Structure, Chirality, and Formation of Giant Icosahedral Fullerenes and Spherical Graphitic Onions[a,b]

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Abstract

We describe the topology, structure, and stability of giant fullerenes exhibiting various symmetries (I, I_h, D_{2h}, T). Our results demonstrate that it is possible to create two new families of nested "chiral" icosahedral (I) fullerenes namely C_{260}@C_{560}@C_{980}@C_{1520}@ … and C_{140}@C_{380}@C_{740}@C_{1220}@ …, which exhibit interlayer separations of ca. 3.4 Å. These chiral fullerenes are thought to possess metalliclike conduction properties. We discuss in detail the transformation of polyhedral graphitic particles into quasispherical nested giant fullerenes by reorganization of carbon atoms, which result in the formation of additional pentagonal and heptagonal carbon rings. These "spherical" structures are metastable and we believe they could be formed under extreme conditions, such as those produced by high-energy electron irradiation. There is circumstantial experimental evidence for the presence of heptagonal rings within these spherical fullerenes.

Keywords

Fullerenes • Spherical onions • Nested fullerenes • Stability and symmetry

Introduction

Graphene sheets, which consist of honeycomb lattices of sp^2 hybridized orbitals of carbon atoms, have proved to be extremely flexible and, as a result, novel nanostructures have been generated. For example, it is possible to curve these sheets by introducing pentagonal rings so as to form closed cages known as fullerenes, e.g., C_{60} and C_{70} [1–3], polyhedral and onionlike particles [4, 5], and elongated fullerenes termed nanotubes [6]. Combinations of five, six, and seven carbon rings (an arrangement of positive and negative curvatures) [7–11] can also lead to other fascinating structures, such as corkscrewlike tubules [7], toroids [12, 13], bent tubular structures [8, 9], nanoboxes [14], or cones [15–17].

Sumio Iijima was the first to report the existence of nested carbon nanocages (known as graphitic onions) using high-resolution transmission electron microscopy (HRTEM), when studying the structure of amorphous carbon films prepared by thermal vacuum deposition (Fig. 1) [4]. In 1988, Kroto and McKay proposed, for the first time, that graphitic onions consisted of nested icosahedral fullerenes (C_{60}@C_{240}@C_{540}@C_{960}…) containing only pentagonal and hexagonal carbon rings (note that C_{60} has icosahedral symmetry) [18, 19]. One reason for considering these icosahedral structures is that the average separation between shells is close to that of graphite (3.35 Å). Four years later, Ugarte widened our appreciation of the curved world of carbon structures by observing the transformation of polyhedral graphitic particles into almost spherical carbon onions [5], when irradiating the

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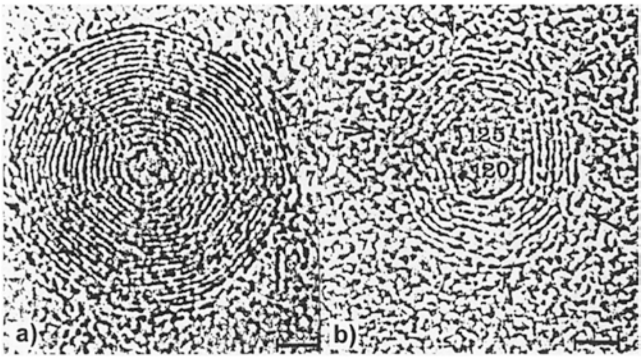

Fig. 1 Two examples (a and b) of HRTEM micrographs of spheroidal carbon particles, first observed by Iijima, exhibiting interlayer spacing close to 3.4 Å (Ref. [4]).

specimens with fast electrons inside an electron microscope. In this context, two of several questions that remain to be answered are: (1) why are onionlike structures quasispherical? and (2) how do graphitic carbon atoms rearrange in order to attain sphericity?

Since the 1970s, it has been known that the structure of carbon blacks (consisting of spherical arrangements of disordered sp^2 hybridized carbon and a few percentage of sp^3 hybridized carbon atoms) resembles that of graphitic onions. At that time, models consisting of platelets of graphite packed into spherical arrangements (Fig. 2) [20, 21] were proposed. However, these models did not account for the presence of pentagonal carbon rings embedded within the hexagonal network. Carbon blacks are now widely used as fillers in order to modify mechanical, electrical or optical properties of various materials.

In 1994, Sarkar and Kroto [22], proposed that the round structures reported by Ugarte could be generated theoretically by removing the cusps (pentagons and neighboring atoms) from the icosahedral fullerenes. The study then suggested that hydrogen or other atoms, such as oxygen or sulfur, stabilized the open-shell arrangement (eliminating dangling bonds). Nowadays, it is possible to generate larger amounts of "graphitic" onions using carbon ion bombardment of silver and copper targets and by arcing graphite rods in distilled water [23, 24]. However, the isolation and the bulk generation of this material have yet to be achieved. More recently, other novel methods for producing carbon onions have been developed. For instance, it is possible to produce bulk amounts of carbon nano-onions by radio-frequency plasmaenhanced chemical vapor deposition over Co and Co-SiO_2 catalysts [25].

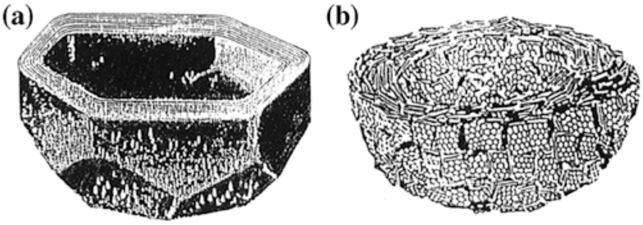

Fig. 2 Models of two possible structures of partially graphitized carbon black particles, which could be considered as concentric giant fullerenes. However, these models never considered the presence of pentagonal rings within the hexagonal network (Refs. [20, 21]).

In this paper, we demonstrate that energy minimization of spherical giant fullerenes is associated with the introduction of additional heptagons and pentagons, a result which may shed light on the mechanism whereby polyhedral graphitic particles transform into round onions. Finally, an energetic study of novel fullerene chiral families exhibiting icosahedral and tetrahedral symmetries is discussed in detail.

Euler's Law in Graphitic Structures

A clear understanding of the geometry and morphology of carbon structures, which consist of hexagonal sp^2 hybridized carbon (e.g., graphite), can be attained by applying Euler's law. The general form of this law can be expressed as $F-E+V=2$, where F is the number of faces, E is the number of edges, V is the number of vertices, and 2 is the Euler characteristic, which is a geometric invariant that characterizes topologically equivalent structures. In the case of all closed cages (polyhedra) = 2, for example in fullerene C_{60}, $F=32$ (12 pentagons and 20 hexagons), $E=90$, $V=60$, and = 2. All closed polyhedra display the same topology as the sphere.

As discussed elsewhere [26], it can be shown that Euler's geometric invariant is related to the genus g (number of handles in a structure) by

$$\chi = 2(1-g) \tag{1}$$

It can be shown that for a sphere = 2 and $g=0$, whereas for a torus = 0 and $g=1$ (one handle). For sp^2 hybridized carbon, such as graphene, and considering pentagonal, hexagonal, heptagonal, and octagonal rings of carbon, we can express

$$F = N_5 + N_6 + N_7 + N_8 \tag{2}$$

and

$$2E = 3V = 5N_5 + 6N_6 + 7N_7 + 8N_8 \tag{3}$$

where N_n is the number of polygons with n sides. Substituting (2) and the constraint (3) into Euler's law yields

$$N_5 - N_7 - 2N_8 = 6\chi = 12(1-g) \tag{4}$$

Within the graphitic structure, the pentagons, heptagons, and hexagons contribute to the curvature and topology of the arrangement and as such can be regarded as "defects." Notice that the number of hexagons is not present in Eq. (4) because they do not contribute to the curvature of the system.

Stability of Giant Icosahedral Fullerenes and Geometrical Rules

Due to the large number of carbon atoms in most of the giant fullerene systems (>250–500 atoms), we have carried out molecular mechanics calculations using the DREIDING force field [27–29] in conjunction with the Tersoff potential [30]. The latter accurately reproduces cohesive energies and elastic properties of graphite and diamond (sp^2 and sp^3 carbon systems) [31, 32]. A comparison of this method with *ab initio* techniques for these giant molecules [33] validated the suitability of the force-field/Tersoff method for studying the systems described herein. Spatial coordinates, generated by the DREIDING force-field method for giant fullerenes were introduced [34] and elastic energies were computed for several graphitelike structures.

An icosahedral carbon fullerene can be constructed by fusing 20 triangular graphene segments, joined by 12 pentagons, one per vertex [35] (Fig. 3). As mentioned earlier, the first proposed family of concentric giant fullerenes (C_{60}@C_{240}@C_{540}@C_{960}@C_{1500}@…) [18, 36] (insert, Fig. 4), exhibiting the same symmetry as C_{60} (I_h), revealed an intershell graphitic spacing of ca. 3.35 Å. The single-shell fullerenes belonging to this family can be constructed using a triangular template, consisting of a three sided graphene sheet delimited by pentagonal rings at the corners. Other giant fullerenes with I_h symmetry have also been generated, using the C_{20} cage [37–39] as a template. In this case, the sequence of consecutive fullerenes (C_{20}@C_{80}@C_{180}@C_{320}@C_{500}@C_{720}@C_{980}@…) is not energetically favorable for graphitic onions due to a discrepancy within the intershell spacing (ca. 2 Å) as compared to that in graphite (ca. 3.35 Å). These families of giant fullerenes consist of nonhelical arrangements within the triangular templates, due to the orientation of pentagonal rings with respect to the hexagonal graphene network (Fig. 5). In other words, if the pentagons are not connected in a straight line (parallel or perpendicular) through hexagonal linear rings, the arrangement is termed helical or chiral (Fig. 5).

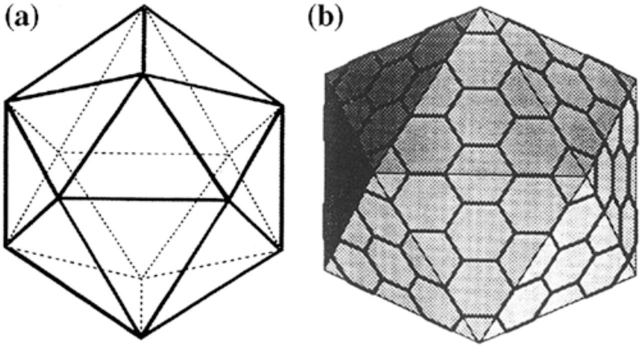

Fig. 3 (**a**) Icosahedron and (**b**) decorated icosahedron with hexagonal and pentagonal carbon rings, showing that the template necessary to generate such structure is an equilateral triangle.

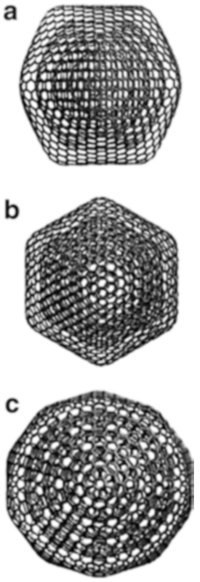

Fig. 4 Molecular models of the icosahedral C_{60}@C_{240}@C_{540}@C_{960}@C_{1500} family proposed by Kroto and McKay showing: (**a**) The 2-fold axis of symmetry; (**b**) The 3-fold axis of symmetry; (**c**) The 5-fold axis of symmetry.

A rule for creating icosahedral fullerenes can be generalized using an equilateral triangle as a building block [35]. In order to create this triangle on a graphene sheet, we first choose an origin [(*0,0*) within the sheet], attaching a pentagonal ring as shown in Fig. 6a. Subsequently, a lattice point, denoted (m, n), is placed in the sheet, and another pentagonal ring is assigned next to it (Fig 6b). At this stage, a third pentagon is located equilaterally with respect to the other two, thus generating a perfect triangle (Fig. 6c), which can be used as the template for constructing an icosahedron. The lattice point (m, n) selected to generate the fullerene determines the number of carbon atoms N_C within the icosahedral shell

$$N_C = 20\left(m^2 + mn + n^2\right) \tag{5}$$

and the cage diameter d

$$d = \frac{5\sqrt{3}}{\pi} a_{C-C} \left(m^2 + mn + n^2\right)^{1/2} \tag{6}$$

where a_{C-C} is the average carbon–carbon distance (ca. 1.44 Å) within the hexagonal network or fullerene cage.

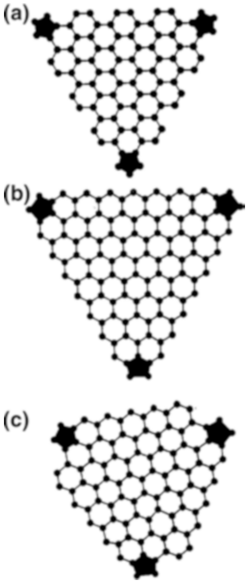

Fig. 5 (**a**, **b**) Nonhelical configurations within the triangular building template necessary for building icosahedral fullerenes; (**c**) helical arrangement, in which pentagons are not aligned through the hexagonal rings.

In particular, it is possible to construct three different families of icosahedral graphitic onions in which their interlayer spacing among shells is ca. 3.4 Å. The *n*th term and the first four elements of the sequence of these families of graphitic onions are shown below.

(i) I_h family (armchair) when $m=n$

$$\begin{aligned} N_C &= 60n^2 \\ (1,1) &= 60 \\ (2,2) &= 240 \\ (3,3) &= 540 \\ (4,4) &= 960 \end{aligned}$$

(ii) I family (helical arrangement) when $m=n+2$

$$\begin{aligned} N_C &= 20\left(3n^2+6n+4\right) \\ (2,0) &= 80 \\ (3,1) &= 260 \\ (4,2) &= 560 \\ (5,3) &= 980 \end{aligned}$$

We should note that C_{80} does not belong to the family, but it could be added in order to have smaller shells in the interior of the onion.

(iii) I family (helical arrangement) when $m=n+1$

$$\begin{aligned} N_C &= 20\left(3n^2+3n+1\right) \\ (2,1) &= 140 \\ (3,2) &= 380 \\ (4,3) &= 740 \\ (5,4) &= 1220 \end{aligned}$$

Using the above procedure, any fullerene or giant fullerene exhibiting icosahedral symmetries (I or I_h) can be generated. Furthermore, structures with other symmetries such as octahedral and tetrahedral can also be created using this method, in addition to other restrictions [39]. In particular, two other new families with icosahedral (I) symmetry, exhibiting intershell spacings close to that of graphite can be generated: (1) C_{260}@C_{560}@C_{980}@C_{1520}@… and (2) C_{140}@C_{380}@C_{740}@C_{1220}@ … These nested fullerenes are helical and possess chiral images with two possible isomers per icosahedral cage (Fig. 7). In any icosahedral cage, as the number of carbon atoms increase, the more faceted the structure becomes. This is due to the fact that only 12 pentagonal rings are necessary to close any cage. Therefore, for systems greater than 540 carbon atoms (which contain more hexagonal rings), sphericity decreases dramatically (Fig. 8).

Laser vaporization of graphite has resulted in the formation of high mass fullerenelike clusters in the 300–350 and 600–700 carbon atom range [40]. This observation provides circumstantial evidence for the formation of icosahedral concentric fullerenes as stable forms of carbon. Specifically, the masses observed in the 300–350 atom range may correspond to single or multiple shells: C_{60}@C_{240}; C_{80}@C_{260}; or to any single helical shell within the same mass range. Furthermore, C_{240}@C_{540}, or single clusters containing roughly the same number of atoms, may match with higher fullerenes reported in the 600–700 carbon atom range.

HRTEM, in conjunction with electron irradiation studies of particles generated by arcing graphite electrodes in inert atmospheres, revealed the presence of graphitelike onions corresponding to: single-shell C_{240} [41], C_{50}@C_{230} [42], C_{120}@C_{390}@C_{760} [42], C_{60}@C_{240}@C_{540}@C_{930} [41, 42], C_{70}@C_{290}@C_{680}@C_{1200}@C_{2000} [42]. These observations suggest that it may be possible to produce helical as well as nonhelical concentric fullerene cages. Moreover, electron diffraction studies of single polyhedral particles reveal *hk0* reflections indicating that the stacking of the graphitic shells is disordered (turbostratic) [43]. This may also be due to helical (I symmetry) concentric cages, which generate turbostraticlike arrangements within the onions.

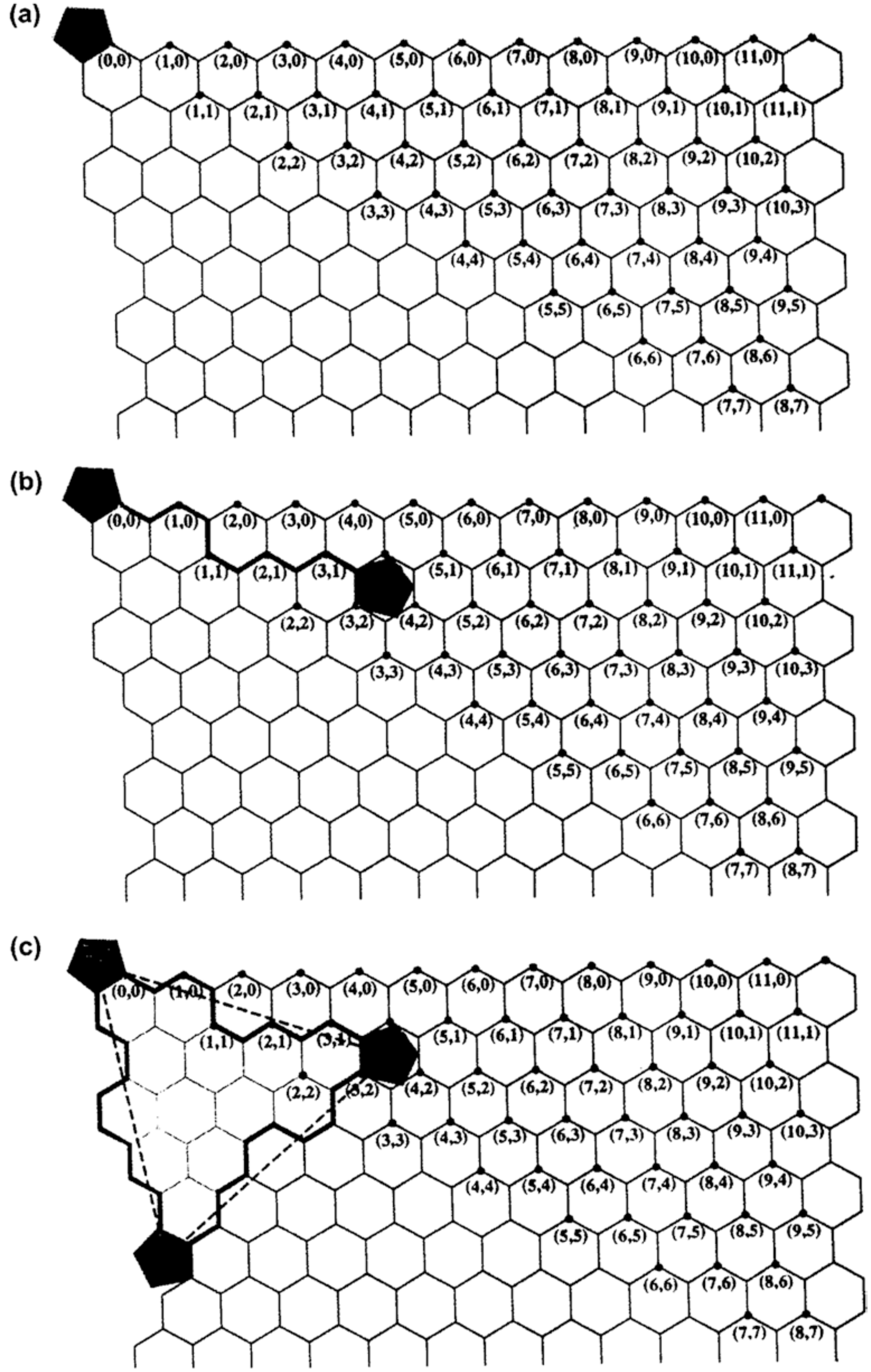

Fig. 6 Procedure followed to generate an icosahedral fullerene: (**a**) select an origin (*0*, *0*) within the graphene sheet and attach a pentagonal ring next to it; (**b**) choose a lattice point (*m*, *n*) and place another pentagon next to it; (**c**) locate a third pentagon equilaterally to the other two pentagonal rings, thus generating the triangular building template. Note that (*m*, *n*) determine the number of atoms and the average diameter of the fullerene.

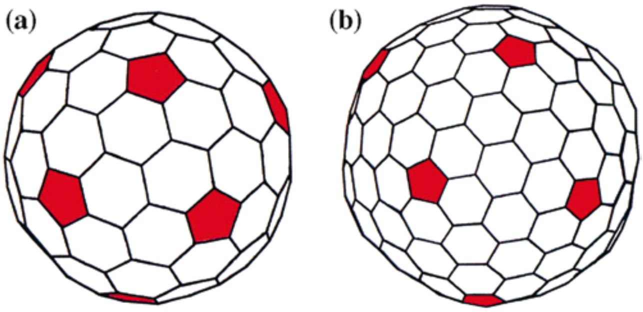

Fig. 7 Generated icosahedral (*I*) fullerenes with a helical arrangement; (**a**) C_{140}; (**b**) C_{260}. The families (C_{80}@C_{260}@C_{560}@C_{980}@C_{1520}@…and C_{140}@C_{380}@C_{740}@C_{1220}@…) are predicted to be metallic (M. I. Heggie, private communication), in contrast to the I_h family (C_{60}@C_{240}@C_{540}@C_{960}@C_{1500}), which is considered a semiconductor.

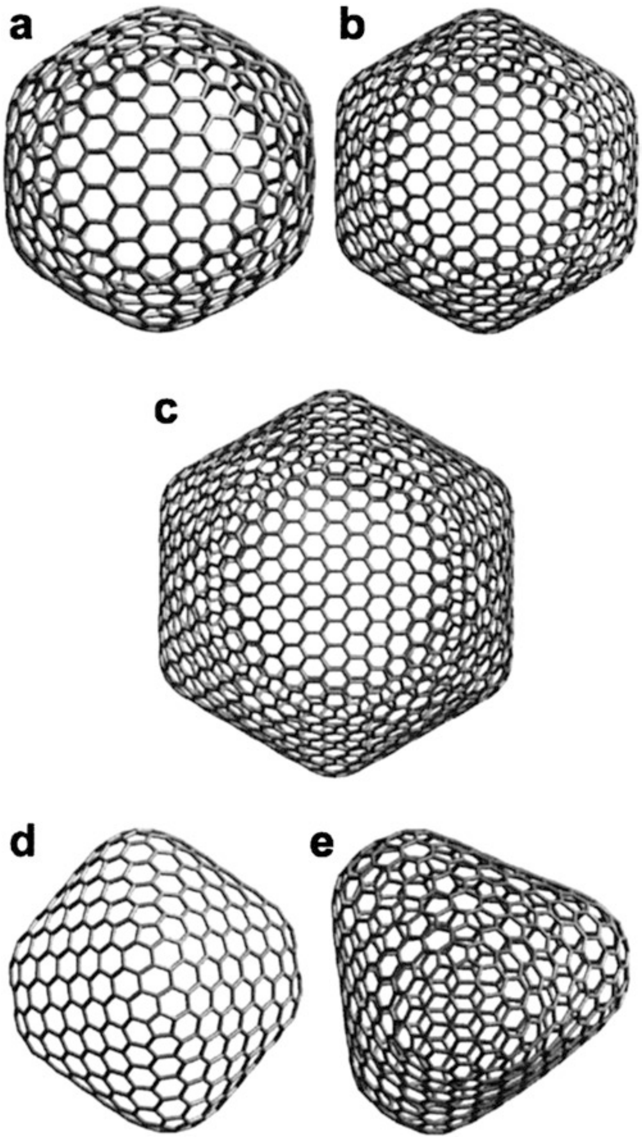

Fig. 8 Fullerenes with 12 pentagonal rings. The faceting increases in icosahedral fullerenes as the structure becomes larger. (**a**) C_{540} (I_h); (**b**) C_{960} (I_h); (**c**) C_{1500} (I_h). Other symmetries: (**d**) D_{2h} with 600 atoms; (**e**) T_d with 660 atoms.

It has been demonstrated experimentally that smallsized and multishell "bucky onions" behave like semiconductors [44]. It has been also noted that as their size increases they exhibit metalliclike behavior because of their nonlinear conducting properties. It is conceivable that single-shell giant fullerenes may be metallic [33], thus propelling viable candidates for the construction of single electron devices. However, the electronic properties of chiral single-shell onions have not yet been reported.

Polyhedral Particles and Graphitic Onion Formation

In 1980, when Iijima first observed (by HRTEM) onionlike graphitized nanoparticles [4] with an interlayer spacing of ca. 3.44 Å, he noted that the angles intersecting the graphitic planes corresponded to ca. 120 ± 20° He then concluded that these angles were fairly close to the ideal angle (109°) of a tetrahedral sp^3 carbon attached to graphite. He explained the latter in terms of tetrahedral bonds or bent trigonal graphitic systems, possibly due to the insertion of pentagonal carbon rings or to the presence of dangling bonds into the graphitic system [4]. Three years after the discovery of C_{60}, Kroto and McKay [18] also suggested that Iijima's structures might be explained as quasi-icosahedral concentric carbon shells that grew through a spiraling mechanism as a result of introducing pentagonal rings into the hexagonal network (Fig. 9).

Ugarte's experiments demonstrated that high electron irradiation over polyhedral particles (generated in the fullerene Krätschmer–Huffman reactor) was able to produce quasi-spherical graphitic arrangements that appeared to be stable [5]. In 1996, Banhart and Ajayan [45] also showed that high electron doses at high temperatures (700–800 °C) resulted in the formation of perfect spherical onions. Continued irradiation at this temperature was responsible for a contraction of the intershell separation, which resulted in the formation of diamond (self-compression phenomenon).

High-energy electron irradiation is capable of producing transformations and atomic rearrangements within the irradiated specimen. These transformations may be due to: (1) bond rupture due to electron excitations; (2) momentum transfer to the atomic nuclei, which may result in the atom displacement to the interstitial sites (*knock-on* effect); (3) excitation of vibrational or rotational modes of the molecules; and (4) energy transfer (loss) from the fast electrons to the specimen, thus raising the average temperature of the irradiated sample [5, 39].

In particular, Ugarte's experiments consisted of irradiating carbon polyhedral particles with a very intense electron beam in a HRTEM, using electron densities 10–20 times higher than those found under normal operating conditions (ca. 10 Å/cm^2) [5]. He noticed that the polyhedral particles transformed gradually into quasispherical graphitic onions, a

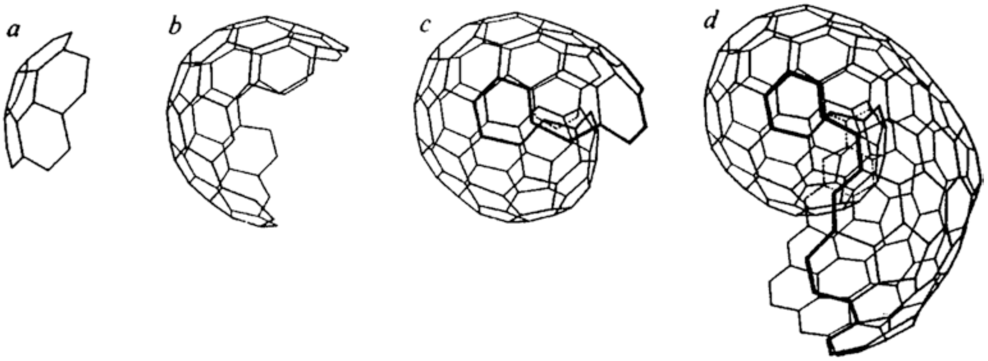

Fig. 9 Hypothetical initial growth sequence (proposed by Kroto and McKay) evolving from: (**a**) a corannulene molecule; (**b**) and (**c**) species in which edge by-pass occurs to (**d**), an embryo in which the second shell is forming. The sequence leads in a natural way to both carbon particles and closed cages, fullerenes (Courtesy of H. W. Kroto).

transformation which can be divided into several steps [46]. Figure 10 shows this sequence. Initially, the polyhedral particle collapses occupying the inner hollow space, thus causing the generation of a disordered particle (Fig 10b). Subsequently, reorganization of the outer layers begins (Fig. 10c), progressing by a kind of internal epitaxy to a final structure, which contains small inner shells, usually very close to the diameter of C_{60} (ca. 1 nm; Fig. 10d).

Ugarte proposed that their transformation under irradiation was caused by the electron beam (resembling high-temperature regimes), thus promoting bond rupture and allowing a degree of structural fluidity [5, 42] responsible for a gradual reorganization into quasispherical arrangements. Notwithstanding this suggestion, Banhart and co-workers discussed [41, 47, 48] onion formation primarily based upon *knock-on* collisions from electrons and carbon atoms, concluding that heating or electronic excitation do not dominate the process [47, 48]. These authors used much higher-energy electron beams (1250 KeV) in order to confirm the latter. It is important to note that high temperature regimes within the process are localized for a few picoseconds. Therefore, it is unlikely that this could lead to an explanation for bucky-onion formation.

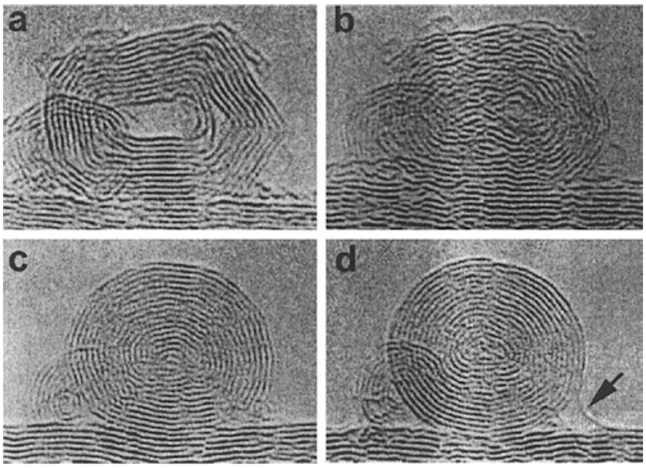

Fig. 10 Formation of quasispherical onionlike particles under electron irradiation. (**a**) polyhedral particle as obtained from the electric arc; (**b**) after 20 s of irradiation the particle collapses and the inner central void disappears; (**c**) after 40 s reordering continues at the surface toward the center progressively; (**d**) 180 s further irradiation yields to quasispherical onionlike particle with a very small central shell (interlayer spacing 0.34 nm; Courtesy of Daniel Ugarte; see also Ref. [46]).

The quasispherical arrangements (onions formed by two to four shells) were reported to be very stable under intense electron bombardment [5, 41]. However, further investigations [47] regarding their stability after irradiation revealed that (when deflecting the electron beam from the irradiated area), the outermost shells dissolved into noncrystalline material, losing their spherical shape and decaying completely into disordered graphitic carbon. Therefore, spherical onions produced by electron irradiation are, indeed, *metastable forms* of carbon.

Sphericity of Graphitic Onions

For giant icosahedral fullerenes containing only 12 pentagons, faceting (i.e., progressive loss of sphericity; Fig. 11) is enhanced as the number of hexagons increases. Transformations of hexagons by heptagon/pentagon pairs will thus increase sphericity at the expense of faceting (discussed by Hare and Fowler) [49]. According to Euler's Law, it is possible to introduce heptagons into a fullerene provided that each heptagon is matched by an additional pentagon, in order to compensate for the negative curvature associated with the heptagon (i.e., $N_5 - N_7 = 12$).

In this section, through energy minimization calculations using the DREIDING force field [27–29] and the Tersoff potential [30], we demonstrate that quasispherical structures containing pentagons and heptagons are metastable, and could be favored under high-energy electron irradiation. From the experimental point of view (Fig. 10), it is possible that the strained regions of polyhedral particles

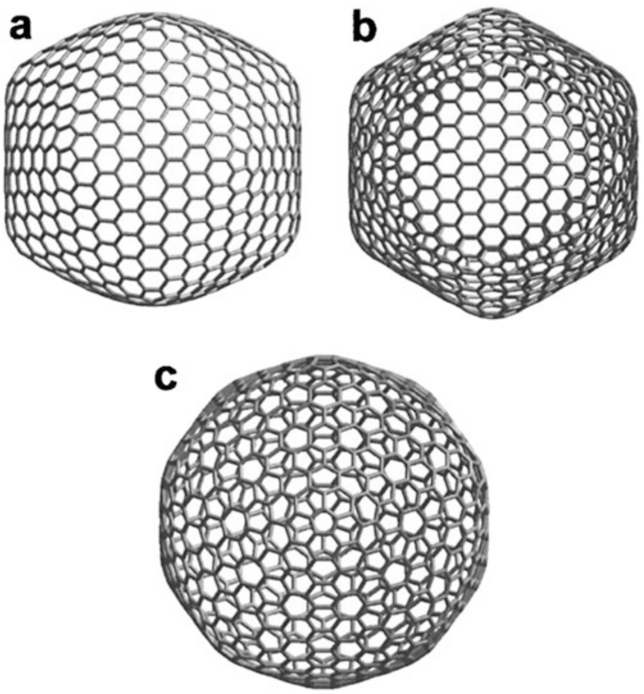

Fig. 11 Molecular model of C_{940} oriented along various symmetry axes: (**a**) C_2; (**b**) C_3; (**c**) C_5. It is clear that as the number of hexagons increases the more faceted the structure becomes.

(Fig. 10a) are selectively disrupted by electron irradiation with ejection of carbon fragments by knock-on effects centered upon the pentagonal cusps, thus generating graphitic domains containing holes (dangling bonds). Such perforated structures are likely to be flexible and could be easily deformed.

In order to generate quasispherical fullerenes theoretically, the following steps should be followed:

1. A polyhedral fullerene (generally exhibiting icosahedral symmetry) possessing hexagons and 12 pentagonal rings is relaxed using the DREIDING force field with the conjugate gradient method in order to find the local minimum of the structure. Subsequently, the Tersoff potential is used to obtain the elastic energy of the structures (For graphite this potential prefers bond distances of 1.46 instead of 1.42 Å) [39].
2. The pentagonal carbon rings and adjacent atoms of the icosahedral fullerene are removed, resulting in perforated structures containing dangling bonds (for larger fullerenes, several carbon atoms surrounding the pentagons need to be removed). It should be noted that the perforations created in the faceted structure emulate experimental observations witnessed under high-electron irradiation (Fig. 10a, b), in which *strained* regions of the structure break and/or fragment, leading to less rigid arrangements [22]. After relaxing using the DREIDING force field in conjunction with the Tersoff potential, these *holey* structures become rounder containing dangling bonds at the edges (Fig. 12). From the experimental point of view, it must be borne in mind that such dangling bonds are energetically costly. Therefore, these voids are likely to be quickly occupied with carbon atoms, possibly by the introduction of heptagon/pentagon arrays (see point 3).
3. The perforations within the *holey* fullerene are subsequently closed by introducing more pentagons (more than 12) and additional heptagons, responsible for maximizing sphericity (Fig. 13).

We believe that, under the electron beam, the rearrangements are caused by *rupture* and/or *knock-on* with subsequent reaggregation of strained regions (pentagonal cusps and defects), in which broken carbon chains, delocalized atoms, interstitials or graphitic fragments arrange in more stable spherical-concentric configurations. Van der Waals interactions should also play a positive role in this context, because a constant interlayer distance between nesting spheres must be maintained.

According to our model, some random reaggregation takes place in order to satisfy dangling bonds once bond rupture occurs. In addition, the initial symmetry of the precursor particle (parent-fullerene) needs to be broken after heptagons and pentagons are introduced in the cage, thus resulting in a more spherical structure (Fig. 13).

The calculations begin with symmetrical polyhedral particles (icosahedral, D_{2h} and tetrahedral), possessing only hexagonal and 12 pentagonal rings of carbon (Tables 1 and 2).

For the D_{2h} system for icosahedral fullerenes with 600 and 540 atoms, respectively (Fig. 13), it is found that the most stable and spherical structure contained 540 atoms, with was obtained from a D_{2h} fullerence with 600 atoms (D_{2h} C_{540}-A in Table 3 and Fig. 13). In this case the structure has lost 60 atoms during rearrangement.

However, starting from icosahedral (I_h) C_{540}, we found highly spherical structures (ico C_{540}-A, B, C, Table 3), which were not as stable as the $D_{2\mathrm{h}}$ C_{540}-A. The data from Tables 1, 2, and 3 are summarized in Fig. 14. For quasispherical fullerenes with additional pentagons and heptagons, the stability decreases due to a reduction in the number of hexagonal rings, confirming that these spherical isomers are *metastable arrangements*.

Another important result is provided by a Stone–Wales-type transformation [50] (Fig. 15), which converts icosahedral fullerenes into quasispherical fullerenes [39, 51–53], with minimal expenditure of energy. This transformation has been applied in the following cases: (1) to convert four adjacent hexagons into two pentagons and two hexagons; (2) three hexagons and one pentagon into two pentagons, one hexagon, and one heptagon; (3) two hexagons and two

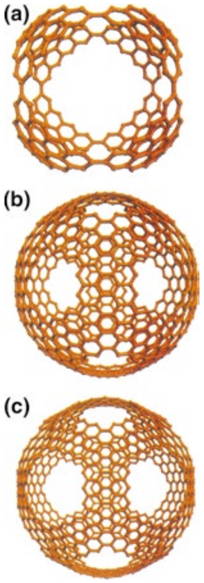

Fig. 12 Quasispherical fullerenes with holes obtained via energy minimization. (**a**) Precursor of D_{2h} C_{540}; (**b**) precursor of ico-C_{888}-A; (**c**) precursor of ico-C_{1500}-A.

pentagons into two pentagons and two hexagons. In the D_{2h} C_{540}, one Stone–Walestype transformation involving two pentagons and two hexagons needs 0.004 eV; on three hexagons and one pentagon requires 0.086 eV; four hexagons require 11.349 eV (Fig. 15). Starting with an icosahedral C_{540}, with heptagons and pentagons, a more spherical structure is obtained via several random Stone–Wales-type transformations, requiring 23.936 eV to generate the ico C_{540}-A fullerene (see Tables 1, 2, and 3).

It is noteworthy that quasispherical onions are not more stable than the symmetrical faceted giant fullerenes on which we based our calculations. However, under the conditions of formation (high-energy electron irradiation), quasispherical structures possessing negative curvature are preferred. Experimentally, it has been found that the maximum energy transfer to the carbon atoms during the high-energy irradiation of 1250 keV is ca. 500 eV [47]. Therefore, the possibility to promote Stone–Wales-type defects is likely. In all cases, except for the D_{2h} C_{228}-A, the quasispherical fullerenes are more stable than C_{60} (see Table 3), provided the isolated pentagon rule is not violated.

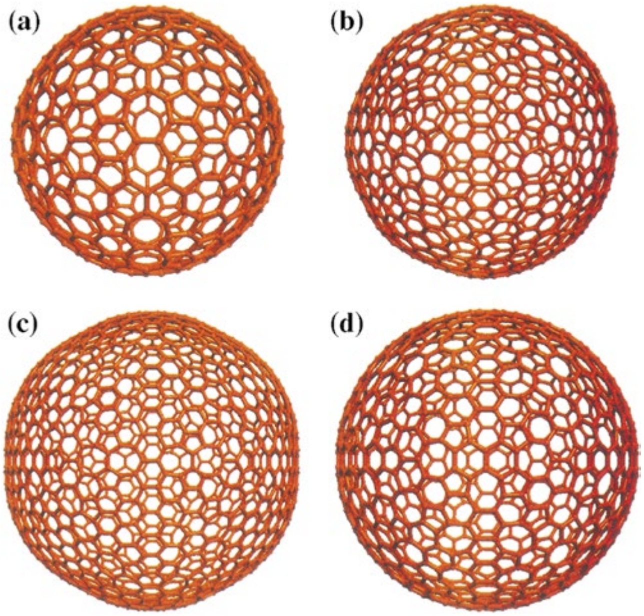

Fig. 13 Quasispherical fullerenes in which the holes have been filled with heptagonal and pentagonal rings. (**a**) D_{2h} C_{540} with 76 pentagons and 64 heptagons; (**b**) ico-C_{888}-A with 60 pentagons and 72 heptagons; (**c**) ico-C_{1500} with 132 pentagons and 120 heptagons (I_h symmetry); (**d**) C_{1020} obtained by adding 132 atoms to the ico-C_{888}, thus generating more heptagon–pentagon pairs responsible for a more spherical isomer.

Table 1 Energy/atom of icosahedral (I_h) and tetrahedral fullerenes relative to graphite, mean radius of fullerene, and difference Δr_i of the largest and shortest distance to the center of mass of fullerene[a]

Structure	Energy/atom (eV)	Mean radius (Å)	Δr_i (Å)
C_{20} (I_h)	−1.7449	2.045	1.09×10^{-4}
C_{60} (I_h)	−0.6600	3.643	6.4×10^{-4}
C_{70} (D_{5h})	−0.6071	3.912	0.647
C_{80} (I_h)	−0.5576	4.182	8.58×10^{-4}
C_{180} (I_h)	−0.3597	6.282	0.1349
C_{240} (I_h)	−0.3136	7.253	0.198
C_{264} (T)	−0.2874	7.591	1.210
C_{320} (I_h)	−0.2586	8.372	0.388
C_{500} (I_h)	−0.1836	10.452	0.753
C_{540} (I_h)	−0.1748	10.860	0.774
C_{660} (I_h)	−0.1305	11.904	4.071
C_{720} (I_h)	−0.1308	12.522	1.144
C_{960} (I_h)	−0.0987	14.440	1.570
C_{980} (I_h)	−0.0961	14.588	1.607
C_{1248} (T)	−0.0753	16.297	8.257
C_{1500} (I_h)	−0.0631	18.014	2.415

[a] All structures possess 1.46 Å C-C bond lengths, the parameter needed for the Tersoff potential

To quantify the degree of sphericity in our structures, the distances r_i between each atom and the center of mass were computed. For a perfect spherical arrangement, r_i corresponds to the radius of a sphere. In the quasispherical structures studied, r_i fluctuates, however, all r_i lie within a small range Δr_i, calculated from the difference between the largest and shortest r_i (Table 3). It is noteworthy that r_i for icosahedral arrangements with just 12 pentagons increases as the fullerene grows. For example, C_{60} is a quasispherical icosahedron $\Delta r_i = 6.4 \times 10^{-4}$ (almost spherical), and can, therefore, be used as the first shell in an onion structure. In the quasispherical particles, the distance between layers is close to that observed experimentally (Fig. 16).

Table 2 Energy/atom of icosahedral/helical (*I*) fullerenes relative to graphite, mean radius of fullerene and difference Δr_i of largest and shortest distance to center of mass of fullerene[a]

Structure	Energy/atom (eV)	Mean radius (Å)	Δr_i (Å)
C_{140} (*I*)	−0.4148	5.539	0.090
C_{260} (*I*)	−0.2789	7.662	0.275
C_{380} (*I*)	−0.2317	9.121	0.496
C_{420} (*I*)	−0.2020	9.7330	0.640
C_{560} (*I*)	−0.1673	11.057	0.851
C_{740} (*I*)	−0.1274	12.694	1.228
C_{980} (*I*)	−0.0961	14.588	1.608

[a] All structures possess 1.46 Å C-C bond lengths, the parameter needed for the Tersoff potential

Table 3 Energy/atom of quasispherical fullerenes relative to graphite, mean radius of fullerene and difference Δr_i of largest and shortest distance to center of mass of fullerene[a]

Structure	Energy/atom (eV)	Mean radius (Å)	Δr_i (Å)
D_{2h} C_{228}-A	−0.8095	7.103	0.399
D_{2h} C_{540}-A	−0.5591	10.962	0.492
D_{2h} C_{540}-B	−0.5588	10.967	0.803
ico C_{540}-A	−0.6287	10.958	0.539
ico C_{540}-B	−0.6002	10.956	0.656
ico C_{540}-C	−0.5987	10.955	0.693
ico C_{888}-A	−0.3648	14.008	0.699
ico C_{1020}-B	−0.5952	15.067	0.159
ico C_{1500}-A	−0.5539	18.201	0.591
ico C_{1620}-B	−0.5938	18.939	0.976

[a] All structures possess 1.46 Å C-C bond lengths, the parameter needed for the Tersoff potential

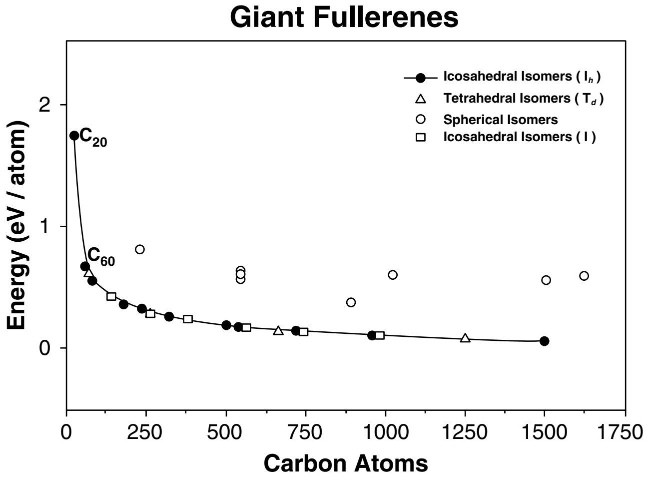

Fig. 14 Energy/atom relative to graphite versus carbon atoms within the fullerenes exhibiting different symmetries and shapes. All fullerenes with twelve pentagonal rings only lie in the same curve (e.g., I_h, I, T_d symmetries). All spherical isomers possess higher energies and, therefore, may be considered as metastable configurations. Energies were obtained using DREIDING force fields and Tersoff potential with 1.46 Å C-C distance.

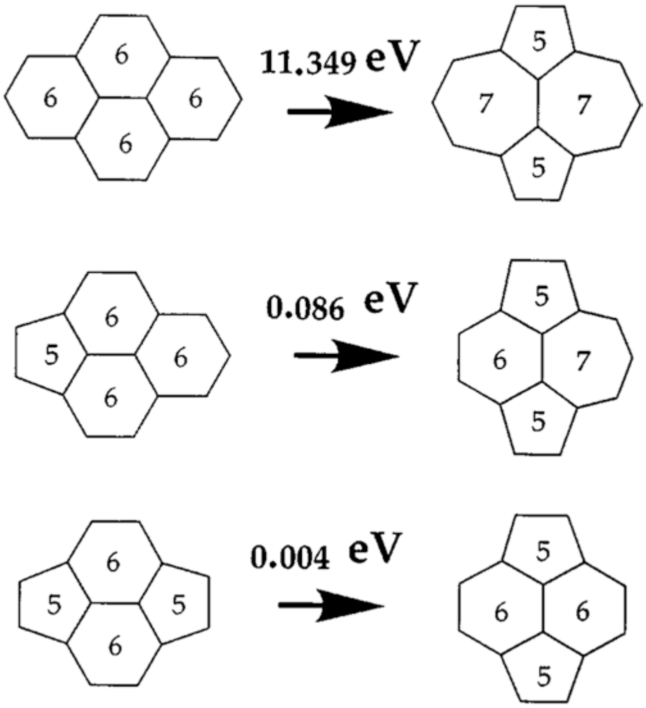

Fig. 15 Energy cost of different Stone–Wales defects for the fullerene D_{2h} C_{540}.

An important experimental observation is the presence of negative curvature [54, 55] (possibly heptagonal rings) in the exterior shells of graphitic onions (see arrow Fig. 10d) [46, 56, 57]. Therefore, it is likely that heptagonal rings are also formed within the carbon shell. Along this line, electron irradiation over diamond, using an intense flux (>10^7 electrons/nm^2 at 200 keV), yields concentric spherical graphitic shells. In the latter, a three step mechanism was followed: comprising displacements, migration, and aggregation [58]. However, further theoretical studies explaining these transformations are awaiting development.

Conclusions

It has been shown that fullerene cages, exhibiting icosahedral symmetries, can easily be generated using equilateral triangles as building templates. As a consequence, two new families of graphitic onions possessing *I* symmetry have been created: (1) C_{260}@C_{560}@C_{980}@ C_{1520}@…and (2) C_{140}@C_{380}@C_{740}@C_{1220}@…. Experimental evidence for their possible existence has also been discussed. Molecular simulation programs based upon force-field techniques and the Tersoff potential had to be considered when dealing with large atomic systems (>250 atoms). In addition, a model which explains the transformation of faceted layered structures into quasispherical graphitic onions under high electron irradiation

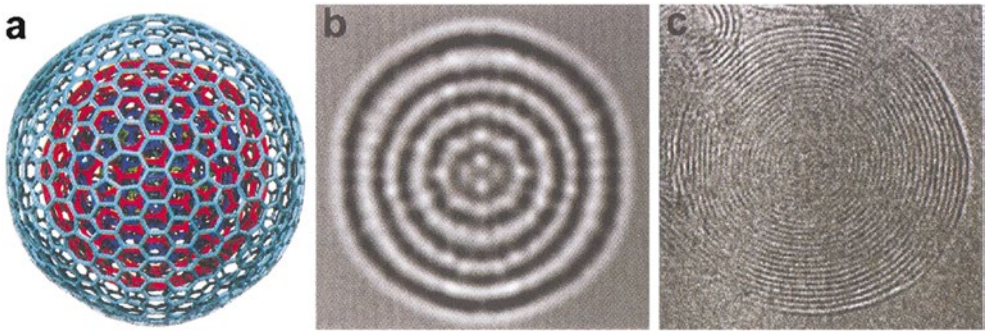

Fig. 16 Nested quasispherical fullerenes created by introducing heptagonal and pentagonal carbon rings. The onion is composed of C_{60}@C_{240}@$D_{2h}C_{540}$@C_{888}-A@C_{1500}-A. (**a**) Molecular simulation model of the minimized structure; (**b**) HRTEM simulation of (**a**); (**c**) experimental spherical carbon onion obtained under high-energy irradiation (interlayer spacing ca. 3.4 Å). Note the almost perfect sphericity of the structure.

has been proposed. This model is based upon the destruction of strained regions, which include pentagonal rings, in order to obtain fullerenes with holes that have more flexibility and which can be filled in different ways with heptagonal and pentagonal carbon rings, generating crystalline or amorphous quasispherical onions. It is believed that the aggregation process, which fills the holes, is random. The introduction and/or production of heptagonal rings via Stone–Wales-type transformations is supported by experimental (HRTEM) observations in onions with negative curvature and related systems reported in the literature. Therefore, quasispherical onions do not need necessarily to follow a predetermined sequence of sizes, such as $60n^2$, and can be considered as *metastable* carbon arrangements. We have ignored the van der Waals interaction. However, this plays an important role in stabilizing the onions, given the adequate interlayer spacing.

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