Fullerenes and their Applications in Science and Technology

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***Abstract*— This paper reviews Fullerenes and their applications in science and technology. Fullerenes are molecules composed entirely of carbon that were discovered in 1985 at Rice University. This paper explores the molecular structure of these molecules and different synthesis methods used nowadays. Many of the practical applications of Fullerenes follow directly from their extraordinary properties. Relevant chemical, physical and optical properties are assessed, which make Fullerenes essential components for the future of nanoelectromechanical systems. In many cases, the necessity of building organic compounds leads to the exploration of nanostructures like Fullerenes. These molecules bring to the word engineering flexibility and promising applications in electrical, military and medical fields.**

***Index Terms*—Applications, Buckminsterfullerene, Fullerenes, Hydrogen Storage, Molecular Wires, Properties, Structure, Solar Cells, Synthesis.**

I. INTRODUCTION

FULLERENES were discovered experimentally for the first time in September 1985. The Buckminsterfullerene, named after the American architect Buckminster Fuller, whose geodesic dome it resembles was observed by a group of scientists including Richard Smalley, Robert Curl and Harry Kroto at Rice University, Huston. For their novel discovery, they shared a Nobel Prize in 1996. Other fullerenes were discovered shortly afterwards with more and fewer carbon atoms; they ranged from 18 atoms to up to hundreds of atoms. Among them, the Buckyball containing 60 carbon atoms is the most popular. C_{60} remains the easiest to produce and the cheapest, with prices rising rapidly for other larger fullerenes. This paper explores the structure and production of fullerenes as well as the chemical, mechanical and optical properties that make them outstanding molecules in several applications in science and technology. The rest of the paper is organized as follows: section II presents the structure and synthesis of Fullerenes; section III shows the most relevant properties of the molecule, and section IV explains scientific and technological potential applications of Fullerenes. Finally, section V draws the conclusions.

II. STRUCTURE AND SYNTHESIS

Fullerenes are composed entirely of carbon. They can be found in three different forms: spherical, elliptical and in the form of tubes.

2.1 Buckyball Structure

The structure of the C_{60} Buckyball is a combination of 12 pentagonal and 20 hexagonal rings, forming a spheroid shape with 60 vertices for 60 carbons. Figure 1 shows the structure of the molecule, which reveals how the pentagonal rings sit at the vertices of an icosahedron such that no two pentagonal rings are next to each other. The average C-C bond distance measured using nuclear magnetic resonance (NMR) is 1.44 A°. A diameter of 7.09 A° is calculated for the C_{60} based on the fact that the C-C distance is equal to 1.40 A° for the hexagon bonds and 1.46 A° for the pentagonal bonds length [1].

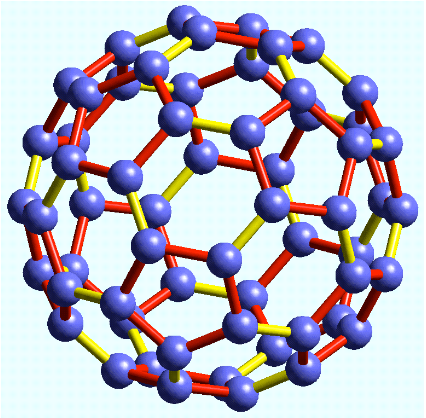

Fig 1 C_{60} Molecular Structure

2.2 Synthesis of Fullerenes

In 1990, Krätschmer and his colleagues developed a contact arc discharge method for macroscopic production, known as the Krätschmer-Huffman method. They discovered that carbon rods heated resistively in a helium atmosphere cloud generate gram quantities of fullerenes embedded in carbon soot, which was also produced in the process. This method consists of graphite electrodes contact arcs passing alternating or direct current through them in an atmosphere of helium in approximately 200 torr. The evaporated graphite takes the form of soot, which is dissolved in a nonpolar solvent. The solvent is dried away and the C_{60} and C_{70} fullerenes can be separated from the residue. Optimal current, helium pressure and flow rate leads to yields of up to 70% of C_{60} and 15% of C_{70} with this method. Laser vaporization is also used for fullerene production. In a typical apparatus a pulsed Nd:YAG laser operating at 532 nm and 250 mJ of power is used as the laser source and the graphite target is kept in a furnace at 1200 °C. Finally, it should be mentioned that fullerenes have also been produced in sooting flames involving, for example, the combustion of benzene and acetylene, although the yields are low [2].

III. PROPERTIES

In this section, Fullerenes' most relevant properties are presented. The study of these properties led scientists to think of the multiple applications that the molecule could have.

3.1 Chemical Properties

The carbon atoms within a Fullerene molecule are sp^2 and sp^3 hybridized, of which the sp^2 carbons are responsible for the considerably angle strain presented within the molecule. C_{60} and C_{70} exhibit the capacity to be reversibly reduced with up to six electrons. This high electron affinity results from the presence of triply-degenerate low-lying LUMOs (lowest unoccupied molecular orbital). Oxidation of the molecule has also been observed; nevertheless, oxidation is irreversible. C_{60} has a localized pi-electron system, which prevents the molecule from displaying superaromaticity properties.

3.2 Physical Properties

Fullerenes are extremely strong molecules, able to resist great pressures—they will bounce back to their original shape after being subject to over 3,000 atmospheres. Theoretical calculations suggest that a single C_{60} molecule has an effective bulk modulus of 668 GPa when compressed to 75% its size [3]. This property makes fullerenes become harder than steel and diamond, whose bulk moduli are 160 GPa and 442 Gpa, respectively. An interesting experiment shows that Fullerenes can withstand collisions of up to 15,000 mph against stainless steel, merely bouncing back and keeping their shapes. This experiment resembles the high stability of the molecule.

3.3 Optical Properties

Delocalized pi electrons in Fullerenes are known to provide exceptionally large nonlinear optical responses. Fullerenes have shown particular promises in optical limiting and intensity-dependent refractive index. Additionally, the transfer of electrons from enclosed atom(s) to the Fullerene enhances the third-order nonlinear optical effect by orders of magnitude compared to empty cage Fullerenes.

IV. APPLICATIONS

4.1 Solar Cells

The high electron affinity and superior ability to transport charge make Fullerenes the best acceptor component currently available. First, they have an energetically deep-lying LUMO, which endows the molecule with a very high electron affinity relative to the numerous potential organic donors. The LUMO of C_{60} also allows the molecule to be reversibly reduced with up to six electrons, thus illustrating its ability to stabilize negative charge.[4] Importantly, a number of conjugated polymer–fullerene blends are known to exhibit ultrafast photoinduced charge transfer, with a back transfer that is orders of magnitude slower. The state of the art in the field of organic photovoltaic is currently the Bulk Heterojunction (BHJ) solar cells based on Fullerene derivate phenyl-C61_butyric acid methyl ester (PCBM), whit reproducible efficiencies approaching 5 % [5].

Conventional silicon solar cells exceed 20% efficiency. Therefore, we can ask ourselves, why is it so important to think of organic solar cells? First, the cost of production of organic light-converting devices compared to the corresponding inorganic analogues is lower by more than two orders of magnitude. And second, an important merit of organic solar cells is their flexibility. They can be rolled up, cut, and spread over any surface. Particularly, such plastic can be used for covering both the inner and outer walls of buildings; cells of any color and texture can be manufactured. For example, a cell phone can be painted with this material, thus walking in a sunny day will be enough to charge the device's battery. American military departments actively support projects associated with organic solar cells because these materials demonstrate high capabilities to be used in new armaments and attendant systems [6].

Finally, great expectations are also associated with the use of organic cells in the advertising and packaging business. These involve autonomous luminous banners, large liquid-crystal line displays and packaging for food.

4.2 Hydrogen Gas Storage

Due to its unique molecular structure, fullerene is the only form of carbon, which potentially can be chemically hydrogenated and de-hydrogenated reversibly [7]. When fullerenes are hydrogenated, the C=C double bonds become C-C single bonds and C-H bonds. The bond strength of single C-

C bonds is 83 kcal/mole, and theoretical calculations show that the bond strength of the hydrogenated C-H bond is 68 kcal/mole[7] . This means that for fullerene hydrides, the H-C bond is appreciably weaker that C-C bonds. Therefore, when heat is applied to fullerene hydrides, the H-C bonds will break before the C-C bonds, and the fullerene structure should be preserved. The considerably lower heat of formation for $C_{60}H_{36}$ indicates that $C_{60}H_{36}$ as a molecule is thermally more stable than C_{60}. Therefore, hydrogenation of C_{60} is thermodynamically favored and can be accomplished under the right chemical conditions. The color of the hydrogenated fullerene changes from black to brown, then to red, orange, and light yellow with increasing hydrogen content. Fullerenes with up to 6.1% hydrogen content has been developed experimentally [7]. A potential application of fullerene hydrides is in hydrogen gas storage devices for electric vehicles that would employ a fuel cell. Currently available hydrogen storage technologies like compressed gas or storage as metal hydrides are potentially hazardous and/or have low hydrogen storage densities. Table 1 [7] shows a comparison of the amount of media required for storage when using Fullerenes versus a metal hydride. The metal hydride storage media used in this comparison is Titanium Zirconium Vanadium.

Table 1 Comparison of Hydrogen storage capacities for internal combustion engines

Comparison of Hydrogen Storage Capacities for Internal Combustion Engines		
	Fullerenes	Metal Hydride
Hydrogen Required to Operate 250 Miles	12 lbs	12 lbs
Amount of Storage Media Required	197 lbs	1200 lbs

4.3 Fullerene Strengthening/Hardening of Metals

Fullerenes offer unique opportunities to harden metals and alloys without seriously compromising their ambient temperature ductility. This is due to the unique characteristics of fullerenes, namely their small size and high reactivity, which enable the dispersion strengthening of metallic matrices with carbide particles that result from in-situ interactions between fullerenes and metals. In a comparison of the hardness of a popular aerospace intermetallic compound Ti-24.5AI-17Nb, with and without fullerene additives, a 30% hardness enhancement was measured for the material with fullerene additives [8].

4.4 Fullerene as Precursor to Diamond

Fullerenes have proven to be an excellent precursor to diamond. This can be attributed in part to the curved structure of fullerenes, which possess a partial sp' (diamond) bonding configuration, as opposed to graphite, which is planar. Argonne National Laboratories and MER Corporation have investigated fullerenes as the source of carbon to CVD deposit diamond with excellent results. MER has demonstrated excellent diamond coatings using fullerenes as the only source of carbon to deposit diamond at five times the growth rate of methane carbon sources, resulting in a projected 70% cost savings [7]. With low cost fullerenes it can be expected that conversion to diamond will be a very important commercial application.

4.5 Optical Application of Fullerene

Optical limiting refers to a decrease in transmittance of a material with increased incident light intensity. The phenomenon of optical limiting has a significant potential for applications in eye and sensor protection from intense sources of light. Based on the optical limiting properties of fullerenes, one can make an optical limiter, which allows all light below an activation threshold to pass and maintains the transmitted light at a constant level below the damage threshold for the eye or the sensor [7]. Figure 2 shows the typical performance of an optical limiter.

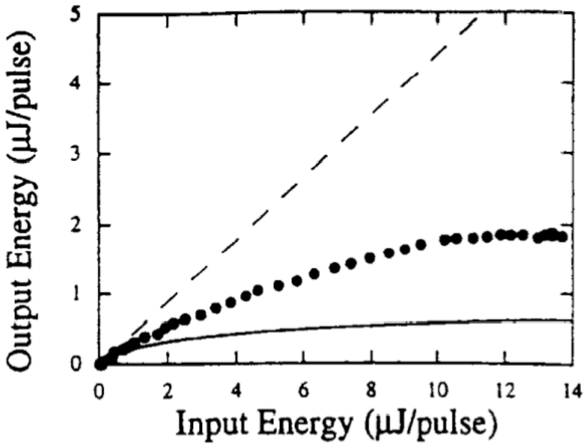

Fig. 2 Optical Limiter Transfer Characteristic

4.6 Fullerenes Based Sensors

Fullerene-based interdigitated capacitors (IDCs) recently have been developed to explore sensor applications. This novel solid-state sensor design is based on the electron accepting properties of fullerene films and the changes that occur when planar molecules interact with the film surface. Fullerene chemistry provides a high degree of selectivity and the IDC design provides high sensitivity. The solid-state chemical sensor's small size, simplicity, reproducibility and low cost make them attractive candidates for fullerene applications development.

Studies of IDC configurations with fullerene films have able to sense water in isopropanol with a resolution of 40 ppm [7]. These results demonstrate the feasibility of using fullerenes as selective dielectric films for IC chemical sensors.

4.7 Fullerenes as Molecular Wires

Recent experiments have documented electron transport through single molecules. Under certain experimental conditions molecular conduction through a single molecule rather than through an ensemble of molecules is guarantee. This phenomenon is possible due the high electron affinity of Fullerenes. If a molecular computer is ever to be built, then it will need molecular wires in order to connect to its various components. Figure 3 shows a computer created scenario of a possible use of Fullerenes in the manufacture of molecular conductors. When a source of UV light is applied to the system in figure 3, the Fullerene molecules get excited and electrons move from the Porphyrin wire towards the Fullerenes. These electrons leave holes in the Porphyrin through which electrical current can flow from one electrode to the other [9].

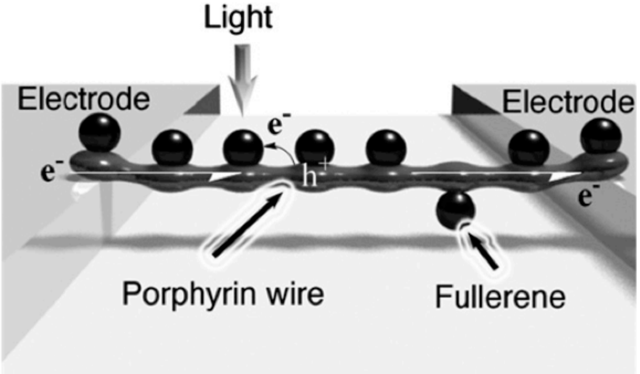

Fig. 3 Molecular Wire System

4.8 Fullerene in Medicine

Interest of scientists in water-soluble fullerene compounds is directly related to their biological activity. Dendrimer 4p containing 18 carboxyl groups is the more promising today. The synthesis and the use of this compound in medicine were patented in the U.S. (C-sixty Corporation); at present, this drug undergoes clinical trials as a promising medication for treatment of AIDS [10]. Fullerene derivatives can be used in the photodynamic cancer therapy as antibacterial agents and medications of neuroprotective action. Because of their ability to enclose atoms, Fullerenes promise to be of great use as drug carriers. Additionally, noble gases have been encapsulated in Fullerenes, which have no desire to bond with the surrounding carbon atoms but can be used in applications such as magnetic resonance imaging (MRI). Researchers at Rice University have designed C_{60} and other fullerenes molecules with an atom of gadolinium inside and with chemical appendages that make them water-soluble. In typical MRI contrast agents, the metal gadolinium is lined to a non-fullerene molecule, which is normally excreted quickly from the body. Fullerenes encapsulated with gadolinium might allow the contrast agent to remain in the body longer, allowing doctors to perform slower studies.

4.9 Endohedral Fullerenes

Endohedral Fullerenes are created when an atom is inserted inside a Fullerene molecule. Figure 4 illustrates an example of a Fullerene containing a non-carbon atom inside.

Fig. 4 Endohedral Fullerene

In one of the methods employed for this purpose, ions are accelerated and implanted to the C_{60} cage. The first collision should absorb and redistribute a good part of the kinetic energy to ensure that the ions have just enough energy to open the cage and enter, without having sufficient kinetic energy left to escape. Metallofullerenes made this way include $M@C_{60}$ with M =Li, Ca, Na, K, Rb. Larger yields can be achieved by co-evaporation of the carbon and the metal in an arc discharge chamber (typical for fullerene production). However, in this process mostly higher endohedral fullerenes, like $M@C_{82}$, are formed. These Metallofullerenes are very stable molecules and can be use in many applications. For example, it has been shown that the bulk modulus of $K@C_{60}$ is higher than that of C_{60}, and while C_{60} rolling dynamics are the same as K $@C_{60}$ rolling dynamics, the sustaining pressure of K $@C_{60}$ intercalated between layers was higher than that of C_{60} intercalated between layers. From this it can be concluded that for nano ball-bearing applications, Metallofullerenes are more effective than fullerene. A crystal of $La@C_{60}$ is predicted to be an air-stable superconductor since there is a complete charge transfer from La to the C_{60} cage resulting in a triply charged molecule. Finally, we want to make use of the spin dynamics of the endohedral fullerenes $N@C_{60}$ and $P@C_{60}$ in molecular spin electronic devices such as a quantum computer. Because the C_{60} fullerene shields the incorporated nitrogen or phosphorus atom from the environment, these molecules have exceptional spin properties, notably very long electron spin relaxation times [11].

V. CONCLUSIONS

Fullerenes, the third form of carbon, have become important molecules in science and technology. Due to their very practical properties, fullerenes are a key topic on nanotechnology and industrial research nowadays. The applications presented in this paper are possible uses of the molecules due to one or more of their extraordinary properties. Fullerenes are used in today’s industry already, mostly in cosmetics, where they play an important role as antioxidants.

The cost of Fullerenes is directly related to the feasibility of implementing several of the applications discussed in this paper. As more applications of Fullerenes become available, the demand for these molecules will increase and we will be able to see a significant decrease on the price of Fullerenes per gram compared to today’s market value.

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