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Full Length Article

1,2,4-Azadiphosphole-based piezoelectric penta-CNP sheet with high spontaneous polarization



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ARTICLE INFO	A B S T R A C T		
<i>Keywords:</i> Penta-sheet Spontaneous polarization Piezoelectricity Molecular precursor	Miniaturizing piezoelectric devices calls for the rational design of two-dimensional (2D) materials with outstanding piezoelectric response and good synthetic feasibility. Here we propose a new ternary 2D pentagonal structure named penta-CNP by assembling the precursor of 1,2,4-azadiphosphole molecule. Based on state-of-the-art theoretical calculations, we find that penta-CNP is dynamically, thermally and mechanically stable with a direct band gap of 2.62 eV, and is anisotropic in its mechanical properties with a negative Poisson's ratio in the [110] direction. Due to its non-centrosymmetric geometry and semiconducting characteristic, penta-CNP possesses a large spontaneous polarization of 4.33×10^{-10} C/m and significant intrinsic piezoelectric response with $d_{16} = 1.80$ pm/V, surpassing the previously reported penta-BCN because of the larger size of phosphorous		

1. Introduction

Piezoelectric materials can realize the interconversion between mechanical and electrical energies [1,2] for applications in various fields including sensing [3], actuating [4] and energy harvesting [5]. However, we can only expect piezoelectric properties from the materials with non-centrosymmetry and non-metallicity [6], as is the case in 2D MoSi₂N₄ [7]. In recent years, 2D piezoelectric materials have attracted extensive attention primarily due to the need of device miniaturization. More importantly, 2D sheets can be piezoelectric even if their 3D counterparts are not [3,8]. Therefore, 2D materials provide more opportunities for piezoelectricity. Among the studied 2D materials, pentasheets composed of pentagons are of special interest because of their unique geometries. For example, although graphene shows no piezoelectricity, penta-graphene is piezoelectric with $d_{36} = -0.065 \text{ pm/V}$ [9], which can be enhanced when going from an unitary to binary sheet by introducing B to form penta-CB₂ with $d_{31} = -0.505$ pm/V and $d_{32} =$ 0.273 pm/V, the enhanced polarization is attributed to the large electronegativity difference between the elements. It would be reasonable to expect that the piezoelectric performance can be further improved when going from a binary to ternary 2D material. This is confirmed by a recent study where a ternary penta-BCN sheet exhibits high spontaneous polarization of 3.17×10^{-10} C/m and a prominent piezoelectricity with

 $d_{21} = 0.878 \text{ pm/V}, d_{22} = -0.678 \text{ pm/V}, \text{ and } d_{16} = 1.72 \text{ pm/V}$ [10]. Thus, it is highly desirable to synthesize such 2D piezoelectric pentasheet.

atom. This study expands the family of 2D ternary pentagonal structures for piezoelectric applications.

It is interesting to note that precursor-based bottom-up approach has been widely used for the synthesis of graphene sheet [11], nanoribbons [12], nanotubes [13], and many other 2D materials such as BCN monolayers [14]. However, so far no any precursor molecules are experimentally available for the synthesis of the theoretically predicted penta-BCN sheet. Hence, an intriguing question arises: can we design a ternary piezoelectric penta-sheet by using available precursors as the structural unit?

To this end, we propose a new ternary pentagon-based 2D structure, penta-CNP, by assembling the precursor of 1,2,4-azadiphosphole molecule that has been synthesized with several well-developed methods. As early as 1991, Ionkin *et al.* prepared 1,2,4-azadiphosphole derivatives using thermal dimerization of amino-substituted phosphaalkyne [15]. Later on, other groups reported stoichiometric reactions of titanium- and vanadium-imide complexes as nitrogen sources with phosphaalkynes for synthesizing 1,2,4-azadiphosphole molecule [16–18]. Very recently, Liang *et al.* succeeded in the development of the first vanadium-catalyzed [2 + 2 + 1] cycloaddition reactions of azobenzenes with phosphaalkynes to synthesize a variety of 1,2,4-azadiphospholes [19]. These experimental progresses motivate us to design the new ternary

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Fig. 1. (a) Pentagonal skeleton of the experimentally synthesized 1,2,4-azadiphosphole molecule and the nitrogen radical for assembling the structure of penta-CNP. (b) Top and side views of the optimized structure. Dashed rectangle represents the unit cell of penta-CNP.

penta-sheet and study its properties, especially its piezoelectricity. We show that the resulting penta-CNP is not only stable, but also exhibits high spontaneous polarization and strong piezoelectric response.

2. Computational methods

The Vienna *ab initio* simulation package (VASP) [20] is used to perform the calculations based on density functional theory. The projector augmented wave method [21,22] with a kinetic energy cutoff of 600 eV is used to describe the interactions between the electrons and nuclei. The Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation [23,24] for the exchange–correlation interactions is used in geometry optimization and properties calculations, while the hybrid Heyd-Scuseria-Ernzerhof (HSE06) functional [25,26] is used for more accurate electronic structure. The first Brillouin zone is represented by a $9 \times 9 \times 1$ *k*-point grid in the reciprocal space using the Monkhorst-Pack scheme [27]. A vacuum space of 21 Å is set along the out-of-plane direction to avoid the interactions between periodic images. The convergence thresholds for total energy and atomic force are set to 10^{-8} eV and 10^{-6} eV/Å, respectively. The finite displacement method [28] implemented in the Phonopy package [29] is used to check the dynamic stability by calculating the phonon spectra. As for the thermal stability, *ab initio* molecular dynamics [30] (AIMD) simulations are conducted by using the Nosé-Hoover thermostat [31].

3. Results and discussion

3.1. Structure and stability

We use the pentagonal skeleton of 1,2,4-azadiphosphole molecule as the precursor and the N radical as the linker to construct the 2D pentasheet, as shown in Fig. 1(a), the optimized geometry is given in Fig. 1(b) which possesses P21 symmetry (space group No. 4) with the lattice constants of a = 3.72 Å and b = 3.69 Å. In this structure, there are two carbon, two nitrogen and two phosphorus atoms in its unit cell, occupying three chemically nonequivalent Wyckoff positions, respectively, i. e. $2a_1$ (0.783, 0.527, 0.500), $2a_2$ (0.920, 0.855, 0.533) and $2a_3$ (0.597, 0.174, 0.557) with the C-N, C-P and N-P bond lengths of 1.47, 1.92 and 1.76 Å, respectively. The top view of Fig. 1(b) shows a pentagonal



Fig. 2. (a) Phonon band structure, and (b) total potential energy fluctuations of penta-CNP with time during the AIMD simulation at 1000 K. Insets show snapshots of the atomic configuration at the end of the simulation.



Fig. 3. Variation of (a) the in-plane Young's modulus and (b) Poisson's ratio with the orientation of penta-CNP.

pattern resembling the geometry of penta-graphene [32]. Thus we name it penta-CNP. The coordinates and lattice parameters of the optimized geometry are listed in Supporting Information (SI).

The buckling height of penta-CNP is 2.41 Å, which is larger than that of penta-graphene and the ternary 2D sheet penta-BCN [10] because of the longer N-P and C-P bond lengths in this structure. On the other hand, the penta-CNP lattice can also be viewed as an orderly modified penta-CN₂ [33] structure by replacing half of the N atoms with P atoms. Such substitution breaks the centrosymmetry of the original structure, leading to the ternary sheet of penta-CNP. The formation energy of penta-CNP is calculated to be -0.29 eV/atom by considering the potential energy of the individual atoms, the one in its most stable conditions. The negative formation energy implies that the synthesis of penta-CNP via the corresponding elementary substances is energetically favorable.

To study the dynamical stability of penta-CNP, we calculate its phonon spectrum. The results are presented in Fig. 2(a). There are no imaginary modes in the entire first Brillouin zone, confirming the dynamical stability of penta-CNP. For checking the thermal stability, we perform AIMD simulations at different temperatures from 400 to 1200 K with every 200 K temperature intervals. For each simulation, we use a 4 \times 4 \times 1 supercell to reduce the fake stability caused by the periodic boundary conditions and a time step of 1 fs for 10 ps. As shown in Fig. 2 (b), one can see that the structure has no obvious distortion at the end of the simulation and the total potential energy fluctuates around a constant value during the simulation, suggesting that the structure is thermally stable at 1000 K. However, when the temperature reaches to 1200 K, some C-P bonds are broken, indicating that this structure can withstand high temperature up to 1000 K. We then investigate the mechanical stability by using the finite distortion method [34] as implemented in VASP code [20]. The linear elastic constants are calculated to be $C_{11} = 173.32 \text{ N} \cdot \text{m}^{-1}$, $C_{22} = 183.57 \text{ N} \cdot \text{m}^{-1}$, $C_{12} = 4.52 \text{ N} \cdot \text{m}^{-1}$ and $C_{66} = 99.01 \text{ N} \cdot \text{m}^{-1}$. For a 2D material with an orthogonal lattice, the Born-Huang elastic stability criteria [35–37] are in the following formulas:

$$C_{11} > 0; C_{22} > 0; C_{66} > 0; C_{11}C_{22} > C_{12}^2$$
(1)

which are fully satisfied with the elastic constants of penta-CNP, confirming the mechanical stability of penta-CNP.

3.2. Mechanical properties

Next, we study the mechanical properties from the calculated linear elastic constants whose specific values are $C_{11} = 173.32 \text{ N} \cdot \text{m}^{-1}$, $C_{22} = 183.57 \text{ N} \cdot \text{m}^{-1}$, $C_{12} = 4.52 \text{ N} \cdot \text{m}^{-1}$ and $C_{66} = 99.01 \text{ N} \cdot \text{m}^{-1}$.

Using the following formulas [38], we calculate the in-plane Young's modulus and Poisson's ratio of penta-CNP along different directions,

$$E(\theta) = \frac{C_{11}C_{22} - C_{12}^2}{C_{11}s^4 + C_{22}c^4 + \left(\frac{C_{11}C_{22} - C_{12}^2}{C_{66}} - 2C_{12}\right)c^2s^2}$$
(2)

$$\nu(\theta) = -\frac{\left(C_{11} + C_{22} - \frac{C_{11}C_{22} - C_{12}^2}{C_{66}}\right)c^2s^2 - C_{12}(c^4 + s^4)}{C_{11}s^4 + C_{22}c^4 + \left(\frac{C_{11}C_{22} - C_{12}^2}{C_{66}} - 2C_{12}\right)c^2s^2}$$
(3)

where $c = \cos \theta$ and $s = \sin \theta$. The calculated results are plotted in Fig. 3. The lowest and highest values of the Young's moduli are 172 N/m and 190 N/m, respectively, exhibiting mechanical anisotropy. Although these values are smaller than those of penta-BCN ($E_a = 223$ N/m and $E_b = 189$ N/m), they are still much larger than that of MoS₂ [39] monolayer (130 N/m), indicating that penta-CNP has relatively strong bonding



Fig. 4. (a) Electronic band structure at the PBE and HSE06 levels, and total DOS and PDOS at the HSE06 level of penta-CNP. (b–e) Band-decomposed charge density of the 2nd VBM, VBM, CBM, and 2nd CBM of penta-CNP. (Isosurface value = 0.008 Å^{-3}).



Fig. 5. Charge distribution on the atoms in penta-CNP.

within the 2D plane and moderate mechanical properties. For $\theta = 45^{\circ}$, 135°, 225° and 315°, the Poisson's ratio has a negative value of -0.04 in the [110] direction and its equivalents.

3.3. Electronic properties

We then calculate the electronic band structure, total density of states (DOS) and partial density of states (PDOS) to study the electronic properties. The calculations for band-decomposed charge density are also carried out to investigate the contribution of atoms to different energy bands. Fig. 4(a) shows the results of electronic band structure. Penta-CNP has a direct band gap of 1.50 eV at the PBE level, which becomes 2.62 eV at the HSE06 level as is well known that the PBE functional underestimates the band gaps. From the PDOS and the band-decomposed charge density distributions, as shown in Fig. 4(a–e), one can see that the valence band maximum (VBM) is mainly contributed from N atoms, while the conduction band minimum (CBM) is almost equally contributed by C, N, and P atoms.

To tune the band gap, we apply tensile strain of 3% and 5%, respectively. Our calculated results suggest that penta-CNP remains dynamically stable, as shown in Fig. S1(a, b) in SI, no any imaginary frequencies appear, while the band gap is slightly reduced from its original value of 2.62 eV to 2.57 and to 2.56 eV, respectively. The calculated band structures under strain are plotted in Fig. S2. It is worth noting that 2D sheets usually become unstable in compressive strain, which is also true for penta-CNP. As shown in Fig. S1(c), the imaginary modes appear near the Γ point even under 1% strain.

3.4. Spontaneous polarization

We then evaluate the charge distribution among the different atoms. The band-decomposed charge density distributions of the valence bands are presented in Fig. 4(b) and (c), which show the asymmetry of electron cloud around the atoms, implying the polarity of the covalent bonds between the different atoms. The results of Bader charge analysis [40,41] shows that each P atom donates 1.26 electrons to its neighboring atoms, while each C and N atom gains 0.02 and 1.24 electrons (see Fig. 5), respectively, demonstrating the highly polarized nature of the N-P bond. The electron transfer from P to N in penta-CNP can be explained with the theory of electronegativity [42], because the electronegativity of C (2.55) falls in between that of P (2.19) and N (3.04). The polarization of the N-P bonds in the penta-CNP lattice adds up in the [010] direction while cancels each other out along the [100] and [001] directions, thus leading to strong spontaneous polarization in penta-CNP.

To quantify the spontaneous polarization, we calculate the dipole moment by using the finite electric field method based on the Berry phase theory [43,44],

$$P_s = P_s^{ion} + P_s^{ele} \tag{4}$$

$$P_s^{ion} = \frac{|e|}{\Omega} \sum_{i=1}^{N_{atom}} Z_i^V \Delta r_i$$
(5)

Table 1

Elastic stiffness tensor (in N/m), piezoelectric stress tensor (in 10^{-10} C/m) and piezoelectric strain tensor (in pm/V) of penta-CNP.

Property	Parameter			
Elastic stiffness tensor	C ₁₁ 173.32	$C_{12} = C_{21}$ 4.52	C ₂₂ 183.57	C ₆₆ 99.01
Piezoelectric stress tensor	e ₂₁ 2.37	$e_{22} = -1.21$	e_{16} 1.78	$e_{36} \\ -0.11$
Piezoelectric strain tensor	d ₂₁ 1.39	$d_{22} = -0.69$	d_{16} 1.80	$d_{36} = -0.1$

where P_s , P_s^{ion} and P_s^{ele} are the total polarization, the ionic contribution and the electronic contribution, respectively, and Ω is the volume of unit cell, and $|e|Z_i^V$ and Δr_i represent the valence charge and the displacement of *i*-th atom, respectively.

The spontaneous polarization is calculated to be 4.33×10^{-10} C/m, which is larger than that of penta-BCN (3.17×10^{-10} C/m). The underlying reason is that the difference in bond length (0.45 Å) between the C—N (1.47 Å) and C—P bonds (1.92 Å) in penta-CNP is three times larger than that (0.14 Å) between the C—N (1.49 Å) and C—B bonds (1.63 Å) in penta-BCN, namely, the geometry of penta-CNP is more noncentrosymmetric than that of penta-BCN. The longer C—P bond length separates the center of positive and negative charges more effectively, similar to the case in CrSe₂ and CrTe₂ [45,46], thus leading to a stronger spontaneous polarization. In addition, the buckling height of 2.41 Å in penta-CNP is larger than the value of 1.34 Å in penta-BCN due to the longer C-P and N-P bond lengths. Usually the larger buckling height of a 2D material provides a broader space for charge accumulation on the edges of the both sides [47]. Thus, penta-CNP exhibits higher spontaneous polarization than penta-BCN.

3.5. Intrinsic piezoelectricity

The semiconducting characteristic, the large permanent dipole and the lack of centrosymmetry of penta-CNP make it promising for piezoelectricity according to the basic principles of data mining for potential 2D piezoelectric monolayer [48]. Based on the lattice symmetry of this structure and the theory of continuum mechanics [49,50], the relationship among the piezoelectric stress tensor, piezoelectric strain tensor and elastic stiffness tensor is given below

$$\begin{pmatrix} 0 & 0 & e_{16} \\ e_{21} & e_{22} & 0 \\ 0 & 0 & e_{36} \end{pmatrix} = \begin{pmatrix} 0 & 0 & d_{16} \\ d_{21} & d_{22} & 0 \\ 0 & 0 & d_{36} \end{pmatrix} \begin{pmatrix} C_{11} & C_{12} & C_{16} \\ C_{21} & C_{22} & C_{26} \\ C_{31} & C_{32} & C_{36} \end{pmatrix}$$
(6)

From Eq. (6), we derive the following Eqs. (7)–(10) to calculate the piezoelectric strain coefficients. The calculated results are given in Table 1.

$$d_{16} = \frac{e_{16}}{C_{66}} \tag{7}$$

$$d_{21} = \frac{C_{21}e_{22} - C_{22}e_{21}}{C_{21}C_{12} - C_{11}C_{22}}$$
(8)

Table 2

Comparison of the piezoelectric coefficients e (in 10^{-10} C/m) and d (in pm/V) of penta-CNP with those of some other 2D materials.

Structure	e	d
Penta-CNP Penta-BCN [10] <i>h</i> -BN [51] H-AIN-H [52]	$\begin{array}{c} 2.37 \ (e_{21}), \ 1.78 \ (e_{16}) \\ 1.93 \ (e_{21}), \ 1.80 \ (e_{16}) \\ 1.38 \ (e_{11}) \\ 0.65 \ (e_{11}) \end{array}$	1.39 (d_{21}) , 1.80 (d_{16}) 0.878 (d_{21}) , 1.72 (d_{16}) 0.60 (d_{11}) 1.15 (d_{11})
H-GaN-H [52] H-InN-H [52]	$0.35 (e_{11})$ $0.40 (e_{11})$	$0.63 (d_{11})$ $1.36 (d_{11})$

$$d_{22} = \frac{C_{12}e_{21} - C_{11}e_{22}}{C_{21}C_{12} - C_{11}C_{22}} \tag{9}$$

$$d_{36} = \frac{e_{36}}{C_{66}} \tag{10}$$

As shown in Table 1, penta-CNP posesses remarkable in-plane piezoelectric responses to both tensile and shear strains with $d_{16} = 1.80 \text{ pm/V}$ and $d_{21} = 1.39 \text{ pm/V}$ along the [100] and [010] directions, respectively. For comparison, the piezoelectric stress and strain tensors of penta-CNP and some other 2D piezoelectric materials are listed in Table 2. One can see that the in-plane piezoelectricity of penta-CNP is stronger than that of *h*-BN [51] and penta-BCN, and much stronger than that of the hydrogenated 2D materials [52]. The d_{21} of penta-CNP is about 1.5 times as large as that of penta-BCN, and the piezoelectricity is enhanced overall. In general, softer materials possess larger *d* coefficient [48]. From the comparison of mechanical properties between penta-BCN and penta-CNP, we note that penta-CNP is softer than penta-BCN, thus leading to a larger value of *d*.

Usually, surface modification can increase the thickness of a nanosheet, and is favorable for enhancing piezoelectric effect [52]. While even if without surface modification, penta-CNP possesses much larger in-plane piezoelectric strain coefficient as compared to the hydrogenated AlN, GaN and InN [52], exhibiting the superiority in piezoelectric effect.

4. Conclusions

In summary, based on first-principles calculations, we have proposed a new 2D ternary pentagonal material, penta-CNP, by using the pentagonal skeleton C2P2N of 1,2,4-azadiphosphole molecule as the precursor and the N radical as the linker. The resulting sheet is purely composed of pentagonal rings and has the following properties: (1) Penta-CNP is dynamically, thermally, and mechanically stable, and is semiconducting with a direct band gap of 2.62 eV at the HSE06 level; (2) It has anisotropic mechanical properties with a negative Poisson's ratio under tensile strain along the [110] direction; (3) The polarized N-P bonds in this structure are responsible for the high spontaneous polarization of 4.33 \times 10^{-10} C/m along the [010] direction; (4) Penta-CNP exhibits large piezoelectric coefficients with $d_{21} = 1.39$ pm/V and d_{16} = 1.80 pm/V, showing advantages in its piezoelectricity and feasibility of synthesis as compared to the previously reported penta-BCN sheet. We hope that this study can stimulate experimental efforts in synthesizing the penta-CNP sheet for expanding the 2D ternary pentagon-based family with promising technological applications.

CRediT authorship contribution statement

Wei Sun: Investigation, Formal analysis, Validation, Writing - original draft, Writing - review & editing. Yiheng Shen: Resources, Validation, Writing - review & editing. Yaguang Guo: Resources, Software, Validation. Yanyan Chen: Resources, Software, Validation. Qian Wang: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2021.149499.

References

- [1] M.-M. Yang, Z.-D. Luo, Z. Mi, J. Zhao, S.P.E.M. Alexe, Piezoelectric and pyroelectric effects induced by interface polar symmetry, Nature 584 (2020) 377–381.
- [2] B. Liu, M. Wang, M. Chen, J. Wang, J. Liu, D. Hu, S. Liu, X. Yao, H. Yang, Effect of TC(002) on the output current of a ZnO thin-film nanogenerator and a new piezoelectricity mechanism at the atomic level, ACS Appl. Mater. Interfaces 11 (2019) 12656–12665.
- [3] W. Wu, L. Wang, Y. Li, F. Zhang, L. Lin, S. Niu, D. Chenet, X. Zhang, Y. Hao, T. F. Heinz, J. Hone, Z.L. Wang, Piezoelectricity of single-atomic-layer MoS₂ for energy conversion and piezotronics, Nature 514 (2014) 470–474.
- [4] S.C. Masmanidis, R.B. Karabalin, I. De Vlaminck, G. Borghs, M.R. Freeman, M. L. Roukes, Multifunctional nanomechanical systems via tunably coupled piezoelectric actuation, Science 317 (2007) 780–783.
- [5] S.H. Baek, J. Park, D.M. Kim, V.A. Aksyuk, R.R. Das, S.D. Bu, D.A. Felker, J. Lettieri, V. Vaithyanathan, S.S.N. Bharadwaja, N. Bassiri-Gharb, Y.B. Chen, H. P. Sun, C.M. Folkman, H.W. Jang, D.J. Kreft, S.K. Streiffer, R. Ramesh, X.Q. Pan, S. Trolier-McKinstry, D.G. Schlom, M.S. Rzchowski, R.H. Blick, C.B. Eom, Giant piezoelectricity on Si for hyperactive MEMS, Science 334 (2011) 958–961.
- [6] R. Ahammed, N. Jena, A. Rawat, M.K. Mohanta, A. De Dimple, Sarkar, Ultrahigh out-of-plane piezoelectricity meets giant Rashba effect in 2D Janus monolayers and bilayers of group IV transition-metal trichalcogenides, J. Phys. Chem. C 124 (2020) 21250–21260.
- [7] B. Mortazavi, B. Javvaji, F. Shojaei, T. Rabczuk, A.V. Shapeev, X. Zhuang, Exceptional piezoelectricity, high thermal conductivity and stiffness and promising photocatalysis in two-dimensional MoSi₂N₄ family confirmed by first-principles, Nano Energy 82 (2021) 105716.
- [8] L.C. Gomes, A. Carvalho, A.H. Castro Neto, Enhanced piezoelectricity and modified dielectric screening of two-dimensional group-IV monochalcogenides, Phys. Rev. B 92 (2015) 214103.
- [9] S.-D. Guo, S.-Q. Wang, Tuning pure out-of-plane piezoelectric effect of pentagraphene: A first-principle study, J. Phys. Chem. Solids 140 (2020) 109375.
- [10] K. Zhao, Y. Guo, Y. Shen, Q. Wang, Y. Kawazoe, P. Jena, Penta-BCN: A new ternary pentagonal monolayer with intrinsic piezoelectricity, J. Phys. Chem. Lett. 11 (2020) 3501–3506.
- [11] Z. Li, P. Wu, C. Wang, X. Fan, W. Zhang, X. Zhai, C. Zeng, Z. Li, J. Yang, J. Hou, Low-temperature growth of graphene by chemical vapor deposition using solid and liquid carbon sources, ACS Nano 5 (2011) 3385–3390.
- [12] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Müllen, R. Fasel, Atomically precise bottom-up fabrication of graphene nanoribbons, Nature 466 (2010) 470–473.
- [13] Y. Tian, Z. Hu, Y. Yang, X. Wang, X. Chen, H. Xu, Q. Wu, W. Ji, Y. Chen, In situ TA-MS study of the six-membered-ring-based growth of carbon nanotubes with benzene precursor, J. Am. Chem. Soc. 126 (2004) 1180–1183.
- [14] S. Beniwal, J. Hooper, D.P. Miller, P.S. Costa, G. Chen, S.-Y. Liu, P.A. Dowben, E.C. H. Sykes, E. Zurek, A. Enders, Graphene-like boron-carbon-nitrogen monolayers, ACS Nano 11 (2017) 2486–2493.
- [15] A.S. Ionkin, S.N. Ignat'Eva, I.A. Litvinov, V.A. Naumov, B.A. Arbuzov, 1,2,4azadiphosphole, Heteroat. Chem. 2 (1991) 577–581.
- [16] F. Geoffrey, N. Cloke, P.B. Hitchcock, J.F. Nixon, D. James Wilson, F. Tabellion, U. Fischbeck, F. Preuss, M. Regitz, Synthetic, structural and theoretical studies on new aromatic 1,2,4-azadiphosphole ring systems: crystal and molecular structure of P₂C₂Bu^t₂NPh, Chem. Commun. (1999) 2363–2364.
- [17] F. Tabellion, C. Peters, U. Fischbeck, M. Regitz, F. Preuss, Imidovanadium(V) complexes as reaction partners for kinetically stabilized phosphaalkynes: synthesis of 1,2,4-azaphosphavanada(V)-cyclobutenes, 1,3,5-triphosphabenzenes, and 1H-1,2,4-azadiphospholes, Chem. - Eur. J. 6 (2000) 4558-4566.
- [18] F.G.N. Cloke, J.C. Green, N. Hazari, P.B. Hitchcock, P. Mountford, J.F. Nixon, D. J. Wilson, Reactions of ^tBuC;P with cyclooctatetraene-supported titanium imido complexes, Organometallics 25 (2006) 3688–3700.
- [19] W. Liang, K. Nakajima, Y. Nishibayashi, Synthesis of 1,2,4-azadiphosphole derivatives based on vanadium-catalyzed [2+2+1] cycloaddition reactions of azobenzenes with phosphaalkynes, RSC Adv. 10 (2020) 12730–12733.
- [20] G. Kresse, F. J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169–11186.
- [21] P.E. Blöchl, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17953–17979.
- [22] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmentedwave method, Phys. Rev. B 59 (1999) 1758–1775.
- [23] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865–3868.
- [24] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple [Phys. Rev. Lett. 77, 3865 (1996)], Phys. Rev. Lett. 78 (1997), 1396–1396.

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- [25] J. Heyd, G.E. Scuseria, M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, J. Chem. Phys. 118 (2003) 8207–8215.
- [26] J. Heyd, G.E. Scuseria, M. Ernzerhof, Erratum: "Hybrid functionals based on a screened Coulomb potential" [J. Chem. Phys. 118, 8207 (2003)], J. Chem. Phys. 124 (2006) 219906.
- [27] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, Phys. Rev. B 13 (1976) 5188–5192.
- [28] K. Parlinski, Z.Q. Li, Y. Kawazoe, First-principles determination of the soft mode in cubic ZrO₂, Phys. Rev. Lett. 78 (1997) 4063–4066.
- [29] A. Togo, I. Tanaka, First principles phonon calculations in materials science, Scr. Mater. 108 (2015) 1–5.
- [30] D. Bucher, L.C.T. Pierce, J.A. McCammon, P.R.L. Markwick, On the use of accelerated molecular dynamics to enhance configurational sampling in *ab initio* simulations, J. Chem. Theory Comput. 7 (2011) 890–897.
- [31] D. Evans, B. Holian, The Nose-Hoover thermostat, J. Chem. Phys. 83 (1985) 4069–4074.
- [32] S. Zhang, J. Zhou, Q. Wang, X. Chen, Y. Kawazoe, P. Jena, Penta-graphene: A new carbon allotrope, Proc. Natl. Acad. Sci. U. S. A. 112 (2015) 2372–2377.
- [33] S. Zhang, J. Zhou, Q. Wang, P. Jena, Beyond graphitic carbon nitride: Nitrogen-rich penta-CN₂ sheet, J. Phys. Chem. C 120 (2016) 3993–3998.
- [34] Y. Le Page, P. Saxe, Symmetry-general least-squares extraction of elastic data for strained materials from *ab initio* calculations of stress, Phys. Rev. B 65 (2002) 104104.
- [35] M. Born, K. Huang, M. Lax, Dynamical theory of crystal lattices, Am. J. Phys. 23 (1955), 474–474.
- [36] Y. Ding, Y. Wang, Density functional theory study of the silicene-like SiX and XSi₃ (X = B, C, N, Al, P) honeycomb lattices: The various buckled structures and versatile electronic properties, J. Phys. Chem. C 117 (2013) 18266–18278.
- [37] F. Mouhat, F.-X. Coudert, Necessary and sufficient elastic stability conditions in various crystal systems, Phys. Rev. B 90 (2014) 224104.
- [38] E. Cadelano, P.L. Palla, S. Giordano, L. Colombo, Elastic properties of hydrogenated graphene, Phys. Rev. B 82 (2010) 235414.

- [39] R.C. Cooper, C. Lee, C.A. Marianetti, X. Wei, J. Hone, J.W. Kysar, Nonlinear elastic behavior of two-dimensional molybdenum disulfide, Phys. Rev. B 87 (2013) 035423.
- [40] G. Henkelman, A. Arnaldsson, H. Jónsson, A fast and robust algorithm for Bader decomposition of charge density, Comput. Mater. Sci. 36 (2006) 354–360.
- [41] W. Tang, E. Sanville, G. Henkelman, A grid-based Bader analysis algorithm without lattice bias, J. Phys.: Condens. Matter 21 (2009) 084204.
- [42] L. Pauling, The nature of the chemical bond. Iv. The energy of single bonds and the relative electronegativity of atoms, J. Am. Chem. Soc. 54 (1932) 3570–3582.
 [43] R. Resta, Macroscopic polarization in crystalline dielectrics: the geometric phase
- [43] R. Resta, indecoscopic polarization in crystalline detectives. the geometric plase approach, Rev. Mod. Phys. 66 (1994) 899–915.
 [44] R.D. King-Smith, D. Vanderbilt, Theory of polarization of crystalline solids, Phys.
- [44] R.D. King-Smith, D. Vanderbilt, Theory of polarization of crystalline solids, Phys. Rev. B 47 (1993) 1651–1654.
- [45] M.N. Blonsky, H.L. Zhuang, A.K. Singh, R.G. Hennig, Ab initio prediction of piezoelectricity in two-dimensional materials, ACS Nano 9 (2015) 9885–9891.
- [46] M.M. Alyörük, Y. Aierken, D. Çakır, F.M. Peeters, C. Sevik, Promising piezoelectric performance of single layer transition-metal dichalcogenides and dioxides, J. Phys. Chem. C 119 (2015) 23231–23237.
- [47] J. Zhang, S.A. Meguid, Piezoelectricity of 2D nanomaterials: characterization, properties, and applications, Semicond. Sci. Technol. 32 (2017) 043006.
- [48] R. Hinchet, U. Khan, C. Falconi, S.-W. Kim, Piezoelectric properties in twodimensional materials: Simulations and experiments, Mater. Today 21 (2018) 611–630.
- [49] H. Ghasemi, H.S. Park, T. Rabczuk, A level-set based IGA formulation for topology optimization of flexoelectric materials, Comput. Method. Appl. M. 313 (2017) 239–258.
- [50] H.V. Do, T. Lahmer, X. Zhuang, N. Alajlan, H. Nguyen-Xuan, T. Rabczuk, An isogeometric analysis to identify the full flexoelectric complex material properties based on electrical impedance curve, Comput. Struct. 214 (2019) 1–14.
- [51] K.-A.N. Duerloo, M.T. Ong, E.J. Reed, Intrinsic piezoelectricity in two-dimensional materials, J. Phys. Chem. Lett. 3 (2012) 2871–2876.
- [52] Y. Guo, H. Zhu, Q. Wang, Piezoelectric effects in surface-engineered twodimensional group III nitrides, ACS Appl. Mater. Interfaces 11 (2019) 1033–1039.

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