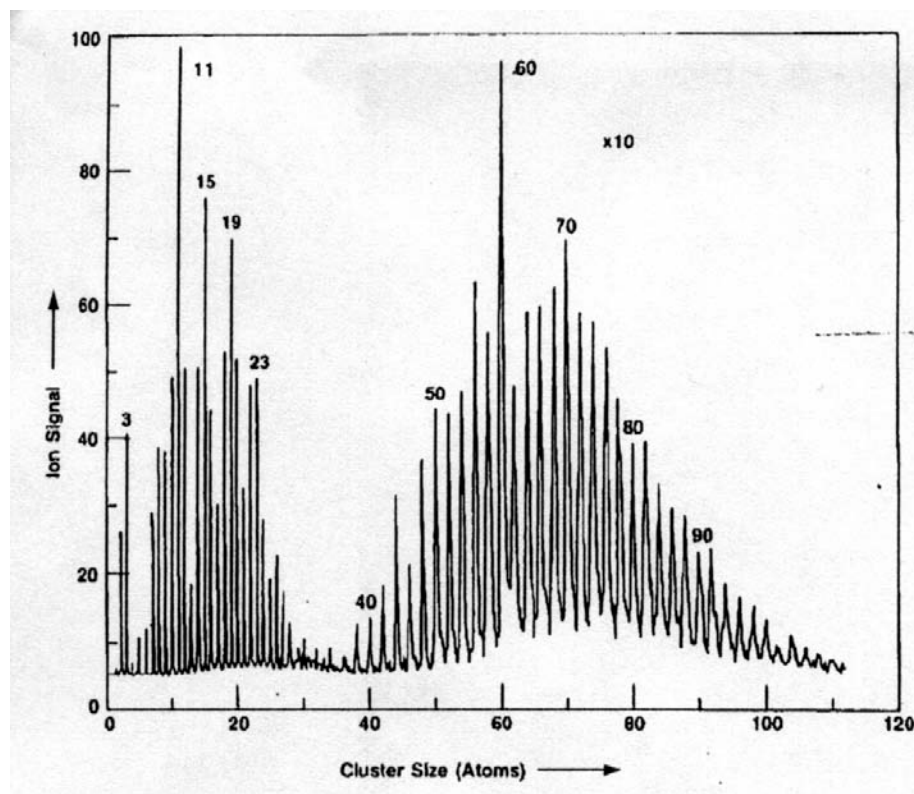
$C_{60}$



$H_2@C_{60}$



Discovery of Deuterium  
Nobel Prize: 1934

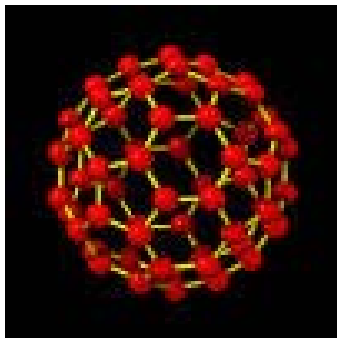


Discovery of  $C_{60}$   
Nobel Prize: 1996

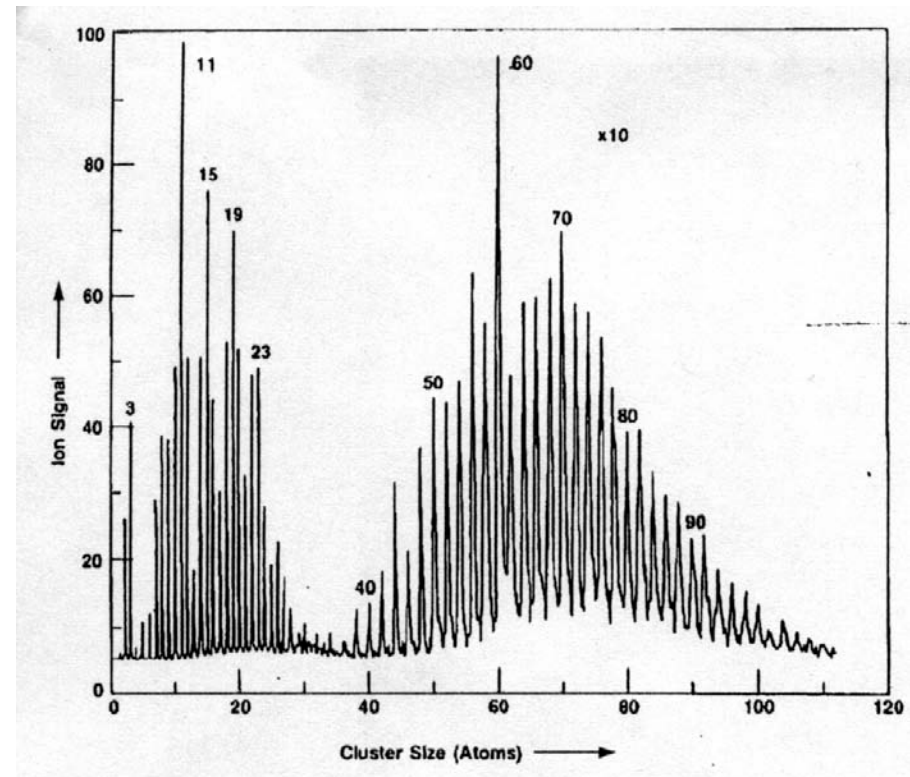


An Extraordinary Claim:  
Carbon can exist in an  
elemental form that has a  
structure reminiscent to a  
soccer ball.

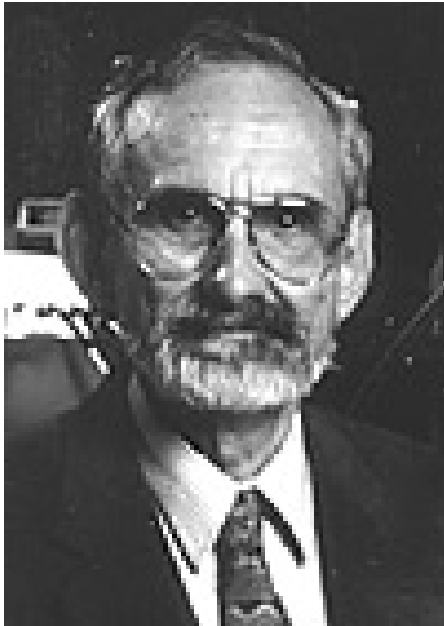
Discovery of  $C_{60}$   
"Buckyballs"  
Pathological Science or  
Revolutionary Science?



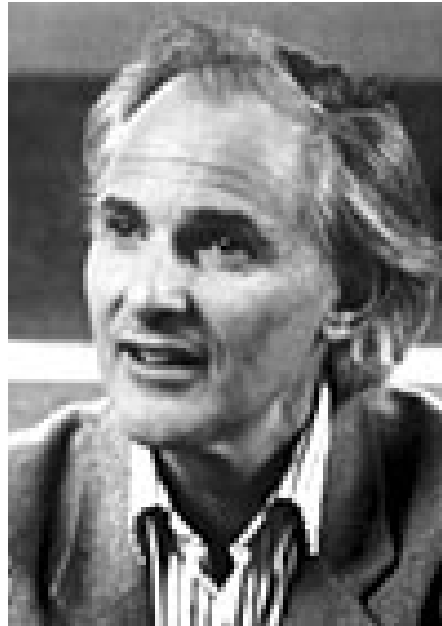
The first "evidence" for  
the special stability of  
 $C_{60}$



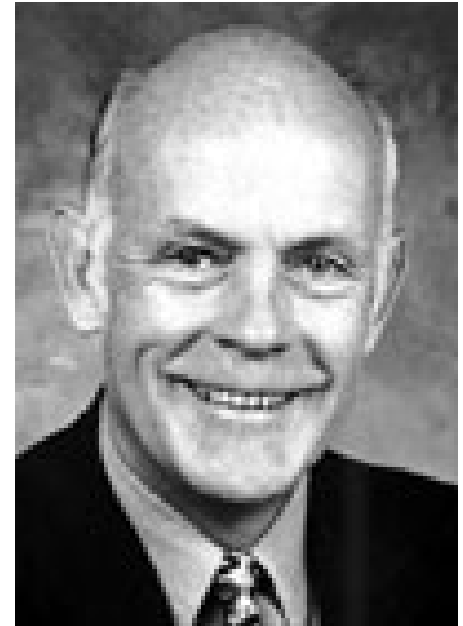
Would you have predicted a Nobel Prize?



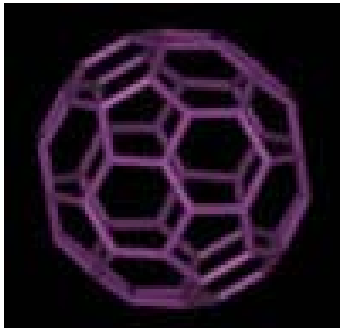
Robert Curl



Harold Kroto



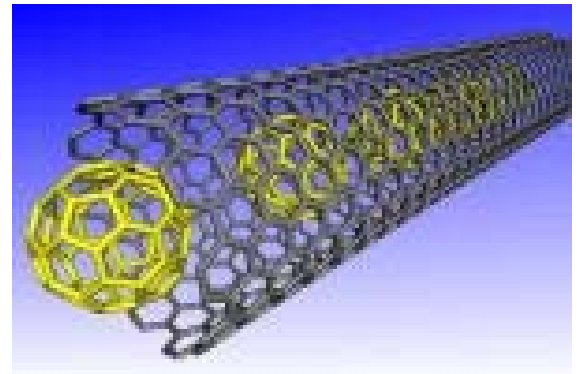
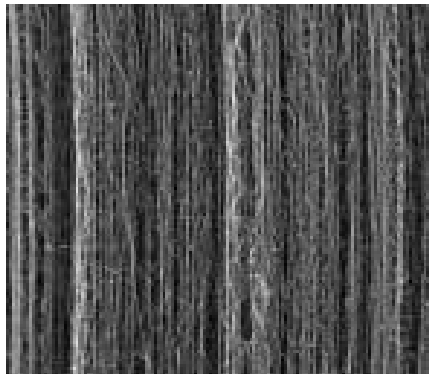
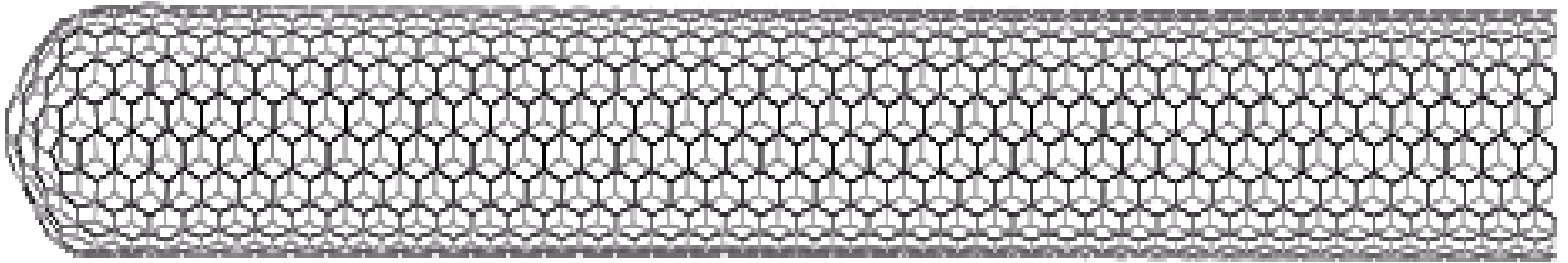
Richard Smalley



The Nobel Prize in Chemistry 1996  
“for the discovery of fullerene”

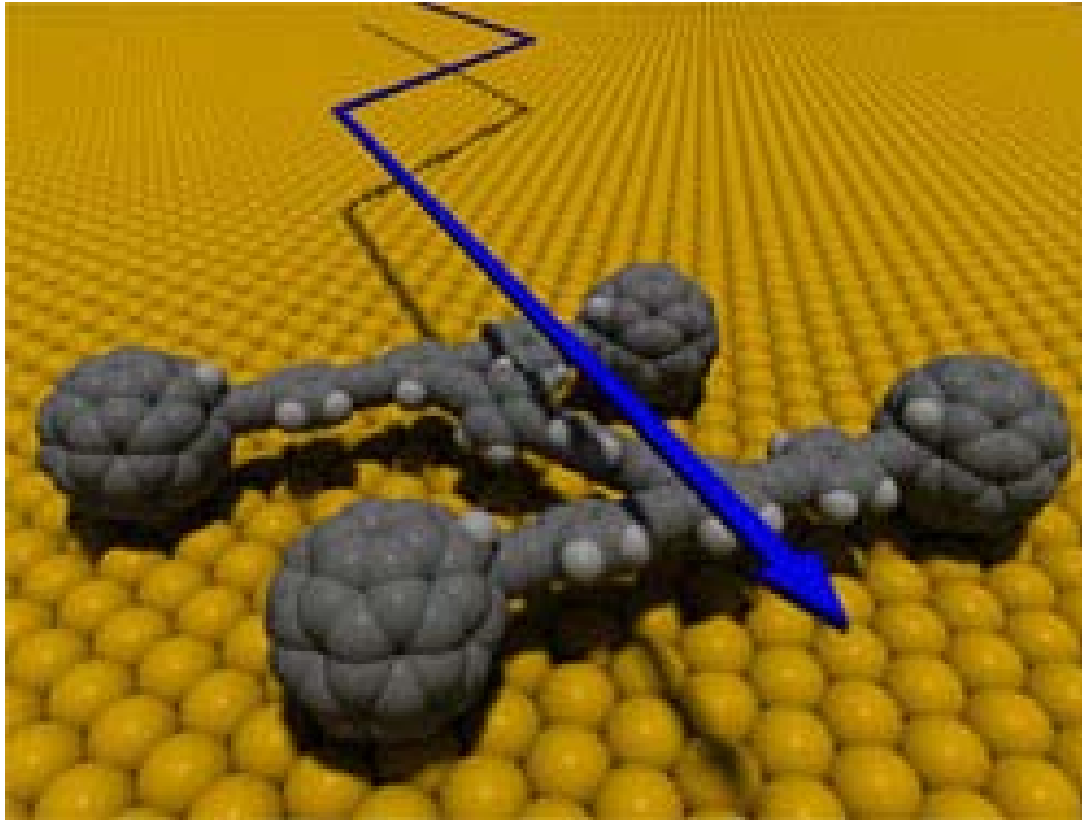
The proposal of Buckeyballs turned out  
to be *revolutionary* science

# Buckyballs pulled into nanowires: Carbon nanotubes!



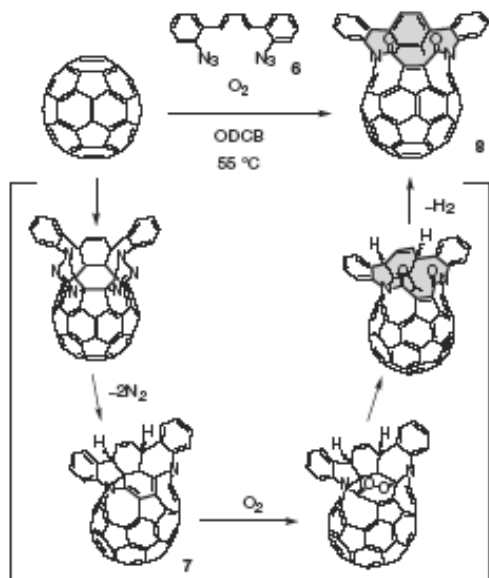


# Nanodevices: A carbon nanocar rolling on a gold surface

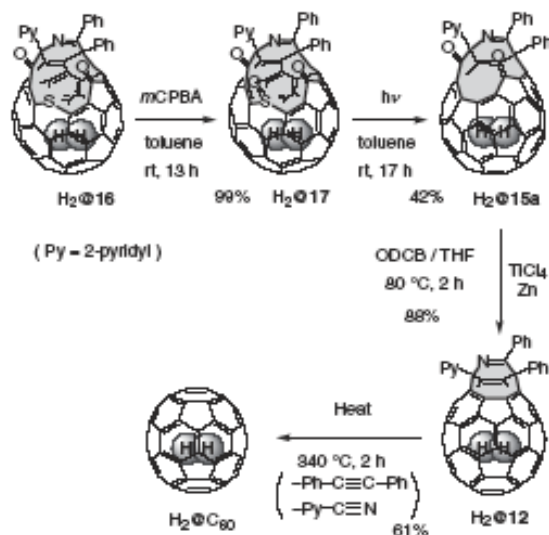


Thanks to Whitney Zoller

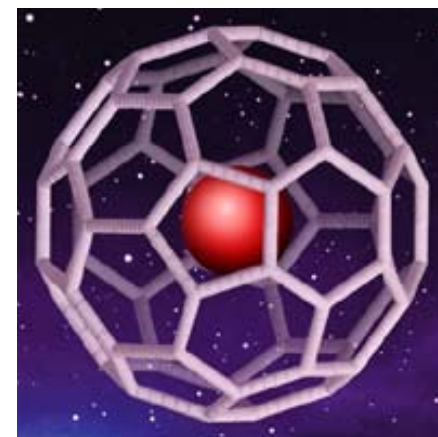
# Putting $H_2$ inside a buckyball!



# Open the buckyball

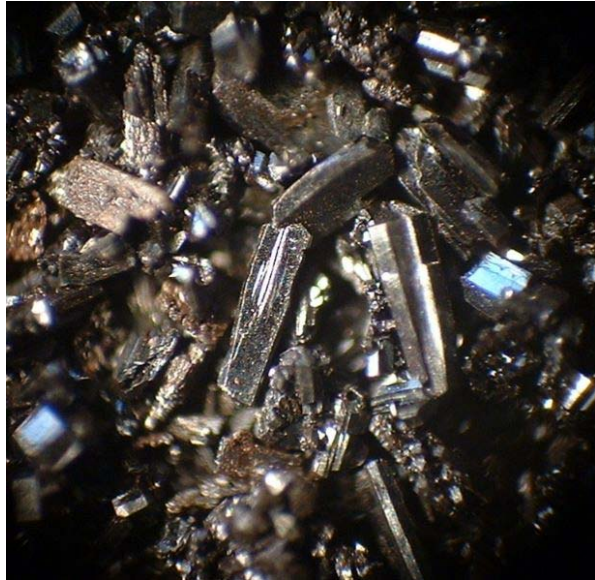


Put in H<sub>2</sub>, then close  
buckyball


$$H_2@C_{60}$$

Collaborator: Professor Koichi Komatsu (Kyoto University)

# Bit More About Buckyballs

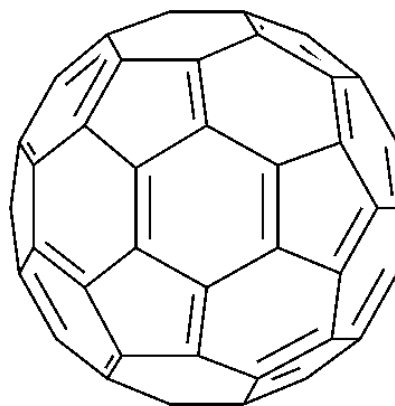
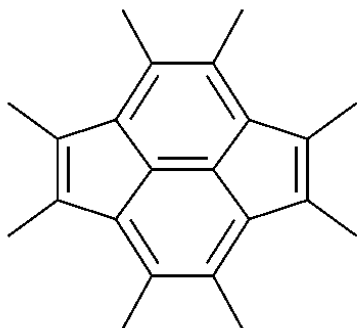


- Buckyballs are also called fullerenes (after architect Richard Buckminster Fuller)
- Buckyballs were discovered in 1985 by Robert Curl, Harold Kroto and Richard Smalley
  - these scientists won the 1996 Nobel Prize in Chemistry for discovering this new allotrope of carbon.

Buckyballs in crystalline form

# The Structure of C<sub>60</sub>

- 12 pentagons surrounded by 20 hexagons (corannulene substructure)
  - Two types of ring junctions (6,6 and 5,6)
  - Isolated pentagon rule (pyracylene subunits)



# Important Properties of C<sub>60</sub>

- Structural
  - Unique geometry
    - High symmetry
    - Closed, spherical structure
  - 7 Å diameter—can encapsulate other atoms
- Electronic
  - Small HOMO-LUMO bandgap (3 degenerate orbitals form LUMO)
    - Easily reduced by up to 6 electrons
  - Strongly electronegative
  - Highly conjugated, but not “superaromatic”
    - Bent  $\pi$  bonds reduce conjugation
- Photosensitizer

# Low Solubility of C<sub>60</sub>

- Highly hydrophobic molecule
  - Limited solubility in many organic solvents
  - Completely insoluble in water

Solvent	Solubility (μg/mL)
<b>Water</b>	--
hexane	40
Dioxane	41
cyclohexane	51
carbon tetrachloride	447
Benzene	1,440
toluene	2,150
carbon disulfide	5,160

# Outline

- Approaches to water-soluble C<sub>60</sub>
  - Non-covalent
  - Covalent
- Biological applications of C<sub>60</sub> derivatives
  - HIV-1 protease (HIVP) inhibition
  - Neuroprotective properties
  - Antibacterial properties
  - Gene transfection and related properties
- Toxicity of C<sub>60</sub> and derivatives
  - Pristine C<sub>60</sub> (unmodified)
  - Functionalized C<sub>60</sub>
- Conclusions and Outlook

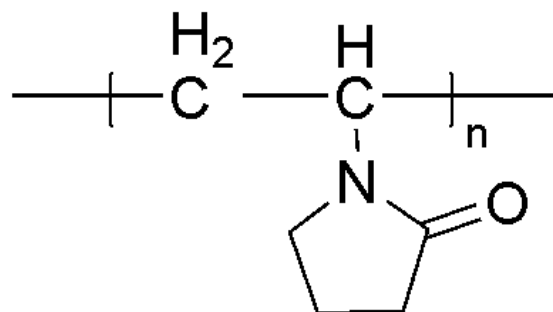
# Water-Soluble C<sub>60</sub>

- Pristine C<sub>60</sub> can be suspended in water
- Biological uses of fullerenes require genuine water solubility and little or no aggregation
- Complexation with water-soluble supramolecules is one effective approach
  - Surfactants
  - Polyvinylpyrrolidone (PVP)
  - Cyclodextrins



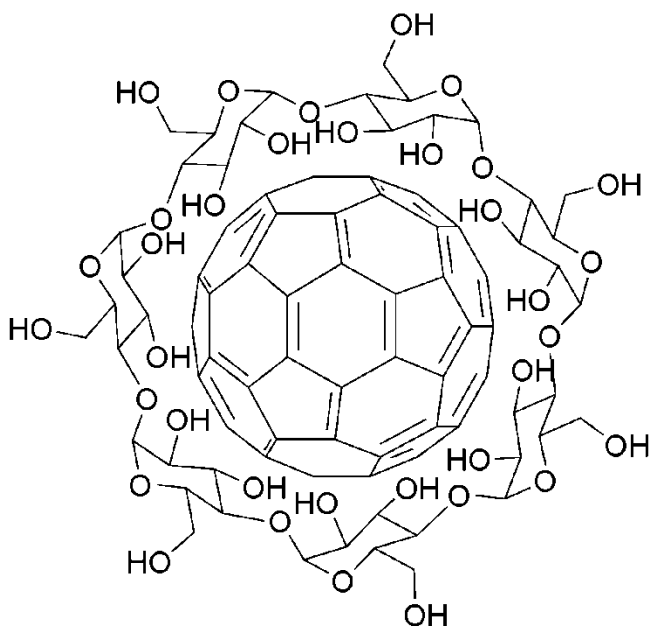
# Non-Covalent Methods: C<sub>60</sub>-PVP Solutions

- PVP is a dispersant used in cosmetics and medicines.
- C<sub>60</sub>-toluene mixed with PVP-chloroform, solvents evaporated, and residue dissolved in water
  - Highest [C<sub>60</sub>] obtained was 400 µg/mL, using 100:0.8 PVP:C<sub>60</sub> w/w

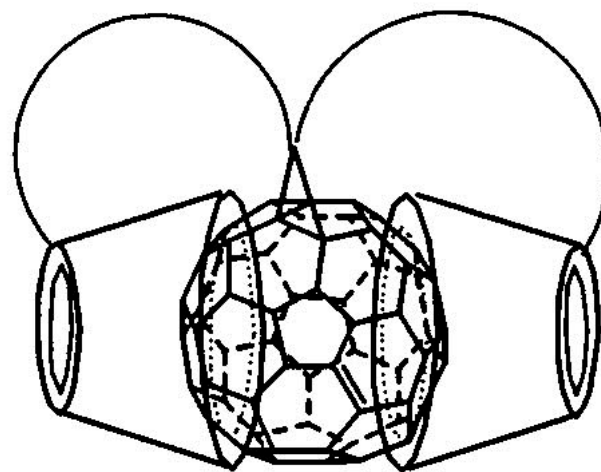


# C<sub>60</sub>-Cyclodextrin Complexes

- Non-covalent or covalent complexes enhance water solubility
  - Aggregation phenomena encountered with 1:1 complexes



$\gamma$ -cyclodextrin



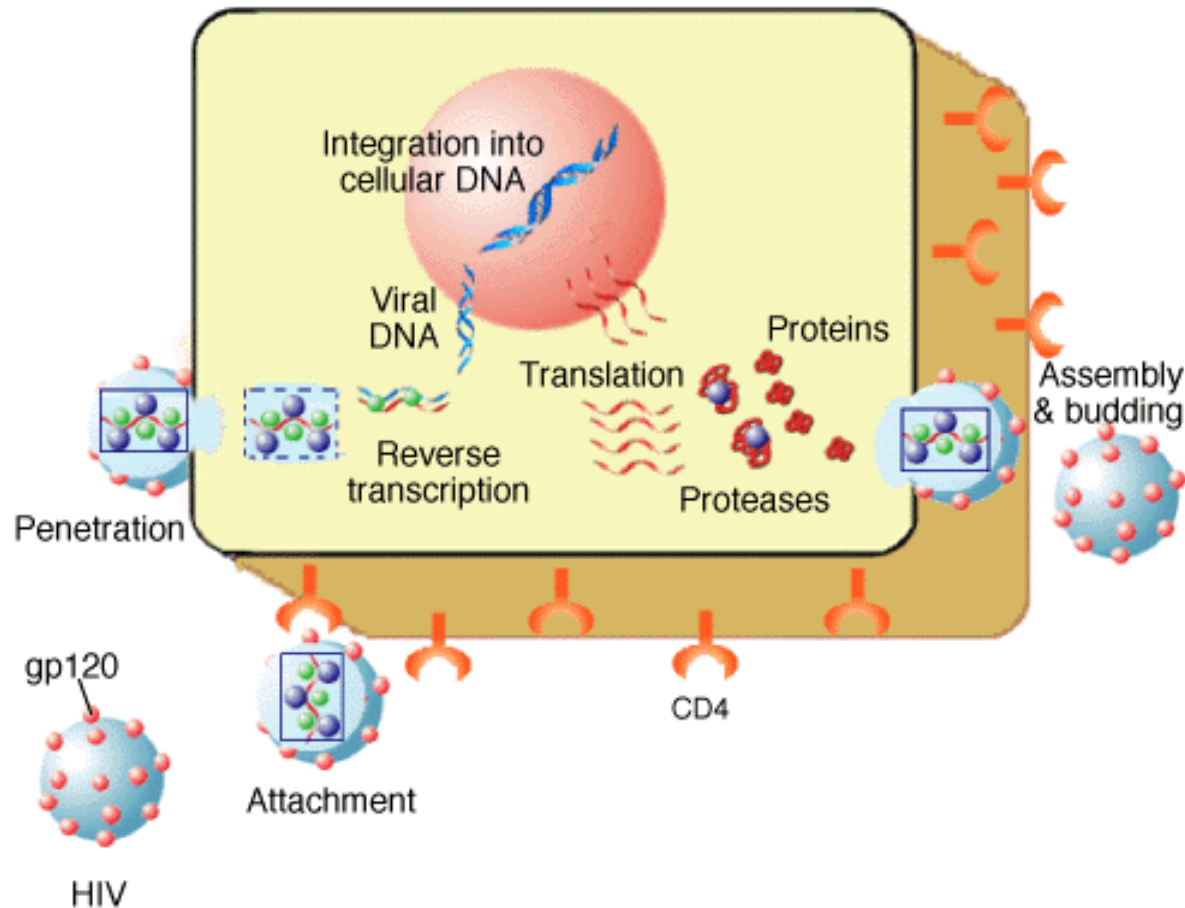
$\beta$ -cyclodextrin

Andersson, T. et al. *Chem. Comm.* **1992**, 604-606; Filippone, S. et al. *Chem Comm.* **2002**, 1508-1509;  
Liu, Y. et al. *Tetrahedron Lett.* **2005**, 46, 2507-2511; Chen, Y. et al. *Tetrahedron* **2006**, 62, 2045-2049. 50

# Overview of Biological Activities of C<sub>60</sub> Derivatives

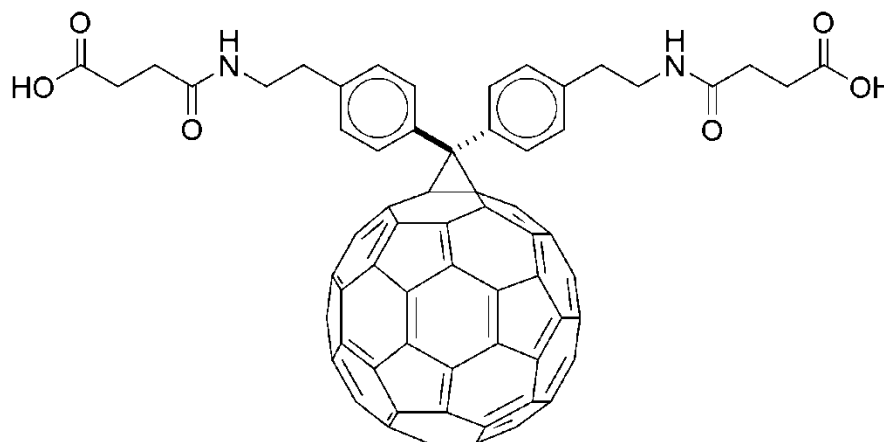
- Antioxidant
- DNA cleavage
- Membrane disruption
- Photodynamic therapy
- Drug delivery (e.g. paclitaxel)
- X-ray contrast agents
- Inhibition of  $\beta$ -amyloid aggregation
- **Free radical sponge**
  - Neuroprotection
- **Antibacterial**
- **Gene transfection**
- **Enzyme inhibition (HIVP, etc.)**
- **And more...**

# Life Cycle of the HIV Retrovirus



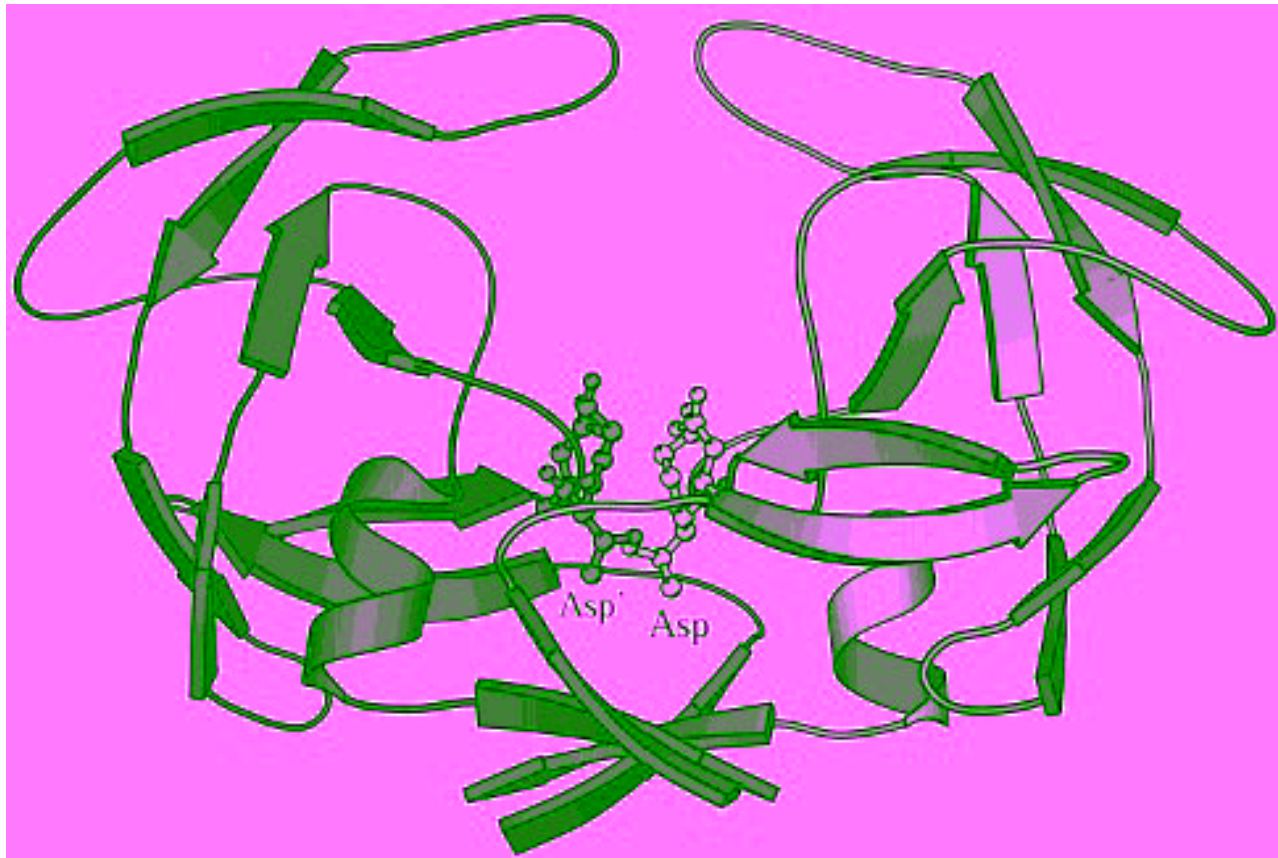
# First Discovery of Biological Activity of a Fullerene

- Hydrophobic, 7-8 Å binding pocket of HIV-1 protease (HIVP) is an attractive target for fullerene inhibition
  - Computational analysis suggested C<sub>60</sub> fits snugly in the active site of HIVP
- Properties
  - $K_i = 5.3 \mu\text{M}$  (Best inhibitors are nanomolar or lower)
  - Toxic even against drug-resistant HIV-variants



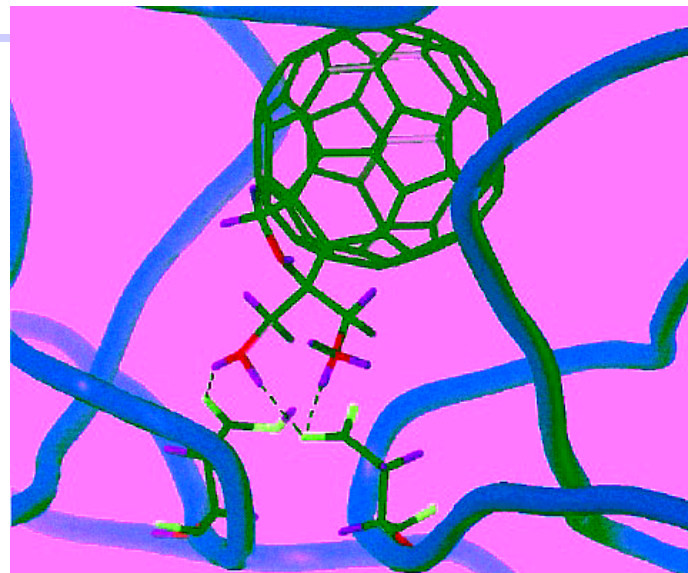
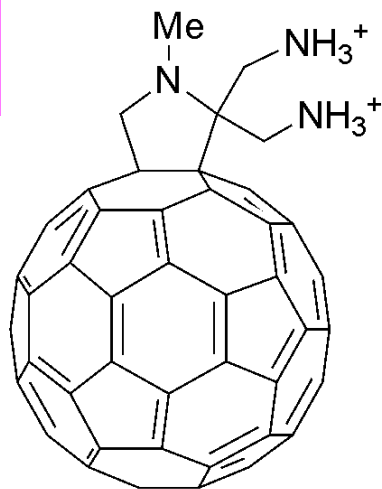
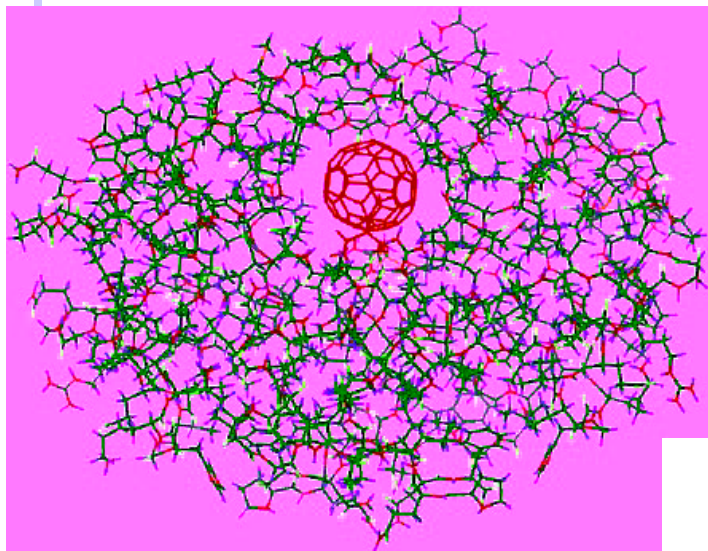
The first fullerene-based inhibitor of an enzyme

# Improving HIVP Inhibitors



Zhu, Z. et al. *Biochemistry* **2003**, 42, 1326-1333.

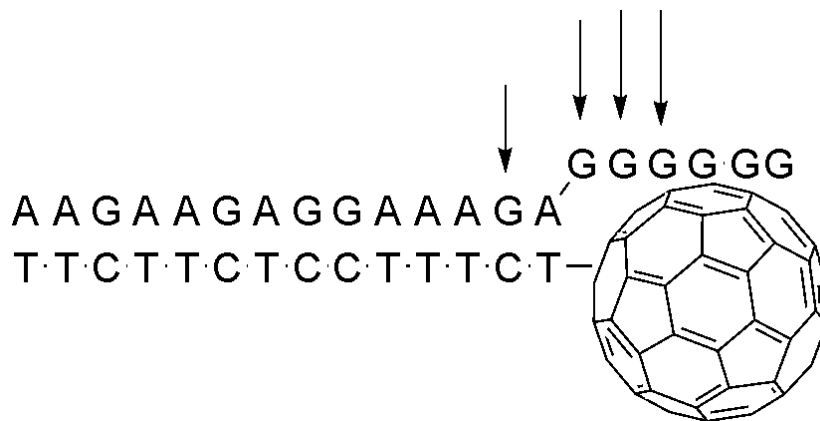
# Improving HIVP Inhibitors



Marcorin, G.L. et al. *Org. Lett.* **2000**, 2, 3955-3958.

# C<sub>60</sub> and DNA

- Water-soluble fullerenes oxidatively cleave DNA when photo-excited
  - C<sub>60</sub>-oligonucleotide complexes enable site-selective cleavage (at G sites) and water solubility
  - Potentially applicable to photodynamic therapy (PEG derivatives)



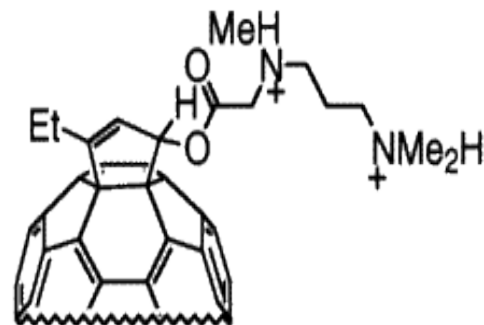
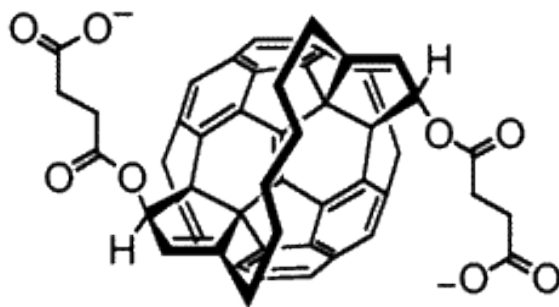
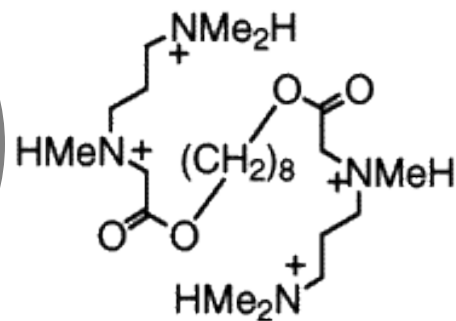
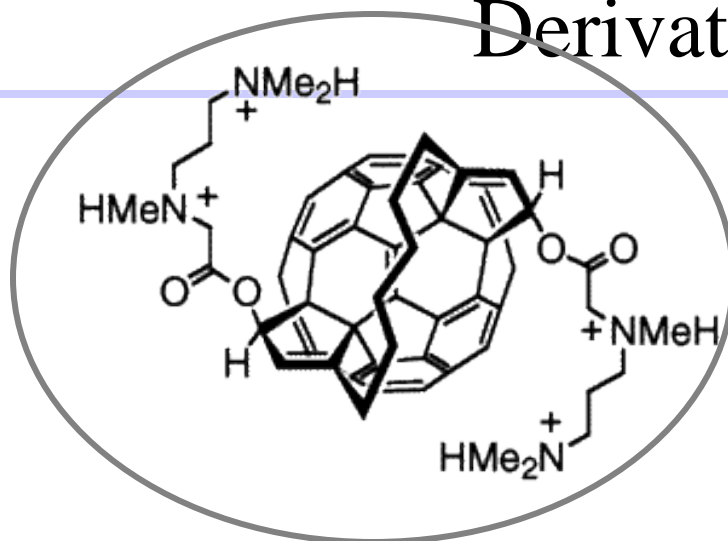
- Can water-soluble fullerene derivatives be synthesized that will bind DNA and transport it through cell membranes, without damaging it?



# Gene Transfection

- Common methods
  - Microinjection
  - Viral vectors (short DNA)
  - Chemical methods
    - Cationic lipids and polymers
    - Commercial reagents for transfection are available
- Discovery of other methods could reduce cytotoxicity and enhance efficiency and reliability of transfection methods

# Non-Viral Gene Delivery with C<sub>60</sub> Derivatives



Nakamura, E. et al. *Angew. Chem. Int. Ed. Engl.* **2000**, 39, 4254-4257.

Isobe, H. et al. *Chem. Lett.* **2001**, 1214-1215.

# Non-Viral Gene Delivery with C<sub>60</sub> Derivatives

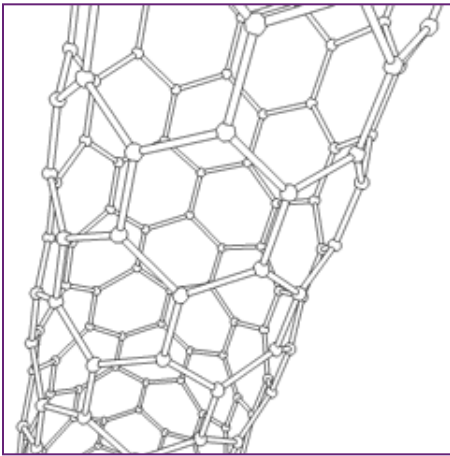
- Fullerene transfection agents proved as good or better than traditional lipofection agents
  - Lower cytotoxicity
  - Higher transfection efficiency
  - Both transient and stable transfection possible
  - Fullerene does not appear to interfere with gene expression (esters cleaved in the cell?)
  - No problems with photo-induced DNA cleavage
- Fullerene transfection agents could be an improvement over viral vectors
  - Not introducing a potentially harmful virus
  - Enable addition of larger nucleotide sequences
- Methodology for large-scale synthesis of related amino-fullerene derivatives could enable commercialization

# Summary

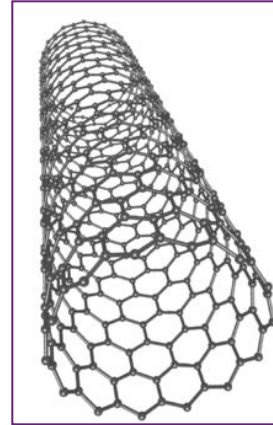
- Unusual properties of the buckyball have generated interest in broadly ranging fields
- Biological applications of fullerenes are broad and rapidly evolving
  - Water-solubility issues have been addressed synthetically
  - Enzyme inhibition, gene transfection, neuroprotection, and other biological applications may become commercially viable

# Nanotubes

- Carbon nanotubes, composed of interlocking carbon atoms, are 1000x thinner than an average human hair – but can be 200x stronger than steel.



# Which Of These Object Are Made From Carbon?



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Water

Diamond

Graphite

Nanotube

Coal

---

# Activity 1

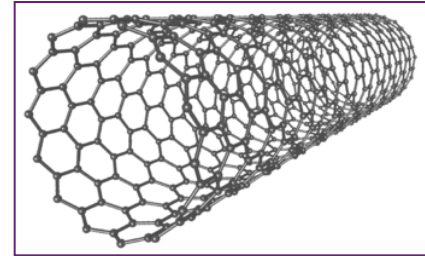
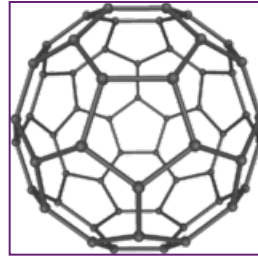
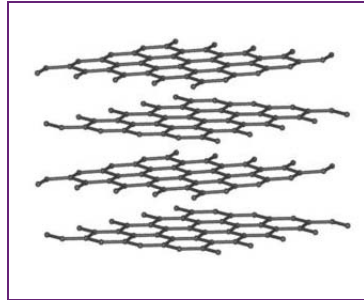
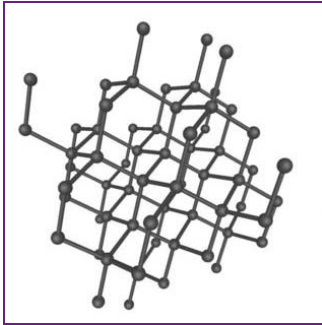
Perform the *Researching Carbon Activity* to learn more about the following allotropes (different forms) of carbon:  
*coal, graphite, diamond, buckyballs, carbon nanotubes.*

# Activity 1 Researching Carbon

Allotrope	Structure	Properties	Uses/ Applications
<b>Coal</b>			
<b>Graphite</b>			
<b>Diamond</b>			
<b>Buckyballs</b>			
<b>Carbon Nanotubes</b>			



Allotropes of carbon have different covalent bonding arrangements.



**diamond**

**graphite**

**buckyball**

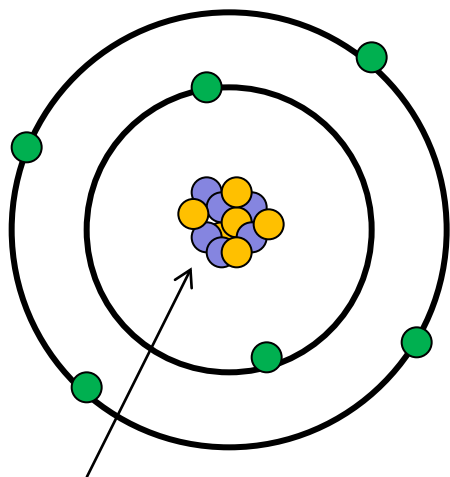
**nanotube**

- Carbon atoms form covalent bonds by sharing outer shell electrons with each other
- Diamond, graphite, buckyballs and carbon nanotubes all have different covalent arrangements of carbon atoms
- The differing covalent arrangements of carbon atoms lead to the different properties of carbon allotropes.

# Covalent Bonding

## Sharing Electrons

- proton
- neutron
- electron



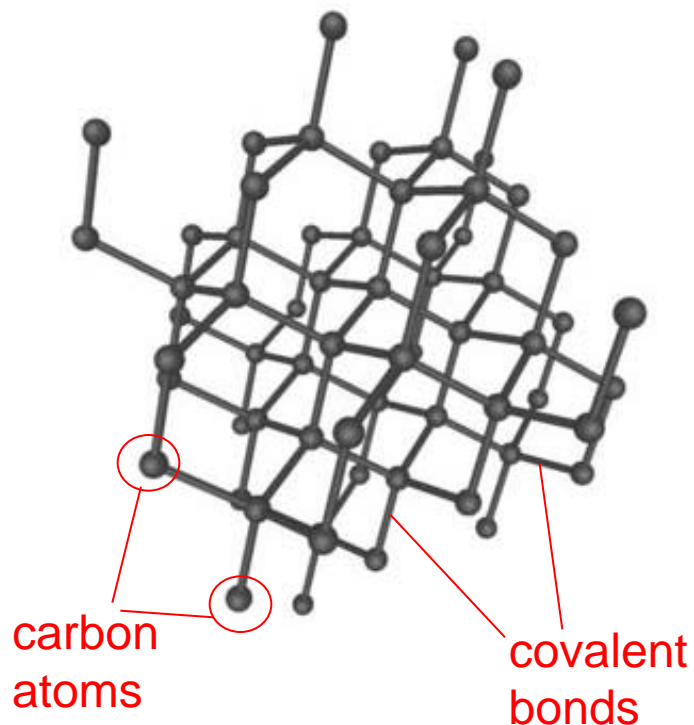
6 protons + 6  
neutrons

A **covalent bond** is a form of chemical bonding that is characterised by the sharing of pairs of electrons between atoms

**Valence electrons** are the electrons in the outer shell or energy level of an atom that form covalent bonds

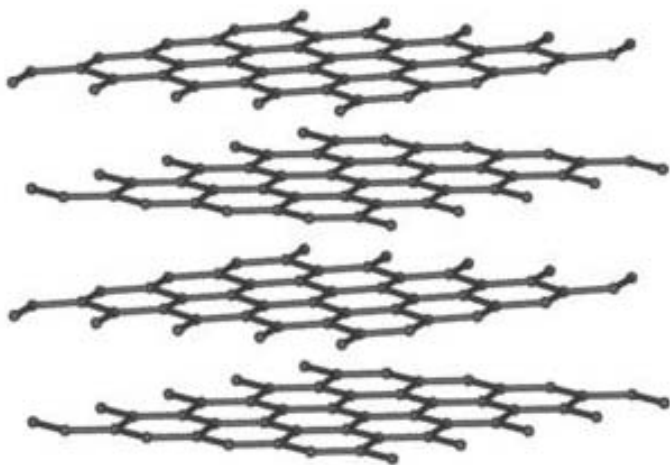
A carbon atom has 6 electrons, 4 of which are Valence electrons  
Therefore, carbon atoms can form up to 4 Covalent Bonds

# Covalent Bonds In Diamond



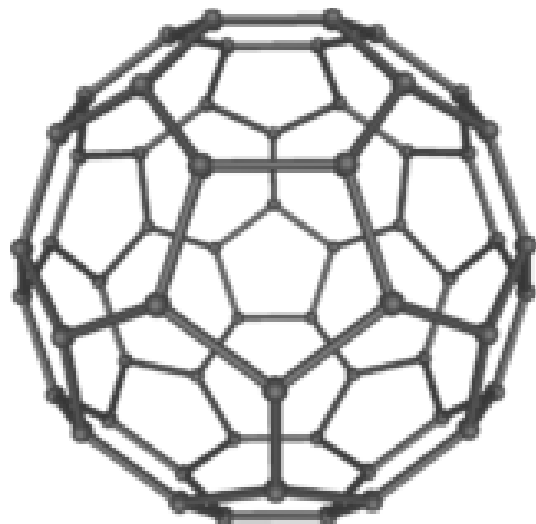
- Diamond is formed by a 3D box-like network of carbon atoms
- The continuous nature of the covalent arrangements forms a giant molecule
- Electrons are fixed.

## Covalent Bonds In Graphite



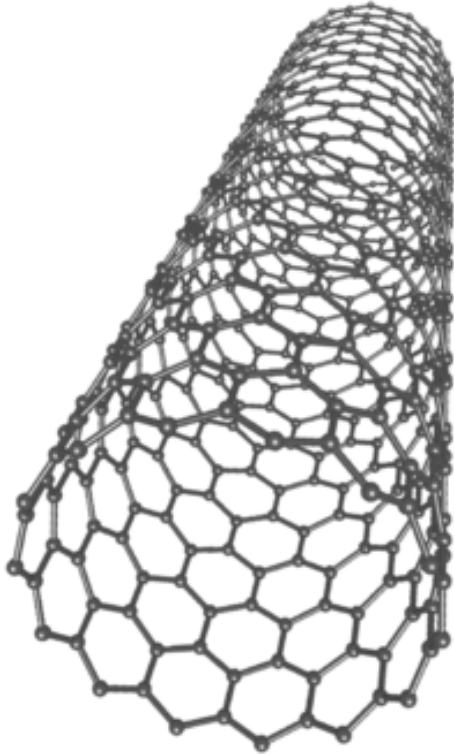
- Graphite is formed by hexagonally-arranged carbon molecules forming 2D layers of sheets
- Electrons are free to move between each carbon sheet.

# Covalent Bonds In Buckyballs



- Carbon atoms in buckyballs are arranged in a soccer ball shape
- C60 Buckyballs have 20 regular hexagon faces and 12 regular pentagon faces
  - these faces come together at 60 carbon atom vertices
- Electrons are localised internally due to the curvature of the structure.

# Covalent Bonds In Carbon Nanotubes



- Carbon nanotubes are formed by a layer of hexagonally-arranged carbon atoms rolled into a cylinder
  - usually have half buckyballs on one or both ends
- Electrons are localised internally, and some can move along the length of the tube by ballistic transport
- Carbon nanotube diameter  $\sim 1\text{ nm}$
- Carbon nanotube length can be a million times greater than its width
- Nanotubes can be
  - single-walled ( $d = 1\text{-}2\text{ nm}$ ), or
  - multi-walled ( $d = 5\text{-}80\text{ nm}$ ).

# Properties of Carbon Allotropes

Allotrope	Hardness	Tensile strength	Conducts heat	Conducts electricity
<b>Coal</b>	+	+	+	no
<b>Graphite</b>	++	++	+++++	+++++
<b>Diamond</b>	+++++	Not known	+++	no
<b>Buckyballs</b>	+++++	++++	+	+
<b>Carbon Nanotubes</b>	+++++	+++++	+++++	+++++

# Unique Properties Of Carbon Nanotubes

- 200x stronger than steel of the same diameter
- The first synthetic material to have greater strength than spider silk
- Excellent conductors of electricity and heat
- Have huge potential for product development.



Space elevator?

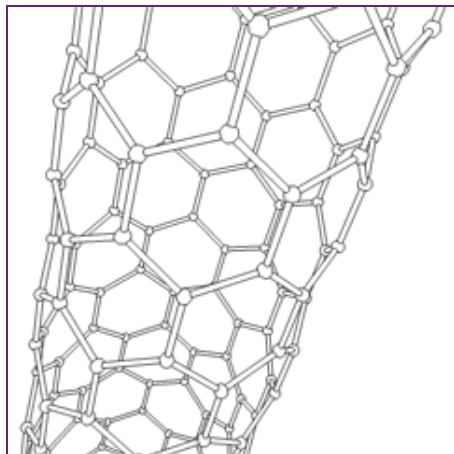


## Activity 2

Perform the *Allotropes of Carbon Activity* to further explore the molecular structure and properties of carbon allotropes.

## Carbon Nanotubes

Given their unique properties, what can carbon nanotubes be used for?



# Nanotubes In Efficient Solar Cells



- Scientists have developed the 'blackest black' colour using carbon nanotubes
- The carbon nanotubes are arranged like blades of grass in a lawn
  - they absorb nearly all light
- Use of carbon nanotubes in solar cells could vastly improve their efficiency.

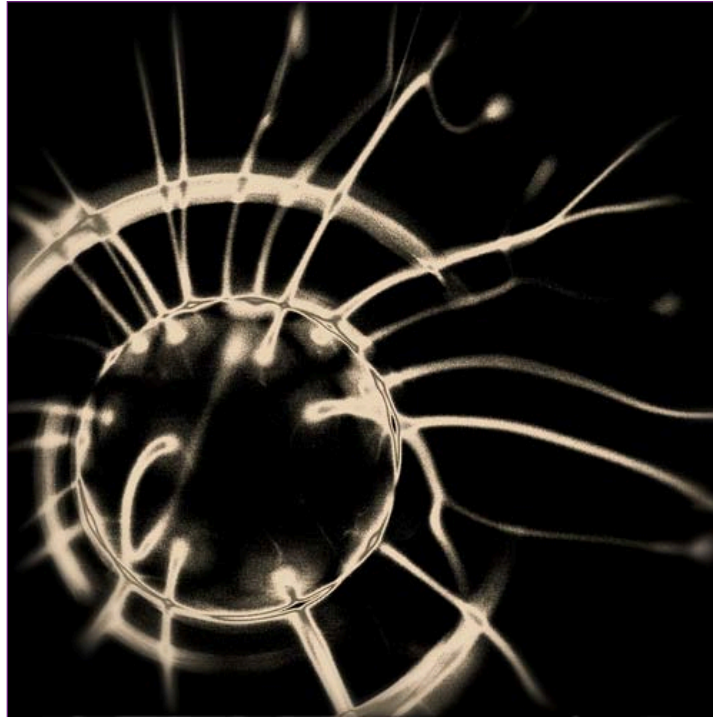
# Nanotubes In Sporting Equipment



- Badminton racquet manufacturer Yonex incorporates carbon nanotubes into their cup stack carbon nanotubes racquets ([www.yonex.com](http://www.yonex.com))
- American baseball bat manufacturer Easton Sports has formed an alliance with a nanotechnology company Zyvex to develop baseball bats incorporating carbon nanotubes
- Tennis racquets also incorporate carbon nanotubes ([www.babolat.com](http://www.babolat.com)).

# Nanotubes In Miniaturised Electronics

- Branching and switching of signals at electronic junctions is similar to what happens in nerves
- A carbon nanotube 'neural tree' can be trained to perform complex switching and computing functions
- Could be used to detect/respond to electronic, acoustic, chemical or thermal signals.



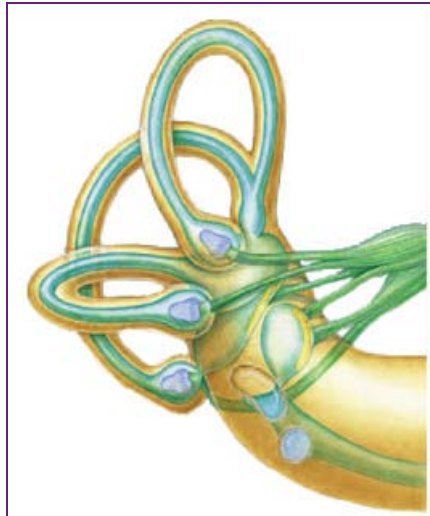
# Nanotubes In AV Technology



- Carbon nanotubes are being used to develop flat screen televisions with higher resolution than the human eye can detect
- Your next TV screen could be thin, ultra-light and foldable...

# Graphene Sheets

A new form of carbon with many potential uses.



- this new form of carbon just one atom thick  
  
“The very unusual electronic properties of graphene sheets means they could be used in solar cells or new battery technology,” he says  
  
“Because of the biological affinity of carbon, they might also be useful as electrodes for a range of medical bionic devices such as cochlear implants”
- Graphene sheets could also be used to create transparent electrodes and coatings that prevent the build up of static electricity.

# How Are Nanosized Carbon Structures Made?





# Manufacturing Carbon Nanotubes

## Molecular Engineering

- Carbon nanotubes can be made using molecular engineering
- Molecular templates are created
  - under the right chemical conditions carbon atoms arrange themselves into nanotubes on the template
- This process is also known as **chemical synthesis** or **self-assembly**, and is an example of the '**bottom-up**' approach to molecular engineering.

# Molecular Engineering

## 2 Approaches

- **‘Bottom-up’** approach: structures are built atom by atom
  - can use self-assembly or sophisticated tools (eg scanning tunnelling microscope, atomic force microscope) which can pick up, slide or drag atoms or molecules around to build simple nanostructures
- **‘Top-down’** approach: traditional engineering techniques such as machining and etching are used at very small scales
  - products tend to be refinements of existing products, such as electronic chips with more and more components crammed onto them.



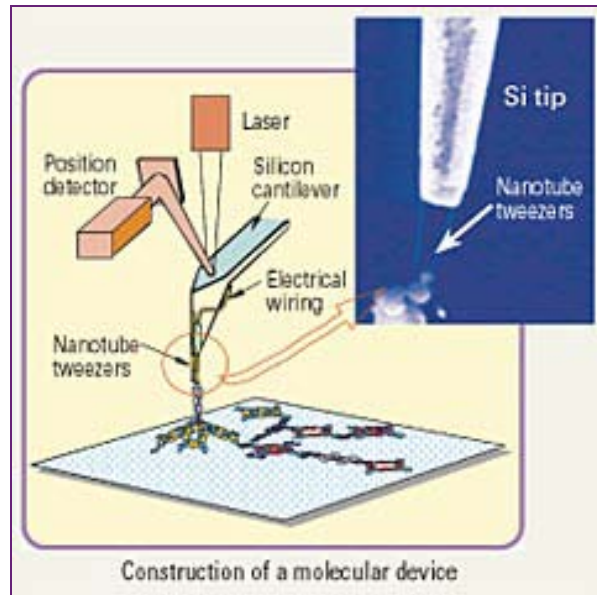
# Down Vs Bottom Up Nanotechnology

Watch the video found at the following website to improve your understanding of the difference between top-down and bottom-up approaches to manufacturing:

[www.nanohub.org/resources/96/](http://www.nanohub.org/resources/96/)

# Bottom Up Approach:

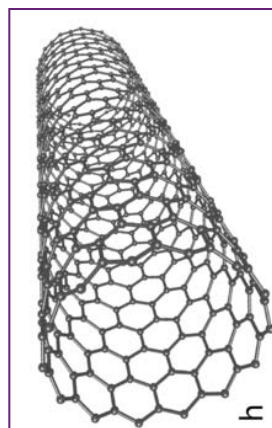
## Using Nanotube Tweezers



- Molecular devices can be constructed using nanotube tweezers
- The tips of the nanotube tweezers can be opened and closed by switching on and off a voltage between the two Carbon Nanotube probes
- Nanotube tweezers are tools for use in the bottom-up approach.

## Activity 3 – Research Questions

Are there any safety issues associated with the use of carbon nanotubes?



*Perform the **Safety Issues of Carbon Nanotubes** activity*

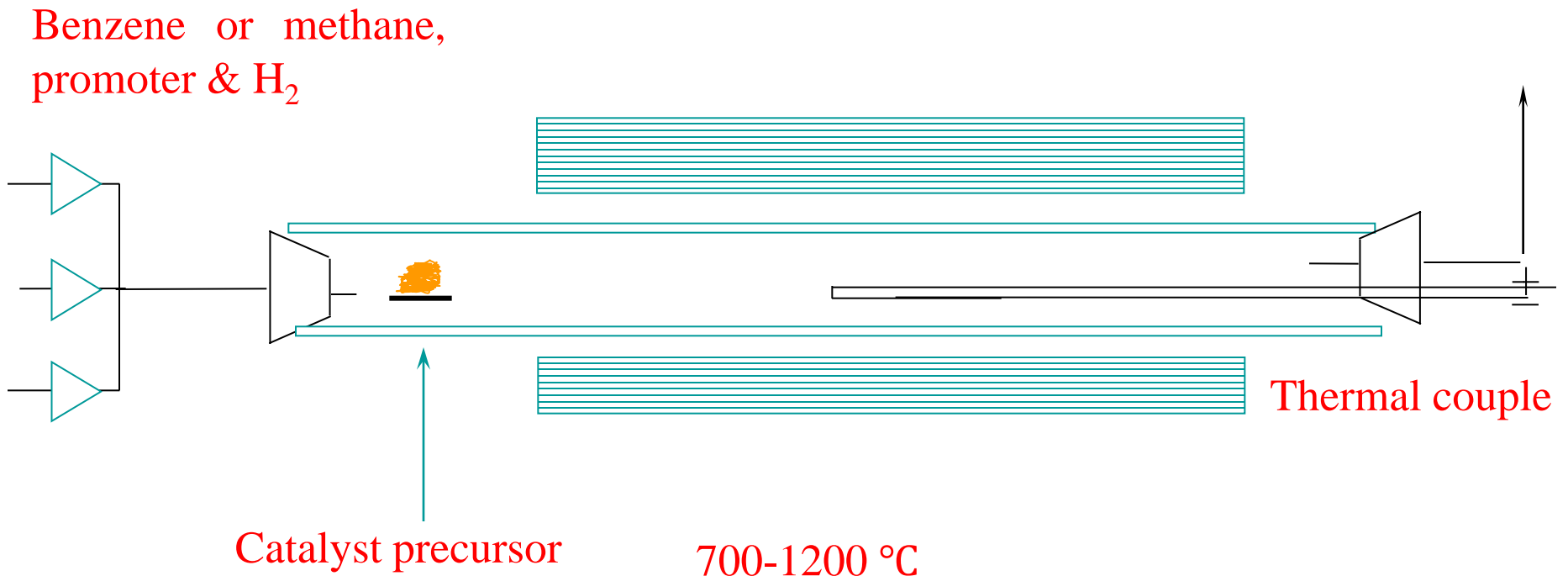
# General classification and diameter range

- **Single-walled carbon nanotubes (SWNTs)**  
**0.4-3nm, usually 1-2 nm**
- **Double-walled carbon nanotubes (DWNTs)**  
**~3nm**
- **Multi-walled carbon nanotubes (MWNTs)**  
**<100 nm**

# Methods for the synthesis of CNTs

- Hydrogen arc discharge
- Floating catalyst technique
- **Laser ablation**

# Apparatus for the floating catalyst method





## **Factors tunable for controlling the diameter and morphology of CNTs**

- **C/H ratio**

**Flux ratio of H<sub>2</sub> and hydrocarbons**

**Selection of carbon sources**

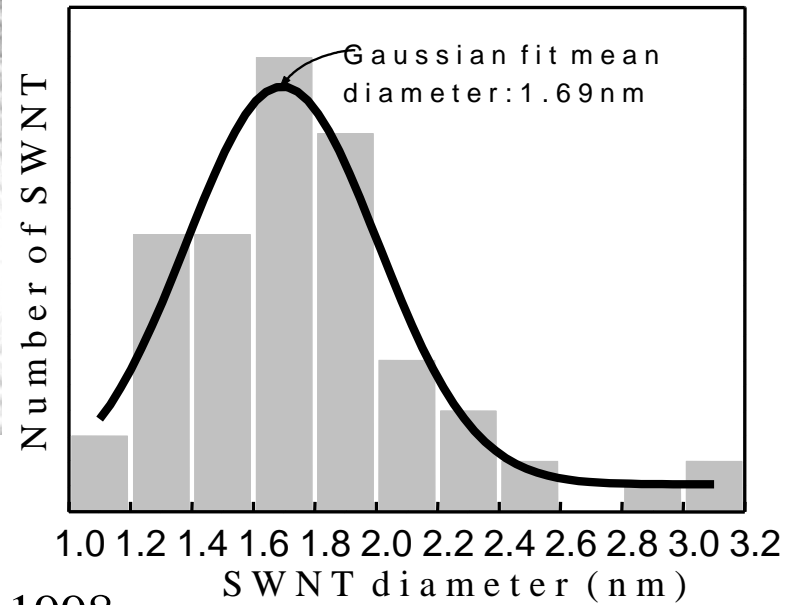
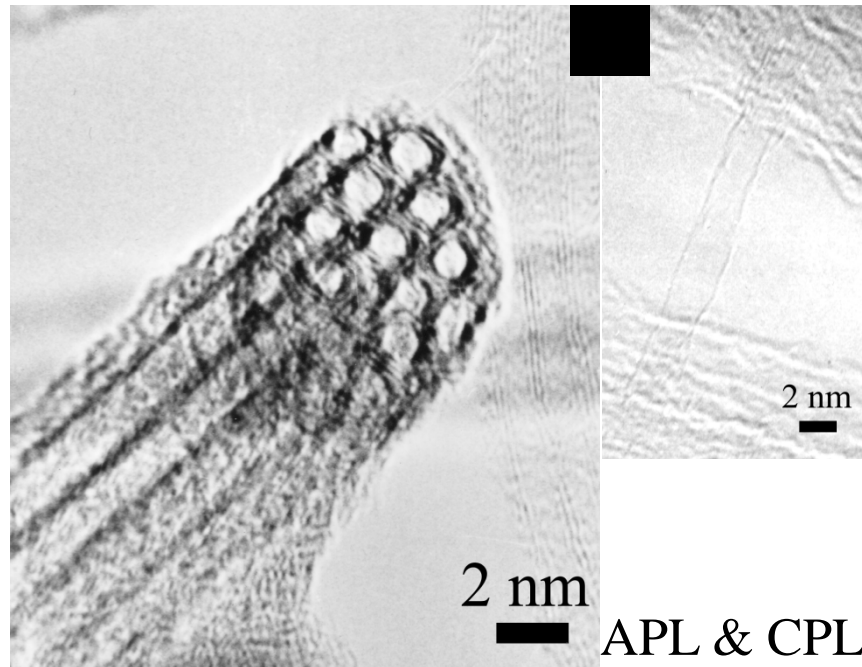
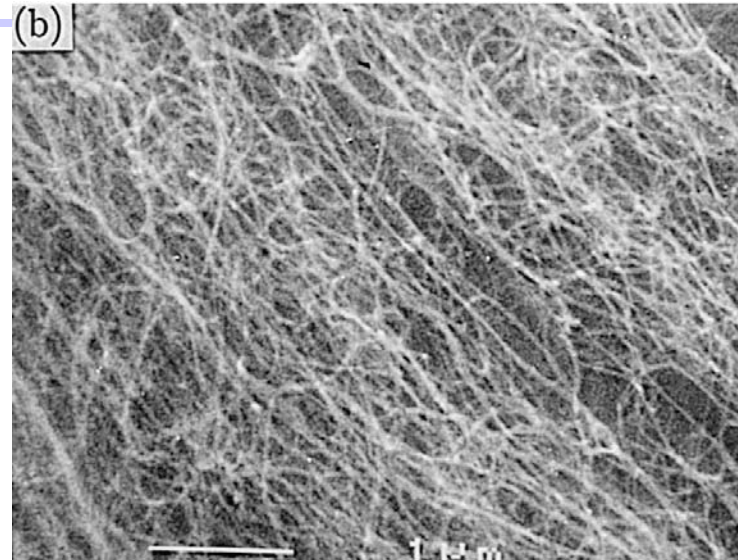
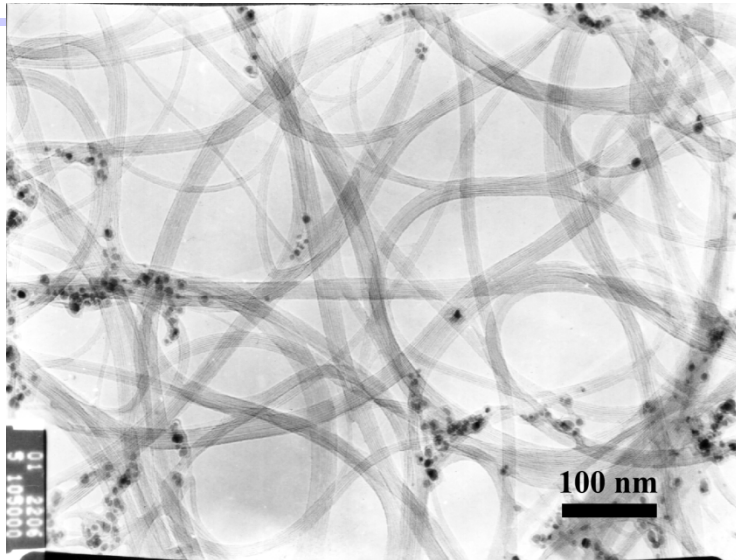
- **Temperature**

- **Carrier gas flux**

- **Amount of sulfur growth promoter**

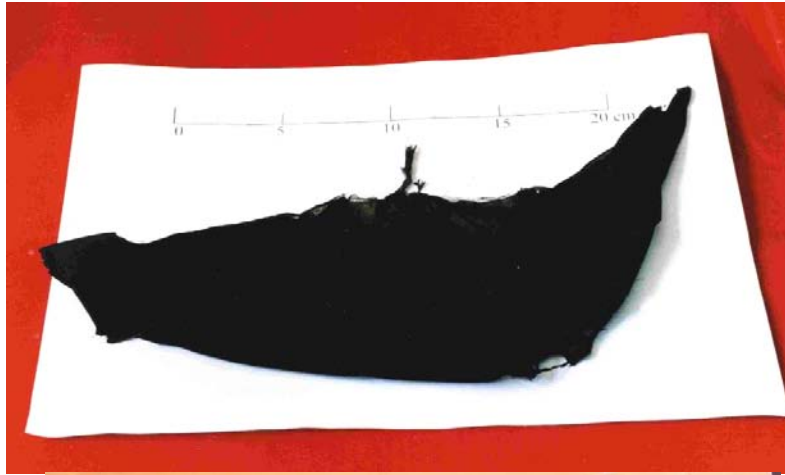
- **Gas flow direction**

# SWNTs

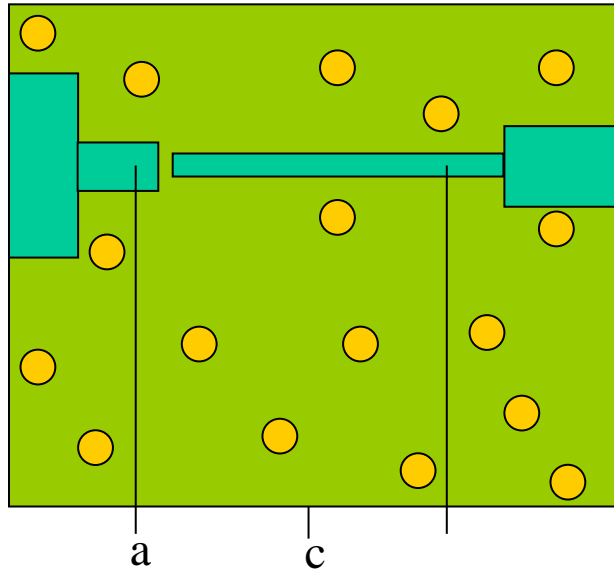


APL & CPL 1998

# Photographs of the as prepared SWNTs



# Synthesis of CNTs by hydrogen arc discharge method

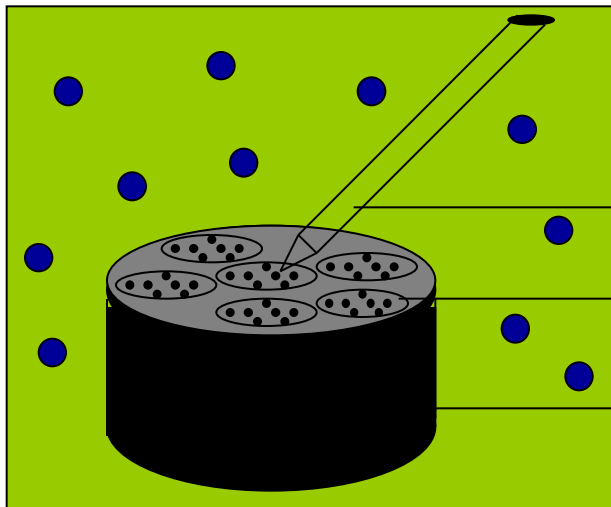


● He 500~600 Torr

a. Graphite cathode

b. Graphite anode

c. Chamber wall



● H<sub>2</sub>

Graphite cathode

Reactants

Graphite anode

Chamber wall





# Summary

- Covalent bonds form when atoms share electrons
- Carbon exists in many forms due to its ability to stably form different covalent bonding arrangements
- The bulk properties of materials are determined by the covalent bonding arrangement of atoms
- Carbon nanotubes have very different properties compared to the other carbon allotropes
  - these unique properties offer huge potential in product development.

# Revision

1. What are carbon nanotubes and why are scientists so interested in them?
2. How are carbon nanotubes made?