Nanochemistry

Project: „Nanostructures and computer simulations in material science”
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Maciej Bobrowski, mate@mif.pg.edu.pl

Gdańsk University of Technology (GUT)

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1. Fullerene
2. Nanodiamonds
3. Quantum dots
4. Graphene
Fullerene’s structure

High symmetry; 120 symmetry operations: rotations, reflections in planes. The \( \text{C}_{60} \) fullerene surface contains 20 hexagons and 12 pentagons. Double bonds are conjugated; nearly 12500 resonance structures can be drawn. In spite of their extreme conjugation, they behave chemically and physically as electron-deficient alkenes rather than electron-rich aromatic systems, i.e., the hexagons could be considered as cyclohexatrienes than as benzene rings.
Izomers of fullerene

The major isomers of fullerenes $C_{60}$, $C_{70}$, $C_{76}$, $C_{78}$, $C_{80}$, $C_{82}$, $C_{84}$. 
Izomers of fullerene

C70

C78

C20

C24

C32
The icosahedral $C_{60}H_{60}$ cage was mentioned in 1965 as a possible topological structure. Eiji Osawa predicted the existence of $C_{60}$ in 1970. He noticed that the structure of a corannulene molecule was a subset of the shape of a soccer ball, and hypothesised that a full ball shape could also exist.

In 1973, a group of scientists from the USSR made a quantum-chemical analysis of the stability of $C_{60}$ and calculated its electronic structure.

In 1985 Harold Kroto of the University of Sussex, working with James R. Heath, Sean O'Brien, Robert Curl and Richard Smalley from Rice University, discovered fullerenes in the sooty residue created by vaporising carbon in a helium atmosphere. In the mass spectrum of the product, discrete peaks appeared corresponding to molecules with the exact mass of sixty or seventy or more carbon atoms. The team identified their structure as the now familiar "buckyballs".

The name "buckminsterfullerene" was eventually chosen for $C_{60}$ by the discoverers as an homage to American architect Buckminster Fuller for the vague similarity of the structure to the geodesic domes which he popularized; which, if they were extended to a full sphere,
Richard Buckminster Fuller

Richard Buckminster „Bucky” Fuller (July 12, 1895 – July 1, 1983) was an American architect, systems theorist, author, designer, inventor and futurist. Fuller published more than 30 books, coining or popularizing terms such as „Spaceship Earth”, ephemeralization, and synergetic. He also developed numerous inventions, mainly architectural designs, and popularized the widely known geodesic dome. Carbon molecules known as fullerenes were later named by scientists for their structural and mathematical resemblance to geodesic spheres.
Total synthesis

The production of higher fullerenes by the classical method of graphite vaporization encounters problems due to the low yield, non-selective carbon cage formation and associated purification issues. A promising route to achieve this goal for the selective synthesis of fullerenes is based on planar polycyclic aromatic hydrocarbon precursor molecules that already contain the carbon framework required for the formation of the target fullerene cage. Such an unfolded fullerene can be stitched up through the intramolecular cyclodehydrogenation to form the desired fullerene isomer. The direct synthesis approach is not limited by synthesis of fullerenes but can be extended to the synthesis of different carbon based nanostructures including buckybowl, nanotubes and nanoribbons.
A $C_{78}$ fullerene related structure has been synthesized and investigated as a pyrolytic precursor. In independent experiments it has been shown that the flash pyrolysis of $C_{78}$ fullerene is very promising for the synthesis of individual isomers of higher fullerenes.


The synthesis of the $C_{84}$-fullerene related hydrocarbon $C_{84}H_{42}$, which possesses more than 83% of the $C_{84}$-fullerene connectivity, and its selective transformation to $C_84$ by flash vacuum pyrolysis (FVP) is reported.

Rational synthesis of C\(_{60}\)
Grignard reaction (organometallic reaction) in which: alkyl, allyl, vinyl, or aryl-magnesium halides (Grignard reagent) add to a carbonyl group in an aldehyde or ketone. This reaction is important for the formation of carbon-carbon bonds. The reaction of an organic halide with magnesium is not a Grignard reaction, but provides a Grignard reagent.

\[
\begin{align*}
R^1\text{MgBr} + R^2\text{R}^3\text{C}=\text{O} & \rightarrow R^1\text{R}^3\text{O} + R^2\text{MgBr} \\
R^1\text{R}^3\text{O} & \rightarrow R^1\text{R}^3\text{OH} + H^+ / H_2O
\end{align*}
\]

Mechanism:
Grignard reagent

Grignard reagent = R–Mg–X, where X is a halogen and R is an organic group, normally an alkyl or an aryl, for instance: methylmagnesium chloride H₃C–Mg–Cl and phenylmagnesium bromide C₆H₅–Mg–Br.

Grignard compounds are popular reagents in organic synthesis for creating new carbon-carbon bonds. For example, when reacted with another halogenated compound R′-X′ in the presence of a suitable catalyst, they typically yield R-R′ and the magnesium halide MgXX′ as a byproduct; and the latter is insoluble in the solvents normally used.

Pure Grignard reagents are extremely reactive solids. They are normally handled as solutions in solvents such as diethyl ether or tetrahydrofuran

Mechanism (the reaction proceeds through single electron transfer):

\[
\begin{align*}
R-X + Mg & \rightarrow R-X^- + Mg^+ \\
R-X^- & \rightarrow R^+ + X^- \\
R^+ + Mg^+ & \rightarrow RMg^+ \\
RMg^+ + X^- & \rightarrow R-Mg-X
\end{align*}
\]
The Wittig reaction or Wittig olefination is a chemical reaction of an aldehyde or ketone with a triphenyl phosphonium ylide (a Wittig reagent) to give an alkene and triphenylphosphine oxide. It is widely used in organic synthesis for the preparation of alkenes.

\[
\begin{align*}
R^1C=O + Ph_3P^+\text{C}^{-}\text{R}^3 & \rightarrow \text{R}^1\text{C} = \text{C}\text{R}^3 + Ph_3P=O \\
R^2 \quad \text{R}^4
\end{align*}
\]

By the way:

Olefin = unsaturated hydrocarbon.

An ylide or ylid is a neutral dipolar molecule containing a formally negatively charged atom (usually a carbanion) directly attached to a heteroatom with a formal positive charge (usually nitrogen, phosphorus or sulfur), and in which both atoms have full octets of electrons. The result can be viewed as a structure in which two adjacent atoms are connected by both a covalent and an ionic bond; normally written \(X^+\text{–}Y^-\).
FriedelCrafts reactions

The Friedel-Crafts are a set of reactions to attach substituents to an aromatic ring, like: alkylation, dealkylation, acylation, hydroxyalkylation and other.

Alkylation:

\[
R-\text{Cl} + \text{FeCl}_3 \rightarrow R^+ + \text{FeCl}_4^- 
\]

\[
\text{catalyst regenerated} 
\]

Acylation:

\[
\text{RCOCl or (RCO)_2O} \quad \text{AICl}_3 \text{ catalyst, reflux} 
\]

\[
\text{anhdyrous conditions} 
\]
Aldol condensation

An **aldol condensation** is a condensation reaction in organic chemistry in which an enol or an enolate ion reacts with a carbonyl compound to form a $\beta$-hydroxyaldehyde or $\beta$-hydroxyketone (an aldol reaction), followed by dehydration to give a conjugated enone.

\[
\text{RCH(OH)H} + \text{R''CH=CHR'''O} \rightarrow \text{RCH=CHR''O} + \text{H}_2\text{O}
\]

**Enol**, i.e. alkene (olefin) with a hydroxyl group.

**Enone**, also called an $\alpha,\beta$-unsaturated carbonyl, is a type of organic compound consisting of an alkene conjugated to a ketone.
Arc discharge

A large electric current is sent between two nearby graphite electrodes in an inert atmosphere. The resulting electric arc vaporizes the carbon into a plasma that then cools into sooty residue. These processes yield a mixture of various fullerenes and other forms of carbon. The fullerenes are then extracted from the soot using appropriate organic solvents and separated by chromatography. (Temperature: 4720–5720°C). 45% of fullerenes in soot, up to 85% of C$_{60}$.
Laser ablation

Alternatively, soot is produced by laser ablation of graphite or pyrolysis of aromatic hydrocarbons. Combustion is the most efficient process, developed at MIT.
Extraction
There are two types of bonds in fullerenes having bond lengths 1.38 Å and 1.45 Å for double and single bonds respectively. In spite of their extreme conjugation, they behave chemically and physically as electron-deficient alkenes rather than electron-rich aromatic systems, i.e., the hexagons could be considered as cyclohexatrienes than as benzene rings. \( C_{60} \) is a strong electron acceptor.

The energy level of triply degenerate LUMO of \( C_{60} \) is almost as low as those of p-benzoquinone or tetracyanoethylene. Hence, a wide variety of reactions have been reported for \( C_{60} \) as nucleophilic addition, \([4+2]\) cycloaddition, 1,3-dipolar addition, radical and carbene additions, metal complexation and so on. \( C_{60} \) fullerene also undergoes supramolecular complexation with various host molecules having electron-donating ability and an adequate cavity size.
Oxidation

\[ \text{C}_{60} \xrightarrow{\text{O}_2, \text{hv}} 18 \text{ h} \text{C}_{60} \text{O} \]

\[ \text{C}_{60} \text{O} + \text{C}_{60} \text{O}_2 + \text{C}_{60} \text{O}_4 \text{ itd.} \]

\[ \text{C}_{60} \text{O} + \text{C}_{60} \xrightarrow{} \text{C}_{60} \text{OC}_{60} \]
C60HyFn = Hydrated C60 Fullerene

Andrievsky et al. developed method of C60HyFn water solution (C60FWS) production. Such solutions of C60HyFn contain single hydrated C60 fullerene molecules as well as their labile nanoclusters (secondary associates). C60HyFn chemically is characterized as highly hydrophilic and highly stable donor-acceptor complexes of C60 associated with molecules of water.

Figure 1: Nanostructure of Hydrated C60 Fullerene – stable supramolecular complex C60 (red) with water molecules (blue) having unique physical-chemical and biological properties http://www.ipacom.com/index.php/en/publications-about-c60hyfn/92).
C60HyFn = Hydrated C60 Fullerene
C60HyFn = Hydrated C60 Fullerene

\[ \text{C60@(H}_2\text{O)}_n \]

C60HyFn water solution with a C60 concentration of 0.22 g/L.
C60HyFn = Hydrated C60 Fullerene

The hydrated C60 fullerene (HyFn = Donor-Acceptor complex of C60@H2O)n is surrounded by ordered water shells. The probable model of HyFn is based on data of Dynamic Light Scattering (DLS), Small-Angle Neutron Scattering (SANS), Low Temperature Differential Scanning Calorimetry (DSC), and Molecular Simulation of Professor M. Chalupa.

Hypothetical Model of Hydrated Fullerene - C60@[H2O]n

The fragment of a structure, C60@{yOH - xH2O}y - xH+n can be substituted by Metal Ions (Me2+).

Close bounded water molecules on C60 fullerene surface

Carbon atoms of electron-acceptor surface of C60 fullerene
C60HyFn = Hydrated C60 Fullerene

Product — “Water with hydrated C60 fullerene” — is a colourless liquid that consists of highly purified water and contains hydrated C60 fullerene (C60HyFn) at a concentration of 0.002 mg/l (2.8 nM) in terms of pure C60 fullerene.

The feedback for its preparation are concentrated aqueous solutions of hydrated fullerene C60.

The specific feature of this product is the fact that single structures C60HyFn, that are dissolved therein with a size of about 2 nm, are able to create and support specific, long, heterogeneously ordered water structures around them. The size of these structures can exceed their own size by dozens or even hundreds of times.

Such water structures, ordered by hydrated C60 fullerene, are consensual and, to a large extent, identical to all water structures of a healthy, normally functioning body.

The unique, multidimensional biomedical effectiveness of this product is also determined by such water structures, including its exceptional antioxidant characteristics.

Official reports on preclinical and clinical trials of this product can be found here and the summary of these reports can be seen here.

A wide range of scientific research and formal testing of this product have confirmed its absolute safety and its high effectiveness, both medically and in terms of preventive characteristics, allowing it to be registered as a dietary supplement in Ukraine. The Safety and Health Certificate from the Ministry of Health of Ukraine no. 05.03.02-94/95179 was issued on December 2, 2010.
http://www1.lsbu.ac.uk/water/fullerene_hydration.html
Halogenofullerenes and hydrofullerenes

Halogenes: F, Cl, I

\[ C_{60} + F_2 \xrightarrow{12 \text{ days}} C_{60}F_{60} + C_{60}F_{44} + C_{60}F_{36} \]

Hydrofullerenes: \( C_{60}H_2, C_{60}H_{18}, C_{60}H_{48} \).
If the hydrogen was added to all double bonds the \( C_{60}H_{60} \) should be obtained. However it was not isolated, as higher hydrofullerenes are unstable.

\[ C_{60} \xrightarrow{\text{Na/NH3 or ROH}} C_{60}H_{18} + C_{60}H_{48} + C_{60}H_{36} \]
Diels-Alder reaction

Diels-Alder reaction

Bingel's reaction
Bingel’s reaction
Complexes
Complexes
Polyfullerenes

- wiszące na łańcuchu
- łańcuchowe
- związane z podłożem
- usięciowane
- dendrymery z fullerenami
Endohedral

La@C60, K2(K@C59B)
Nonmetals inside the cage: Helium, Neon, Argon, Hydrogen

Synthesis:
- arc discharge (graphite + guest atom as oxide or carbide)
- Laser ablation
- Ionic implantation
- High pressure implantation
- Total synthesis
Total synthesis: $H_2$ inside $C_{60}$

Rys. 7.10. Schemat funkcyjonalizacyjnego chemicznego otwarcia (A) i zamknięcia (B) fulerenu $C_{60}$ w celu umieszczenia wewnątrz cząsteczki wodoru [326]
Fullerenes’ applications

Potential Applications of Fullerenes

- Magnetic Record Toner
- Photosensitive Material Nonlinear Optical Element
- Superconductivity
- Superconductivity circuit FET, Photolithography
- Gas Separation
- Free Radical Scavenger
- Electron Acceptor
- Photosorbent
- Low Thermal Conductivity
- Nano-size Molecule
- Nanoporous Adsorption
- Cage Structure (connoted Metal)
- Information Communication
- Electrical Device
- Bio/Medicine
- Environmental
- Energy/Transport
- Industrial Usage
- Sensor (Photo, Gas)
- Gas Storage
- Lithium Ion Battery
- Fuel Cell, Solar Cell
- Diagnostics Agent Medicine Cosmetics

Fullerenes’ functionalization

Nanodiamonds

Carbon dots
Nanodiamonds
Nanodiamonds, synthesis

(a) **Top-down**

**ND of Static Synthesis**

High Pressure High Temperature (HPHT) Nanodiamond

- High Pressure: 7-10 GPa
- High Temperature: 1500-2200°C
- Catalyst (Fe, Ni)

[Microdiamond image]

- Smallest: 10-20 nm
- Substitutional N 100-200 ppm

(b) **Bottom-up**

**ND of Dynamic Synthesis**

Detonation Nanodiamond (DND)

- Detonation process
- Size: Up to 500 nm
- Nitrogen: up to 10,000 ppm
- Optically inactive conglomerates

[Detonation image]
Nanodiamonds: properties and applications.

DOPANTS/INTERNAL DEFECTS
- Color centers (fluorescence, phosphorescence, magneto-optics)
- Boron doping (electroconductivity)
- Vacancies (photoacoustics)
- $^3$H doping (radionucleic)

CORE
- Mechanical/chemical stability
- Inherent biocompatibility
- Large bandgap (transparency)
- High refractive index (strong UV scattering)
- "Quality" of color centers
- High thermal conductivity

SURFACE CHEMISTRY
- Colloidal stability
- Uniformity of NDs distribution in nanocomposites
- Formation of shells/coatings
- Conjugation with biomolecules
- Drug adsorption
- Electron affinity (e.g. negative)
- Catalytic properties
- Activity of subsurface color centers
- Self-assembly into photonic crystals
- Biocompatibility

SIZE AND SHAPE
- Size of DNDs is ~4-5nm
- Shape close to spherical (DND) or blocky (HPHT)
- Influence reactivity
- Interactions with cells
- Ball rolling in nanolubricants
- Quantum confinement

NON-DIAMOND CARBON
- EM radiation absorption
- Fullerene-like reactivity
- Influence biocompatibility
- Influence colloidal stability
Nanodiamonds: properties and apps.
Nanodiamonds: properties and appls.

[Diagram showing the functionalization of nanodiamonds with various steps involving chemical reactions and functional groups.]

Maciej Bobrowski, mate@mif.pg.edu.pl (Gdańsk University of Technology (GUT))

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Fluorescence spectra and corresponding images under 254 nm UV exposure of ND-PMA-Eu_xTb_y: (a, e) ND-PMA-Eu; (b, f) ND-PMA-Eu1Tb1; (c, g) ND-PMA-Eu1Tb5; (d, h) ND-PMA-Tb, respectively. (i) CIE chromaticity diagram of the hybrid materials. (j, k) Images of UV-LED coated with the ND-PMA-Eu and ND-PMA-Tb.
**Carbon dots**

- **Top-down approach**
  - Laser ablation
  - Electrochemical
  - Arc discharge

- **Bottom-up approach**
  - Ultrasonic
  - Hydrothermal
  - Microwave pyrolysis

*Carbon resources: Fullerene, Carbon, Graphene, Nanotube, Graphite*