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ORIGINAL PAPER

Classification of hypothetical doubly and triply periodic porous graphitic structures by tilings of neck-like units

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Abstract In this study, we extend the concept of constructing high-genus fullerenes with neck-like structures to the classification of a wide family of doubly periodic graphitic structures. The neck structures are obtained by peeling the outer (positively curved) part of a toroidal carbon nanotube off, meanwhile leaving the central hole unchanged. A doubly periodic structure is then characterized by the original tiling and the shape of the necks used. Through the consideration of the coloring problem of uniform tilings, a systematic method of constructing similar structures with periodicities along all three dimensions is developed. The P type Schwarzite, extensively studied in the literature, can be classified within the scheme if the shape of the necks is carefully chosen.

Keywords Fullerenes · Doubly periodic structures · Triply periodic structures

1 Introduction

Romo-Herrera et al. introduced the concept of hierarchy in the construction of 2D and 3D ordered molecular networks [1–3]. By replacing the atoms in a 2D or 3D lattice with "superatoms" and the bonds with "superbonds", complex molecular networks having similar global structures as the parent lattice can be formed. In the context of sp^2 carbon structures, the superatoms are porous carbon clusters that contain

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nonhexagons and the superbonds are simply straight carbon nanotubes (CNT) of suitable diameters. Depending on the configuration of the atoms (e.g. planar trivalent, planar tetravalent, cubic hexavalent, or tetrahedral tetravalent), the superatoms are designed to have their "holes" directing at the orientations of the bonds of the parent atoms. These holes are then loaded with CNTs of the same diameter thereby forming the corresponding "superlattice".

However, a detailed classification of possible porous graphitic structure was not illustrated by Romo-Herrera et al. And the existing literature mostly focuses on the minimal surfaces realized by graphitic films [4–11]. Here in this paper we propose such a classification scheme and put special attention on the application of 2D tiling theory [12]. We show that by replacing regular polygons in a periodic polygonal tiling with prescribed neck-like structures, doubly periodic high-genus graphitic structures with various sizes of pores can be obtained, where the neck structures are obtained by cutting the outer regions of corresponding toroidal CNTs off. Similarly, triply periodic structures deriving from colored polygonal tilings and suitably chosen neck-like structures can also be classified.

2 Neck structures

In the previous report from our group [13], two kinds of neck-like graphitic structures were proposed as the basic units for the classification of a wide family of high-genus fullerenes (HGF). These neck structures are basically the inner parts of toroidal CNTs (TCNT), where a large family of TCNTs with nonhexagonal rings were classified by the present authors [14,15]. By suitably choosing the geometric parameters of necks, e.g. the width of their polygonal rims and the length of necks themselves, HGFs with various shapes and topologies can be formed by assembling the necks in ways that regular polyhedra are formed by assembling sets of polygons. For example HGF of genus five can be constructed by placing six square necks at the faces of a cube, and HGF of genus eleven by placing twelve pentagonal necks at the faces of a dodecahedron. We deliberately called them HGF polyhedra, for the construction scheme is in general applicable to a wide family of polyhedra.

A polyhedron, in a narrow sense, can be viewed as tilings of regular polygons on a sphere. However we use the word "tiling" usually in the context of periodic planar arrangements of polygons like one paved on a pedestrian crossing. Thus it seems straightforward to generalize the concept of constructing HGF from neck structures to the planar tiling of them. In the following we present a detailed discussion of this generalization. But before entering the discussion, we would like to mention that planar tilings are all "planar", i.e. they possess zero Gaussian curvature. It is this reason that for the following proposed structures to be stable, it is vital that the two ends of the necks therein are of the same side lengths. Here we show two examples of such neck with D_{6h} and D_{3h} point group symmetries, respectively, in Fig. 1. The dual lattice of the sp^2 carbon is also drawn in thin line (blue), so it is easier to see that the rims of the necks are indeed polygonal. The D_{3h} neck shown in part (b) is obtained by alternating removing the sides of the neck shown in part (a), and eight-member, instead of seven-member, rings form at the central hole. Note that it takes three parameters

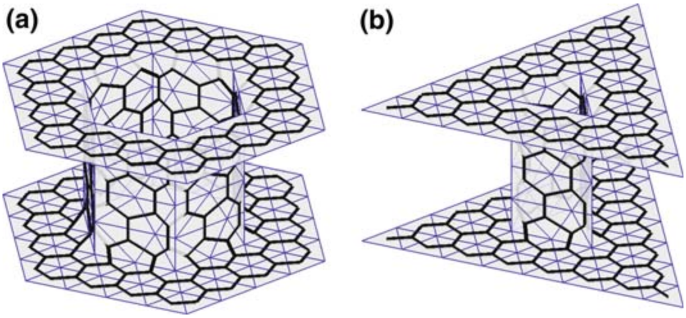

Fig. 1 The neck structures. The carbon sp^2 σ bonding is drawn in thick line and the dual lattice of the molecular graph is drawn in thin line. **a** A D_{6h}-symmetric neck. Its rims are both regular hexagonal, and it has twelve heptagons around its central hole. **b** D_{3h}-symmetric neck obtained by alternating removing three sides of the neck shown in (**a**). The twelve heptagons now pair up and "fuse" into six octagons. Both of the necks shown are denoted as $(z, m, g) = (2, 2, 2)$

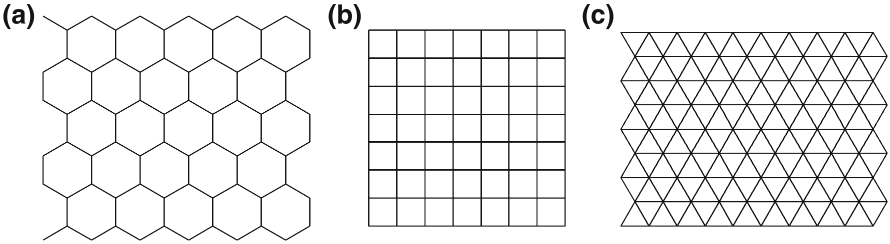

Fig. 2 The three Platonic tilings. **a** Honeycomb tiling (6^3). **b** Square tiling (4^4). **c** Equilateral triangular tiling (3^6)

to specify a neck given its rotational symmetry: the side length of the rims $(z + m)$, the size of the central hole (z), and the height of the neck (g). Readers of interest may refer to the Fig. 2 of the reference [13].

3 Planar tilings of necks

3.1 Platonic tilings

The simplest uniform tilings of regular polygons are the three Platonic tilings. By uniform we mean that the graph of the tiling is vertex-transitive, i.e. its vertices are all shared by a particular set of polygons in a particular order. These tilings can be conveniently symbolized as p^q, representing that a vertex is shared by q regular p-gons. There are three kinds of Platonic tilings, which are the honeycomb tiling (6^3), the square tiling (4^4), and the equilateral triangular tiling (3^6), as shown in Fig. 2.

By replacing the hexagons in the honeycomb tiling with D_{6h} necks, we obtain a doubly periodic graphitic structure with a hole at the center of each hexagon, as shown in Fig. 3a. The corners of three necks, each contributes two carbon atoms, meet at a vertex and a hexagon forms. Whereas at the edges of the honeycomb the rims of two

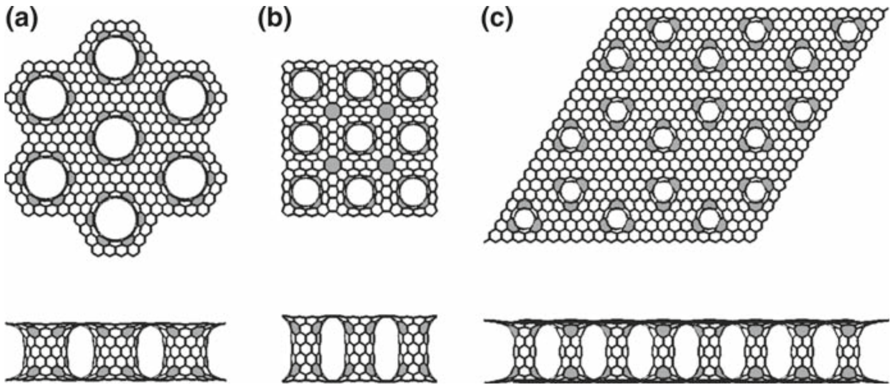

Fig. 3 The doubly periodic graphitic structures obtained from the Platonic tiling the necks. The *upper row* are the top views and the *lower row* are the side views. **a** Honeycomb tiling of D_{6h} necks. **b** Square tiling of D_{4h} necks. **c** Equilateral triangular tiling of D_{3h} necks. All necks used in these examples are indexed by $(z, m, g) = (2, 2, 2)$

necks join to form a line of hexagons. The resulting structure is like connecting a two-layered graphene with straight CNTs at the vertices of an underlying triangular lattice. In the part (b) and (c) of the figure, the square tiling and the equilateral triangular tiling of corresponding necks are shown. For the square lattice, we simply use only four of the six unit cells in a D_{6h} neck to complete the revolution. Since each of the eight corners is composed of two atoms as well, the loci of the vertices of the lattice are now octagons (shaded). And the heptagons distribute around the central hole of each neck. As for the triangular tiling, which is the *dual* of the honeycomb tiling, the resulting tiling of necks can be seen as connecting a two-layered graphene with CNTs at the vertices of an underlying honeycomb lattice.

3.2 Archimedean tilings

In analogy to the Platonic and Archimedean solids, if we allow regular polygons of different numbers of sides to be tiled at the same time, then Archimedean tilings can be obtained. There are total eleven kinds of uniform Archimedean tilings [12], and here we only report three examples for brevity. Whereas other Archimedean tilings of necks can be constructed in similar fashion. In Fig. 4, we show the (3, 6, 3, 6), $(4, 8^2)$, and $(3^2, 4, 3, 4)$ Archimedean tilings of neck structures. For the (3, 6, 3, 6) tiling, two triangular necks each contributes one carbon atom and two hexagonal necks each contributes two. These sum up to form a hexagonal ring at every vertex of the tiling. For the $(4, 8^2)$ case the square and the two octagonal necks all contribute two atoms to a vertex, thus hexagonal rings form at the vertices, too. Contrary to the above two tilings, heptagons form at the vertices of the $(3^2, 4, 3, 4)$ tiling. It is interesting to note that in the $(4, 8^2)$ tiling shown in Fig. 4b there are two kinds of edges, one formed between two octagons and one formed between a square and an octagon. One can see that the σ bondings formed along pairs of octagons are greatly elongated, indicating that the metric in fourfold necks is different from one in eightfold necks. The same

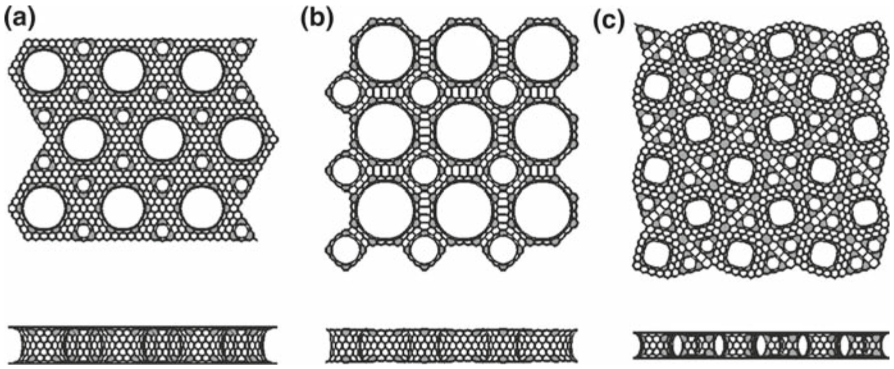

Fig. 4 Archimedean tilings of neck structures, with the same viewing convention as used in Fig. 3. **a** (3, 6, 3, 6) tiling. **b** $(4, 8^2)$ tiling. **c** $(3^2, 4, 3, 4)$ tiling

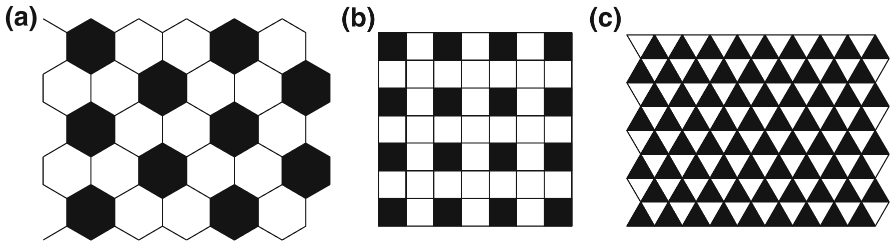

Fig. 5 Three possible coloring schemes of the Platonic tilings. **a** $(6^3)112$. **b** $(4^4)1112$. **c** $(3^6)121212$. The numbers read afterward indicate the colors drawn on the polygons, 1 for *white* and 2 for *black*

situation can also be found in the $(3^2, 4, 3, 4)$ tiling. This is in general true for all Archimedean tilings except for ones containing threefold and sixfold necks only, e.g. the (3, 6, 3, 6) tiling illustrated here.

4 Coloring of the regular tilings: triply periodic structures

With the knowledge of constructing doubly periodic graphitic structures from planar tilings of necks, one can make a step further to the classification of extended graphitic structures with periodicities along all three dimensions. Let us consider the coloring of regular uniform tilings discussed above. By coloring we mean that the polygonal tiles are painted with colors, and polygons with different colors are considered to be different even if they are of the same number of sides. In Fig. 5 we show three examples of uniform colorings from the three Platonic tilings each. Following the notation of Grünbaum and Shephard, the three examples are denoted as $(6^3)112$, $(4^4)1112$, and $(3^6)121212$, respectively, with the numbers following the brackets indicating the colors used in the tilings. Specifically, 1 stands for white and 2 stands for black tiles in these cases.

As before, the necks with appropriate rotational symmetries are arranged in the ways shown in the colorings. Additionally, this time we intently shift the necks which

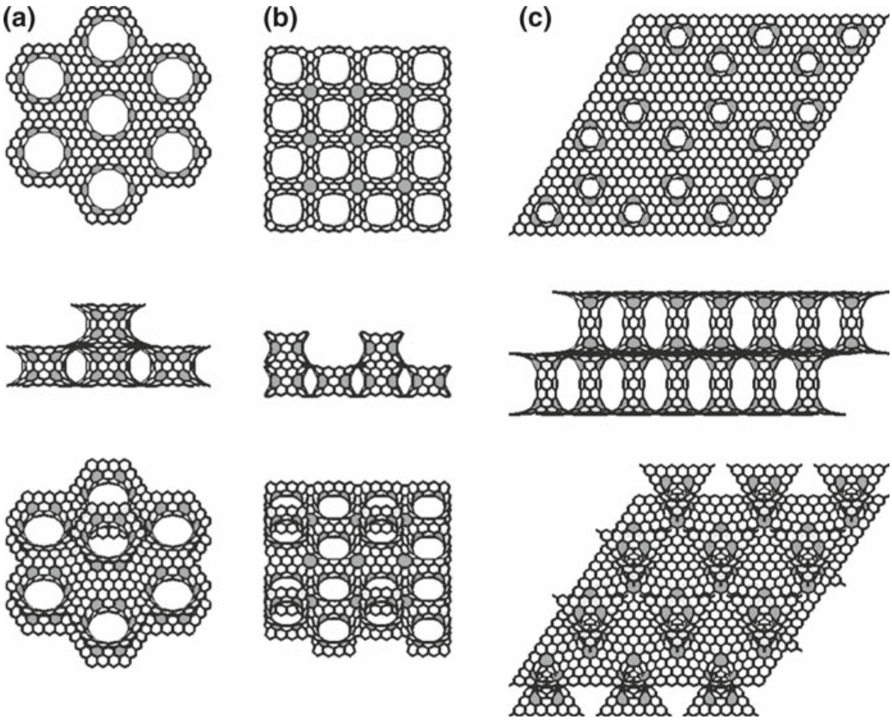

Fig. 6 Triply periodic graphitic structures corresponding to the three colorings illustrated in Fig. 5. **a** $(6^3)112$ coloring using necks with $(z, m, g) = (2, 2, 1)$. **b** $(4^4)1112$ coloring with $(2, 2, 0)$ necks. **c** $(3^6)121212$ with $(2, 2, 2)$ necks

correspond to black tiles up to certain extent, so the lower rims of the shifted necks now match up with the upper rims of the unshifted necks. It follows that the third dimension of periodicity can be achieved by repeating the colorings along z-axis (out of the plane of paper) so that adjacent layers are connected by the upper rims of the lower layer and the lower rims of the upper layer. The thus obtained triply periodic graphitic structures for the three colorings are illustrated in Fig. 6. It is not surprising that if we view along the z-axis (the first row of the figure), these triply periodic structures look almost the same as their planar parents shown in Fig. 3, apart from that the rims of the necks are moderately compressed along the x and y directions. On the other hand, the translational vector along z-axis is proportional to the length of the necks used.

We would like to mention that the coloring of the uniform tilings is not restricted to only two colors, for example it is well known that hexagons in the honeycomb lattice can be classified into three Clar families [16], denoted as $(6^3)123$. However the above discussed construction method for triply periodic graphitic structures applies to uniform colorings with only two colors.

Readers may notice that the structures deriving from the $(3^6)121212$ coloring of triangular necks are isomorphic to the Schwarz's H surface. It is noteworthy that the well studied P type Schwarzite actually belongs to a special case of the structures

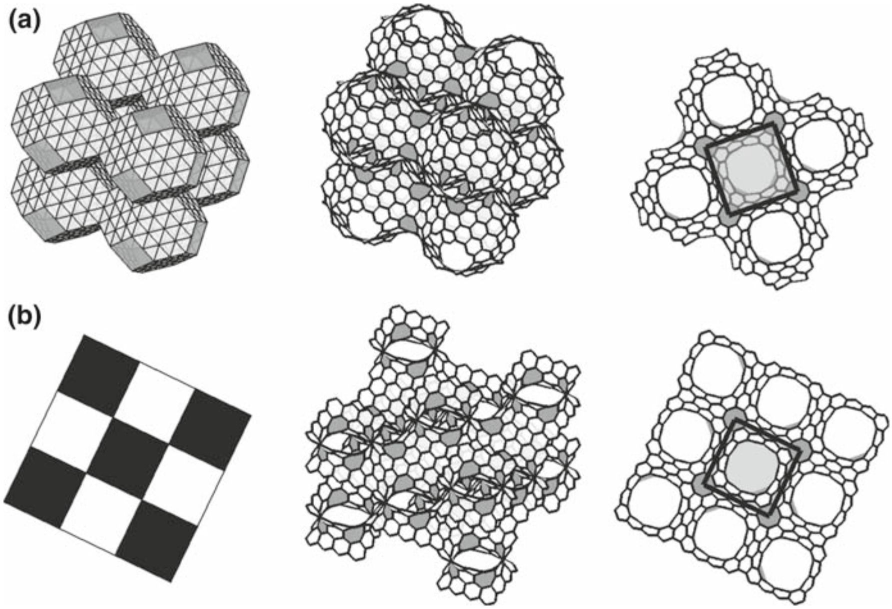

Fig. 7 Two kinds of representations of P type Schwarzite. **a** The "connected truncated octahedra" representation. The dual of the structure, where sp^2 carbon atoms are represented by *triangles*, is shown on the *left*. And the top view of the structure is shown on the *right*, where the framed portion corresponds to a square neck. **b** The $4^4$1212 coloring of *square necks*. And the top view of the structure is also shown on the *right*, where the central one neck is framed for clarity

classified in this scheme. Consider the (4^4)1212 coloring (shown in the leftmost column of Fig. 7b), if fourfold necks with $z = m$ and $g = 0$ are chosen then the resulting periodic structure is identical to the P type Schwarzite. The P type Schwarzite is usually illustrated as connecting truncated octahedra along their fourfold rotational axes in all three dimensions, as shown in Fig. 7a. Nevertheless we can identify a fourfold neck at an angle of 45° to the cubic cell, shown in the rightmost column of the figure. Thus it can be said that the decomposition of P type Schwarzite into square necks is a choice of unit cell in addition to the decomposition into connected truncated octahedra.

5 Conclusion

In this paper, we apply the concept of building high-genus fullerenes with neck-like structures [13] to the classification of a wide family of doubly periodic porous graphitic structures. Specifically, this is done by replacing the regular polygons in a planar tiling with their corresponding neck structures, given a set of indices specifying the shape of the necks. Generalization to triply periodic structures can be obtained by considering the coloring problem of the regular uniform tilings. Necks corresponding to different colors are assigned with different altitudes, and the magnitude of the translational vector along z-axis is determined by the height of the necks used. The P type Schwarzite extensively studied in the literature also belongs to a special case of the graphitic structures given by this scheme. The extended porous structures studied in this paper may be promising hydrogen-storing material, however further works characterizing the physical and chemical properties of these kind of graphitic structures are needed.

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