Fullerenes, Carbon Nanotubes and Carbon Nano-Onions —They could Be Plasma Crystals

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A large variety of polyhedral carbon forms, based on closed network of 5/6 rings of carbon, was discovered near the end of 20th century and named fullerenes. Typical forms of the members of fullerenes, including C_{60}, carbon nanotubes and carbon nano-onions are briefly introduced. In spite of unprecedented vigor in research and developmental activities into the properties and applications of fullerenes, the origin of exotic forms in fullerenes still remains unknown. We propose here that the fullerenes could be the results of crystallization of complex plasma of carbon. Close analogy between carbon nano-onions and mm-sized Coulomb balls is mentioned. The latters are nested spherical shells consisting of micron-sized plastic spheres and crystallized in spherical potential field.

Key words: Polyhedral Carbons, Cage Molecules, Complex Plasma, Nested Balls

1. Introduction

Shown in Fig. 1 is the most beautiful (Aldersey-Williams, 1994) and the most famous molecule in chemistry, buckminsterfullerene, discovered by Kroto *et al.* (1985). It is also called "bucky ball" for brevity. The molecule is a truncated icosahedron and consists of 60 carbon atoms, all chemically and magnetically equivalent and distributed evenly on the surface of circumscribing sphere. Chemists often call it simply as C_{60} despite the fact that there are 1812 structural isomers for this formula (Fowler and Manolopoulos, 1995). When first published, C_{60} has not been isolated (Kroto *et al.*,1985). Hence C_{60} became the most attractive target to synthesize, and vigorous race to the first synthesis began. After five years a surprisingly simple method, consisting of evaporating carbon rod by resistive heating under the atmosphere of helium, was found by Krätchmer and Huffman (1990). C_{60} spontaneously crystallized on the cold surface in the reactor. Later, arc discharge between a closely spaced pair of graphite rods, was found to be the most convenient method for vaporization of carbon to crystalize into C_{60}. The research on fullerenes flourished, and enormous number of papers has been published (estimated to exceed 15,000). Nobel Prize for Chemistry was given to the first discoverers in 1996. Readers are referred to books describing more details of the stories on the discovery and research on fullerenes, which are exciting to read even for non-scientists (Kroto and Walton, 1993; Aldersey-Williams, 1994; Baggott, 1994).

Soon after the discovery of C_{60}, it was soon realized that there are a large variety of shapes exist among the closed networks of five- and six-membered sp^2-carbon rings including not only the classical spheres and polyhedral solids but also novel forms never known in chemistry. These are now summarily called "Fullerenes". In this small review, we will briefly mention a couple of the most unusual forms of fullerenes, namely tubes and onions, but also discuss the origin of these forms, which is called *formation mechanism* in chemistry.

2. Carbon Nanotubes

An instructive review on carbon nanotubes was given by Marcaccio and Paolucci (2014). The most well-studied form of fullerene is not C_{60} but carbon nanotubes, which were discovered many times, at first without really recognizing its atomistic structure by Oberlin *et al.* (1976), but finally the correct structure was deduced by Iijima by analogy with C_{60} in 1991 (Iijima, 1991). During the first stage of research, only multi-walled carbon nanotubes (MWCNT) were known (Fig. 2), but single-walled carbon nanotubes (SWCNTs) naturally proved more interesting and were soon found out (Fig. 3). At present, most of the scientific works on carbon nanotubes are performed using SWCNT. The thinnest model of SWCNT is an elongated C_{60}, formally made by cutting the latter into two halves and inserting tightly rolled graphene sheet between them to give an edgeless and capped tubular network. When caps contain pentagons in numbers smaller or larger than six, carbon nanohorns (CNH) will be obtained by the same procedure as mentioned above. CNH are also known and being studied intensively. After the research on C_{60} subsided around the turn of century, the popularity of CNT is still continuing strong among research scientists.

One of the most remarkable achievements that came out of CNT research is the utilization of space inside nanotubes as a reactor vessel. Caps of CNT can be readily removed by

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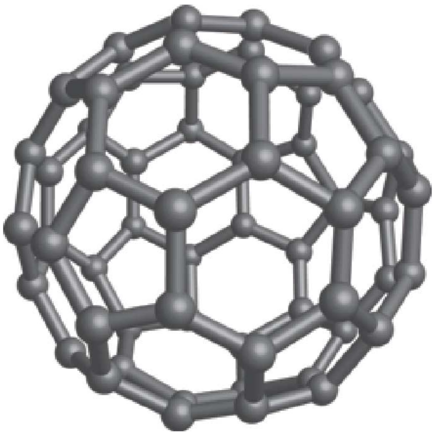
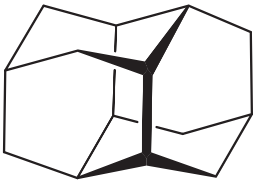


Fig. 1. Ball-stick model of buckminsterfullerene, C_{60}. Van der Waals diameter of this molecule is almost exactly 1 nm, thus C_{60} represents the smallest nanoparticles (definition: 1 to 100 nm). However, C_{60} is somehow soluble in various solvents, and subliminal, hence behaves like a molecule.

heating under vacuum to give open-ended CNTs enclosing precisely predictable nano-sized space. The first success in using this space was reported by Smith-Monthiou-Luzzi when they packed this space with a single column of C_{60} molecules by heating uncapped CNT in the presence of C_{60} to give so-called "pea-pods", which further gave double-walled CNTs by heating to fuse all the C_{60} molecules inside the host CNT into the thinnest SWCNT (Smith *et al.*, 1998). Many other, larger molecules like ferrocene could be introduced likewise in SWCNT. Shinohara and his group (Zhang *et al.*, 2013) packed diamantane (**1**) molecules into thick CNTs and upon heating obtained a diamond nanowire tightly fit inside the host CNTs. They are now trying to take out the wire from the CNTs.



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In spite of tremendous possibilities in CNTs and CNHs as research targets and for applications, there are two obstacles that might hinder further developments. These are concerns on the possible health risk of researchers and impossibility of controlling the structures in the syntheses. Whereas the first problem is likely to be overcome sooner or later by advancing operational safety, it is at the moment still difficult to produce CNTs with desired length, diameter, orientation of tube (either armchair **2** or zigzag **3** type), and chirality. This latter difficulty is caused by the fact that the mechanism of CNT formation still remains unknown. Actually formation mechanism is unknown to any member of fullerene carbons. Thus, the *origin of form* is a common source of deadlock in the fullerene research. We will come back to this problem in Section 4.

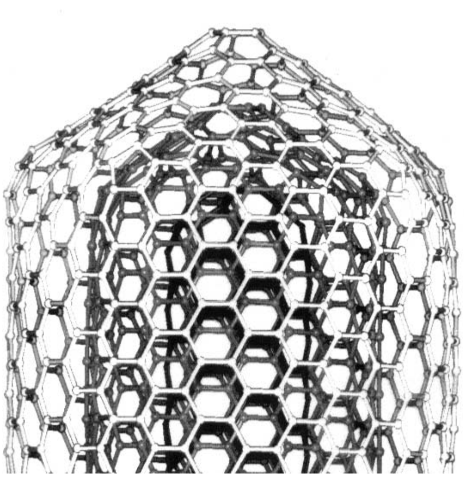


Fig. 2. A partial view of a ball-and-stick model of three-layered carbon nanotube. Inter-wall distances are all identical and equal to the sum of van der Waals radius of carbon. Drawn by Dr. Mitsuho Yoshida.

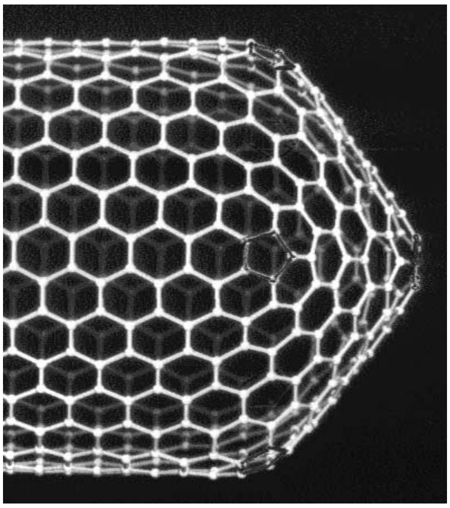
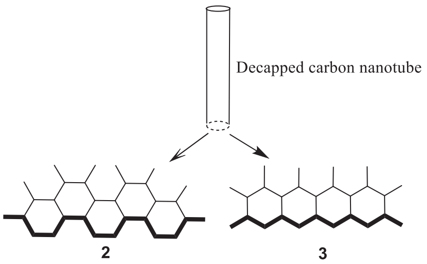


Fig. 3. A partial image of relatively thick single-walled carbon nanotube. Cap portion contains six pentagons (marked red) in local eicosahedral disposition. Drawn by Dr. Mitsuho Yoshida.



3. Carbon Nano-onions

As can be understood from the structural requirements for the fullerenes mentioned above, countless isomeric forms with similar energies exist for fullerenes and CNTs. Therefore it is generally difficult to isolate monodisperse fullerene. However, carbon nano-onions (CNO) with concentric multi-shell structure represents one notable exception, for which only one electronically stable configuration exists: $C_{60}@C_{240}@C_{540}@C_{960}\cdots C_{60n^2}$ ($n = 1, 2, 3\cdots$) (see Fig. 4 for the case of $n = 3$) (Yoshida and Ōsawa,

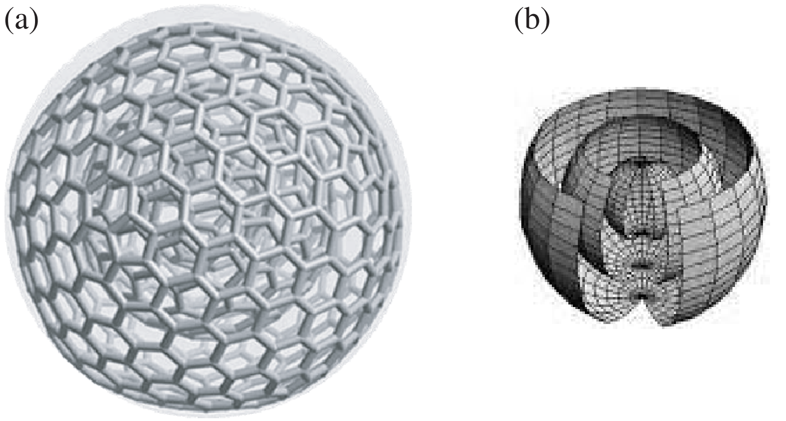


Fig. 4. (a) Wire-frame and (b) multiple-element models of three-layered carbon nano-onion $C_{60}@C_{240}@C_{540}$. Never isolated in pure form, but highly defective nano-onion particles are considered to be major constituents of soot from incomplete combustion process.

1993). The inter-shell distance of this series is constant; 0.35 nm, almost exactly equals to the sum of carbon van der Waals radii. The reason for such a fortuitous relation between structure and energy is unknown. At sufficiently high temperatures all the shells are supposed to take spherical instead of polyhedral shape to acquire freedom of rotation around the common central axis, providing an interesting nano-levitation/rotation system with fascinating electromagnetic properties. So far various sizes of CNOs are undesirable side products in the fullerene synthesis, but it is hoped to isolate homogeneous and uniform CNOs in macroscopic amounts in the near future.

4. Origin of the Fullerene Forms

It is tempting to think of the reason why people were so much surprised and excited when C_{60} was discovered. One likely answer would be that no one has ever expected its emergence. The discoverers originally intended to see short linear-chain carbon molecules to form upon laser evaporation of graphite. In chemistry, the origins of the known molecules are pretty well classified and understood. In other words, each of the known molecular classes belongs to one or the other of the "registered domiciles." For example, the most common home village of sp^2-hybridized carbon compounds is planar polyaromatic hydrocarbons (PAH). No spherical or closed ball forms have ever been registered in the PAH domicile. That's why we were so much surprised by the sudden on-stage of C_{60} and fullerenes in general.

In the past 30 years, intensive search was made for the formation mechanism of C_{60}, using all available knowledge including detection of intermediates by modified mass spectroscopic analysis, and predicting a number of new reaction modes under the conditions of arc discharge or laser ablation graphite. The most extensive and promising approach was made by Irle-Morokuma, who used a combined quantum mechanical-molecular dynamics (QM/MD) simulation to carefully follow the time-evolution of any ordered structures from a mixture of 100–120 C_2 molecules confined in a cubic cell having edge lengths of 10–20 Å at temperatures 2000–3000 K (Irle *et al.*, 2006). Here the adopting diatomic carbon molecule C_2 (**4**) as the building (and shrinking as well, see below) unit is a reasonable choice, in view of frequent observation of Swan bands during the growth and decomposition of fullerenes, in arc, comets, atmosphere of planets, interstellar matters and blue flame of hydrocarbon combustion.

:C=C:

4

In these non-equilibrium and irreversible systems, they observed with high probability the following sequence of events: at first small and linear chains are generated, which grow to bowl-shaped graphene-like polycyclic fragments and then close themselves to a giant fullerene C_{120}–C_{200}. The thermally excited giant fullerene then starts to expel C_2 one by one to shrink to smaller fullerenes. However, the shrinking process slowed down rapidly as the size of intermediate fullerenes decreases smaller and smaller and the final computational yields of C_{60} were much too small compared to the experimental observations (Ōsawa, 2012). It is likely that the present computers are still much too slow and small to perform more realistic simulation of the formation of fullerenes.

We propose here a state of matter which has never been considered in the studies of C_{60} formation mechanism but should be seriously taken into account, which is plasma. Since around 2010, astrophysicists began reporting detection of fullerenes mostly in planetary nebulae in Milky Way and further Mazellanic Clouds. Possibilities of formation of C_{60}, C_{70}, C_{80}, C_{240}, C_{320}, C_{540}, $C_{60}@C_{240}$, and $C_{60}@C_{240}@C_{540}$ have been suggested by analyzing infrared spectra of planetary nebulae and interstellar dust caught by Space Telescope Spitzer of NASA or UV spectra taken at Very Large Telescopes of European Southern Observatory in Chile. Especially strong evidence was found by Cami *et al.* (2010) for the formation of C_{60} and C_{70}: sharp IR spectra from a planetary nebulae Thackeray 1 (IC 1266) surrounding a central star HD161044 in the constellation Altar, visible in the southern hemisphere, containing exactly the same characteristic absorption lines of these fullerenes have been taken by Spitzer Telescope ship. In addition, two famous reflection nebulae, Iris in the constellation Cepheus (Fig. 5) and NGC 2013 in the Orion also produced some of the

Fig. 5. Partial infrared evidence for the existence of C_{60} was reported (Sellgren *et al.*, 2010) in Iris nebula, or NGC 7023, located in the constellation Cepheus of the galaxy in the Northern hemisphere, 1,300 light years away and 6 light years across (1 ly is about 10 billion km). Photo reproduced by courtesy of NASA.

Table 1. Five phases of evolution in small to medium planets ($0.8 \sim 8\ M_{\odot}$). Superscripts a, b, c and d indicate Asymptotic giant branch star, Planetary nebule, involving C, N, O gases evolution at several km/sec to outside, By gravity, and Due to increased temperature, respectively.

Phase	Duration year	Size change	Nuclear fusion	Temperature, K		Luminosity
				Core	Nebule	
II. Beginning	$10^7 \sim 10^{10}$	expand shrink^c	H→He Hydrogen exhausted	15 million decrease	-	-
II. Red giant	short	expand^d	-	100 million	-	increase
III. AGB^a	$2 \cdot 10^4$	expand	He→C,O	100 million	30,000	Very high
IV. PN^b	10^4	-	He→C,O		100,000	(hidden)
V. White dwarf	?	-	-			low

prominent infrared peaks of C_{60} (Sellgren *et al.*, 2010).

The possibility of fullerene formation in outer space has long been predicted by Kroto and Jura (1992). Medium to small planets nearing the end of its life cycle often pass through planetary nebula phase, wherein successive nuclear fusion of hydrogen and helium accumulates enough amounts of C, N and O in its core, the whole star glows red and temperature reaches 100 million K. Then "heavy" gases are ejected at supersonic speed from the surface of star for about 10,000 years (Table 1).

IR spectroscopic evidence mentioned above strongly suggests that the cloud (nebule) of gases floating around the dying star in the planetary nebule phase provides excellent environment for C_{60} and C_{70} to form. Let us compare the conditions in the nebule and in the experimental fullerene formation in laboratories. First of all, temperature in the nebule can be much higher (100,000 K) than the estimated fullerene formation temperature of 2,000 to 3,000 K in the arc discharge experiments. Actually the highest possible temperature in the arc discharge set-up could be higher than 5,000 K. Then, it would be interesting to use the temperature above 5,000 K in the next simulation. Atmosphere of Tc 1 nebule is reported to be hydrogen, but we cannot completely exclude a possibility of helium atmosphere in the reaction zone in the absence of adequate information on site.

More critical problem to understand the formation mechanism of fullerene could be to recognize the characteristics of carbon plasma in the planetary nebule. According to the recent advance in plasma physics, reactive species in the C_{60} formation belong to complex plasmas (Tsytovich *et al.*, 2008). Grains of complex plasma interact strongly among each other, often giving well-definable crystals and liquids. Interstellar dusts and dark matters that emit diffuse interstellar bands (DIB) are typical examples of complex plasma. Since 1994, complex plasma was recognized to crystallize under properly adjusted laboratory conditions (Tsytovich *et al.*, 2008). Understandably, DIB and other IR-UV peaks could have arisen from plasma crystals. We are attracted to re-consider fullerene formation processes as a sort of crystallization of reactive complex plasmas. This is a reasonable proposition, in view of the fact that both grains of complex plasma and small carbon cluster intermediates, which accumulate during fullerene formation, are strongly coupled (note that the word *coupling* in physics is used as the same meaning like *bonding* in chemistry). Another characteristic of complex plasma is that grains are very highly charged. It is likely that carbon clusters also carry large number of free electrons at high temperature above 5000 K. The largest difference between complex plasma and fullerene intermediate clusters exists in the size, the former being micron-sized compared to the sub-nano to nano size in the latter.

In this regard, a recent report on interesting plasma crystals, Coulomb balls, by Bonitz *et al.* (2006) should be mentioned here. Coulomb balls consist of 100–500 particles of micro-meter sized plastic spheres, which carry high electric charge and arrange themselves into a highly ordered set of nested spherical shells with local icosahedral order inside the shell. All of the Coulomb balls they prepared have a spherical shape with diameters ranging 4–5 mm. There is a striking similarity between Coulomb balls and carbon nano-onions mentioned in the previous section. The most interesting aspect of the former is that they grow in a spherical confinement potential field. Arc discharge and laser evaporation plasma region is also basically spherical with the tip of electrode in the center. Then the curved surface of C_{60} may have been primarily created by the spherical potential field but not by the appearance of pentagonal rings. In the planar- or cubic confinement potential field in simulating complex plasma in laboratory, planar and 3D plasma crystals are formed (Tsytovich *et al.*, 2008). Furthermore, application of NCC-DFTB (non-selfconsistent charge-density functional tight binding) theory constructed on the basis of ordinary phases (Irle *et al.*, 2006) may not be suitable for describing electronic states at extremely high temperature. In the simulation of Coulomb balls, pair-wise Coulomb interactions and Yukawa potential proved sufficient (Bonitz *et al.*, 2006).

5. Conclusions

Forms in chemistry and physics are often originated from the functional requirements of the object in question. In the case of fullerenes in nano-size, however, it proved essential to understand the origin of forms in order to gain complete control to promote their applications. Sudden decline of research activities of C_{60}, which occurred around the turn of century, attests to this proposition. Unless we have control over the form, we cannot effectively produce what we really need at reasonable cost. We hope we can finish the long overdue homework soon.

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