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Two-Dimensional Borane with 'Banana' Bonds and Dirac-Like Ring *

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Designing new two-dimensional (2D) semiconductors with novel topological characters is highly desirable for further material innovation. We propose a theoretical design of a stable 2D inorganic material, namely, borane, which is jointly stabilized by traditional B–B localized and unique B–H–B delocalized chemical bonds. In borane, the bonding natures along different directions are distinguishing, which lead to huge differences in mechanical strengths of 142.73 and 97.47 N/m for a and b directions, respectively. In a unit cell, each hydrogen atom binds to two boron atoms forming a three-center-two-electron (3c-2e) bridge bond B–H–B. This can be considered as an extension of diborane molecules from 0D to 2D. The collaboration of localized and delocalized chemical bonds endows borane with high structural stability, as indicated by its favorable cohesive energy, high mechanical strength, absence of imaginary modes in the phonon spectrum, and moderate melting point. Remarkably, borane has a fascinating electronic property featured with a Dirac-like ring in the electronic band structure. The unique bonding nature and electronic property in borane would attract intensive interests in both theory and experiment.

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As one of the most important and popular elements, boron (B) has huge flexibility to participate in varied multicenter bonding due to its electron-deficient property,[1,2] resulting in the formation of many allotropes that have already been realized experimentally. [3−9] With hydrogen, B can form a series of molecules called boranes.[10,11] The simplest isolable borane is diborane (B_2H_6), which has been extensively studied and is one of the most synthetically useful chemical intermediates.[12−14] In its ground state, diborane adopts a D_{2h} configuration containing four terminal and two bridging hydrogen atoms. The bonds between boron and the terminal hydrogen atoms are conventional two-center-two-electron (2c-2e) B–H covalent bonds, leaving a total of four electrons to share between the two bridging H atoms and the two B atoms. Consequently, two three-center B–H–B bridge bonds are formed, each of which consists of two electrons. The 3c-2e B–H–B bond is also known as a 'banana' bond as it is not linear but bent. This kind of bond also exists in other larger boranes and plays an important role in stabilizing these molecules.[15]

Designing new materials is always desirable for the promise of new properties and potential applications, and it would be particularly interesting when the material contains some peculiar topological properties, such as reduced dimensionality and novel chemical bonding. This is because unique geometry structures could probably lead to exotic physicochemical properties. In recent years, inspired by the intensive studies of graphene[16,17] and inorganic two-dimensional (2D) materials,[18−20] there have been several theoretical efforts on designing 2D structures that contain rule-breaking chemical bonding, such as planar hypercoordinate carbon,[21−25] planar hypercoordinate silicon,[26−28] and planar hypercoordinate transition metals.[29] With quite unique structural properties, these 2D materials can present some rather intriguing electronic and mechanical properties. For example, Wang *et al.* recently reported the design of a novel inorganic 2D material, namely, Be_5C_2 monolayer, in which each C atom binds to five beryllium atoms to form a planar-pentacoordinate-carbon (ppC) moiety.[30] Especially, Be_5C_2 monolayer is semimetallic and has an unusual negative Poisson's ratio, which is promising for wide applications in electronics and mechanics.

The highly sought after 2D structures with rule-breaking chemical bonding and the recent progress on fabricating 2D borophene[31−33] promote us to ask an interesting question: Is it possible to extend the novel 3c-2e B–H–B bond into periodic solids? The address of this issue would probably deliver some unique structures as well as some intriguing properties, which is of theoretical and practical importance. To our best knowledge, neither experimental nor theoretical attempt in this regard has been reported.

Inspired by the bonding nature of diborane molecular, in this Letter we design an inorganic 2D material, namely borane, on the basis of comprehensive density functional theory (DFT) computations. In a unit cell of borane, each H atom binds to two B atoms to form a 3c-2e B–H–B bridge bond. *Ab initio* molecular dynamics (*ab initio* MD) simulations reveal that borane is kinetically and thermodynamically stable, and its high mechanical strength endows the possibility of experimental realization at room temperature. Especially, borane is a semi-metallic material, which

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has an intriguing character of the Dirac-like ring.

Our DFT computations based on first-principles were carried out using the plane-wave technique implemented in the Vienna *ab initio* simulation package (VASP).[34] The ion-electron interaction was described using the projector-augmented plane wave (PAW) approach.[35,36] The generalized gradient approximation (GGA) expressed by the PBE functional[37] and a 460 eV cutoff for the plane-wave basis set were adopted in all computations. We adopted a vacuum thickness of 20 Å in the z-direction. The geometry optimizations were performed using the conjugate gradient method, and the convergence threshold was set to be 10^{-5} eV in energy and 10^{-4} eV/Å in force. The Brillouin zone was represented by a Monkhorst-Pack special k-point mesh of $6 \times 10 \times 1$ for geometry optimizations. As standard DFT methods systematically underestimate the band gaps of semiconducting materials with small- or medium-gaps, thus the HSE06 screened hybrid functional was always utilized.[38,39] Since borane is a zero-gap semiconductor, the HSE06 is not necessarily more reliable than the conventional PBE result. At this point, for comparison, both the PBE and HSE06 methods are used and the results are presented in this work. Moreover, the effect of the van der Wals force is very weak and is not considered in this work. The phonon spectrum was computed using the finite displacement method[40] as implemented in phonopy codes.[41] *Ab initio* MD simulations were performed to assess the thermal stability of borane. The PAW pseudo-potential and PBE functional were used, as implemented in VASP software. The initial configuration of borane was annealed at different temperatures. At each temperature, the *ab initio* MD simulation in NVT ensemble lasts for 30 ps with a time step of 1.0 fs. The temperature was controlled using the Nosé–Hoover method.[42]

Our design of 2D borane was initially inspired by the diborane molecule (Fig. 1(a)), in which the central B_2H_2 ring is held together by two 3c-2e B–H–B bonds. Following this hint, we constructed several possible structures of borane (Fig. S1), which can be seen as 2D networks of the D_{2h}-B_2H_2 rings. Figure 1(b) presents the optimized atomic structure of the most stable 2D borane, which consists of one B atomic layer sandwiched between two H atomic layers. Borane has a rectangular unit cell with the lattice constants a and b being 5.30 and 3.00 Å, respectively. One unit cell of borane consists of four B atoms and four H atoms, resulting in a formula of BH for the 2D network. Therefore, borane is isoelectronic to graphene and can be seen as obtained by replacing the C–C dimers in graphene with B_2H_2 rings. In borane, each B atom binds to two B atoms and two H atoms while one H atom is shared by two B atoms. The B–H length in borane is 1.33 Å, which is quite close to that of diborane molecule computed at the same theoretical levels. The B–B lengths between two B_2H_2 rings and within a B_2H_2 ring are 1.82 and 1.72 Å, respectively. According to the Hirshfeld charge population analysis, the net charges on B and H atom are -0.02—e— and 0.02—e—, respectively, indicating that the bonding between B and H atoms is mainly of covalence. Moreover, a spin-polarized computation was also performed to determine the ground state of borane. However, there is no energy difference between spin-polarized and spin-unpolarized computations, indicating that borane has a nonmagnetic ground state and all electrons are paired.

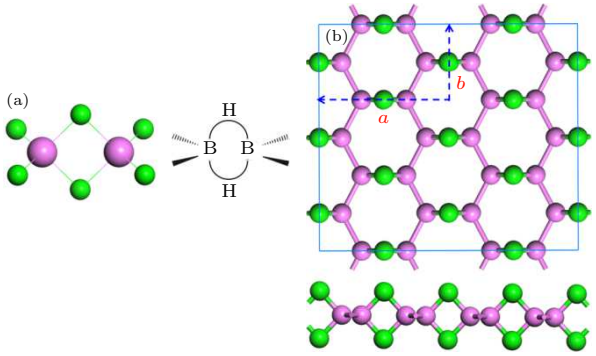

Fig. 1. (a) Geometry structure of diborane molecule (left) and a D_{2h}-B_2H_2 motif structure (right). Pink and green balls represent B and H atoms, respectively. (b) Top (upper) and side (bottom) views of geometric structure of 2D borane. The blue dashed lines denote a unit cell, a and b represent the lattice vectors.

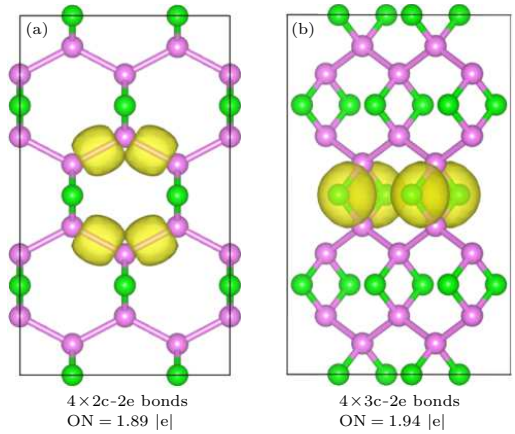

Fig. 2. Schematic of SSAdNDP chemical bonding pattern for a unit cell of borane. 'ON' is short for occupation number. The iso-surface value is $0.12e/\text{Å}^3$.

The chemical bonding pattern of borane was then analyzed utilizing the recently developed solid-state adaptive natural density partitioning (SSAdNDP) method,[43] which can well interpret the chemical bonding patterns in terms of classical lone pairs, 2c-2e bonds, as well as multi-center delocalized bonds in bulk solids, surfaces, and nanostructures. Since B has three valence electrons while H has only one valence electron, thus there are sixteen valence electrons in one unit cell of borane. According to our computational results, there are four 3c-2e B–H–B bonds (responsible for the bonding within B_2H_2 rings) and four 2c-2e B–B bonds (responsible for the bonding between B_2H_2 rings) in one unit cell of borane, accounting for 16 valence electrons (Fig. 2). Specifically, one B atom of borane is involved in two 2c-2e B–B bonds and two 3c-2e B–H–B bonds. The occupation numbers of 2c-2e and 3c-2e bonds are 1.89 and 1.94$|e|$, respectively. The above results reveal that the B atom in borane

actually has the same bonding nature as that of the B atom in the diborane molecule.

Then, is borane a stable structure? We calculated the cohesive energy of borane by $E_{\rm coh} = (4E({\rm Be}) + 4E({\rm H}) - E({\rm Be_4H_4}))/8$, where $E({\rm Be})$, $E({\rm H})$ and $E({\rm Be_4H_4})$ represent the energies of the isolated Be, H atom, and Be_4H_4 monolayer, respectively. According to the definition, it means that a higher $E_{\rm coh}$ represents a higher stability. Our computations reveal that the cohesive energy of borane is as high as 4.72 eV/atom, which is 1.05 eV/atom larger than that of the all-N 2D nitrogen (3.67 eV/atom),[31] intermediate between those of the silicene (3.99 eV/atom) and graphene (7.96 eV/atom) at the same theoretical level. Although it is hard to identify the stability of materials by directly comparing the cohesive energies, a high cohesive energy of 4.72 eV/atom is a direct proof that borane is a strongly bonded 2D crystal.

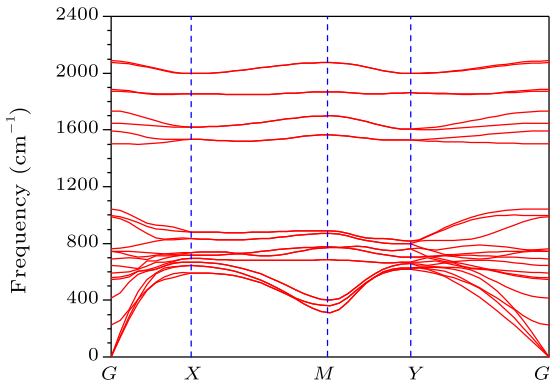

Fig. 3. Phonon spectrum of 2D borane.

Mechanically, a stable tetragonal 2D structure should meet the following criteria: $C_{11}C_{22} - C_{12}^2 > 0$, $C_{66} > 0$, where C_{ij} are the elastic constants. We hence computed the elastic constants of borane to examine its mechanical stability. According to our computations, the elastic constants of borane are $C_{11} = 151.85$ GPa, $C_{22} = 103.70$ GPa, $C_{12} = C_{21} = 30.75$ Pa, and $C_{66} = 59.67$ GPa, which comply well with the mechanical stability criteria. The in-plane Young's modulus along (Y) for borane, which can be deduced from the elastic constants by $Y_a = (C_{11}C_{22} - C_{12}C_{21})/C_{22}$ and $Y_b = (C_{11}C_{22} - C_{12}C_{21})/C_{11}$, are 142.73 and 97.47 N/m for a and b directions, respectively. Computed at the same levels of theory, the in-plane Young's moduli of borane are about 40% and 27% of that of graphene ($Y = 355.35$ N/m), while much higher than those of silicene ($Y_a = Y_b = 71.2$ N/m)[44] and phosphorene ($Y_a = 101.60$ N/m, $Y_b = 28.94$ N/m),[45] indicating that borane has high mechanical strength.

The stability of borane can be further confirmed by computing its phonon dispersion curves. As shown in Fig. 3, there is no appreciable imaginary mode in the phonon spectrum, indicating the high kinetic stability of borane. Remarkably, the highest frequency of borane is ~2100 cm^{-1}, higher than the highest frequency of ~1600 cm^{-1} in graphene[46] and ~1200 cm^{-1} in the experimentally realized 2D borophene,[47] indicative of robust B–H–B bonds in borane. Moreover, the *ab initio* MD at a temperature of 298 K was performed to access the thermodynamic stability of borane. Snapshots of the geometric structure of borane at the end of each *ab initio* MD simulation are presented in Fig. S2. Our computations demonstrated that the structure of borane can be well kept throughout a 30 ps *ab initio* MD simulation up to 298 K, but collapses at 1000 K, suggesting good thermodynamic stability for borane. Moreover, we also performed geometry optimizations for the structures from *ab initio* MD simulations. After full atomic relaxation, the structures from *ab initio* MD simulation at 298 K can easily recover the initial configuration of borane, indicating that borane has rather good phase stability.

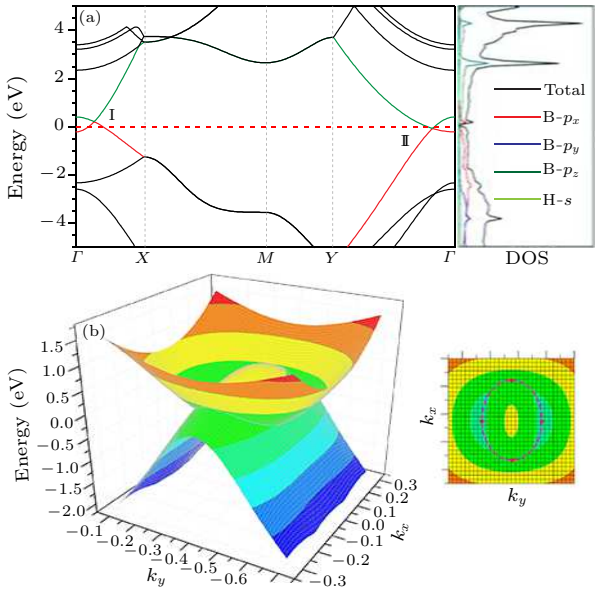

Fig. 4. (a) Electronic band structure (left) and density of states (right) of borane. The red and green lines stand for the valence and conductance bands for borane monolayer, respectively. The black dashed line denotes the position of Fermi level. I and II label two distorted Dirac-like cones. (b) The 3D band structure of borane (left). The fermi level is set at 0 eV. Top view of the 3D band structure (right). The violet ellipse represents the Dirac ring between the valence and conductance bands.

Being isoelectronic to graphene, could borane present different electronic properties from those of graphene? To answer this question, we computed the electronic band structure of borane using the hybrid HSE06 functional. As shown in Fig. 4(a), borane is semi-metallic without an appreciable band gap. The conduction and valence energy levels meet at the Fermi level and show two distorted Dirac-like cones along the G–X (cone-I) and Y–G (cone-II) paths. Specifically, the cone-I is 134 meV above the Fermi level while the cone-II is 130 meV below the Fermi level. The dispersion of those energy levels at the two Dirac-like cones is quite linear in both G–X and Y–G directions. For cone-I, the slopes of two involved bands, i.e., the first derivatives of the band energies in reciprocal space are equal to −14 and 32 eV/Å, which are comparable with those in graphene (±34 eV/Å). For cone-II, the slopes of two involved

bands are −10 and 27 eV/Å, which are slightly less than those of cone-I. Quite recently, Ma *et al.* reported that 2D ionic boron has similar electronic properties to borane.[48]

The density of states of (DOS) of borane were computed to obtain deeper insight into its electronic properties. As shown in Fig. 4(a), the DOS is zero near the Fermi level, which further supports the presence of the Dirac-like cones. The partial DOS analysis shows that the states at Fermi level are mainly contributed by the p_x and p_z orbitals of B atoms. To elucidate the origin of Dirac-like cones, we also computed the partial charge densities corresponding to the highest occupied electronic state (HOES) and the lowest unoccupied electronic state (LUES) at two Dirac-like cones (Fig. S3). For cone-I, the HOES is localized at B–B and B–H–B bonds while the LUES is mainly contributed by the B–B bonds. In contrast, both the HOES and LUES of cone-Ⅱ correspond solely to the B–B bonds.

Moreover, as elaborated in Fig. 4(b), we also plotted the 3D band structure of borane to give a more intuitive picture of the Dirac-like cones. Remarkably, the band crossings with linear dispersions along G–X and Y–G directions form a semi-closed ring in the Brillouin zone, namely, a Dirac-like ring. The Dirac-like ring observed in low-dimensional structures is quite unusual and could lead to novel electronic properties and important applications. For example, Lee *et al.*[49] suggested that materials with a Dirac-like ring can exhibit much stronger nonlinear electromagnetic response than ordinary Dirac cone materials (e.g., graphene). The features of borane open new possibilities for electronic applications of boron-based two-dimensional materials and derived nanostructures.

With such fascinating electronic properties, it is desirable to realize borane in the laboratory. A promising approach is to grow borane on the substrate via polymerization of diborane molecules, just similar to the growth of silicene[50] and borophene[31–33] on the surface of metals. In this case, the lattice constant mismatch between borane and the substrate could hardly be avoided, which could consequently induce an external strain. To investigate whether the Dirac-like cones can remain under the external strains, we also computed the band structures of strained borane. According to our computations, the electronic properties of the monolayer are rather robust in response to the external strains. The Dirac-like cones can be well preserved with a biaxial strain up to ±5% while the positions of the cones are slightly changed (Fig. S4).

To summarize, inspired by the unique bonding nature of diborane molecules, we designed a new inorganic 2D crystal of borane by systematic DFT computations. In borane, each boron atom is involved in two 3c-2e B–H–B bridge bonds, which is confirmed by the SSAdNDP analysis. Our DFT computations demonstrated that borane is a stable 2D structure, as indicated by its favorable formation energy, moderate melting point, high mechanical strength, and absence of imaginary modes in the phonon spectrum. Particularly, borane has rather intriguing electronic properties featured with a Dirac-like ring in the electronic band structure. With the development of experimental techniques for fabrication of 2D materials, it would be desirable to confirm the existence of borane in the laboratory.

Supplementary material: The online version of this study contains supplementary material, which is available to authorized users. The optimized structures and relative energies of three possible configurations of boranes, snapshots of FPMD simulations, the partial charge densities corresponding to the highest occupied electronic state and the lowest unoccupied electronic state at two Dirac cones, band structures of strained borane.

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Supplementary Material: Two-dimensional borane with “banana” bonds and Dirac-like ring*

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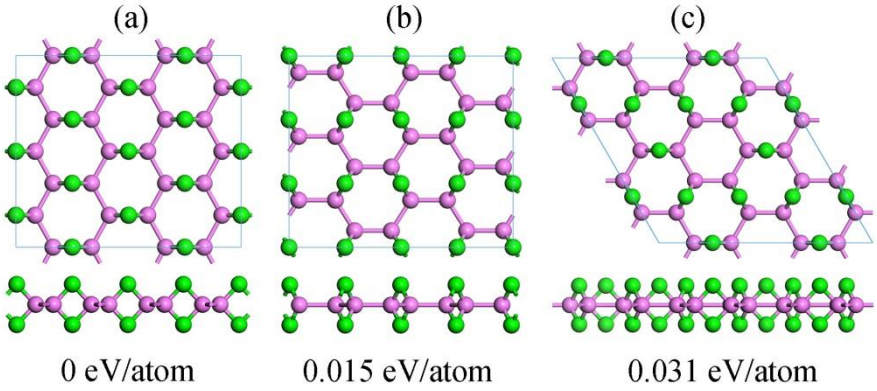
Figure S1: The optimized structures and relative energies of three possible configurations of boranes.



* The online version of this article contains supplementary material, which is available to authorized users. The optimized structures and relative energies of three possible configurations of boranes, snapshots of FPMD simulations, the partial charge densities corresponding to the highest occupied electronic state and the lowest unoccupied electronic state at two Dirac cones, band structures of strained borane.

Figure S2: Snapshots of the geometry structure of borane at the end of each *ab*-initio MD simulation at a temperature of (a) 298 K and (b) 1000 K are presented to access the thermodynamic stability.

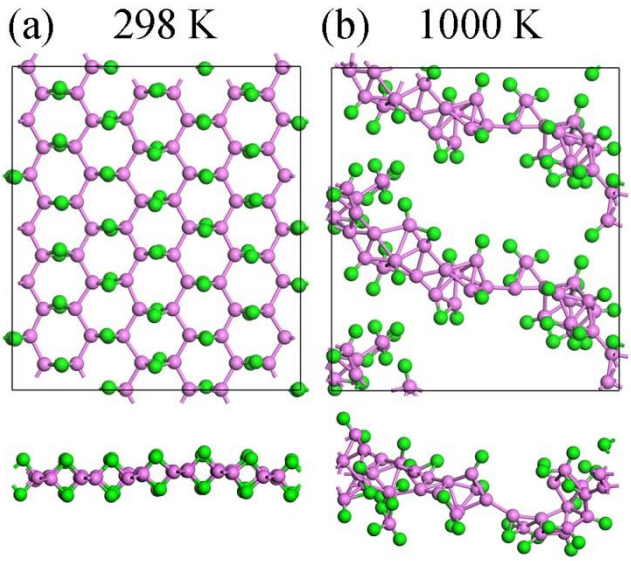


Figure S3: (a) Electronic band structures and (b) partial density of states of borane at the HSE06 level. Top and side view of the partial charge densities plots of the valence band maximum and conduction band minimum. The iso-value is 0.01 e $Å^{-3}$.

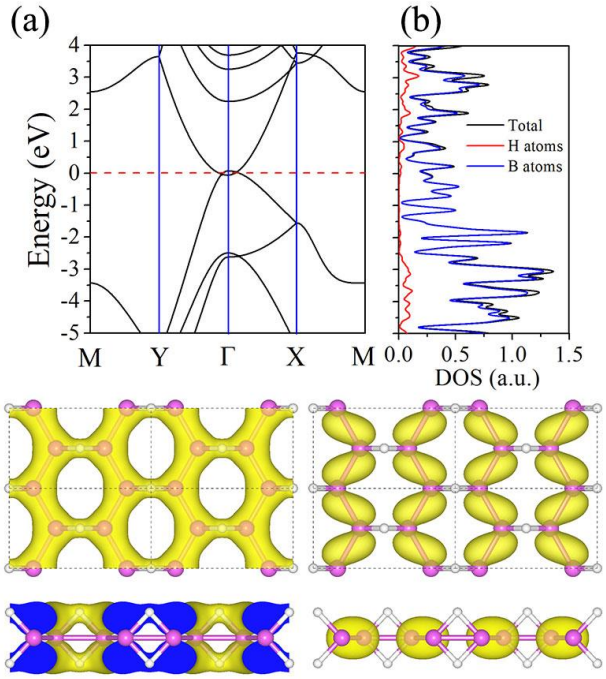
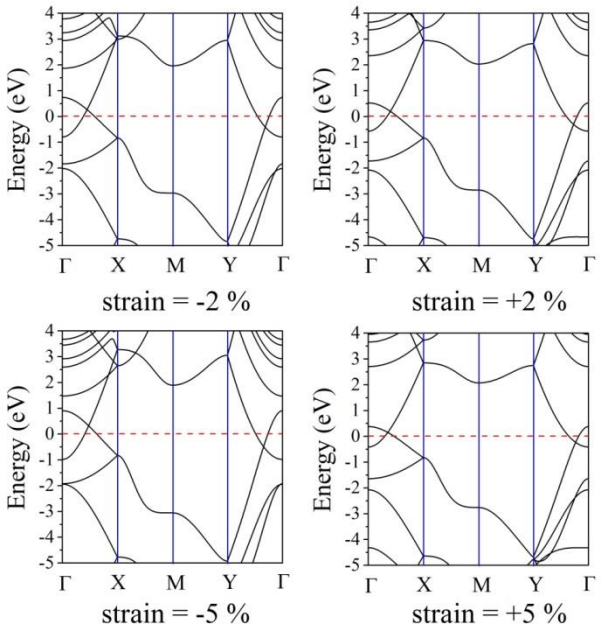



Figure S4: Electronic band structures calculated at the PBE level with a biaxial strain of –5 %, –2 %, 2 % and 5 %, and indicating a rather robustness in response to the external strains.