First-principles prediction of two atomic-thin phosphorene allotropes with potentials for sun-light-driven water splitting

Na Jiao, Pan Zhou, Lin Xue, Chaoyu He and Lizhong Sun

1 School of Physics and Physical Engineering, Qufu Normal University, Shandong, Qufu 273165, People’s Republic of China
2 Hunan Provincial Key Laboratory of Thin Film Materials and Devices, School of Material Sciences and Engineering, Xiangtan University, Hunan 411105, People’s Republic of China
3 College of Physics and Optoelectronics, Taiyuan University of Technology, Taiyuan 030024, People’s Republic of China
4 Hunan Key Laboratory for Micro-Nano Energy Materials and Devices, School of Physics and Optoelectronics, Xiangtan University, Hunan 411105, People’s Republic of China

E-mail: lzsun@xtu.edu.cn and hechaoyu@xtu.edu.cn

Received 5 October 2018, revised 25 November 2018
Accepted for publication 10 December 2018
Published 7 January 2019

Abstract
Based on first-principles, the structures, stabilities, electronic and optical properties of two new atomic-thin phosphorene allotropes, named as stair-P and zipper-P, are systematically investigated. Stair-P and zipper-P are constructed based on the previously proposed stair-graphane and zipper-graphane, respectively. They are confirmed to be dynamically stable phosphorene allotropes with energetic stabilities comparable to the experimentally synthesized black-P and blue-P. Stair-P and zipper-P are all semiconductors with indirect band gaps of 2.32 eV and 2.00 eV, respectively. These band gaps can be effectively modulated by in-layer compressive and stretching strains. The band edges of stair-P and zipper-P are proper for water splitting at both acidic (PH = 0) and neutral (PH = 7) environments and their sun-light adsorbing abilities are better than black-P and blue-P in the visible range.

Keywords: phosphorene, 2D semiconductor, photocatalysis

(Some figures may appear in colour only in the online journal)
configuration [13, 14], δ-P [19], ε-P [19] and green-P [20], the bi-layered θ-P [19], γ-P [19], B1 [21], G1 [21] and some other interesting allotropes [22, 23].

Experimentally, the black-P have been successfully fabricated through mechanically exfoliating [9, 12] from its 3D counterpart black phosphorus or other chemical deposition method [24–26] and the blue-P can be fabricated on Au(1 1 1) by molecular beam epitaxial growth with black phosphorus as precursor [27]. The black-P and blue-P based heterostructures, such as MXene/blue phosphorene, BSe/blue phosphorene and black phosphorene, were confirmed as excellent photocatalysts [28–31] for sun-light-driven water splitting. Previous literature [23] has also shown that both the CBM and VBM positions of phosphorene allotropes match well with the chemical reaction potential of H2/H+ and O2/H2O, showing potential ability in sun-light-driven water splitting as photocatalysts. These works show that phosphorus based nano-materials have desirable potentials in photocatalysts.

In this letter, we predict two new phosphorene allotropes, named as stair-P and zipper-P, with crystalline structures based on the previously proposed stair-graphane and zipper-graphane [32]. The structures, stabilities, electronic and optical properties, as well as their photocatalytic properties of stair-P and zipper-P were systematically investigated through the density functional theory (DFT) based first-principles calculations. They are confirmed to be dynamically viable phosphorene allotropes with energetic stabilities comparable to black-P and blue-P. The calculated results show that both stair-P and zipper-P are semiconductors with proper band gaps and band edges for photocatalytic applications.

2. Computational details

The DFT based first-principles calculations as implemented in Vienna ab initio simulation package (VASP) [33] is employed to investigate the structures, stabilities, electronic and optical properties, as well as the photocatalytic properties of stair-P and zipper-P. The projector augmented wave (PAW) potentials is adopted to describe the interactions between nucleus and the valence electrons. The exchange and correlation are approximated by the general gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functionals [34]. A plane-wave basis set with the kinetic energy cutoff of 400 eV is employed to expand the wave functions and the Brillouin zone (BZ) sample meshes is set to be denser enough. Both the lattices and atomic positions of all systems are fully optimized up to the residual force on every atom to be less than 0.01 eV Å−1 before property investigations. To evaluate the dynamic stabilities of these phosphorene allotropes, their vibrational spectrum were simulated though phonopy package [35] with the forces calculated from VASP. We have also considered using HSE06 functionals [36] to evaluate more accurate band gaps and band edges of the systems, for further evaluating if stair-P and zipper-P are proper materials as visible-light photocatalysts for water splitting.

3. Results and discussion

Stair-P and zipper-P are constructed based on the carbon frameworks of the previously proposed stair-graphane and zipper-graphane [32]. Their optimized crystals are shown in figures 1(a) and (b), respectively. Similar to the previously proposed α-P, β-P, γ-P, δ-P, red-P and θ1-P, stair-P and zipper-P contain only 6-member rings in their body, with different up and down sequences of phosphorus atoms. As listed in table 1, stair-P has a monoclinic lattice with P2/M (No.10) symmetry. Its optimized lattice parameters are a = 9.85 Å, b = 3.289 Å, c = 25 Å, α = γ = 90° and β = 86.06°. There are four inequivalent phosphorus atoms in stair-P as indicate in figure 1(a) in different colors, locating at positions of P1 (0.013, 0.00, 0.454), P2 (0.160, 0.50, 0.436), P3 (0.298, 0.500, 0.504) and P4 (0.429, 0.00, 0.466). The puckered thickness of stair-P is t = 3.669 Å, which is the largest one among these phosphorene allotropes. There are only four inequivalent bonds in stair-P. They are P1–P2, P2–P3, P3–P4 and P4–P1 with length of 2.223 Å, 2.259 Å, 2.262 Å and 2.261 Å, respectively. Zipper-P is a rectangular phase possessing symmetry of Pmma (No.51), as summarized in table 1. Its optimized lattice parameters are a = 10.67 Å, b = 3.27 Å, c = 25 Å and α = β = γ = 90°. From figure 1(b), we can see that there are two inequivalent phosphorus atoms in zipper-P. They locate at positions of P1 (0.103, 0.50, 0.491) and P2 (0.142, 0.00,
0.90 eV, 1.58 eV, 2.76 eV, 1.97 eV, respectively. This result is consistent well with those corresponding direct band gap of 1.58 eV. That is to say, the PBE-based/HSE06-based indirect band gap of stair-P is 1.57 eV, which is slightly smaller than the corresponding indirect band gap of black-P, blue-P, red-P, and green-P. The PBE-based/HSE06-based band gaps of black-P, blue-P, red-P, and green-P are 0.90 meV/atom, 1.93 meV/atom, 1.22 eV, and 1.96 eV, respectively. We can see that there are no imaginary frequencies appearing in the phonon band structures. Such results confirm that both stair-P and zipper-P are dynamically stable phases.

Further investigations show that the band gaps of stair-P and zipper-P can be effectively modulated by in-layer strains from different directions. Based on PBE functionals, the modulating effects of uniaxial in-layer strains on the band gaps of stair-P and zipper-P are shown in figures 5(a) and (b), respectively. We can see that the compressive strains along the zigzag direction (\(\sigma_y\)) change stair-P to be a quasi-direct band gap semiconductor, with the band gaps increased under small strains and then decreased at larger strains. For zipper-P, both the compressive and stretching strains along the zigzag direction (\(\sigma_y\)) translate stair-P from quasi-direct to indirect band gap semiconductor, with the band gaps increased under small strains and then decreased at larger strains. For zipper-P, both the compressive and stretching strains along the zigzag direction (\(\sigma_y\)) cannot affect the types of band gap. However, they can decrease the band gap from 1.26 eV to 0.2 eV. The compressive strains along armchair direction (\(\sigma_x\)) change zipper-P to be quasi-direct band gap semiconductor and correspondingly decrease its band gaps. Stretching strains along armchair direction (\(\sigma_x\))
just slightly affect the band gaps but do not change the types of band gap.

We noticed that the band gaps of stair-P and zipper-P are suitable for harvesting visible light. A good material for photo-catalyzed application needs not only the suitable band gaps but also the appropriate band edges compared with the reduction and oxidation potentials. To investigate the potential applications of stair-P and zipper-P in photocatalysis, we need to align the material’s band edges potentials with respect to the redox potentials. And, the work function of the photocatalyst material is important for confirming the band edges. Then, we firstly calculated the work function of stair-P, zipper-P, black-P and blue-P. The results of the work function (WF, the Fermi energy level is set as the reference) of these four allotropes are all calculated by DFT-PBE and HSE06 methods, as summarized in table 1. Furthermore, the HSE06-based work functions of stair-P (5.92 eV) and zipper-P (5.81 eV) are close to the standard reduction potential of H$^+$/H$_2$ ($-4.44$ eV) and oxidation potential of O$_2$/H$_2$O ($-5.67$ eV). These electronic properties are benefit for photocatalytic water splitting. We then turn our attentions to evaluate if their band edges (VBM and CBM) are also proper for photo-catalyzed water splitting. The HSE06-based VBM and CBM for black-P, blue-P, red-P, green-P, stair-P and zipper-P are shown in figure 6(a). The results for black-P and blue-P are good consistent with those reported in the previous work [23, 28, 29]. For the situation of PH = 0/PH = 7, the CBM of stair-P is 0.5944/0.1814 eV higher than the reduction potential of H$^+/H_2$ and the VBM of stair-P is 0.4917/0.9047 eV lower than the reduction potential of O$_2$/H$_2$O. These band edges in both acidic and neutral situations are appropriate for sun-light-driven water splitting. For zipper-P, its band edges show that it possesses potential for sun-light associated water splitting in acidic situation.
CBM is 0.3283 eV higher than the reduction potential of H⁺/H₂ and its VBM is 0.4458 eV lower than the reduction potential of O₂/H₂O at situation of PH = 0. However, the band edges of zipper-P are not suitable for water splitting at neutral situation of PH = 7. Our results also show that the previously proposed green-P and red-P have potentials for water splitting at neutral situation of PH = 7.

The investigations on optical absorptions of stair-P and zipper-P further confirm their potential applications in sunlight-driven water splitting. As shown in figure 6(b), the optical absorption spectrum of stair-P, zipper-P, black-P, blue-P, red-P and green-P are calculated based on HSE06 functional. We can see that stair-P and zipper-P show better absorbing abilities in the energy range of 2.0 eV to 4.0 eV than black-P and blue-P. These results suggest that stair-P and zipper-P are good visible sun-light absorbers. The results also show that the previously proposed green-P and red-P possess excellent absorbing abilities in the energy range of 2.0 eV to 4.0 eV, which is not reported in previous literatures.

4. Conclusions

Using first-principles calculations based on density-functional theory, we proposed two new stable phosphorene allotropes (stair-P and zipper-P) to extend phosphorene allotropes family. The structures, stabilities, electronic, optical properties and the potentials for photocatalysis of these two new phosphorene allotropes were systematically investigated. Our results show that both stair-P and zipper-P are dynamically stable phases with remarkable stabilities comparable to the experimentally synthesized black-P and blue-P. Stair-P and zipper-P are all indirect band gap semiconductors with HSE06-based band gaps of 2.32 eV and 2.0 eV, respectively. The proper energy band gaps and band edges, as well as the good sun-light absorbing abilities indicate that both stair-P and zipper-P possess potential for applications in sun-light-driven water splitting, which are also desirable to be synthesized in future experiment in views of their remarkable energetic stabilities and positive dynamical stabilities.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 11647170, 11647063, 11604180, 11704319, 11274262 and 11574260) and Higher Educational Science and Technology Program of Shandong Province (Grant Nos. J16LJ01).

ORCID iDs

Na Jiao https://orcid.org/0000-0003-2732-7209
Pan Zhou https://orcid.org/0000-0002-5570-2427
Lizhong Sun https://orcid.org/0000-0002-0086-9625

References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Science 306 666
[2] Bolotin K I, Sikes K J, Jiang Z, Klima M, Fudenberg G, Hone J, Kim P and Stormer H L 2008 Solid. State. Commun. 146 351
[3] Kim K S, Zhao Y, Jang H, Lee S Y, Kim J M, Kim K S, Ahn J H, Kim P, Choi J Y and Hong B H 2009 Nature 457 706
[4] Frank I W, Tanenbaum D M, van der Zande A M and McEuen P L 2007 J. Vac. Sci. Technol. B 25 2558
[5] Lee C, Wei X, Kysar J W and Hone J 2008 Science 321 385
[6] Balandin A A, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F and Lau C N 2008 Nano Lett. 8 902
[7] Jin C, Lin F, Suenaga K and Iijima S 2009 Phys. Rev. Lett. 102 195505
[8] Chhowalla M, Shin H S, Edu G, Li L-J, Loh K P and Zhang H 2013 Nat. Chem. 5 263
[9] Liu H, Neal A T, Zhu Z, Luo Z, Xu X, Tománek D and Ye P D 2014 ACS Nano 8 4033
[10] Huda M and Kleinman L 2006 Phys. Rev. 102 195505
[11] Chhowalla M, Shin H S, Eda G, Li L-J, Loh K P and Zhang H 2013 Nat. Chem. 5 263
[12] Liu H, Neal A T, Zhu Z, Luo Z, Xu X, Tománek D and Ye P D 2014 ACS Nano 8 4033
[13] Huda M and Kleinman L 2006 Phys. Rev. 102 195505
[14] Mak K F, Lee C, Hone J, Shan J and Heinz T F 2010 Phys. Rev. Lett. 105 136805
[15] He C, Zhang C X, Sun L Z, Jiao N, Zhang K W and Zhong J X 2012 Phys. Status Solidi 6 427
[16] Sluiter M H F and Kawazoe Y 2003 Phys. Rev. B 68 085410
[17] Zhu Z and Tománek D 2014 Phys. Rev. Lett. 112 176802
[18] Sofo J O et al 2007 Phys. Rev. B 75 153401
[19] Guan J, Zhu Z and Tománek D 2014 Phys. Rev. Lett. 113 046804
[20] Zhao T, He C Y, Ma S Y, Zhang K W, Peng X Y, Xie G F and Zhong J X 2015 J. Phys.: Condens. Matter 27 265301
[21] Han W H, Kim S, Lee I-H and Chang K J 2017 J. Phys. Chem. Lett. 8 4627
[22] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[23] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[24] Parlinski K, Li Z Q and Kawazoe Y 1997 Phys. Rev. Lett. 78 4063
[25] Heyd J, Scuseria G E and Ernzerhof M 2003 J. Chem. Phys. 118 8207