Recent progress in epitaxial growth of two-dimensional phosphorus

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Abstract
Phosphorus is an important non-metal element with many allotropes and tunable electronic properties. As one of the most important allotropes of phosphorus, two-dimensional (2D) black phosphorus (BP) possesses many extraordinary properties, such as high charge carrier mobility with high on/off ratio, thickness-dependent direct bandgap varying from 0.3 to 2 eV, and anisotropic electrical, optical and thermal properties. Inspiring by the success of 2D BP, other 2D phosphorus allotropes with intriguing properties for next-generation electronic and optoelectronic devices have also attracted much attention. However, large-scale growth of high-quality 2D single/few-layer phosphorus remains a great challenge. In this review, we highlight recent progress achieved on 2D phosphorus, with special focus on the epitaxial growth of 2D BP films, blue phosphorus (BlueP) monolayers as well as phosphorus-metal porous networks. The remaining challenges and future perspectives on the development of monolayer phosphorus or phosphorus-metal alloys are also provided.

KEYWORDS
black phosphorus, blue phosphorus, epitaxial growth, metal-phosphorus networks

1 | INTRODUCTION

Black phosphorus (BP), a group-V elemental two-dimensional (2D) material, has attracted substantial research interest since its rediscovery in 2014,¹ offering a variety of unique properties such as high hole mobility up to ~1000 cm²/(V s) at room temperature accompanied with a high on/off ratio of 10⁵,¹,² thickness-dependent direct bandgap (0.3–2 eV) that covers the range from visible to mid-infrared region,¹,³,⁶ and the in-plane anisotropic electronic, optical, thermal and mechanical properties.²,⁵–⁷ All these distinctive characteristics make BP a
promising candidate for electronic, optoelectronic, energy storage, and biological applications, and significant advancements have been made for the uses in field-effect transistors (FETs), photodetectors, solar cells, lithium-/sodium-ion batteries, supercapacitors, photothermal therapy, drug delivery, bioimaging, and so on. The success of BP has inspired great interest in searching for new phosphorus structures. Many 2D phosphorus allotropes with varied electronic properties have been proposed theoretically, including $\alpha$-P, $\beta$-P, $\gamma$-P, $\delta$-P, red phosphorene, green phosphorene, $\alpha\beta$-P, $\beta\gamma$-P, $\gamma\delta$-P, $\alpha\gamma$-P, $\alpha\delta$-P, $\beta\delta$-P, $\varepsilon$-P, $\zeta$-P, $\eta$-P, $\theta$-P, $\alpha\varepsilon$-P, $\beta\varepsilon$-P, $\gamma\varepsilon$-P, $\zeta\varepsilon$-P1, $\zeta\varepsilon$-P2, $\psi$-P, violet phosphorus, Kagome phosphorus and porous phosphorus (Figure 1). It is noted that some of these phosphorus structures are constructed through the hybridization of different basic phosphorus phases, greatly enriching the 2D phosphorus family (Figure 1Q–U). Contrary to the flourishing and fast developments in theoretical predictions, the experimental synthesis of 2D phosphorus is less progressed. Up to now, some of these allotropes, $\alpha$-P (black phosphorus, BP), $\beta$-P (blue phosphorus, BlueP) and violet phosphorus, red phosphorus nanosheet, have been experimentally realized, while the others are still awaiting experimental verification.

In this review, we highlight the recent progress in the experimental synthesis of single/few-layer phosphorus. We begin with a brief summary of the top-down fabrication methods for preparing 2D BP flakes, and then the

**FIGURE 1**  Atomic structures of phosphorus allotropes. (A) $\alpha$-P, (B) $\beta$-P, (C) $\gamma$-P, and (D) $\delta$-P. Reproduced with permission. Copyright 2014, American Physical Society. (E) Red phosphorene. Reproduced with permission. Copyright 2015, IOP Publishing. (F) Green phosphorene. Reproduced with permission. Copyright 2017, American Chemical Society. (G) $\alpha\beta$-P, (H) $\beta\gamma$-P, (I) $\gamma\delta$-P, (J) $\alpha\gamma$-P, (K) $\alpha\delta$-P, and (L) $\beta\delta$-P. Reproduced with permission. Copyright 2019, American Chemical Society. (M) $\varepsilon$-P, (N) $\zeta$-P, (O) $\eta$-P, (P) $\theta$-P, (Q) $\alpha\varepsilon$-P, (R) $\beta\varepsilon$-P, (S) $\gamma\varepsilon$-P, (T) $\zeta\varepsilon$-P1, and (U) $\zeta\varepsilon$-P2. Reproduced with permission. Copyright 2015, American Chemical Society. (V) $\psi$-P. Reproduced with permission. Copyright 2017, Royal Society of Chemistry. (W) Violet phosphorus. Reproduced with permission. Copyright 2016, American Chemical Society. (X) Kagome phosphorus. Reproduced with permission. Copyright 2015, IOP Publishing. (Y) Porous phosphorus. Reproduced with permission. Copyright 2016, American Chemical Society.
bottom-up growth of BP ultrathin films. A comparison of the qualities and the corresponding device performances of BP thin films prepared by different techniques is also presented. Subsequently, the recent developments of the epitaxial growth of BlueP and BlueP related metal-phosphorus porous networks are discussed. Finally, challenges and prospects on developing controllable methods to grow large-area and high-quality 2D phosphorus films are outlined, as well as the dilemmas that need to be addressed to achieve 2D phosphorus-based nanodevices.

2 | FABRICATION OF 2D BLACK PHOSPHORUS

Similar to other 2D van der Waals materials (e.g., graphene, boron nitride, etc.), single- and few-layer BP can be obtained from its bulk crystals by top-down techniques, such as mechanical cleavage, liquid-phase exfoliation, chemical intercalation, plasma thinning, and so on. Mechanical exfoliation by “Scotch tape” was the first method to prepare single-layered BP with high quality, however, suffering from the limited flake size and the low production rate. In comparison, liquid-phase exfoliation and chemical intercalation via the assistance of chemical solvents or intercalants are promising for large-scale production at the expense of flake size, but bring in extrinsic chemical residuals to the BP nanosheets. In addition to exfoliation, atomically thin BP has also been obtained by Ar or O2 plasma treatments. In particular, the oxide layers (e.g., P2O5) formed during the O2 etching process can further improve the stability of the BP films by preventing deep degradation.

BP films can also be prepared on substrates through the phase transformation from red phosphorus under high pressure and/or high temperature. For example, Xia’s group has demonstrated the conversion of red phosphorus to BP on a flexible polyester substrate at room temperature under a pressure of 8 GPa. They further developed this strategy to fabricate ~50 nm thick BP films on sapphire at 700°C and 1.5 GPa, with a grain size up to 70 μm and a hole mobility up to 160 cm²/(V s) along the armchair direction. In the meantime, Ji’s group reported the synthesis of 2D BP on Si substrate from red phosphorus by chemical vapor deposition (CVD), using a high pressure of 27.2 atm and the assistance of SnI4 as a mineralizer. The average areas of the thin film are >3 μm² for the ~4-layer BP films with, which reach >100 μm² for the thicker samples.

Based on the mineralizer-assisted method, Xu et al. developed a nucleation and lateral growth strategy to prepare large-scale crystalline BP films, as illustrated in Figure 2A. A SiO2/Si wafer coated with Au thin film was used as the substrate, and red phosphorus, Sn and SnI4 were the precursors. The regular Au3SnP7 islands (Figure 2B) formed at 750°C further serve as nucleation seeds for the growth of BP at a moderate temperature of ~500°C. The lattice constants of the Au3SnP7 are 3.2 Å and 5.4 Å along the (010) and (110) directions, respectively, matching well with the lattice parameters of BP to facilitate the seeded growth of the single crystalline BP films. The cross-sectional TEM image in Figure 2C reveals the atomically sharp interface between BP and Au3SnP7. In the following transition stage, small BP nanosheets with a thickness of ~5 nm thermodynamically grew (Figure 2D), and finally fuse across with each other to form the large-area BP thin films. Figure 2E shows a ~150 nm BP film with a lateral size of over 200 μm. The as-grown ~8 nm BP films demonstrate high field-effect mobility of ~1200 cm²/(V s) and Hall mobility of ~1400 cm²/(V s) at room temperature, comparable to the values reported for those exfoliated samples.

Pulsed laser deposition (PLD) method is another scalable approach to prepare a variety of ultrathin films. For the PLD method, the use of laser pulse instead of conventional thermal heaters can facilitate the formation of energetic BP clusters within the confined region near the target substrate, and thus enable the large-scale growth of 2D BP films (Figure 3A). Lau et al. have grown wafer-scale amorphous BP ultrathin films on SiO2/Si substrate at 150°C by conventional PLD. The bandgap of the polycrystalline BP films decreased from 0.80 to 0.21 eV as the thickness increased from 2 to 8 nm. The fabricated FET based on the 2 nm thick amorphous BP exhibits a hole mobility of 14 cm²/(V s), and an on/off current ratio of 10⁵. Recently, the successful growth of centimeter-scale ultrathin BP films by a controlled PLD strategy was reported by using bulk BP crystals as the source and mica wafer as the substrate. As presented in Figure 3B, a precise control of the film thickness was achieved by manipulating the laser pulses during the deposition. The formation of the unidirectional, homogeneous BP thin films was verified by a combination of atomic force microscopy (AFM) (Figure 3C), X-ray diffraction (XRD), Raman mapping, TEM (Figure 3D,F,E), and so on. Furthermore, the fabrication of large-scale FET arrays based on 5-nm BP films reveals high hole mobilities of 213 and 617 cm²/(V s) at 23°C (room temperature) and −23°C (Figure 3F–H), respectively, which are comparable to the values obtained from exfoliated or CVD-grown BP samples with similar thickness. More importantly, highly uniform electrical performance was observed over the centimeter-scale BP films, as revealed by the three-dimensional mapping of the carrier mobilities extracted from the 25 FET arrays shown in Figure 3H. Considering the much smaller-sized BP flakes obtained by other approaches, such laser-assisted physical vapor deposition method is very promising for the growth of large-scale 2D
BP thin films, paving the way for the further development of BP-based devices.

Table 1 summarizes the film quality, device performance, advantages, and disadvantages of the BP films obtained via all the aforementioned methods. Although significant progress has been achieved in the fabrication of 2D BP thin films, challenges remain on the precise control of the thickness and domain size. Feasible approaches for the controllable large-scale growth of atomically thin BP films are desired for wafer-scale optoelectronic devices and compact integrated circuits.

3 EPITAXIAL GROWTH OF BlueP

Due to the novel physical and chemical properties of BP, various phosphorus allotropes with exotic properties have been predicted.24–32 Among them, BlueP, which was firstly predicted by Zhu et al. in 2014,24 has received much attention for its attractive thermoelectric properties,27 strain- and fluorination-induced quantum spin Hall effect,58 electric field-induced band gap engineering,59 and tunable quantum phase transitions,60 which promise its potential applications in electronic and optoelectronic nano-devices. BlueP is also a promising candidate for gas sensors due to the distinguishable structures, charge transfer, and electronic properties resulted from the various adsorbed gas molecules.61 Furthermore, a transition metal-N$_3$ (W-N$_3$) centers on BlueP have exhibited excellent catalytic performance for nitrogen reduction reaction (NRR) with an ultra-low limiting potential (the lowest potential for electrochemical reaction to occur) of $-0.02$ V,62 indicating its potential applications in electrocatalysis.

As displayed in Figure 4A, BlueP possesses a buckled honeycomb structure similar to silicene, and the unit cell of BlueP is highlighted by the black rhombus with lattice constant of $b_1 = b_2 = 3.28$ Å. Here, each phosphorus atom covalently bonds with three neighboring atoms via the $sp^3$ hybridization to stabilize the formation of BlueP. In comparison, the atomic structure of BlueP is significantly different from BP, which possesses a distinct armchair ridge configuration with lattice constants of $a_1 = 3.31$ Å and $a_2 = 4.37$ Å (Figure 1A). The electronic band gaps of monolayer BlueP and BP are both $\sim 2$ eV,24,59 Furthermore, BlueP shows no anisotropic properties in contrast to the anisotropic BP. Tristant et al.63 have compared the finite-temperature stability of BP and BlueP deposited on Au (111) by first-principles calculations, and revealed that BlueP is more energetically stable with a lower formation energy of 46 meV/atom at room temperature.

Subsequent experimental efforts have been devoted to the synthesis of BlueP via MBE under ultra-high vacuum (UHV) conditions on various substrates, for example, Au,37,64,65 Cu,66,67 Ag,68 Pt,65 and so on. However, interactions between the metal substrates and P atoms significantly affect the growth behaviors of phosphorus. For instance, the direct thermal evaporation of bulk BP crystals as precursor results in a gold-phosphorus network on
Au(111),64,65 phosphorus clusters on Cu(111),67 long-range ordered nanostripe arrays composed of phosphorus monomers and dimmers on Cu(110),66 and BlueP clusters with sizes of several nanometers on Ag(111).68 Meanwhile, many other experimental results and theoretical studies69–71 suggest that moderate phosphorus-substrate interactions can decompose the P clusters into individual atoms and facilitate the formation of continuous 2D phosphorus films.72 Thus, searching or constructing a supporting surface with moderate phosphorus-substrate interactions is essential for the synthesis of 2D BlueP as well as other allotropes.

Currently, BlueP can be fabricated on Au(111) surface with a gold silicide intercalation layer (AuSIL).37 Si atoms were firstly deposited onto the Au(111) surface to form the AuSIL layer with short-range ordering.73 By subsequently evaporating phosphorus precursors onto the AuSIL interlayer held at 280°C, BlueP monolayer can be fabricated (Figure 4B). Here, two BlueP phases with and without visible moiré patterns can be observed, labeled as 1 × 1 BlueP1 (Figure 4C) and 1 × 1 BlueP2 (Figure 4D), respectively. The lattice constant of both phases is 0.33 nm, consistent well with the theoretically predicted value of the freestanding BlueP. As thus, the appear and disappear of moiré patterns in BlueP1 and BlueP2 originate from their different orientations with respect to the underlying Au (111) substrate. Furthermore, the transition state of BlueP nanoclusters (Trans BlueP) can be observed in Figure 4B, and atomically sharp boundaries formed between the Trans BlueP and 1 × 1 BlueP phases reveal the transition process.
Table 1: Summary of the film quality, device performance, advantages, and disadvantages of BP thin films prepared by various methods

| Preparation method                  | References | Thickness | Lateral size | Current on/off ratio | Mobility (cm²/(V s)) | Advantages | Disadvantages |
|-------------------------------------|------------|-----------|--------------|----------------------|----------------------|------------|---------------|
| Mechanical exfoliation              |            | 10 nm     | /            | ~10⁵                 | ~1000                | High quality | (1) Unscalable |
|                                     |            | 8 nm      | /            | 10⁴                  | 197                  |             |               |
|                                     |            | 5 nm      | /            | 10                   | 55                   |             | (2) Low yield rate |
|                                     | 44         | 4–8 nm    | /            | >10⁴                 | 95.6                 |             |               |
|                                     | 45         | 5 nm      | /            | >10⁴                 | 286                  |             |               |
| Liquid-assistant exfoliation        | 46         | ~7.4 nm   | 190 and 532 nm | 10⁵               | 0.58                 | (1) Controllable | Bring in extrinsic chemical residuals |
|                                     | 47         | /         | 190–620 nm   | /                   | /                    | (2) Coating accessible |               |
|                                     | 48         | 16–128 nm | /            | ~10⁴                 | ~50                  |             |               |
|                                     | 49         | Quasi-monolayer | /            | >10⁴                 | ~800                 |             |               |
| Chemical intercalation              |            | 1–5 layers | /            | /                    | 1150                 | (1) Controllable | The formation of non-transparent oxide layers |
|                                     | 50         | 2–10 nm   | /            | ~10⁵                 | /                    |             |               |
|                                     | 51         | 4–28 nm   | 60 nm nanoribbon | >10⁵               | 862                 | (2) Improved stability with the formation of oxide layers |               |
|                                     | 55         | >200 µm   | /            | /                    | /                    |             |               |
| Chemical vapor deposition types     | 33         | ~4 layers | >3 μm²       | ~10⁴                 | /                    | Controllable | Require high pressure and high temperature conditions |
|                                     | 35         | ~50 nm    | 40–70 µm     | /                    | ~160                 |             |               |
|                                     | 53         | ~5 nm     | >200 µm      | /                    | ~1200                |             |               |
|                                     | 56         | ~6 nm     | 3 mm         | 10⁴                  | 1744                |             |               |
| Pulsed laser deposition             | 36         | 2–10 nm   | ~50 nm       | ~10³                 | 14                   | (1) High controllability | /               |
|                                     | 54         | 5 nm      | >1cm²        | /                    | 213                  | (2) High production rate | (3) High quality |
Very recently, Zhou et al. reported that copper oxides can be used as buffer layers for the synthesis of phosphorene. The Cu$_3$O$_2$ buffer layers were prepared by annealing Cu(111) at 320°C in 5 × 10$^{-7}$ mbar O$_2$ for 10 min. By depositing P atoms onto the Cu$_3$O$_2$/Cu(111) surface held at 80°C and subsequently annealing at 250°C, it forms a flat BlueP monolayer with a graphene-like structure instead of the buckling configuration. More interestingly, the flat phosphorene exhibits metallic nature because of the enlarged atomic lattice constant of 4.2 Å, which is much larger than that of the buckling BlueP.

Interestingly, the Au–P bonds can be broken by intercalating atoms, resulting in the formation of BlueP monolayers. As shown in Figure 5G,H, Zhang et al. reported that monolayer BlueP can form by depositing Si atoms onto the gold-phosphorus networks at 280°C. Here, the intercalating Si atoms break the P–Au bonds within the Au–P networks to release the P clusters, and also permeate into the Au substrate to break the interfacial bonds/coupling.

Similar to MOFs, MIFs possess tunable nanostructures and periodic potential valleys as well, which can serve as nano-templates for selective adsorption/trapping of functional molecules or single atoms. For instance, Si et al. demonstrated that the 2D gold-phosphorus networks can be used to trap water molecules, offering a platform to explore the structure and dynamics of water clusters. Zhang et al.

**FIGURE 4** Epitaxial growth of monolayer BlueP and Au-BlueP network. (A) Atomic model of BlueP phosphorus in top and side views. (B) Coexistence of two BlueP phases grown on the AuSIL buffer layer. Atomically resolved STM image of (C) 1 × 1 BlueP$_1$ phase and (D) of 1 × 1 BlueP$_2$ phase. (E) Atomic model of the Au-BlueP network on Au (111). (F) Au-BlueP network directly grown on Au (111). (G) Intercalation of Si into the Au-BlueP network leading to the partial formation of BlueP. (H) Coexistence of BlueP and Au-BlueP network. Reproduced with permission, Copyright 2020, American Chemical Society. BlueP, blue phosphorus; STM, scanning tunneling microscope
found that the 2D gold-phosphorus networks can provide preferential binding sites to anchor individual Sn atoms. The potential valleys of the networks can prevent these Sn atoms from aggregating into large-sized clusters, resulting in highly dispersed Sn single-atom clusters with high surface density. Furthermore, a new ternary metal–inorganic porous network, namely nitrogen-substituted gold-phosphorus network, can be constructed by depositing P onto Au(111) under a nitrogen environment.79 Different substrates can be used to tune the as-grown nanostructures. For example, 1D porous gold-phosphorus chain arrays can be synthesized on Au(110) surface, in which periodic P₄ clusters are interconnected by Au atoms.⁸⁰

Recently, Sun et al.⁷⁴ successfully constructed a Kagome lattice based on the 2D gold-phosphorous networks decorated with potassium (Figure 5A,B). The pristine gold-phosphorous network (referred to Au₃P₄) on the clean Au (111) possesses a triangular lattice configuration and two potential valleys along each edge. The electron doping from the adsorbed potassium atoms can induce the formation of a new gold-phosphorous phase, namely Au₅P₄ networks (Figure 5B). At the same time, the potassium atoms spontaneously trapped into the potential valleys to form the ternary gold-phosphorus-potassium network. This process is depicted in Figure 5C. The constructed potassium-gold-phosphorus lattice exhibits the Kagome arrays of periodic potential valleys and possesses a typical Kagome band structure, that is, one flat band coexisting with one Dirac crossing band, as highlighted by the blue lines in Figure 5D. Furthermore, the flat band can be tuned by varying the Kagome lattice constants (Figure 5E), in which larger lattice parameters lead to smaller hopping and flatter band dispersions. In particular, the width of the flat band approaches zero with the parameters increasing to 16.00 Å. This study provides a new strategy for constructing Kagome lattices, which serve as an ideal platform to study topological and flat band phenomena.⁸¹,⁸² The studies about MBE growth of 2D phosphorus and phosphorus-related materials on various substrates was summarized in Table 2.

5 | OUTLOOK

Bottom-up growth of 2D phosphorus is still at the early stage of development, offering great opportunities for further exploration. Many 2D phosphorus allotropes have been theoretically predicted, but most of them still require experimental validation. Among them, BP
represents one of the most promising candidates for applications in electronic and optoelectronic devices, which has been intensively investigated. Controllable synthesis of large area and high quality few-layer especially single-layer BP and its allotropes remains a significant challenge. The additives (Au, Sn, and SnI4) assisted ambient pressure growth of bulk BP stimulated the rapid development of chemical vapor transport methods to fabricate high quality BP crystals and thin films. However, the mechanisms of such the mineralizer-assisted growth of BP at low pressure is still controversial, that is, whether it is the catalyzed growth with the assistance of the Sn24P22−xI8 ternary alloy or the epitaxial growth on the surface of the Au3SnP7 buffer layer. It is highly desired to reveal the growth mechanism at the atomic scale.

Similarly, monolayer BlueP has been successfully synthesized by MBE method on Au(111) with the assistance of Si intercalation. A flat BlueP has also been grown on Cu(111) with copper oxide buffer layers. For such MBE methods, the sample size can reach up to ~1 cm. As thus, large-scale growth of BlueP is possible by MBE with further optimization. Further research effort should be devoted to the understanding of the growth mechanism and the development of other bottom-up technology (e.g., CVD). The growth of BlueP on other substrates, for example, insulating SiO2, is also of great interest for practice device applications.

Precise band structure engineering of 2D phosphorus is essential to modulate the electronic and optical properties for desired device applications. Various strategies have been applied to modulate the electronic structure of few/single-layer BP in the past several years, including ion implantation, plasma treatment and surface charge transfer doping. However, these approaches either introduce significant amount of defects into the thin films or suffer from the chemical instability. Stable in-situ substitutional doping during the synthesis of 2D phosphorus (e.g., nitrogen doping of BlueP) represents a promising approach to extend their application in multifunctional devices, but is rarely investigated. It is also important to explore other nondestructive doping strategies, for example, combining with other organic and inorganic quantum materials to construct 2D phosphorus-based heterojunctions.

Another critical issue is the poor chemical stability of 2D phosphorus. For few-layer BP, several different mechanisms have been proposed, including the degradation and oxidation assisted by water, oxygen, water together with light, water together with oxygen, as well as the synergistic effect of water, oxygen, and light. However, the direct evidence of the initial degradation process are not sufficient and solid, and therefore the sole and collective roles of water, oxygen and light during the BP degradation are under debate. Liu and Zhou have explored the adsorption behaviors of environmental gas molecules on monolayer BlueP by first-principles calculations. They found that most of environmental gas molecules (e.g., N2, NO, NO2, CO, CO2, etc.) are physisorbed, while O2 tends to dissociate and chemisorb on BlueP surface, which indicates that BlueP is relatively stable under ambient environment. Very recently, a reversible adsorption and desorption of O atoms on the BlueP nanoclusters (i.e., gold-phosphorus network) on Au (111) has been observed, revealing the good stability against oxidation. Atomic scale investigations and understanding of the BP oxidation under controlled environment can promote the development of effective protection strategies for 2D phosphorus thin films.

Furthermore, the fabrication of 2D binary and even ternary phosphorus-based alloys with high tunability
represents a promising strategy to enrich the 2D family. For instance, the formation of highly ordered AuP$_2$ and Au$_3$P$_4$ MIFs with different stoichiometries and versatile nanostructure have been presented in Section 4. Ternary nitrogen-substituted and potassium-decorated gold-phosphorus networks have also been fabricated and exhibited extraordinary properties, such as Kagome flat band. With a careful selection of different elements and a precise control of the stoichiometries, it is possible to develop novel predesigned 2D alloys with robust quantum properties and phenomena. We believe that the field of 2D phosphorus and phosphorus-based materials will flourish in the coming years.

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CONFLICT OF INTERESTS
The authors declare no conflict of interest.

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REFERENCES
1. Li L, Yu Y, Ye GJ, et al. Black phosphorus field-effect transistors. Nat Nanotechnol. 2014;9:372-377.
2. Qiao J, Hu ZX, Yang F, Ji W. High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus. Nat Commun. 2014;5:4475.
3. Liu H, Deng Y, Ye PD. Semiconducting black phosphorus: synthesis, transport properties and electronic applications. Chem Soc Rev. 2015;44:2732-2743.
4. Ling X, Liang L, Huang S, et al. Low-frequency interlayer breathing modes in few-layer black phosphorus. Nano Lett. 2015;15(6):4080-4088.
5. Lee S, Yang F, Suh J, et al. Anisotropic in-plane thermal conductivity of black phosphorus nanoribbons at temperatures higher than 100K. Nat Commun. 2015;6:8573.
6. Fei r, Soklaski R, Yan JA, Lo C, Yang L. Enhanced thermoelectric efficiency via orthogonal electrical and thermal conductances in phosphorene. Nano Lett. 2014;14(11):6393-6399.
7. Smith B, Vermeersch B, Carrete J, et al. Temperature and thickness dependences of the anisotropic in-plane thermal conductivity of black phosphorus. Adv Mater. 2017;29(5):1603756.
8. Kim S, Myeong G, Shin W, et al. Thickness-controlled black phosphorus tunnel field-effect transistor for low-power switches. Nat Nanotechnol. 2020;15(3):103-206.
9. Buscema M, Blanter SI, Steele GA, van der Zant HSI, Castellanos-Gomez A. Fast and broadband photoresponse of few-layer black phosphorus field-effect transistors. Nano Lett. 2014;14(6):3347-3352.
10. Yang Y, Gao J, Zhang Z, et al. Black phosphorus based photocathodes in wideband bifacial dye-sensitized solar cells. Adv Mater. 2016;28(40):8937-8944.
11. Ren X, Lian P, Xie D, et al. Properties, preparation and application of black phosphorus/phosphorene for energy storage: a review. J Mater Sci. 2017;52:10364-10386.
12. Luo S, Zhao J, Zou J, et al. Self-standing polypyrrole/black phosphorus laminated film: promising electrode for flexible supercapacitor with enhanced capacitance and cycling stability. ACS Appl Mater Interfaces. 2018;10(4):3538-3548.
13. Shao J, Xie H, Huang H, et al. Biodegradable black phosphorus-based nanospheres for in vivo photothermal cancer therapy. Nat Commun. 2016;7:12967.
14. Zhao Y, Qiao J, Yu Z, et al. Stable and multifunctional dye-modified black phosphorus nanosheets for near-infrared imaging-guided photothermal therapy. Chem Mater. 2017;29(17):7131-7139.
15. Luo M, Zhou Y, Zhang H, Mei L. 2D black phosphorus-based biomedical applications. Adv Funct Mater. 2019;29(13):1808306.
16. Deng L, Sun C, Yun B, Sun Q, Zhao C, Li Z. Functionalization of small black phosphorus nanoparticles for targeted imaging and photothermal therapy of cancer. Sci Bull. 2019;63(14):917-924.
17. Xing C, Chen S, Qiu M, et al. Conceptually novel black phosphorus/cellulose hydrogels as promising photothermal agents for effective cancer therapy. Adv Healthc Mater 2018; 7(7):1701510.
18. Luo M, Fan T, Zhou Y, Zhang H, Mei L. 2D black phosphorus-based biomedical applications. Adv Funct Mater. 2019;29(13):1808306.
19. Qiu M, Singh A, Wang D, Swihart M, Zhang H, Prasad PN. Biocompatible and biodegradable inorganic nanostructures for nanomedicine: silicon and black phosphorus. Nano Today. 2019;25:135-155.
20. Xie Z, Peng M, Lu R, et al. Black phosphorus-based photothermal therapy with a CD47-mediated immune checkpoint blockade for enhanced cancer immunotherapy. Light: Sci Appl. 2020;9:161.
21. Pei J, Yang J, Yildirim T, Zhang H, Lu Y. Many-body complexes in 2D semiconductors. Adv Mater. 2018;31(2):1706945.
22. Xie Z, Fan T, An J, et al. Emerging combination strategies with phototherapy in cancer nanomedicine. Chem Soc Rev. 2020;49:8065-8087.
23. Chen S, Xing C, Huang D, et al. Eradication of tumor growth by delivering novel photothermal selenium-coated tellurium nanoheterojunctions. Sci Adv. 2020;6(15):eaay6825.
24. 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.
25. Zhao T, He CY, Ma SY, et al. A new phase of phosphorus: the missed tricycle type red phosphorene. J Phys Condens Matter. 2015;27:265301.
26. Han WH, Lee IH, Chang KJ. Prediction of green phosphorus with tunable direct band gap and high mobility. J Phys Chem Lett. 2017;8:4627-4632.
27. Geng W, Brown JJ, Page AJ, Ke Z. New phosphorene by phase combination with tunable electronic and mechanical properties. J Phys Chem C. 2019;123:10788-10794.
28. Wu M, Zhou L, Yao K, Zeng XC. Nine new phosphorene polymorphs with non-honeycomb structures: a much extended family. Nano Lett. 2015;15:3557-3562.
29. Wang H, Liu Z, Yang J. ψ-Phosphorene: a new allotrope of phosphorene. Phys Chem Chem Phys. 2017;19(13):2402-2408.

30. Schusteritsch G, Pickard CJ. Single-layered Hittorf's phosphorus: a wide-bandgap high mobility 2d material. Nano Lett. 2016;16(5):2975-2980.

31. Yu G, Li W, Zheng Y. Two-dimensional Kagome phosphorus and its edge magnetism: a density functional theory study. J Phys Condens Matter. 2015;27:255006.

32. Zhou Z, Yang J. Two-dimensional phosphorus porous poly-morphs with tunable band gaps. J Am Chem Soc. 2016;138(22):7091-7098.

33. Smith JB. Growth of 2D black phosphorus film from chemical vapor deposition. Nanotechnology. 2016;27:215602.

34. Jiang Q, Chen N, Zhang H, Dai L, Wang S. Facile synthesis of black phosphorus: an efficient electrocatalyst for the oxygen evolving reaction. Angew Chem Int Ed. 2016;128:14053-14057.

35. Li C, Wu Y, Deng B, et al. Synthesis of crystalline black phosphorus thin film on sapphire. Adv Mater. 2018;30:1703748.

36. Yang Z, Yuan S, Lin S, Yau HM, Dai J, Lau SP. Field-effect transistors based on amorphous black phosphorus ultrathin films by pulsed laser deposition. Adv Mater. 2015;27:3748-3754.

37. Zhang JL, Zhao S, Sun S, et al. Synthesis of monolayer blue phosphorus enabled by silicon intercalation. ACS Nano. 2020;14(3):3687-3695.

38. Zhou D, Meng Q, Si N, et al. Epitaxial growth of flat, metallic monolayer phosphorene on metal oxide. ACS Nano. 2020;14:2385-2394.

39. Zhang L, Huang H, Zhang B, et al. Structure and properties of violet phosphorus and its phosphorene exfoliation. Angew Chem Int Ed. 2020;132:1090-1096.

40. Zhang L, Gu M, Li L, et al. High yield synthesis of violet phosphorus crystals. Chem Mater. 2020;32:7363-7369.

41. Sun Y, Ren Z, Liu Y, Fu R. Facile synthesis of ultrathin red phosphorus nanosheets with excellent photocatalytic performances. Mater Lett. 2019;236:542-546.

42. Akhtar M, Zhao R, Alruqi A, Mroczkowska JE, Sumanasekera G, Jasinski JB. Recent advances in synthesis, properties, and applications of phosphorene. npj 2D Mater and Appl. 2017;1:5.

43. Castellanos-Gomez A, Vicarelli L, Prada E, et al. Isolation and characterization of few-layer black phosphorus. 2D Mater. 2014;1:025001.

44. Liu H, Si M, Du Y, Ye PD. The effect of dielectric capping on few-layer phosphorene transistors: tuning the Schottky barrier heights. IEEE Electron Device Lett. 2014;35:795-797.

45. Liu H, Zhu Z, Luo Z, Xu X, Tománek D, Ye PD. Phosphorene: an unexplored 2d semiconductor with a high hole mobility. ACS Nano. 2014;8:4033-4041.

46. Yasaee P, Kumar B, Foroozan T, et al. High-quality black phosphorus atomic layers by liquid-phase exfoliation. Adv Mater. 2015;2015(27):1887-1892.

47. Hanlon D, Backes C, Doherty E, et al. Liquid exfoliation of solvent-stabilized few-layer black phosphorus for applications beyond electronics. Nat Commun. 2015;6(1):1-11.

48. Kang J, Wells SA, Lee JH, Liu X, Chen KS, Hersam MC. Solvent exfoliation of electronic-grade, two-dimensional black phosphorus. ACS Nano. 2015;9:3596-3604.

49. Tan SJR, Abdelwahab I, Chu L, et al. Quasi-monolayer black phosphorus with high mobility and air stability. Adv Mater. 2018;30:1704619.

50. Lu W, Nan H, Hong J, et al. Plasma-assisted fabrication of monolayer phosphorene and its Raman characterization. Nano Res. 2014;7(6):853-859.

51. Jia J, Lai S, Xu J, Choi YJ, Park JH, Lee S. Plasma-treated thickness-controlled two-dimensional black phosphorus and its electronic transport properties. ACS Nano. 2015;9(9):8729-8736.

52. Li X, Deng B, Wang X, et al. Synthesis of thin-film black phosphorus on a flexible substrate. 2D Mater. 2015;2:031002.

53. Xu Y, Shi X, Zhang Y, et al. Epitaxial nucleation and lateral growth of high crystalline black phosphorus films on silicon. Nat Commun. 2020;11:1330.

54. Wu Z, Lyu Y, Zhang Y, et al. Large-scale growth of few-layer two-dimensional black phosphorus. Nat Mater. 2021;20:1203-1209.

55. Feng X, Chen L, Tan WC, Wang L, Ang KW. High mobility anisotropic black phosphorus nanoribbon field-effect transistor. Adv Funct Mater. 2018;28:1801524.

56. Zhang Z, Yan Q, Li Q, Yang Y, Ren TL. Two-step heating synthesis of sub-3 millimeter-sized orthorhombic black phosphorus single crystal by chemical vapor transport reaction method. Sci China Mater. 2016;59(2):122-134.

57. Sevik C, Sevincli H. Promising thermoelectric properties of phosphorenes. Nanotechnology. 2016;27:355705.

58. Yang G, Liu Z, Jin S, Zhang H, Ding Z. Strain- and fluorination-induced quantum spin hall insulators in blue phosphorene: a first-principles study. J Phys Chem C. 2017;121(23):12945-12952.

59. Agnihotri SPR, Chauhan YS, Agarwal A, Bhowmick S. Significant enhancement of the stark effect in rippled monolayer blue phosphorus. J Phys Chem C. 2018;122(9):5171-5177.

60. Zhu L, Guan S, Liu Y, Tingting Zhang, Chen G, Yang SA. Blue phosphorene oxide: strain-tunable quantum phase transitions and novel 2D emergent fermions. Nano Lett. 2016;16(10):6548-6554.

61. Liu N, Zhou S. Gas adsorption on monolayer blue phosphorus: Implications for environmental stability and gas sensors. Nanotechnology. 2017;28:175708.

62. Zhang ZM, Yao X, Lang XY, Zhu YF, Gao W, Jiang Q. W-N3 center supported on blue phosphorus as a promising efficient electrocatalyst with ultra-low limiting potential for nitrogen fixation. Appl Surf Sci. 2021;536:147706.

63. Tristant D, Cupo A, Meunie V. Finite temperature stability of single-layer black and blue phosphorus adsorbed on Au(111): a first-principles study. 2D Mater. 2018;5:035044.

64. Zhang JL, Zhao S, Han C, et al. Epitaxial growth of single layer blue phosphorus: a new phase of two-dimensional phosphorus. Nano Lett. 2016;16:4903-4908.

65. Tian H, Zhang JQ, Ho W, et al. Two-dimensional metal-phosphorus network. Mater. 2020;2(1):111-118.

66. Zhang JL, Zhao S, Sun S, et al. Phosphorus nanostripe arrays on Cu(110): a case study to understand the substrate effect on the phosphorus thin film growth. Adv Mater Interfaces. 2017;4:1601167.
67. Gu, C., Zhao, S., Zhang, J.L., et al. Growth of quasi-free-standing single-layer blue phosphorus on tellurium monolayer functionalized Au(111). ACS Nano. 2017;11(5):4943-4949.
68. Yang, S., Wang, W., Cheng, P., Chen, L., Wu, K. Regular arrangement of two-dimensional clusters of blue phosphorene on Ag (111). Chin Phys Lett. 2020;37:096803.
69. Zhou, D., Si, N., Li, H., Fuchs, H., Niu, T. Epitaxial growth of main group monoelemental 2D materials. Review. Adv Funct Mater. 2020;32:2006997.
70. Zhao, S., Li, Z. Blue phosphorus growth on different noble metal surfaces: from a 2D alloy network to an extended monolayer. J Phys Chem C. 2021;125(1):675-679.
71. Zhang, J.L., Hu, Z., Wang, L., Liu, L., Wee, A.T.S., Chen, W. 2D phosphorene: epitaxial growth and interface engineering for electronic devices. Adv Mater. 2018;30:1802207.
72. Gao, J., Zhang, Y.W. The critical role of substrate in stabilizing phosphorene nano flakes: a theoretical exploration. J Am Chem Soc. 2016;138:4763-4771.
73. Okamoto, H., Massalski, T.B. The Au–Si (Gold-Silicon) system. Bull Alloy Phase Diagr. 1983;194:190-198.
74. Sun, S., Zhao, S., Luo, Y.Z., et al. Designing Kagome lattice from potassium atoms on phosphorus–gold surface alloy. Nano Lett. 2020;20:5583-5589.
75. Riedl, C., Coletti, C., Iwasaki, T., Zaharov, A.A., Starke, U. Quasi-free-standing epitaxial graphene on SiC obtained by hydrogen intercalation. Phys Rev Lett. 2009;103(24):246804.
76. Yang, Y., Fu, Q., Li, H., et al. Creating a nanospace under an h-BN cover for Adlayer growth on nickel (111). ACS Nano. 2015;9:11589-11598.
77. Si, N., Shen, T., Zhou, D., et al. Imaging and dynamics of water hexamer confined in nanopores. ACS Nano. 2019;13:10622-10630.
78. Zhang, J.L., Zhao, S., Sun, S., et al. Atom by atom condensation of Sn single clusters within gold–phosphorus metal–inorganic porous networks. J Phys Chem Lett. 2021;12:745-751.
79. Zhang, J.L., Zhao, S., Sun, S., et al. On-surface synthesis of nitrogen-substituted gold-phosphorus. Chem Mater. 2020;32:8561-8566.
80. Sun, S., Yang, T., Ma, Z., et al. Experimental realization of one-dimensional metal-inorganic chain gold–phosphorus chain. ACS Mater Lett. 2020;2:873-879.
81. Ruostekoski, J. Optical Kagome lattice for ultracold atoms with nearest neighbor interactions. Phys Rev Lett. 2009;103:080406.
82. Jo, G.B., Thomas, C.K., Hosur, P., Vishwanath, A., Stamper-Kurn, D.M. Ultracold atoms in a tunable optical Kagome lattice. Phys Rev Lett. 2012;108:045305.
83. Li, S., Liu, X., Fan, X., et al. New strategy for black phosphorus crystal growth through ternary clathrate. Cryst Growth Des. 2017;17(12):6579-6585.
84. Lange, S., Nilges, T., Au, SnP2@black phosphorus: an easy access to black phosphorus. Inorg Chem. 2007;46(10):4028-4035.
85. Koenig, S.P., Doganov, R.A., Seixas, L., et al. Electron doping of ultrathin black phosphorus with Cu adatoms. Nano Lett. 2016;16(4):2145-2151.
86. Kuriakose, S., Ahmed, T., Balendhran, S., et al. Effects of plasma treatment on the electrical and optoelectronic properties of layered black phosphorus. Appl Mater Today. 2018;12:244-249.
87. Kiraly, B., Rudenko, A.N., Katsnelson, M.I., Khajetoorians, A.A. Probing single vacancies in black phosphorus at the atomic level. Nano Lett. 2017;17:3607-3612.
88. Yang, B., Wan, B., Zhou, Q., et al. Te-doped black phosphorus field-effect transistors. Adv Mater. 2016;28(42):9408-9415.
89. Si, N., Shen, T., Liu, X., et al. Lateral epitaxial growth of two-dimensional heterostructure linked by gold adatoms. Nano Res. 2021;14:887-892.
90. Zhou, D., Si, N., Tang, Q., et al. Defect generation and surface functionalization on epitaxial blue phosphorene by C60 adsorption. J Phys Chem C. 2019;123:12947-12953.
91. Yao, M., Zhang, X., Wu, T., Liu, B., Li, M., Long, M. First-principles study on photoelectric and transport properties of CsXBr4 (X = Ge, Sn) and blue phosphorus van der Waals heterojunctions. J Appl Phys. 2021;129:035302.
92. Liu, B., Long, M., Cai, M.Q., Yang, J. Two-dimensional van der Waals heterostructures constructed via perovskite (C6H5NH3)2XBr4 and black phosphorus. J Phys Chem Lett. 2018;9:4822-4827.
93. Ziletti, A., Campbell, D.K., Coker, D.F., Castro, N., Neto, A.H. Oxygen defects in phosphorene. Phys Rev Lett. 2015;114:046801.
94. Wang, G., Pandey, R., Karna, S.P. Degradation of phosphorene in air: understanding at atomic level. 2D Mater. 2016;3:025011.
95. Favron, A., Gaufrès, E., Fossard, F., et al. Photooxidation and quantum confinement effects in exfoliated black phosphorus. Nat Mater. 2015;14:826-832.
96. Hu, Z., Li, Q., Lei, B., et al. Water-catalyzed oxidation of few-layer black phosphorous in a dark environment. Angew Chem Int Ed. 2017;56(31):9131-9135.
97. Wood, J.D., Wells, S.A., Jariwala, D., et al. Effective passivation of exfoliated black phosphorus transistors against ambient degradation. Nano Lett. 2014;14(12):6964-6970.
98. Zhou, Q., Tong, Y., Wang, J. Light-induced ambient degradation of few-layer black phosphorus: mechanism and protection. Angew Chem Int Ed. 2016;55(38):11437-11441.
99. Zhang, J.L., Zhao, S., Telychko, M., et al. Reversible oxidation of blue phosphorus monolayer on Au(111). Nano Lett. 2019;19:5340-5346.

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