



# Can an element form a two-dimensional nanosheet of type 15 pentagons?

Lei Liu, Immanuella Kankam, Houlong L. Zhuang\*

School for Engineering of Matter Transport and Energy, Arizona State University, Tempe, AZ 85287, USA

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## ABSTRACT

Type 15 pentagon was recently discovered three decades since the 14th type of pentagon was reported in 1985. In contrast to such a long time span, the list of two-dimensional (2D) materials keeps growing longer on a monthly (if not daily) basis according to emerging experimental and theoretical reports. Combining these two seemingly irrelevant topics, we apply density functional theory (DFT) calculations to examine the possibility of forming a 2D nanosheet with the vertices of type 15 pentagons occupied by boron, carbon, silicon, phosphorous, sulfur, gallium, germanium, or tin atoms. We find that none of the optimized eight nanosheets remain the same initial structure filled with type 15 pentagons after the geometry optimizations by a DFT calculator. Instead, we obtain different rearranged structures for each nanosheet, most of which have not yet been reported before. For example, gallium atoms form a 2D nanosheet structure with a triangular pattern similar to single-layer boron sheet called borophene. These new 2D materials exhibit formation energies comparable to that of single-layer silicene, implying the feasibility of being grown on a substrate. The electronic structure shows that all the eight nanosheets are metallic (or semi-metallic for the carbon nanosheet), compensating for the dearth of metallic systems in existing 2D materials that are mostly semiconducting. Our work shows that linking a pentagonal geometry with DFT calculations yields both educational and scientific merits.

## 1. Introduction

The essential point in the definition of a crystal is its periodicity denoting the existence of translational vectors by which the atoms in the crystal repeat themselves. In addition to translation vectors, a crystal often exhibits other symmetry elements such as rotation and inversion axes [1]. However, translation cannot necessarily coexist with any of these other symmetry elements. For example, it is well known and also straightforward to prove that a crystal cannot possess fivefold rotation axes [2].

Similarly, tiling a plane with regular (*i.e.*, equiangular and equilateral) pentagons without rendering a gap in-between the pentagons is impossible. But tiling a plane with irregular, convex pentagons is an exception. In fact, how many types of irregular, convex pentagons that can tile a plane has been a long-standing geometry problem puzzling many mathematicians for a century—the first such convex pentagon was found in 1918 and the latest one in 2015 by Mann, McCloud, and Von Derau [3]. 15 types of convex pentagons have been discovered so far to be capable of tiling a gapless plane. More recently, Rao claims to have proved that there exist only 15 types of convex pentagons for tiling a plane [4].

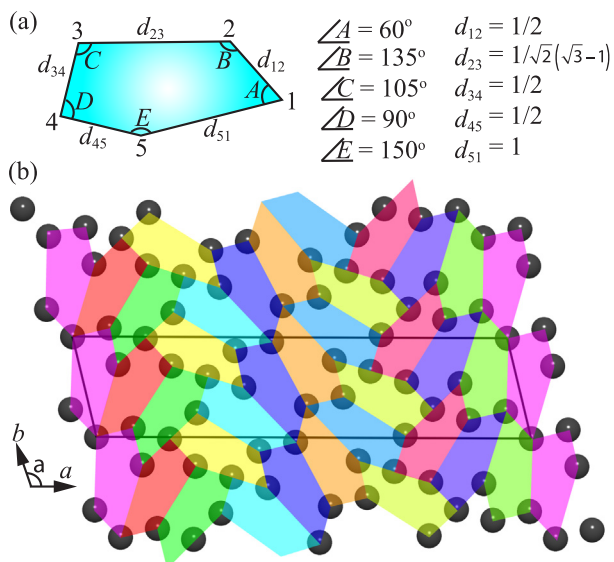
Analogizing a planar structure with that of a two-dimensional (2D)

material (*e.g.*, graphene [5]) and the vertices of convex pentagons with atomic coordinates provides natural ingredients for density functional theory (DFT) calculations. As a result of this analogy, an intriguing question to ask is: can an element form a 2D nanosheet of one of the existing types of convex pentagons?

DFT is established by Hohenberg and Kohn who prove that the external potential that electrons experience is completely dependent on the ground state electron density [6]. Instead of using the many-body wave function, DFT uses the electron density as a key variable to solve the Schrödinger equation:  $H\Psi = E\Psi$ . Kohn and Sham recast the still many-body problem into an independent-particle problem [7,8]. The Hamiltonian  $H$  is a square matrix whose eigenvectors and eigenvalues need to be solved. Furthermore, many software use a linear combination of plane waves for approximating the wave function  $\Psi$  [9–12]. The obtained energy  $E$  can be used to derive a variety of properties such as the elastic modulus measuring the rigidity of a material [13]. The practical simplicity of DFT calculations lies at the dependence of  $H$  and  $\Psi$  on the initial lattice parameters and atomic coordinates of a simulation cell for a material. DFT calculations have been widely applied to predict new structures owing to this simplicity [14]. Benefitted from DFT calculations, numerous 2D materials have been predicted to associate with unexpected crystal structures and exotic properties

\* Corresponding author.

E-mail address: [zhuanghl@asu.edu](mailto:zhuanghl@asu.edu) (H.L. Zhuang).



**Fig. 1.** (a) Sketch of type 15 pentagon and its angles and side lengths. (b) 2D crystal structure with the atoms represented by spheres located at the vertices of type 15 pentagons. A unit cell of the 2D crystal is enclosed by solid lines.

[15–22].

To answer the previous question, we use the most recently discovered type 15 pentagon as an example to demonstrate the robustness of DFT calculations in predicting 2D crystal structures and obtaining their electronic structure. We use a unit cell by placing boron, carbon, silicon, phosphorous, sulfur, gallium, germanium, or tin atoms at the vertices of type 15 pentagons. The reason for choosing these elements is because a single element can form different allotropes of 2D materials often named with a suffix of “-ene” like borophene [23], silicene [24], and germanene [25], which have been reported in theoretical or experimental studies. We then apply DFT calculations to the unit cell and fully relax the geometry to examine the resulting structure. Based on the optimized single-layer nanosheets, we compute the electronic structure to determine whether they are metallic or semiconducting.

## 2. Methods

Fig. 1(a) shows a type 15 pentagon along with its angles and side lengths. Being a convex pentagon, all of the angles lie between 0 and  $180^\circ$ . Three of the five side lengths ( $d_{12}$ ,  $d_{34}$ , and  $d_{45}$ ) are the same and they are also shorter than the other two side lengths ( $d_{23}$  and  $d_{51}$ ). Fig. 1(b) illustrates a unit cell of a 2D material formed from one of the eight elements. Each unit cell contains 20 atoms. The two lattice vectors are: [26]  $a = ((10 + 7\sqrt{3})/4, (3 + 2\sqrt{3})/4)$  and  $b = (-(1 + \sqrt{3})/4, (3 + \sqrt{3})/4)$ . The angle between vectors  $a$  and  $b$  is thus  $\alpha = 103.7^\circ$ . To avoid overlapping atoms in the input configuration, we scale the lattice vectors by factors that range from 2.5 to 4.0 depending on the different sizes of atoms.

We use the Vienna *Ab-initio* Simulation Package (VASP) to perform the DFT calculations [9]. The electron-electron exchange-correlation interaction is a part of the Hamiltonian treated by the Perdew-Burke-Ernzerhof (PBE) functional [27]. The potential data sets describing the electron-nucleus interactions are based on the projector augmented wave method [28,29]. The periodic boundary conditions are applied in all three directions of a surface slab of 2D nanosheet. A vacuum spacing of the surface slab is set to 18.0 Å that is thick enough to isolate image interactions. For all the calculations, the plane waves with the kinetic cutoff energy below 500 eV are involved to approximate the total electronic wave function. For the integration in the reciprocal space, a  $4 \times 8 \times 1$   $\Gamma$ -centered  $k$ -point grid generated with the Monkhorst-Pack method is used. We employ the conjugate-gradient method [30] to

optimize the 2D structures [31]. The in-plane lattice constants and atomic positions are fully updated during the optimization process until the criterion of force convergence that is smaller than 0.01 eV/Å is met.

## 3. Results and discussion

Fig. 2(a)–(h) displays the optimized structures of the eight nanosheets resulting from the DFT calculations. Table 1 lists the lattice parameters and the shortest bond length. We observe that these optimized structures are vastly different from the input ones. In particular, B atoms occupy the vertices of nearly regular pentagons separated by triangles; C atoms form hexagonal carbon rings and restore the structure of graphene with a typical C–C bond length of 1.42 Å; Si atoms locate at the vertices of pentagon and rectangles; Similar to bulk Si in the diamond structure, several Si atoms in the unit cell favor a fourfold coordination resembling the  $sp^3$  hybridization; P atoms appear to generate a chain structure, each of which consists of a combination of different shapes of polygons; S atoms also prefers to form chain structures while the types of polygons are not as visible; Ga atoms weave a web of triangles that are also found in an allotrope of borophene denoted as  $B_\Delta$ ; [32] Ge atoms create a similar pattern of triangles. However, embedded in the pattern are squares to connect the triangles; Sn atoms adopt a mixture of polygons (parallelogram, pentagons, and hexagons); The resulting diverse structures is due to the fact that the atoms resist the same geometry constraint imposed on them in a different manner, as these elements have their own preferred chemical bonding environments [33]. Although type 15 pentagons are completely destroyed in the nanosheets, the unit cell remains periodic. The DFT simulator (*i.e.*, VASP) therefore behaves like a skilled tile installer to assemble a gapless plane using a blend of various polygons.

To assess the energy cost of obtaining each optimized structure of the eight nanosheets, we calculate the formation energy  $E_f$  defined as the energy difference between a nanosheet and its most stable bulk counterpart [34], whose structure is listed in Ref. [35]. Table 1 shows that the calculated  $E_f$  ranges from 0.09 to 0.91 eV/atom. The smallest  $E_f$  expectedly belongs to the carbon nanosheet (graphene) that has been mechanically exfoliated from graphite [5]. Aside from graphene, the  $E_f$  of the other nanosheets are generally too high to lead to a suspended nanosheet. However, most of the  $E_f$  are comparable to that of silicene (0.76 eV/atom) [36], which has been grown on a Ag substrate. Therefore, a suitable substrate may stabilize these 2D nanosheets [37], among which Ga nanosheet appears to be a promising 2D system not only because of its moderate  $E_f$  but also due to the structural similarity with the  $B_\Delta$  structure that has already been synthesized on the Ag(111) surface [38].

Fig. 2(i)–(p) shows the density of states (DOS) of the optimized eight nanosheets. As can be seen, all the DOS at the Fermi level of the nanosheets except graphene are non-zero, confirming that these nanosheets are metallic. The DOS of graphene at the Fermi level is zero because of the Dirac cone associated with semi-metallic behavior. The DOS of the P, S, and Sn nanosheets exhibit a typical feature of 1D system—abundant peaks arising from the Van Hove singularities. This feature in the DOS of the P, S, and Sn nanosheets is consistent with their chain structures as shown in Fig. 2(d), (e) and (h). A number of 2D materials are attractive because they are semiconductors, valuable for optical, electrical, or photocatalytic applications [37,39]. Metallic 2D materials are much less, but exhibit similarly promising applications in such as nanoplasmonics [32] and superconductors [40]. As graphene has found a plethora of applications, we expect the other seven predicted metallic nanosheets to be useful additions to the large family of 2D materials.

## 4. Conclusions

We explored the possibility of forming a 2D crystalline material with atoms located at the vertices of type 15 pentagons by performing

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