Opportunities and Challenges of Black Phosphorus for Electrocatalysis and Rechargeable Batteries

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As an emerging 2D layered material, black phosphorus (BP) has received intensive attention in recent years, particularly in electrocatalysis and rechargeable batteries. With further structural modifications, BP-based heterostructured composites have exhibited attractive physical and chemical properties regarding to enhanced conductivity, ion transport, and catalysis activity, endowing them as potential candidates for electrochemical ions storage and electro/chemical catalysis. In this perspective, a brief summary is first given on the recent progress of BP and BP-derived materials in electrocatalysis, such as hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and nitrogen reduction reaction (NRR), and in rechargeable batteries, such as lithium-ion batteries (LIBs), sodium-ion batteries (SIBs), and potassium-ion batteries (PIBs), followed by a critical review on the current opportunities and challenges. It is expected that this class of emerging materials will bring about new potential solutions to address the current energy crisis and inspire researchers to develop more novel materials toward future multifunctional applications.

1. Introduction

Black phosphorus (BP), an emerging 2D layered material, is the most stable phosphorus allotrope. The BP bulk can be produced by following either a high-temperature/pressure or a mineralizer auxiliary synthesis and using the white/red phosphorus as the starting material.[3] BP bulk material has a layered structure with weak van der Waals force at the interlayers, which is easy for the ion intercalation and diffusion for further exfoliation. As the most thermodynamically stable phosphorus allotrope, BP demonstrates high theoretical electrochemical ion storage capacities, for example, over 2500 mA h g⁻¹ for lithium storage, which is much larger than that of graphite (372 mA h g⁻¹). Exceptionally, BP features relatively high carrier mobility and shows favorable electronic merits for the application in electrocatalysis. Phosphorene, a monolayer exfoliated from the bulk BP crystals, exhibits various unique properties to enrich the family of 2D materials.[4,5] Different to some 2D structures with flat atomic configurations in the plane, phosphorene has a puckered structure along the armchair direction, endowing it attractive anisotropic physical and chemical properties in batteries and electrocatalysis. Similar to the preparation of other 2D nanomaterials, the preparation of 2D phosphorene can be classified into two main categories: top-down approaches (e.g., mechanical exfoliation, liquid exfoliation, plasma etching, and electrochemical exfoliation) and bottom-up approaches (e.g., vapor deposition, phase transition, and wet-chemistry synthesis).[6-8] Black phosphorus quantum dots (BP-QDs) are further developed as a versatile functional nanomaterial for a wide range of sustainable energy and environmental technologies.[9] One of the typical features for BP is the thickness-dependent bandgap, which can be easily modulated from 0.3 eV for the bulk phase to 2.0 eV for the monolayer phosphorene.[10,11] This unique characteristic on the band tunability enables BP to be optimized for various opto/electronic applications, including field effect transistors (FETs), solar cells, photodetectors, sensors, batteries, photocatalysis, electrocatalysis, etc.[12-15] Despite the obvious advantages of BP, some intrinsic properties are not satisfactory for some specific applications. For example, the chemical instability and the weak conductivity of the pristine BP may pose negative influences on electrochemical performance when used for energy conversion and storage devices.[3,16] As an effective method to address these issues, the construction of BP-based heterostructures can significantly improve the properties and thus can broaden the application of BP-based materials.[16]

This perspective aims to review the applications of BP in emerging electrocatalysis and rechargeable batteries. BP has been explored as potential electrocatalysts toward various reactions, such as oxygen evolution reaction (OER), hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), nitrogen reduction reaction (NRR), etc.[17,18] For the widely studied HER...
and OER, the pristine BP catalyst manifests too strong adsorption for OER intermediates and too weak adsorption for HER intermediates, which generate unfavorable catalytic reaction steps and greatly hinder its practical catalytic applications.\[^{[19]}\]

Physically constructing BP-based heterostructures is an effective solution for increasing active sites, promoting surface reconstruction, and achieving desired adsorption pathways for electrolysis.\[^{[20–23]}\]

In the BP-based heterostructures, it has been revealed that BP could be degraded upon exposure to oxygen/water during electrocatalysis, leading to irreversible phosphorus loss. This phosphorus degradation, however, can increase the numbers of active centers onto the surface of counterpart, giving rise to an acceptable activity overall.\[^{[24]}\]

On the other hand, BP is one promising electrode material used in rechargeable batteries, due to its ultrahigh theoretical capacity of 2596 mA h g\(^{-1}\) based on the Li\(_{3}\)P/Na\(_3\)P compounds in lithium ion batteries (LIBs)/sodium ion batteries (SIBs), and its large interlayer channel space of 3.08 Å for fast diffusion of metallic ions.\[^{[25–27]}\]

To further improve the battery performance, BP-derived heterostructure electrodes have been investigated for enhancing the conductivity, restricting the large volume swelling, and inducing the stable solid-electrolyte interphase.\[^{[28–30]}\]

In this perspective, the recent progress on the regulation strategies of BP and BP-derived hybrids in electrocatalysis, including HER, OER, NRR, and ORR, and in rechargeable batteries, including LIBs, SIBs, potassium ion batteries (PIBs), and Li–S batteries, are briefly summarized. Then, the current opportunities and challenges are outlined for the applications of this emerging material in energy-related devices and technologies. It is expected that this fast-growing BP-based materials and their applications will bring about new solutions to address the current energy crisis toward sustainable future, as identified by the United Nation’s Sustainable Development Goals (e.g., affordable and clean energy, and sustainable cities and communities), and enrich the knowledge basis of nanoscience and nanotechnology.

## 2. BP and BP-Derived Catalysts for Electrocatalysis

### 2.1. Effect of Structural Parameters of Individual BP Nanosheets on Electrolysis

It has been well addressed that the sizes and shapes of nanostructures have significant impact to the physical and chemical properties and thus lead to dramatically varied performance within device applications.\[^{[31,32]}\]

The electrocatalytic activities of the BP are largely affected by some structural parameters, such as thicknesses, substrates, functionalized groups, and defects. The effects of these major structural parameters on the catalytic performance are summarized as follows.

i) Thicknesses: The thickness of 2D materials is closely associated with the band structures and charge/carrier mobility.\[^{[33,34]}\]

BP nanosheets with different thicknesses can be separated by using different centrifugation rates. As illustrated in Figure 1a,\[^{[35]}\] four types of BP nanosheets with different average thicknesses were obtained at different centrifugation rates, namely, 70 nm for 0–500 rpm, 54 nm for 500–1000 rpm, 22 nm for 1000–1500 rpm, and 6 nm for above 1500 rpm, and examined for OER catalysis. It was concluded that the BP nanosheets obtained at a low centrifugation rate below 1000 rpm were inferior to the unselected BP. The BP nanosheets collected at a rate above 1500 rpm, however, delivered greatly enhanced OER performance (Figure 1b). Furthermore, the current density at an overpotential 1.8 V for the BP nanosheets obtained at a high centrifugal rate above 1500 rpm was 19.6 mA cm\(^{-2}\), which was more than three times higher than that of the unselected BP (6.1 mA cm\(^{-2}\), Figure 1c).\[^{[36]}\]

ii) Substrates: The substrates for the growth of 2D materials can lead to significant influence on the band structure and charge/carrier transport behavior when works as current collector or supporting material. For example, BP directly grown on a Ti foil (BP-Ti) and a CNT network substrate (BP-CNT) exhibited efficient alkaline OER performance.\[^{[37]}\]

Specifically, the BP-CNT catalyst manifested better activity with a potential of 1.6 V to achieve the desired density of 10.0 mA cm\(^{-2}\), which was close to that of the commercial RuO\(_2\) (1.59 V) and IrO\(_2\) (1.57 V).\[^{[38]}\]

iii) Functionalized groups: Functional groups adsorbed on the surface of 2D materials can alter the surface chemistry and electronic structure as well as the interaction with the reactants.\[^{[39]}\]

It was reported that the succinic acid (SA)-functionalized BP nanosheets (SA-BP) presented the overpotentials at 10 mA cm\(^{-2}\) of 369.8 mV for OER and 235 mV for HER, outperforming the l-ascorbic acid-functionalized BP nanosheets (L-AA-BP) with overpotentials of 459.5 and 224 mV for OER and HER, respectively.\[^{[40]}\]

Also, a direct comparison of BP exfoliated in various DMSO solutions consisting of different tetrabutylammonium salts (TBAX; X = PF\(_6\), BF\(_4\), or ClO\(_4\)) verified that the TBAPF\(_6\)/DMSO-processed BP exhibits better HER activity than these exfoliated in the presence of BF\(_4\) and ClO\(_4\) ions.\[^{[41]}\]

iv) Doping states: Doping plays a critical role in modulating the electronic structure and regulating the intermediate adsorption behaviors of electrocatalysts.\[^{[42]}\]

The metallic dopants, such as Co, Mo, and Ni, into BP could induce metal-P active sites, with optimized electronic structures for desired adsorption energy and enhanced HER activity. Particularly, the Co-doped BP delivered a HER potential of \(\approx 0.3\) V at 10 mA cm\(^{-2}\), which was better that that of the Ni- or Mo-doped BP catalysts.\[^{[43]}\]

v) Compositions: Few-layer BP nanosheets could promote the chemisorption of N\(_2\) molecules and activate the inert N≡N bonds, demonstrating a NH\(_3\) production rate of 31.37 mg h\(^{-1}\)mg\(^{-1}\)cat. for NRR under an acidic condition.\[^{[44]}\]

To further promote the active centers for NRR, single-metal atoms could be further embedded into BP frameworks. As identified in the report, the W, Ta, and Nb atoms dispersed onto BP can lower the energy barriers of the NRR limiting step.\[^{[45]}\]

## 2.2. Effect of Coupling Materials of BP-Based Heterostructures on Electrolysis

As an effective approach to counter with the challenge of individual 2D materials to meet diverse requirements in widespread applications, the construction of 2D-based heterostructures allows the combination of two or more property-complementary components together to achieve altering electronic...
structures, modulating interfaces, regulating charge and mass transport properties, and tailoring responsibility toward mechanical, physical, and chemical stimuli. To address the undesired catalytic activities of BP, BP-derived catalysts have received much attention due to the significantly enhanced electrocatalytic performance toward OER, HER, ORR, and NRR. This types of electrocatalysts mainly include three categories as summarized as follows.

i) BP coupled with noble metals or alloys. Pt has been used to activate the HER activity of BP, where the existing Pt–P bonds induced unique and strong synergistic ligand effects. The optimized Pt/BP catalyst delivered an improved activity of 6.1 times higher than that of the Pt/C catalyst. Specifically, a maximum current density of 82.89 mA cm$^{-2}$ was reached at an overpotential of 70 mV in 1.0 M KOH for the BP/Pt catalyst with only 1.0 µg of Pt. Au has also been used to modify BP for promoting the OER activity, which led to the transition of the semiconducting characteristic of BP into the metallic feature with faster carrier mobility. The electrocatalysis measurements showed that the Au/BP catalyst exhibited a low on-set potential of 1.36 V and a Tafel slope of 68.1 mV dec$^{-1}$. Besides Pt and Au, metallic Ir was introduced to modify the BP nanosheets toward ideal intermediates adsorption for both HER and OER catalysis, thus reached bifunctional activity for pH-universal overall water splitting. With the presence of the Ir modifier into the BP/Ir heterostructured catalyst (IRBP), the Gibbs free energy ($\Delta G^\circ$) was nearly thermoneutral for HER (Figure 1d), and the OER potential on the rate-limiting step was the lowest compared to the individual Ir and BP catalysts (Figure 1e). Experimental catalysis results confirmed that the optimized BP/Ir heterostructured catalyst exhibited a superior HER activity with an overpotential as low as 1.98 and 125 mV, respectively, to reach 10 and 400 mA cm$^{-2}$ in the alkaline solution (Figure 1f), and an excellent OER performance with only 1.0 M KOH solution. Inset in (j) shows the interfacial electron transfer within EBP@NG structure. Reproduced with permission.© 2019, American Chemical Society.
290 mV required for 10 mA cm\(^{-2}\) in both acidic and alkaline solutions (Figure 1g).\(^{[44]}\) Consequently, only 1.54 and 1.57 V of the overall cell voltages for achieving the desired density of 10 mA cm\(^{-2}\) were required for using the resultant Ir-modified BP catalyst under acidic and alkaline conditions, respectively.\(^{[44]}\)

Beyond elementary noble metals, noble metals-based alloys have been implanted into the BP nanosheets for improving catalytic activities. For instance, a hybridized catalyst composed of PtRu clusters and BP nanosheets was applied for enhancing the alkaline HER activities. Due to the unique electronic interaction between the PtRu clusters and the BP that could accelerate the water dissociation and realize the optimal H\(^{\alpha}\) adsorption, the BP/PtRu catalyst delivered an overpotential of 22 mV at 10 mA cm\(^{-2}\), a Tafel slope of 19 mV dec\(^{-1}\), and a current density of 88.5 mA cm\(^{-2}\) at 70 mV in 1.0 M KOH solution.\(^{[52]}\)

BP coupled with non-noble metals/derivations. Some non-noble metals, such as Co and Cu, can be used for modifying BP for OER and HER catalysis. Specifically, HER performance of few-layer BP and graphene nanosheets loaded by Cu nanoparticles was verified in the acidic solution and the 30 wt% Cu@BP catalyst performed a lower overpotential and a smaller Tafel slope compared to the 30 wt% Cu@graphene catalyst.\(^{[53]}\) Furthermore, with the in situ growth of Co nanoparticles onto BP, the alkaline OER performance of BP could be improved, with an overpotential of 310 mV at 10 mA cm\(^{-2}\).\(^{[54]}\)

Non-noble metal-based phosphides, as these containing Co and Ni, have been recognized as promising candidates to be hybridized with BP for improving the electrocatalytic activities. For example, an in-plane BP/CoP heterostructures were synthesized by selectively growing nanosized CoP at the reactive edges of BP.\(^{[45]}\) Owing to the improved conductivity and the increased active sites, the BP/CoP catalyst exhibited better activities for HER in both acidic and alkaline solutions (Figure 1h) and for OER in an alkaline solution compared with the pristine BP.\(^{[45]}\) It was reported that Ni/P/BP heterostructures delivered improved electrical conductivity up to 6.25 \(\times\) 10\(^{-3}\) S m\(^{-1}\), which led to an increased charge carrier concentration up to 1.37 \(\times\) 10\(^{20}\) cm\(^{-3}\), resulting in a continuous stable HER cycling over 3000 cycles.\(^{[55]}\)

Another large family for coupling with BP for electrocatalysis is non-noble metal-based oxides. Some effective BP/metal oxide heterostructures, such as BP-QDs/CoO\(_{x}\),\(^{[56]}\) BP-QDs/MnO\(_{2}\),\(^{[57]}\) CoFeO/BP,\(^{[46]}\) and BP-QDs/SnO\(_{2}\)\(_{x}\),\(^{[58]}\) have been successfully developed.\(^{[58]}\) As shown in Figure 1i, a CoFeO/BP catalyst prepared by depositing amorphous CoFeO onto BP nanosheets was worked as an efficient bifunctional electrocatalyst for catalysing both HER and OER, in which the overpotentials were 88 mV for HER and 266 mV for OER at 10 mA cm\(^{-2}\) in the 1.0 M KOH solution.\(^{[46]}\) Further investigation confirmed that the excellent catalytic performance of the CoFeO/BP was highly associated with the adaptive surface structure toward applied potentials during the catalysis process. Specifically, at reduction potentials, the CoFeO/BP was transformed into CoFe phosphide as the real active sites for HER, while at oxidation potentials, an amorphous and O-vacancy-rich CoFeO phase formed to proceed the OER through a lattice oxygen oxidation mechanism (LOM).\(^{[46]}\) In addition to the OER and HER catalysis, the introduction of non-noble metal oxide catalysts to couple with BP nanosstructures, such as by confining BP QDs into SnO\(_{2}\)\(_{x}\) nanotubes, could induce active metal-P bonds or coordination, and thus increase the electrocatalytic ammonia yield and the Faradaic efficiency.\(^{[50]}\)

Besides phosphides and oxides, the BP-based heterostructures coupled with non-noble metal-based sulfides (e.g., MoS\(_{2}\)/BP\(^{[59]}\)), carbides (e.g., BP-QDs/MXene\(^{[60]}\)), nitrides (e.g., Ni\(_{3}\)N/BP\(^{[61]}\)), and borides (e.g., BP/CoFeB\(^{[62]}\)) have been explored for electrocatalysis. For example, due to the higher Fermi level of BP compared to MoS\(_{2}\), MoS\(_{2}/BP\) heterostructured nanosheets were designed with electrons flowing from BP to MoS\(_{2}\), presenting a low HER overpotential of 85 mV at the density of 10 mA cm\(^{-2}\).\(^{[59]}\) Contributed by the electronic interactions and the oxygen affinity difference, a 2D/2D heterostructure composed of amorphous CoFeB sheets and exfoliated BP sheets (BP/CoFeB) showed an optimal oxygen-containing intermediates absorption for OER, leading to an overpotential of 227 mV for achieving 10 mA cm\(^{-2}\) and a small Tafel slope of 36.7 mV dec\(^{-1}\).\(^{[62]}\)

BP coupled with metal-free materials. Metal-free catalysts, such as g-C\(_{3}\)N\(_{4}\) and doped graphene, have evidenced to deliver attractive electrocatalytic activities for OER and HER, which can also be used to couple with BP to form heterostructures. As illustrated in Figure 1g, 2D/2D BP/N-doped graphene heterostructured catalysts (EBP@NG) consisting of exfoliated black phosphorus and N-doped graphene were rationally designed.\(^{[47]}\) Due to the lower Fermi level of BP, the electronic interaction within the interfaces could induce directional electron transfer. This could enrich the electron density of BP and optimize the H\(^{\alpha}\) adsorption to improve the HER activity. In the meanwhile, the interfacial charge transfer introduced positively charged carbon centers in the N-doped graphene, which are beneficial to the formation of OOH\(^{\alpha}\) intermediates and the promotion of OER activity. As a result, the EBP@NG manifested good activities toward HER and OER for overall water splitting under an alkaline condition, in which a low cell voltage of 1.54 V was required at 10 mA cm\(^{-2}\), superior to the Pt/C@RuO\(_{2}\) catalyst (1.60 V) (Figure 1j).\(^{[47]}\)

Another explored metal-free counterpart for coupling with BP is g-C\(_{3}\)N\(_{4}\), which is a conjugated organic polymer with an N-substituted graphite framework. By covalently bonding BP nanosheets with g-C\(_{3}\)N\(_{4}\) to form a BP-CN-c heterostructure with the presence of polarized P–N bonds, the electron transfer from the BP to the g-C\(_{3}\)N\(_{4}\) was efficiently regulated and the OOH\(^{\alpha}\) adsorption on the P atoms was significantly promoted. Consequently, the resultant BP-CN-c catalysts delivered good activities toward the OER with an overpotential of 350 mV at 10 mA cm\(^{-2}\) together with a 90% retention after continuous operation for 10 h, and the OER with a half-wave overpotential of 390 mV.\(^{[61]}\)

As summarized in Figure 2, three primary types of BP-based catalysts, namely BP with noble metals or alloys, BP with non-noble metals or derivations, and BP with metal-free materials were developed for effective electrocatalysis. For the BP heterostructured with noble metals, the superior catalytic performance to the individual components is highly related to the introduced interfacial electron transfer between the BP and the metals, in
combination with some unique merits of BP nanosheets, such as large surface area and high carrier mobility. Depending on the stability of noble metals, the BP/noble metals catalysts can sustain good cycling stability at a low overpotential. However, the major barrier of this class of heterostructures is the high costs of noble metals.

For BP combining with non-noble metals or derivations, a large family has been developed covering from common elementary non-noble metals, such as Co and Ni, to various non-noble metals-based compounds, including phosphides, oxides, sulfides, carbides, borides, and nitrides (Table 1). The production costs of these counterparts are relatively low and the catalytic activities of these BP with non-noble metals or derivations are comparable or even better than the noble metals-based hybrids. One of the major issues for these types of heterostructures is the weak structural stability from the non-noble metals during the catalysis process and in the reactive solutions, which lead to rapid structural change and fast performance decay, particularly under harsh conditions. BP with metal-free materials can well overcome some issues existing in the metal-containing catalysts, such as the leaching of active metal elements and loss of active sites, as there are no metallic active centers. However, the overall catalytic performance still needs improvement. Furthermore, compared with the well-studied HER and OER catalysis, the studies of BP and BP-based catalysts for NRR and ORR catalysis are yet limited until now.

3. BP and BP-Derived Composites for Rechargeable Batteries

Similar to the case for BP used in electrocatalysis as discussed above, the structural modifications on the bare BP can also be adapted to ions storage involved in the rechargeable batteries. It is sure that the morphology of the BP affects the battery performance. For example, few-layer BP nanosheets exfoliated in acetone with 7 nm in thickness of 7 and 30 nm in lateral presented a reversible capacity of 480 and 345 mA h g⁻¹ at the densities of 100 and 1000 mA g⁻¹, respectively. As demonstrated in Figure 3a, the thickness control on BP for LIBs was achieved via a laser-assisted exfoliation method in low-boiling point solvents.

For Li-/Na-ion intercalation channels, the orthorhombic BP structure, in which each P atom is covalently bonded to three adjacent atoms along the open and the across directions (zigzag and armchair) (Figure 3b), endows a unique ion-intercalation path along the zigzag direction with a broad channel spacing. Comparative investigations on the electrochemical Li-/Na-intercalation processes the orthorhombic BP structure verified that the favorable intercalation channels are along the zigzag direction. However, obvious anisotropic intercalation behaviors were identified within the storage of Li- and Na-ions. Specifically, the Li-ions could activate the effective intercalation along the armchair direction, whereas the Na-ions could dominantly diffuse along the zigzag direction. Further comparison on the energy profiles of the diffusion through two different channels (Figure 3c) confirmed that the Li-/Na-ions diffusion along the zigzag direction is energetically favorable, but the energy barriers diffusing along the armchair direction are significantly increased and even insurmountable for Na-ions. Apart from Li- and Na-ions, some theoretical calculation works verified the possible diffusion of Mg-ions along the zigzag and the armchair directions of BP. Besides metallic...
ions storage, BP was evidenced to hold the capability for trapping the soluble polysulfides, catalyzing the polysulfide conversion reactions, and thus promoting the reversibility and stability of Li-S batteries.\(^{83,84}\)

With respect to BP-derived composites for rechargeable batteries, including LIBs, SIBs, and PIBs, the most widely studied case is the BP/graphene (graphene) hybrid.\(^{85}\) In spite of the high initial discharge capacity of BP in LIBs, the rechargeability is unsatisfactory, accounting by the low initial coulombic efficiency (≈57%) and the rapid capacity fading caused by undesired volume change (≈300%) upon lithiation.\(^{86,87}\) It has been well recognized that carbon could well restrain the undesired edge reconstruction of BP to provide abundant open edges for fast ions entry, and the coating of the polyaniline could form a stable solid-electrolyte interphase for efficient ions transport. At an area loading of 1.2 mg cm\(^{-2}\), the (BP-G)/PANI anode demonstrated reversible capacities of 910, 790, and 440 mA h g\(^{-1}\) after 2000 cycles at 2.6, 5.2, and 13.0 A g\(^{-1}\), respectively (Figure 3e), which means that less than 10 min was required to recharge a LIB at 13.0 A g\(^{-1}\) to a cell-level density of ≈350 Wh kg\(^{-1}\).\(^{78}\)

In another case, the rational combination of 2D BP with 2D graphene to produce 2D/2D heterostructured hybrids could be used as the flexible electrodes for LIBs.\(^{89,90}\) Furthermore, some other active materials, such as metal oxides, can be introduced into the 2D/2D BP/graphene heterostructures to enhance the electrochemical ion storage capability.\(^{91}\) BP/graphene hybrid materials have been widely investigated for SIBs.\(^{92}\) Figure 3f illustrates the sodiation mechanism for BP, in which the ion intercalation was first conducted and then an alloy reaction occurred to form Na\(_3\)P.\(^{79}\) Within the BP/graphene heterostructure, the liquid-exfoliated BP can reduce the ions/electrons diffusion distance and the graphene can facilitate the electrons transport. Moreover, the phosphorene-graphene interlayer space benefits for accommodating the unfavorable anisotropic expansion. As a result, the 2D/2D BP/graphene hybrid presented a specific capacity as high as 2440 mA h g\(^{-1}\) based on the P mass (Figure 3g) and an 83% capacity retention after 100 discharge/charge cycles.\(^{78}\) Similar heterostructures can be synthesized via room-temperature pressurization\(^{89}\) and the combination of electrochemical exfoliation and solvothermal method.\(^{94}\) Different to the formation of alloys of Li\(_3\)P in LIBs and Na\(_3\)P in SIBs, K\(_3\)P alloy can also be produced in PIBs which possesses the highest formation energy and the lowest diffusion coefficient. By limiting the formation of K\(_3\)P via the control of discharge depth, the BP/graphite hybrid presented a reversible potassiation capacity of 600 mA h g\(^{-1}\) for 50 cycles.\(^{79}\) High concentration electrolyte was also introduced to form robust solid electrolyte interphases for stabilizing the PIBs with the BP/graphite electrode.\(^{96}\)

Coupling BP with CNTs to form a 3D conductive structure is another strategy for achieving favorable electrochemical ion diffusion and significantly improved battery performance. It has been reported that the BP/CNTs electrode for LIBs exhibited a discharge capacity of 1088 mA h g\(^{-1}\) at 0.1 A g\(^{-1}\), an electrical conductivity of 88.9 Ω, a cycling stability with 7573 mA h g\(^{-1}\) at 0.5 A g\(^{-1}\) for 650 discharge/charge cycles, and a rate performance with 552 mA h g\(^{-1}\) at a high rate of 2.5 A g\(^{-1}\).\(^{79}\) A black phosphorus/Ketjenblack-multiwalled carbon nanotubes (BPC) composite with a 70 wt% BP loading was prepared through a simple ball milling method and applied for LIBs and SIBs. For LIBs, an initial Coulombic efficiency of ≈91%, a specific capacity of 2512.4 mA h g\(^{-1}\), and a cycle stability of over 2000 mA h g\(^{-1}\) after 100 cycles were achieved.\(^{98}\) For SIBs, an initial Coulombic efficiency of over 90% and a capacity of about 1700 mA h g\(^{-1}\) after 100 discharge/charge cycles at the current density of 1.3 A g\(^{-1}\) based on the P mass were achieved.\(^{99}\) Recently, a nanostructured BP/graphite/CNTs composite anode (BP/G/CNTs, 50 wt% BP, 40 wt% graphite, 10 wt% CNTs) was prepared by using a ball-milling method, which presented capacities of 1375 mA h g\(^{-1}\) in the first cycle at 0.15 A g\(^{-1}\), 1031.7 mA h g\(^{-1}\) after 450 cycles, and 508.1 mA h g\(^{-1}\) after 3000 discharge/charge cycles at 2.0 A g\(^{-1}\).\(^{100}\)

**Table 1.** Comparison on HER/OER performance of BP-based electrocatalysts.

| Electro catalysts | Electrocatalysis | Overpotentials [mV] | Tafel slopes [mV dec\(^{-1}\)] | Ref. |
|-------------------|-----------------|---------------------|-------------------------------|------|
| NH\(_2\)BP         | HER (alkaline)  | 290                 | 63                            | [64] |
| BP/N-graphene     | HER (alkaline)  | 325                 | 76                            | [47] |
| BP-Ph/graphite    | HER (alkaline)  | 21                  | 46.9                          | [50] |
| BP_{Ir,be}        | HER (alkaline)  | 2.1                 | 91                            | [44] |
| PtRu/BP           | HER (alkaline)  | 22                  | 19                            | [65] |
| CoFeO@BP          | HER (alkaline)  | 88                  | 51                            | [46] |
| BPQD/MoS\(_2\)    | HER (alkaline)  | 600                 | 162                           | [66] |
| MoS\(_2\)/BP      | HER (alkaline)  | 233                 | 99                            | [67] |
| BP QDs/MXene      | HER (alkaline)  | 190                 | 83                            | [60] |
| Prussian blue/BPQDs| HER (acidic)    | 148                 | 79                            | [68] |
| BP_{Ir,be}        | HER (acidic)    | 26                  | 30.9                          | [44] |
| Ni\(_3\)P/BP      | HER (acidic)    | 185                 | 61                            | [69] |
| Ni\(_3\)P@BP      | HER (acidic)    | 107                 | 38.6                          | [55] |
| MoS\(_2\)/BP      | HER (acidic)    | 85                  | 68                            | [70] |
| MoSe\(_2\)/BP     | HER (acidic)    | 380                 | 97                            | [71] |
| MoS\(_2\)/BP      | HER (acidic)    | 126                 | 68                            | [67] |
| Co(OH)\(_2\)/BP   | HER (acidic)    | 276                 | 57                            | [72] |
| BP@Ti foil        | HER (alkaline)  | 370                 | 91.5                          | [36] |
| BP/N-graphene     | HER (alkaline)  | 265                 | 89                            | [47] |
| N-BP-QDs          | HER (alkaline)  | 430                 | 48                            | [73] |
| BP-QDs/CoO\(_2\)  | HER (alkaline)  | 360                 | 58.5                          | [56] |
| Co\(_3\)O\(_2\)/BP| HER (alkaline)  | 400                 | 63                            | [74] |
| Co/BP             | HER (alkaline)  | 310                 | 61                            | [54] |
| BP/Co\(_3\)P      | HER (alkaline)  | 380                 | 78                            | [45] |
| CoFeO@BP          | HER (alkaline)  | 266                 | 42                            | [46] |
| Ni\(_3\)N/Ni\(_3\)P/BP | HER (alkaline) | 247                 | 78                            | [75] |
| Ni\(_3\)N/BP-graphite | HER (alkaline) | 233                 | 64                            | [61] |
| BP_{Ir,be}        | HER (alkaline)  | 290                 | 64                            | [44] |
| BP QDs/MXene      | HER (alkaline)  | 360                 | 64.3                          | [60] |
| BPO\(_4\)/MoS\(_2\)| HER (alkaline)  | 370                 | 46                            | [66] |
As summarized in Figure 4, three major BP and BP-derived composites were developed for the application in rechargeable batteries, including the pristine BP, the BP coupled with carbon, and the BP heterostructured with other 2D materials. Although the regulation on some intrinsic parameters, such as thicknesses and sizes, can affect the electrochemical ion storage performance, the most effective approach to date is to couple the BP with other components for improving the capacity and promoting the cycling stability. Pairing BP with carbon is a facile and cost-effective method, in which a simple ball milling of BP and graphite could achieve uniform mixing and stable P–C bonding.\[^{[101]}\] For other BP-derived electrode materials (Table 2), such as BP/PEDOT,\[^{[102]}\] BP/h-BN,\[^{[103]}\] BP/phosphorus oxide,\[^{[104]}\] and BP/MXene,\[^{[105]}\] explored for LIBs and SIBs,\[^{[106]}\] the costs of these hybrids are usually relatively high, due to the high cost of the counterparts (e.g., PEDOT, h-BN, and MXene). Even though the heterostructures consisting of BP and non-carbon materials sometimes presented significantly enhanced performance, the BP-C composites are more promising in the possible practical applications for their relative low-cost and acceptable electrochemical performance. In rechargeable batteries, current studies primarily concentrate on the application of BP and BP-derived composites as the anode for LIBs and SIBs, while few reports were found for PIBs and other rechargeable batteries.
4. Challenges and Outlook

As a summary, BP and BP-derived composites have been intensively explored as effective catalysts for various electrocatalytic reactions, including HER, OER, NRR, and ORR, and as electrode materials for different rechargeable batteries, including LIBs, SIBs, PIBs, and Li-S batteries. In spite of achieved plausible progress, several challenges yet exist to push this promising class of materials into practical applications, as summarized in Figure 5.

i) Synthesis: The BP obtained from different synthetic approaches, however, possesses diverse electrochemical properties, due to the varying quality and surface and chemical states. For example, it was reported that the BP obtained from white phosphorus presented an initial discharge capacity of 2505 mA h g\(^{-1}\) at 4 GPa and 400 °C, while the BP prepared from red phosphorus delivered an initial discharge capacity of 2649 mA h g\(^{-1}\) at 4.5 GPa and 800 °C.\(^{[107]}\) Also, the large-scale production and safe storage for BP is significantly challenging, and the current price is extremely high. Limited by the synthetic methods, the accurate control on the quality and assembly of BP-based heterostructures is very challenging. This needs innovations on the synthetic approaches and manufacture technologies for practical device applications.

ii) Stability and degradation: BP is sensitive to external oxygen, moisture, and light. The exposure of BP to these sources will result in irreversible structural degradation, constraining its practical applications in electrocatalysis and rechargeable batteries.\(^{[108]}\) Hence, the passivation of BP from significant performance deterioration is needed. Surface coating, doping, or modifications have been effective strategies to promote the stability of BP.\(^{[109]}\)

iii) Electrochemical ion storage: The current research focuses on BP mainly include LIBs and SIBs, in which the electrochemical ion storage mechanisms (e.g., insertion, extraction, redox reactions) have been extensively studied. Table 2 summarizes the performance of BP-based electrode materials in LIBs and SIBs. The rate capability and cycling stability are crucial parameters for practical applications. The rate capability reflects the fast charge/discharge capability, while the cycling stability indicates the durability and retention of the initial capacity over multiple cycling. These parameters are important for determining the practicality and performance of the BP-based electrodes.

Table 2. Comparison on LIBs/SIBs performance of BP-based electrode materials.

| Electrode materials          | Batteries | Rate capability [mAh g\(^{-1}\)/density] | Cycling stability [mAh g\(^{-1}\)/cycle number] | Ref. |
|------------------------------|-----------|------------------------------------------|-----------------------------------------------|-----|
| Few-layer BP                 | LIBs      | 345/1 A g\(^{-1}\)                      | 480/100                                       | [80]|
| L-BP-S\(_{\text{hexane}}\)   | LIBs      | 273.6/5 A g\(^{-1}\)                   | 404.4/200                                     | [76]|
| BP/graphite                  | LIBs      | 1240/4.5 C                               | 1849/100                                      | [87]|
| BP/graphite/PANI             | LIBs      | >700/13 A g\(^{-1}\)                   | ≥500/2000                                     | [78]|
| BP/carbon                    | LIBs      | —                                        | >600/100                                      | [86]|
| BP/PEDOT                     | LIBs      | 434/10 A g\(^{-1}\)                     | 1092/100                                      | [102]|
| BP/Ketjenblack-MWCNTs        | LIBs      | ≥1600/6.24 A g\(^{-1}\)                | ≥2000/100                                     | [98]|
| Few-layer BP/graphene        | LIBs      | 141/2.5 A g\(^{-1}\)                   | 402/500                                       | [89]|
| BP@CNTs                      | LIBs      | 552/2.5 A g\(^{-1}\)                   | 757.3/650                                     | [97]|
| BP/graphite/CNTs             | LIBs      | ≥900/3 A g\(^{-1}\)                     | 508.1/3000                                    | [100]|
| BPNs@TiO\(_2\)/graphene     | LIBs      | 271.1/5.0                                 | 502/180                                       | [91]|
| BPQD/MXene                   | LIBs      | 167/2 A g\(^{-1}\)                     | 520/2400                                      | [105]|
| Phosphorene/graphene         | SIBs      | 645/26 A g\(^{-1}\)                    | ≥490/100                                      | [79]|
| Phosphorene/graphene         | SIBs      | 1499/5 A g\(^{-1}\)                    | 1120.6/200                                    | [94]|
| BP/PEDOT                     | SIBs      | 370/10 A g\(^{-1}\)                    | 1078/100                                      | [102]|
| BP/Ketjenblack-MWCNTs        | SIBs      | 928/3 A g\(^{-1}\)                     | ≥1700/100                                     | [99]|
| BP/rGO                       | SIBs      | 720.8/40 A g\(^{-1}\)                  | 640/500                                       | [93]|

Figure 4. Schematic illustration of BP and BP-derived composites and their main features for rechargeable batteries.
iv) Electrocatalytic activities: BP-based heterostructured catalysts show good activities toward HER and OER. However, the in-depth understanding regarding the specific roles of BP in the heterostructured catalysts during electrocatalysis is yet unclear. The first concern is the irreversible structural degradation of BP in contact with electrolytes, which results in inferior environmental durability in long-term service. The other one is the possible roles of the as-produced P-O(H) species during electrocatalysis. To date, the structural origin of the reaction mechanisms for the reaction activity of the BP-based electrocatalysts has yet to be clearly understood. Further investigations with the employment of emerging in situ characterization techniques and the art-of-the-state theoretical calculations and simulations are urgently demanded.

In the light of current achievements and existing challenges, the research on BP for electrocatalysis and rechargeable batteries is full of opportunities as the full potential of BP has yet to be discovered until now. Further efforts aiming at structural stability and catalytic activities of BP-based materials are highly required. The in-depth reaction mechanisms need to be revealed through a combination of theoretical calculations and experimental investigations. For example, i) ideal structural modifications on BP need further exploration for addressing the volume expansion and the sluggish kinetic issues in rechargeable batteries; ii) general synthetic standards should be considered, because the electrochemical performance is dependent on the product quality and the preparation methods of BP, in which the possible contaminations and the unintentional surface adsorptions are often brought from the preparation; iii) in the design of heterostructure, optimal composite ratios should be investigated during the performance evaluation process, which is much helpful for identifying the possible reaction mechanisms and clarifying the roles of each

**Figure 5.** Schematic illustration of key issues for BP and its derivations for electrocatalysis and rechargeable batteries.
component; iv) more attention should be given on the environment-induced degradation of BP in contact with air, water, or light, and propose some effective passivation strategies for stabilizing the BP structures; v) in spite of significantly enhanced performance for BP-based materials in batteries and electrolysis, the gap between the lab-scale tests and the industrial manufacture is still very large, which is limited by the environmental sensitivity of the pristine BP and the small volume production technologies for nanomaterials. Furthermore, BP and BP-derived materials have been initiated for the applications in some emerging electrocatalytic reactions and next-generation rechargeable batteries, which will boom the research in multifunctional BP-based materials. Through the combined material discovery and mechanism understanding on batteries or electrocatalysis, rational design and synthesis of effective and air-stable BP-based heterostructures will become one of major research goals in the future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

batteries, black phosphorus, electrocatalysis, hydrogen evolution reaction, lithium-ion batteries, oxygen evolution reaction, sodium-ion batteries

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