

EIJI ŌSAWA

NanoCarbon Research Institute Limited  
Ueda, Nagano, 386-8567, Japan, osawaeiji@aol.com

## LOOKING BACK THE MOST BEAUTIFUL MOLECULE $C_{60}$ AFTER QUARTER CENTURY OF DISCOVERY

*On the occasion of silver anniversary of the  $C_{60}$  discovery, the present situation of  $C_{60}$  research is briefly analyzed from three distinct angles: molecule, solid and nanoparticle. With regard to molecular angle, the long pending problem of formation mechanism is almost solved by molecular dynamics approach hinted by Prigogine's nonequilibrium thermodynamics. The  $C_{60}$  research is at the moment most active in chemistry, and some of the recent results are discussed here. Though  $C_{60}$  is closer to molecule than to the smallest nanoparticle in its outlook, a big future seems hidden in its application in nanotechnology.*

*Keywords: buckminsterfullerene, formation mechanism, dyadic electronic system, fullerenol polisher, elixir.*

### INTRODUCTION

$C_{60}$  (Fig. 1, see insert) was first found in 1985 [1] and then isolated in 1990 [2] as a new molecule and aroused tremendous interests from chemists. Next year, physicists found superconductivity in alkali-doped  $C_{60}$  films [3]. Excitement quickly spread to engulf scientists and engineers of all disciplines, and enormous surge of research on *buckminsterfullerene* began. In addition to the scientific novelty,  $C_{60}$  is also called as the most beautiful molecule [4] with perfect symmetry [5]. Everyone seemed to like it. The fever continued to about 1996, when the discoverers were awarded Nobel Prize for Chemistry. Then, all of sudden interests of scientists shifted to carbon nanotubes, the tubular kin of  $C_{60}$ . CNT fever continued somewhat longer, until about 2010, but then graphene took over the leading position of international scientific race, after Nobel Prize for Physics went to the re-discoverers of graphene. Graphene is a lengthwise opened and extended carbon nanotube. Where do we go after graphene in the journey on  $sp^2$ -networks?

Clearly, carbon research is undergoing *Sturm und Drang* period in the past 20 years. For just an example of the intensity of impact, the *Nature* paper by Kroto and others [1] that started all these research activities has been cited

about 8,800 times by June 2012 according to *Google Scholar* statistics. Iijima's first paper on CNT [6] obtained still higher citations of about 24,900! Scientists are working hard everywhere as if they are driven by strong force, and with high enthusiasm in one or the others of these new carbons. We would like to know why the popular targets of carbon research change so quickly. What would be the next target? Will any of the recognized targets produce useful products some day?

In this short review, we will try to answer at least some of the above questions. For personal reason, we will limit our discussion to  $C_{60}$ , and analyze the reason for its rise and fall. We hope that the fall in the number of research outputs of fullerene is temporary and will recover in due time.

### FORMATION MECHANISM

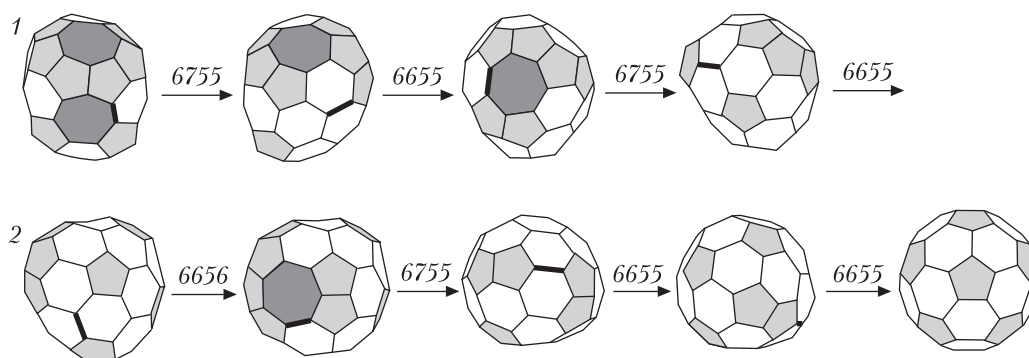
A persistent weak point of  $C_{60}$  as the raw industrial material is the high production cost (end price = ¥30,000/2.5 g). Actually not only  $C_{60}$  but also all the breeds of new carbon networks including single-walled carbon nanotubes and graphenes have the same problem of forbiddingly high price. In order to bring down price, we must improve the production method. These are new carbons are being produced by one or the other variations of bottom-up methods that involve generation of carbon plasma at extremely high temperatures like 5000 K.

These conditions are different from those which chemists used to work in the past two-centuries, thus posing us an entirely new and difficult task when we want to probe into their formation mechanism. In spite of hard work for a quarter of century, none of the known bottom-up nanocarbons has yielded atomistic details in the formation mechanism. If we do not know the mechanism of formation, we cannot improve the production process. Let us start looking at the formation mechanism of  $C_{60}$ .

In the beginning only the traditional, deterministic, equilibrium and multi-step approach was earnestly followed [7, 8]. This approach assumes that nature knows the shortest possible but energetically most economical pathway of building up carbon atoms step by step to  $C_{60}$  with icosahedral symmetry, where the surface pattern of soccer ball or truncated dodecahedron is reproduced with a bewildering network of 12 pentagons and 20 hexagons. In the absence of techniques to study phenomena occurring at 5000 K, we had to guess what nature knows and confirm the guess by some objective means. Many people including ourselves felt challenged and were adsorbed in the puzzle (Fig. 2), but this traditional approach turned out to be surprisingly futile: about a dozen of seemingly reasonable mechanisms have been suggested but neither experimental nor computational support could be obtained [9].

Then the second, non-traditional approach surfaced from about the turn of century. This method is essentially non-empirical simulation with the help of molecular dynamics algorithm as the basic tool. Namely a few hundreds of  $C_1$  or  $C_2$  species are confined in a small space of nanometer size, and heated at 2000–3000 K as long as one can afford, generally up to pico seconds, to see what happens in computer. As the number of carbon atoms must be large enough so as to reproduce real phenomena, the load of computation became quite large, hence energies were at first calculated by fast empirical potential functions like Brenner's reactive bond order types [10]. However, no  $C_{60}$  was formed. It was finally felt that energy must be evaluated by quantum chemical method. At this point, Irle – Morokuma group began using NCC-DFTB level of theory in 2003 [10]. Even with this lowest possible level, they succeeded to observe hot  $C_2$  species self-assemble into a hot giant fullerene consisting of 100 to 200 carbon atoms, which then releases  $C_2$  species to shrink close to  $C_{60}$  [7].

However, this remarkable breakthrough is still incomplete as they have hardly reached  $C_{60}$  itself. It seems that some unknown but crucial condition is missing to accelerate the strongly endothermic shrinking step. Addition of helium, carbon monoxide and oxygen did not work, even though He did occasionally lead to  $C_{60}$  but not so often as to reproduce the



**Fig. 2.** An example of traditional mechanistic pathway from an arbitrary  $C_{60}$  isomer (2) to buckminsterfullerene (1) as obtained by a combined topological and semi-empirical quantum mechanical approach using only Stone – Wales rearrangement as the elementary step. Four integers above arrow indicate the four adjacent rings participating in the rearrangement, wherein the central C–C bond (bold) formally rotates by a right angle. Taken from [4]

high yields observed in experiments, ca 20% in arc discharge and 100% in combustion methods [12, 13].

Nevertheless, their Shrinking Hot Giant Fullerene Road avoids difficulties in the traditional approach, like including a number of unstable intermediates, passing through high transition states of Stone – Wales rearrangements and compensating large entropy loss in forming closed systems. We believe that the SHGFR theory is the most likely among all the other theories of  $C_{60}$  formation. When eventually completed, the mechanism will be the most remarkable examples of Prigogine's non-equilibrium and irreversible physics, where a highly ordered structure like  $C_{60}$  emerges from completely disordered starting mixture by dynamic self-assembling process at very high temperature.

The Irlé – Morokuma theory explains at least one well-observed but so far enigmatic experimental observation: initial formation of large amounts of high-mass peaks and their subsequent disappearance in MS. Their simulation results strongly support a long-held interpretation that each of the large cluster peaks represents a giant fullerene. Giant fullerenes should be practically strain-free but kinetically highly unstable at such high temperatures of 2,000 to 3,000 K, hence it is perfectly reasonable that they release  $C_2$  to shrink into smaller and smaller fullerenes until it reaches the distinguished kinetic energy minimum of  $C_{60}$ . This picture fits to the absence of mass peaks below  $C_{58}$  fullerenes and appearance of several intermediates below  $C_{100}$  like  $C_{70}$ . If closed network growth mechanism holds, the distribution pattern around  $C_{60}$  must be the other way around. The most likely places of  $C_2$  expulsion will be the central bond of abutting pentagons, or the places with high curvatures in very large giant fullerenes.

Failure to reproduce the shrinking process by computer simulation is likely caused by the neglect of vibronic coupling outside the Born – Oppenheimer approximation. Electronic states of giant fullerenes in very high vibrational excited states must be greatly influenced by non-adiabatic nuclear movements.

Accordingly bonds are the more readily broken as the curvature of surface increases. In other words,  $C_2$  expulsion will become faster and faster as the fullerene shell shrinks smaller and smaller towards  $C_{60}$ , which is an outstanding kinetic energy minimum.

If we assume that the Irlé – Morokuma theory will be sooner or later completed along the direction they proposed, we can then proceed to improve the yield of  $C_{60}$  production. Some more details of the production process will be given later in this review.

#### MOLECULE OR NANOPARTICLE?

$C_{60}$  is often referred as the first member of nanoparticles. However, this statement should be taken with some reservation. According to the formal definition of nanoparticle (1–100 nm in diameter),  $C_{60}$  with its nuclear-nuclear distance of 0.71 nm, or van der Waals diameter of 1.0 nm, only marginally qualifies as the smallest nanoparticle. In more general terms like amenability to purification (Table I, see insert),  $C_{60}$  is closer to molecule rather than nanoparticle. It would be more appropriate to categorize  $C_{60}$  as a borderline case between molecule and nanoparticle.

Mass production and cost reduction of material are not necessarily as important in nanotechnology as in modern chemical technology. This assessment came out in the course of comparison between the two technologies (Table I). As far as the classification of a material to either molecule or nanoparticle is concerned, the most pertinent criteria would be the ways of application (origin of function) and the units used (the lowest two lines in Table I). Nanoparticles are generally used as individual particles, hence counted by the number, whereas chemical substances are treated as a collection of molecules and counted by the weight (actually in terms of mole numbers).  $C_{60}$  may be used, if used at all, either as individual particle or as a mass of molecules depending on the purpose due to its border-line nature. In the latter case, mass production and low cost is certainly an important asset. In that case, combustion method is by far the most advantageous.

**Production of  $C_{60}$  by combustion.** Formation of  $C_{60}$  in the flame of hydrocarbon combustion was discovered by J. Howard of MIT [14] and K.-H. Homann of Darmstadt TH [15] immediately after the first isolation of  $C_{60}$  from carbon vapor by Krätschmer *et al.* [2]. It has long been considered that the two methods follow different mechanisms. However, Homann and his coworkers have long recognized the formation of large variety of giant carbon clusters just below fullerene formation zone in flame, and named it as aromers for aromatic oligomers and thought the smaller of them as fullerene precursors (Fig. 3, see insert) [15]. In the light of Irle – Morokuma theory, aromers could well be giant fullerenes. Then an inevitable conclusion is that the two  $C_{60}$  syntheses, arc discharge and combustion, follow the same mechanism.

Independently, Howard continued to improve the combustion synthesis of  $C_{60}$ , almost single-handedly after Homann retired. The yield of  $C_{60}$  in the solid black product from combustion increased from 1% in the earliest period, to 20% by the effort of Mitsui Chem. Co., which built a plant with this yield level, then Howard reached 100% before 2003. By this time Howard had set up a venture company and stopped publishing his results even though he continued to keep his teaching post at MIT. Unfortunately, he suffered from brain cancer and died on July 7, 2008. Thus, the most precious records on the optimum conditions of combustion synthesis of  $C_{60}$  remained in secrecy and will never be published. Nevertheless, it would be challenging for us to take the best advantage of Irle – Morokuma mechanism and to reproduce the Howard conditions posthumously. It appears important to keep the flame temperature very high near 3000 K even at the end of long flame. External heating may be necessary.

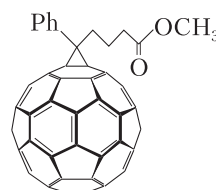
#### RECENT DEVELOPMENTS

On the industrial sector and investment market, activities around  $C_{60}$  have long diminished. Some of the continuing moves in the commercial sector will be briefly touched at

the end of this section. However, in the academia,  $C_{60}$  research is still going on rather strong. Here again we need a small remark on its relation to the fullerene fever. As a molecule, or chemical reagent,  $C_{60}$  is definitely one of the most favored companions among chemists. Its outstanding chemical features include strong electron-withdrawing property, high reactivity to addition reactions, and high symmetry. For this reason,  $C_{60}$  is still a very popular topic in chemistry.

#### Electron acceptors in dyadic systems.

One of the most favored strategies in current scenes of *green energy* is to arrange a pair of electropositive and electronegative molecules or their fragments in nano-vicinity, let light absorbed by the former to excite its frontier electrons, to migrate them to the latter by orbital interactions through bonds (OITB) or through space (OITS), and to take them out as electric current. Here skill in the organic synthesis is required in order to construct elaborate molecular architecture. Graphene is a classical electron acceptor but  $C_{60}$ , which is a spherical graphene, is preferred due to high electronegativity (the low energy vacant molecular orbitals are in the bonding energy levels), and reactivity. For these reasons,  $C_{60}$  and a simple derivative [6,6]PCBM (phenyl- $C_{61}$ -butyric acid methyl ester) has been the best-used electron acceptors (or n-type semiconductor as physicists prefer to call) in the research of photosynthesis and photovoltaic cells [16, 17]. About the turn of century, porphyrin-fullerene dyad systems have been extensively studied, but the light-harvesting efficiency still cannot compete with natural systems [18].



**Designer syntheses.** Due to its high symmetry ( $I_h$ , next only to sphere),  $C_{60}$  can be derivatized to novel polyfunctional structures while still retaining many of its symmetry elements [19, 20]. These novel structures are at the moment one of the attractive playgrounds of synthetic organic chemists. It is fascinating to see that such a large and complicated structure like  $C_{60}$  are incorporated at will into intricate molecular architectures like fashion designers creating original costumes one after the other. Interested readers are referred to the original publications.

**Surgery on  $C_{60}$  cage.** The  $C_{60}$  cage is large enough to cut open, place foreign atoms or even a molecule into the inside of cage, then close the opened mouth by stitching together by means of chemical bonds. Komatsu and Murata succeeded in encapsulating a  $H_2$  molecule inside  $C_{60}$  through a 13-membered ring orifice and then closing it again [21]. In reality, the opening and closing of cage involve many steps of elaborate chemical transformations and it will need a lot more work to simplify and generalize the technique. Nevertheless, this is a flexible and valuable approach to the novel endohedral  $C_{60}$  derivatives.

**Endohedral metallofullerenes.** An alternative physical method of encapsulation of foreign matters in  $C_{60}$  cage structure has been explored since soon after the discovery of  $C_{60}$ . Still now, synthesis of  $M@C_{60}$  ( $M$  = metal atoms or ions) is achieved only with extremely low yields, and the type of  $M$  strictly limited (Fig. 4, see insert) [22]. Clearly metal encapsulation into  $C_{60}$  comprises one of the most challenging subjects in the  $C_{60}$  research. It is hoped that QM/MD simulation will be able to solve many mysteries in  $M@C_{60}$  that cannot be solved by experimental approaches.

**Fullerenols.** One other type of fullerene derivatives of  $C_{60}$  that has attracted much attention of chemists is those exhaustively substituted with small heteroatoms like  $C_{60}H_{60}$  and  $C_{60}F_{60}$ , wherein cage skeleton will be still a perfect sphere but inflated due to  $sp^3$  hybridization, with longer and equal C–C bonds and smaller angle strain. However, the reaction stopped af-

ter 44 substituents have entered, due to steric crowding. Beyond this limit, the cage skeleton starts to break apart [23]. Exactly the same situation was observed when OH radicals were forced to add to  $C_{60}$  as many as possible [24]. In these  $C_{60}X_{60}$  systems, C–X bonds are supposed to be considerably elongated due to severe steric crowding with the neighboring X atoms. Thus, there will be a hard and rigid spherical shell consisting of spherically aligned, non-bonded X-atoms concentrically enclosing above the spherical  $C_{60}$ . Thus, from the outside the  $C_{60}X_{60}$  molecule will look like a very hard sphere filled with X atoms on the surface. Such a molecule must be very unique and new, chemically inert and show highly positive surface potential.

Originally, the synthesis of  $C_{60}X_{60}$  was suggested by Kroto as ideal nanolubricants in analogy with the known lubrication property of poly(tetrafluoroethylene). No frictional constant has been reported for  $C_{60}X_{44}$  ( $X = H, F, OH$ ) so far, but we can easily guess that these are too small for solid spacers with approximate diameter of only about 1 nm to perform effective lubrication for usual surfaces. Perhaps super-lubrication may be realized for the  $C_{60}X_{44}$ /PTFE systems. However, this is not the whole story.

Surprisingly enough,  $C_{60}(OH)_{44}$  (and  $C_{60}(OH)_{36}$  as well) proved to be an excellent and practicable polisher for copper surface of multi-layered integrated circuits [25, 26]. Fullerenol is dissolved in water and the copper device is treated in agitating fullerenol solution only for a few minutes to achieve the novel mechano-chemical polishing. Mechanism of the MCP action is still not well understood. Although vicinal surface OH groups may act like ethylene glycol to form pentagonal chelate ring, a chelating agent is already added in the polishing liquid from the beginning. We imagine that hard and rigid ball of  $C_{60}(OH)_{44}$  plays some unknown but critical role to smooth out the copper surface by chopping off tiny asperities only one or two atomic layers thick. We imagine that this fullerenol/copper polishing system will be the beginning of polishing in the atomic scale.

**Radical sponge for elixir.** Remarkable success in polyhydroxylation of  $C_{60}$  confirms its high capacity to absorb radicals. The «radical sponge» characteristics of  $C_{60}$  have been used for photodynamic therapy of skin cancer and for scavenging harmful singlet oxygen [27]. For the same reason, when a French research group found that olive oil dissolves small but certain amount of  $C_{60}$ , they tested the effect of daily dose of 1.2 mg  $C_{60}$ /kg·day to mice upon their life [28]. Astonishingly the life-length of  $C_{60}$ -treated group proved almost doubled than that of un-treated group. On the other hand, Cataldo and Braun [29] have already reported that  $C_{60}$  could be dissolved in many kinds of unsaturated plant oils but only to much smaller saturation concentrations. Damage of cells by  $C_{60}$  is also known to occur *in vivo* [cited in 29].

#### PERSPECTIVES AND CONCLUDING REMARKS

The result of explosive expansion of  $C_{60}$  research on unprecedented scale produced thousands of publications, which led to a new problem: it is impossible to write a comprehensive review or book, simply because the volume of literature on  $C_{60}$  grew too large to be handled by a single person or even by a small group of authors. The same remark will also apply to carbon nanotubes. For this reason I picked up the topics in the foregoing section from among those papers which I happened to come across. Hence this and the preceding sections must be taken as very subjective and intuitive, but here I have to answer the questions I posed to myself at the outset.

I better start with an interpretation of a new social phenomenon called «research fever». This interpretation may be already obvious to many, but quite fast propagation of news by internet, e-mails and on-line publications must be largely responsible to the sudden breakout of feverish research activities. Nowadays big scientific discoveries propagate almost instantly around the earth. An inevitable consequence of such efficient information flow is that we are always chased by the news, but not the other

way around as it used to be. Life and time are moving faster and faster. It is partly true that one research topic will be soon digested and overworked in a matter of few months.

In the case of  $C_{60}$ , it has three faces due to of its special shape and functions. One is the face of a molecule for chemists, the second one the face of a solid for physicists, and the last one that of a nanoparticle for material scientists. *Molecular face* is still being explored among chemists as shown above [30]. *Solid face* is almost lost as exemplified by the disappointingly small increase in the superconductive transition temperature by only 2 K in 20 years [31]. However, *nano face* is still mostly hidden as illustrated by the less well-known case of unique polishing ability of fullereneol with atomic precision.

It is hoped that more and more examples of  $C_{60}$ 's performance as the smallest nanoparticle will appear, but the development is still slow. Once the basic rules and concepts of nano-science and technology are better understood [32–34], we are sure  $C_{60}$  will come back to the front scene. Large specific number density and surface area are the definitive advantages of  $C_{60}$  like the primary particles of detonation nanodiamond, other typical smaller nanoparticle (Table II, the lowest two lines). Perhaps a quarter of century is too short to complete the whole story of truncated eicosahedrane which began about 2200 years ago by Archimedes (Fig. 5, see insert).

#### REFERENCES

1. Kroto H.W., Heath J.R., O'Brien S.C. et al.  $C_{60}$ : Buckminsterfullerene // Nature. — 1985. — V. 318. — P. 162–163.
2. Krätschmer W., Lamb L.D., Fostiropoulos K., Huffman D.R. Solid  $C_{60}$ : a new form of carbon // Nature. — 1990. — V. 347. — P. 354–358.
3. Haddon R.C., Hebard A.F., Rosseinsky M.J. et al. Conducting films of  $C_{60}$  and  $C_{70}$  by alkali-metal doping // Nature. — 1991. — V. 350. — P. 320–322.
4. Aldersey-Williams H. The Most Beautiful Molecule: An Adventure in Chemistry. — London: Aurum Press, 1995. — 340 p.
5. Baggott J. Perfect Symmetry: The Accidental Discovery of Buckminsterfullerene. — Oxford: Oxford University Press, 1994. — 315 p.

6. *Iijima S.* Helical microtubules of graphitic carbon // *Nature*. — 1991. — V. 354. — P. 56–58.
7. *Irle S., Zheng G., Wang Z., Morokuma K.* The C<sub>60</sub> formation puzzle «solved»: QM/MD simulations reveal the shrinking hot giant road of the dynamic fullerene self-assembly mechanism // *J. Phys. Chem. B*. — 2006. — V. 110. — P. 14531–14545.
8. *Irle S., Pag A.J., Saha B., Wang Y. et al.* Atomistic mechanism of carbon nanostructure self-assembly as predicted by non-equilibrium QM/MD simulations // *Practical Aspects of Computational Chemistry II. An Overview of the Last Two Decades and Current Trends* / Leszczynski J., Shukla M.K. (eds.). — Berlin: Springer – European Academy of Sciences, 2012. — P. 59.
9. *Dunk P.W., Kaiser N.K., Hendrickson C.L. et al.* Closed network growth of fullerenes // *Nature Commun.* — 2012. — V. 3:855. — doi: 10.1038/ncomms1853.
10. *Brenner D.W., Shenderova O.A., Harrison J.A. et al.* A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons // *J. Phys. Condens. Matter*. — 2002. — V. 14. — P. 783–802.
11. *Irle S., Zheng G., Elstner M., Morokuma K.* From C<sub>2</sub> molecules to self-assembled fullerenes in quantum chemical molecular dynamics // *Nano Lett.* — 2003. — V. 3. — P. 1657–1664.
12. *Howard J.B.* Private communication.
13. *Howard J.B., Kronholm D.F.* Fullerenes production technology for large-scale commercial applications // *NanoTechnology Forum*, Nov. 5, 2003, Taipei.
14. *Howard J.B., McKinnon J.T., Makarovskiy Y. et al.* Fullerenes C<sub>60</sub> and C<sub>70</sub> in flames // *Nature*. — 1991. — V. 352. — P. 139–141.
15. *Homann K.-H.* Fullerenes and soot formation – new pathways to large particles in flames // *Angew. Chem. Int. Ed.* — 1998. — V. 37. — P. 2434–2451.
16. *Hasobe T., Imahori H., Kamat P.V. et al.* Photovoltaic cells using composite nanoclusters of porphyrins and fullerenes with gold nanoparticles // *J. Am. Chem. Soc.* — 2005. — V. 127, N 4. — P. 1216–1228.
17. *Imahori H., Umeyama T., Ito S.* Large  $\pi$ -aromatic molecules as potential sensitizers for highly efficient dye-sensitized solar cells // *Acc. Chem. Res.* — 2009. — V. 42, N 11. — P. 1809–1818.
18. *Milanesio M.E., Alvarez M.G., Rivarola V. et al.* Porphyrin-fullerene C<sub>60</sub> dyads with high ability to form photoinduced charge-separated state as novel sensitizers for photodynamic therapy // *Photochem. Photobiol.* — 2005. — V. 81. — P. 891–897.
19. *Matsuo Y., Nakamura E.* Selective multiaddition of organocopper reagents to fullerenes // *Chem. Revs.* — 2008. — V. 108. — P. 3016–3028.
20. *Matsuo Y., Muramatsu A., Kamikawa Y. et al.* Synthesis and Structural, Electrochemical, and Stacking Properties of Conical Molecules Possessing Buckyferrocene on the Apex // *J. Am. Chem. Soc.* — 2006. — V. 128, N 30. — P. 9586–9587.
21. *Komatsu K., Murata M., Murata Y.* Encapsulation of molecular hydrogen in fullerene C<sub>60</sub> by organic synthesis // *Science*. — 2005. — V. 307. — P. 238–240.
22. *Aoyagi S., Nishibori E., Sawa H. et al.* A layered ionic crystal of polar Li@C<sub>60</sub> superatoms // *Nature Chem.* — 2010. — V. 2, N 8. — P. 678–683.
23. *Touhara H., Okino F.* Fluorinated fullerenes // *Advanced Inorganic Fluorides: Synthesis, Characterization and Applications* / Nakajima T., Žemva B., Tressaud A. (eds.). — Amsterdam: Elsevier, 2000. — P. 555–590.
24. *Kokubo K., Matsubayashi K., Tategaki H. et al.* Facile synthesis of highly water-soluble fullerenes more than half-covered by hydroxyl groups // *ACS Nano*. — 2008. — V. 2. — P. 327–333.
25. *Takaya Y., Tachika H., Hayashi T. et al.* Performance of water-soluble fullerene as novel functional molecular abrasive grain for polishing nanosurfaces // *CIRP Annals. Manuf. Technol.* — 2009. — V. 58. — P. 495–498.
26. *Takaya Y., Kishida H., Hayashi T. et al.* Chemical mechanical polishing of patterned copper wafer surface using water-soluble fullerene slurry // *CIRP Annals. Manuf. Technol.* — 2011. — V. 60. — P. 567–570.
27. *Tabata Y., Ikada Y.* Biological functions of fullerene // *Pure Appl. Chem.* — 1999. — V. 71. — P. 2047–2053.
28. *Baati T., Bourasset F., Gharbi N. et al.* The prolongation of the lifespan of rats by repeated oral administration of [60]fullerene // *Biomater.* — 2012. — V. 33. — P. 4936–4946.
29. *Cataldo F., Braun T.* The Solubility of C<sub>60</sub> Fullerene in Long Chain Fatty Acids Esters // *Fullerenes, Nanotubes and Carbon Nanostructures*. — 2007. — V. 15, N 5. — P. 331–339.
30. *Ōsawa E.* Formation Mechanism of C<sub>60</sub> under Non-equilibrium and Irreversible Conditions – An Annotation // *Fullerenes, Nanotubes and Carbon Nanostructures*. — 2012. — V. 20, N 4–7. — P. 299–309.
31. *Matsushita E.* Attempt at extending BCS-like theory to explain fullerene superconductors // *Prog. Theor. Phys.* — 2011. — V. 125, N 5. — P. 1021–1034.
32. *Ōsawa E., Ho D.* Nanodiamond and its application to drug delivery // *J. Med. Allied Sci.*, in press.
33. *Ōsawa E.* Nanodiamond – an Emerging Nanocarbon Material // *Handbook of Advanced Ceramics* / S. Soumiya (ed.). — 2<sup>nd</sup> Edition. — Elsevier, 2012, in press.
34. *Barnard A., Sasaki S., Ōsawa E.* Statistical modelling of ensembles of nanoparticles: approaches to diversity and polydispersity // *Cryst. Growth & Design*, submitted for publication.

Received 02.07.2012

*Ейджі Осава*NanoCarbon Research Institute Limited  
Ueda, Nagano, 386-8567, Japan, osawaeiji@aol.comПОГЛЯД НА НАЙКРАСИВІШУ МОЛЕКУЛУ  $C_{60}$   
ЧЕРЕЗ ЧВЕРТЬ СТОЛІТТЯ ПІСЛЯ ВІДКРИТТЯ

З нагоди срібної річниці з часу відкриття фулеренів коротко проаналізовано нинішню ситуацію з їх дослідженням.  $C_{60}$  розглянуто в трьох різних аспектах — молекула, тверде тіло та наночастинка. Стосовно молекулярного аспекту варто зазначити, що давню проблему механізму утворення фулеренів майже розв'язано за допомогою молекулярно-динамічного підходу, підказаного нерівноважною термодинамікою І. Пригожина. Нині найактивніше досліджують хімію  $C_{60}$ . У статті розглянуто деякі з нещодавніх результатів у цій галузі. Хоча за своїми характеристиками  $C_{60}$  ближчий до молекул, ніж до найдрібніших наночастинок, його застосування в нанотехнологіях, схоже, таїть у собі великі перспективи.

*Ключові слова:* бакмінстерфулерен, механізм утворення, діадна електронна система, полірувальний фулеренол, еліксир життя.

*Эйджи Осава*NanoCarbon Research Institute Limited  
Ueda, Nagano, 386-8567, Japan, osawaeiji@aol.comВЗГЛЯД НА САМУЮ КРАСИВУЮ МОЛЕКУЛУ  $C_{60}$   
ЧЕРЕЗ ЧЕТВЕРТЬ ВЕКА ПОСЛЕ ОТКРЫТИЯ

По случаю серебряной годовщины со времени открытия фуллеренов кратко проанализирована нынешняя ситуация с их исследованием.  $C_{60}$  рассматривается в трех различных аспектах — молекула, твердое тело и наночастица. Касательно молекулярного аспекта нельзя не отметить, что давно занимавшая умы ученых проблема механизма образования фуллеренов почти решена с помощью молекулярно-динамического подхода, подсказанного неравновесной термодинамикой И. Пригожина. Сегодня наиболее активно изучаются химические свойства  $C_{60}$ . В статье обсуждаются некоторые последние результаты в этой области. Хотя по своим характеристикам  $C_{60}$  ближе к молекулам, чем к мельчайшим наночастицам, его применение в нанотехнологиях, похоже, таит в себе большие перспективы.

*Ключевые слова:* бакминстерфуллерен, механизм образования, диадная электронная система, полирувочный фуллеренол, эликсир жизни.





ЕЙДЖІ ОСАВА

## МОЯ КОРОТКА НАУКОВА БІОГРАФІЯ

Я народився в місті Тояма в Японії в 1935 році. 1960 року на факультеті промислової хімії в Університеті Кіото здобув ступінь магістра за спеціальністю «промислова хімія». Кілька років працював інженером на виробництві.

Щасливий для мене збіг обставин стався в 1961 році — Радянський Союз запустив перший космічний корабель «Восток», пілотований Юрієм Гагаріним. Він здійснив виток навколо Землі і благополучно приземлився. Ця подія спровокувала посилення холодної війни між СРСР і США, причому останні явно програвали в ній. Незабаром США і Японія подвоїли кількість студентів природничих спеціальностей у великих університетах. У результаті виникла гостра нестача викладачів природничих наук. У такий спосіб я дістав можливість повернутися в академічний світ. Проте невдовзі я зрозумів, що експериментальні дослідження — це не моя стежа.

Хоча пошук свого місця в науці був для мене досить складним, інший щасливий випадок допоміг мені: у 1985 році Г. Крото, Р. Смоллі і Р. Керл відкрили фулерен  $C_{60}$ . З цього моменту я усвідомив себе як ученого і творчу особистість, оскільки ще в 1970 році я передбачив можливість існування молекули  $C_{60}$  та її високу стабільність.

Удача ще раз усміхнулася мені в 2002 році — врешті-решт було виділено первинні частинки наноалмазів, отримані детонаційним способом. Цей об'єкт виявився «найтвердішим горішком», з яким я будь-коли мав справу в своєму житті. З цієї причини я все ще продовжую працювати над цією темою.

### Науковий шлях

1960–1964 — науковий співробітник Teijin Co. Ltd., Осака

1964–1967 — асистент кафедри синтетичної хімії, Університет Кіото, Кіото

1966–1967 — докторантура Університету Віконсина (професор R. West)

1967–1969 — докторантура Принстонського університету (професор P.v.R. Schleyer)

1970–1990 — доцент кафедри хімії Університету Хоккайдо, Саппоро

1990–2001 — професор кафедри Knowledge-Based Information, Технологічний університет Тойохасі

2001 — донині — президент NanoCarbon Research Institute Limited, Уеда, Нагано

### Наукові інтереси

Останнім часом: дисперсні наноалмази (діаметром  $3,7 \pm 0,6$  нм) та їх застосування.

Раніше: наука і технології нановуглецевих сполук, у тому числі  $C_{60}$  та інших фулеренів, наноцибулинки (nano-onions), Маккей-кристали (McKay crystals) та детонаційні наноалмази.

У минулому: хімія вуглеводнів, обчислювальна хімія.

### Публікації

336 наукових статей у журналах з імпаکت-фактором, 71 книг/розділів у книгах; 108 публікацій за матеріалами міжнародних конференцій, 24 патенти і патентні заявки, 208 статей у науково-популярних журналах (станом на липень 2010). h-індекс — 35.