Planar Hexacoordinate Carbon

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Be_2C Monolayer with Quasi-Planar Hexacoordinate Carbons: A Global Minimum Structure**

Yafei Li, Yunlong Liao, and Zhongfang Chen**

Dedicated to Professor Henry F. Schaefer III on the occasion of his 70th birthday

Abstract: *The design of new materials is an important subject in order to attain new properties and applications, and it is of particular interest when some peculiar topological properties such as reduced dimensionality and rule-breaking chemical bonding are involved. In this work, we designed a novel two-dimensional (2D) inorganic material, namely Be_2C monolayer, by comprehensive density functional theory (DFT) computations. In Be_2C monolayer, each carbon atom binds to six Be atoms in an almost planar fashion, forming a quasi-planar hexacoordinate carbon (phC) moiety. Be_2C monolayer has good stability and is the lowest-energy structure in 2D space confirmed by a global minima search based on the particle-swarm optimization (PSO) method. As a semiconductor with a direct medium band gap, Be_2C monolayer is promising for applications in electronics and optoelectronics.*

The spatial tetrahedral preference of tetracoordinate carbon has been one of the foundations of organic chemistry and biochemistry since it was deduced by van't Hoff and Lebel in 1874.[1] Carbon can be planar when it adopts sp^2 hybridization, as in graphite. In 1968 Monkhorst first put forward the interesting question about the possibility of planar tetracoordinate carbon (ptC) by taking hypothetical planar methane as an example.[2] Hoffmann et al. suggested that ptC could be stabilized electronically, mechanically, or by a combination of both in their seminal 1970 paper.[3] Following this line, Schleyer and co-workers designed the first ptC molecule (1,1-dilithiocyclopropane) by ab initio computations in 1976.[4] Ever since ptC chemistry has been a subject of intensive studies.[5] Numerous stable ptC-containing molecules have been designed theoretically,[6] and some global minima, such as CAl_4^-,[7] CAl_4^{2-},[8] and CAl_3Si^-[9] have been detected experimentally. More interestingly, at the beginning of this century, Schleyer et al. theoretically predicted numerous penta-coordinate carbon (ppC)[10] and hexa-coordinate carbon (phC)[11] minima.

In recent years, there has been growing interest in the design of ptC-containing extended systems.[12] Motivated by the intensive studies of graphene[13] and its inorganic analogues,[14] several groups designed ptC-containing 2D materials. For example, on the basis of ptC molecule CB_4, Wu et al. designed B_2C graphene, in which each C atom binds to four boron atom to form a ptC moiety.[15] Recently, Zhang et al. designed a semiconducting 2D structure, namely TiC monolayer, which is fully composed by quasi-planar tetracoordinate carbon atoms.[16] These materials not only possess fascinating structural properties, but also have many potential applications. For example, B_2C graphene is predicted to be metallic and superconductive.[17]

The active quest of ptC-containing solids promoted us to ask an interesting question: is it possible to develop planar carbon with coordination numbers more than four in periodic solids? If the answer is yes, what novel properties would these materials present? To our best knowledge, attempts in this regard have never been reported.

Here, on the basis of comprehensive density functional theory (DFT) computations, we report the design of a new 2D structure, namely Be_2C monolayer, in which each C atom binds to six Be atoms to form a quasi-planar hexacoordinate (phC) moiety, thus representing the first example of a phC-containing solid. Our DFT computations demonstrate that Be_2C monolayer has excellent stability. Particularly, the phC-containing Be_2C monolayer is the global minimum structure in 2D space, which holds potential for experimental synthesis. Be_2C monolayer is semiconducting with a moderate direct band gap, thus promising for applications in electronics and optoelectronics.

Our design of Be_2C monolayer was initially inspired by the previously studied BeB_2 monolayer,[18] in which a Be atom lies above each boron hexagon. Be_2C monolayer is isoelectronic to BeB_2 monolayer and can be considered as formed by substituting Be and B atoms of BeB_2 monolayer with C and Be atoms, respectively. Figure 1a presents the optimized structure of our designed Be_2C monolayer. One unit cell of Be_2C monolayer consists of two Be atoms and one C atoms, with the optimized lattice constants of $a = b = 2.99$ Å.

However, different from BeB_2 monolayer, in which B atoms are in the same plane, and from the exactly planar graphene, every two neighboring Be atoms in Be_2C monolayer are buckled into two different atomic planes, 0.46 Å

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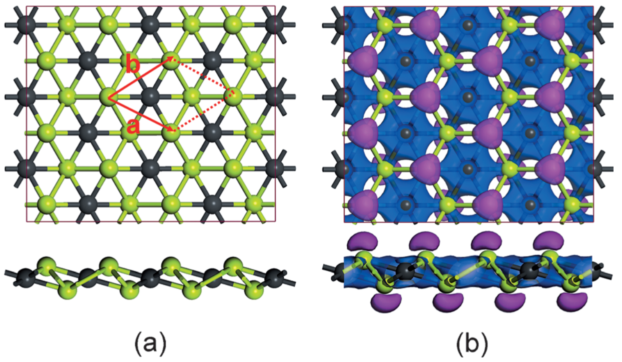

Figure 1. a) Top (upper) and side (lower) views of the geometric structure of 2D Be_2C monolayer; *a* and *b* represent the lattice vectors. Black and green balls represent C and Be atoms, respectively. b) Deformation charge density of 2D Be_2C monolayer. Blue and pink refer to electron accumulation and depletion regions, respectively. The iso-surface value is 0.05 e/au.

above and below the C atomic plane, respectively. Particularly, each C atom of Be_2C monolayer binds to six neighboring Be atoms to form a quasi-phC moiety (Be-C-Be bond angle 66.5°), while each Be atom is shared by three phC atoms. In Be_2C monolayer, the C–Be and Be–Be bond lengths are 1.73 and 1.98 Å, respectively, much shorter than in bulk Be_2C (1.88 and 2.17 Å for C–Be and Be–Be bonds, respectively). We performed a spin-polarized computation for Be_2C monolayer to determine its ground state, however, no energy difference between spin-polarized and spin-unpolarized computations was observed, indicating that Be_2C monolayer has a nonmagnetic ground state and there is no unpaired electron or unsaturated dangling bond in Be_2C monolayer.

To get insights into the chemical bonding and the stabilizing mechanism of quasi-phC in Be_2C monolayer we computed the deformation electronic density, which is defined as the total electronic density of Be_2C monolayer substracted by the electronic densities of isolated Be and C atoms. As shown in Figure 2b, there is remarkable electron transfer from the p orbitals of Be atoms to C atoms. The transferred electrons are well delocalized around the six C–Be bonds, which is crucial for stabilizing the phC moiety and illustrates the covalent character of C–Be bonds. Hirshfeld charge analysis shows that the net charges on C and Be atom are −0.32 and 0.16 e, respectively. So C and Be atoms in Be_2C monolayer are also considerably ionized. To minimize the repulsion interactions, Be atoms buckle into two planes to ensure that two neighboring cations are not in the same plane. Note that there is no visible electron accumulation between Be atoms, indicating weak Be–Be bonding. The computed bond order is 0.58 and 0.18 for the C–Be and Be–Be bond, respectively.

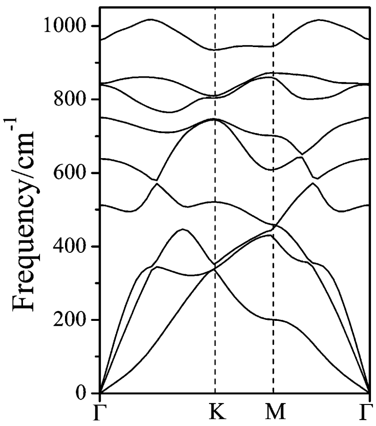

Figure 2. Phonon spectrum of Be_2C monolayer.

Before examining the electronic properties of Be_2C monolayer, we need to answer the question if Be_2C monolayer is a stable structure. To evaluate the stability of Be_2C monolayer, we first computed its cohesive energy defined as $E_{coh} = (nE_C + 2nE_{Be} - E_{Be2C})/3n$ (E_C, E_{Be} and E_{Be2C} are the total energies of a single C atom, a single Be atom, and Be_2C monolayer, respectively). According to our computations, Be_2C monolayer has a cohesive energy of 4.86 eV/atom. For comparison, at the same theoretical level, the cohesive energies of graphene, 2D BC_3 monolayer,[19] and silicene are 7.95, 7.26, and 3.71 eV/atom, respectively. Although the relative stabilities of these materials with different compositions cannot be determined directly by comparing their cohesive energies, a 4.86 eV cohesive energy is clear evidence that Be_2C monolayer is a strongly bonded network.

We then focused on the mechanical properties of Be_2C monolayer. As a validation, the in-plane stiffness of graphene computed at our theoretical levels is 330 $N\,m^{-1}$, which agrees well with experimental measurement[20] and previous theoretical studies.[21] For Be_2C monolayer, its in-plane stiffness was computed to be 162 $N\,m^{-1}$, which is lower than that of graphene, but higher than those of silicene (59 $N\,m^{-1}$) and MoS_2 monolayer (121 $N\,m^{-1}$) computed at the same theoretical levels. Therefore, Be_2C monolayer also has good mechanical properties.

To test the kinetic stability of Be_2C monolayer, we computed its phonon spectrum. As shown in Figure 2, no appreciable imaginary phonon modes are presented, indicating that Be_2C monolayer is kinetically stable. Particularly, the highest frequency of Be_2C monolayer reaches up to 1020 cm^{-1}, which is much higher than the highest frequency of 580 cm^{-1} in silicene,[22] 473 cm^{-1} in MoS_2 monolayer,[23] and 810 cm^{-1} in TiC monolayer,[16] indicating robust C–Be bonds in Be_2C monolayer.

Finally, we assessed the thermal stability of Be_2C monolayer by performing first-principles molecular dynamics simulations. We used a 4 × 4 supercell and carried out three individual MD simulations for Be_2C monolayer at temperatures of 1000, 1500, and 2000 K. Snapshots of Be_2C monolayer at 10 ps were plotted for three simulations (see Supporting Information). The structure of Be_2C monolayer does not collapse throughout a 10 ps MD simulation up to 1500 K. However, at 2000 K, the structure is seriously disrupted, indicating that the melting point of Be_2C is probably between 1500 and 2000 K. The above results reveal that the Be_2C monolayer has very good thermal stability and can maintain its structural integrity in high-temperature environment.

Although Be_2C monolayer has good stability, this only means it is a local minimum. As a global minimum structure is more likely to be realized experimentally, we investigated if the quasi-phC-containing Be$_2$C monolayer is the global minimum structure in 2D space. To address this issue, we performed a global search for the lowest-energy structure for Be$_2$C in 2D space by using the first-principles based particle-swarm optimization (PSO) method.[24] As a benchmark, the PSO method predicted the hexagonal structure with a two-atoms unit cell as the global minimum structure for graphene by only one generation.

After 30 generations we obtained two stable structures for 2D Be$_2$C, named Be$_2$C-I and Be$_2$C-II (Figure 3). Be$_2$C-I is the above discussed quasi-phC-containing Be$_2$C monolayer. Be$_2$C-II also has very interesting structural properties, in which each carbon atom binds to four Be atoms in the same plane to form a ptC moiety. Interestingly, when the system was constrained to be an exact plane in the PSO searching process, Be$_2$C-II was predicted to be the most stable structure for 2D Be$_2$C monolayer and is 6 meV/atom lower in energy than Be$_2$C-I. However, when the constraint was removed, Be$_2$C-I prefers an out-of-plane buckling while Be$_2$C-II still favors the planar structure. In this case Be$_2$C-I becomes 183 meV/atom lower in energy than Be$_2$C-II. Therefore, the phC-containing Be$_2$C monolayer is the global minimum structure in the 2D space. This result is very inspiring because Be$_2$C monolayer is the first global minimum of phC-containing structure. Previously predicted phC-containing molecules (e.g. CB_6^{2-}) were all local minima.[25]

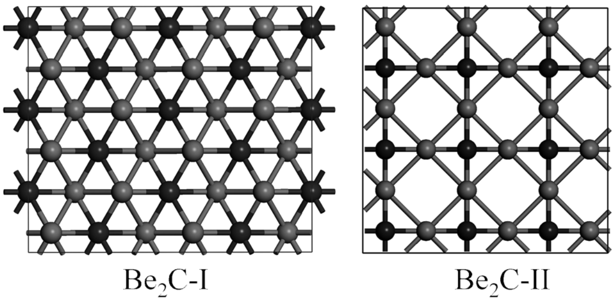

Figure 3. Geometric structures of Be$_2$C-I and Be$_2$C-II.

Since the phC-containing Be$_2$C monolayer is the global minimum structure in the 2D space it holds great potential to be realized experimentally. We propose to grow the Be$_2$C monolayer on substrates by chemical vapor deposition (CVD) method similar to the growth of silicene on the surface of metal[26] or metal oxide.[27] Particularly, it was found that the cohesive energy difference between Be$_2$C monolayer and Be$_2$C bulk (4.86 vs 5.31 eV/atom) is less than that between silicene and Si bulk (3.71 vs 4.54 eV/atom) implying that it would be energetically more favorable to obtain Be$_2$C monolayer from the bulk phase than the synthesis of silicene. Note that the formation of Be$_2$C may require high temperature, and the problem of toxicity is also a challenge for experimental realization.

We next investigated the potential electronic properties of Be$_2$C monolayer. To address this issue, we computed the band structure of Be$_2$C monolayer as well as its density of states (DOS). As shown in Figure 4a, a direct gap of about 1.52 eV appears in the band structure, with the valence band maximum (VBM) and the conduction band minimum (CBM) both located at the Γ point. Therefore, different from graphene and BeB$_2$ monolayer which are both semi-metallic, Be$_2$C monolayer is semiconducting with a sizable band gap. Moreover, we re-computed the band gap of Be$_2$C monolayer by using the hybrid HSE06 functional[28] to get a more accurate band gap. HSE06 predicted a 2.34 eV direct band gap with similar dispersion of energy bands to that of PBE functional (see Supporting Information).

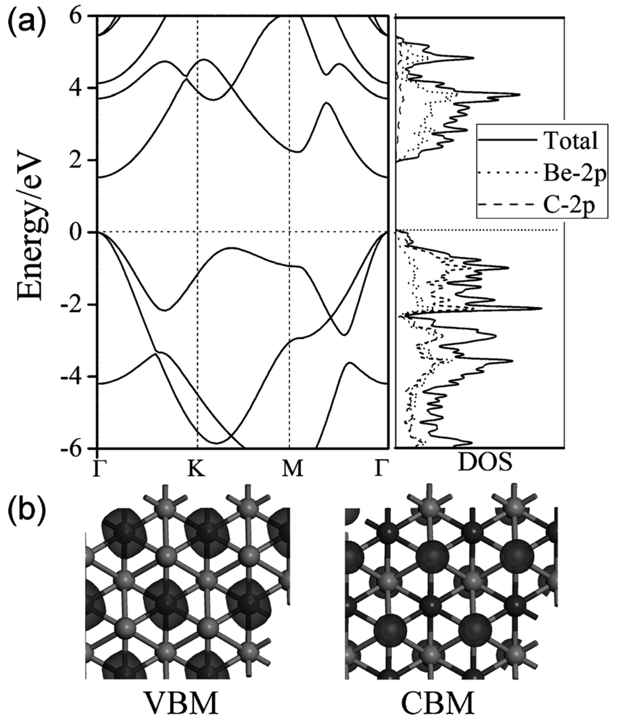

Figure 4. a) Band structure (left) and density of states (DOS) of Be$_2$C monolayer. The Fermi level is assigned at 0 eV. b,c) The iso-surfaces of partial charge densities for the b) valence band maximum and c) conduction band minimum of Be$_2$C monolayer. The isovalue is 0.05 e$Å^{-3}$.

The PDOS analysis shows that the VBM of Be$_2$C monolayer is contributed by C-2p and Be-2p states while the CBM is mainly contributed by Be-2p states. There is apparent hybridization between C-2p and Be-2p states below the Fermi level. To get more information, we also computed the partial charge densities corresponding to the VBM and CBM of Be$_2$C monolayer (Figure 4b). The VBM is mainly localized at the multicenter σ-bonding between C and Be atoms while the VBM corresponds solely to the 2p orbitals of Be atoms, consistent with the PDOS analysis.

To summarize, by systematic DFT computations we designed a new inorganic 2D crystal of Be$_2$C monolayer which is semiconducting with a moderate band gap. In Be$_2$C monolayer, each C atom binds to six Be atoms to form a quasi-phC moiety, representing the first example of a phC-containing periodic structure. Be$_2$C monolayer has a strong chemical bonding and a high in-plane stiffness, is absence of imaginary phonon modes, and can be stable up to at least 1500 K in our simulation. Particularly, the PSO method confirmed that the phC-containing Be_2C monolayer is the global minimum structure in the 2D space. Overall, our studies not only put forward the novel phC into periodic nanomaterial, but also provide a new candidate for future electronics and optoelectronics. Considering the rapid development of experimental techniques for fabrication of low-dimensional materials in recent years, we are optimistic that Be_2C monolayer can be realized experimentally.

Computational Methods

DFT computations based on first-principles were performed using the plane-wave technique implemented in Vienna ab initio simulation package (VASP).[29] The ion–electron interaction was described using the projector-augmented plane wave (PAW) approach.[30] The generalized gradient approximation (GGA) expressed by PBE functional[31] and a 420 eV cutoff for the plane-wave basis set were adopted in all computations. To account the Be–Be interactions which would have a substantial van der Waals (vdW) contribution, we adopted the PBE + D2 (D stands for dispersion) method with the Grimme vdw correction.[32] The convergence threshold was set as 10^{-4} eV in energy and 10^{-3} eV Å^{-1} in force. For 2D Be_2C monolayer, we set the x and y directions parallel and the z direction perpendicular to the layer plane, and adopted a supercell length of 15 Å in the z direction. The Brillouin zone was sampled with a $12 \times 12 \times 1$ centered k points grid for 2D systems. The phonon band structure of Be_2C monolayer was computed using the density functional perturbation theory (DFPT)[33] as implemented in the Phonopy program,[34] which adopts the quasi-harmonic approximation method to analyze the potential energy hypersurface in the neighborhood of the minimum-energy structure.

First principles molecular dynamics (MD) simulations were performed to assess the thermal stability of Be_2C monolayer. The PAW pseudo-potential and PBE functional were used as implemented in VASP software. The initial configuration of Be_2C monolayer was annealed at different temperatures. At each temperature, MD simulation in NVT ensemble lasts for 10 ps with a time step of 1.0 fs. The temperature was controlled by using the Nosé–Hoover method.[35]

The particle-swarm optimization (PSO) method within the evolutionary scheme as implemented in the CALYPSO code was employed to search the low-energy structures of 2D Be_2C monolayer. As an unbiased global optimization method, the PSO algorithm was inspired by the choreography of a bird flock and can be viewed as a distributed-behavior algorithm that performs multidimensional search. This method has been successfully employed to predict the lowest-energy structures of 2D boron-carbon sheets,[36] 2D boron sheet,[37] 2D boron-silicon sheets[38] as well as many 3D structures.[39] In our PSO simulation, the population size was set to be 30, and the number of generation was maintained at 30. Unit cells containing total atoms of 6, 12 and 18 were considered. The structure relaxations during the PSO simulation were performed using the PBE functional, as implemented in VASP software.

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