

Fullerenes Revisited

Materials Chemistry and Applications of C₆₀ Molecules

Pradeep P Shanbogh and Nalini G Sundaram

The serendipitous discovery of C₆₀ fullerene, which resulted in the prestigious Nobel Prize in Chemistry in 1996, spurred the finding of other fullerenes possessing carbon atoms ranging from 16 to hundreds. In this article, we offer a bird's eye view of the synthesis, properties and recent applications of this class of carbon allotropes with special emphasis on C₆₀ molecules. The versatility of the molecule and its applications interlinking the various interdisciplinary areas of science are described.

History of the Fullerene

Fullerenes are the carbon allotropes composed entirely of carbon and exist in the form of a hollow sphere (buckyballs), ellipsoid or tube (bucky tubes or carbon nanotubes). The existence of fullerenes was first predicted by Eiji Osawa of Toyohashi University of Technology in 1970 and was discovered experimentally for the first time in September 1985. It was detected in the time-of-flight mass spectrometer from the product of laser vaporization of graphite. Fullerene C₆₀, the most abundant molecule, was first synthesized in 1990 by Kramster *et al*, by an electric arc resistive heating of graphite rods [1].

Interestingly, the first fullerene discovered, known as the Buckminster fullerene, is also called the Bucky ball [2]. It derives its name from the geodesic dome designed by the architect Buckminster Fuller, which it resembles (*Figure 1*). These fullerene molecules contain 60 carbon atoms arranged in interlocked pentagons and hexagons similar to a soccer ball [2]. The discovery of C₆₀ fullerene spurred the finding of other fullerenes, which had carbon atoms ranging from 16 to hundreds. Though other fullerenes with varied number of carbon atoms were subsequently



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Keywords

Fullerenes, allotropes, C₆₀, functionalization.



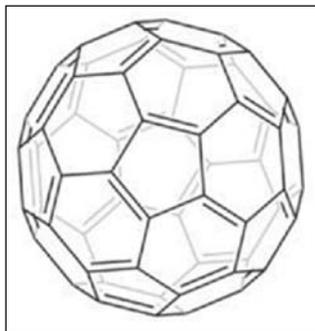


Figure 1. Structural illustration of fullerene.

It is noteworthy that fullerene was discovered by scientists working in different fields of science, and to this date is known to have applications that transcend the barriers of various disciplines of physics, chemistry and biology. The discovery of these molecules has been the foundation for research in many other interdisciplinary areas of science.

discovered, C_{60} remains to be the most easy-to-produce and thus is most popularly applied in a variety of fields ranging from medicine to solar cells. It is noteworthy that fullerene was discovered by scientists working in different fields of science, and to this date is known to have applications that transcend the barriers of various disciplines of physics, chemistry and biology. The discovery of these molecules has been the foundation for research in many other interdisciplinary areas of science especially in nanotechnology, carbon nanotubes and most recently in graphenes. The porous and geometrical structures of fullerenes have also resulted in encapsulation of atoms and molecules in the core, initiating work in the area of endohedral fullerenes.

Other fascinating physical and chemical properties such as electrical properties, capacity to form endohedral and exohedral derivatives, electron accepting nature, mechanical strength and negligible bio-toxicity of these new forms of carbon led many scientists to predict several technological applications. This has resulted in an increased number of research publications in recent years, making it a happening and hot field.

Symmetry, Structure and Chemistry of Fullerene

The cage-like structure of a fullerene consists of 12 five-member rings and a number of six-member rings depending on the number of carbon atoms [3]. It was postulated that the five-member rings need to be separated from each other to reduce the localization of the strain caused by the bending of the sp^2 -hybridized carbon atoms. This is the essence of the isolated pentagon rule (IPR) [3] which dramatically reduces the possible number of isomers for a given fullerene family. *Figure 2* shows the major isomers of fullerenes (C_{60} to C_{84}). Fullerenes are described by the general chemical formula C_{20+2H} where H is the number of hexagonal faces.

An important property of the C_{60} molecule is its high symmetry. There are 120 symmetrical operations, like rotation around an axis and reflection in a plane, which map the molecule onto itself. This makes C_{60} the most symmetrical molecule [4]. The C_{60} fullerene



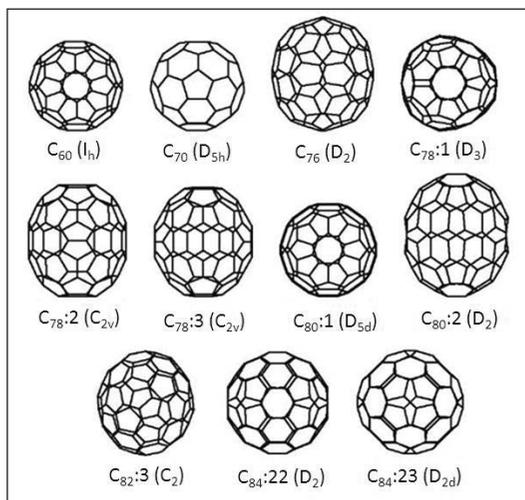


Figure 2. The major isomers of fullerenes C_{60} , C_{70} , C_{76} , C_{78} , C_{80} , C_{82} , and C_{84} .

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surface contains 20 hexagons and 12 pentagons. All the rings are fused and the double bonds are conjugated. Nearly 12500 resonance structures can be drawn for fullerene C_{60} . Nevertheless, only one structure really represents it most appropriately: the one in which all C=C double bonds are in the hexagons. There are two types of bonds in fullerenes having bond lengths 1.38 Å and 1.45 Å for double and single bonds respectively (Figure 3). In spite of their extreme conjugation, they behave chemically and physically as electron-deficient alkenes rather than electron-rich aromatic systems [5], i.e., the hexagons could be considered as cyclohexatrienes than as benzene rings. C_{60} is a strong electron acceptor. The geodesic and electronic bonding factors in the structure account for the stability of the molecule. Hence, the C_{60} molecule with the interlocked 12 pentagons and 20 hexagons has the lowest pressure, and therefore, is the simplest to purify. In theory, an infinite number of fullerenes can exist; their structure is based on pentagonal and hexagonal rings, constructed according to rules for making icosahedra.

C_{60} : The Most Symmetrical Molecule

Since the C_{60} molecule shows a high symmetry, many point group symmetry operations such as rotations around an axis, reflection in a perpendicular plane and also inversions can be observed

Figure 3. Representation of nature of bonds in fullerene C_{60} .

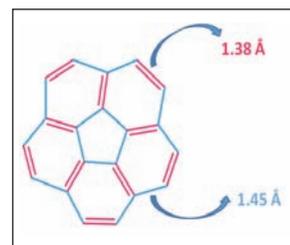
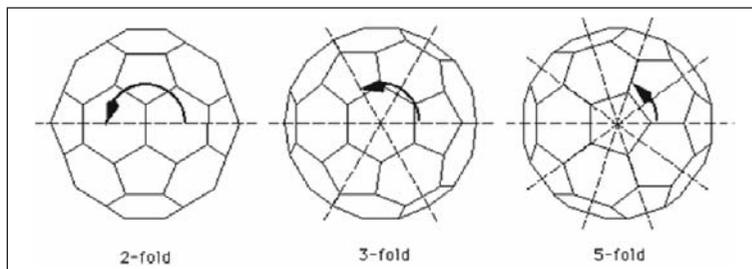


Figure 4. Rotation axes of the C_{60} molecule.

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Totally, the C_{60} molecule has 120 different symmetry operations, and thus, has the icosohedral point group making it one of the most symmetric molecule synthesized.

(Figure 4). As all symmetry operations should result in an equivalent structure, most of them go through the center of mass of the molecule. The highest symmetry axis, i.e., the 5-fold axis operates at the centers of two pentagons. There are six 5-fold axes, 10 different 3-fold axes, each passing through the center of every two of the 20 hexagons in the molecule. 2-fold axes can also be observed passing through the center of the edges of two hexagons. Since there are three neighbors for every hexagon (30 edges between two hexagons), we can find 15 2-fold axes. Additionally, there are 15 different mirror planes and finally one center of inversion of the molecule. Totally, the C_{60} molecule has 120 different symmetry operations, and thus, has the icosohedral point group making it one of the most symmetric molecule synthesized. More information on the geometric considerations underlying the structure of fullerenes can be found in [6]. Table 1 shows the physical properties of C_{60} .

Table 1. Physical properties of C_{60} (fullerene).

Color	Black Solid
Odor	Odorless
Formula	C_{60}
Weight	720.65
Density	1.7 to 1.9 gcm^{-3}
Standard heat of formation	9.08 k calmol^{-1}
Index of refraction	2.2 (600nm)
Boiling point	Sublimes at 800K
Resistivity	1014 ohms m^{-1}
Crystal form	Hexagonal cubic
Optical band gap	1.68 eV
Vapor pressure	5×10^{-6} torr at room temperature and 8×10^{-4} torr at 800K
Solubility	Benzene, toluene and chloroform



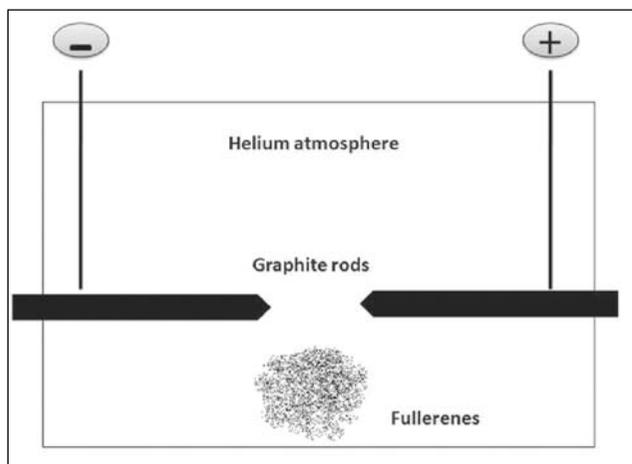


Figure 5. Synthesis of graphite by arc heating (method b).

Synthesis of Fullerene, C_{60}

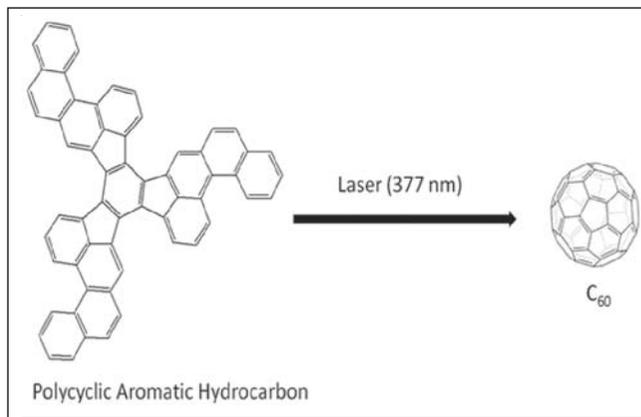
Large quantities of fullerene C_{60} can be synthesized by the following ways:

- Resistive heating of graphite.
- Arc heating of graphite: Arc generated between graphite rods under inert conditions (He gas) slowly evaporates graphite and forms fullerene (Figure 5). The gap between the two graphite rods is kept constant as the graphite converts into soot. By this method, > 95% pure C_{60} can be obtained along with other isomers of fullerene and impurities. Purification is carried out by chromatography.
- Inductive heating of graphite or other source (acetylene, etc.).
- Pyrolysis¹ of hydrocarbon (naphthalene).
- Total synthesis of fullerene (Figure 6): Apart from the above mentioned methods, another attractive synthesis approach has been developed as it results in selectively forming large amounts of fullerenes. A polycyclic aromatic hydrocarbon (PAH) with the formula $C_{60}H_{30}$, which consists of 60 carbon atoms, forms the fullerene C_{60} . C_{60} product is formed on laser irradiation of this PAH at 337nm wavelength [7].

¹ Decomposition brought about by high temperatures.



Figure 6. Generation of C_{60} by cyclodehydrogenation of polyarene.



² The addition of specific groups of atoms or bonds to certain molecules which results in a characteristic chemical reaction or specific applications of those molecules.

Functionalization² of Fullerenes

It is known that fullerene is not super aromatic; it behaves like a polyene and is a good electron acceptor [8]. The fullerene molecule by itself cannot be utilized in many applications due to its hydrophobic nature and limited solubility in many organic solvents. Deviation from planarity has been observed due to geometrical constraints which results in a loss of strain due to change in its hybridization from sp^2 to sp^3 .

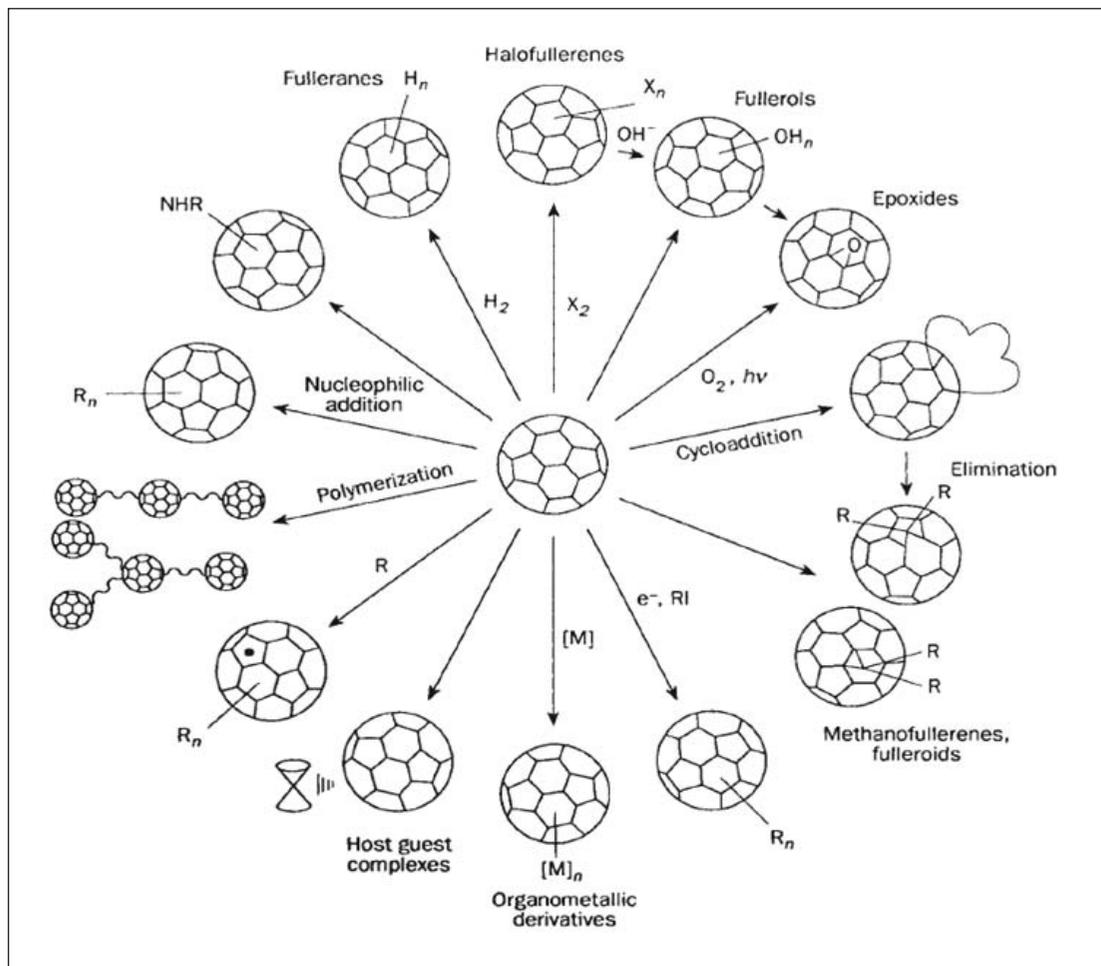
This causes the molecule to be more reactive and therefore more versatile for several applications. There are several covalent and non-covalent approaches available to functionalize the fullerene C_{60} molecule (*Figure 7*).

Functionalization: Covalent Approach

Fullerene can be reduced by up to 6 electrons and most reactions occur at 6, 6-ring junction forming thermodynamically stable products. Due to the electron-poor nature of C_{60} , it is an excellent substrate for nucleophilic additions. Given below are several reactions from which one can obtain functionalized fullerenes:

1. Synthesis of Fullerols [9]: This is the first water soluble derivative of fullerene (*Figure 8a*).
2. Synthesis of fulleropyrrolidines (*Figure 8b*) [10].

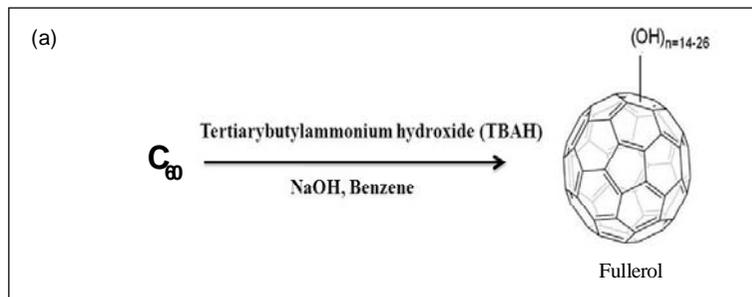
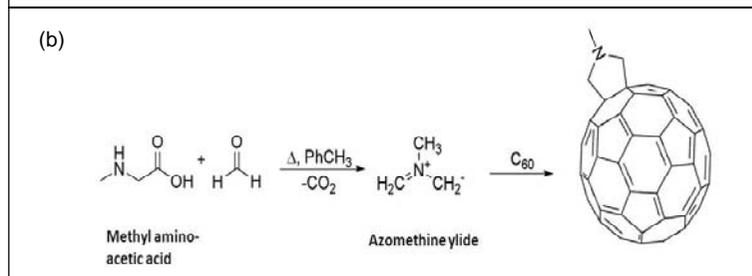
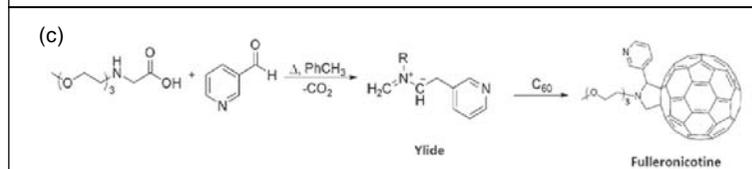
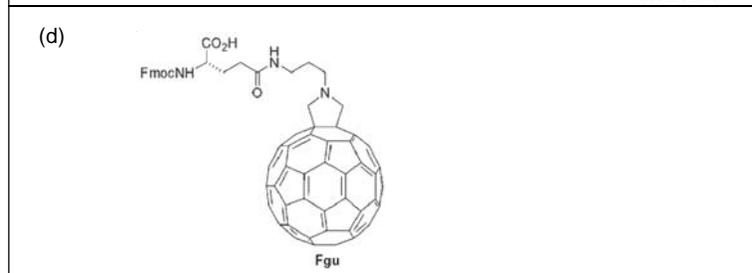
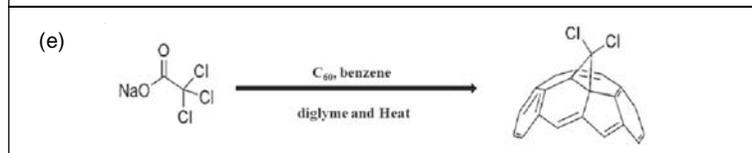
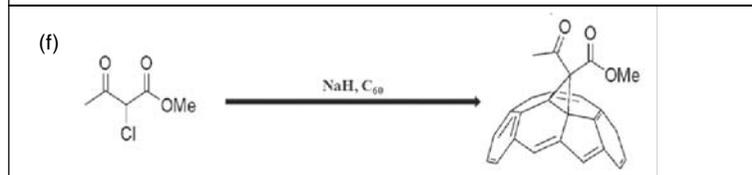




3. Synthesis of fulleronicotine – Prato's reaction: The reaction of amino acid sarcosine with paraformaldehyde heated and refluxed with toluene forms an ylide (Figure 8c). This reaction is at a higher temperature and the ylide reacts with the fullerene to yield a N-methylpyrrolidine derivative or pyrrolidinofullerene or pyrrolidino. This is used to form the metallofullerenes otherwise known as endohedral fullerenes.

4. Synthesis of fulleropeptides: Fulleropeptides were synthesized by Fmoc protocols. Fluorenylmethyloxycarbonyl (Fmoc) group is introduced as a protecting group for the amines in the peptides (Figure 8d).

Figure 7. Few general reactions of C_{60} . Reprinted with permission from *Nature Reviews*, Vol.363, No.6431, Macmillan Publishers Ltd., June 1993.

Figure 8a. Synthesis of fullerol.**Figure 8b.** Synthesis of fulleropyrrolidines.**Figure 8c.** Synthesis of Fulleronicotine.**Figure 8d.** Synthesis of fulleropeptides.**Figure 8e.** Carbene addition.**Figure 8f .** Bingel Cyclopropanation.

5. Synthesis of methanofullerenes. Carbene addition and Bingel cyclopropanation are the approaches to synthesize methanofullerenes (Figure 8e & 8f).



Figure 9. Functionalization with PVP.

Functionalization: Non-Covalent Approach

Supramolecular chemistry allows the preparation of functional architectures by means of non-covalent interactions, including hydrogen bonding, p-p, and metal coordination. One example is given below.

Functionalization with PVP: Polyvinyl pyrrolidone, a surfactant in presence of chloroform mixed with C₆₀, interacts non-covalently with C₆₀. When the solvent is evaporated, the residue is soluble in water (*Figure 9*).

Formation of Endohedral Fullerenes: Atoms, molecules, or ions can be trapped inside the cavity of a fullerene cage to form endohedral fullerenes. H₂, N₂, and a wide variety of noble gases and transition metal atoms have been successfully encapsulated [8]. Physical methods for the preparation of endohedral fullerenes are tedious and lack efficiency, reaching isolated yields of only 1%. Recently, a new creative concept called ‘molecular surgery’ has been developed to introduce guests inside the fullerene sphere. The procedure starts with a ring opening or a ring expansion generally induced by cycloadditions or radical-oxidation reactions in order to open a ‘hole’ in the sphere and put in the desired species (*Figure 10*). The reconstitution of the cage after the encapsulation is achieved at high temperatures.

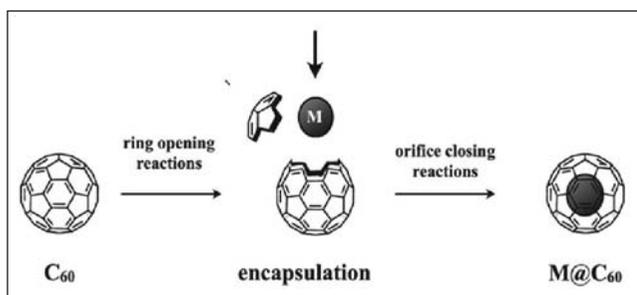


Figure 10. Schematic diagram of encapsulation in endohedral fullerene. Reproduced from *J. Mater. Chem.*, Vol.21, pp.1305–1318, 2011 with permission from The Royal Society of Chemistry.

When hydrogenated, they form a C–H bond, whose strength is lower than the strength of the C–C bond.

Therefore, when heated, the C–H bond breaks, preserving the distinctive structure of the fullerene. This characteristic makes fullerenes the ideal molecules for hydrogen storage.

³ The interface between two layers or regions of dissimilar crystalline semiconductors.

Applications of Fullerenes

Research in fullerene chemistry is currently well-established and mature. This paved the way to explore the applications of this molecule and its functionalized derivatives in different potential areas such as pharmaceuticals, medicine, photovoltaics, etc. Here, we focus on some of the established and recent applications of the functionalized C₆₀ fullerenes [8, 15].

Functionalized Fullerenes for Photovoltaics/Solar Cells: As mentioned before, the C₆₀ is an electron-deficient system and thus, acts as an electrophile in many organic reactions. Some examples which were discussed are addition of carbene, to form methanefullerene; solid state synthesis in the presence of KCN leading to dimers and high pressure synthesis to obtain polymers. Many of these polymer-fullerenes are used in organic photovoltaics since they exhibit ultrafast photo-induced charge transfer, while the reversible reaction is slower. Currently, the bulk heterojunction³ solar cell widely uses the fullerene derivate phenyl –C₆₁ butyric acid methyl ester (PCBN) with good efficiencies (about 5%). Stanford scientists built the first all-carbon solar cells.

Antioxidants and Biopharmaceuticals: Since fullerenes react readily with free radicals, which are dangerous to the body, they could potentially act as antioxidants [15]. Fullerenes hold great promise in the health and personal care industry, especially the pharmaceutical sector. Much research is being carried out in the control of nervous damage caused due to diseases such as Alzheimer's and Lou Gehrig's disease (ALS) by the applications of fullerenes. The sponge-like effect of fullerenes towards radicals, results in destruction of 20 free radicals per C₆₀ radical. The bioactivity of the fullerene-based antioxidants is 100 times more effective than the current leading drugs in the market.

Hydrogen Storage: Fullerenes are able to retain a maximum of 6.1% of hydrogen due to their cage-like molecular structure. When hydrogenated, they form a C–H bond, whose strength is



lower than the strength of the C–C bond. Therefore, when heated, the C–H bond breaks, preserving the distinctive structure of the fullerene. This characteristic makes fullerenes the ideal molecules for hydrogen storage. The extent of hydrogenation can be determined from the change in the color of this molecule which changes from black to brown, then to red, orange and light yellow with increasing hydrogen intake. Since most of the hydrogen-storing hydride materials are dangerous and have low storage capabilities, fullerene hydrides can be used in fuel cells of electric cars safely.

Endohedral Fullerenes: Insertion of a metal ion in the cages of the C_{60} molecule produces an endohedral fullerene [8]. Rare earth ions such as Gd inserted in the fullerene could potentially be used as diagnostic MRI contrast agents for several diseases. These materials are highly stable even at higher temperatures and more effective than fullerenes. N @ fullerenes is explored in molecular spin electronic devices as quantum computers. Since the cage-like structure of the fullerene screens the magnetic ion from the external environment, these molecules have exceptional spin properties.

Fullerenes for Drug Delivery: Attachment of hydrophilic moieties to the hydrophobic C_{60} fullerene makes it soluble in water. Consequently, they become capable of transporting drugs to the cells [16]. These functionalized fullerenes can cross the cell membrane and bind with the mitochondria [17]. Some functionalized fullerenes can be regulated so as to deliver the drug slowly to get maximum therapeutic effect. DNA-functionalized fullerenes show better efficiency as compared to the available lipid-based vectors. It was found that the derivatized fullerene forms a protective sheath around the DNA, thus increasing its lifetime in endosomes, which in turn supports chromosomal incorporation.

Summary

The C_{60} fullerene molecule has been a hot area of research since its discovery 20 years ago. The first decade of research included

Initially found to be an inert molecule, functionalization of fullerenes has radically changed the research direction and given impetus for effective utilization of these molecules.



Future research directions include exploring applications of the fullerene C_{60} in catalysis, water purification, biohazard protection, portable power, vehicles and medical use.

studying and understanding the properties of this fascinating allotrope of carbon. Initially found to be an inert molecule, functionalization of fullerenes has radically changed the research direction and given impetus for effective utilization of these molecules. Derivatized fullerenes have been exploited, both in academic laboratories as well as R&D centres in industries, as mentioned above. Many of the applications are in the fledgling state and it is only recently that fullerenes have been used for non-invasive cancer imaging, cancer therapy and also for novel optical applications. It is apparent that further research is on the integration of these molecules to form supramolecular assemblies as well as nanostructures that are able to achieve high capabilities in their specific tasks. Future research directions include exploring applications of the fullerene C_{60} in catalysis, water purification, biohazard protection, portable power, vehicles and medical use.

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