Controlling quantum spin Hall state via strain in various stacking bilayer phosphorene

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Quantum spin Hall (QSH) state of matter has a charge excitation bulk bandgap and a pair of gapless spin-filtered edge-states, which can support backscattering-free transport. Bilayer phosphorene possesses a large tunable bandgap and high carrier mobilities, and therefore has the widely potential applications in nanoelectronics and optics. Here, we demonstrate an strain-induced electronic topological phase transition from a normal to QSH state in bilayer phosphorene accompanying by a band inversion that changes $\mathbb{Z}_2$ from 0 to 1, which is highly dependent on the interlayer stacking. When the bottom layer is shifted by 1/2 unit cell along axial direction with respect to the top layer, the topological bandgap reaches up to 92.5 meV, which is sufficiently large to realize the QSH effect at room temperature. Its optical absorption spectrum becomes broadened, and even extends to the far-infra-red region leading to a wider range of brightness, which is highly desirable in optic devices.
Two dimensional (2D) topological insulator (TI), namely, the quantum spin Hall (QSH) insulator, has charge excitation bulk energy gap and a pair of gapless spin-filtered edge states with a Dirac-cone-like linear energy dispersion\textsuperscript{11}. The special edge states are topologically protected by the time reversal (TR) symmetry and can immune to nonmagnetic scattering and geometry perturbations, thus open new ways for backscattering-free transport. Such systems have stimulated enormous research activity in condensed matter physics due to their novel quantum spin Hall effect and hence the potential application in quantum computation and spintronics\textsuperscript{2,3}.

Phosphorene, a new two-dimensional (2D) material, has been successfully isolated by mechanical exfoliation\textsuperscript{4} and gained rapidly attention\textsuperscript{5–12}. Unlike graphene, phosphorene takes a puckered non-planar structure although it is composed of the basic hexagon as shown in Fig. 1(a). Phosphorene is chemically inert and has great transport properties with high carrier mobilities (around 1000 cm\textsuperscript{2}/V·s) and drain current modulation (four orders of magnitude larger than that in graphene)\textsuperscript{5,6,13}, which makes the phosphorene a potential candidate for future nanoelectronic applications\textsuperscript{5}. Furthermore, phosphorene has been predicted as an ideal direct band-gap material at the $\Gamma$ point of the first Brillouin zone\textsuperscript{8,14}, which is very important for electronic and optical application. A large number of 2D buckled honeycomb structures have been predicted in nontrivial QSH states by the first-principle calculations, including bilayers of group III elements with Bi\textsuperscript{15}, 2D stable dumbbell stanene\textsuperscript{16}, and so on\textsuperscript{15–18}. It is reasonable to ask whether or not a trival insulator phosphorene can be a topological nontrivial insulator, which maybe largely improve its application on optical and transport properties. Manifestation of the nontrivial topology of occupied bands in a TI is attributed to band inversion (BI) between occupied and unoccupied bands at
the time reversal invariant momenta (TRIM) in the bulk Brillouin zone by large enough spin-orbit coupling \cite{19,20}, or external strain \cite{21,22}. There are two common approaches to create or annihilate the TI states \cite{23}: (1) To undertake chemical tuning but often entails uncontrolled effect of chemical disorder, (2) To change the band topology of a physical system by adjusting lattice constants or internal atomic positions in the unit cell \cite{21,24}, which is an accepted way for phosphorene due to its highly sensitive of band gap to external strain. Different from monolayer phosphorene, few-layer phosphorene with weak interlayer van der Waals (vdW) interaction has various interlayer stacking orders, which can provide an exciting approach to tuning their optical and electronic properties. Further, few-layer phosphorene has the smaller tunable bandgap by external strain, and thus it was the more likely to exhibit band inversion and the ensuing topological insulator behavior. And bilayer phosphorene is the thinnest multilayer system, which can provide fundamental information on the interlayer interaction, and the stacking-dependent electronic and optical properties, a feature akin to the bilayer graphene systems \cite{25–27}.

In this work, we explore the possibility of converting normal insulating state into QSH one in bilayer phosphorene, through a systematic investigation of electronic structure on interlayer stacking and external strain. Our results reveal that the tuning of topological behavior in bilayer phosphorene is highly dependent on interlayer stacking order and the direction of the applied in-plane strain, i.e., the direction with the maximum atomic wavefunction overlap. Meanwhile, reversible direct to indirect and semiconductor to metal transitions can be found by adjusting the weight of vdw. The optical property of the QSH in bilayer phosphorene is examined based on a real-space and real-time time-dependent density functional theory, which proves that the absorption spec-
trum becomes broadened, and even extends to the far-infra-red region and leads to a wider range
of brightness. Such improvement in optical responds property is highly desirable in broadband
photodetection and infrared detector.

Results

Crystal structures and electronic structures of bilayer phosphorene for four different stack-
ing orders. Bulk black phosphorus belongs to the space group Cmca, and phosphorene can been
viewed as cleaved from the (0001) surface of black phosphorus. Bilayer phosphorene is held to-
gether by weak interlayer forces with significant van der Waals character, which allows formation
of several polytypes due to the possibility of different stacking. In this study we consider four
possible high-symmetry stacking orders: (1) the top layer is stacked vertically on the bottom layer
in the Pmna (Ta), (2) the bottom layer is shifted by half of one unit cell along x or y with respect to
the top layer in the Pbcm (Tb), (3) the bottom layer is shifted by one unit cell along x or y direction
with respect to the top layer, and thus the top and bottom layers are mirror images of each other
in the Pnma (Tc), (4) the bottom layer is shifted by one and a half of one unit cell along x or y
direction with respect to the top layer in the Pccm (Td), as shown in Fig. 1(c)-1(f), respectively.
Table 1 gives the optimized lattice constants, bond length and other structural parameters of bilayer
phosphorene for the four stacking orders, which are well consistent with the previously theoretical
data\textsuperscript{28} with errors lower than 0.5%. For the different stacking order, the bond length $R_1$ is almost
same as the bond length $R_1'$ but always shorter than the bond length $R_2$. The bond angles $\alpha$ is shorter
than the $\beta$. The smallest layer interval $d_{int}$ in the vertical direction is 3.503 Å (Ta), 3.085 Å (Tb),
3.739 Å (Tc) and 3.291 Å (Td). Our total energy calculations indicate that the Ta-, Tb-, Tc- and Td-stacked orders have same structural stability with the difference of the cohesive energy below 10 meV. (The stability of Tb-stacked order is proved in the supplementary information, which has the lowest cohesive energy.)

Fig. 2 gives the electronic structures for the four stacking orders. The band gaps at Γ are 0.434 eV (Ta), 0.442 eV (Tb), 0.264 eV (Tc) and 0.002 eV (Td). Since our HSE06 band structures have indicated that these PBE band gaps are underestimated by ~ 0.56 eV (see Supplementary Fig. S2), thus all four stacking orders should have a band gap in excess of 0.56 eV, which agrees with the previously theoretical data using the same method. The iso-surfaces of the band-decomposed charge density at Γ point of the valence band maximum (VBM) and conduction band minimum (CBM) for the four stacking orders are shown in Fig. 2(e)-(h), respectively, which show very similar charge density distribution, and thus they have very similar bonding character. A prominent in-plane anti-bonding-like feature of VBM (marked by blue dashed box) and in-plane bonding-like features of CBM (marked by red dashed box) are shown for each four stacking order. The similar out-plane bonding and out-plane antibonding features are also found in the CBM and VBM, respectively. We observe the overlap of layer-layer charge density of CBM in Tc- and Td-stacked orders, showing the bonding-like character, which is absent in Ta- and Tb-stacked orders. We can expect that VBM and CBM are mainly originated from the localized and delocalized states of P atoms, respectively, in the interfacial area between the top and bottom layers. Hence, the different interaction strength and band gaps are related to the different π-π interaction distance between the delocalized states, which due to the different stacking order.
**x-y plane strain-induced quantum spin Hall state in bilayer phosphorene.** The band gap $E_g$ changes with the in-plane strain $\sigma$ of bilayer phosphorene for four stacking orders are shown in Fig. 3. We consider three types of in-plane strains $\sigma_x$, $\sigma_y$ and $\sigma_{xy}$ along x direction, y direction, and both x and y directions, respectively. When the strain is applied in given direction, the lattice constants in the other directions are relaxed fully through the technique of energy minimization in order to ensure that the force on atoms is less than 0.01 eV/Å. Our calculation shows that all four orders are highly anisotropic. Band gaps of four stacking orders are highly sensitive to in-plane strain, where the band gap is more sensitive to $\sigma_{xy}$ as compared with those of strains $\sigma_x$, $\sigma_y$. Hence, for the remainder of this study, we mainly focus on the effect of $\sigma_{xy}$ on band gap in Fig. 3. When $\sigma_{xy}>0$ (tensile), we can find the band gaps increase with $\sigma_{xy}$ increasing, then turn to decrease at $\sigma_{xy} = 4.0\%$ (Ta) and $\sigma_{xy} = 3.0\%$ (Tb). When $\sigma_{xy}<0$ (compression), or near zero strain for Td-stacked order, the band gap decrease with $\sigma_{xy}$ increasing, then turn to increase at $\sigma_{xy} = -3.0\%$ (Ta and Tb), and $\sigma_{xy} = 0.02\%$ (Tc). This corresponding BI process, as shown in inset in Fig. 3(d), indicates a possible topological phase transition. The direct-indirect band gap transition can be found when $\sigma_{xy}=-2.0\%$ in Tc- and Td-stacked orders. With the further compression strain increasing, The band gaps are closed and turn into metal states when $\sigma_{xy}=-7.0\%$ (Tb), $\sigma_{xy}=-3.0\%$ (Tc), and $\sigma_{xy}=-5.0\%$ (Td).

In Fig. 4(a)-(c), we further analyze the electronic band structures for Tb-stacked order at $\sigma_{xy}$ values. We note that, as $\sigma_{xy}$ increases, its VBM and CBM start approaching each other and then overlapping when $\sigma_{xy} = -2.77\%$. For stronger compression strain ($\sigma_{xy}=-3.0\%$), repulsion between the electronic bands leads to shift VBM at $\Gamma$ and CBM at $\Gamma$ away from each and enlarges
the band gap, accompanied by the inversion of the top of valence and bottom of the conduction band at the \( \Gamma \) point. The band parity also change its sign due to BI. Such band-inversion character is also observed in the density of states (DOS) and the orbital-projected band structures when \( \sigma_{xy}=-3.0\% \) [see Fig. 4(e)-(g)]. The \( P - p \) makes a significant contribution to the total DOS, and the conduction band near \( E_F \) is from the \( p_z \) and \( p_y \) orbitals, while the valence band around \( E_F \) is mainly contributed by the \( p_z \) orbital. By observing the orbital-projected band structures under \( \sigma_{xy}=-3.0\% \), we find that the weight of \( p_z \) orbital is very large at the local region of CBM around \( \Gamma \) point. The weight of \( p_y \) orbital is significantly large at the local region of VBM around \( \Gamma \) point. This phenomenon shows a obvious BI process when the compression strain \( \sigma_{xy} \) is increased.

Here, we use a rigorous method of Fu and Kane\textsuperscript{29} to prove that Tb-stacked order when \( \sigma_{xy}=0 \) is a topologically trivial band insulator with \( \mathbb{Z}_2=0 \), while for larger compression strain \( \varepsilon_{xy}=-3.0\% \), it is in a nontrivial QSH state with \( \mathbb{Z}_2=1 \). The method is valid since the Tb-stacked bilayer has both spatial inversion and time reversal symmetries (four time reversal invariant points in the 2D Brillouin zone). Inversion center in the crystal ensures \( \varepsilon_{n\alpha}(k) = \varepsilon_{n\bar{\alpha}}(-k) \), where \( \varepsilon_{n\alpha}(k) \) is the electron energy for the \( n \)-th band with spin index \( \alpha \) at \( k \) wave vector in the Brillouin zone. The time reversal symmetry makes \( \varepsilon_{n\alpha}(k) = \varepsilon_{n\bar{\alpha}}(-k) \), where \( \bar{\alpha} \) is the spin opposite to \( \alpha \). The calculated parities of all occupied bands at four time-reversal invariant momenta are listed in Table 2. We can find the product of parities of occupied bands contributes a +1 at the four time-reversal invariant momenta when \( \sigma_{xy}=0 \), yielding a trivial topological invariant \( \mathbb{Z}_2=0 \). As the strain is increased up to \( \sigma_{xy}=-3.0\% \), band inversion at the \( \Gamma \) point takes place. The product of parities of occupied bands is -1 at \( \Gamma \) while +1 at the three other time-reversal invariant momenta. Thus the Tb-stacked
order under the compression strain $\sigma_{xy} = -3.0\%$ are identified as topological insulators with $\mathbb{Z}_2 = 1$. The results shown in Fig. 4(d) suggest that the QSH state in Tb-stacked order survives under the compression strain $\sigma_{xy}$ from $-2.77\%$ to $-7.0\%$, where the maximum band gap $E_g = 92.5$ meV can be found when $\sigma_{xy} = -5.0\%$. (The calculated critical strain $\sigma_{xy} = -5\%$ where Tb-stacked order is in quantum spin Hall state by HSE06 method, which is presented in Supplementary Fig.S3).

We do not observe the topological phase transition in Tc-stacked order because BI do not appears by adjusting in-plane strain. We also do not find topological phase transition in Td-stacked order because the VBM and the CBM have the same parity, which is not closely relate to the details of the atoms orbitals or bond types but implies different signs of overlap integral of the atomic orbitals. The detailed topological phase transition process for Ta-stacked order is given in supplementary information.

**Universal reversible semiconductor-metal transition by interlayer interaction.** We have employed a semi-empirical van der Waals (vdW) approach, as proposed by Grimme known as the DFT-D2 method to correctly describe the interlayer interaction between the top and bottom layers of bilayer phosphorene. The total energy of system is defined as $E_{DFT-D} = E_{KS-DFT} + E_{vdW}$, where $E_{KS-DFT}$ is the conventional Kohn-Sham DFT total energy and $E_{vdW}$ the total energy can be described via a simple pair-wise force field which is optimized for several popular DFT functionals. To focus on the effect of interlayer interaction in electronic structure, a scaling factor is added in the front of the $vdW$ term in the computations, referring as the weight of $vdW$ ($W_{vdW}$).

The dependence of the band gaps on $W_{vdW}$ for four different stacking orders are presented
in the Fig. 5(a). As compared with the monolayer phosphorene, the band gap of the bilayer phosphorene is smaller and each band becomes doubly degenerate at $W_{vdW}=0t$ ($t=1$ is the energy unit) as shown in Fig. 5(b) and (c), indicating the absence of chemical interaction between the top and bottom layers in Td-stacked order. As $W_{vdW}$ increases, the double degeneracy of the band is broken because the top and bottom layers start to bond together. The change of the band gap on $W_{vdW}$ is more strongly in Td-stacked order, compared with that of Ta-, Tb- and Tc-stacked orders. As shown the inset in Fig. 5(a), the band gap is closed when $W_{vdW}=\sim 1.05t$, then opens up again for the larger $W_{vdW}$, which indicates a BI process. The weight of $p_z$ in CBM has a clear saltation when $W_{vdW}=1.14t$, compared with that when $W_{vdW}=0t$ as shown in Fig. 5(b) and (c), proving BI of VBM and CBM. However, Td-stacked bilayer phosphorene can not be the topological insulator by adjusting $W_{vdW}$ because the parities of its VBM and CBM are the same. With the $wvdW$ further increasing beyond 2 $t$, the band gaps of all four structures are closed due to overlap of VBM and CBM, indicating that the four structures undergo semiconductor to metal transition. In the whole process, their band gaps have the large variation, but we do not observe any sign of topological phase transition, indicating topological phase transition can not be induced by $W_{vdW}$. Hence, we can expect that the topological phase transition is closely relationship with the direction of the applied strain, which would be the one along bonding direction, i.e., the direction with maximum atomic wave function overlap.

**Optical responds of Tb-stacked bilayer phosphorene under the $x-y$ plane train $\sigma_{xy}$.** According to the above discussion, we know the Tb-stacked bilayer phosphorene is in a nontrivial state when the compression strain $\sigma_{xy} = 3.0\%$, and have verified its stability by calculating the vibra-
As we know, phosphorene has promising optical properties. Here, we mainly study the optical responds of Tb-stacked bilayer phosphorene when $\sigma_{xy} = -3.0\%$ in order to make a compare.

As shown in Fig. 6 (b), the obtained photonic band gap (PBG) are 0.5 eV and 0.01 ev, respectively, when $\sigma_{xy} = -3.0\%$ and $\sigma_{xy} = 0$. The PBG is close to the band gap calculated by VASP, which means that OCTOPUS is reliable on calculation for the optical property. When the impulse excitation polarizes in the armchair-edge direction ($y$-direction) or the zigzag-edge direction ($x$-direction), there is always a main absorption peak around 10 eV, because there is only a $\sigma$ plasmon resonance mode in bilayer phosphorene. When the impulse excitation polarizes in the zigzag-edge direction, the main absorption peak when $\sigma_{xy} = -3.0\%$ becomes smaller and shows blue shift comparing to that when $\sigma_{xy} = 0$. This is because the resonance level spacing increases with the interatomic spacing increasing in the zigzag-edge direction. When the impulse excitation polarizes in the armchair-edge direction, the main absorption peak around 10 eV when $\sigma_{xy} = -3.0\%$ is almost unchange compared to that when $\sigma_{xy} = 0$. In the low-energy resonance zone from 0 eV to 2 eV, their strength of optical absorption for both $\sigma_{xy} = -3.0\%$ and $\sigma_{xy} = 0$ are nearly zero, when impulae excitation polarizes in the zigzag-edge direction. Meanwhile, the optical absorption are highly active in the energy band gap of bilayer phosphorene, when the impulse excitation polarizes in the armchair-edge direction. This phenomenon is the result of selection rules associated with the anisotropic symmetries of bilayer phosphorene. Interestingly, when the impulse excitation polarizes in the armchair-edge direction, compared with that when $\sigma_{xy} = 0$, the absorption spectrum is red-shift. Furthermore, we find a weak absorption closed to zero (0.01
eV) owing to the decrease in energy gap when $\sigma_{xy} = -3.0\%$. To elucidate the mechanism of the optical absorption in low-energy resonance behind the resonance phenomena, the induced charge response has been analyzed in real-time propagation, as shown in Fig. 6(c)-(f).

We analyze the induced charge density at the low-energy resonance zone. Fig. 6(c)-(f) presents the Fourier transform of the induced charge density when $\sigma_{xy} = 0$ and $-3.0\%$ along the armchair-edge direction and the zigzag-edge direction. We set the induced density plane to parallel the bilayer phosphorene plane, and to locate the middle of the top pucker-layer in the vertical direction. When the impulse excitation polarizes in the zigzag-edge direction, the induced electron density is separate from the induced hole density roughly, and they locate at the left side and the right side (seen in the black box and the white box), respectively, as shown in the Fig. 6(c) at $\sigma_{xy} = 0$ and 6(e) at $\sigma_{xy} = -3.0\%$. Hence, we can find a common characteristic that the induced charge at the most resonance points is distributed at the boundary region in Fig. 6(c) and 6(e). The induced charge density of $\sigma_{xy} = 0$ is more plentiful than at $\sigma_{xy} = -3.0\%$ by comparing Fig. 6(c) and 6(e). This phenomenon supports that absorption spectrum of $\sigma_{xy} = -3.0\%$ becomes weaker compared to $\sigma_{xy} = 0$. When the impulse excitation polarizes in the armchair-edge direction as shown in Fig. 6(d) at $\sigma_{xy} = 0$ and 6(f) at $\sigma_{xy} = -3.0\%$, the induced electron density is also separate from the induced hole density, but they locate at the up and down (seen the black box and the white box), respectively, as shown in the Fig. 6(d) at $\sigma_{xy} = 0$ and 6(f) at $\sigma_{xy} = -3.0\%$. Furthermore, the induced charge density of the $\sigma_{xy} = -3.0\%$ is richer and concentrated in the center of the bilayer phosphorene when the impulse excitation polarizes in the armchair-edge direction. What is because that the shielding effect becomes stronger with the interatomic spacing becoming smaller.
Discussion

we demonstrate an in-plane strain-induced electronic topological transition from a normal to QSH state in bilayer phosphorene, accompanying by a band inversion that causes the change in the $\mathbb{Z}_2$ topological invariant from 0 to 1. Our investigate shows that the topological phase transition in bilayer phosphorene is closely related to interlayer stacking and the direction of applying strain, which would be the one along bonding direction, i.e., the direction with maximum atomic wave function overlap. The topologically non-trivial bandgap in Tb-stacked bilayer phosphorene can reach up to 92.5 meV when $\sigma_{xy}=-5.0\%$, which is sufficiently large to realize the QSH effect at room temperature. Meanwhile, reversible direct to indirect and semiconductor to metal transitions can be found by adjusting the weight of vdW. The optical absorption spectrum of the QSH state in bilayer phosphorene becomes broadened, and even extends to the far-infra-red region and leads to a wider range of brightness, which is highly desirable in broadband photodetection and infrared detector.

Note added in proof: during the review process for this manuscript, we noted an theoretical work that in few-layer (> 2) phosphorene there will be a normal-to-topological phase transition induced purely by applying an electric field\textsuperscript{[13]}. However, the normal-to-topological phase transition in various stacking bilayer phosphorene has not yet been explored.
Methods

$\mathbb{Z}_2$ calculation technique. We use the method of Fu and Kane$^{29}$ to calculate topological invariant $\mathbb{Z}_2$. $H$ is a time-reversal invariant periodic Hamiltonian with $2N$ occupied bands characterized by Bloch wave functions. A time-reversal operator matrix relates time-reversed wave functions is defined by

$$A_{\alpha\beta}(\Gamma_i) = \langle \mu_\alpha(\Gamma_i) | \Theta | \mu_\beta(\Gamma_i) \rangle$$

where $\alpha, \beta = 1, 2, ..., N$, $| \mu_\alpha(\Gamma_i) \rangle$ are cell periodic eigenstates of the Bloch Hamiltonian, $\Theta = \exp(i\pi S_y)K$ is the time-reversal operator ($S_y$ is spin and $K$ complex conjugation), which $\Theta^2 = -1$ for spin 1/2 particles. Since $\langle \Theta \mu_\alpha(\Gamma_i) | \Theta \mu_\beta(\Gamma_i) \rangle = \langle \mu_\beta(\Gamma_i) | \mu_\alpha(\Gamma_i) \rangle$, $A(\Gamma_i)$ is antisymmetric at TRIM $\Gamma_i$. The square of its Pfaffian is equal to its determinant, i.e., $\det[A] = \text{Pf}[A]^2$. Then $\delta_i = \text{(det}[A(\Gamma_i)])^{1/2}/\text{Pf}[A(\Gamma_i)] = \pm 1$.

Hence, the topological invariant $\mathbb{Z}_2$ can be defined as

$$(-1)^{\mathbb{Z}_2} = \prod_{i=1}^{4} \delta_i$$

When solids have space-reversal symmetry, $\mathbb{Z}_2$ can be simplified as

$$(-1)^{\mathbb{Z}_2} = \prod_{i=1}^{M} \xi_{2m}(\Gamma_i)$$

where $\xi$ is the parities of all occupied bands at $\Gamma_i$, and $M$ is the number of the time-reversal invariant points.

Electronic structure calculation technique. We calculate the lattice configurations as well as electronic band structures of bilayer phosphorene with four different stacking orders based on the density functional theory (DFT) implemented in the Vienna Ab-initio Simulation Package.
The projector augmented wave (PAW) method and the Perdew-Erk-Ernzerhof (PBE) exchange-correlation functional are adopted. Long-range dispersion corrections have been taken into account within a semi-empirical van der Waals approach proposed by Grimme known as the DFT-D2 method (where D2 stands for the second generation of this method). The kinetic energy cutoff for the plane wave basis set is chosen to be 600 eV, and the reciprocal space is meshed at $14 \times 10 \times 1$ using Monkhorst-Pack method. A vacuum space of at least 25 Å along the $z$ direction is used to separate the bilayer systems in order to avoid spurious interactions due to the nonlocal nature of the correlation energy. In order to correct the PBE band gaps, we apply a hybrid Heyd-Scuseria-Emzerhof (HSE) functional in which the exchange potential is separated into a long-range and a short-range part, where $1/4$ of the PBE exchange is replaced by the Hartree-Fock exact exchange and the full PBE correlation energy is added. Hence the HSE functional is thought to correct the GGA band gaps significant by partially correcting the self-interaction.

**Optical property calculation technique.** We calculate the optical response of the Tb-stacked bilayer phosphorene under the strains $\sigma_{xy} = 0.0\%$ and $\sigma_{xy} = -3.0\%$, based on a real-space and real-time time-dependent density functional theory (TDDFT) as implemented in the OCTOPUS code. The Hartwigsen-Goedecker-Hutter pseudopotentials and Generalized Gradient Approximation (GGA) with PBE functional for the exchange-correlation are used to calculate both the ground state and excited state. We mainly investigated the plasmon excitation in the direction that is parallel to the plane of the phosphorene. Geometries of phosphorene which we mainly discussed is rectangular. The simulation zone was defined by assigning a sphere around each atom with a radius of 6 Å and a uniform mesh grid of 0.3 Å. In the real time propagation, excitation spectrum
was extracted by Fourier transform of the dipole strength induced by an impulse excitation\cite{ref1}. In the real-time propagation, the electronic wave packets were evolved for typically 6000 steps with a time step of $\Delta t = 0.005 \ \text{Å/eV}$. 
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**Figure 1 Four stacking orders of bilayer phosphorene.** (a) The monolayer black phosphorus (phosphorene), where the top and bottom P atoms of the nonplanar sublayers are represented by green and purple atoms. (b) The projection of monolayer black phosphorus on x-y plane, where $R_1$ and $R'_1$ are two types of P-P in-plane bond lengths, and $\alpha$ is the angle between two $R_1$ bonds. One unit cell has four atoms as included by the blue shadowed region. Note that filled and opened dots with the same color are two different sublattice. (c)-(f) The four different stacking orders: (Ta) the top layer is stacked vertically on the bottom layer, (Tb) the bottom layer is shifted by half of one unit cell along x or y with respect to the top layer, (Tc) the bottom layer is shifted by one unit cell along x or y direction with respect to the top layer, and thus the top and bottom layers are mirror images of each other, (Td) the bottom layer is shifted by one and a half of one unit cell along x or y, where $R_2$ is the length of the out-of-plane bond, $\beta$ is the angle between the in-plane and out-plane bonds and $d_{int}$ is the smallest layer interval in the vertical direction.

**Figure 2 The electronic structures of bilayer phosphorene for four different stacking orders.** (a)-(d) The band structures. The maximum valence band and the minimum conduction band are represented by purple and red lines, and valence band maximum (VBM) and conduction band minimum (CBM) are denoted by purple and red real boxes. The band gaps $E_g$ are indicated by blue shadowed regions. The inset in (d) is the result of enlarging the region close to the Fermi level. The Fermi level is set to zero. $\Gamma$ (0.0, 0.0, 0.0), $X$ (0.0, 0.5, 0.0) and $Y$ (0.5, 0.0, 0.0) refer to special points in the first Brillouin zone. (e)-(h) The isosurface of band-decomposed charge densities on y-z plane corresponding to VBM and CBM at $\Gamma$ point, where the top and bottom P atoms of the nonplanar sublayers are represented by green and purple atoms. The bonding and
antibonding features are highlighted by red and blue dashed boxes. The isosurface in subfigures (e)-(h) is set to be 0.0037 e/Å³.

**Figure 3 The band gap $E_g$ changes with the in-plane strain $\sigma$ of bilayer phosphorene for four stacking orders.** (a)-(d) The band gaps for four different stacking orders on the in-plane strain, where $\sigma_x$, $\sigma_y$ and $\sigma_{xy}$ mean the strain along x direction (zigzag direction), y direction (armchair direction) and both x and y directions, respectively. We consider tension strain ($\sigma > 0$), and compression strain ($\sigma < 0$). The direct-indirect band-gap transition can be delineated by vertical blue dashed line, and the condition under which bilayer phosphorene becomes metallic is highlighted by blue shaded region. We find the band gap is reopened when in-plane strain up to the critical value, as denoted by green dashed box. The inset in (d) is the enlarged result of green dashed box.

**Figure 4 Electronic structures of bilayer phosphorene for Tb-staked order.** (a)-(c) The band structures of bilayer phosphorene for Tb-stacked order when the in-plane strain $\sigma_{xy}$ is 2.0%, 2.77% and 3.0%, where the maximum valence band and minimum conduction band are represented by the purple and red lines, and (even, odd) parity is denoted by (+, -). The inset in (c) is the result of enlarging the region close to the Fermi level. The Fermi level is set to zero. $\Gamma$ (0.0, 0.0, 0.0), X (0.0, 0.5, 0.0) and Y (0.5, 0.0, 0.0) refer to special points in the first Brillouin zone. (d) The valence band maximum (VBM) and conduction band minimum (CBM) of bilayer phosphorene for Tb-stacked order changes with the compression strain $\sigma_{xy}$, where the CBM and VBM are represented by red and purple lines, the CBM and VBM at $\Gamma$ are represented by red and purple
dashed lines, and the VBM, CBM and CBM along \( \Gamma -X, \Gamma -X \) and \( \Gamma -Y \) are represented by orange, green and blue dashed lines. The condition under which Tb-stacked bilayer phosphorene becomes metallic is highlighted by red shadowed region. (e) The density of states of Tb-stacked bilayer phosphorene when \( \sigma_{xy} = -3.0\% \), where the total density of states (DOS) is represented by the gray dotted lines, the \( s \)- and \( p \)-orbitals of P atom are represented by the purple and orange dotted lines, and the \( p_x \), \( p_y \) and \( p_z \) orbitals are represented by red and blue dotted lines. (f) and (g) The \( p_y \) and \( p_z \) orbital-projected band structures of Tb-stacked bilayer phosphorene, where the radii of circles are proportional to the weight of corresponding orbital.

**Figure 5 The electronic structures changes with \( W_{vdW} \) of bilayer phosphorene for four stacking orders.** (a) The band gap \( E_g \) changes with \( W_{vdW} \), where the band gaps \( E_g \) of Ta-, Tb-, Tc- and Td-stacked bilayer phosphorene are represented by the red, green, orange and blue points, and their fitted lines can be denoted by the corresponding color-lines. We find the band gap of Td-stacked bilayer phosphorene is reopened when \( W_{vdW} \) up to critical value, as shown the inset in (a). (b) and (c) The \( p_z \) orbital-projected band structures of Td-stacked bilayer phosphorene when \( W_{vdW} = 0 \) and \( W_{vdW} = 1.14t \), where the weights of \( p_z \) orbital are proportional to the radii of circles, and (even, odd) parity is denoted by (+, -). The inset in (c) is the enlarged result of green dashed box. The Fermi level is set to zero. \( \Gamma(0.0, 0.0, 0.0), \ X(0.0, 0.5, 0.0) \) and \( Y(0.5, 0.0, 0.0) \) refer to special points in the first Brillouin zone.

**Figure 6 The optical property of bilayer phosphorene for Tb-stacked order.** (a) The top and side views of Tb-stacked bilayer phosphorene, where up and bottom P atoms of the nonplanar
sublayers are represented by the purple and green atoms, and hydrogen atom is represented by the red atom to passivate the dangling $\sigma$ bonds at the edges. (b) The optical absorption of Tb-stacked bilayer phosphorene when the compression strain $\sigma_{xy} = 0.0\%$ and $\sigma_{xy} = -3.0\%$. We consider two polarized directions, $x$ (zigzag) and $y$ (armchair) directions. Red arrows point out the moving direction of the absorption peaks after applying in-plane strain $\sigma_{xy}$, as shown the inset in (b). (c) and (d) The induced charge density of Tb-stacked bilayer phosphorene without strain to an impulse excitation polarized in the $x$- and $y$-directions. (e) and (f) The induced density of Tb-stacked bilayer phosphorene when the compression strain $\sigma_{xy} = -3.0\%$ to an impulse excitation polarized in the $x$- and $y$-directions. The regions where electron and hole density mainly locates, are highlighted by black and white dashed boxes. The selected energy resonance points are 4.96 eV (c), 1.11 eV (d), 4.96 eV (e) and 1.22 eV (f).
Band gap is reopened.
Eg = 0.136
eglecting Eg = 0.0
eglecting Eg = 0.005

-0.5
-0.25
0
0.25
0.5
X/2

Y/2

Metal

Reopened maximun
Eg = 0.0925

Eg = 0.0925

DOS (arb. units)
Table 1: The calculated structural parameters of the four different stacking orders, other previous theoretical data and the corresponding bulk experimental values, where $a$ (Å) along x direction, $b$ (Å) along y direction are the lattice constants, $d_{int}$ (Å) is the smallest layer interval in the vertical direction, $R_1$ (Å), $R'_1$ (Å) are the in-plane bonds length, $R_2$ (Å) is the out-plane bond length, $\alpha$ ($^\circ$) is the in-plane bond angle and $\beta$ ($^\circ$) is the out-plane bond angle. $E_{coh}$ (eV/atom) is the cohesive energy with respect to isolated atoms, and $\Delta E_{coh}$ (meV/atom)=$E_{coh}$-E_{coh}(Tb-stacked order) is the relative stability of the different stacked bilayers with respect to the Tb-stacked bilayer phosphorene.

|      | $a$  | $b$  | $d_{int}$ | $R_1$ | $R'_1$ | $R_2$ | $\alpha$ | $\beta$ | $E_{coh}$ | $\Delta E_{coh}$ |
|------|------|------|-----------|-------|--------|-------|----------|---------|-----------|-----------------|
| Ta   | 3.314| 4.519| 3.503     | 2.221 | 2.226  | 2.256 | 96.45    | 103.26  | -3.6550   | 8.0             |
| Theory | 3.326| 4.550| 3.495     | 2.243 | 2.235  | 2.283 |          |         |           |                 |
| Tb   | 3.319| 4.505| 3.108     | 2.223 | 2.226  | 2.253 | 96.55    | 103.17  | -3.6630   | 0.0             |
| Theory | 3.331| 4.526| 3.214     | 2.242 | 2.238  | 2.277 |          |         |           |                 |
| Tc   | 3.312| 4.546| 3.739     | 2.223 | 2.224  | 2.251 | 96.34    | 103.54  | -3.6556   | 7.4             |
| Theory | 3.324| 4.535| 3.729     | 2.238 | 2.236  | 2.274 |          |         |           |                 |
| Td   | 3.315| 4.524| 3.291     | 2.221 | 2.225  | 2.255 | 96.50    | 103.34  | -3.6559   | 7.1             |
| Bulk(Exp) | 3.314| 4.376| 3.503     | 2.224 | 2.244  | 96.34 |         |         |           | 102.09          |
Table 2: Products of parity eigenvalues at four time-reversal invariant momentum for 0.0% and −3.0% strain. Positive parity is denoted by + while negative denoted by −. The resulting $Z_2$ values are shown.

| Strain | $\Gamma$ | $X$ | $Y$ | $M$ | $Z_2$ |
|--------|---------|-----|-----|-----|-------|
| 0.0%   | +       | +   | +   | +   | 0     |
| −3.0%  | −       | +   | +   | +   | 1     |