Predicting Two-Dimensional Boron—Carbon Compounds by the Global Optimization Method

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Supporting Information

ABSTRACT: We adopt a global optimization method to predict two-dimensional (2D) nanostructures through the particle-swarm optimization (PSO) algorithm. By performing PSO simulations, we predict new stable structures of 2D boron—carbon (B—C) compounds for a wide range of boron concentrations. Our calculations show that: (1) All 2D B—C compounds are metallic except for BC3 which is a magic case where the isolation of carbon six-membered ring by boron atoms results in a semi-conducting behavior. (2) For C-rich B—C compounds, the most stable 2D structures can be viewed as boron doped graphene structures, where boron atoms typically form 1D zigzag chains except for BC3 in which boron atoms are uniformly distributed. (3) The most stable 2D structure of BC has alternative carbon and boron ribbons with strong in-between B—C bonds, which possesses a high thermal stability above 2000 K. (4) For B-rich 2D B—C compounds, there is a novel planar-tetracoordinate carbon motif with an approximate C2v symmetry.

INTRODUCTION

Graphene, a two-dimensional (2D) single layer of carbon atoms arranged in a honeycomb lattice, has been the focus of recent research efforts,1–4 due to its unique zero-gap electronic structure and the massless Dirac Fermion behavior. The unusual electronic and structural properties make graphene a promising material for the next generation of faster and smaller electronic devices. The need for miniaturization of electronic devices calls for continued development of new materials with reduced dimensionality. Besides graphene, some other 2D materials were fabricated as well. Recently, Coleman et al.5 reported that a straightforward liquid exfoliation technique can efficiently produce monolayer 2D nanosheets from a variety of inorganic layered materials such as BN, MoS2, and WS2. There is a growing interest in exploring the structures and properties of boron nanostructures because boron possesses a richness of chemistry. This element has been extensively investigated both theoretically,6,7 and experimentally8 in various forms (e.g., bulk boron, nanotubes,9 clusters, and quasi-planar sheets). The general perception of a monolayer boron sheet is that it occurs as a buckled sheet with a triangular lattice.10 Recently, monolayers of boron comprising triangular and hexagonal motifs, known as “α-sheets”,11,12 have been predicted to be energetically more stable than the flat triangular sheets, which have not been experimentally synthesized. This leads to the postulation of the existence of the B80 fullerene.13 The stability and electronic properties of boron nanoribbons were also explored.14 These novel nanostructures with a number of interesting properties offer numerous potential applications in tribology, high-energy-density batteries, sensors, photoconversion of solar energy, and nanoelectronics. In particular, 2D materials are of special importance because they are usually parent structures of one-dimensional nanotubes and zero-dimensional nanocages.

Some 2D boron—carbon (B—C) alloy structures were studied both experimentally and theoretically. A novel material with the composition BC3 with a graphite-like structure was confirmed by electron diffraction data.15 This BC3 honeycomb sheet with excellent crystalline quality was grown uniformly over a macroscopic surface area of NbB2 (0001).16 Theoretically, a first-principles study17 showed that a monolayer of BC3 is an indirect-gap semiconductor. By varying the ratio between benzene and BCl3, BxC1−x compounds with x = 0.17 have been synthesized at 900 °C by Way et al.18 who suggested the existence of an ordered BC3 compound and proposed a possible structure of BC3. The speculated monolayer BC3 was later predicted to be metallic by density functional calculations.19 On the boron-rich side, Wu et al. recently proposed a 2D B2C sheet in which the boron and carbon atoms are packed into a mosaic of hexagons and rhombuses.20 In this 2D B2C graphene, each carbon atom is bonded with four boron atoms, forming a planar-tetracoordinate carbon (ptC) moiety.20 Despite the recent discovery of these novel 2D B—C nanostructures, a complete understanding of the structures and properties of 2D B—C compounds with a wide...
range of boron concentrations is still elusive. This stems from the fact that the 2D boron sheet differs from graphene, making the prediction of the structures of 2D B–C compounds extremely difficult.

In this work, we propose a general global optimization method to predict 2D nanostructures based on the particle swarm optimization (PSO) technique as implemented in the Crystal structure AnaLysis by Particle Swarm Optimization (CALYPSO) code. Our extensive tests show that the new method is very efficient in finding the stable 2D nanostructures. Utilizing our method, we study 2D B2Cn compounds with several B concentrations. Our simulations reveal new 2D ground-state structures of BC4, BC6, BC8, B2C, B3C, and B2C. We show that 2D C-rich B–C compounds adopt the graphene-like honeycomb structure and therefore can be treated as B-doped graphene. The B-rich compounds have less similarity with that of boron α-sheet, although they both consist of different arrangements of hexagons and triangles. It is also interesting to see that a common feature of B-rich B–C compounds is that they all have similar C2v-like ptC motifs.

**METHODS**

**PSO Algorithm for 2D System.** Previously, several approaches have been proposed to predict the ground-state structures of crystals and clusters. Recently, we developed a method for 3D crystal structure prediction through the PSO algorithm within the evolutionary scheme. PSO is designed to solve problems related to multidimensional optimization, which is inspired by the social behavior of birds flocking or fish schooling. The key idea is to have a swarm of interacting particles, each representing a candidate solution to a given optimization problem. Thus, particles are embedded in the search space and explore the solution space by flying around. Moreover, the particles are also attracted to high fit regions located by other particles. Recently, we have applied the PSO algorithm into the field of crystal structure prediction for materials with the only known information of chemical compositions at given external conditions (e.g., pressure) as implemented in the CALYPSO code. In this application, each particle is treated as a specific PSO Algorithm for 2D System. Previously, several approaches have been proposed to predict the ground-state structures of crystals and clusters. Recently, we developed a method for 3D crystal structure prediction through the PSO algorithm within the evolutionary scheme. PSO is designed to solve problems related to multidimensional optimization, which is inspired by the social behavior of birds flocking or fish schooling. The key idea is to have a swarm of interacting particles, each representing a candidate solution to a given optimization problem. Thus, particles are embedded in the search space and explore the solution space by flying around. Moreover, the particles are also attracted to high fit regions located by other particles. Recently, we have applied the PSO algorithm into the field of crystal structure prediction for materials with the only known information of chemical compositions at given external conditions (e.g., pressure) as implemented in the CALYPSO code. In this application, each particle is treated as a specific structure in a high dimensional space which adjusts its own flying according to its flying experience as well as the flying experience of other structures. The system is initialized with a population of random structural solutions and searches for optima by updating generations. We have demonstrated that the PSO algorithm on crystal structure prediction is highly efficient with a faster and cheaper way compared with other methods. The CALYPSO method has been successful in predicting structures for various high-pressure systems including the semi-conducting phase of lithium, the electrode structure of Mg, and the super-conducting phases of Bi2Te3.

Our earlier PSO algorithm is specially designed for 3D crystal structure prediction. Here, we have, for the first time, applied the PSO algorithm to 2D systems. In this application, we only consider single atomic layer 2D systems. It should be noted that a straightforward extension of our method can be applied to 2D systems with finite thickness, e.g., MoS2. In our method, we first generate a set of random 2D structures with a randomly chosen symmetry. Different from the 3D crystal case where the 230 space groups are used, we randomly select a 2D symmetry group among the 17 plane space groups. Once a particular plane space group is selected, the lateral lattice parameters are then confined within the chosen symmetry. The atomic coordinates are randomly generated with the imposed symmetry constraint. The generation of random structures ensures unbiased sampling of the energy landscape. The explicit application of symmetric constraints leads to significantly reduced search space and optimization variables, and thus fastens global structural convergence. Subsequently, local optimization including the atomic coordinates and lateral lattice parameters is performed for each of the initial structures. In the next generation, a certain number of new structures (the best 60% of the population size) are generated by PSO. The other structures are generated randomly, which is critical to increase the structure diversity. Within the PSO scheme, a structure in the searching phase space is regarded as a particle. A set of particles (structures) is called a population or a generation. The positions of the particle are updated according to the following equation:

\[
x_{i,j}^{t+1} = x_{i,j}^t + v_{i,j}^{t+1}
\]

where \( x \) and \( v \) are the position and velocity, respectively (\( i \) is the atom index, \( j \) refers to the dimension of structure with \( j \in \{1, 2, \ldots, \} \), and \( t \) is the generation index). The new velocity of each particle is calculated on the basis of its previous location \( x_{i,j}^t \), before optimization, previous velocity \( v_{i,j}^t \), current location pbest\(_{i,j}^t \), with an achieved best fitness (i.e., lowest energy), and the population global location gbest\(_{i,j}^t \) with the best fitness value for the entire population:

\[
v_{i,j}^{t+1} = \omega v_{i,j}^t + c_1 r_1 (pbest_{i,j}^t - x_{i,j}^t) + c_2 r_2 (gbest_{i,j}^t - x_{i,j}^t)
\]

where \( \omega \) (in the range of 0.9–0.4) denotes the inertia weight, \( c_1 = 2 \) and \( c_2 = 2, r_1 \) and \( r_2 \) are two separately generated random numbers and uniformly distributed in the range \([0, 1]\). The initial velocity is generated randomly. All the structures produced by the PSO operation are then relaxed to the local minimum. Usually, 10s of iterations are simulated to make sure that the lowest-energy structures are found. By symmetry, the local optimization and the PSO operation keep the 2D nature of the structures. We have implemented the PSO algorithm for 2D systems into the CALYPSO code.

In our calculations, we usually set the population size to 30. We consider all possible cell sizes with the total number of atoms no more than 20. The number of generations is fixed to 30.

**DFT Calculations.** In the PSO simulations, we use density functional theory (DFT) to relax the structures and calculate the energies. In the DFT plane-wave calculations, we use the local density approximation (LDA). The ion–electron interaction is treated using the projector augmented wave (PAW) technique as implemented in the Vienna ab initio simulation package (VASP). For relaxed structures, the atomic forces are less than 0.01 eV/Å. Because the 3D periodic boundary condition is adopted in VASP, we simulate the 2D systems by constraining all the atoms in an \( ab \)-plane which is perpendicular to the \( c \) lattice vector with the length fixed to 10 Å. For the Brillouin zone integration, we generate the \( n \times m \times 1 \) k-mesh according to the Monkhorst–Pack scheme, where \( n \) and \( m \) are determined by the lateral lattice constant. The phonon calculations are performed using the direct method as implemented in the Phonopy program.

**RESULTS AND DISCUSSION**

**Known 2D Systems.** We first apply the designed PSO method through the CALYPSO code to predict the most stable 2D structure of carbon. As expected, the global optimization method successfully predicts the graphene structure with a two-atom unit cell by only one generation. We also find the most stable 2D hexagonal BN structure within one generation. Although bulk ZnO takes the wurtzite structure, previous experiment showed that single-layer ZnO has a planar structure similar to that of BN. We perform four separate PSO simulations to find the most stable 2D structure of ZnO. All four simulations predict the correct most stable hexagonal ZnO structure: Three of them use only one generation, while the hexagonal structure emerges in the third generation in the other simulation. For boron, we again find the known most stable 2D structure, i.e., the α-sheet with...
eight B atoms,\textsuperscript{11,12} within only two generations. These benchmarks suggest that our PSO algorithm is rather effective in predicting stable 2D materials.

2D Boron–Carbon Compounds. We consider the 2D B–C compounds with seven different B concentrations: BC\textsubscript{5}, BC\textsubscript{3}, BC\textsubscript{2}, BC, B\textsubscript{2}C, B\textsubscript{3}C, and B\textsubscript{5}C. The low-energy 2D structures for B–C compounds predicted from our PSO simulations via the CALYPSO code are shown in Figures 1–7. We use I, II, III, ..., to name the structures in the order of increasing energy. We can see that for carbon-rich compounds (BC\textsubscript{5}, BC\textsubscript{3}, and BC\textsubscript{2}), the 2D sheets can be viewed as boron-doped graphene structures. Interestingly, there are isolated 1D zigzag boron chains in the most stable 2D structures of BC\textsubscript{5} (i.e., BC\textsubscript{5}-I) and BC\textsubscript{2} (i.e., BC\textsubscript{2}-I). For BC\textsubscript{3}, it was suggested that BC\textsubscript{3}-III where the isolated boron atoms are uniformly distributed is the most stable boron-doped graphene structure.\textsuperscript{18,19} However, our calculations show that BC\textsubscript{3}-III is energetically less favorable and has a much higher energy than BC\textsubscript{3}-I by 51 meV/atom. This might be due to the fact that BC\textsubscript{3}-I has more C–C π bonds than BC\textsubscript{3}-III, similar to the cases of the hydrogenation and oxidation of graphene, where hydrogen atoms or oxygen atoms prefer to stays close to each other in graphene.\textsuperscript{32,33} However, we find that the full phase separation does not occur in boron-doped graphene structures because the 2D graphene-like boron structure has a higher energy. Different from BC\textsubscript{2} and BC\textsubscript{5}, BC\textsubscript{3} with 1D zigzag boron chains is not the most stable 2D structure. Instead, the structure with uniformly distributed boron atoms (BC\textsubscript{3}-I) is more favorable with a lower energy of 52 meV/atom. Below we will show...
that the stability of BC$_3$-I is originated from its peculiar semi-conducting electronic structure. BC$_3$-I with two boron atoms at the 1 and 4 positions of the carbon six-membered ring was previously observed experimentally. For the first time, we confirm by global optimization technique that BC$_3$-I is indeed the most stable 2D structure.

For BC, the stable 2D structure (BC-I in Figure 4) is strip-like with alternative boron chains and armchair carbon chains. Every carbon atom is sp$^2$ hybridized, forming two C–C bonds and one B–C bond. Each boron atom has four neighbors with one B–C bond and three B–B bonds. The boron atoms in BC-I can be viewed as connected prismatic B$_4$. Carbon atoms in the meta-stable BC structures (BC-II and BC-III in Figure 4) are either three-fold or four-fold bonded.

The lowest-energy 2D structure for B$_2$C can be seen as the addition of boron atoms to the center of the B$_4$C$_2$ six-membered ring (with C at the opposite side of the ring) of the B$_3$C$_3$ graphene structure. As a result, boron atoms form six-, four-, and three-fold bonds. Our calculations also find the B$_2$C structure with the ptC moiety (D$_{3h}$ symmetry, T$_{11}$ in the notation by Pei and Zeng) previously proposed by Wu et al. However, this structure has a higher energy (49 meV/atom) than the most stable structure (B$_2$C-I) (Figure 5). It is interesting to note that the most stable B$_2$C structure contains the ptC atoms but with a different motif (approximate C$_{2v}$ symmetry, see Figure 11b).

This intriguing ptC motif was earlier proposed to be present in a metastable configuration of C$_2$B$_6$ (T$_7$ in the notation by Pei and Zeng). Here, we show that the T$_7$ ptC motifs can in fact be stabilized in a stable 2D structure of B$_2$C. Previously, experiments have indicated that some aluminum-containing ptC species in the gas phase, such as CAl$_4$, CAl$_3$Si, CAl$_3$Ge, neutral CAl$_4$Si, and neutral CAl$_4$Ge, have been isolated and detected in photoelectron spectroscopy experiments. The boron-containing ptC species have not been observed. This might be due to the fact that most experimental work focused on the carbon-rich 2D B–C compounds. Future experiments on boron-rich 2D B–C systems might confirm our prediction of this novel ptC motif.

The most stable 2D B$_3$C structure (B$_3$C-I) is shown in Figure 6. This structure contains alternative zigzag boron chains and zigzag boron–carbon chains. And there are similar ptC motifs as that in B$_2$C-I. It is noteworthy that the two metastable 2D B$_3$C structures (B$_3$C-II and B$_3$C-III) are closely related to B$_3$C-I: B$_3$C-II can be obtained by moving half of the boron atoms in the zigzag boron–carbon chain toward the zigzag boron chain to form more B triangles; The zigzag boron–carbon chains in B$_3$C-III are equivalent as a result of swapping a carbon atom in the zigzag boron–carbon chain with its neighboring boron atom in the zigzag boron chain in B$_3$C-I. The most stable 2D structure of B$_3$C (Figure 7) is similar to B$_2$C-I except that the ribbon width of the triangular boron sheet is now four instead of two. In the metastable structures (B$_3$C-II and B$_3$C-III), all carbon atoms are three-fold coordinated. Interestingly, there is a large hole formed by six boron atoms and two carbon atoms in B$_3$C-III. To summarize, boron-rich 2D B–C compounds have peculiar ptC motifs and boron triangles, and they do not resemble clearly the structural feature of α-sheet boron structures, in contrast to the carbon-rich case.

In our structural searches, we constrain the systems to be an exact 2D monolayer structure. It might be possible that the predicted structures are not stable against out-of-plane distortions. We therefore perform phonon calculations to check the dynamic stability of the predicted stable 2D structures. Our calculations show that all the 2D structures have no appreciable unstable phonon modes except for the 2D B$_2$C-I and B$_3$C-I structures. B$_2$C-I has a large imaginary frequency (6.7i THz) at zone center Γ point. By distortion of the atoms along the vibrational eigenvectors of the zone center soft phonon mode, we derive a stable structure with a 0.42 Å buckling which is more stable than the exact 2D B$_2$C-I structure by 24 meV/atom. Due to the structural similarity, a similar distortion occurs in B$_3$C-I.

We also perform first-principles molecular dynamics (MD) simulations to examine the thermal stability of the 2D structures. The constant temperature and volume (NVT) ensemble was adopted. The time step is 3 fs and the total simulation time is 15 ps for each given temperature. We find that almost all the lowest energy 2D structures are stable up to 1000K. In particular, the structure of BC-I remains almost intact at 2000 K [see Figure 8b]. The high thermal stability of BC-I should be due to the high stability of carbon armchair chain and the fact that each boron has one relatively strong B–C bond. However, B$_3$C-I is unstable at 1000 K. Some B–B bonds in the zigzag B–C chains might be broken to form more B–B bonds, resulting in a motif similar to that in B$_2$C-II [Figure 8a]. This is not unreasonable since B$_3$C-II is structurally closely related to B$_2$C-I and has only a slightly higher energy than B$_2$C-I, with which only a small kinetic barrier between B$_2$C-I and B$_3$C-II is expected.

Our electronic band calculations show that all the 2D B–C compounds are metallic except for BC$_3$-I (See Figure 9 for representative band structures). The metallicity stems from the delocalized 2p$_z$ π electrons of carbon and boron atoms,
similar to those in graphene and boron 2D α-sheet.11 The LDA
calculation shows that BC2-I has an indirect gap of 0.52 eV with
the valence band maxima at Γ, which is in agreement with the
reported value (0.66 eV) from a local orbital pseudopotential
calculation.37 It is interesting to note that we recently found 2D
NC3 has the same structure as BC2-I and is also a semi-
conductor.36 The semi-conducting behavior is due to six-member-
red “benzene” rings isolated by boron atoms: The boron atom
is $sp^2$ hybridized, and all of its three 2p electrons are participating
in the formation of σ bonds; For the “benzene” ring, there are
three bonding orbitals and three antibonding orbitals separated
via an energy gap.

The partial density of states (PDOS) of the predicted 2D B–C
compounds is analyzed carefully. By the 2D nature, there is a
mirror plane symmetry (the basal plane) in each of the 2D
compounds is analyzed carefully. By the 2D nature, there is a

Figure 10. Partial density of states for (a) BC2-I, (b) BC-I, and (c) B2C-
I. The vertical dashed lines denote the Fermi level.

optimal filling of σ bonding states, while the other 2D B–C
compounds do not.

To gain more insight into the chemical bonding in 2D
boron–carbon nanostructures, we plot the electron localization
function (ELF) for representative systems using the formulation
of Silvi and Savin.37 The topological analysis of ELF is used
to classify chemical bonds rigorously.38 Because the σ states are
more localized than π states, the ELF distribution with a large
value (e.g., 0.7) for B–C compounds mostly reflects the in-plane
σ states. The ELF isosurface (0.7) plot (Figure 11a) for BC2-I
shows that the p orbitals of the 1D zigzag boron chain are rather
delocalized, which might explain the stability of the 1D zigzag
boron chain motif (lower panel of Figure 11a). For BC-I, there
are four C–C σ bonds, four B–C σ bonds, one B–B two-center
σ bond, and two three-center B bonds in each unit cell (each unit
cell has four B atoms and four C atoms). The total number (11)
of σ bonds is consistent with the number (22) of occupied σ
electrons integrated from the in-plane PDOS. The other six
electrons occupy the π states.

For B2C-I, ELF is significantly distributed around the center
of the boron triangles, indicating the presence of the boron three-
center bond. Around each three-fold coordinated carbon atom,
the ELF localizes at the bond centers of the three B–C bonds,
similar to the ELF distribution of graphene (see Figure 11a for
the ELF of the graphene part of BC2). For the pC atom in B2C-I,
the ELF mainly distributes between carbon and B1, B2, and B3
(lower panel of Figure 11c), whereas the bonding between the
pC atom and B3 is weak. For comparison, we also show the ELF
for B2C-IV with D2h pC motifs (lower panel of Figure 11d).
In this case, the ELF is symmetrically distributed along each B–C
bond. We note that there is no boron three-center bond in B2C-
IV, which might explain the physical origin of its higher energy.
It was recently shown that there is no two-center B–B bond in
the α-sheet boron structure.39 Here, we find that there are two-
center σ B–B bonds in 2D B–C compounds, especially in some
boron-rich B–C compounds (see Figure 11b and c).

CONCLUSION

To predict 2D nanostructures, we develop a global optimization
method based on the PSO algorithm as implemented in
CALYPSO code. Using the PSO algorithm, we predict new
stable structures of 2D B–C compounds for a wide range of
boron concentrations. For some of the system such as BC3 and
B2C, the predicted structures have much lower energies than
previous proposed structures. Our calculations show that: (1) almost all 2D B–C compounds are metallic except for BC3 which is a magic case where the isolation of carbon six-membered ring by boron atoms results in a semi-conducting behavior; (2) for C-rich B–C compounds, the most stable 2D structures can be viewed as boron-doped graphene structures. Usually boron forms 1D zigzag chain except for BC3 where boron atoms are uniformly distributed; (3) the most stable 2D structure of BC has alternative carbon and boron ribbons with strong in-between B–C bonds, resulting in a high thermal stability above 2000 K; (4) for B-rich 2D B–C compounds, there is a novel planar-tetracoordinate carbon motif with an approximate C3 symmetry. ELF analysis of the nature of the bonding shows that the delocalized p states of 1D zigzag boron chain in the carbon-rich compounds and the three-center boron bonds in the boron-rich case play an important role in the structural stability. The new 2D B–C compounds predicted in this work might be promising candidates for nanoelectronics applications, energy materials (electrode in Li-ion battery, hydrogen storage, and cheap catalysis in fuel cell). From the predicted 2D B–C compounds, one can derive many new nanostructures (e.g., nanoribbons, nanotubes, nanocages) which might have a wealth of exotic electronic and/or magnetic properties.

**ASSOCIATED CONTENT**

Supporting Information. Complete ref 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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