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More spherical large fullerenes and multi-layer fullerene cages

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Abstract

According to the experimental investigation, the carbon nano-particles have spherical multi-layer structure (also called onion-like carbon structure). Theoretically, the optimum structures of these large fullerenes contain highly faceted shapes with icosahedral symmetry. This discrepancy in structure may be attributed to the formation mechanism. Thus, a method is devised to construct spherical large fullerenes (C_{240} , C_{340} , C_{560} , C_{2160} , C_{2940} , C_{3840} , C_{4860}) by using the triangular motif. The 5–7–5–7 shape defect is applied in this method for assembling the large spherical fullerenes which could transform the graphene sheet to a spherical motif via SW rearrangement. The geometry-optimized structures of large spherical fullerenes have been generated by molecular mechanics calculation. Then, the average radius and standard deviation of these large fullerenes were obtained to verify the spherical shape. The multi-layer fullerene with spherical shape was confirmed by the TEM observation. According to the structure analysis, the distance between two neighboring encapsulating carbons is about 3.5 Å, which approximately coincides with the distance between two layers of graphite. The van der Waals force per carbon atom and of multi-layer fullerene with the spherical shape generated by force field calculation, predict their relative stability. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Spherical large fullerenes; Multi-layer fullerene; van der Waals force

1. Introduction

According to the formation mechanism of fullerenes for the structure of giant fullerene is C_n , where the number n may be any even integer. C_n with $n > 100$ is called large fullerene (or giant fullerene) [1]. Recently, using transmission electron micrographs (TEM) spherical multi-layer carbon nano-particles with onion-like structure and single shell large fullerenes have been observed during the electron irradiation of graphite particles by Iijima, Ugarte and Ru's groups [2–5]. According to the structure analysis, these large

fullerenes may have either a faceted shape with icosahedral symmetry or a spherical shape. For the theoretical studies of large cages, Klein proposed the isolated pentagon rule (IPR) to construct this closed shell molecules and Fowler et al. generated the shape for multi-shell polyhedral using the Euler–Schlafli theorem [6,7]. Then, Chiu et al. proposed the geometric structures with different symmetry by using the 2-D planar diagram. This can predict the structure of large fullerenes systemically [8]. In particular, these fullerenes should contain 12 pentagons and a number of hexagons. Several theoretical calculations (including ab initio, semiempirical, molecular dynamics, ...) predict that these structures have highly faceted shapes (graphene

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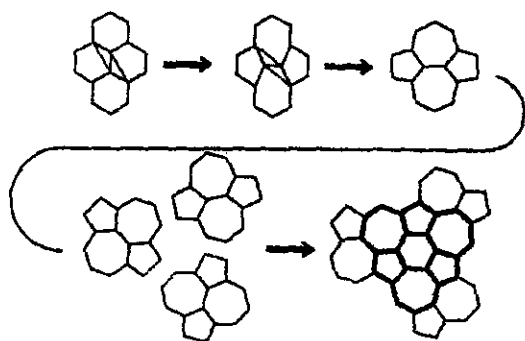


Fig. 1. 5–7–5–7 shape defects via SW rearrangement from graphene sheet and three motifs generate the new C_3 symmetric motif to be an assembling unit forming large fullerene.

sheets) and could be viewed as a spherical shape along the C_3 axis only [9–13]. Later, Brabec et al. proposed the structure defects via carbon atom insertions and generated the shape as well as the stability of large fullerenes by using equilibrium statistical mechanics methods [14]. In 1997, Banhart et al. proposed that the shapes with edges and facets are less stable than structures with smooth curvature [15]. Very recently, Scuseria et al. proposed a mechanism of 5–7–5 defect introduction which may occur by C_2 removal from 5–6 bond on the surface of fullerenes and lead to more spherical shape [16,17]. This calculation showed that the molecules with the defect compare favorably with I_h fullerenes for large system. Although the faceted large fullerene has favorable energy, the onion-like carbon particle needs more spherical shape to be assembled by it. Theoretically, Maiti et al. concluded that the spherical shape of individual shell is enhanced in an onion shape because of the attractive interlayer van der Waals coupling [10]. In this work, we proposed a method to construct more spherical larger fullerenes up to C_{4860} based on the icosahedral symmetry. This method applied the triangular motif with respect to regular icosahedron, and it contains 5–7–5–7 defects via a modified Stone–Wales (SW) rearrangement from graphene sheets [18]. This intra-molecular rearrangement does not change the number of carbons in these large fullerenes during the formation processing. The more spherical larger fullerenes and multi-layer fullerene cages (up to C_{4860}) can be built by using these triangular motifs. Then, the molecular mechanics method has been applied to generate the lowest energy structures

of large fullerene. Simulated multi-layer fullerene cage should be viewed as a spheroid in any direction. In order to confirm the more spherical shapes of large fullerene, the average radius, the standard deviation and the coefficient of variation of the average radius were generated. More spherical large fullerenes were found by a computer program with the molecular mechanics method. The van der Waals force per carbon atom in the multi-layer fullerene cage has been generated by DREIDING force field and these data were compared to find the relative stability of this molecule [19].

2. Computation

Particularly, the triangular facial fragment has been used to build large icosahedral fullerenes. The regular shape of icosahedron contains 20 equivalent triangular motifs. It is seen that the triangular motif provides a clear and simple geometric way to build a large fullerene family. The graphene sheet contains a number of hexagons and keeps the planar structure. According to the experimental observation, the large fullerene structure has more spherical shape, which may contain pentagons, hexagons and heptagons. Fig. 1 shows the method, which could modify a planar graphite sheet to a more spherical motif via the modified SW rearrangement [18]. In this rearrangement, four hexagons are hereafter designated as two pentagons and two heptagons (which is also called 5–7–5–7 defect on fullerene shape). Furthermore, three motifs generate a new C_3 symmetric motif that could be the assembling unit forming large fullerene.

The geometry-optimized structures of the large fullerenes are determined by using the DREIDING force field, which is useful for predicting structures and dynamics of organic molecules [19]. This force field is implemented in the Cerius² 4.0 package [20]. The average radii of each large fullerene can be obtained from these structures. In order to verify a more spherical shape for large fullerene, the standard deviation (SD) of the radii of these fullerenes and coefficient of variation (CV) for Δr (being the distance between the radii of i th atom and its average radii) were calculated. These data provide the degree of sphericity of the large fullerenes. When the values of SD and CV are close to zero, a large fullerene will have a more spherical shape.

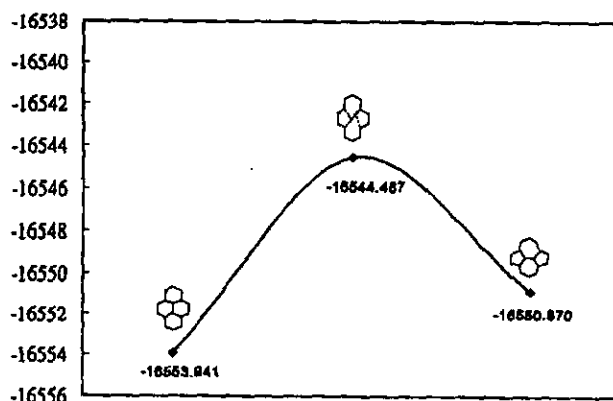


Fig. 2. Energy (eV) diagram for the formation of the 5–7–5–7 shapes defects from graphene sheet by the ab initio calculation. Two bonds form and two bonds break in the SW rearrangement process, in which the intermediate has sp^3 carbon bonding center.

In order to generate the energy barrier in the above intra-molecular rearrangement, the Hartree–Fock calculation with a 6-31G basis set has been used employing the GAUSSIAN 94 program [21].

The van der Waals force of these fullerenes was generated by the DREIDING force field [19]. In order to determine the effective van der Waals attraction per atom in the multi-layer fullerene cage (e.g. three-layer shell N_1 , N_2 and N_3), the following equation is given:

$$E^{vdW} = [E(N_1, N_2, N_3) - E(N_1) - E(N_2) - E(N_3) - E(N_3)] / (N_1 + N_2 + N_3), \quad (1)$$

where E^{vdW} is the effective van der Waals force per

Table 1
Radius, SD and CV for the faceted and the spherical large fullerenes

C_n^a	r (Å)	SD	CV (%)	C_n^b	r (Å)	SD	CV (%)
C_{60}	3.50	0.000	0.00				
C_{240}	7.04	0.124	1.77				
C_{540}	10.53	0.308	2.92	C_{540}	10.59	0.076	0.72
C_{960}	14.00	0.483	3.45	C_{960}	14.14	0.072	0.51
C_{1500}	17.48	0.643	3.68	C_{1500}	17.63	0.239	1.36
C_{2160}	20.96	0.795	3.79	C_{2160}	21.16	0.223	1.06
C_{2940}	24.44	0.941	3.85	C_{2940}	24.70	0.245	0.99
C_{3840}	27.93	1.085	3.89	C_{3840}	28.26	0.201	0.71
C_{4860}	31.41	1.227	3.91	C_{4860}	31.75	0.275	0.87

^a The faceted fullerene.

^b The spherical fullerene.

atom of the (N_1, N_2, N_3) multi-layer structure. $E(N)$ and $E(N_1, N_2, N_3)$ are total energy for a single shell fullerene with N atoms and for a (N_1, N_2, N_3) three layers multi-layer fullerene cage, respectively. This equation could be extended to more than three shells. In this work, we compare the van der Waals force of the spherical multi-layer fullerene cage and the related single shell fullerene of per carbon atom.

3. Results and discussion

The original faceted large fullerene with the icosahedral symmetry contains 12 isolated pentagons and hexagons. However, the number of atoms in these large fullerenes follows $60n^2$ where $n = 1, 2, 3, \dots$. Actually, these large fullerenes do not possess the spherical shapes except they were viewed from a higher symmetry axes. Several TEM pictures show that the polyhedral carbon cages can appear in spheroid shapes. Thus, the faceted large fullerenes should be modified to have a more spherical shape via intra-molecular rearrangement, which have been described in Fig. 1. In particular, this rearrangement is in terms of triangular motif. This intra-molecular rearrangement generates the 5–7–5–7 structural defect in the large fullerene shape. These defects spread out the fullerene shape and lead to a much more spherical cage. Fig. 2 displays the calculated pathway from graphite plane to this 5–7–5–7 shape defect. In which the sp^3 bonding intermediate was assumed in

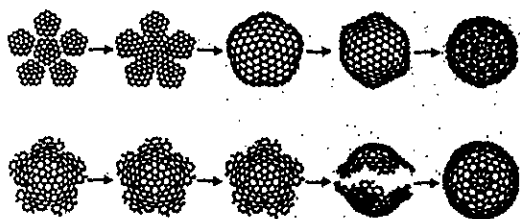


Fig. 3. Assembling process for a C_{340} large fullerene.

this calculation. Its energy barrier is about 9.45 eV by HF/6-31G method using GAUSSIAN 94 program. Particularly, this value should be preserved in the backward isomerization upon cooling to room temperature because the large fullerene is formed at very high temperature.

In order to determine the spherical structure of large fullerene, the average radii, SD and CV of large fullerenes up to C_{4860} are given in Table 1, which includes both faceted and spherical shapes. Comparing the SD and CV, the shapes of these fullerenes are more spherical than that of large fullerene with faceted shape. According to the structure analysis, the calculated CV values for large spherical shape fullerenes are lower than 1% that could confirm their more spherical shape even up to C_{4860} . Their SD values are lower than 0.27, which agrees with Scuseria's calculation results [17]. The faceted large fullerenes are not spherical so that their SD values increase with the number of carbons in fullerenes. Since the values of SD and CV for C_{240} are very close to that of the spherical shape, we ignore this fullerene in the calculation.

Constructing large fullerene is a difficult and tedious work. In this work, we use the triangular motif of icosahedron as an assembly unit to generate the spherical shape of large fullerene, and employ the DREIDING force field to minimize the large fullerene

structure. Fig. 3 shows the assembling process for C_{340} large fullerene based on the triangular motif. The energy minimum structures of C_{2940} , C_{3340} and C_{4860} are shown in Fig. 4 that could be viewed in any direction as a spherical shape.

Table 2 shows the total energies of these large fullerenes after the force field minimization. We compare the potential energy per carbon atom in this study. The large fullerenes have the lower energy per atom than that of C_{60} . According to the energy analysis, the spherical large fullerenes have larger E_{bonds} and E_{angles} than those of faceted fullerenes. Theoretically, the spherical large fullerenes are the other possible isomers for the large fullerene structures. In conclusion, the bonding of the spherical large fullerene is not the exact sp^2 bonding. Thus, it has larger E_{bonds} and E_{angles} than that of graphite and the faceted large fullerenes. The potential energy differences per carbon atom between the spherical and the faceted large fullerenes are very small.

The experimental observation shows that the multi-layer carbon cage has a spherical shape. According to Table 1, the distance between any two neighboring shells is about 3.5 Å, which is close to the distance between graphite layers. According to the experimental observation, these structures could be multi-layer fullerene cages. Ruff and Maiti's calculation reveals that van der Waals binding energies of onion-like fullerene cages play a very important role for stabilization of such structures [8]. Table 3 gives the van der Waals energy per atom in multi-layer fullerene cages up to C_{4860} with nine shells. Eq. (1) can give the effective van der Waals force per atom in multi-layer fullerene cages. The minimum energy structures of multi-layer fullerene cages were determined by the DREIDING force field. The van der Waals forces for two-layer, three-layer, four-layer, five-layer and six-layer fullerene cages are -0.0387 eV, -0.0456 eV, -0.0495

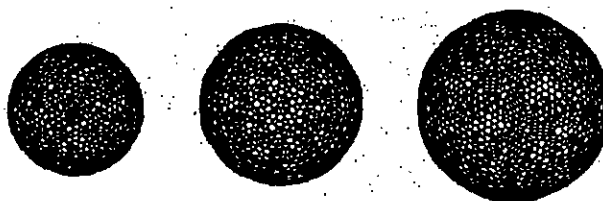


Fig. 4. C_{2940} , C_{3340} and C_{4860} large fullerenes could be viewed as spheroid in any direction.

Table 2
Potential energy of large fullerenes by molecular mechanics calculation (eV)

Fullerene	E_{bonds}	E_{angle}	E_{torsions}	$E_{\text{inversions}}$	$E_{\text{van der Waals}}$	E_{total}	Energy per carbon atom
C ₆₀	1.04	5.71	19.21	17.91	6.21	50.09	0.83
C ₂₄₀	10.22	7.86	27.58	20.86	35.67	102.20	0.43
C ₃₄₀ ^a	19.78	7.69	39.52	25.25	84.05	176.30	0.33
C ₅₄₀ ^b	28.05	80.64	27.37	20.22	51.54	207.82	0.38
C ₉₆₀ ^b	31.36	7.37	49.35	28.72	150.96	267.78	0.28
C ₉₆₀ ^a	33.45	128.86	29.99	21.32	92.54	306.17	0.32
C ₁₅₀₀ ^b	46.44	7.25	56.68	31.26	236.76	378.40	0.25
C ₁₅₀₀ ^a	74.99	215.33	35.77	23.28	146.79	496.16	0.33
C ₂₁₆₀ ^a	64.97	7.21	62.46	33.25	341.54	509.44	0.24
C ₂₁₆₀ ^b	121.28	372.84	54.89	30.18	211.54	790.72	0.37
C ₂₉₄₀ ^a	86.94	7.20	67.24	34.90	465.28	661.56	0.23
C ₂₉₄₀ ^b	175.05	471.11	43.01	25.88	314.81	1029.86	0.35
C ₃₈₄₀ ^a	112.30	7.20	71.35	36.31	607.99	835.14	0.22
C ₃₈₄₀ ^b	164.98	549.52	32.06	21.76	371.78	1140.10	0.30
C ₄₈₆₀ ^a	141.05	7.20	74.95	37.54	769.66	1030.40	0.21
C ₄₈₆₀ ^b	258.07	737.02	54.62	30.16	513.18	1593.04	0.33

^a Faceted.

^b Spherical.

and -0.0528 eV, respectively. To conclude, the van der Waals force in the multi-layer fullerene cage per atom increases as the number of layer increases. This calculation results support that the giant fullerenes occurred with the multi-layer structure. Since the multi-layer fullerene cage has strong van der Waals force, it may generate a more concentric carbon cage. Recently, Banhart et al. proposed that the core of carbon-onions could be transformed to diamond [22]. We conclude that the van der Waals force in

this fullerene may play a very important role in the formation of diamond. Comparing the radius of single shell and multi-layer of C₃₄₀ fullerene, it decreases by about 0.02 \AA for this radius investigation (Tables 1 and 3).

The results of our work provide a framework by which experimental observations of large fullerenes and multi-layer fullerene cage can be understood in terms of I_h fullerenes systematically. This assembling process for large fullerene applies the triangular motif

Table 3
Comparison of the van der Waals force of multiple-layered fullerene cages (eV) and onion radius (Å)

	van der Waals ^a	Energy per carbon	Onion radius
C ₆₀ -C ₂₄₀ -C ₃₄₀	-32.541	-0.0387	10.581
C ₆₀ -C ₂₄₀ -C ₃₄₀ -C ₉₆₀	-82.095	-0.0456	14.121
C ₆₀ -C ₂₄₀ -C ₃₄₀ -C ₉₆₀ -C ₁₅₀₀	-163.221	-0.0495	17.636
C ₆₀ -C ₂₄₀ -C ₃₄₀ -C ₉₆₀	-288.487	-0.0528	21.146
C ₁₅₀₀ -C ₃₁₆₀			
C ₆₀ -C ₂₄₀ -C ₃₄₀ -C ₉₆₀	-456.163	-0.0543	24.692
C ₁₅₀₀ -C ₂₁₆₀ -C ₃₉₄₀			
C ₆₀ -C ₂₄₀ -C ₃₄₀ -C ₉₆₀	-687.247	-0.0562	28.216
C ₁₅₀₀ -C ₂₁₆₀ -C ₃₉₄₀ -C ₅₈₄₀			
C ₆₀ -C ₂₄₀ -C ₃₄₀ -C ₉₆₀	-987.028	-0.0577	31.729
C ₁₅₀₀ -C ₂₁₆₀ -C ₃₉₄₀ -C ₅₈₄₀			
C ₄₈₆₀			

^a van der Waals energy is generated by Eq. (1).

with simple geometrical consideration via SW rearrangement to construct the spherical large fullerenes, which could give the chemists and theoreticians structural information about new carbon allotropes. The shape of spherical multi-layer fullerene cage could be viewed as spheroid in any direction and it provides a reliable interpretation of TEM image. The van der Waals force per atom in multi-layer fullerene cage can support the existence of carbon nano-particles. Thus, the investigation of the chemical and physical properties of large fullerenes and their derivatives will certainly lead to the discovery of new and interesting materials.

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