Review

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Review

Exploring Properties and Synthesis Procedures of Fullerenes from Historical Perspective

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Abstract: The theoretical prediction of icosahedral carbon molecules preceded their experimental discovery by decades. In 1985, Kroto et al. synthesized C_{60} - commonly known as buckminsterfullerene or buckyball - pioneering research into fullerenes and earning the Nobel Prize in Chemistry in 1996. Fullerenes exhibit a unique truncated icosahedral structure with remarkable symmetry (I_h group), which influences their electronic properties and stability. C_{60}'s π-electrons follow energy states dictated by spherical harmonics modified by its lower symmetry. This robust structure enables applications like endohedral fullerenes, where foreign species are encapsulated within the carbon cage. Synthesis methods such as laser vaporization, arc discharge, pyrolysis, and flame combustion have been developed to produce fullerenes, each offering distinct advantages. This historical overview explores the evolution of fullerene synthesis techniques and their structural and electronic properties, underscoring their significance in materials science.

Keywords: fullerene; arc discharge; CVD; pyrolysis

1. Introduction

Historically the theoretical prediction of possible existence of icosahedral molecules was reported several decades before their experimental discovery in the laboratory[1]. In early works, Tisza[2]described the point group symmetry for icosahedral molecules, Schultz[3] showed that different kinds of carbon hydrogenated cages are possible along with truncated icosahedron. Moreover, Osawa [4] predicted the chemical stability of icosahedral C_{60} molecule with I_h symmetry.

The nearly spherical, closed-cage molecule C_{60} was experimentally identified in 1985 by Kroto et al. [5], a discovery that ultimately led to the awarding of the Nobel Prize in Chemistry in 1996. The researchers noted a striking similarity between the molecular structures observed in their experiments and the geodesic domes conceptualized and constructed by R. Buckminster Fuller [6]. This resemblance inspired the naming of these molecules as "fullerenes”. Moreover, The C_{60} molecule, commonly referred to as “buckminsterfullerene” or simply as a “buckyball”, rapidly garnered significant interest. This was largely due to its distinct structure and remarkable properties, placing C_{60} and its related fullerene derivatives at the forefront of scientific research [7].

The C_{60} molecule adopts a structural configuration known as a truncated icosahedron, a polygon comprising 60 vertices and 32 faces, of which 12 are pentagonal and 20 are hexagonal. The carbon atoms in C_{60} are situated at these vertices, and 90 covalent bonds interconnect them. Notably, the single bonds in C_{60} are slightly longer than its double bonds, which results in a deviation from a perfectly regular truncated icosahedral geometry (Figure 1) [8,9]. Additionally, variations of this topological structure, such as C_{20}, C_{70}, C_{80}, C_{140}, and C_{260}, have also been documented in the literature [10–12].

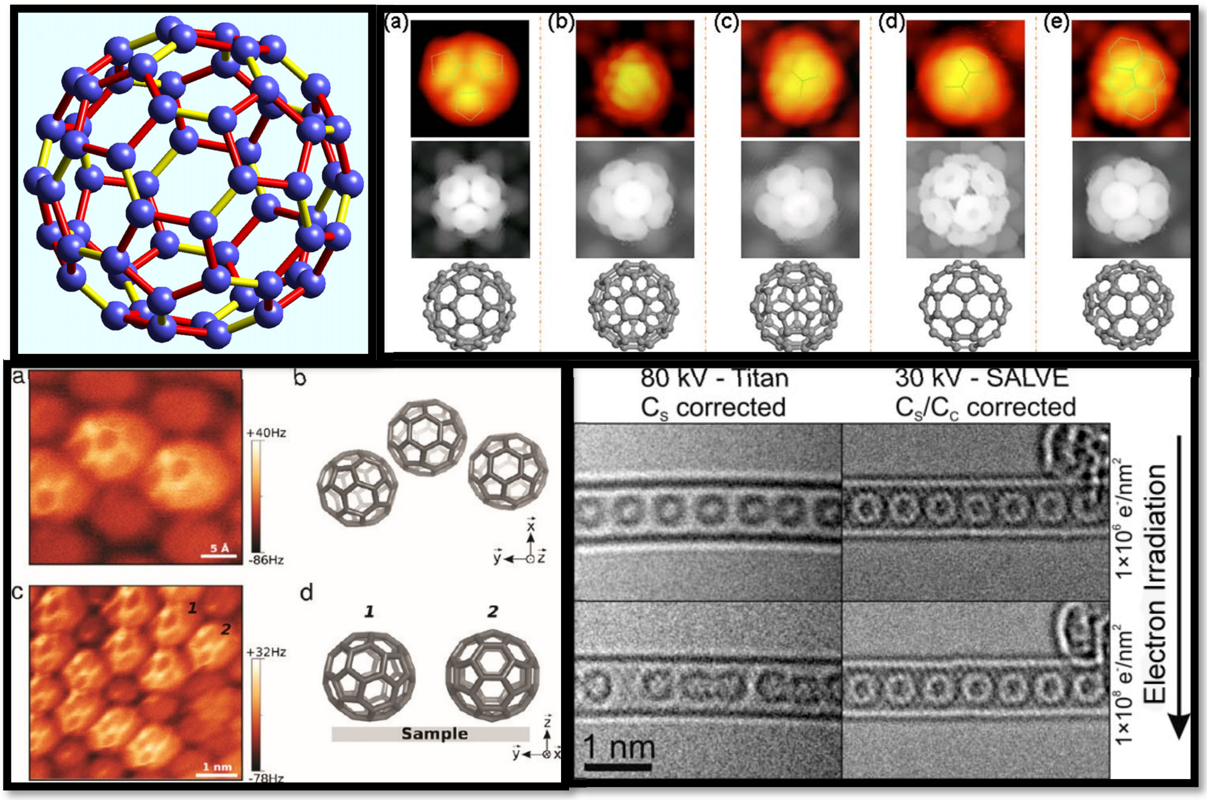

Figure 1. (Top left) The buckyball structure is shown with single bonds highlighted in red and double bonds highlighted in yellow. **(Top right**) The upper panel presents high-resolution STM images of a single fullerene molecule positioned at five distinct adsorption sites. The central panel displays the corresponding simulated STM images for fullerene molecules at each of these sites. Meanwhile, the lower panel illustrates the proposed molecular orientations of individual fullerene molecules at the respective adsorption sites. [13].**(Bottom left)** (a) nc-AFM image obtained under constant current conditions, displaying the topmost atoms of three C60 molecules adsorbed onto a molecular island. (b) A schematic representation illustrating the proposed self-assembly model. (c) A larger-area nc-AFM image under constant current, showing two distinct adsorption configurations, labeled as 1 and 2. (d) A model representing the observed adsorption configurations.[14]. **(Bottom right)** High-resolution transmission electron micrographs (HRTEM) of C_{60} molecules (fullerenes) in single-walled carbon nanotubes. Left: Figure in aperture-corrected (Cs-corrected) FEI titanium at 80 kV; Right: Illustration in opening and chromatic aberration-corrected SALVE TEM at 30 kV © Dr. Johannes Biskupek[15].

1.1. Structure and Properties of Fullerene

One of the remarkable characteristics of fullerenes is their ability to serve as durable containers for encapsulating other molecules or atoms. When a fullerene traps a material within its carbon framework, the resulting structure is referred to as an "endohedral fullerene" (Figure 2). The term "endohedral" was first introduced in 1991 by Cioslowski et al. [16] and independently by Weiske et al. [17]. If the encapsulated species is metallic, the structure is specifically termed an "endohedral metallofullerene" [18], whereas the inclusion of non-metallic species leads to the designation "non-metal doped fullerene."

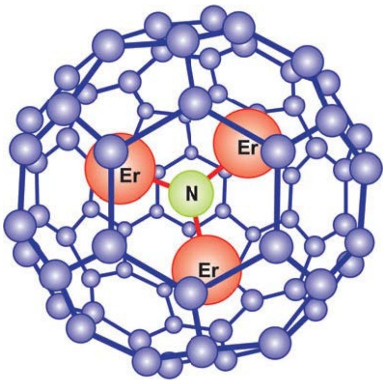

Figure 2. The chemical structure of the $Er_3N@C_{80}$endohedral fullerene. A Er_3N nitride cluster is enclosed by an icosahedral C_{80} carbon cage[19].

The C_{60} molecule exhibits exceptionally high symmetry, characterized by numerous transformations that map the molecule onto itself. These symmetry operations include rotations about specific axes, reflections through planes, and inversions while maintaining the center of mass at a fixed position. Three distinct types of rotational axes are observed in the C_{60} molecule (Figure 3). Firstly, the molecule possesses 5-fold rotational axes that pass through the centers of two opposite pentagons, corresponding to a rotation of 72 degrees (360°/5). Secondly, there are 3-fold rotational axes that traverse the centers of two opposing hexagons, where a rotation of 120 degrees (360°/3) restores the molecule's symmetry. Lastly, 2-fold rotational axes exist through the midpoints of edges shared by two hexagons, associated with a rotation of 180 degrees (360°/2). In total, the C_{60} molecule contains six 5-fold axes, ten 3-fold axes, fifteen 2-fold axes, fifteen mirror planes, and one inversion center. The combination of all these symmetry elements results in 120 distinct symmetry operations, collectively forming a symmetry group equivalent to the icosahedral group I_h. Consequently, C_{60} is often regarded as one of the most symmetric molecules known [20].

The icosahedral group (Ih) can be broken down into its irreducible representations, which correspond to dimensions d = 1, 3, 3, 4, 5, and are denoted as A, T_1, T_2, G and H, respectively. Because of the inversion symmetry, the irreducible representations are either symmetric (labelled as g) or anti-symmetric (labelled as u) for each representation. The molecular vibrations and electronic states are labelled by irreducible representations, using uppercase and lowercase characters, respectively.

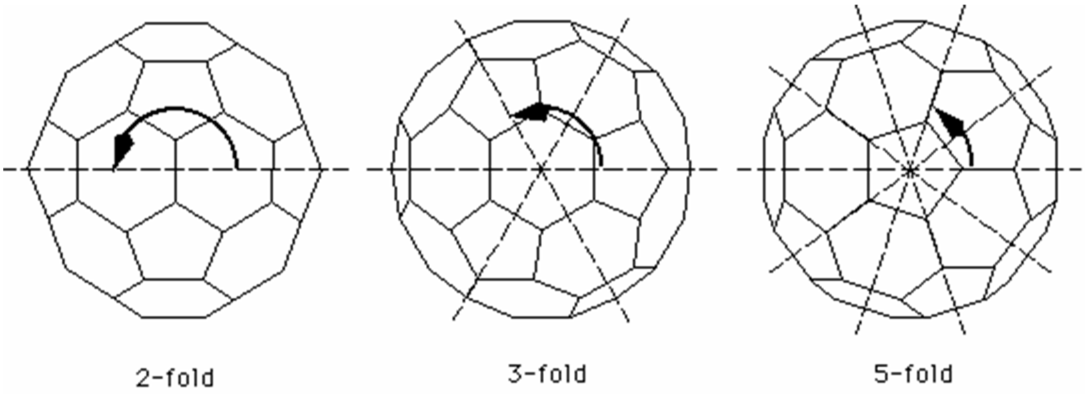

Figure 3. Rotation axes of the C_{60} molecule.

As C_{60} molecule has spheroidal geometry thus the electronic states can be described by spherical harmonics. However, spherical harmonic wave functions representing the 60π electrons of C_{60} has to be tailored slightly by the icosahedral symmetry, because of the presence of truncated icosahedral symmetry group (I_h) in its structure. The 60π electrons are distributed among the allowed energy states following the aufbau principle, Pauli Exclusion Principle and Hund’s rule. The resulting energy states corresponding to $l = 0$ to $l = 4$ are completely filled whereas the highest energy level

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corresponding to $l = 5$ has 10 unpaired electrons. The unpaired electrons indicate the truncated icosahedral symmetry of C_{60} which is a lower symmetry compared to a perfect sphere and splits the degeneracies of all levels above $l = 2$ as shown in Figure 4.

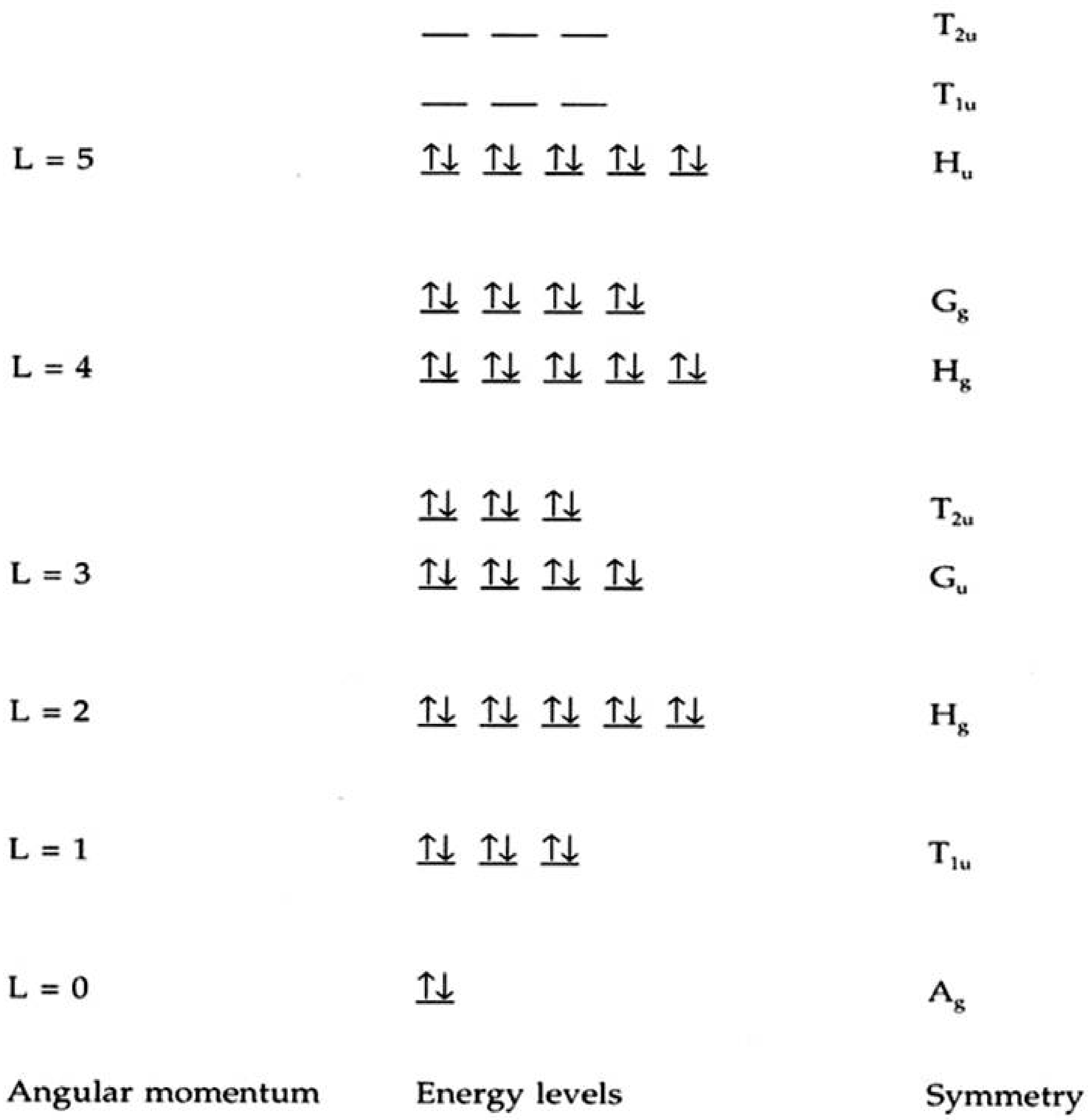


Figure 4. An energy level diagram for the π electrons of C_{60}, illustrating the division of the pertinent angular momentum states in accordance with icosahedral symmetry.[21].

The distribution of electrons is consistent with highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and LUMO+1 levels of the Huckel molecular orbital calculation on C_{60} [22,23].The theoretically calculated electronic structure of isolated C_{60} molecule and fcc form of solid C_{60} using local density approximation (LDA) in the density functional theory are shown in Figure 5.

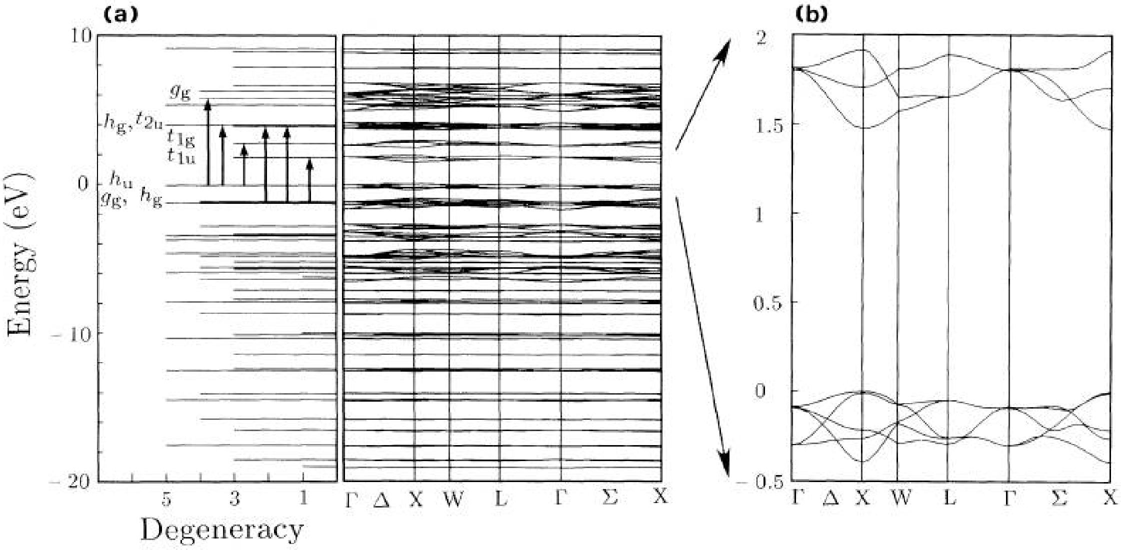


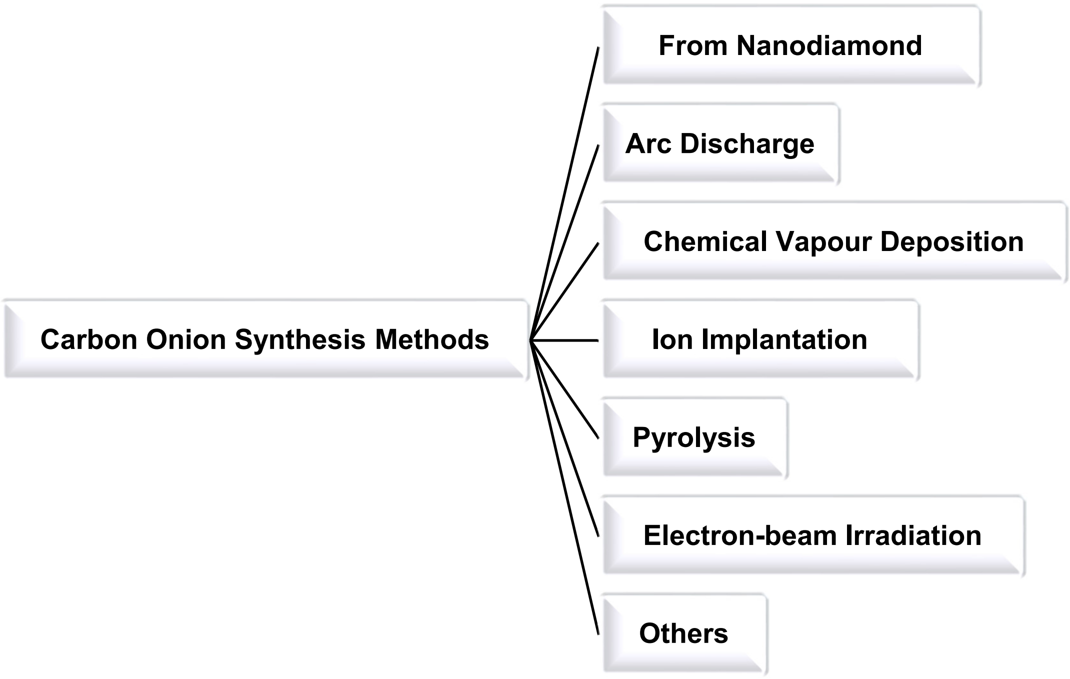
Figure 5. (a) The left panel illustrates the electronic energy levels of the C_{60} cluster, while the right panel depicts the band structure of the face-centered cubic (fcc) C_{60} crystal. The fcc C_{60} crystal exhibits semiconducting behaviour, with the valence band maximum located at the X point, which is designated as the zero-energy reference. To align the electronic states, the energy levels of the C_{60} cluster are shifted such that the highest occupied state (hu) corresponds to the average energy of the five uppermost occupied bands of the fcc C_{60} at the Γ point. Arrows indicate optically allowed transitions with excitation energies below 6 eV. (b) The band structure of fcc C_{60} near the energy gap is presented, showing that both the top of the valence band and the bottom of the conduction band occur at the X point.[24].

The valence band structure matches with results of the x-ray photoemission studies of solid C_{60}, and also consistent with the plane-wave basis-set calculation[25]. The HOMO–LUMO energy gap (between the h_u state and the t_{1u} state) is 1.9 eV however the first optically allowed transition is allowed between the h_u state to the t_{1u} +1 (t_{1g}) state (required minimum energy of 2.87 eV). The large energy gap between the occupied and unoccupied orbital levels is partially accountable for the astonishing thermal stability of C_{60}[26].

The reported electrical conductivity at room temperature of a C_{60} single crystal is 1.7×10^{-8} S/cm[27] and for films it is in the range of 10^{-5}-10^{-8} S/cm[28]. Dependence of electrical conductivity of C_{60} on temperature (below[29] and above[30,31]the room temperature) and pressure[32] was also reported. The thermal conductivity of C_{60} single crystal is 0.4 W/mK [33,34]. Temperature and pressure dependence of thermal conductivity were also studied[35].

2. Synthesis of Fullerene

In this section different methods to synthesize fullerenes specially C_{60},are discussed. Some of the methods such as laser vaporization and arc discharge, require very high temperatures because these use solid graphite as a precursor material. However, other methods work with easily decomposable carbon sources, such as pyrolysis and electron irradiation (Scheme 1).



Scheme 1. Different synthesis methods of fullerene.

2.1. Laser Vaporization Method

In this process the atoms of a refractory material (such as carbon) is vaporised by a high power laser into a carrier gas (usually helium). In the carrier gas, the atoms nucleate and glided into a molecular beam for further analysis by time-of-flight mass spectrometry. In 1985 Kroto et al.5used laser ablation method employing a Nd:YAG laser pulse to vaporize graphite target in helium atmosphere to synthesise the C_{60} molecule and detected it by a mass spectrometer (Figure 6). Hunter et al.[36] first produce C_{60}^{+} cluster ions and later on annealed them to synthesise fullerenes. Lieber et al.[37] pointed out that when fullerenes are prepared at room temperature then the dense carbon plasma cools rapidly and does not provide sufficient time for the growing carbon fragments to rearrange into the stable, closed fullerene structures. Whereas ablating graphite at an elevated temperature (preferably at 1200°C) cools plasma slowly enough so that growing carbon clusters have adequate time to reorganize themselves into stable fullerenes. Oyama et al.[38] found that the amount of grown fullerene depends on temperature of graphite rod and pressure of buffer gas. Xie et al.[39] ablated Perchloroacenaphthylene($C_{12}C_{l8}$) by Nd:YAG laser in a vacuum which resulted in the production of C_{60} and various perchlorinated carbon clusters. The graphite rod supported by movement assisting device in the pumped liquid helium bath was ablated using Nd:YAG laser by Aratono et al.[40] to produce C_{60}.

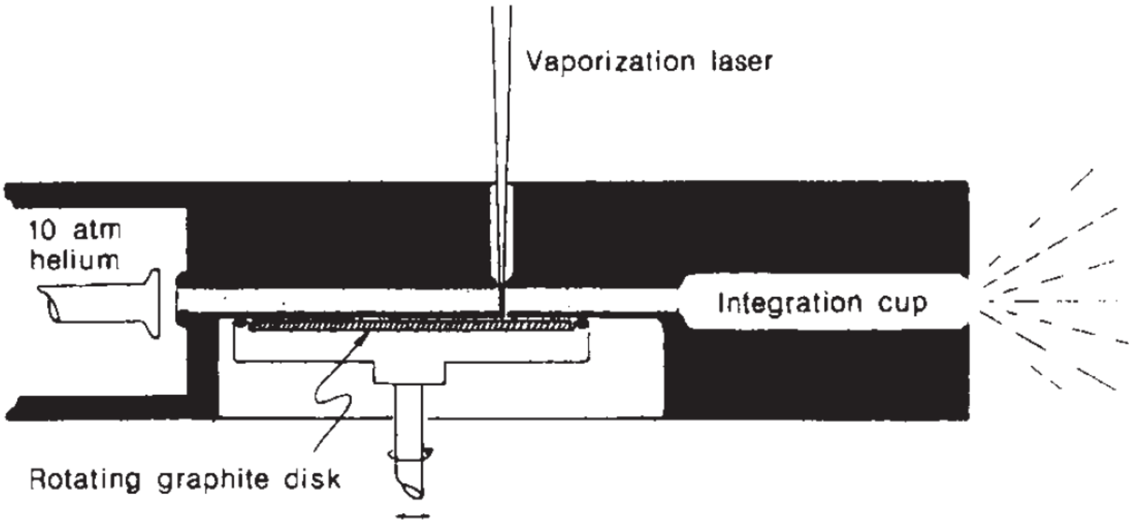


Figure 6. The schematic illustrates a pulsed supersonic nozzle system employed for the generation of carbon cluster beams. The integrating cup can be detached along the designated line. A vaporization laser beam, delivering 30-40 mJ of energy at a wavelength of 532 nm in a 5-ns pulse duration, is focused through the nozzle to strike a graphite disk. The disk undergoes slow rotation to maintain a consistent vaporization surface. High-density helium gas flows across the vaporization region via the pulsed nozzle, serving as a carrier gas to facilitate thermalizing collisions. These collisions are essential for cooling, enabling reactions, and promoting clustering of species within the graphite plasma. Additionally, the helium flow propels the resulting carbon clusters through the nozzle. At the nozzle's exit, the cluster-laden gas undergoes free expansion, forming a supersonic beam. This beam is analyzed 1.3 meters downstream using a time-of-flight mass spectrometer. [5].

2.2. Resistive and Inductive Heating

In this method carbon evaporation is carried out by resistive/inductive heating in presence of a quenching gas atmosphere to obtain large amount of fullerene containing soot. In 1990, Krätschmeret al.[41]evaporated graphite electrodes placed under an inert gas atmosphere by resistive heating[42]to synthesise large amount of C_{60} (Figure 7).Since a high yield of C_{60} was achieved in this process, thus a huge interest among scientists was created and numerous articles were published regarding the study of its physical and chemical properties. Stability of the fullerene family was also evident from the report of Taylor et al.[43]where they showed that C_{70}has a closed cage structure. Diederich et al.[44] used the same method to synthesise higher order fullerenes. Funasaka et al.[45] produced both endohedral fullerenes and exohedral fullerenes by the resistive heating with graphite crucible filled with lanthanum oxide. Otsuki et al.[46]used Joule resistive heating to study the influences of different carbon materials on weight yields of (C_{60}+C_{70}) and weight ratios of C_{60} to (C_{60}+C_{70}) in soot at varying He gas pressures. However, Peters et al.[47] used inductive heating to prioritise the thermal evaporation of carbon at significantly lower temperatures for fullerene formation and used carbon rod of various quality to optimize the process.

Figure 7. Fullerene generator "in action". It is a slightly modified carbon evaporator originally designed and used for TEM sample preparation. The device is currently showcased at the Deutsches Museum in Bonn, Germany..©Wolfgang Krätschmer[48].

2.3. Arc Discharge

In this method an arc voltage is employed across two graphite electrodes under an inert gas atmosphere and fullerenes are deposited as soot inside the chamber. An excellent theoretical background was put forward by Alekseyev et al.[49] covering all the aspects of the problem. Haufler et al.[50] prepared gram quantities of C_{60} using AC contact-arc vaporization of graphite rod in helium atmosphere with a pressure of a 100-Torr (Figure 8). Koch et al.[51]put forward a design of a simple bench-top AC arc discharge reactor for preparation of fullerene. Man et al.[52]found that fullerenes are the minimum energy products while studying the standard energy of combustion of fullerene soot generated in arc discharge and this energy criteria is responsible for the remarkable yield of fullerenes in arc discharge. Scrivens et al.[53]used DC arc discharge method to synthesise C_{60} in gram quantities and found that the absolute pressure, the flow rate of helium gas, the current level of the arc, and the arc gap were important parameters to achieve high yield of fullerenes. Moreover, various carbonaceous solids even coal[54,55] was used as electrode materials to synthesise fullerenes using AC and DC arc discharge. Modified arc discharge methods, for example hybrid plasma (RF and DC)[56],pulsed arc discharge[57], combination of resistive heating and arc discharge[58]etc were also employed for the production of C_{60}.

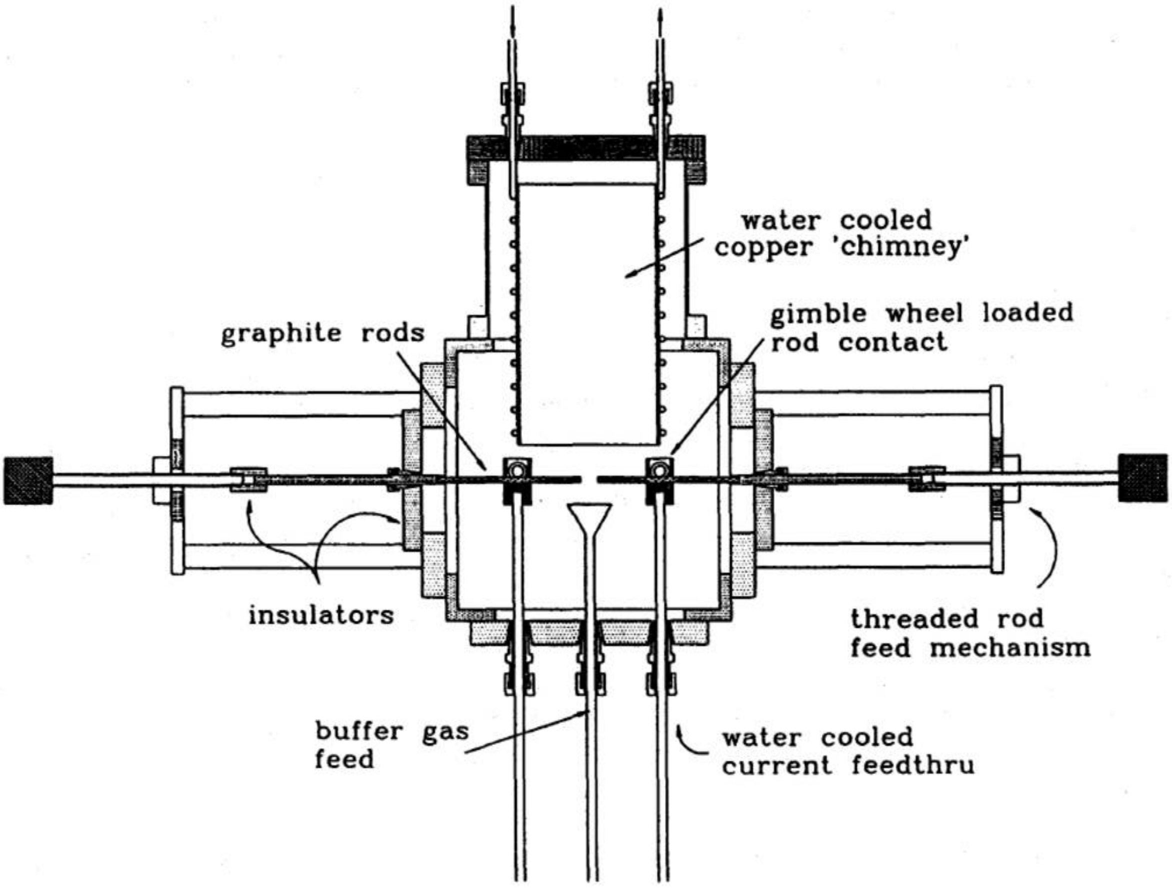


Figure 8. Schematic cross-sectional view of a carbon AC arc C_{60} generator[59].

2.4. Pyrolysis

The process temperature of laser ablation and arc-discharge methods is of the order of 4000°C[60] which demand high thermal budget and also creates great inconvenience to thoroughly understand the fullerene creation process (Figure 9). To decrease the thermal budget and to achieve more control over the process parameters several attempts were made by using hydrocarbons with lower decomposition temperature than graphite as carbon precursors. In 1993, Taylor et al.[61] reported a process to produce C_{60} using pyrolysis of naphthalene at 1000°C. Pyrolysis of other organic precursors such as decacyclene and acenaphthylene[62], benzene/oxygen and acetylene/oxygen mixtures [63],single-wall carbon nanotubes[64], binaphthyl and oligonaphthylene [65], perchlorofulvalene [66] etc. were also reported to produce C_{60}.Osterodt et al.[67] used wide range of hydrocarbons, cyclopentadienide metal complexes, and mellitic acid anhydride to synthesise fullerenes.

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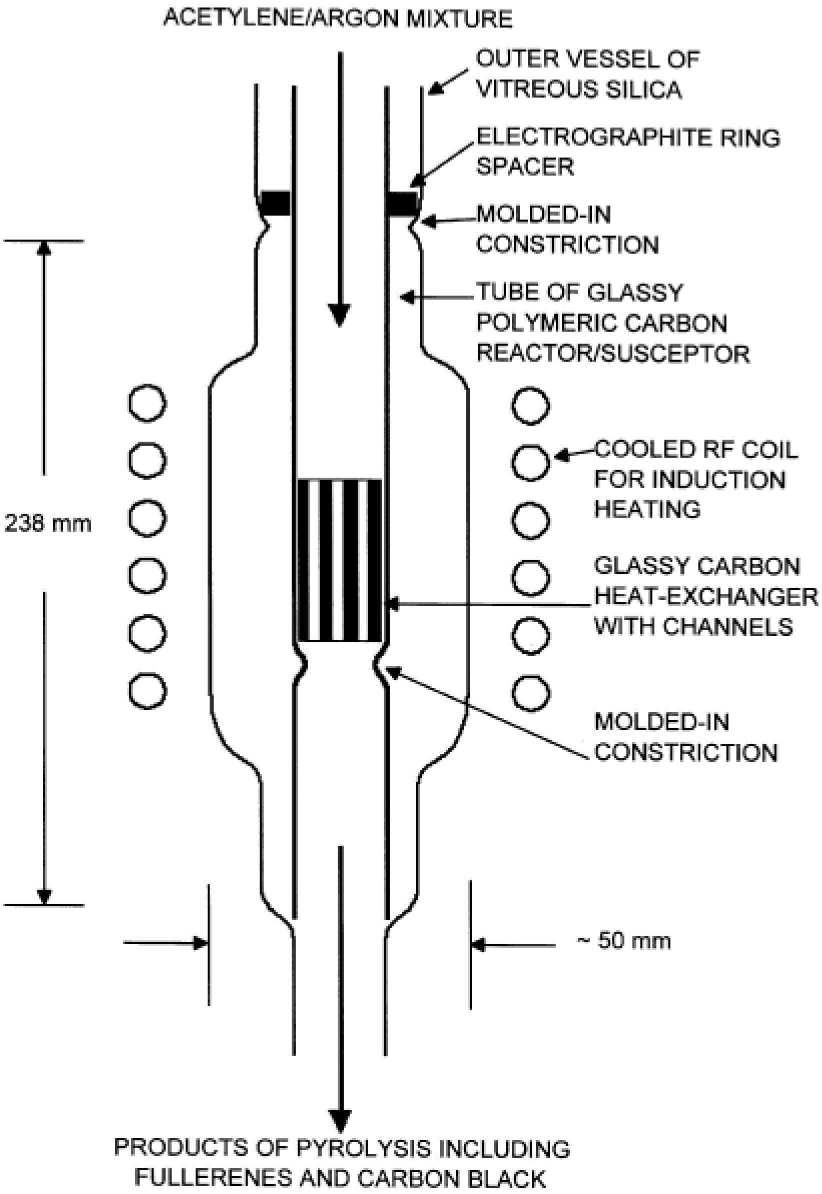

Figure 9. Schematic layout of the reactor for generating fullerene from acetylene[68].

2.5. Combustion/ Flame Synthesis

In the year of 1991 Howard et al.[69]first reported the synthesis of fullerenes using hydrocarbon (such as benzene) combustion (Figure 10).They found that the temperature, pressure, and carbon/oxygen ratio are the deterministic parameter for the resulting C_{60}/C_{70} ratio. They also used[70]premixed laminar benzene/oxygen/argon flames for the synthesis of C_{60} and $C_{70}$by varying the process parameters including pressures and C/O ratio. Combustion method can also be employed to synthesise higher fullerenes using benzene/oxygen/argon at pressures of 40 Torr [71].They also compared the combustion method to the arc discharge and found that the combustion method is superior for the production of higher fullerenes. Reilly et al.[72]used real-time aerosol mass spectrometry for direct observation of the chemical evolution of flame-generated soot containing fullerenes. Ozawa et al.[73]reviewed the advancement in the synthesis of fullerenes from flaming soot with respect to the experimental conditions, characteristics in the product distribution, and formation mechanisms.

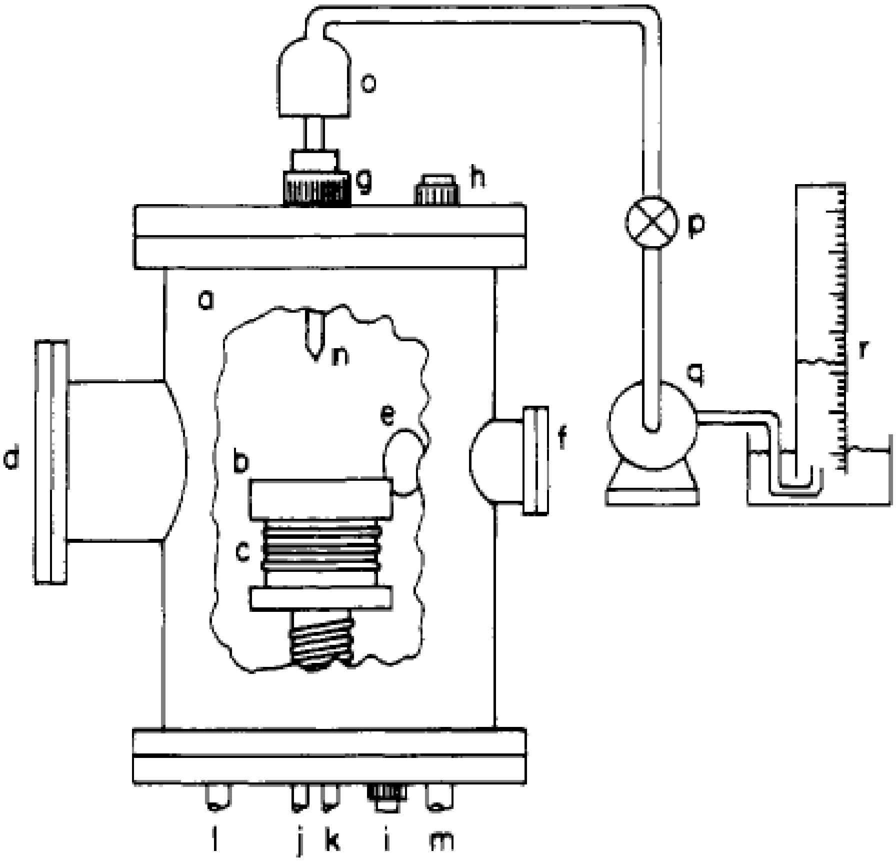

Figure 10. The burner and its related components include: a) a low-pressure chamber; b) a copper burner plate; c) a water cooling coil; d, e, and f) windows; g, h, and i) feed-throughs; j) an annular-flame feed tube; k) a core-flame feed tube; l and m) exhaust tubes; n) a sampling probe; o) a filter; p) a valve; q) a vacuum pump; and r) a gas meter.[74].

Other than the above mentioned methods solar energy[75,76], electron beam irradiation[77] and chemical methods[78] can be applied to prepare fullerenes.

3. Conclusion

Fullerenes, particularly C_{60}, represent a landmark discovery in carbon nanomaterials due to their exceptional symmetry, stability, and versatile properties. Advances in synthesis techniques—from high-energy processes like laser vaporization and arc discharge to lower-temperature methods like pyrolysis and combustion—have enabled scalable production. The icosahedral structure and electronic configuration of fullerenes drive their potential applications in fields such as nanotechnology and materials science. As research continues, further refinements in synthesis and characterization promise to unlock new functionalities and applications for these fascinating molecules.

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