New Phosphorene Allotropes Containing Ridges with 2- and 4-Coordination

Jie Liu,^{†,‡} Yaguang Guo,^{†,‡} Shunhong Zhang,^{†,‡} Qian Wang,^{*,†,‡,§} Yoshiyuki Kawazoe,[∥] and Puru Jena[§]

[†]Center for Applied Physics and Technology, College of Engineering, Peking University, Beijing 100871, China [‡]Key Laboratory of High Energy Density Physics Simulation, and IFSA Collaborative Innovation Center, Ministry of Education, Beijing 100871, China

[§]Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284, United States

^{II}New Industry Creation Hatchery Center, Tohoku University, Sendai, 980-8577, Japan

ABSTRACT: In all of the phosphorus monolayers reported to date, phosphorus is 3-fold coordinated. However, flexible chemistry of phosphorus allows it to have varying coordination number up to 6. Here, we report three new phosphorus monolayers (labeled α -P₆, β -P₆, and 558-P₆) having 2-, 3-, and 4-fold coordination, which can be observed in epitaxial growth where flakes merge forming ridges at the boundaries. On the basis of state-of-the-art theoretical simulations, we show that these three new monolayer allotropes are thermally and dynamically stable, and they have comparable energetic stability with some reported monolayers such as δ -P, γ -P, and ε -P. Because of their special atomic configurations, they



exhibit exceptional properties, including extremely high electron mobility, anisotropic Young's moduli, and optical absorbance in visible and ultraviolet regions. These findings can extend the family of phosphorenes with novel properties and potential for applications.

INTRODUCTION

Unusual properties together with the tremendous technological applications of graphene^{1,2} have stimulated considerable interest in the search of other two-dimensional (2D) materials with novel properties. Recently, successful synthesis of monolayer black phosphorus,^{3,4} phosphorene (α -P), has led to considerable interest in exploring the stability and electronic properties of other layered allotropes of phosphorus. A number of other 2D phosphorus allotropes have been studied such as β -P (blue phosphorus),⁵ γ -P, and δ -P,⁶ and some newly discovered phosphorene polymorphs.^{7,8} Most of them are predicted to be semiconductors from first-principles calculations, but exhibit very different electronic, optical, and mechanical properties. For instance, α -P has a direct band gap of 1.53 eV, while β -P possesses a much larger band gap of 2.69 eV, which can be exploited in nanoelectronics and optoelectronics devices.^{9,10} α -P has an unusual negative Poisson's ratio¹¹ and exhibits a highly anisotropic rippling pattern,¹² which are useful in nanomechanics, and selective adsorption, which enables it to serve as a superior gas sensor.¹³ ζ -P shows nonvolatile ferroelastic switching, which can be used as a shape memory material.⁷ These discoveries indicate that the novel properties of phosphorene polymorphs are closely related to the topological arrangement of phosphorus atoms.

The equilibrium geometry of α -P is puckered because the three-coordinated phosphorus atoms retain sp³ hybridization character.¹⁴ β -P possesses the hexagonal honeycomb structure

where each atom is in three-coordinated configuration forming a silicene-like sheet,⁵ while γ -P and δ -P⁶ have rectangular Wigner-Seitz cells. Although the recent prediction of some new phosphorene polymorphs⁷ with nonhoneycomb structures greatly enriches the diversity of 2D phosphorus allotropes, we believe that the search for stable phosphorene structures is still incomplete. Motivated by the findings of new types of phosphorene through hybridization of different polymorphs,⁷ and the existence of one-dimensional (1D) topological defects of carbon ridges in epitaxial growth of graphene, which plays an important role in mediating the electronic properties of graphene and its related structures,¹⁵⁻¹⁷ we conceived the idea of building 2D new phosphorus sheets by introducing 1D phosphorus ridges into some predicted phosphorene polymorphs. In this work, on the basis of a series of state-of-the-art theoretical calculations, three new phosphorene polymorphs are designed by implanting 1D phosphorus ridges into β -P with the buckled hexagonal lattice. The resulting new structures are stable and exhibit exceptional properties.

COMPUTATIONAL METHODS

Our studies are based on density functional theory (DFT) and the projector augmented wave (PAW) method¹⁸ as imple-

Received:September 3, 2015Revised:October 5, 2015Published:October 7, 2015

The Journal of Physical Chemistry C

mented in the Vienna Ab initio Simulation Package (VASP).¹⁹ The plane-wave cutoff energy for wave function is set to 500 eV. The electronic exchange-correlation interaction is incorporated in the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).²⁰ The Heyd-Scuseria-Ernzerhof (HSE06)^{21,22} functional is used for high accuracy calculations of electronic structure and optical properties. For geometry optimization, the convergence thresholds are set at 10^{-4} eV and 10^{-3} eV/Å for total energy and force component, respectively. Monkhorst-Pack kmeshes²³ of 7 × 16 × 1 for α -P₆, 3 × 15 × 1 for β -P₆, and 6 \times 8 \times 1 for 558-P₆ are adopted to represent the first Brillouin zone. The 2D systems are separated by a vacuum spacing of 20 Å in the nonperiodic direction. Thermal stability is studied using the Canonical ensemble (NVT) ab initio molecular dynamics (AIMD) simulations with temperature controlled by Nosé thermostat.²⁴ Phonon calculations are performed using the finite displacement method as implemented in the Phonopy program.²⁵

RESULTS AND DISCUSSION

Geometric Structures. It has been reported that 1D topological defects of carbon ridges exist in the epitaxial growth of graphene,¹⁶ where two half-lattices of graphene grow on Ni (111) with fcc (face-centered cubic) and hcp (hexagonal closed-packed) sites, respectively, and the 1D ridges are formed at the boundary of the two half-lattices. On the basis of this experimental finding, we have proposed a similar epitaxial growth process of β -P to simulate the formation of 1D phosphorus ridges as β -P shares the common structural feature of the honeycomb lattice with graphene. To better describe the experimental process, a supercell is built to simulate the two half-lattices of β -P with a translation relative to one another by a translation vector $(a_1 + a_2)/3$ (indicated by a red dashed line with an arrowhead in Figure 1a), where a_1 and a_2 are the basic vectors of β -P lattice (indicated by red solid lines with arrowheads). We fixed the cell and the nonboundary atomic positions to perform structural optimization to let the structure reconstruction only occur on the atoms around the boundaries of the two half-lattices (marked by the green rectangles in



Figure 1. Structure and schematic illustrations of the formation of a ridge embedded in the β -P lattice. Top and side views of (a) initial and (b) optimized structures used to simulate the two half-lattices of β -P. Gray dashed rectangles denote the supercells. Yellow spheres represent phosphorus atoms formed at the 1D ridge. Schematic drawings of (c) the collision of two crustal plates moving in opposite directions, and (d) the formation of a ridge at the boundary when two crustal plates collide.

Figure 1a). Starting from the initial structure in Figure 1a, the optimized structure with a zigzag ridge is obtained, as shown in Figure 1b. The formation of the zigzag ridge makes the structure more puckered to relieve the intralayer stress resulting from the mismatch of the two half-lattices. Therefore, we demonstrate that the 1D ridge composed of two- and four-coordinated phosphorus atoms can be formed at the boundary of two β -P half-lattices during epitaxial growth. This is reminiscent of the formation of ridges when two crustal plates, moving in the opposite directions, collide with each other, as schematically shown in Figure 1c and d.

We then constructed new phosphorene polymorphs by introducing a structural unit containing the 1D ridges (see Figure 2a) into β -P. The structural unit contains six



Figure 2. (a) Structure of P_6 unit viewed from different directions. Top and side views of the optimized structures of (b) α -P₆ and (c) β -P₆.

nonequivalent phosphorus atoms (named P_6) where there is only one phosphorus atom with 2- or 4-fold coordination, while the other four are 3-fold coordinated. Here, two different monolayer structures are generated, as shown in Figure 2b and c. In Figure 2b, the 3-fold coordinated phosphorus atoms adjacent to P₆ units are tetrahedrally connected to the structural unit, forming a distorted α -P-like hexagon as shown in the green rectangle of Figure 2b. We name this structure as α -P₆. The two-coordinated phosphorus atoms in α -P₆ are lined up in the same direction, and the structural units are distorted as they reach the energetically preferred structure. Similarly, in the structure of Figure 2c, P₆ units antisymmetrically connect to each other, and the three-coordinated phosphorus atoms are tetrahedrally connected to P_6 units forming a β -P like hexagon as shown in the green rectangle in Figure 2c. We name this structure β -P₆. The α -P₆ and β -P₆ monolayers possess PM symmetry (space group no. 6) and PMMA symmetry (space group no. 51), respectively. The optimized lattice constants are given in Table 1. The average P-P bond lengths are 2.25 and 2.24 Å for α -P₆ and β -P₆, respectively, which are very close to that in the honeycomb structures⁶ (α -P, β -P, γ -P, and δ -P).

Energetic Stability. Total energies are calculated to investigate the thermodynamic stabilities of α -P₆ and β -P₆. The results are presented in Table 1. We can see that the α -P₆ and β -P₆ structures are about 0.14 and 0.09 eV in energy higher than that of α -P, respectively. However, the energy differences are very small as compared to the γ -P, δ -P,⁶ and ε -P phases,⁷ implying that they are energetically nearly degenerate with the

Table 1. Calculated Parameters of Some Phosphorene Polymorphs: Lattice Constants *a* and *b* (in Å), Total Energy ΔE (in eV/atom) Relative to α -P, and Energy Band Gap $E_{\rm g}$ (in eV) Computed at the HSE06 Level

	phase								
	α-P ₆	β -P ₆	558-P ₆	<i>α</i> -Ρ	β -P	<i>δ</i> -Ρ	γ-P	e-P	
а	7.33	14.78	9.50	4.63	3.28	5.53	3.26	5.39	
Ь	3.27	3.25	6.70	3.30	3.28	5.42	5.42	5.39	
ΔE	0.14	0.09	0.13	0	0.01	0.08	0.09	0.14	
$E_{\rm g}$	1.36	0.67	0.80	1.53	2.69	0.66	1.05	0.94	

previously reported allotropes. Thus, due to the bonding flexibility of the phosphorus atom, various 2D phosphorus structures with comparable stability can be formed.

Dynamical Stability. To examine the dynamical stability of α -P₆ and β -P₆, we calculated the phonon spectra of the two phases. The results are plotted in Figure 3a₁ and b₁, which show



Figure 3. Phonon band structures of $(a_1) \alpha - P_6$ and $(b_1) \beta - P_6$. Total potential energy fluctuation during AIMD simulations of $(a_2) \alpha - P_6$ and $(b_2) \beta - P_6$.

that both α -P₆ and β -P₆ are dynamically stable because all of the vibrational modes are real in the first Brillouin zone. Similar to α -P⁵ the phonon spectra of both α -P₆ and β -P₆ have three distinct acoustic branches: the in-plane transverse acoustic (TA) mode, the longitudinal acoustic (LA) mode, and the outof-plane acoustic (ZA) mode. The TA and LA modes have linear dispersion near the Γ point, whereas the ZA mode has quadratic dispersion near the Γ point. Cai et al.²⁶ described α -P as a 2D puckered honeycomb structure consisting of weakly coupled quasi-1D chains. The vibrational atoms in α -P are weakly coupled along the armchair direction as compared to the zigzag direction. The phononic properties of α -P₆ and β -P₆ exhibit a distinct anisotropy similar to that of α -P. As shown in Figure $3a_1$ and b_1 , the LA and TA modes along the Γ -X direction near the Γ point show a lower group velocity as compared to those along the Γ -Y (zigzag) direction as both of the two branches have larger slope along the Γ -X direction, implying that the coupling between phosphorus atoms along the x direction is weaker than that along the y direction.

Thermal Stability. To study the thermal stabilities of α -P₆ and β -P₆ at room temperature, we performed ab initio molecular dynamics (AIMD) simulations at 300 K with a large supercell of $4 \times 4 \times 1$ for α -P₆ and $2 \times 6 \times 1$ for β -P₆. We found that the geometries of both α -P₆ and β -P₆ remain nearly

intact after heating for 8 ps with a time step of 1 fs, and the total energies remain almost constant during the simulation (see Figure 3a₂ and b₂). These results suggest that the α -P₆ and β -P₆ are thermally stable at room temperature.

Mechanical Stability. To guarantee the positive-definiteness of stain energy resulting from finite distortions of the lattice, the linear elastic constants of a mechanically stable 2D sheet haste to obey the Born–Huang criteria:²⁷ $C_{11}C_{22}-C_{12}^2 >$ 0 and C_{11} , C_{22} , $C_{44} > 0$. To check the mechanical stability, we calculated the elastic constants of α -P₆ and β -P₆ from the strain–stress relationship. For the 2D sheet, there are four nonzero elastic constants: C_{11} , C_{22} , C_{12} , and C_{44} .²⁷ We calculated the linear elastic constants by using the finite distortion method²⁸ implemented in the Vienna Ab initio Simulation Package (VASP). The 2D elastic constants are derived from the strain–stress relationship. For comparison, the calculations were also carried out for α -P. The results are listed in Table 2. The calculated elastic constants of α -P are in

Table 2. Calculated Elastic Constants of α -P₆, β -P₆, and α -P

structure	α -P ₆	β -P ₆	<i>α</i> -P
C_{11} (N/m)	41.7	76.6	26.6
C_{12} (N/m)	5.8	9.2	18.4
C_{22} (N/m)	89.0	109.0	103.6
C_{44} (N/m)	14.6	24.9	21.7

good agreement with previous work.²⁹ One can see that both α -P₆ and β -P₆ are mechanically less anisotropic as compared to α -P, because the difference between C_{11} and C_{22} is smaller. The elastic constants of both α -P₆ and β -P₆ satisfy the Born–Huang criteria,²⁷ implying that the two structures are mechanically stable.

Mechanical Properties. Next, we studied the mechanical properties of α -P₆ and β -P₆. The Young modulus $E(\theta)$ and Poisson's ratio $\nu(\theta)$ along an arbitrary in-plane direction $\theta(\theta)$ is the angle relative to the *x* direction) can be expressed as³⁰

$$E(\theta) = \frac{C_{11}C_{22} - C_{12}^2}{C_{11}s^4 + C_{22}c^4 + \left(\frac{C_{11}C_{22} - C_{12}^2}{C_{44}} - 2C_{12}\right)c^2s^2},$$

$$\nu(\theta) = \frac{\left(C_{11} + C_{22} - \frac{C_{11}C_{22} - C_{12}^2}{C_{44}}\right)c^2s^2 - C_{12}(c^4 + s^4)}{C_{11}s^4 + C_{22}c^4 + \left(\frac{C_{11}C_{22} - C_{12}^2}{C_{44}} - 2C_{12}\right)c^2s^2}$$

where $c = \cos \theta$ and $s = \sin \theta$. For α -P₆ and β -P₆, the polar diagrams of $E(\theta)$ and $\nu(\theta)$ are plotted in Figure 4a and b, respectively. The deviations of $E(\theta)$ and $\nu(\theta)$ from a perfect circle indicate that both α -P₆ and β -P₆ have anisotropic Young moduli and Poisson's ratios. α -P₆ exhibits a comparable Young's modulus with α -P along the y direction, but is larger than that of α -P along the x direction. The Yong's modulus of β -P₆ has a shape similar to that of α -P₆, but with obviously larger values (see Figure 4a), indicating that β -P₆ is more rigid than α -P₆. The diagrams of the Poisson's ratio of α -P₆ and β -P₆ are similar both in shape and in magnitude. However, the magnitudes of Poisson's ratios along the x and y directions are significantly smaller than that of α -P due to their different atomic configurations.

Electronic Properties. To study the electronic properties of α -P₆ and β -P₆, we calculated their electronic band structures as well as the band decomposed charge densities for both the



Figure 4. Polar diagrams of (a) Young's modulus $E(\theta)$, and (b) Poisson's ratio $\nu(\theta)$ of α -P₆, β -P₆, and α -P.

valence band maximum (VBM) and the conduction band minimum (CBM). The results are displayed in Figure 5. At the



Figure 5. Electronic band structures of $(a_1) \alpha$ -P₆ and $(b_1) \beta$ -P₆ (blue lines, GGA/PBE; red lines, HSE06). Charge density isosurfaces for the VBM of $(a_2) \alpha$ -P₆ and $(b_2) \beta$ -P₆, and the CBM of $(a_3) \alpha$ -P₆ and $(b_3) \beta$ -P₆.

GGA/PBE level, the α -P₆ sheet is predicted to be a direct band gap semiconductor with a band gap of 0.76 eV, because both the VBM and the CBM are at Y point in the Brillouin zone, as shown in Figure 5a₁. The band structure of β -P₆, on the other hand, exhibits an indirect band gap, as the VBM is located at the Y point whereas the CBM lies between the Γ and Y points. The energy difference between the VBM and CBM is only 0.14 eV. Therefore, the band gap of β -P₆ is 0.14 eV, which is much smaller than that of α -P₆. It is well-known that the GGA/PBE functional significantly underestimates band gaps. Consequently, we used a more accurate HSE06 functional to correct the band gaps. The calculated results are also plotted in Figure 5a1 and b1, showing that, although both functionals give very similar band dispersions, the band gaps of α -P₆ and β -P₆ at the HSE06 level are increased to 1.36 and 0.67 eV, respectively. As compared to other previously studied phosphorene polymorphs

(see Table 1), α -P₆ shares the direct band gap feature with α -P, δ -P, and ε -P phases.^{6,7} However, its fundamental gap is smaller than that of α -P (1.53 eV), but larger than that of δ -P (0.66 eV) and ε -P (0.94 eV). The band gap of β -P₆, on the other hand, is much smaller than that of β -P (2.69 eV).⁵ Thus, we find that the band gap of the phosphorene polymorphs changes over a wide range from 0.66 eV (δ -P) to 2.69 eV (β -P) due to the change of their atomic configurations. We also find that introducing the 1D phosphorus ridges can effectively change the band gap of α -P and β -P. According to the Shockley–Queisser limit,³¹ the maximum theoretical solar conversion efficiency of a single cell can reach 33.7% with the band gap of 1.34 eV. The band gap of α -P₆ is very close to this value, indicating a potential application in solar absorber.

To better understand the electronic structures of α -P₆ and β -P₆, we further calculated the band decomposed charge densities for both the VBM and the CBM to visualize the electronic states near the Fermi level. The results plotted in Figure 5a₂ and b₂ show that the electron distributions in the VBM for both of the two sheets are mainly localized on the two-coordinated phosphorus atoms. This is because the low coordination of phosphorus atoms leads to electron lone pairs, which are much higher in energy than those of the paired electrons. The charge density distributions in the CBM (Figure 5a₃ and b₃) for both of the systems are quite isolated along the *y* direction, but exhibit a remarkable overlap in the *x* direction. Such anisotropic character has a direct impact on phonon–electron scattering, which plays an important role in carrier transport properties.

Carrier mobility is known to be a crucial factor for electronic and optoelectronic applications, because large mobility can prevent electrons and holes from recombination.³² Therefore, we calculated the carrier transport properties of both α -P₆ and β -P₆ monolayers by using deformation potential approximation.³³ The carrier mobility of a 2D sheet can be written as μ_{2D} = $e\hbar^3 C_{2D}/k_{\rm B}Tm_{\rm e}^*m_{\rm d}(E_1)^{2}$,^{34,35} where E_1 represents the deformation potential, which is obtained by studying the energy changes of the VBM and CBM under lattice compression and dilation. $m_{x/y}^*$ is the carrier effective mass determined by quadratic fitting of conduction and valence

Table 3. Carrier Effective Masses (*m* in the Unit of Rest Electron Mass), Deformation Potential Values *E* (in eV), 2D Elastic Modulus *C* (in GPa·nm), and Carrier Mobility μ (in 10³ cm²/V·s) along the *x* and *y* Directions

carrier type	phase	m_x	m_y	E_{1x}	E_{1y}	C_{x_2D}	$C_{y_{2D}}$	μ_x	μ_y
electron	α -P ₆	0.64	0.61	7.79	0.58	41.67	89.03	0.04	14.91
	β -P ₆	0.43	0.35	2.22	0.76	76.60	109.08	2.02	29.75
hole	α -P ₆	-1.55	-2.21	2.93	2.25	41.67	89.03	0.04	0.09
	β -P ₆	-0.28	-0.42	5.37	3.58	76.60	109.08	0.60	1.15

bands in different directions, and m_d is given by the expression $m_d = (m_x^* m_y^*)^{1/2}$. The elastic modulus C_{2D} refers to the elastic constants, where C_{11} and C_{22} denote values along the *x* and *y* directions, respectively. The calculated parameters of carrier mobility for both α -P₆ and β -P₆ are listed in Table 3.

It is well-known that black phosphorus exhibits an anisotropic character with different carrier types along different directions.^{36,37} For α -P, Qiao et al.³⁷ predicted that the electron mobility along the x direction is about 14 times as large as the value along the y direction, while the hole mobility along the xdirection is about 25 times smaller than the value along the y direction. However, the situation is different in the systems studied here. For example, the electron mobility along the ydirection is about 370 and 15 times as large as the values along the x direction for α -P₆ and β -P₆, respectively, while the hole mobility along the y direction for both of them is 2 times as large as that along the x direction. Especially, the electron mobility in the *y* direction for both of the two sheets can reach $10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (see Table 3), which is comparable with the hole mobility along the y direction of α -P.³⁷ The underlying reason is that the deformation potential for electrons in the ydirection is extremely small as compared to typical values, making electrons less prone to acoustic scattering.³ ⁸ As mentioned above, the charge density distributions in the CBM of both sheets are quite isolated along the y direction. This will lead to little change in band edge energy upon lattice compression and dilation, because the wave functions of band edge state have a small overlap. In addition, the effective mass is also a decisive factor, as the band dispersion is relatively significant in the first conduction band, which results in a small electron mass along the *y* direction. Our calculations show that, unlike α -P, both α -P₆ and β -P₆ exhibit large electron mobility of the order of 10^4 cm² V⁻¹ s⁻¹, making them very promising for application in electronic devices.

Optical Properties. The direct band gap of α -P makes it a potential candidate for optoelectronic applications.³⁷ Because α -P₆ also possesses a direct band gap, we calculated the imaginary part of its dielectric function at the HSE06 level. For comparison, calculations for β -P₆ and α -P were also performed by using the same procedure. The results are displayed in Figure 6. According to the photon energy, we divide the



Figure 6. Imaginary part of the dielectric function of α -P₆, β -P₆, and α -P at HSE06 level.

spectrum into three parts, the infrared, visible, and ultraviolet regions, respectively. All of the structures start to absorb the sunlight with photon energy close to its band gap value. It is known that diamond silicon, the most common solar cell material, has an indirect band gap (\sim 1.1 eV) and a large optical gap (\sim 3.3 eV),^{39,40} which makes it inefficient for solar absorption. However, in α -P, because of the direct band gap,

the dipole transition at the Γ point is allowed,³⁷ which results in a significant absorption in infrared and visible regions. As mentioned above, the material with band gap near 1.34 eV will have the maximum solar conversion efficiency. Because of the proper band gap (1.36 eV) in α -P₆, its absorption curve is much higher than that of α -P from the photon energy over ~1.70 eV, resulting in a remarkable coverage over the solar spectrum. For α -P, the direct band gap of 1.53 eV (at HSE06 level as shown in Table 1) combined with its high carrier mobility make it promising for fast and broadband photodetection and solar cell application.⁴¹ As compared to α -P, α -P₆ exhibits an even better performance in sunlight absorption with comparable carrier mobility (see Table 3).³⁷ For β -P₆, although the band gap is indirect, the optical gap at Y point in the Brillouin zone (see Figure 5b) is only about 1.0 eV, which is much smaller than that of diamond silicon. This will lead to absorption comparable with that of α -P. According to our results, we conclude that both α -P₆ and β -P₆ exhibit a good optical absorption in the visible range. Combined with their high electron mobility, these new two phosphorus sheets may have potential for solar absorber applications.

Ridge-Linked 558 Sheet. The six-membered rings are the main structural units of phosphorene polymorphs such as β -P,⁵ γ -P, and δ -P,⁶ while some other polymorphs are composed of the 3-, 4-, 5-, 7-, 8-, and 12-membered rings.⁸ Combination of different rings gives rise to different layered structures. Thus, we constructed a new monolayer structure by combining the 1D phosphorus ridge with five- and eight-membered rings, as shown in Figure 7a. We name this as 558-P₆, because the unit



Figure 7. (a) Top and side views of optimized structure of $558-P_6$. (b) Phonon spectrum and (c) electronic band structure (red lines, GGA/PBE; blue lines, HSE06) of $558-P_6$. (d) Variation of potential energy during AIMD simulations at 300 K.

cell is composed of two five-membered rings, one eightmembered ring, and two P₆ units. We carried out similar calculations for the 558-P₆ monolayer. Geometry optimization and total energy calculations indicate that 558-P₆ is 0.13 eV/ atom higher in energy than α -P, and is energetically as stable as α -P₆ (see Table 1). AIMD simulations and phonon calculations reveal that 558-P₆ is both thermally and dynamically stable, as shown in Figure 7b and d. The electronic band structure of 558-P₆ is calculated at both the PBE and the HSE06 levels. The results are plotted in Figure 7c. Although α -P₆ and 558-P₆ are energetically degenerate, they display very different band structures; the corresponding band gaps are 1.36 and 0.8 eV,

The Journal of Physical Chemistry C

respectively, indicating again that geometry can significantly affect the electronic properties of phosphorus monolayers.

CONCLUSIONS

In summary, we show that three new phosphorene polymorphs, α -P₆, β -P₆, and 558-P₆, can be obtained by introducing the structural unit (P₆) containing 1D phosphorus ridges into β -P, or combining the structural unit with the five- and sixnumbered rings. The resulting new 2D structures have 2-, 3-, and 4-coordinated P atoms, showing the structural flexibility of the phosphorus bond, well-known in chemistry. Although these new polymorphs are metastable as compared to α -P, they are dynamically, thermally, and mechanically stable at ambient conditions; α -P₆ and 558-P₆ monolayers are energetically nearly degenerate with the recently reported ε -P sheet,⁷ and β -P₆ is energetically comparable to δ -P and γ -P.⁶ We demonstrated that α -P₆ and β -P₆ possess exceptional mechanical, electronic, and optical properties via a comprehensive first-principles DFT study. The Young's moduli and Poison's ratios of α -P₆ and β -P₆ are both anisotropic, and β -P₆ is found to be stiffer than the α - P_6 and α -P monolayers. Extremely high electron mobilities of 14 900 and 29 800 cm² V⁻¹ s⁻¹ are found for α -P₆ and β -P₆, respectively. The carrier mobilities of α -P₆ and β -P₆ exhibit intriguing anisotropic features. In α -P₆ and β -P₆, the *y* direction (zigzag) is electrically more conductive as compared to the xdirection (armchair), and electrons are more mobile than holes. α -P₆ has much better optical absorbance than β -P₆ and α -P when the photon energy is in the region of 2.29-4.60 eV. These findings expand and deepen our understanding of Pbased monolayers with unique geometries and exceptional properties for potential applications.

AUTHOR INFORMATION

Corresponding Author

*E-mail: qianwang2@pku.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is partially supported by grants from the National Natural Science Foundation of China (NSFC-51471004, NSFC-11174014), the National Grand Fundamental Research 973 Program of China (Grant no. 2012CB921404), and the Doctoral Program of Higher Education of China (20130001110033). P.J. acknowledges support by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award no. DE-FG02-96ER45579. We thank the crew of the Center for Computational Materials Science, the Institute for Materials Research, Tohoku University (Japan), for their continuous support of the HITACHI SR11000 supercomputing facility.

REFERENCES

 Neto, A. C.; Guinea, F.; Peres, N.; Novoselov, K. S.; Geim, A. K. The Electronic Properties of Graphene. *Rev. Mod. Phys.* 2009, *81*, 109.
 (2) Geim, A. K. Graphene: Status and Prospects. *Science* 2009, *324*, 1530–1534.

(3) Wang, X.; Jones, A. M.; Seyler, K. L.; Tran, V.; Jia, Y.; Zhao, H.; Wang, H.; Yang, L.; Xu, X.; Xia, F. Highly Anisotropic and Robust Excitons in Monolayer Black Phosphorus. *Nat. Nanotechnol.* **2015**, *10*, 517–521.

(4) Kou, L.; Chen, C.; Smith, S. C. Phosphorene: Fabrication, Properties, and Applications. J. Phys. Chem. Lett. 2015, 6, 2794–2805.

(5) Zhu, Z.; Tománek, D. Semiconducting Layered Blue Phosphorus: A Computational Study. *Phys. Rev. Lett.* **2014**, *112*, 176802.

(6) Guan, J.; Zhu, Z.; Tománek, D. Phase Coexistence and Metal-Insulator Transition in Few-Layer Phosphorene: A Computational Study. *Phys. Rev. Lett.* **2014**, *113*, 046804.

(7) Wu, M.; Fu, H.; Zhou, L.; Yao, K.; Zeng, X. C. Nine New Phosphorene Polymorphs with Non-Honeycomb Structures: A Much Extended Family. *Nano Lett.* **2015**, *15*, 3557–3562.

(8) Guan, J.; Zhu, Z.; Tománek, D. Tiling Phosphorene. ACS Nano 2014, 8, 12763–12768.

(9) Liu, H.; Neal, A. T.; Zhu, Z.; Luo, Z.; Xu, X.; Tománek, D.; Ye, P. D. Phosphorene: An Unexplored 2d Semiconductor with a High Hole Mobility. *ACS Nano* **2014**, *8*, 4033–4041.

(10) Xia, F.; Wang, H.; Jia, Y. Rediscovering Black Phosphorus as an Anisotropic Layered Material for Optoelectronics and Electronics. *Nat. Commun.* **2014**, *5*, 4458.

(11) Jiang, J.-W.; Park, H. S. Negative Poisson's Ratio in Single-Layer Black Phosphorus. *Nat. Commun.* **2014**, *5*, 4727.

(12) Kou, L.; Ma, Y.; Smith, S. C.; Chen, C. Anisotropic Ripple Deformation in Phosphorene. *J. Phys. Chem. Lett.* **2015**, *6*, 1509–1513. (13) Kou, L.; Frauenheim, T.; Chen, C. Phosphorene as a Superior Gas Sensor: Selective Adsorption and Distinct I–V Response. *J. Phys.*

Chem. Lett. 2014, 5, 2675–2681. (14) Rodin, A.; Carvalho, A.; Neto, A. C. Strain-Induced Gap Modification in Black Phosphorus. *Phys. Rev. Lett.* 2014, *112*, 176801. (15) Botello-Méndez, A. R.; Declerck, X.; Terrones, M.; Terrones, H.; Charlier, J.-C. One-Dimensional Extended Lines of Divacancy

Defects in Graphene. *Nanoscale* **2011**, *3*, 2868–2872. (16) Lahiri, J.; Lin, Y.; Bozkurt, P.; Oleynik, I. I.; Batzill, M. An Extended Defect in Graphene as a Metallic Wire. *Nat. Nanotechnol.* **2010**, *5*, 326–329.

(17) Kou, L.; Tang, C.; Guo, W.; Chen, C. Tunable Magnetism in Strained Graphene with Topological Line Defect. *ACS Nano* **2011**, *5*, 1012–1017.

(18) Blöchl, P. E. Projector Augmented-Wave Method. Phys. Rev. B: Condens. Matter Mater. Phys. **1994**, 50, 17953.

(19) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 11169.

(20) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(21) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid Functionals Based on a Screened Coulomb Potential. *J. Chem. Phys.* 2003, 118, 8207–8215.

(22) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Erratum:"Hybrid Functionals Based on a Screened Coulomb Potential"[J. Chem. Phys. 118, 8207 (2003)]. J. Chem. Phys. 2006, 124, 219906.

(23) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* 1976, 13, 5188.

(24) Nosé, S. A Unified Formulation of the Constant Temperature Molecular Dynamics Methods. J. Chem. Phys. **1984**, 81, 511–519.

(25) Togo, A.; Oba, F.; Tanaka, I. First-Principles Calculations of the Ferroelastic Transition between Rutile-Type and CaCl₂-type SiO₂ at High Pressures. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, *78*, 134106.

(26) Cai, Y.; Ke, Q.; Zhang, G.; Feng, Y. P.; Shenoy, V. B.; Zhang, Y.-W. Giant Phononic Anisotropy and Unusual Anharmonicity of Phosphorene: Interlayer Coupling and Strain Engineering. *Adv. Funct. Mater.* **2015**, *25*, 2230–2236.

(27) Zhang, S.; Zhou, J.; Wang, Q.; Chen, X.; Kawazoe, Y.; Jena, P. Penta-Graphene: A New Carbon Allotrope. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 2372–2377.

(28) Cadelano, E.; Colombo, L. Effect of Hydrogen Coverage on the Young's Modulus of Graphene. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *85*, 245434.

(29) Wang, L.; Kutana, A.; Zou, X.; Yakobson, B. I. Electro-Mechanical Anisotropy of Phosphorene. *Nanoscale* **2015**, *7*, 9746– 9751.

The Journal of Physical Chemistry C

(30) Cadelano, E.; Colombo, L. Effect of Hydrogen Coverage on the Young's Modulus of Graphene. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *85*, 245434.

(31) Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of P-N Junction Solar Cells. J. Appl. Phys. **1961**, 32, 510–519.

(32) Priolo, F.; Gregorkiewicz, T.; Galli, M.; Krauss, T. F. Silicon Nanostructures for Photonics and Photovoltaics. *Nat. Nanotechnol.* **2014**, *9*, 19–32.

(33) Bardeen, J.; Shockley, W. Deformation Potentials and Mobilities in Non-Polar Crystals. *Phys. Rev.* **1950**, *80*, 72.

(34) Fei, R.; Yang, L. Strain-Engineering the Anisotropic Electrical Conductance of Few-Layer Black Phosphorus. *Nano Lett.* **2014**, *14*, 2884–2889.

(35) Aaditya, M.; Atanu, S.; Tribhuwan, P.; Abhishek, K. S. Semiconductor to Metal Transition in Bilayer Phosphorene under Normal Compressive Strain. *Nanotechnology* **2015**, *26*, 075701.

(36) Ling, X.; Wang, H.; Huang, S.; Xia, F.; Dresselhaus, M. S. The Renaissance of Black Phosphorus. *Proc. Natl. Acad. Sci. U. S. A.* 2015, 112, 4523–4530.

(37) Qiao, J.; Kong, X.; Hu, Z.-X.; Yang, F.; Ji, W. High-Mobility Transport Anisotropy and Linear Dichroism in Few-Layer Black Phosphorus. *Nat. Commun.* **2014**, *5*, 4475.

(38) Long, M.; Tang, L.; Wang, D.; Li, Y.; Shuai, Z. Electronic Structure and Carrier Mobility in Graphdiyne Sheet and Nanoribbons: Theoretical Predictions. *ACS Nano* **2011**, *5*, 2593–2600.

(39) Xiang, H.; Huang, B.; Kan, E.; Wei, S.-H.; Gong, X. Towards Direct-Gap Silicon Phases by the Inverse Band Structure Design Approach. *Phys. Rev. Lett.* **2013**, *110*, 118702.

(40) Wang, Q.; Xu, B.; Sun, J.; Liu, H.; Zhao, Z.; Yu, D.; Fan, C.; He, J. Direct Band Gap Silicon Allotropes. *J. Am. Chem. Soc.* **2014**, *136*, 9826–9829.

(41) Dai, J.; Zeng, X. C. Bilayer Phosphorene: Effect of Stacking Order on Bandgap and Its Potential Applications in Thin-Film Solar Cells. J. Phys. Chem. Lett. 2014, 5, 1289–1293.