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A novel two-dimensional material B₂S₃ and its structural implication to new carbon and boron nitride allotropes

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The two-dimensional (2D) semiconductor materials and the related device fabrication have become a new focus of electronics and materials science recently. Comparing with three-dimensional (3D) semiconductor, the choice of the 2D materials is very limited. The recently emerging enthusiastic goal of fabricating functional heterojunctions of 2D semiconductors spurred a strong need in searching 2D materials that have large variety of band gaps and band edges. Here, we propose a single layer B₂S₃ as a new potential 2D material conceived directly from its existing layered 3D crystal. Using an advanced hybrid functional method, we demonstrated that 2D B₂S₃ has a gap of 3.75 eV, filling a missing energy range for 2D materials. Furthermore, by adding extra B atoms at the 'vacancy' sites of B₂S₃ structure toward 1:1 stoichiometry, we constructed new 2D BN and graphene allotropes that show large variation in the electronic structure. The BN allotrope exhibits a gap that is 0.99 eV lower than h-BN. Although the structure is significantly different to graphene, the new C allotrope contains a Dirac cone. However, the Dirac point is slightly lower than the Fermi level because of the electron transfer from an adjacent valence band to the Dirac cone states, resulting at a metallic state with both 'massless' electrons and massive holes.

Introduction

Since graphene was first made in the laboratory in 2004 by Geim's group,¹ it has inspired enormous experimental and theoretical studies. Many peculiar properties of this atomically thin film have been discovered, including ballistic charge transport, ambipolar field effect and room-temperature quantum Hall effect,¹⁻⁵ making graphene a very promising candidate materials for future nanoelectronic,^{5,6} optoelectronic^{7,8} and spintronic applications.⁹ However, graphene alone can not satisfy all the needs of a 2D based electronic device, especially considering that graphene sheet possesses no gap. To this end, h-BN¹⁰ is a good complementary since it is isoelectronic to graphene and has a gap as large as 5.74 eV, making it an ideal candidate for gate dielectrics.⁴ From graphene to BN, there is a large energy gap difference and there is lack of 2D materials covering the spectrum. Recently several transition metal chalcogenides such as MoS₂ and WSe₂ etc. got strong attention.¹¹⁻¹³ However, their band gaps varies in a small range (from 0.7 eV to 2.1 eV).^{11,14} g-C₃N₄, which is constructed from tri-s-triazine units connected by amino groups, possesses a direct band gap of 2.7 eV.¹⁵ Its capability for photocatalysis¹⁵⁻¹⁷ and solar energy conversion^{18,19} is currently pursued.

Besides investigating new 2D materials, much effort has been made in exploring the novel carbon allotropes²⁰⁻²⁶ that may either maintain the Dirac point²⁰⁻²³ or open a gap.²⁴⁻²⁶ Along this line, several allotropes have been proposed and studied using first principles methods, including the T-graphene,²¹ S-graphene²³ and graphyne.²² One important problem with these allotrope is that they can transform to graphene honeycomb structure through a direct path.²³ The stacking of a few graphene layers has also been shown as an effective method to open a gap.²⁶⁻²⁸ However, such method can only vary the gap for a small range. There is still a great need to search new 2D materials and/or new structures for graphene allotropes, in order to advance the electronics based on 2D materials. One successful approach is the exfoliation techniques that obtain single layered sheets from any layered bulk material probable.²⁹ As a matter of fact, there are many compounds adopting layered structure, including metals, insulators and semiconductors. Among them, B₂S₃ has a unique layered structure and a band gap of 3.75 eV, making it an ideal candidate for single layer fabrication through exfoliation. In this work, we propose a new two-dimensional material, B₂S₃, which can be obtained from the layered bulk B₂S₃ crystal. Bulk B₂S₃ has attracted tremendous interest due to its usage in high-

tech glasses^{30–32} and preparation of organosulfur compounds.^{33,34} The structure and electronic properties of 2D B_2S_3 are studied using first principle calculations. This 2D materials has an orthorhombic lattice. Based on calculations, we found that B_2S_3 is a wide band gap semiconductor with a direct Γ_v to Γ_c band gap of 3.75 eV. Furthermore, by observing the structure features of the 2D B_2S_3 , we constructed new allotropes of BN and C. Different to many previously proposed C allotropes, there is no direct transformation path from the new structure back to original graphene honeycomb structure. From electronic structure calculations, we found that the new allotrope also exhibit Dirac points and therefore is metallic. The unit cell of the new carbon allotrope is rectangular, which provides another example of Dirac cone without the hexagonal symmetry.

Methodology

All the calculations were performed based on density functional theory using Vienna Ab-Initio Simulation package (VASP).³⁵ Projector augmented wave (PAW)³⁶ approach was used to describe the ionic potential. Generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE)³⁷ functional was employed in structure relaxations, while both

Heyd-Scuseria-Ernzerhof (HSE)³⁸ hybrid functional and PBE functional were used to calculate the band structures and DOS. Periodic boundary conditions (PBC) were applied and a vacuum space of about 15 Å along the z-direction was included in the model to avoid interactions between layers. Monkhorst-Pack scheme³⁹ with a $4 \times 2 \times 1$ k -mesh was used for the Brillouin zone integration. The energy cutoff for the calculations was set to 900 eV. The conjugated gradient (CG) method was used to optimize the structures.

Results and Discussions

The crystal structure of bulk B_2S_3 has been available since 1962^{40,41} and it was first characterized by Harald and Bernt in 1977.⁴² In this crystal, boron and sulfur atoms form strong covalent bonds within single B_2S_3 layer, and the neighboring layers are connected by weak van der Waals forces. From this structure, we can construct a single layer B_2S_3 . This two-dimensional B_2S_3 has a rectangular unit cell and the calculated lattice constants are 10.859 and 21.507 Å as shown in Fig. 1a. In each unit cell, there are 16 boron atoms and 24 sulfur atom. All boron atoms are bonded with three sulfur atoms; whereas sulfur atoms bonded with two borons. The boron and sulfur atoms can be categorized into four and six types based on their

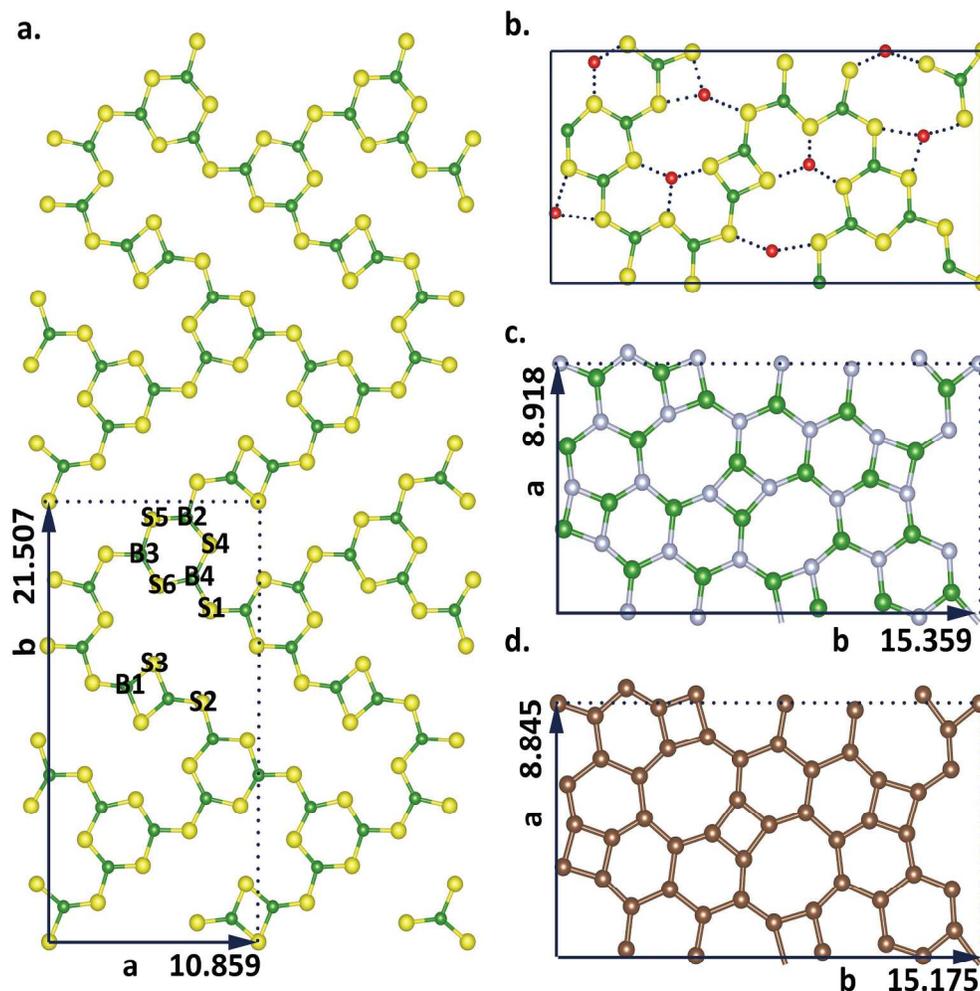


Figure 1. Two dimensional structures of (a) single layer B_2S_3 , (b) B_2S_3 plus extra B atoms filling the ‘vacancy’ sites, (c) conceived r-BN, and (d) conceived r-graphene. The unit of the lattice constants is angstrom. Boron, sulfur, nitrogen, carbon and added atoms are shown in green, yellow, grey, brown and red colors.

symmetry positions and chemical environments. Parallel to *b*, every two six-membered rings and one four-membered ring form a zigzag chain. Adjacent chains are linked by sulfur atoms between two six-membered rings and some vacancies present between the zigzag chains. Similar to layers in bulk B_2S_3 material,⁴³ the optimized structure of 2D B_2S_3 shows a small buckling in the *z* direction, with the largest coordinate difference of 0.0815 Å in *z* direction. The structure consists of B_3S_3 six-member rings and B_2S_2 four-member rings linked by sulfur atoms.

The stability of the single layer B_2S_3 is an important issue. We first calculate the enthalpy of formation (ΔH^f) by comparing the total energies of B_2S_3 layers and the elementary B and S solids. Both B and S form many allotropes at ambient condition. We choose the α -rhombohedral and the orthorhombic S8 (Fddd) structures for B and S respectively. Our calculations show that ΔH^f is -211.09 kJ/mole for single layer B_2S_3 . Furthermore, we

would like to compare the energies of single layer and bulk B_2S_3 . Because the B_2S_3 layers are bound by van der Waals (vdW) interaction, we include this weak interaction by using a DFT-D2 approach.⁴⁴ We found that single layer B_2S_3 is 0.265 eV/ B_2S_3 higher than its bulk materials. This is actually similar to the energy difference between graphene layer and graphite. Using the same computation method and parameter set-ups, we found that graphene is 0.056 eV/Carbon higher in energy than graphite. Considering that each B_2S_3 formula contains 5 atoms, these two energy differences are quite close. This indicates that single layer B_2S_3 can likely be obtained by exfoliation methods analogy to graphene preparation. At last, we performed molecular dynamics (MD) simulations of single layer B_2S_3 at 700 K to examine whether the materials is stable under finite temperature. The MD simulation was run for 3ps containing 3000 MD steps. The structure becomes stable after 3ps. We found the B_2S_3 network remains the same at 700 K, although

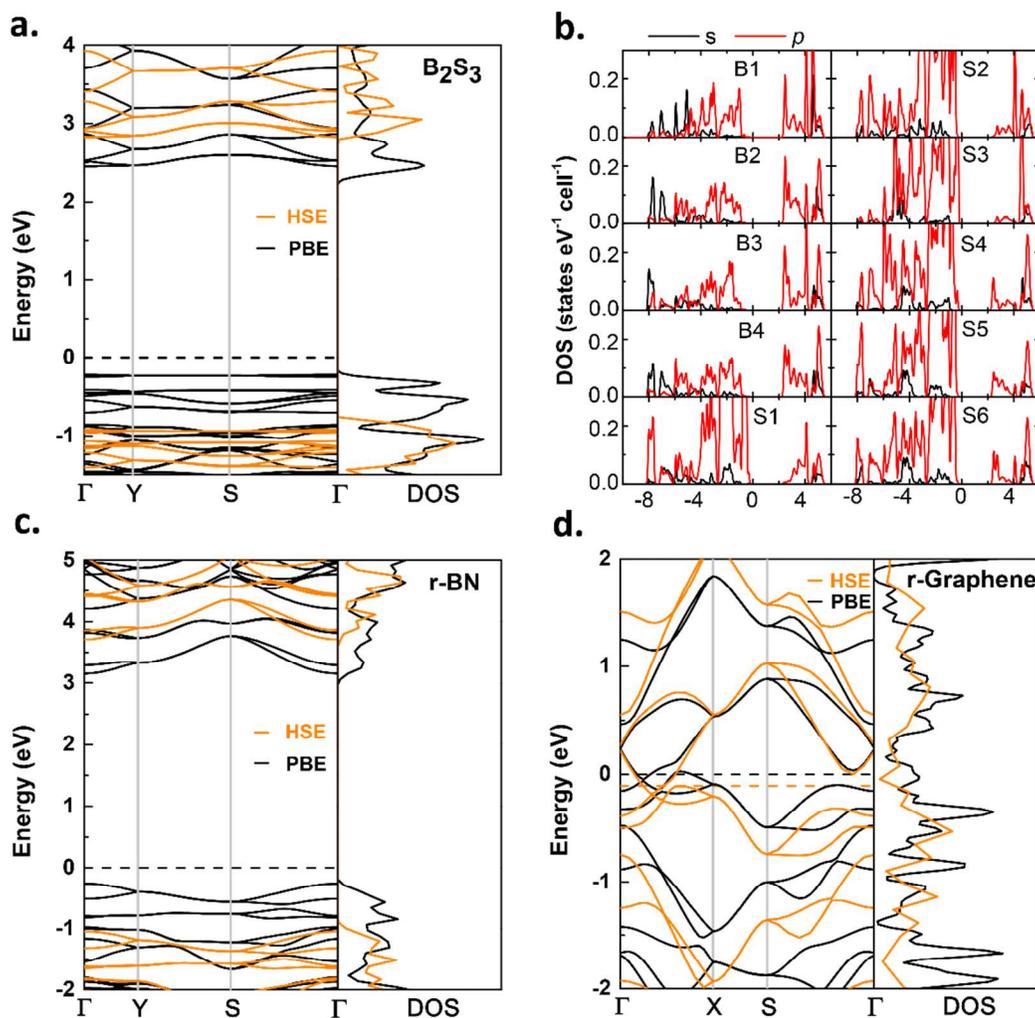


Figure 2. The band structures and DOS of (a) B_2S_3 , (c) r-BN, (d) r-graphene. The black and the orange lines represent the band structures and DOS calculated using PBE and HSE functionals, respectively. For B_2S_3 and r-BN, the Fermi levels for PBE and HSE results are set as identical; whereas for r-graphene the Fermi levels are shown by black and orange dashed lines. (b) PDOS of boron and sulfur atoms in B_2S_3 .

the atoms shifted along perpendicular direction, developing a ripple-like structure. This structure is typical for two-dimensional materials. Actually by running MD simulation for 5x5 unit cell graphene, we also found similar ripples.

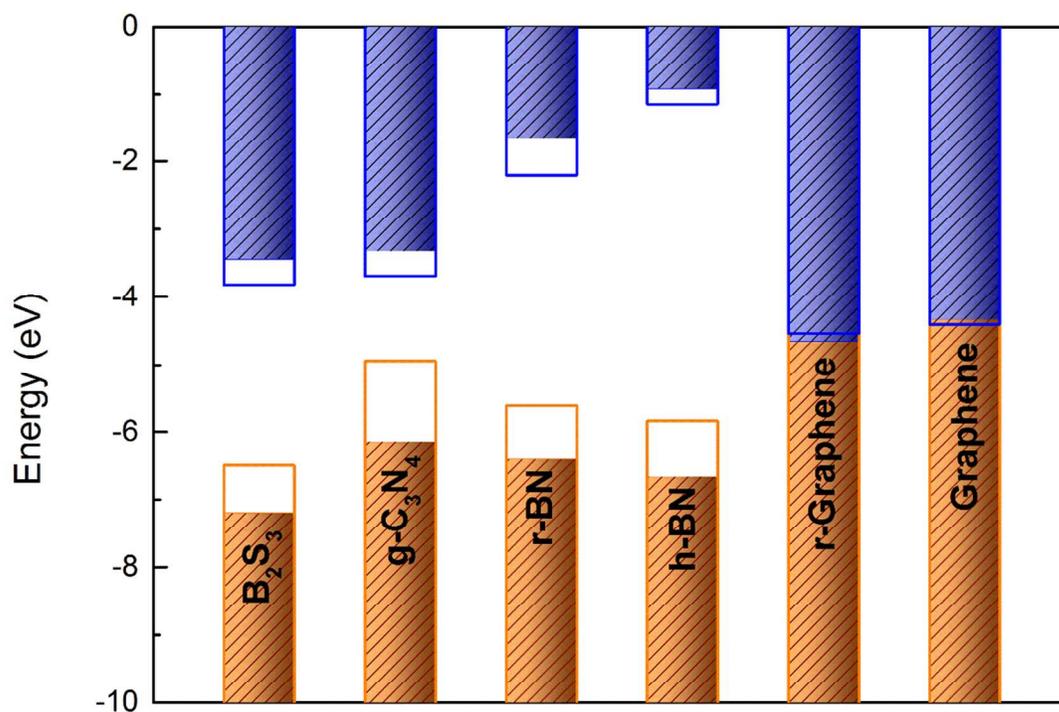
The structure and the stoichiometry of 2D B_2S_3 indicate the possibility of conceiving new allotropes for BN and C. As a matter of fact, by adding extra B atoms at the vacancy sites of B_2S_3 , we will change the stoichiometry from 2:3 to 1:1. The positions for the eight added boron atoms are illustrated in Fig. 1b. By replacing S atoms with N atoms, we can eventually construct a new allotrope of BN. The new structure consist of four-, six-, and eight-membered B-N rings. The geometry of this resulted boron nitride allotrope was optimized and shown in Fig. 1c. The unit cell of this boron nitride allotrope is also *rectangular*, therefore we name it r-BN. Our calculations showed that r-BN is 0.25 eV/atom less stable than h-BN. But it is 0.17 eV/atom more stable than inorganic graphenylene,⁴⁵ which is a boron nitride porous two-dimensional nanosheet reported recently. The optimized lattice constants of r-BN are 8.918 and 15.359 Å that are much smaller than that of B_2S_3 , because the average B-N bond length in r-BN is 0.35 Å shorter than the average B-S bond length in B_2S_3 . In r-BN, boron and nitrogen atoms exist alternatively and both of them exhibit trigonal coordination as in h-BN.¹⁰ Different to B_2S_3 , r-BN is strictly two-dimensional without any buckling in z direction.

Furthermore, we can replace the boron and nitrogen atoms in r-BN with carbon atoms, and construct a new C allotrope, which we name as r-graphene. The structure was illustrated in Fig. 1d. It contains in total 48 C atoms in one unit cell. r-graphene and r-BN are isoelectronic and their relaxed structures and lattice constants are very similar. Both are purely planar without buckling in z direction. The calculated in-plane lattice constants of r-graphene are 8.845 and 15.175 Å separately. Our

calculations showed that r-graphene is 0.42 eV/atom less stable than graphene. We also compared the stability of r-graphene with that of the other carbon allotropes with 4-, 6- and 8-membered rings. We found that r-graphene is 0.091, 0.21 and 0.045 eV/atom more stable than t-graphene,^{21,46} graphenylene⁴⁷ and the recently synthesized isomeric graphene⁴⁸ with biphenylene as the smallest subunit, respectively. More importantly, there is no simple transformation path from r-graphene to honeycomb graphene.

Next, we study the electronic structures of B_2S_3 , r-BN and r-graphene. The band structures and density of states (DOS) for the three 2D materials are plotted in Fig. 2. It is well known that the local and semilocal functionals such as PBE functional significantly underestimate the band gaps of semiconductor materials comparing with the experimental values. It has been demonstrated by many studies that the HSE hybrid functional can yield quite accurate band gaps.^{49–52} We employed both HSE and PBE functionals to calculate the electronic structures.

In previous studies,⁴³ bulk B_2S_3 was found to be a semiconductor with an indirect band gap from the Γ point to the X point. Its gap value was 2.43 eV obtained by GGA. In contrast, 2D B_2S_3 is calculated to be a semiconductor with a direct band gap at the Γ point as shown in Fig. 2a. This indirect to direct gap transition has been found in the case of two-dimensional transition metal dichalcogenides.^{29,53} The gap value of 2D B_2S_3 is 3.75 eV as obtained by HSE and 2.68 eV by PBE. The HSE corrections to the PBE results happen to both valence and conduction bands. Comparing with the PBE bands, the valence band maximum (VBM) is shifted downwards for 0.70 eV and the conduction band minimum (CBM) upwards for 0.38 eV by HSE functional. The overall effect increases the band gap significantly for 1.08 eV. The bands around both VBM and CBM exhibit very flat feature. By fitting the bands



around VBM and CBM to quadratic polynomials, we found that the effective masses of electrons and holes are $7.062 m_e$ and $6.443 m_e$. The large effective masses indicate low mobilities of both electron and the holes in this 2D material. By analyzing the projected density of states (PDOS) as shown in Fig. 2b, we found that the states around the VBM consist of mainly the S $3p$ orbitals, whereas the states around the CBM both B $2p$ and S $3p$. The differences of PDOS between boron and sulfur atoms in different symmetry groups are very small.

In Fig. 2c, the band structure for r-BN is plotted along the high symmetry lines of the Brillouin zone. Although also an insulator, r-BN possesses a band gap that is considerably smaller than that of h-BN. The HSE and PBE gap values are 4.75 eV and 3.41 eV, respectively. Similar to the case of B_2S_3 , the HSE functional shifts both the VBM and CBM toward larger gap for 0.79 eV and 0.56 eV, respectively. Comparing with B_2S_3 , r-BN shows larger dispersions for both the bands around the VBM and around the CBM, which are comparable to those in h-BN. The effective masses of electrons and holes are calculated to be $0.599 m_e$ and $0.998 m_e$. These values are close to those in h-BN, which are $1.175 m_e$ and $0.792 m_e$.²⁹ This result suggests that the large structure modification from h-BN to r-BN does not cause large change of the carrier mobility. Compare with r-BN, the effective masses of electrons and holes are much larger. This is likely originated from the sparse bonding network in B_2S_3 . The fact that the B-S bond length is 25.5% larger than that of B-N may contribute significantly to this effect.

The band structure of r-graphene is presented in Fig. 2d. Because the HSE functional only makes a slight change to the ground state charge distribution, so we assume that the energy difference between the average electrostatic potential of r-graphene and the vacuum level is the same for both PBE and HSE calculations. Therefore, the band structures of r-graphene calculated using PBE and HSE are aligned as shown in Fig. 2d. The energy difference between the PBE and HSE Fermi levels is obtained directly from the calculated Fermi energies of the two cases. r-graphene shows distinguish features in its band structure while comparing with graphene. First, the band structure shows a Dirac point along the Γ -X line. The hexagonal symmetry of graphene was originally thought to be necessary for the presence of Dirac points. However, several 2D carbon allotropes that are not hexagonal symmetric were shown to possess Dirac points,²¹⁻²³ recently. r-graphene adds another example that the presence of Dirac points does not depend on the hexagonal symmetry. Different to graphene, the Dirac point of r-graphene does not locate on the Fermi level. This is true for both PBE and HSE results. $E_\Gamma - E_d$, the difference between the energy of Fermi level and the energy at Dirac point, is calculated to be 0.061 and 0.079 eV using PBE and HSE, respectively. The DOS is not zero at the Fermi level, but a small value. While inspecting the band structure, we found this is caused by the intersection of the Fermi level with a valence band at a point along the Γ -X line and right to the Dirac point. This feature can be seen in both PBE and HSE bands. It is not very clear to us what causes the increase of energy for these

maximum-point states along the Γ -X line (closer to X) which exceeds the energy of the Dirac point. It may related to the presence of 4-membered rings in this structure, since the wavefunctions of the maximum-point states are largely localized around the 4-membered rings, whereas the wavefunctions of the states at the Dirac point are localized more around the 6-carbon rings. This unique feature of the r-graphene leads to self-doping of the material. Therefore, r-graphene contains electron carriers even without n-type doping or electron transfer from the side group. Meanwhile, massive holes will be present as charge carriers in the valence band.

Not only are the band gaps important. While forming heterojunctions, the band edge energies determine the band offsets of adjacent semiconductors. Band edges states are also the important factors determining the photolysis capability. We thus calculated the band edges of B_2S_3 , r-BN and r-graphene, by aligning the electrostatic potentials at the 2D atomic sheet and the void region far from the atomic layer, representing the vacuum. A potential average in the atomic plane and a running average in z direction was performed in order to smooth the rapid variation of the potentials. Both the HSE and PBE results are plotted in Fig. 3. Comparing with HSE, the electron affinities (CBM) are overestimated and the ionization energies (VBM) are underestimated by PBE functional. Thus, the PBE band gaps are reduced by both of these two factors. The HSE gaps agree well with available prior experimental studies. For example, the band gap of g- C_3N_4 is estimated to be 2.7 eV by ultraviolet-visible spectrum,¹⁵ and the calculated band gap for g- C_3N_4 in this work is 2.8 eV.

Comparing with other members of the 2D materials such as h-BN, graphene and g- C_3N_4 , B_2S_3 has a unique band gap of 3.75 eV. It is in the energy range of blue to UV lights that not any other 2D materials can absorb. More interestingly, B_2S_3 has a conduction band edge very close to g- C_3N_4 ; however, its VBM is much lower. Although the band edge states of g- C_3N_4 straddle the water redox potential,¹⁵ its VBM is only slightly lower than the O_2^-/O_2 potential. It needs to be noticed that B_2S_3 can react with water while exposed. However, it might be contained by other more stable materials such as BN or graphene. r-BN has a similar ionization energies to h-BN, but its electron affinity is 0.72 eV larger. Both graphene and r-graphene are metals, and their Fermi levels relative to Vacuum is very close.

Conclusions

In this work, we propose the possibility of attaining a new 2D material, B_2S_3 , based on its layered crystal structure of bulk B_2S_3 . Using advanced hybrid functional, we found that the band gap of B_2S_3 is 3.75 eV. Comparing with g- C_3N_4 , the larger gap of B_2S_3 mainly comes from the lower VBM (about 1.05 eV) and their CBM values are very close. By filling the vacancy sites in the B_2S_3 structures, we constructed h-BN and graphene allotropes, r-BN and r-graphene, that cannot transform into common structure through simple paths. These allotropes all possess unique electronic structures. r-BN is an insulator with a

gap that is significantly smaller than that of h-BN. r-graphene exhibits a Dirac point that is slightly below its Fermi level. Therefore, it is a self-doped metal containing both ‘massless’ electron and massive holes.

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Notes and references

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We propose a single layer B_2S_3 as a new potential 2D material conceived directly from its existing layered 3D crystal. New 2D BN and graphene allotropes are constructed from B_2S_3 .

