

## Systematics of High-Genus Fullerenes

Chern Chuang and Bih-Yaw Jin\*

Department of Chemistry and Center for Theoretical Sciences, National Taiwan University, Taipei, Taiwan, ROC

Received March 30, 2009

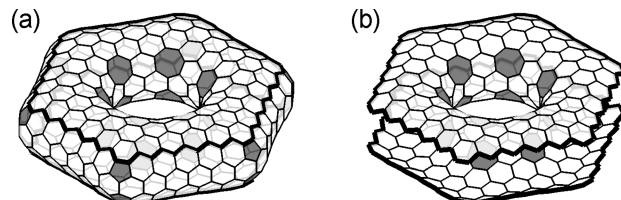
In this article, we present a systematic way to classify a family of high-genus fullerenes (HGFs) by decomposing them into two types of necklike structures, which are the negatively curved parts of parent toroidal carbon nanotubes. By replacing the faces of a uniform polyhedron with these necks, an HGF polyhedron corresponding to the vertex configuration of the polyhedron can be obtained. HGF polyhedra including tetrahedron, cube, octahedron, dodecahedron, icosahedron, and truncated icosahedron are proposed under the same construction scheme, which contains nonhexagons other than heptagons. Moreover, simple criteria for determining the stabilities of the proposed HGFs based on four geometric parameters are discussed.

### INTRODUCTION

Over the past two decades, fullerene molecules continually received vast attention from scientific society since the discovery of  $C_{60}$ <sup>1</sup> and carbon nanotubes (CNTs).<sup>2</sup> It is well-known that inserting nonhexagonal defects into a honeycomb lattice can lead to critical influence on the geometry and physical properties of the graphitic structures.<sup>3</sup> In particular, fullerene molecules with negative Gaussian curvature are of practical and theoretical interests because of their exotic geometries and topologies and potential applications as promising materials in hydrogen storage.<sup>4–8</sup>

Terrones et al. proposed a family of high-genus fullerenes (HGFs) possessing  $I_h$  and  $O_h$  symmetries having genus 11 and 5, respectively, in a series of studies.<sup>9–13</sup> These HGF molecules are composed of an inner and an outer layer of defective graphene interconnected by straight carbon nanotubes along certain high-symmetry directions. Heptagons in addition to hexagons are required to form the HGFs without dangling bonds, and they are distributed solely around the “holes” of the molecular structures, and hence these HGFs possess negative Gaussian curvature. HGFs can be said to be the finite version of schwarzites (i.e., periodic negatively curved graphene)<sup>7,14–19</sup> and are typically composed of hundreds to thousands of carbon atoms. These particular kinds of porous molecular structures maybe plausible candidates for hydrogen storage in the sense of host–guest chemistry and are of theoretical interests for its relevance to the problem of the influence of nonhexagonal defects on the physical properties of graphite.

The general construction and classification of HGFs, however intriguing, were not reported by Terrones’s group or found in the literature. Here we propose such a construction scheme to classify the high-symmetric HGFs proposed by Terrones et al., based on the decomposition of HGFs into smaller identical pieces called neck structures. This has enabled us to construct HGF Platonic polyhedra other than dodecahedron and cube, as in the case of Terrones’s group. Application of the same scheme to more general Archimedean polyhedra is also presented in this article. The stability



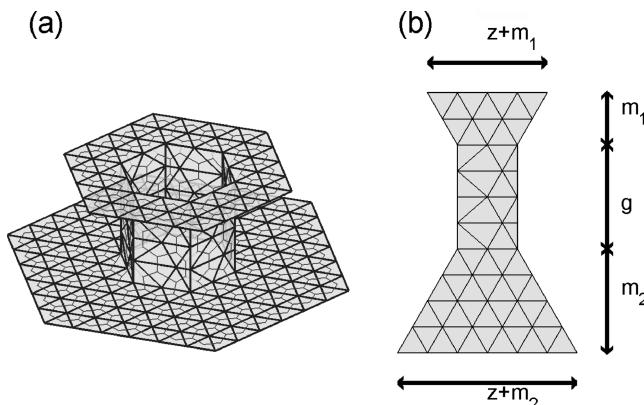
**Figure 1.** (a) Typical  $D_{6h}$ -symmetric TCNT with pentagons and heptagons. (b) H-type neck structure formed from removing the outer rim of the TCNT shown in (a).

constraints on the possible geometries of the necks in different HGF polyhedra are also discussed.

### NECK STRUCTURE

Tamura et al.<sup>20</sup> proposed a cut-and-fold approach to specify a family of polygonal TCNTs belonging to the  $D_{nh}$  point group by four parametric indices. In Figure 1a, a  $D_{6h}$ -symmetric TCNT is shown with all the nonhexagons shaded. Note that pentagons are located at the outer rim of the torus and heptagons are at the inner rim, which is consistent with the curvature distribution of a torus because adding pentagons (heptagons) into the planar honeycomb introduces positive (negative) curvature. By removing the cyclic strip of hexagons sandwiched between the thickened lines at the outer rim, we obtain a catenoid-shaped structure as shown in Figure 1b, and we shall call this kind of structure an H-type neck in this article. Since the neck structures contain hexagons and heptagons only, they possess nonpositive curvature throughout. In particular, we show a neck structure in dual space in the sense of graph theory,<sup>21</sup> where trivalent nodes (atoms) of a graph (molecule) are represented by triangles (Figure 2a). For clarity, we intentionally bend the neck in a way to make it look like two flat polygonal discs with a polygonal tube connecting their central holes. A neck structure can be specified by five parameters, with four of them describing the shape of the neck and one for the rotational symmetry number  $n$ , as shown in Figure 2b, where only one rotational unit cell is unfolded. For the remaining four parameters, we define them to be the distance between the vertices of the idealized neck shown in Figure 2a. Here, by the word “distance” we mean the number of edges of

\* Corresponding author e-mail: byjin@ntu.edu.tw.



**Figure 2.** (a) Dual space representation of a distorted H-type neck, where  $sp^2$  carbon atoms are represented by triangles. (b) Unfolded rotational unit of an H-type neck with the definitions of the specifying parameters, in this case  $(z,g,m_1,m_2) = (2,2,2,4)$ .

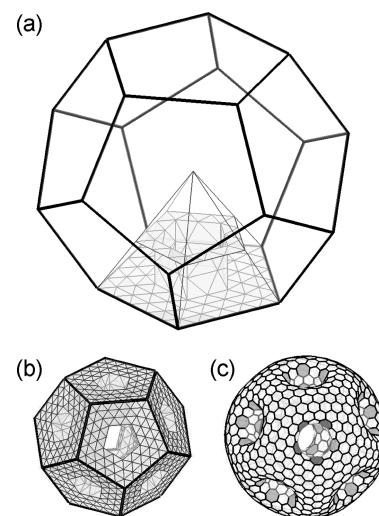
triangles between two given points in the dual space. The four parameters are defined as followed.  $z$  is the horizontal distance between heptagons, which is the smallest horizontal width of a unit cell shown in Figure 2b (two in this case).  $2g$  is the vertical distance between heptagons. Since the height of the rectangular part is four, here we have  $g = 2$ .  $m_1$  is the side length of the upper trapezoidal patch, and  $m_2$  is the side length of the lower one, where in this case they are, respectively, two and four. With the neck structure defined, we proceed to show the construction of high-genus fullerenes by assembling a number of identical necks of suitably chosen parametric indices.

#### PLATONIC POLYHEDRA

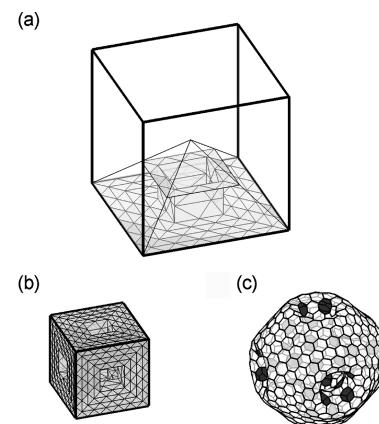
HGFs proposed by Terrones et al. can be seen as fullerenes with two layers, an inner core and an outer layer, connected by CNTs along the directions of  $n$ -fold rotation axes. They proposed HGFs belonging to two different point groups and topologies, namely  $I_h$  symmetry with genus 11 and  $O_h$  symmetry with genus 5. As we are about to see, these two kinds of HGFs can be constructed by patching  $g + 1$  necks side-by-side with each neck located along the directions of symmetry axes of the point group, where  $g$  is the genus of the HGF.

As will be shown in the following sections, a typical HGF can be formed by replacing the regular polygons of a polyhedron template by the neck structures defined previously, thus resulting in two concentric polyhedra connected by cylinders at the holes on the faces. We shall call this kind of HGFs the “HGF polyhedra”, depending on which kind of polyhedron is chosen as the template. Among the infinite possibilities of polyhedra, we will start with the simplest ones, namely, the five Platonic polyhedra.

**Dodecahedron.** First we consider the  $I_h$ -symmetric HGFs of genus 11. The  $I_h$  point group has only two-, three-, and fivefold rotational symmetry elements, so the necks in this type of HGFs can only have three- or fivefold rotational symmetries to satisfy the symmetry constraint (digons, polygons with two edges only are not discussed here). Since necks with threefold symmetry are obviously highly strained, only those necks with fivefold symmetry can be used to construct this type of HGFs. Recalling that a dodecahedron is made of 12 regular pentagons, it is intuitive to replace the pentagons with necks of  $n = 5$  (Figure 3a). Suitably altering



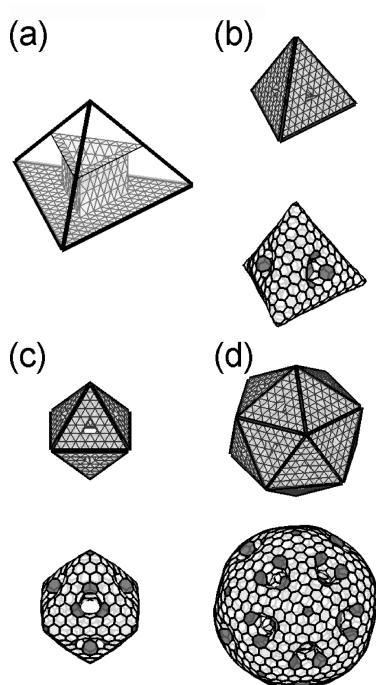
**Figure 3.** (a) H-type neck as the twelfth part of a dodecahedron. (b) Dual space representation of the HGF dodecahedron shown in (a). (c) Optimized structure of the HGF dodecahedron.



**Figure 4.** (a) H-type neck as a sixth part of a cube. (b) Dual space representation of the HGF cube shown in (a). (c) Optimized structure of the HGF cube.

the height of the necks, we come up with two concentric dodecahedra with a pentagonal hole on every face of them and 12 pentagonal prisms connecting the holes, as shown in Figure 3b. After suitable geometric optimization, one can obtain the final smooth structure of HGF dodecahedron as given in Figure 3c. It is noteworthy that, since three necks meet at each vertex of the dodecahedra and each of them contributes two carbon atoms (triangles) at its own vertices, 20 new hexagons form at the vertices of the two dodecahedra.<sup>22</sup> Similarly, by merging these necks to form the final HGF dodecahedron,  $z + m_1 - 1$  ( $z + m_2 - 1$ ) hexagons formed at each edge of the inner (outer) dodecahedron. By the definition of the neck, the dodecahedron inside has edge length  $z + m_1$ , while the outer one has length  $z + m_2$ . Because of this, the height of the necks  $g$  is not an independent parameter as long as we have first chosen a set of  $(z, m_1, m_2)$ . We shall come back to this point later when discussing the stabilities of HGFs.

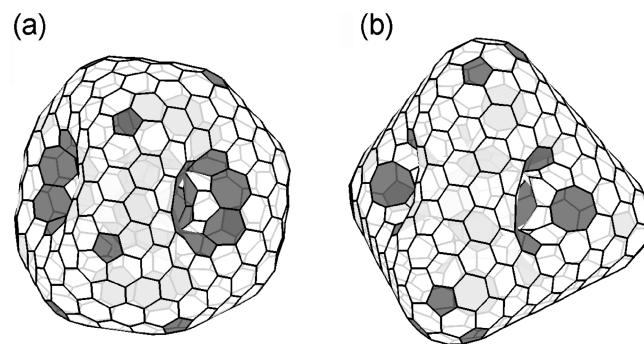
**Cube.** Similar to the dodecahedron case, we can construct a cubical HGF with genus 5 by using six necks with fourfold rotational symmetry as shown in Figure 4. Figure 4a illustrates how to replace the face in a cube by a suitably constructed neck. One can then obtain the resulting HGF cube by merging six necks together. Interestingly, though



**Figure 5.** (a)  $C_3$ -symmetric H-type neck composed of hexagons and octagons. (b) HGF truncated tetrahedron  $C_{564}$ . (c) HGF octahedron  $C_{672}$ . (d) HGF icosahedron  $C_{2100}$ .

the constructed HGF cube, shown in Figure 4b, has sharp corners and apexes like ordinary cubes, the optimized geometry shown in Figure 4c is quite smooth and flat and shaped like a rhombicuboctahedron instead of a cube. This rather contradictory result originates from the fact that we first drastically distorted the honeycomb to fit the boundary condition imposed by fourfold rotational symmetry of the neck. Here, as in the case of dodecahedron, only hexagons form at the vertices and edges of the cubes, and therefore no intrinsic curvature can be generated around these vertices.

**Tetrahedron, Octahedron, and Icosahedron.** In addition to the above-mentioned two Platonic solids, there are three more solids purely consisting of equilateral triangles, namely tetrahedron, octahedron, and icosahedron. Although the construction method described above can be applied immediately to these three cases, the H-type necks with threefold rotational symmetry contain only six heptagons which are highly strained as mentioned before. Nevertheless, it is possible to construct stable triangular necks other than the present ones. As shown in Figure 5a, a  $C_3$ -symmetric neck is formed by alternatively removing the carbon atoms between adjacent heptagons of a parent  $C_6$  H-type neck shown in Figure 2a. Now two neighbored heptagons merge into an octagon, so there are six octagons in each neck in total. Compared to original necks with heptagons, the ones with octagons bear sufficient intrinsic curvature ( $4\pi$  in number) and less strain energy for the molecular graph to complete the revolution. Note that all four geometric parameters for the specification of necks in this situation follow simply by replacing the heptagons in the original definitions mentioned above by octagons. Figure 5b–d shows three examples of HGFs composed of these kind of necks, one for each Platonic solid. Carefully examining these structures, we can see that triangles, quadrilaterals, and pentagons form at the vertices of the tetrahedron, octahedron, and icosahedron, respectively. Because in these cases the



**Figure 6.** (a) HGF truncated tetrahedron with pentagons and heptagons,  $C_{524}$ . (b) HGF truncated tetrahedron with pentagons and octagons,  $C_{532}$ .

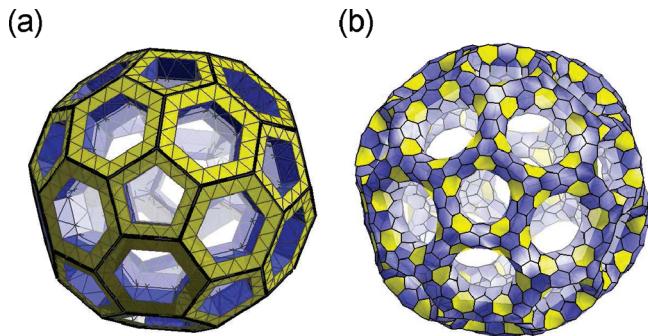
necks are not distorted to fit the rotational boundary conditions in contrast to dodecahedron and cube, the formation of these nonhexagons exactly reflects the local curvature of the polyhedra, or the *angular deficit* in the language of the polyhedron theory.

One may argue that the triangles in the HGF tetrahedron are not chemically stable, but the presence of them can be avoided easily. For instance, replacing the sharp triangular cones at the four vertices of a tetrahedron by four equilateral triangles can lead to a smooth truncated tetrahedron as shown in Figure 6a. Note that, instead of triangles, three pentagons form at each vertex and each neck is surrounded by six pentagons. It is obvious that we are free to use the H-type neck defined at the very beginning, which contains heptagons instead of octagons, again in this case, as shown in Figure 6b. This is actually the generalization of the same construction method to a family of regular polyhedra called Archimedean polyhedra, which is addressed in the next section.

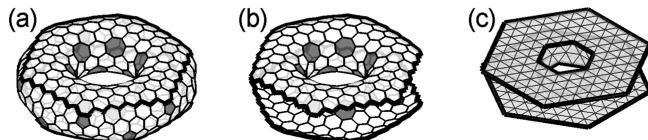
## ARCHIMEDEAN POLYHEDRA

Unlike Platonic polyhedra, faces of an Archimedean polyhedron can be a collection of regular polygons with a different number of sides. The truncated tetrahedrons previously discussed are composed of equilateral triangles and regular hexagons. We can then replace the hexagons by hexagonal necks and triangles by  $k^2$  tiled planar triangles, where  $k$  is the size of the replaced triangular cone. If we replace all the regular  $n$ -gons in an Archimedean polyhedron by  $D_{nh}$ -symmetric necks, an HGF Archimedean polyhedron can then be constructed. We do not intend to give examples here for all 13 Archimedean polyhedra, since this is not particular intriguing. Instead, we present the case of the most celebrated Archimedean polyhedron among chemists and physicists: the truncated icosahedron, which is realized in the physical world as the soccer ball or the famous  $C_{60}$  molecule (Figure 7).<sup>23</sup>

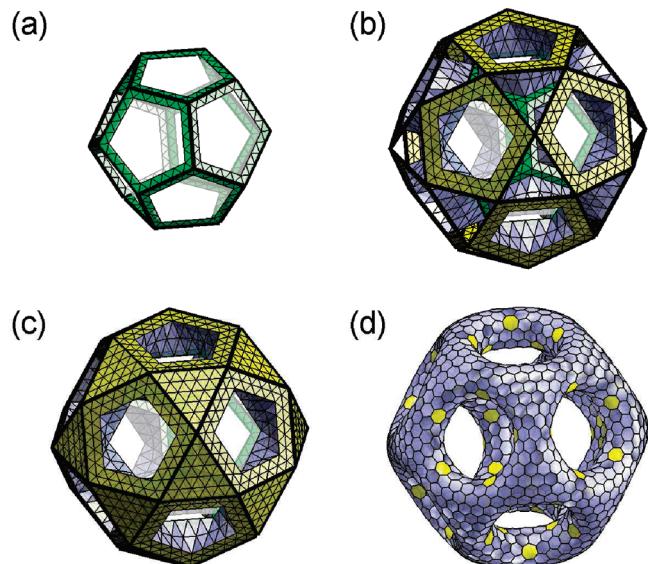
It should be noted that the regularity of faces of polyhedron is *not* a necessary condition for the HGF polyhedron to exist. In fact, all 3D networks can be HGF-ized in the sense of graph theory. Concerning the physical stability, fullerenes other than  $C_{60}$ <sup>24</sup> may be good candidates for the construction of their HGFs, since they are all composed of pentagons and hexagons<sup>23</sup> and they have a rather smooth variation of curvature over their molecular graphs.



**Figure 7.** (a) Dual space representation of an HGF truncated icosahedron  $C_{2340}$ . (b) Optimized molecular structure of the HGF truncated icosahedron.



**Figure 8.** (a)  $D_{6d}$ -symmetric TCNT with pentagons and heptagons. (b) D-type neck structure formed from removing the outer rim of the TCNT shown in (a). (c) Dual space representation of the D-type neck.



**Figure 9.** (a) Inner layer of an HGF dodecahedron (red), which consists of the inner part of 12 necks. (b) Patching the rest of the D-type necks (blue and yellow), leaving 20 triangular holes at the outer side. (c) Complete icosidodecahedron-shaped HGF is formed by patching up the remaining holes with 20 triangular graphenes. (d) Corresponding optimized HGF, a  $C_{3420}$ .

#### D-TYPE NECK

In addition to the H-type neck structure described above, there is another kind of neck possessing geometric configurations different from the H-type ones, the D-type neck. They can be obtained from the truncation of parent  $D_{nd}$ -TCNTs (Figure 8). However, it is obvious that with D-type necks alone we cannot construct an HGF without seriously distorting them, since their edges have staggered conformation. As shown in Figure 9a, we start from patching the inner part of 12 fivefold necks (shown in red) to form the inner layer of an HGF dodecahedron. Next, in part (b), we put the rest of the D-type necks (blue and yellow) onto the inner layer. Here it is obvious that there are triangular holes appearing

**Table 1.** Optimal Values for  $\Delta m$ -to- $g$  Ratio of the HGF Platonic Polyhedra

polyhedron	optimal $(\Delta m)/(g)$
tetrahedron	$2(2)^{1/2}$
octahedron	$(2)^{1/2}$
icosahedron	$3 - (5)^{1/2}$
cube	$2(3)^{1/2}$
dodecahedron	$\{2(3)^{1/2}[(10 - 2(5)^{1/2})^{1/2}\}/[3 + (5)^{1/2}]$

at the threefold rotation axes, and therefore we need to add 20 triangular graphene patches of suitable size to obtain a closed HGF with no dangling bonds, as shown in Figure 9c. Finally, the relaxed molecular structure is shown in part (d).

Now the outer layer of the resulting HGF polyhedron approximates an icosidodecahedron, while the inner layer is still shaped like a dodecahedron. Interestingly, this HGF still possesses  $I_h$  symmetry. It is possible, too, to construct an HGF with its inner side an icosidodecahedron and the outer side a dodecahedron, and naturally this applies to all the cases described above with H-type necks.

#### STABILITY

Since the number of atoms in the outer layer of an HGF must be larger than that in the inner core, the four parameters ( $z, g, m_1, m_2$ ) of the necks are not independent variables for stable HGFs. To be more specific,  $z + m_1$  and  $z + m_2$  suffice to specify the sizes of the inner and the outer polyhedron, respectively, and the difference of these two parameters,  $\Delta m = m_2 - m_1$ , in turn determines the distance between the layers or the length of the tubule part of the necks. However,  $g$  independently describes this length by specifying the distance between the heptagons at the two layers. Therefore, given the polyhedron and parameters  $z$  and  $g$ , the optimal values<sup>25</sup> for  $\Delta m$  are uniquely determined, leaving us only three independent parameters to vary. The optimal values for the  $\Delta m$ -to- $g$  ratio of the HGF Platonic polyhedra are summarized in Table 1. It should be noted that these values are calculated by assuming that atoms are fixed on the faces of the polyhedra, which are not strict physical restrictions but suggestions for chemically reasonable sets of indices. Both the HGF dodecahedra and cubes previously studied by Terrones et al. have the  $\Delta m$  close to the values given here. Interestingly, for the three HGF Platonic polyhedra composed of triangles, the tetrahedron, octahedron, and icosahedron, the ratio of  $\Delta m$  over  $g$  decreases monotonically. This is because when the number of faces increases, the inradius, the radius of the sphere inscribed in the polyhedron, also increases and its variation over the change of  $m_1$  and  $m_2$  decreases.

#### CONCLUSIONS

In summary, we developed a construction scheme of high-symmetric and high-genus fullerenes based on the decomposition of them into pieces of two types of necklike structures, which originate from removing the positively curved parts out of parent toroidal carbon nanotubes. The construction of HGF Platonic polyhedra including tetrahedron, octahedron, and icosahedron, which is first proposed in the present article, is systematically discussed. Application of the same construction rule to more complicated Archimedean

Polyhedra is also shown possible, where only the HGF truncated icosahedron of genus 31 was given as an example. Their stability was briefly discussed, and simple rules for determining the proper parameters of the neck were derived for the HGF Platonic polyhedra. Their physical properties may be interesting because of the exotic topologies and geometries and require further studies in the future.

#### ACKNOWLEDGMENT

We acknowledge the financial support of NSC, Taiwan, ROC. B.-Y.J. thanks the support from the Center of Quantum Science and Engineering, NTU, Taiwan.

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- (21) The dual of a zigzag sp<sup>2</sup> carbon chain is a straight strip of alternating triangles, so the neck structures discussed in this article have clear edges in dual space, which in turn facilitates the presentation. For more related discussions, see ref 26 and references therein.
- (22) There are special cases when  $m_1 = 0$ , where the rims of the pentagonal prisms are identified at the edges of the inner dodecahedron. In these cases, each face contributes three atoms instead of two and 10 nonagons form on the inner dodecahedron as a result.
- (23) There is one more reason for making this choice: Because truncated icosahedron has pentagonal and hexagonal faces only, while necks of these two rotational symmetries are more stable.
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CI9001124