Fullerenes—an attractive nano carbon material and its production technology

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Carbon has three allotropes: graphite, diamond, and a molecular form known as fullerene. This article describes the first low cost, high volume process for manufacturing fullerenes, introduced by the Frontier Carbon Corporation (FCC) (Figure 1). FCC is a venture company in Japan whose shareholders are the Mitsubishi Chemical Corporation (MCC), the largest chemical company in Japan, and the Mitsubishi Corporation (MC). It was founded in December 2001. Fullerenes have been commercially available since 2002 in Japan.

Figure 1. FCC commercial products and production plant.

Fullerenes are one of the most famous nano carbon materials, together with carbon nanotubes. Fullerene[1–4] is a kind of a family name whose members are spherical molecules made entirely of carbon atoms with a symmetric three dimensional structure. Of the fullerenes, C_{60} is the most

[1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl & R.E. Smalley, "C_{60}: buckminsterfullerene", *Nature*, **318** (1985) 162–163.
[2] W. Kratschmer, L.D. Lamb, K. Fostiropoulos & D.R. Huffman, "Solid C_{60}: a new form of carbon", *Nature*, **347** (1990) 354–358.
[3] Third Allotrope of Carbon—Fullerene Chemistry (Furaren no Kagaku), *Kikan Kagaku Sosetsu*, No. 43 (1999) 1–254.
[4] M. Arikawa, "New carbon material: fullerene production and recent trend of fullerene application", *Journal of Japan Society of Powder and Powder Metallurgy*, **52** (2005) 109–114.

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common molecule, and can be produced by a variety of syntheses. The structure of C_{60} is very similar to that of a soccer ball. Each carbon atom is located at the positions corresponding to the cross points of a soccer ball's pentagons and hexagons. Professor Osawa predicted the existence of this molecule, and it was discovered in 1980 by Drs Kroto, Curl and Smalley, an achievement recognized by the award of the 1996 Nobel Prize for Chemistry. Figure 2 shows the molecular model of C_{60}. Its diameter is 0.71 nm, and around 1 nm when including the orbital electrons. In the fullerene family, there are also C_{70} (whose shape is similar to that of a rugby ball), C_{76}, C_{80}, C_{82} and so on to possibly some few hundreds of carbon atoms. Other types of fullerenes also exist, like endohedral metallofullerenes, which have other atoms like gadolinium (Gd) inside their cage structures; or fullerene derivatives that have a function added to the cage by organic synthesis methods.

Fullerenes can be dissolved into organic solvents, whereas other kinds of carbon material can not be. Fullerenes themselves are a black powder, whose appearance resembles that of carbon black. The true density of C_{60} is 1.73 g/cm^3, and the bulk density is 0.6 g/cm^3. When placed into an organic solvent, e.g. toluene, and mixed well, the powder is dissolved into the solvent to yield a coloured solution. The colour of C_{60} in solution is violet like grape juice, while C_{70} in solution is reddish brown; the solution of each fullerene has its own different colour according to the carbon atom number. "Dissolving" is defined in the sense that nothing is caught by the finest filter, or that coherent light is not diffracted during its passage through the solution. Some typical features are summarized in Figure 3.

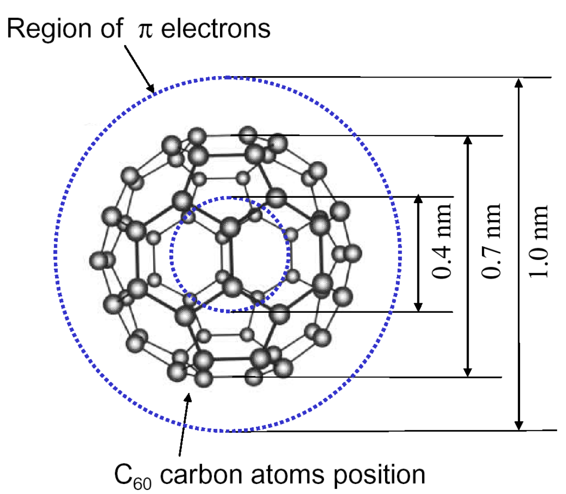

Figure 2. Molecular model of C_{60}.

- Carbon molecule w/diameter of 1 nm
- Cage structure
- Can be dissolved
- Can be functionalized
- Guest-host complexation
- Excellent electron acceptor
- Efficient radical scavenger
- Photoexcitation
- Thermally stable
- Low thermal conductivity
- Can be sublimed
- Can be polymerized

Figure 3. Some typical features of fullerene.

The double electron bond makes fullerenes easy to synthesize into different molecules. Fullerene chemical reactions, leading to for example hydrogenated fullerene ($C_{60}H_n$), hydroxylated fullerene ($C_{60}(OH)_n$) or halogenated fullerene, have been reported. Some compounds are known to form a kind of self-assembly structure. For example, it has been found that a kind of fullerene derivative, C_{60} with five functions added to fixed positions, forms a double layer molecular film and adopts a vesicular structure with a diameter from 29 to 54 nm.[5,6] Figure 4 shows the fullerene derivatives that can be supplied by FCC up to kg quantities.

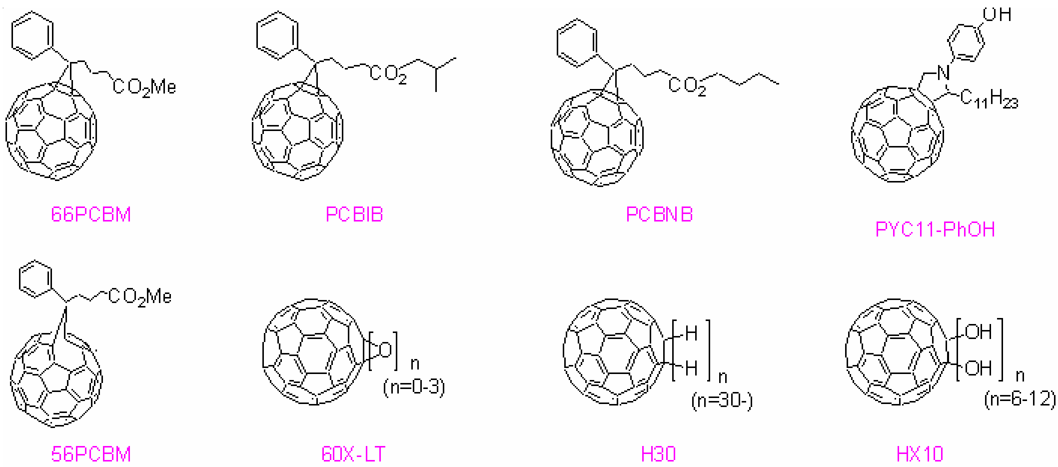

Figure 4. Some fullerene derivatives supplied by FCC.

Dissolving is one of the key aspects of obtaining pure fullerenes, for example, over 99% pure C_{60} is available. The most popular method to produce pure fullerene is by high performance liquid chromatography (HPLC). Both the pharmaceutical and the semiconductor applications require the fullerene molecules to be very pure without any contaminants.

Another characteristic that is different from those of most other carbon materials is electrical resistance. Usually, carbon materials are good electrical conductors, but fullerenes are insulators like diamond. This characteristic is usually found in the bulk powder form, and under the special conditions of a thin film with a thickness of few molecules, where quantum effects modify the conductivity.

The final noteworthy characteristic is the thermal behaviour. Fullerenes start to be oxidized at about 300 °C, but in an inert environment, like a nitrogen atmosphere, fullerenes sublime at a definite temperature. This temperature is dependant on pressure, and is around 550–650 °C at a pressure of one atmosphere. Among the allotropes of carbon, only fullerenes may be sublimed, and by using this property, a thin fullerene film may be deposited on the surface of many kinds of substrates by using conventional processing techniques familiar in the semiconductor industry.

Fullerene applications

A decade after the discovery of artificial fullerene synthesis in 1990, over seven hundred application patents using fullerenes had been filed in many countries. Figure 5 depicts the potential applications envisaged by the patentees. Nevertheless, very few commercial products

[5] E. Nakamura et al., "Spherical bilayer vesicles of fullerene based surfactants in water: a laser light scattering study", *Science*, **291** (2001) 1944–1947.
[6] E. Nakamura et al., "Stacking of conical mesogens with a fullerene apex into polar columns in crystals and liquid crystals", *Nature*, **419** (2002) 702–705.

have been realized. The reason was the high price of fullerene, more expensive than that of gold before 2001, and the total amount of fullerene produced in the world was very limited.

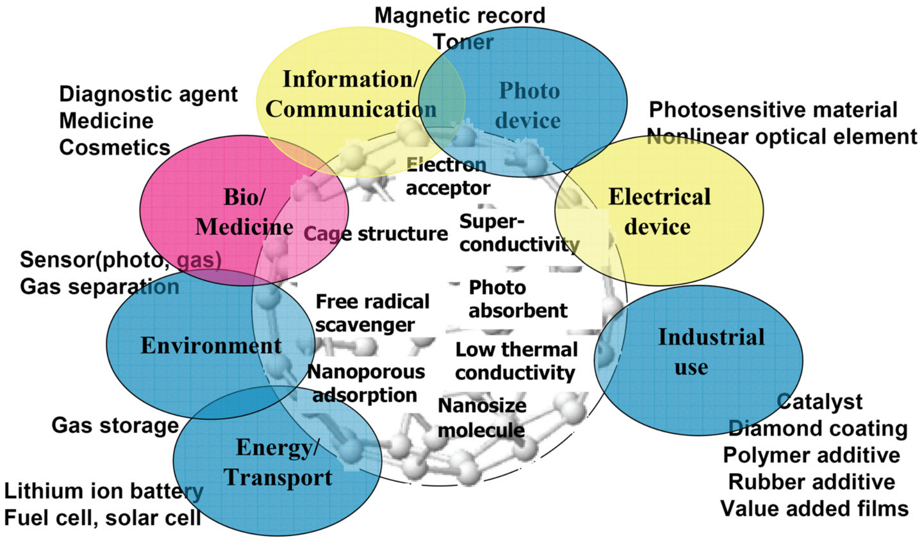

Figure 5. Application patent map (covering the period 1990 to 2000).

In 2002, FCC completed its pilot fullerene production system and by 2003 had completed the first commercial production plant with a capacity of several tens of cubic tons. This helped the boom in nanotechnology by enabling many new application studies, one of which was the appearance of the bowling ball in which the surface plastic is endowed with dispersed fullerenes to improve its rolling characteristics.

Current fullerene application products that the public can access are the following:

1) Bowling ball
2) Golf clubs with titanium golf heads, carbon fibre reinforced plastic (CFRP) shafts and golf balls
3) Badminton rackets using CFRP frames and strings
4) Tennis rackets using CFRP frames and strings
5) Snowboards using CFRP components and wax
6) Plastic eyeglass frames
7) Additives to compressor oil in automotive air conditioners.

The functions that fullerenes fulfill in each product differ, but may be categorized according to the following functions.

A) Interaction or reaction with radicals
B) Nano filler properties
C) Carbon source
D) Interfacial material between organic and inorganic materials
E) Basic component of fullerene derivatives.

Many fullerene applications are being investigated, for example, as organic electronics devices like organic photocells, organic transistors, battery components, materials for the next generation of semiconductors, as pharmaceutical products, and so on.

A medicine for cancer using a light-induced technique, an anti-HIV medicine using fullerenes as objects of a definite molecular size, and other kinds of medicine are being developed.[7] Fullerene derivatives are being developed as drugs for Lou Gehrig's and Parkinson's diseases by adding different functional groups to fullerene. Animal testing has shown that some fullerene derivatives protect neurons from degradation. There is further interest in self-assembled clusters of fullerene derivatives as drug delivery vessels. Fullerene derivatives can provide therapeutic benefits in a variety of fields. Endohedral metallofullerenes, which contain a metal atom within the cage, may have application as media for tomography diagnosis.

Production of fullerenes

In general the fullerene production process is composed of the following five subprocesses:

1) Synthesis process of fullerenes or fullerene-containing soot
2) Extraction process of fullerenes from the fullerene-containing soot
3) Separation & purification process for each fullerene molecule giving pure fullerene such as C_{60}
4) Synthesis of fullerene derivatives using the techniques of organic synthesis
5) Post-processing, e.g. dispersion of fullerene into water or other media.

The production flow based on combustion synthesis is shown in Figure 6. Each actual, realized process must satisfy the following three requirements for an industrial production system:

A) Reasonable production cost
B) Supply reliability in terms of amount and delivery time
C) Established and assured quality.

Two methods are mainly used for fullerene synthesis in practice. One is the arc method[3] and the other is the combustion method.[8–11] Figure 7 shows both methods. In the arc method, two graphite rods are placed with small gap between them in the reactor chamber filled with an inert gas below atmospheric pressure. When a high DC voltage is applied to the rods, an arc is formed, and the carbon of the rod is evaporated and decomposed. On cooling, the carbon atoms recombine and fullerenes are synthesized simultaneously with soot. This fullerene and soot is accumulated on the surface of the inner wall of the reactor chamber. The soot is collected and the fullerenes are extracted by the solvent. The problem of this method lies in its production scale. It is hard to produce large amounts of fullerenes by this method, as a stable broad arc seems to be impossible to achieve.

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[7] S.R. Wilson, "The potential of fullerenes in biology and medicine", *Proc. Electrochem. Soc.* **97-42** (1997) 321–322.

[8] Jack Howard et al., "Method to produce fullerenes", Japanese patent 3404632 (2003).

[9] Michel J. Alford et al., "Burner for carbon nano material production and its combustion system", Japanese patent 2003–525710 (2002).

[10] H.Takehara, "Production method for fullerene", Japanese patent 3718516 (2004).

[11] H.Takehara et al., "Experimental study of industrial scale fullerene production by combustion synthesis", *Carbon* **43** (2005) 311–319.

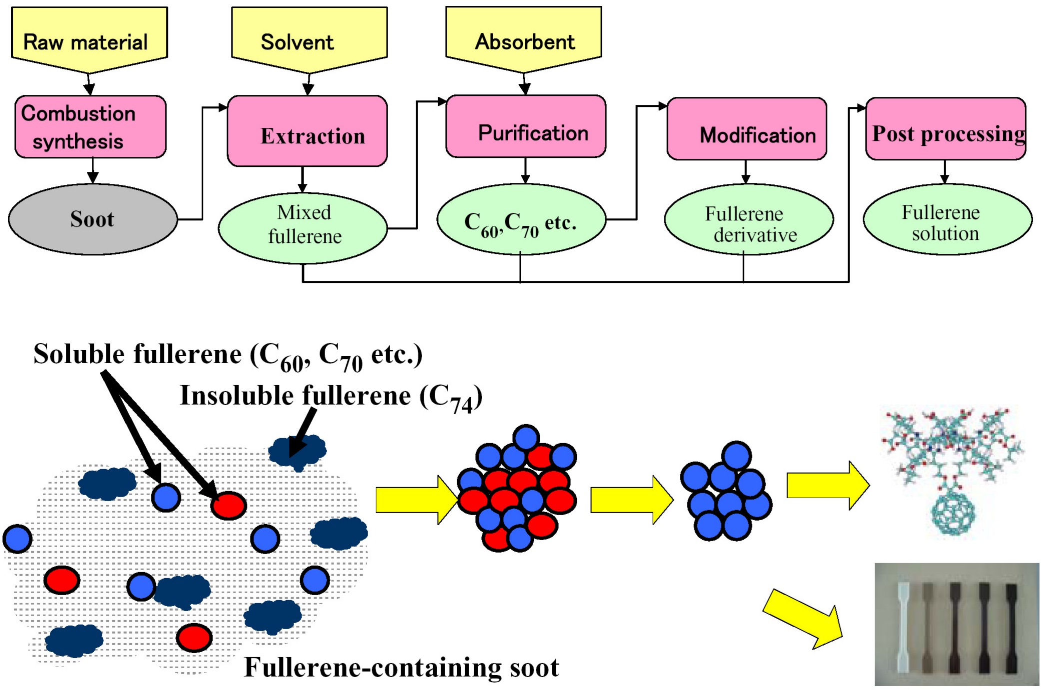

Figure 6. Fullerene production flow (combustion method).

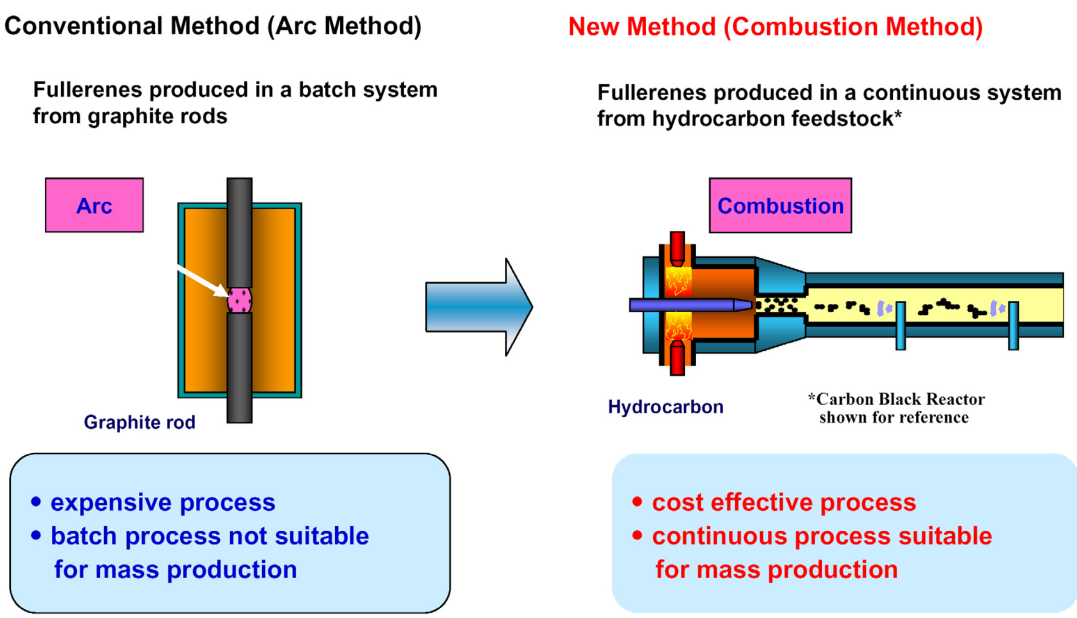

Figure 7. Fullerene synthesis methods; arc method and combustion method.

In spite of many producers and suppliers who used the arc method, the total amount of fullerene on the world market was not large until 2003.

The combustion method was discovered at the Massachusetts Institute of Technology when fullerenes were found in a flame under special conditions. TDA Research Inc., Denver, Colorado demonstrated a prototype of a large fullerene production burner system, and through collaboration between TDA and FCC, this prototype was improved. In 2003, FCC finished constructing their commercial fullerene production plant, and capacity rose to about 40 cubic tons per year of mixed fullerenes.

A hydrocarbon fuel is burnt under fuel-rich conditions, which results in imperfect combustion and soot is produced. The soot production process is similar to that for carbon black or charcoal black, but under special conditions much fullerene is generated in the flame. The carbon black process produces a tiny amount of fullerene, but not in quantities sufficient for commercial production. In the fullerene combustion method, the yield and the composition can be controlled by the combustion conditions. One of them is the ratio of fuel to oxygen.

The details of this process are as follows;

1) Introduce the fuel and oxygen into the combustion system

2) Burn them using a special burner system

3) With high temperature and the imperfect combustion, fullerene is synthesized along with soot

4) After cooling, the fullerene-containing soot is filtered from the combustion gas by the filter system

5) Periodically the fullerene-containing soot is taken out of the system.

Using an automatic system for pulsing the filter, the fullerene-containing soot can be taken out continuously.

In 2001 the typical price of fullerene was about 50 U.S. dollars per gram. By using the combustion method, FCC realized large capacity production and started to sell at a price of 5 dollars per gram.

The fuel can be an aromatic hydrocarbon especially benzene or toluene, or acetylene.

The typical types of burner are the diffusion type and the premix type. The premixing burner has shown good results in many published papers and patents.

Some fuel is burnt to create the high temperature field, and the rest is used as the raw material for the fullerenes. The dehydration reaction is critical and by tuning the carbon-oxygen ratio, the yield and the composition of fullerene within the soot can be controlled.

Other methods like thermal plasma or pyrolysis have been reported, but none has shown more production capability than the combustion method. By understanding the fullerene synthesis mechanism, new synthesis processes with more productivity or higher yield than the current technology may be expected in the future.

The link between development speed and collaboration

There are many reasons for the surprisingly rapid development of fullerene production, one key aspect of which has been collaboration with other research venture companies, Universities, Government organizations, and so on. Once production is sorted out, the next challenges are the real industrial applications that consume much fullerenes in a short interval, and their realization has been started by FCC and its customers.

Conclusions

Fullerene is a new material with many valuable characteristics. The commercial production of fullerene has already been realized, and abundant stocks are now accessible. The price is already only one tenth of that prevailing in 2001, and will be further reduced in the near future, but the science and technology regarding fullerene production, the corresponding materials science and the applications development, are still in progress.