Review on the Energy Transformation Application of Black Phosphorus and Its Composites

Hao Liu 1, Zehui Peng 1, Mengdi Hu 1, Xin Xu 1, Shuai Lou 2* and Shancheng Yan 1,*

1 School of Geography and Biological Information, Nanjing University of Posts and Telecommunications, Nanjing 210023, China
2 Department of Materials Science and Engineering, University of California, Berkeley, CA 94720, USA
* Correspondence: yansc@njupt.edu.cn

Abstract: Black phosphorus (BP) is a unique two-dimensional material with excellent conductivity, and a widely tunable bandgap. In recent years, its application in the field of energy has attracted extensive attention, in terms of energy storage, due to its high theoretical specific capacity and excellent conductivity, black phosphorus is widely used as electrode material in battery and supercapacitors, while for energy generating, it has been also used as photocatalyst and electrocatalysts to split water and produce hydrogen. Black phosphorus demonstrates even better stability and catalytic performance through further construction, doping, or heterojunction. This review briefly summarizes the latest research progress of black phosphorus and its composites in energy preparation and storage, as well as ammonia nitrogen fixation, and also looks into the possible development directions in the future.

Keywords: black phosphorus; energy; catalyst; composites

1. Introduction

With the development of industrialization, the energy crisis and environmental pollution have become increasingly serious [1–8]. The development and utilization of clean energy, such as solar, wind and hydrogen have become the key to solving the problem. However, solar, and wind energy sources are highly dependent on natural weather and thus have low stability, while hydrogen generated from water splitting relies on high-performance catalysts [7,9–17]. As a solution to both issues, black phosphorus has attracted increasing interest due to its unique and stable structure and excellent physical and chemical properties [18]; moreover, it has proven an excellent candidate to be both negative/positive electrode material for batteries to store electricity converted from unstable solar and wind energy [19–23], as well as efficient photocatalyst [24–27] and electrocatalyst [20,28] for water splitting since the first exfoliation of bulk black phosphorus into mono- or few-layered phosphorene in 2014 [29].

Phosphorus is abundant in nature (white phosphorus, red phosphorus, black phosphorus, blue phosphorus ese etc.), and the structure of black phosphorus is different from that of typical graphene [30–36]. The difference is that each layer of atoms of black phosphorus is not on the same plane, but with folded Z-linked arrangement. Strong covalent bonds form within single layers, in between which it is van der Waals force [37–43]. With this unique lattice structure, black phosphorus shows better stability than its allotropes (white and red phosphorus), and it also has high carrier mobility, anisotropic in-plane properties and specific capacity [21,44–46], which makes it ideal as negative electrode material for lithium and sodium batteries [30,47–53], as well as photocatalysts. With construction [54–58], doping [59–64], or heterojunctions [65–71], the stability, charge transport, and catalytic performance of black phosphorus can be further improved. Therefore, black phosphorus composites can be applied to other many fields.
In this review, the application of black phosphorus and its composites in the field of energy is summarized, the problems existing in the preparation and applications are also covered, and the prospect of black phosphorus will be discussed.

2. Application of Black Phosphorus and Its Composites in Energy Storage

Recent advances in the field of energy storage devices such as batteries (including lithium-ion battery, sodium-ion battery, potassium-ion battery, etc.) and supercapacitors have helped mankind to cater to their power demands to a greater extent. As is well known, the lithium-ion battery has been the dominant technology in the rechargeable energy storage market for more than twenty years. The need for an efficient method to increase higher energy densities strategy emerges. Compared with graphene, black phosphorus has a wider range of lithium ion channels, and the double-layer structure provides a gap space for lithium ion insertion and extraction [22,72]. As shown in Figure 1, Wang et al. proposed the black phosphorus anchored commercial copper foam, BP@Cu, fabricated with a simple electrophoretic deposition (EPD) method. It is found that black phosphorus can effectively improve the affinity between copper foam and lithium, conducive to the intercalation and propagation of lithium ions [73]. With the rapid development of the functional applications of portable and wearable electronic products, there is an urgent need to fabricate flexible supercapacitors with high power density, high charging/discharging rates, and a long cycling lifespan that can provide sufficient power support. With superior saturation absorption characteristics and good mechanical flexibility, black phosphorus can also be used, and the supercapacitors show a long lifetime and good capacitance characteristics after 30,000 cycles on pet substrate [74].

Figure 1. (a) Schematic illustration of the electrophoretic deposition of BP on Cu foam. (b) Comparison of the ζ-potential and conductivity of BP in isopropanol before and after adding Mg(NO$_3$)$_2$. (reproduced with permission from Ref. [73], © American Chemical Society 2020).

Discovering and designing novel anode materials for potassium-ion batteries have become a significant challenge. Among different anode materials, phosphorus-based (including composites) anodes have been recognized as one of the most promising materials because of their high theoretical capacity (2596 mAh.g$^{-1}$ for phosphorus) and the abundance of phosphorus resources [75]. Nonetheless, phosphorus-based anodes exhibit low conductivity and large volume expansion, resulting in inferior cycling performance and rating property. Black phosphorus heterostructures were found to be used to enhance the storage of capacity. As an example, He et al. found that BP/GeSe undergoes the phase transition from semiconductor to metal after potassium salinization, indicating better conductivity than single-layer GeSe, which will benefit the transport of free electrons (Figure 2). In addition, compared with monolayer GeSe, the potassium removal barrier on BP/GeSe surface is reduced to 0.92 eV. The potassium atom on GeSe/BP heterostructure can accommodate up to five layers of negative and stable structure, which greatly improves the storage capacity. These studies show that BP/GeSe heterostructure can also be used as an excellent electrode material for potassium ion batteries [76]. Black phosphorus can also be used as the active component of potassium ion battery. KP alloy synthesized by Sultana
et al. takes black phosphorus as its active ingredient, and has the highest weight capacity among all known potassium ion anode materials [77].

![Figure 2](image-url)  
**Figure 2.** Top and side views of the three nonequivalent stacking patterns of the BP/GeSe interface. (a) H-style, (b) T-style, and (c) B-style. (reproduced with permission from Ref. [76], © American Chemical Society 2019).

### 3. Application of Black Phosphorus and Its Composites in Photocatalysts

Among various physical, chemical and biological technologies for pollution control, advanced oxidation technologies such as photochemical oxidation, ozone oxidation and so on. These technologies are more and more widely used in the treatment of organic pollutants [78–80]. Sunlight has the advantages of easy availability, regeneration, and no secondary pollution, which makes the photocatalytic degradation technology to have a good application prospect in this field [80–83]. Two-dimensional semiconductor catalysts for heterogeneous photocatalytic reaction under light illumination have been widely used in the treatment of organic pollutants [84], to be decomposed into harmless CO2 and H2O [85–89]. The black phosphorus (0.03–2.2 eV) is different from the lack of bandgap in graphene, or the low carrier mobility of transition metal dichalcogenides (TMDs). It has a layer-dependent bandgap from visible to infrared, and high carrier mobility of over 1000 cm²/Vs [76], and therefore can more effectively transport the electrons and holes generated by light excitation to the catalyst surface and greatly speed up the photochemical reaction catalytic rate [90,91]. It has been considered as a promising metal-free photocatalyst for solving the energy crisis and environmental problems. The combination of BP with carbon nitride (CN) strengthens the visible-light harvesting ability, facilitates the charge separation in the photocatalytic process, and renders the promoted activity of photoinduced molecular oxygen activation, such as superoxide radicals (O₂⁻) evolution and H₂O₂ production.

One representative work is the first design of a binary nanohybrid (BP/CN) of two dimensional (2D) black phosphorus (BP) and graphitic carbon nitride (CN) by Zhu et al. [92]. They used methanol as a sacrificial electron donor to burst holes generated by band gap excitation for photocatalytic hydrogen precipitation on BP/CN. A proposed schematic diagram for the visible and NIR light activated photocatalytic H₂ evolution using BP/CN in the presence of methanol is shown in Figure 3. They also found that the best hydrogen precipitation rate of 427 µmol·g⁻¹·h⁻¹ was achieved at a BP:CN ratio of 1:4, while the hydrogen production rate was 101 µmol·g⁻¹·h⁻¹ under 780 nm light irradiation. Compared to relatively conventional catalysts, Pt/CN at the hydrogen production rate under 780 nm light irradiation was almost zero, so it is said that BP/CN showed stronger catalytic activity in the visible near infrared region. When BP/CN is irradiated with >780 nm light, the excited electrons in the CB band of BP are trapped by interfacial P-N defects, thereby enhancing the photocatalytic performance. The hydrogen production rate of pure graphitic carbon nitride is approximately 168 µmol·g⁻¹·h⁻¹, compared to which BP/CN...
has a better catalytic performance [93]. Wen et al. significantly improved the efficiency of photocatalytic H₂ and rhodamine B (RhB) degradation using a BP/CN heterostructure with efficient charge separation capabilities and abundant active sites [94]. Later Li et al. studied an efficient infrared photocatalyst, using black phosphorus to build heterojunctions and improve the photocatalytic efficiency of polymer carbon nitride (CN) [95]. Carbon nitride can be indirectly excited by infrared light, and excitons can be decomposed into free carriers at the heterojunction interface. Holes are injected into black phosphorus, and electrons are still stored in carbon nitride. The unique photoexcitation process effectively improves the conversion and selectivity of the reaction. The photocatalytic ability of black phosphorus can also be enhanced by the use of co-catalysts. Yuan et al. found that the photocatalytic performance of layered black phosphorus enhanced with the reduction in the number of layers when assisted by MoS₂, while the presence of this two-dimensional heterogeneous structure resulted in faster photogenerated charge separation and higher photocatalytic hydrogen production activity [96].

![Figure 3. Proposed schematic diagram for the visible and NIR light activated photocatalytic H₂ evolution using BP/CN in the presence of methanol. (reproduced with permission from Ref. [92], © American Chemical Society 2017).](image-url)

Efficient photocatalytic nitrogen fixation is key to the development of efficient catalysts for the production of ammonia under ambient conditions. Bian et al. synthesized an edge-rich black phosphorus nanosheet with good catalytic nitrogen fixation efficiency under visible light irradiation [97]. Shen et al. selectively grew Ni₂P at the edges of the black phosphorus nanosheets [98]. The interface between BP and Ni₂P is a natural electron transfer channel, which effectively reduces the potential barrier for charge transfer and thus increases the ammonia generation activity. Of course, black phosphorus quantum dots and black phosphorus 2D materials can also be modified with other 2D materials to improve the efficiency of photocatalytic nitrogen fixation. Qiu et al. used graphitic carbon nitride nanosheets modified with black phosphorus (BP) nanosheets as photocatalysts, using black phosphorus as a co-catalyst, which greatly increased the number of excited electrons and significantly improved the efficiency of photocatalytic nitrogen fixation compared to pure carbon nanotubes [99]. Later, Dong et al. demonstrated that coupling black phosphorus quantum dots with defective semiconductors could effectively improve the performance of photocatalytic nitrogen fixation by surface anchoring of black phosphorus quantum dots and doping with bulk iron in W₁₈O₄₉ nanowires, which significantly improved the photocatalytic activity [100]. In addition, black phosphorus is an excellent catalyst for hydrogen precipitation [101, 102]. Guan et al. grew BP quantum dots on a sea urchin-like TiO₂ surface. the BP/TiO₂ heterostructure greatly improved the efficiency of hydrogen production and no co-catalyst was used [103]. The results show that under visible light irradiation, the H₂ production rate of BP/TiO₂ heterojunctiions is 2.4 times higher than that of pure TiO₂. Yuan et al. also proposed a strategy to grow Co₂P on the edges of black...
phosphorus nanosheets to achieve accurate control of charge separation. The Co-P bond formed improved the photogenerated carrier transfer between the nanosheets and the co-catalyst, effectively improving the production efficiency of H₂ [104]. Song et al. used black phosphorus as an electron accelerator and immobilized it on Cs₂AgBiBr₆, resulting in enhanced photocatalytic efficiency and under visible light, hydrogen production rate reached 104.6 μmol·h⁻¹·g⁻¹ [105]. As compared to those commonly used photocatalysts such as TiO₂, Pt, Co and g-C₃N₄, black phosphorus exhibits wider and stronger absorption in the visible and near-infrared (NIR) regions, which can harvest more light to drive photocatalytic hydrogen generation reactions [106]. We have compared the properties of some of these black phosphorus-based materials in Table 1 and several groups of black phosphorus-based materials with and without black phosphorus in Figure 4, so it can be said that black phosphorus is well-suited for use as a photocatalyst.

Table 1. Comparison on hydrogen production rates of a number of black phosphorus-based materials.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Apparent Quantum Yield (%)</th>
<th>H₂ Evolution Rate (μmol g⁻¹ h⁻¹)</th>
<th>Wavelength Range (λ)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP/g-C₃N₄</td>
<td>3</td>
<td>427</td>
<td>&gt;420 nm</td>
<td>[92]</td>
</tr>
<tr>
<td>BP/CN</td>
<td>1.25</td>
<td>101</td>
<td>&gt;780 nm</td>
<td>[94]</td>
</tr>
<tr>
<td>BP/MoS₂</td>
<td>1.2</td>
<td>1286</td>
<td>&gt;420 nm</td>
<td>[96]</td>
</tr>
<tr>
<td>BP/TiO₂</td>
<td>/</td>
<td>341</td>
<td>&gt;550 nm</td>
<td>[103]</td>
</tr>
<tr>
<td>Co₃P/BP</td>
<td>2.42</td>
<td>1191</td>
<td>&gt;420 nm</td>
<td>[104]</td>
</tr>
<tr>
<td>BP/Cs₂AgBiBr₆</td>
<td>/</td>
<td>104.6</td>
<td>&gt;420 nm</td>
<td>[105]</td>
</tr>
<tr>
<td>Pt/BP</td>
<td>4</td>
<td>447</td>
<td>&gt;420 nm</td>
<td>[106]</td>
</tr>
</tbody>
</table>

Figure 4. H₂ evolution rate of several groups of black phosphorus-based materials with and without black phosphorus. The reference involved in the diagram includes Refs. [92,93,103,105].

4. Application of Black Phosphorus and Its Composites in Electrocatalysis

Layered black phosphorus is one promising electrocatalyst toward hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) catalysis [107–109]. Water electrolysis,
a promising green technology, is limited in efficiency by HER and OER. One representative work is the 2D Heterostructure of Amorphous CoFeB Coating Black Phosphorus Nanosheets to improve the efficiency of electrocatalytic water oxidation carried out by Chen et al. [110]. Exfoliated black phosphorus (EBP) nanosheets have high carrier mobility due to their two-dimensional (2D) layered structure but are limited by an excess of oxygen-containing intermediate adsorption and rapid deterioration in air. To address this issue, they prepared nanohybrids of amorphous CoFeB nanosheets on BP nanosheets. Through electronic interactions and oxygen affinity differences between EBP and CoFeB nanosheets, the heterostructure is able to balance the uptake of oxygen-containing intermediates to achieve the optimum state for facilitating the OER process. In addition, the EBP (crystalline) and CoFeB (amorphous) hybrid displays the superiorities of quick charge carrier transfer and abundant reactive sites, respectively. Schematic diagram of the typical processes for OER and MOR is shown in Figure 5. Li, et al. propose a method to catalyze OER kinetically and efficiently by growing amorphous multi-transition-metal (cobalt and iron) oxide on two-dimensional black phosphorus [111]. To further improve the catalytic efficiency, Qian et al. used gold nanoparticles to modify the black phosphorus nanosheets to give them excellent electrocatalytic oxygen evolution performance [112]. The applications of BP and its related composites in the fields of electrochemistry and bioelectrochemistry have been summarized by Han Zhang et al. (Figure 6) [113]. Black phosphorus also shows great potential in electrocatalytic nitrogen fixation. The efficiency of ammonia synthesis with black phosphorus has exceeded 100 \( \mu \text{g} / (\text{h} \cdot \text{mg}) \), and it is the best among non-metallic nitrogen fixation catalysts [114]. Doping other elements in situ during the preparation of black phosphorus crystals is another effective way to improve the stability of black phosphorus. Yang et al. used red phosphorus as raw material to prepare black phosphorus crystals, about 0.1% of tellurium (Te) was added to obtain Te-doped black phosphorus [115]. After doping, Te tends to be dangling bonds. The form is adsorbed on the surface of black phosphorus, so that the bottom of the conduction band of black phosphorus is lower than the redox potential of \( \text{O}_2/^-\text{O}_2 \), so it is difficult to generate active oxygen \( \text{O}_2 \), and the stability of black phosphorus is improved. The carrier mobility of Te-doped black phosphorus is as high as 1850 \( \text{cm}^2 / (\text{V} \cdot \text{s}) \). After being placed in the air for 21 d, it can still maintain the electron mobility of \( >200 \text{ cm}^2 / (\text{V} \cdot \text{s}) \) and the switching ratio of \( >500 \), showing good stability, while the mobility and switching ratio of undoped black phosphorus are reduced to 0. However, in the process of preparing black phosphorus crystals, the selection of doping elements is limited, and the doping concentration is extremely low. Moreover, if doping/loading is carried out during the preparation of black phosphorous nanosheets, it can be further expanded.

Figure 5. Schematic diagram of the typical processes for OER and MOR. (reproduced with permission from Ref. [110], © American Chemical Society 2021).
At present, the conversion of carbon dioxide (CO₂) to carbon monoxide products is one of the more promising of the many methods of carbon dioxide emission reduction. The use of electrocatalysis technology to promote carbon dioxide emission reduction offers advantages over other CO₂ recovery strategies because of its relatively simple operating conditions (it can be carried out at ambient temperature and pressure) and its ability to convert CO₂ into usable fuel using clean renewable energy sources, which has multiple benefits. However, the efficiency of electrocatalytic reduction in CO₂ is still very low. This is because the chemical bonds in carbon dioxide are very stable. To explore this problem, we found that copper, silver, gold, and their alloys are currently the most active electrocatalysts for reducing CO₂ in aqueous solutions to CO. However, these alloys have certain limitations, such as higher surface energy and lower surface activity. Based on the above phenomenon, semiconductor two-dimensional nanomaterials will give full play to their advantages, which can provide high specific surface area, expose abundant catalytic active centers, and promote carrier separation. As one of the two-dimensional materials, black phosphorus (BP) forms a folded honeycomb orthorhombic lattice with strong interlayer bonding. Therefore, it will be considered as a promising candidate for the electrocatalytic reduction in CO₂. Huang et al. reported a facile direct solid-state reaction strategy using black phosphorus coupled black titania to prepare uniform BP-BT (black titania, TiO₂) materials with enhanced wide-spectrum sunlight absorption properties. BP-BT possesses a typical crystalline core-amorphous shell (TiO₂@TiO₂-x) structure with numerous oxygen vacancies and electron-rich P dosage in the layer and exhibits excellent solar-to-chemical conversion for efficient photocatalytic CO₂ reduction to CH₄. The electrochemical index of black phosphorus can also be used as an H₂O₂ sensor. Pumera et al. constructed a sensing system based on black phosphorene @ biological enzyme [116]. In the reductive sensing system (BP/HRP), black phosphorus can significantly improve the current signal and keep the structure intact. GC/BP/HRP electrode can detect H₂O₂ with high sensitivity, and the linear range is as wide as 5–275 μmol·L⁻¹, with a detection limit of 0.14 μmol·L⁻¹.

In terms of electrocatalytic hydrogen production, Wan et al. constructed a heterostructure with MoSe₂ and black phosphorus; BP nanosheets are used as 2D substrates to stabilize MoSe₂ aggregation and provide a short path for electron transfer, while MoSe₂ provide rich active sites released from aggregation. At 10 mA·cm⁻², it shows an overpotential of 380 mV. In the heterostructure, BP nanosheets can not only be used as a conductive network for rapid electron transfer, but also prevent MoSe₂ nanosheets from aggregation to expose more active sites. It shows that black phosphorus can promote charge transfer and expose more active electrocatalytic sites through a simple combination with other TMDs. As shown in Figure 7, the combination of black phosphorus and another metallic electrocatalyst can further improve the catalytic efficiency. Wang et al. reported the strong activation of platinum catalyst by black phosphorus (BP), and the subsequent modulation
has greatly changed the surface electronic structure of Pt, to improve the catalytic activity of hydrogen evolution reaction (HER). The strong Pt-P bond makes the d-band center of Pt move down to the Fermi level, resulting in the lowest energetics of the intermediate products in the electrocatalytic reaction. When the number of Pt-P bonds increases, the activity can also increase, and BP-activated platinum catalyst can reach up to 6.1 times higher than the most advanced industrial Pt/C catalyst in terms of activity. Layered black phosphorus as a catalyst for hydrogen evolution reaction also has some problems, such as few active sites and instability under environmental conditions [117,118]. In the application process, it is necessary to ensure that the layered black phosphorus is not oxidized. It is found that the selective bonding of C60 at the edge of few-layered black phosphorus can protect the BP from oxidation [119]. At the same time, the excellent conductivity of carbon materials with SP2 bond and structure can also improve the catalytic performance of layered black phosphorus electrocatalyst [120]. In addition, the carbon material covering the layered black phosphorus not only avoids the direct contact between the layered black phosphorus and the electrolyte, but also enhances the stability and efficiency of the electrode [121–123]. Yu et al. prepared Nafion stabilized black phosphorus nanoparticles (BNPs) and 6-o-α-Maltose group-β-Cyclodextrin (G2)-β-CD,6-O-α-mal-tosyl-β- Cyclodextrin modified composite electrode (BNPs-G2)- β- CD/GCE [124]. Host guest recognition based on cyclodextrin, BNPs-g2-β-CD/GCE can be used as an electrochemical sensing platform for chiral recognition of tryptophan (TRP). In this system, black phosphorus nanoparticles can be used as carrier material for target recognition unit cyclodextrin and improve the electron transport performance of the electrode.

Figure 7. Schematic of illustration of BPed-Pt/Gr (reproduced with permission from Ref. [118], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2019).

5. Conclusions

In this review, the latest research on BP and its composite materials in energy storage, photoelectric catalysis, etc. are summarized. However, there are still some problems to be solved. For example, since the number of layers of BP significantly affects its characteristics, there is an urgent need for a controllable mass production method of layered BP, which can also promote the cost reduction of BP-related materials. Moreover, instability limits the potential applications of BP-related composite materials. The currently reported stabilization methods have their limitations. Simple and effective stabilization strategies are issues that need further consideration, which may have an impact on the preparation, processing, and application of BP-related materials. The research on black phosphorus requires more effort in scientific exploration and investigation of the possibility of final commercial application.

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