2D Black Phosphorus for Energy Storage and Thermoelectric Applications

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Recent progress in the currently available methods of producing black phosphorus bulk and phosphorene are presented. The effective passivation approaches toward improving the air stability of phosphorene are also discussed. Furthermore, the research efforts on the phosphorene and phosphorene-based materials for potential applications in lithium ion batteries, sodium ion batteries, and thermoelectric devices are summarized and highlighted. Finally, the outlook including challenges and opportunities in these research fields are discussed.
1. Introduction

The successful exfoliation of black phosphorus (BP) into monolayer or few-layer BP, dubbed phosphorene, has attracted tremendous research interest since 2014. It is known that the discovery of graphene in 2004 has inspired considerable efforts devoted to the active exploration of 2D crystals and their potential applications. For example, transition metal dichalcogenides (TMDs) (e.g., MoS$_2$, MoSe$_2$, ReS$_2$, ReSe$_2$, WSe$_2$, MoS$_3$), layered metal oxides/hydroxides, graphitic carbon nitride, and MXenes have been intensively studied and tested in numerous applications, such as catalysis, batteries, light harvesting devices, and as lubricants. Recently, phosphorene, as another elementary 2D material after graphene, has triggered numerous theoretical and experimental investigations in many fields owing to its unique structure and intriguing anisotropic properties, which are rarely found in other 2D materials. In addition, BP quantum dots, phosphorene nanoribbons, phosphorene nanotubes, and MXenes have also attracted much research interest. Being chemically and electronically active, phosphorene shows vast potential for photodetectors, field-effect transistors (FETs), rechargeable batteries, thermoelectric (TE) devices, and other applications.

The discovery of BP crystals can be traced back to 100 years ago. It was noticed as the most stable one compared to other phosphorus allotropes (e.g., black, red, and violet phosphorus). BP crystal is composed of puckered-honeycomb layers stacked by weak van der Waals interactions, giving to other phosphorus allotropes (e.g., white, red, and violet). Despite the recent progress of phosphorene in (opto)electrical, optical, and electrical properties, apart from its anisotropic structure and fascinating properties, BP shows a layer-dependent bandgap, which can be tuned from 0.3 to 2 eV with decreasing thickness from bulk to single layer. The tunable bandgap of BP can be kept direct in a wide range of thickness, which is a great challenge in TMDs. The widely tunable direct bandgap means that BP exhibits great potential bridging the gap between zero-gap graphene and large-gap TMDs (1–2 eV). Moreover, the bandgap of phosphorene and its nanoribbons has also been predicted theoretically that can be engineered by the plane strain and edge structures. Recently, phosphorene has attracted much attention as promising anodes for rechargeable batteries including lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) due to its high theoretical specific capacity (2596 mAh g$^{-1}$) and ultrafast Li/Na ions diffusion along the zigzag direction. Both the intrinsic in-plane anisotropy and moderate bandgap of phosphorene have also stimulated considerable efforts in developing its potential role in TE application, which benefits from the large Seebeck coefficient and high carrier mobility. Despite the recent progress of phosphorene in (opto)electrical or electrochemical devices, it faces major challenges of low yield in preparation of phosphorene as well as its poor air stability. Therefore, large-scale preparation methods and effective passivation strategies are still necessary before the direct application of phosphorene into these areas.

In this Review, the state-of-the-art studies of phosphorene and phosphorene-based materials for energy storage as well as TE devices are summarized, aiming to give an overview of this emerging material in the energy research field. In the following context, the recent progress in preparation methods of phosphorene are introduced first, followed by currently developed passivation techniques to increase the air stability. Then, a detailed description of phosphorene and phosphorene-based materials for LIBs, SIBs, and TE devices are classified and highlighted. Moreover, simple discussions on other energy storage applications of phosphorene are provided, including lithium–sulfur batteries and supercapacitors, due to their early research stage. Finally, our insights on the challenges and opportunities of phosphorene in this research area will be proposed.

2. Synthesis of Black Phosphorus Crystals and Phosphorene

BP crystals have been prepared by several methods, such as high pressure synthesis, high-energy ball-milling technique, and chemical vapor transport (CVT) deposition process, and so on. For the synthesis of phosphorene, a top-down method of exfoliating BP bulk has been largely used, which is realized by weakening the interaction of adjacent layers of BP. However, very...
limited bottom-up methods, such as chemical vapor deposition (CVD) or wet-chemical process, have been reported due to the complicated chemistry of phosphorene.

2.1. Synthesis of Black Phosphorus Crystals

In 1914, Bridgman reported an accidental discovery of BP crystals for the first time during converting white phosphorus to red phosphorus under the high pressure of 1.2 GPa at 200 °C.[114] Subsequently, a few methods were used in an attempt to synthesize BP single crystals with large size, such as modified Bridgeman’s method,[115,116] mercury catalysis,[117] and liquid bismuth,[118,119] and so on. However, highly flammable white phosphorus was often used as the precursor and the as-obtained BP crystals were not large enough (e.g., needle-like BP single crystal with the size of 5 x 0.1 x 0.07 mm²).[118,120] Until 1982, BP single crystals larger than 5 x 5 x 10 mm² (Figure 1a) were prepared by Endo et al. via converting red P into melting black P at 900 °C and then slowly cooling down through a high isobaric pressure of 1 GPa.[102] This method solved the deficiency of big-size and high-quality BP crystals, but still largely limited by high-pressure apparatus in terms of the large-scale applications. Recently, high-energy mechanical ball-milling of commercial red phosphorus has also been demonstrated as a viable method of synthesizing BP bulk (Figure 1b), indicating that BP may be prepared with a simple and potentially scalable process with low cost. However, it produces small BP crystals.[121] Therefore, a nontoxic and effective preparation method is still desired for industrial applications.

Very recently, Lange et al. prepared high-quality BP crystals by simply using Au, Sn, and SnI₄ as mineralizers in evacuated silica ampules.[122] This method, named as CVT process, endows the synthesis of BP free from using toxic agents (e.g., mercury and liquid bismuth) and complicated apparatus. It was further modified by Köpf et al. in 2014 only using Sn/ SnI₄ as the mineralizer, resulting in a short reaction and large, high-quality BP crystals.[108] In the method, red phosphorus together with Sn and SnI₄ as the starting materials was set to a temperature of 650 °C and then slowly cooled to 550 °C after 7.5 h. A representative silica glass ampoule after the synthesis of black phosphorus is shown in Figure 1c. SnI₄ (orange) and red phosphorus (red) from the gas phase are condensed at the right hand side of the ampoule. BP is formed in large bunches. Excessive Sn reacted to form Sn phosphides, which are present in small round spheres. Compared to the Lang’s method, byproducts like Au₂SnP₇, AuSn, or Au₃P₃ were successfully avoided by removing Au as the mineralization additive. This method provides easy access to high-quality BP crystals with facile fabricating process. Actually, Sn and I from SnI₄ are the still possible candidates to form side phases. In addition, the yield of BP crystals is still not high enough. Generally, 500 mg of red phosphorus are used as precursor in this method, indicating the maximum yield of BP is 500 mg considering the complete phase transformation. Therefore, growing BP crystals with improved purity as well as high yield is still challenging and needs further investigation.

2.2. Synthesis of Phosphorene

Reliable methods for preparing high-quality phosphorene are critical for practical applications. Two categories, e.g., the top-down and bottom-up approaches, are generally utilized for the preparation of ultrathin layered materials.[123] The top-down methods mainly rely on exfoliation of bulk crystals into mono- or few-layer nanosheets by weakening the interlayer interaction chemically or mechanically, while the bottom-up methods are based on the chemical synthesis, such as CVD, wet-chemical synthesis, and epitaxial process. Currently, intensive studies are reported on the phosphorene preparation via the top-down methods, such as mechanical exfoliation (scotch-tape technique) and liquid-phase exfoliation in various solvents.[124]
It is known that scotch-tape technique resulted in the discovery of graphene by repeatedly peeling off layers from the bulk material. Currently, this method has been wildly used for the preparation of graphene analogues nanosheets (e.g., MoS$_2$,[125–127] BN,[128–130] mica,[131–133] etc.). Phosphorene is also prepared using the scotch-tape technique from BP crystals. The method can be optimized to produce high-quality phosphorene with the thickness of 1.6–10 nm and the lateral size of several micrometer (Figure 1d).[134] Although mechanical exfoliation of BP crystals is widely used, it is limited due to its extremely low yield. Large-scale synthesis of phosphorene in processable dispersions is still necessary for applications such as batteries, supercapacitors, solar cells, etc.

Alternatively, liquid-phase exfoliation and shear mixing[75,135] or their combination[73] are viable options as promising large-scale production techniques. The size selection of as-exfoliated phosphorene can be realized by controlling different centrifuge speeds.[136] Up to date, numerous efforts have been made on exploring efficient organic/inorganic molecules used in the liquid-phase exfoliation of BP crystals. Recently, high-quality phosphorene with controllable sizes was prepared by liquid phase sonication in N-cyclohexyl-2-pyrrolidone (CHP).[137] The low-magnification transmission electron microscopic (TEM) images of phosphorene obtained in CHP was shown in Figure 1e. Dimethylformamide and dimethyl sulfoxide are also demonstrated as suitable solvents for preparing stable dispersions of ultrathin phosphorene.[138] Formamide was identified in our previous study as an efficient solvent with a high yield of phosphorene, outperforming several other common solvents as parallel control experiments (Figure 1f).[136] However, the appropriate solvents for exfoliating BP bulk with high yield tend to be those with high boiling points. Therefore, the difficulty in removal of the liquid from the as-exfoliated phosphorene limits their practical implement. Recently, ultrathin phosphorene (the thickness of ≈2 nm) with clean surface was prepared by exfoliating BP bulks in the distilled (DI) water.[139,140] However, the yield of exfoliating BP in DI water is still not high enough. Therefore, it is necessary to explore proper solvents with low boiling points and high exfoliation efficiency or developing other effective synthesis methods.
3. Air Instability of Phosphorene and Passivation Approaches

Although BP bulk stands out as the most thermodynamically stable allotrope of phosphorus, the atomically thin phosphorene gradually degrades in the presence of air.\cite{144,145} It is found that unprotected phosphorene possesses strong affinity for oxygen or water molecules upon exposure to ambient conditions, which presents a fundamental obstacle hindering the potential adoption of phosphorene in (photo) electronics and electrochemical devices. This has been largely reported since the successful fabrication of phosphorene. Island et al. demonstrated an increase of over 200% in volume of phosphorene during the continuous exposure (122 h) to ambient conditions.\cite{146} The atomic force microscopy scans of a BP flake were taken in air during the observation time, as shown in Figure 2a. The large volume increase of exposed phosphorene could be ascribed to the irreversible reaction between phosphorene and the ambient species, particularly O$_2$/H$_2$O, promoting the formation of PO$_x$ (e.g., phosphoric acid). In addition, flowing and growing bubble-like features were also observed on the surface of exposed bare phosphorene under transmission electron microscopy (TEM) observation.\cite{136}

The ready degradation of phosphorene in ambient conditions leads to the deterioration of its physical and electric properties. Recently, a few works have proposed effective passivation approaches by protecting phosphorene from ambient atmosphere, including implementing protective layers to encapsulate phosphorene or covalent surface modification of phosphorene. Several studies have deposited capping overlayers to provide enhanced environmental stability of phosphorene and phosphorene-based devices.\cite{120,121} Atomic layer deposition of a AlO$_x$ capping layer on phosphorene has been demonstrated as an effective and scalable approach as shown in Figure 2b.\cite{147} Similarly, the SiO$_2$ layer deposited on bare phosphorene by the inductively coupled plasma chemical vapor was reported with an extended lifetime of phosphorene.\cite{148} A fully encapsulated phosphorene was also realized by contacting phosphorene with monolayer graphene and then fully encapsulated the device with hexagonal boron nitride (h-BN) in a layer-by-layer configuration. Compared to those passivation composites such as deposited AlO$_x$ and SiO$_2$, h-BN is chemically inert and pinhole free, minimizing the possible reaction of phosphorene with air. However, recent studies by Kim et al. reveal that even a thick Al$_2$O$_3$ layer is inadequate to provide long-term stability of phosphorene, which may be due to the slow diffusion of adsorbents through the capping layers and causing eventual breakdown. Therefore, they developed a double-layer capping strategy by further coating a hydrophobic fluoropolymer film on top of the Al$_2$O$_3$ capping layer. The hydrophobic layer is critical for preventing the adsorption of moisture from air and diffusion into the device, giving much enhanced air stability during months-long observation.

Except for depositing capping layers on the surface of phosphorene, covalent surface modification of phosphorene has also been reported as a helpful passivation approach toward air stable phosphorene. Recently, a titanium sulfonate ligand was coordinated with phosphorene, resulting in good air stability of phosphorene dispersion in water and exposure to air.\cite{149} The successful passivation was demonstrated due to surface coordination occupying the long pair electrons of phosphorus, suppressing the oxidative reaction of phosphorene with oxygen and water molecules effectively. Very recently, covalent functionalization of phosphorene (Figure 2c) was further realized by simply immersing phosphorene in aryldiazonium salt solutions (4-nitrobenzenediazonium: 4-NBD and 4-methoxybenzenediazonium: 4-MBD tetrafluoroborate salts) for a series of reaction times (0–180 min).\cite{150} During the soaking process, the modification proceeds spontaneously. The P=C bonds formed after phosphorene reacting with 4-NBD and 4-MBD for 30 min. This spectral feature for both molecules was further enhanced after increasing reaction time to 180 min. With a formation of covalent P=C bonds, the morphology of the chemically modified BP remains constant within 10 d of exposure to ambient conditions. On the contrary, the unprotected phosphorene appears with large protrusions, indicating its severe oxidation. Therefore, those covalent functionalization strategies may provide insight into feasible and easy protection of phosphorene.

Actually, those passivation approaches discussed above, including both depositing protective layers and covalent surface modification on the surface of phosphorene, are demonstrated on one piece of mechanically cleaved phosphorene. So far, limited studies have been presented on passivating large amount of phosphorene simultaneously, which is critical for volume applications of phosphorene in some fields, such as sensors, energy storage and conversion, and so on. Recently, a densely packed few-layer BP and reduced graphene oxide (rGO) composite was
reported to show excellent air stability. Briefly, spark plasma sintering (SPS) process was used to enhance the stacking of phosphorene and rGO. As shown in their cross-sectional scanning electron microscopy (SEM) images (Figure 2d), the PG-SPS sample shows a much more densely packed structure as compared to the loosely stacked phosphorene–graphene hybrid. As a result, the as-obtained densely packed phosphorene–rGO composite possesses excellent air stability within 60 d observation, as confirmed by their X-ray diffraction (XRD) analysis (Figure 2e). The enhanced air stability of phosphorene was attributed to effectively suppressing the permeation of water or oxygen molecules into the sample. Actually, this method still relies on utilizing the large amount of graphene oxide, which may limit its applications. Therefore, it is still challenging to develop effective in situ passivation methods on large amounts of phosphorene.

4. Black Phosphorus for Lithium-Ion Batteries

The theoretical specific capacity of BP as anodes for LIBs is as high as 2596 mAh g$^{-1}$ based on the formation of Li$_3$P$^{[151,152]}$. This value is almost ten times that of commercially used graphite (372 mAh g$^{-1}$)$^{[153,154]}$ which renders BP a promising anode of LIBs with high gravimetric and volumetric energy density. In addition, as the most thermodynamically stable allotrope of phosphorus, BP can be stable up to 450 °C under N$_2$ atmosphere, indicating that the BP could be considered for application of high energy-density batteries.
with proper package and sealing process.\textsuperscript{[120]} However, BP is faced with the challenges of large volume change (\(\approx 300\%\)) as well as sluggish reaction kinetics as a typical alloying anode, leading to low initial reversible specific capacity and fast capacity fading.\textsuperscript{[125]} During past decade, extensive studies have been focused on the electrochemical mechanism,\textsuperscript{[155]} first-principles calculations,\textsuperscript{[156,157]} and developing BP–carbon composites,\textsuperscript{[63]} and so on.

### 4.1. Electrochemical Activities

The puckered layer structure of BP provides 2D interstitial space for Li insertion and extraction. Owing to the unique properties of phosphorene, numbers of theoretical calculations have been carried out related to the diffusion of Li ions in phosphorene.\textsuperscript{[158,159]} It is found that stronger interaction between Li and phosphorene than that in graphene could potentially provide high open circuit voltage and enhance the electrochemical performance accordingly.\textsuperscript{[82]} In addition, the ultrafast diffusion of Li ions along the zigzag directions of phosphorene due to the low shallow energy barrier (0.08 eV) is almost 10\(^4\) and 10\(^2\) times faster than that in graphene and MoS\(_2\), respectively, indicating that phosphorene possesses potentially excellent Li storage properties.\textsuperscript{[159]} Good reversibility has been also reported due to the self-recovery of phosphorene monolayer when it is distorted during the intercalation of Li ions at high Li/P ratio.\textsuperscript{[158]} Therefore, favorable features of phosphorene as anodes of LIBs including ultrafast diffusivity, good reversibility, and high open circuit voltage have been demonstrated theoretically as a promising candidate as anodes toward high-performance LIBs.

Recently, the electrochemical behavior of BP with high purity and crystallinity has also been experimentally studied by controlling different discharge termination voltages.\textsuperscript{[160]} As shown in Figure 3a,b, ex situ XRD patterns were conducted at the different discharging and charging potential. When the potential is lowered from 2 to 0.78 V, various Li\(_x\)P phases (e.g., LiP\(_7\), LiP\(_5\), Li\(_3\)P\(_7\) in sequence) are formed. The LiP phase produced is analyzed by high-resolution TEM (Figure 3c) when the potential is held at about 0.78 V. At the potential of 0.63 V, the molar ratio of Li and P is determined to be 1.93:1 characterized by Auger electron spectroscopy, assumed to be the theoretical phase of Li\(_3\)P. When the discharge termination voltage is further lowered to 0 V, the main product becomes Li\(_3\)P. Upon charging process, the Li\(_3\)P phase disappeared and Li\(_3\)P reappeared at the potential of 1.12 V. Finally, amorphous phosphorus was believed to form with no obvious diffraction peaks at fully charged state. Therefore, the reactions of BP involved as anodes of LIBs could be as follows:

\[
\text{BP} \rightarrow \text{Li}_3\text{P} \rightarrow \text{LiP} \rightarrow \text{Li}_3\text{P} \rightarrow \text{Li}_3\text{P} \quad (1)
\]

However, BP bulk or microsized particles suffer from rapid capacity fading due to its large volume change as well as sluggish reaction kinetics.\textsuperscript{[161]} Isolating BP bulk into ultrathin phosphorene has been demonstrated as an answer to prolonging its cycling life. As evidenced by in situ TEM,
phosphorene exhibits excellent structural integrity even after several lithiation/delithiation cycles.[135] Nevertheless, they exhibit poor initial reversible capacity of 210 mA h g\(^{-1}\) accompanied by the low first-cycle Coulombic efficiency (11.5%), which is far from its theoretical capacity (2596 mA h g\(^{-1}\)).[136] Therefore, improvement of initial reversible capacity of BP nanosheets is still challenging before practical applications.

**4.2. BP–Carbon Composites**

Coupling conductive carbon with BP has been demonstrated theoretically and experimentally as an effective strategy to boost the electrochemical performance of BP as anodes for LIBs due to improved electrical conductivity as well as enhanced accommodation ability of large volume change.[103] During the past years, different carbon materials have been used to combine with BP, such as carbon black (super P), carbon nanotube, and graphene, etc. Recently, BP–carbon (super P) composites with an optimum ratio of 7:3 were synthesized by high energy mechanical milling (HEMM) technique with red phosphorus and super P as the starting materials.[160] As a result, a high initial reversible capacity of 1814 mA h g\(^{-1}\) with an improved 1st- cycle coulombic efficiency (CE) of about 90% could be achieved compared to that of pure BP (1279 mA h g\(^{-1}\), CE of 57%). In addition, the cycling performance was further increased by controlling the voltage range. When the BP–carbon composite is cycled within the potential of 0–2.0 V versus Li\(^+\)/Li, the capacity degrades fast with about 10% retention during 30 cycles due to the large volume change originating from generating Li\(_2\)P phase. For the potential range of 0.78–2.0 V, good cycling performance with no obvious fading over 100 cycles was observed by avoiding the formation of the Li\(_2\)P phase. However, the reversible reaction between P and LiP only exhibits a specific capacity of 600 mA h g\(^{-1}\). Stable cycling performance has not been achieved with a specific capacity close to the full capacity of BP (2596 mA h g\(^{-1}\)).

Recently, robust phosphorus–carbon (P–C) bonds in BP–carbon composites (the ratio of P and C = 1:3) prepared via HEMM are demonstrated to be critical to improve the high capacity retention.[162] The stable P–C bonds are a key factor to maintain good electrical connection between BP and the conductive carbon matrix, affording a high initial charge specific capacity of 2382 mA h g\(^{-1}\) and a good cycling life with a specific capacity retention of 1849 mA h g\(^{-1}\) over 100 cycles. Furthermore, the BP/graphite composite shows highest reversible capacity as well as the most stable cycling performance among the various composites, including BP/carbon black, BP/graphene oxide, and BP/C\(_{60}\). Therefore, it is found that carbon structures also play a critical role in boosting the BP anodes for LIBs. Although good performance of BP as anodes for LIBs is achieved via those effective strategies, the BP used above is still the bulk/microsized BP crystals. Thin nanosheets with sufficient active sites may be beneficial to provide effective transport pathways for charge transfer and diffusion, which may show better rate performance.

Theoretically, phosphorene/graphene heterostructure (P/G) has been investigated as a good candidate for LIBs based on first-principles calculations due to improved binding energy and high diffusion mobility of Li ions in the P/G anodes.[163] Very recently, a paper-like flexible LIB electrode was experimentally prepared by combining exfoliated phosphorene (80 wt%) with conductive graphene sheets (20 wt%).[160] The characterizations including its photograph, SEM images, STEM-HAADF (scanning transmission electron microscopy high-angle annular dark-field) image and the corresponding EDS elemental mappings are shown in Figure 4a–f, respectively. The as-prepared porous phosphorene-G paper possesses mechanical robustness benefiting from the flexible 2D structure of both graphene and phosphorene. On the contrary, a BP nanoparticle–G hybrid paper prepared via the same procedure with phosphorene-G paper is very brittle due to the intimate contact between phosphorene and graphene. This demonstrates that phosphorene exhibits favorable features for flexible electrochemical energy storage applications. In addition, high specific capacities (920 mA h g\(^{-1}\) at 100 mA g\(^{-1}\), Figure 4g), good rate capability (141 mA h g\(^{-1}\) at 2500 mA g\(^{-1}\), Figure 4h), and prolonged cycle performance (402 mA h g\(^{-1}\) over 500 cycles at 500 mA g\(^{-1}\), Figure 4i) could be achieved for the freestanding phosphorene–G paper electrode based on its total mass.

As discussed above, a densely packed phosphorene–graphene composite (PG-SPS) was prepared with a high packing density of 0.6 g cm\(^{-3}\). The good air stability of PG-SPS is beneficial for maintaining its lithium storage properties over 60 d observation. On the contrary, the phosphorene in the porous phosphorene–graphene composite were severely oxidized, leading to the degraded electrochemical properties. However, so far there have been limited reports on applicable strategies toward passivating phosphorene and phosphorene-based anode materials for LIBs. Therefore, the practical use of the air stable phosphorene in LIBs could be of interest.

**4.3. BP–Noncarbon Composites**

As discussed above, developing BP–carbon composites has been demonstrated as effective strategies toward overcoming the challenges of sluggish reaction kinetics and large volume change of BP as anodes for LIBs. However, high portion of conductive carbon materials possibly lead to reduced specific capacity based on the overall mass of the whole electrode, considering that carbon materials exhibit relatively low specific capacities compared to the bare phosphorene. Constructing controllable and well-designed heterostructures based on ultrathin 2D nanosheets (e.g., MoS\(_2\)/WS\(_2\),[39,40] Fe\(_2\)O\(_3\)/MoS\(_2\),[61] WSe\(_2\)/MoSe\(_2\),[164] GaSe/MoS\(_2\),[160] polyaniline/MoS\(_2\)[164]) are fundamentally and technologically attractive in batteries or electronic devices. Therefore, hybridization of phosphorene with other electrochemical active materials, such as transition metal oxides, metal chalcogenides, and metal phosphides, has been identified as an intriguing route to engineer their properties through taking advantages of different building blocks. Very recently, multifunctional 0D–2D Ni\(_2\)P/BP (Figure 5) has been reported as high-capacity anodes for LIBs due to sufficient active sites and enhanced electrical conductivity compared to the pure phosphorene.[160]
Different from carbon materials in BP-based composites, the component of Ni$_2$P contributes to the Li storage with a high theoretical specific capacity of 742 mAh g$^{-1}$ via the following conversion reaction

$$\text{Ni}_2\text{P} + 3\text{Li}^+ + 3e^- \rightarrow \text{Li}_3\text{P} + 2\text{Ni}$$

Currently, the investigation of BP–noncarbon composites, especially for LIBs applications, is still in its infancy. The absence of dangling bonds on BP basal plane presents a difficulty to further modify phosphorene. Therefore, efforts could be devoted to conjugate functional groups (e.g., $\text{–OH, –COOH, thiol ligands}$) on the surface of phosphorene for further hybridization. However, considering the sensitive property of phosphorene to oxidizing and aqueous conditions, careful processing under inert atmosphere to construct phosphorene-based heterostructures would be necessary and also challenging in order to minimize the phosphorene oxidization.

Figure 4. a) Photograph of a BP–G hybrid paper. b) Top-view and c) cross-sectional-view SEM images of the BP–G hybrid paper. d) STEM-HAADF image, and the corresponding EDS elemental mappings of e) the C-K line, and f) P-K line, of a region of the BP–G hybrid paper. g) The second galvanostatic charge/discharge profiles of the BP nanosheet, G paper, and BP–G hybrid paper electrodes at a current density of 100 mA g$^{-1}$ within a potential window of 0.001–3 V (vs Li$^+$/Li). h) Rate performance of the BP nanosheet, graphene paper, and BP–G hybrid paper electrodes at different current densities. i) Cycling stability and Coulombic efficiency of the BP–G hybrid paper electrode at 500 mA g$^{-1}$ for 500 cycles after the rate capability test. Reproduced with permission.[140] Copyright 2017, John Wiley & Sons, Inc.
5. Black Phosphorus for Sodium-Ion Batteries

Sodium shares similar chemical properties with lithium in many aspects. Therefore, the development of Na battery technologies could learn from the accumulated experience of LIBs. Recent studies on cathode materials for SIBs have demonstrated comparable performance to the LIBs counterparts. However, identifying viable anodes is the major scientific challenge for competitive SIBs technology. The development of anodes for SIBs has been largely based on hard-carbon materials, which provides a relatively low specific capacity, especially a low volumetric capacity. Recently, BP has been considered as one of the most promising anodes due to its high sodium storage capacity, layered structure, and suitable operating potential (≈0.45 V vs Na/Na⁺). Numerous theoretical investigations have been focused on the monolayer phosphorene as anodes for SIBs using a first-principle calculation. It is found that Na diffusion on phosphorene is ultrafast and anisotropic, potentially endowing phosphorene with excellent electrochemical response. Therefore, phosphorene is also demonstrated as a promising anode for SIBs.

The sodiation of phosphorene proceeds according to two steps including both intercalation (1.5–0.54 V vs Na/Na⁺) and alloying (0.54–0.0 V vs Na/Na⁺), finally forming the Na₃P phase recognized by ex situ XRD techniques. Upon alloying, an anisotropic volumetric expansion with a 92% expansion along y-axis and 0% along x-axis was observed using in situ TEM. However, the complete sodiation of BP leads to a large volume expansion (∼500%) and thus fast capacity fading during cycling. To achieve stable cyclability, these authors fabricated a layer-by-layer phosphorene–graphene hybrid as anodes of SIBs for the first time as illustrated in Figure 6a,b. Graphene in such a sandwich structure plays a critical role in buffering the anisotropic expansion as well as facilitating the electron transport. With increasing content of graphene in the composite, excellent sodium storage performance in terms of cyclability was achieved benefiting from these advantages as shown in Figure 6c. In addition, the phosphorene–graphene hybrid with 48.3% of phosphorus exhibited a high reversible capacity (2440 mA h g⁻¹ at 0.02 C) and good capacity retention (2080 mAh g⁻¹ after 100 cycles) based on the mass of phosphorus (Figure 6d). Therefore, phosphorene–graphene hybrids and other phosphorene–carbon-based materials could be suitable anodes for SIBs in
the future. Actually, considering the electrochemically inactive property of graphite/graphene and low specific capacities of other carbon materials, phosphorene for SIBs also face the similar challenge to LIBs. That is, high percent of carbon materials would lead to reduced specific capacities based on the whole mass of the composite electrodes. Therefore, developing phosphorene-based hybrid heterostructures with high-capacity nanomaterials could be an effective strategy, as discussed above in the Section 4.2 of BP–carbon composites for LIBs.

Furthermore, electrolyte additives have been considered as an indispensable role for the improvement of SIBs. Na₃P, as an electrochemically reduced product of BP during sodiation process, has much shorter intersodium distances (2.98–3.22 Å) due to covalent character of Na–P bonds than metallic sodium (3.71 Å).[179,180] This favorable feature endows BP with higher volumetric energy densities than other Na alloys (e.g., Sn, Sb). However, the highly reactive surface of Na₃P induces severe electrolyte decomposition, leading to large irreversible capacity.[181] Electrolyte additives with no more than 5% either by weight or by volume have been largely studied in LIBs as one of the most economic and effective methods for the improvement of LIBs performance.[182–184] Therefore, the successful experience of LIBs could be learnt by SIBs due to the similar electrochemical properties. Actually, among those additives (transdifluoroethylene carbonate, vinylene carbonate, fluorooethylene carbonate (FEC), and ethylene sulfite) used for LIBs, FEC has been demonstrated as the efficient one for SIBs to stabilize the solid-electrolyte interphase (SEI) and thus suppress the electrolyte decomposition.[185–187] For example, enhanced cycling performance (~1000 mAh g⁻¹ after 80 cycles) was achieved for P/C composite by adding FEC in the electrolyte.[152] On the contrary, dramatically capacities degrade happened after 40th cycle due to the unstable SEI film. Currently, the study of the most suitable electrolyte additives for BP-based anode materials for SIBs is still in early stage. Therefore, further systematic exploration and study of optimal electrolyte additives is still necessary.

### 6. Thermoelectric Applications

TE energy generation based on semiconductor materials has attracted immense attention, as the process can be directly used to convert waste heat into electricity. The TE properties of these materials are quantified by the dimensionless figure of merit ZT, which is defined as $ZT = \sigma T/\kappa \alpha$ where $\sigma$, $\alpha$, $\kappa$, and $T$ are electrical conductivity, Seebeck coefficient, thermal conductivity, and absolute temperature, respectively.[188,189] The state-of-the-art TE materials usually possess a relatively large power factor ($\sigma \alpha$) and a low thermal conductivity to maximize the ZT values.[189] And the current development of advanced TE materials is mainly focused on band...
engineering,

lorically low thermal conductivity,

2D device material employed in nanoelectronic devices

and batteries,

exploitation of its TE applications is still in its infancy. BP has been reported to retain a large Seebeck coefficient ($\approx 335$ $\mu$V K$^{-1}$ at RT),

a high carrier mobility ($1000$ cm$^2$ V$^{-1}$ s$^{-1}$ at RT),

and a moderate bandgap ($0.3$ eV for bulk BP),

which makes it a potential candidate for TE applications. However, most of these studies have been focused on theoretical calculations without further verification by experimental data. In the following section, the TE properties of BP in both bulk and thin sheet forms are reviewed. The potential applications and related challenges are also discussed.

To the best of our knowledge, few reports have been aimed at illustrating the TE properties of bulk BP. The electrical properties of BP polycrystalline bulks prepared by applying high-pressure were first reported in 1950s, which demonstrated a bandgap of $0.33$ eV, an electrical resistivity of $1.5$ $\Omega$cm, and a hole mobility of $350$ cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature.

It was a decade later that a positive Seebeck coefficient was reported in the range of $330$–$413$ $\mu$V K$^{-1}$ for bulk BP, and the Young’s modulus was $6.89$ GPa. The ultimate tensile strength and compressive strength were measured to be $34$ and $350$ MPa, respectively. These properties indicated that BP could be considered as a potential candidate for strain and hydrostatic gauges and transducers. In 1965, Slack

studied the thermal conductivity of bulk BP at $3$–$300$ K and a room-temperature $\kappa$ of $12$ W m$^{-1}$ K$^{-1}$ was reported. In 1983, Akahama et al.

prepared BP single crystal with the dimension of $5 \times 5 \times 10$ mm$^3$ under high pressure and investigated the electrical properties along the three principal crystal axes. Undoped BP crystals presented p-type conduction with an effective acceptor concentration of $2.5 \times 10^{15}$ cm$^{-3}$, and the room temperature resistivities were in the range of $0.4$–$2.3$ $\Omega$cm, of which the resistivity along $b$-axis was about one order of magnitude higher than that along $c$-axis. On the other hand, Te elements were employed as dopants for the first time to achieve n-type BP crystals, which exhibited a higher electron concentration of $2.3 \times 10^{16}$ cm$^{-3}$ and slightly lower resistivity compared with those of p-type BP. Based on the previous data acquired at room temperature, the ZT value was calculated to be $10^{-4}$ in accordance with the literature report.

The poor TE performance is mainly ascribed to the inferior $\sigma$ and high $\kappa$ due to the low carrier concentration and preferential orientation along $b$-axis, which may have hindered further research and progress in BP crystals thereafter. Higher doping should presumably increase the power factor, reaching toward an optimal value similar to other semiconductors, but this has not been demonstrated experimentally yet.

It is not until recently that researchers have successfully exfoliated few-layer BP from its bulk crystal, namely phosphorene, which has been implemented in the FET configuration. The prototype FETs show superior performance at room temperature with a current on/off ratio of up to $10^5$ and a maximum field-effect mobility of $1000$ cm$^2$ V$^{-1}$ s$^{-1}$, thus unveiling the potential application of 2D BP in nanoelectronics and optoelectronics.

The recent two years have witnessed an explosion of attention paid to both theoretical and experimental research of BP and related applications.

The carrier concentration of intrinsic BP crystal is manifested in the range of $10^{19}$–$10^{21}$ cm$^{-3}$, which, however, is about 4–5 orders of magnitude lower than the optimal concentration required for good TE materials. Recently a series of theoretical studies have predicted the excellent TE properties of BP with optimized carrier concentration. Zhang et al.

utilized first-principles calculation and Boltzmann transport theory to systematically investigate the TE properties of BP provided with a reasonable carrier concentration in the range of $10^{19}$–$10^{21}$ cm$^{-3}$. Results indicate that BP exhibits a peak ZT of 1.1 with an electron concentration of $1.5 \times 10^{20}$ cm$^{-3}$ and a maximum ZT of 0.6 with a hole concentration of $3.2 \times 10^{19}$ cm$^{-3}$, as shown in Figure 7 at 800 K. Furthermore, the authors indicate in the modeling that the substitution of Sb for P can enhance the density of states around the Fermi level and also introduce alloy scattering to reduce the lattice thermal conductivity. The resultant ZT value is predicted to reach up to 5.4 at 800 K for 25 at% Sb-doped BP, while reducing the Sb concentration to 12.5 at% contributes to an average ZT of over 2.0 over a broad temperature range of 450–800 K. However, to date no experimental research has verified the feasibility of Sb-substitution for P. Ly et al.

predicted that the power factor of n-type bulk BP can approach as high as $11.8 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ upon an optimized electron concentration of $1.9 \times 10^{20}$ cm$^{-3}$. Combined with the large thermal conductivity (12 W m$^{-1}$ K$^{-1}$ at RT), the ZT value was deduced to be 0.22 at room temperature, which is far below that of the state-of-the-art Bi$_2$Te$_3$-based materials. Meanwhile the authors also evaluated the TE performance of phosphorene with appropriate p-type doping, which shows a large power factor of $13.9 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ and that a maximum ZT of 1.78 can be achieved by assuming an order of magnitude lower in the lattice thermal conductivity compared to the previous data. Furthermore Qin et al.

reported that a peak ZT of 0.72 could be obtained at 800 K for bulk BP, which could be enhanced to 0.87 under certain strain. But these theoretical results turn out to be controversial considering that BP crystals become unstable and sublimate above 450 °C.

Based on various approximations and methods, these theoretical calculations indeed provide essential guidance for the performance optimization of BP crystals. But more experimental efforts are required in order to further verify and calibrate these predicted data.

The band structure of BP was first calculated by using the tight-binding approximation, which demonstrated that BP was a narrow bandgap (0.3 eV) semiconductor with a direct energy gap at the zone edge in the $(00k_z)$ direction. It was one year later in 1982 that researchers employed self-consistent pseudopotential method to study the band structure of BP in order to validate and precisely analyze the previous data. Their calculation verified that the minimum direct gap of BP crystal was 0.3 eV, which appeared at $Z$ point in Brillouin zone in (001) direction consistent with the conclusion from tight-binding approach.
Recently Du et al.\cite{216} analyzed the electronic structure of bulk BP based on ab initio calculation and an energy gap of 0.19 eV was observed which opens at $\Gamma$ point. Li et al.\cite{86} verified the band structure of bulk BP by employing angle-resolved photoemission spectroscopy (ARPES) measurements and ab initio calculation. The electronic structure of bulk BP is presented in Figure 8a. As evident by the red dashed lines, which indicate the filled bands, the observed bandgap is around 0.2 eV in reasonable agreement with the aforementioned calculation and testing.\cite{101,115,118} On the other hand, the effects of strain or pressure on the band structures of BP crystals and layers have been investigated. The energy gap of BP is inversely proportional to the pressure applied, which is probably due to the decrease of van...

![Figure 7](https://www.advancedsciencenews.com)

Figure 7. Theoretical calculation of a) Seebeck coefficient, b) electrical conductivity, and c) ZT value of BP as a function of carrier concentration at 300 K. d) The Seebeck coefficient, e) electrical conductivity, and f) ZT value of BP as a function of carrier concentration at 800 K. Reproduced with permission.\cite{92} Copyright 2015, Royal Society of Chemistry.

![Figure 8](https://www.advancedsciencenews.com)

Figure 8. a) Band structure of bulk BP measured by ARPES. The blue solid lines and red dashed lines stand for empty and filled bands, respectively. Reproduced with permission.\cite{86} Copyright 2014, Nature Publishing Group. b–d) Band structure of BP monolayer under a uniaxial compression along the direction normal to the layer for three imposed heights $h/h_0$ (continuous line). The dotted lines correspond to the band structure of pristine BP (dotted lines). e) Bandgap as a function of the height. The original layer thickness is $2h_0$. Reproduced with permission.\cite{218} Copyright 2014, American Physical Society.
nder Waals gap of two adjacent layers with the increasing pressure. A semiconductor–metal transition was observed in BP crystal when the pressure reaches \( \approx 1.7 \text{ GPa} \). By further increasing the pressure imposed on BP up to 5 GPa, it exhibited a structural transition from orthorhombic to rhombohedral and then to cubic structure at \( \approx 10 \text{ GPa} \). Likewise, as presented in Figure 8b–e, researchers have also predicted that exerting uniaxial stress along the direction perpendicular to the BP monolayer primary surface can result in the gap modification and semiconductor–metal transition, of which the pressure is estimated to be around 24 GPa. Recently, Konabe et al. investigated the TE properties of bilayer BP under tensile strain by applying first-principle calculation. The simulation results show that interlayer coupling is critical in adjusting the TE performance, of which the power factor increases monotonically as a function of tensile strain up to 6%. Ascribing to the puckered structure of BP, the electrical and thermal transport properties exhibit strongly anisotropic behavior along the armchair and zigzag directions, i.e., \( b \)- and \( a \)-axis, respectively. For bulk BP crystals, the hole mobility is much higher than the electron mobility along the same crystal axis. In 1980s, the hole mobility along \( c \)-axis was reported about 3 and 6 times that of electron along \( a \)- and \( b \)-axes, respectively, which is mainly due to the anisotropy of effective mass. As a consequence, the anistropy nature of BP has accelerated the development of BP-based flexible devices.

Interestingly, not only are the electrical properties of BP anisotropic, but the different symmetries in the armchair (AC) and the ZZ-directions also cause a large anisotropy in the phonon thermal conductivity. This was predicted theoretically and proven experimentally both in the few-layer phosphorene limit as well as for thin films and bulk samples. With higher quality samples, the anisotropy ratio was seen to be \( \approx 2 \) at all temperatures where the ZZ-direction has a larger thermal conductivity than the AC-direction for all samples, as shown in Figure 9. The difference in the absolute values could be attributed to different levels of defect density in BP but the overall physics is identical in all these measurements. These measurements were all performed on undoped as-obtained crystals of BP and hence the electrical measurements of optimally doped samples remain challenging. Most intriguingly, the electrical anisotropy is exactly opposite of the thermal conductivity, where the ZZ crystal direction is expected to have a smaller electrical conductivity compared to the AC direction, which makes the study of BP for thermoelectrics all the more enticing.

BP emerges as one of the potential elemental thermoelectrics other than Si, Ge, and Te. Its TE properties, however, have not garnered equal attention as the previous IV- and IV-group elements. According to the doping theory in classical semiconductor, both n- and p-type conduction can be achieved by replacing phosphorus atoms with neighboring group elements. The intrinsic BP crystal exhibits hole-dominated transport behavior, which has been

Figure 9. a) An illustration of the anisotropy in crystal direction arising from the puckered structure in BP named as zigzag (ZZ) and armchair (AC). b) High-resolution TEM taken from a typical BP flake (adapted with permission. Copyright 2015, Nature Publishing Group. c,d) Summary of thermal conductivity at 300 K in ZZ and AC directions, respectively, showing larger thermal conductivity in the ZZ direction (reproduced with permission. Copyright 2017, John Wiley & Sons, Inc.)
manifested experimentally but the mechanism needs further clarification. On the other hand, Te-doped BP had been reported to present n-type conduction, which was attributed to the substitution of hexavalent Te for pentavalent P.[101] However, the doping concentration of Te was not revealed in the report. Recently, Yang et al.[232] reported the enhanced stability of BP field-effect transistors (FETs) by 0.1 at% Te doping. In addition, the Hall-effect measurement confirmed its p-type conducting behavior, which is contradictory to the previous data.[101] The underlying reason is probably due to the trace amount of Te incorporation; however, further increase of Te up to 0.5% molar ratio will result in Te residues. This also indicates that the solubility of Te in BP should be in the range of 0.1–0.5 at%. For the first time, Luo et al.[190] synthesized n-type BP nanosheets embedded with Ni0.6P nanocrystals (denoted as Ni0.6P@BP heterostructure), which demonstrate around two orders of magnitude enhancement in the electrical conductivity from 2.12 × 10^2 S m^−1 for pristine BP to 6.25 × 10^4 S m^−1 for Ni0.6P@BP at 300 K. This is mainly due to the remarkable improvement of the carrier concentration (from 1.25 × 10^17 to 1.37 × 10^20 cm^−3). Ascribing to the enhanced phonon scattering by grain boundaries and impurities, the thermal conductivity of Ni0.6P@BP has been reduced to about one sixth that of BP single crystal (from 44.5 to 7.69 W m^−1 K^−1) at 300 K. Consequently, 0D–2D heterostructuring has been manifested as an effective way to improve the TE performance of BP crystals.

Despite the tremendous efforts in promoting layered and bulk BP as potential candidates in TE application, certain issues and challenges still remain ahead regarding the stability and further optimization. On the one hand, effective alloying, doping or compositing in BP are necessary to improve the carrier concentration up to optimal values and to balance between the electrical conductivity and Seebeck coefficient and to further reduce the thermal conductivity to make it attractive for thermoelectrics. On the other hand, in addition to the traditional crystal growth of BP, other synthesis methods, such as mechanical alloying, are required for the scalable production and then commercial applications of BP.

7. Other Energy Storage Applications

Exploring phosphorene or phosphorene-based materials in a variety of applications is one of the most active research areas. In addition to LIBs, SIBs, and TE, phosphorene has been demonstrated as a promising candidate for many other energy storage and conversion devices (e.g., modern reversible batteries,[233] electrocatalysis,[139] photocatalysis,[234–236] solar cells,[237] etc.) due to its intriguing properties. For example, Li–S batteries have attracted intensive research as a promising alternative of the current LIBs due to their superior theoretical capacity (1675 mAh g^−1) and high energy density (2600 Wh kg^−1).[236–240] However, the dissolution of intermediate polysulfides into the electrolyte results in gradual loss of active sulfur and rapid capacity fade accordingly. Recently, Li and co-workers demonstrated that the incorporation of phosphorene into a porous carbon nanofiber network could serve as an effective polysulfides immobilizer due to a high binding energy of LiS, to phosphorene, largely enhancing the cycling performance of Li–S batteries.[140] Very recently, a phosphorene as a coating layer, with high electrical conductivity and ultrahigh Li diffusion, was also introduced onto a commercial polypropylene separator to trap and activate the soluble polysulfides in Li–S batteries.[241] Phosphorene has also been explored as a promising anode of Mg-ion batteries, but current studies are mainly focused on the theoretical calculations by means of first-principles analysis.[242–244]

Supercapacitors are another important energy-storage system due to their high power density, fast charging/discharging rate, and excellent cycle stability.[245–247] According to the charge storage mechanism, supercapacitors are classified into electrical double layer capacitors (EDLCs) and pseudocapacitors. EDLCs work is based on the charge storage at the interface of electrodes and electrolyte, while pseudocapacitors are based on the reversible redox process at or near the electrode surface. Very recently, a flexible all-solid-state supercapacitor was reported based on the exfoliated phosphorene as electrode materials.[248] As shown in Figure 10, typically, the as-obtained dispersion of phosphorene in acetone was drop-casted on a Pt-coated polyethylene terephthalate (PET) substrate. Subsequently, polyvinyl alcohol (PVA)/H3PO4 as the gel electrolyte was sandwiched between the two as-prepared BP films on PET, followed by protection against the ambient exposure. As a result, the fabricated device based on EDLCs exhibited a high stack capacitance of 13.75 F cm^−2 at a scan rate of 0.01 V s^−1, good mechanical flexibility as well as outstanding cycling stability over 30 000 cycles with only 28.2% capacity decay.

8. Summary and Outlook

In this Review, the recent progress in preparation of phosphorene and their applications in energy storage and TE energy generation have been discussed. The liquid-phase exfoliation of BP crystals provides a straightforward way for the scalable and size controllable production of phosphorene. Importantly, phosphorene exhibits great potential in numerous promising applications due to their attractive physical, chemical, and mechanical properties.

Although great progress has been made in this area, challenges remain at this very early stage. Currently, scotch-tape technique and liquid-phase exfoliation for the phosphorene preparation have been only used in laboratories level, and its yield is still relatively low to meet the requirement of large-scale industrial applications. Furthermore, the difficulty in removal of organic molecules from the surface of exfoliated phosphorene presents a challenge in their applications. In addition, passivation of phosphorene to increase the air stability is important, since they degrade upon exposure to the ambient air. So far, various approaches including implementing protective layers to encapsulate phosphorene or covalent surface modification of phosphorene have been proven applicable. However, the current methods have not been demonstrated on scalable processes. Furthermore, although phosphorene provides a high theoretical capacity of
2596 mAh g\(^{-1}\) assuming the formation of Li\(_3\)P and Na\(_3\)P, their large volume change as well as sluggish reaction kinetics limit its performance as anodes of LIBs and SIBs, especially concerning their 1st-cycle Coulombic efficiency and the cycling stability. With respect to the TE application of BP, the main challenges are the inferior electrical conductivity and high thermal conductivity due to the low intrinsic carrier concentration and anisotropic structure of BP crystals, respectively, which exert a detrimental influence on the overall ZT value. The highest ZT value of BP has been predicted to reach over 2.0, however, it requires experimental verification in the future.

Note that the study of phosphorene within three years is still in its infant stage. In the light of current achievements, there are still lots of opportunities in this field. Except for scotch-tape technique and liquid-phase exfoliation, CVD and wet-chemical methods have also shown unique advantages in preparing ultrathin 2D nanosheets and their lateral/vertical epitaxial heterostructures. Therefore, one of the future directions is to construct phosphorene or their heterostructures by developing effective CVD or wet-chemical methods. In addition, to suppress the oxidation of massive phosphorene against the air, easily scale-up methods are highly desirable. One possible way is to in situ grow protective overlayers on the phosphorene surface via solution-based methods. It is worth noting that the absence of dangling bonds on BP basal plane might present a difficulty to further growing other materials on phosphorene due to lack of chemical or physical interaction. Therefore, modification of phosphorene with functional groups on their surface might be necessary. Furthermore, although facing the problems of large volume change and sluggish reaction kinetics for LIBs and SIBs, phosphorene possesses large spacing between the layers and fast Li/Na diffusion along the zigzag direction, which are favorable features for reversible batteries. So far, phosphorene-conductive carbon composites have been intensively studied with enhanced performance as anodes for LIBs and SIBs. To further improve their electrochemical performance, the preparation of phosphorene-based heterostructures with metal oxides/sulfides or conductive polymers is desirable for LIBs, SIBs, and other energy storage devices due to the synergistic effect. In addition, reduction of thermal conductivity and proper control of the charge carrier concentration through doping and nanostructuring can be effective approaches to improve the TE properties of BP and expand their applications in thermoelectrics and wearable electronics.

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**Conflict of Interest**

The authors declare no conflict of interest.
