Abstract

The discovery of monolayered black phosphorus (phosphorene) in 2014 gives rise to enormous research enthusiasm for its unique electrical and physicochemical properties. Since then, the applications of black phosphorus and its nanostructures have been extended to various fields covering field effect transistors, rechargeable batteries, electrocatalysis, sensors, thermoelectric materials, and so forth. However, controllable and scalable synthesis of BP and its nanostructures remains a challenge. In this review, we provide a state-of-the-art overview of the progress towards the synthesis of bulk BP and its typical nanostructured counterparts, including the 0D BP (quantum dots), 1D BP (nano/micro-belts), 2D BP (phosphorene), and 3D BP (sponges). Special focus will be made on the various synthetic methods, the characterizations of products, and the corresponding necessary improvements. We close the review with a look at the challenges and perspectives regarding future studies.

1. Introduction

Elemental phosphorus is among the eleven most abundant elements in the earth's crust (up to 100 billion tons). It has several allotropes including white phosphorus (WP), red phosphorus (RP), violet phosphorus, and black phosphorus (BP) [1–4]. Among these, BP as the most stable allotrope of phosphorus has been emerging as a novel 2D semiconductor material due to its tunable and direct bandgap, high carrier mobility, and in-plane anisotropic properties [5–8]. To date, BP crystals have been found to exist in three crystalline structures, including orthorhombic, rhombohedral, and simple cubic structures, as well as in an amorphous form [9–11]. The discovery of bulk orthorhombic BP can be traced back to 1914, but it gained little attention until the successful exfoliation of orthorhombic BP into phosphorene by using the scotch-tape microcleavage method in 2014 [12]. A variety of synthetic methods of phosphorene were then further reported, including liquid-phase exfoliation, hydrothermal reaction, electrochemical exfoliation and so forth [13–16]. These achievements enable many new findings of interesting properties, such as the thickness-dependent bandgap (from 0.3 eV for the bulk to 2.0 eV for the monolayer), perfectly linearly polarized light emission from monolayer and few-layer forms, and tunable topological/electronic properties [17–19]. These distinct features render BP with wide applications ranging from energy storage and catalysis to electronic devices [3, 20–29].

Shaping 2D materials into low-dimensional structures (0D and 1D) has demonstrated its wide benefits in nanomaterial fields [30–33]. A typical example is the exfoliation of graphite into graphene, which gives rise to comprehensive investigations due to its large surface area and unique physicochemical/electronic properties relative to its bulk counterpart [34, 35]. Extensive research was later focused on the synthesis of graphene quantum dots, graphene nanobelts, and 3D graphene, which largely broaden their potential applications owing to the structure-dependent properties [36–38]. Inspired by the studies of graphene, a lot
of effort was immediately devoted to the preparation of different forms of nanostructured BP in addition to phosphorene. To date, those including 0D BP (quantum dots), 1D BP (nano/micro-belts), 2D BP (phosphorene), and 3D BP (sponges) have been largely reported and efforts are still dedicated to improving their synthetic methods [39–42]. However, different from the stable graphene, the nanostructured BP is oxygen/light sensitive and low-melting (lower than 400 °C), resulting in inconsistent structures along with degraded electronic or physicochemical properties [43, 44]. In addition, it is prone to undergo phase transition (e.g., WP as a byproduct) during the synthetic process [14]. Therefore, although great achievements have been made, it is still a challenge to realize the controllable synthesis of bulk BP and its different nanoforms with good quality and high yield.

In this review, we aim to provide an overview of the recent progress in the synthesis of BP and its nanostructures with different dimensions. The various synthetic strategies will be emphasized and characterizations of the corresponding products will be discussed. Note that BP-based composites, such as BP/graphene, BP/MXene, and others as well as their applications, are not included in this review. The challenges and perspectives in this field are presented last.

2. Preparation of bulk black phosphorus

Bulk BP is generally used as a precursor for downsizing into its nanostructures. Therefore, its quality, including crystallinity, size, and purity, is of primary concern. BP crystals were accidentally discovered in 1914 by Bridgman during the conversion of WP to RP under a high pressure of 1.2 GPa at 200 °C [45]. Afterwards, several methods were developed to improve the quality of the produced BP crystals, including the modified Bridgman’s method [46], mercury catalysis [47], liquid bismuth [48], and so on. A breakthrough was achieved in 1982 when Endo et al converted RP into melting BP at 900 °C and then slowly cooled it down at a high isobaric pressure of 1 GPa. This method can produce BP single crystals with a size of larger than 5 × 5 × 10 cm [3, 49]. However, these synthetic methods above are highly dependent on high-pressure apparatus, presenting practical obstacles for cost-effective and scalable synthesis of BP crystals. To overcome these challenges, effective strategies including the chemical vapor transport (CVT) deposition process, mechanical ball-milling technique, and wet-chemical methods have been extensively reported.

2.1. Chemical vapor transport (CVT)

The CVT method has been regarded as an elementary method for the synthesis of pure crystals [50, 51]. It involves the phase transformation from the solid to the gas phase, followed by deposition onto another region. Currently, it is largely used to produce bulk BP crystals or doped BP crystals (e.g., sulfur-, selenium-, and tellurium-doped) with high crystallinity, which are further used as parents for producing BP nanostructures [52–54].

In 2007, Nilges’s group discovered the CVT method for the synthesis of BP crystals, which was a breakthrough regarding the improvement of BP quality and synthesis simplicity [55]. In this method, BP crystals were prepared from RP in an evacuated silica ampule under a low temperature of 873 K with the addition of small amounts of Au, Sn, and SnI₄ as mineralizers. The synthetic process takes 5–10 d and impurities including Au₂SnP₇, AuSn, Sn₂P₃, and SnI₄ were found in the products. Afterwards, they focused on the optimization of the reaction mineralizers and found that the Sn/SnI₄/red-P system was beneficial for reducing both the cost and impurities simultaneously [56]. Figure 1(a) shows a photograph of the produced BP crystals with the size of several millimeters in a silica glass ampule.

However, SnI₄, as one of the important components, is difficult to synthesize due to the required temperature gradient of 45 °C–50 °C. Fluctuations in the temperature gradient might instead produce other products including Hittorf’s phosphorus (HP) and WP. In this regard, Zhao et al further developed the Sn/I₄/red-P system using the muffle furnace instead of the evacuated ampules [58]. Therefore, it is simpler considering the tedious synthesis of SnI₄ as well as the vacuum conditions. Based on this system, Yan’s group developed in 2016 a two-step heat process using the Sn/I₄/red-P system with two independent heating zones in the tube furnace (figure 1(b)) [59]. The produced BP shows high crystallinity as demonstrated by X-ray diffraction (XRD, figure 1(c)). This method only produces the tin phosphide as a by-product, which can be removed by washing the product with diluted hydrochloric acid. Therefore, the purification process of BP crystals was largely simplified. The X-ray rocking curve shows a full width at half maximum of 21.65 arc sec (figure 1(d)), suggesting an eminent crystallinity of the produced BP crystals. However, the CVT method can currently only produce 5–10 g per batch. In addition, impurities including the Sn-I-based by-products as well as WP are also likely to be present in the product. Therefore, a profound understanding of the growth mechanism from experimental and theoretical aspects is highly desirable, although numerous efforts have been under way [57].
Although the CVT method has demonstrated its feasibility for producing orthorhombic BP single crystals, the synthetic mechanism is still poorly understood. Questions regarding the role of mineralization additives, the nucleation and growth modes, and other issues during the phase transformation remain unclear. Various species, such as Sn, I₂, SnI₂, SnI₄, and Au were used as mineralization additives for BP growth, while their exact functions are unknown. Recently, Yu's group demonstrated that the solid ternary inverse clathrate Sn₂₄P₂₂−ₓI₈ was critical for BP growth instead of the commonly accepted vapor mineralizer, which could provide insipirable strategies for BP synthesis \([60]\). The mediate was determined as Sn₂₄P₁₉.₃I₈ by Chen et al \([61]\). Yan's group revealed the presence of crystalline monoclinic violet or HP during the synthetic process, which was characterized by several structural and optical experimental identification approaches (e.g., micro-Raman spectroscopy) \([62]\). It was identified as having a critical role in the transformation from RP to BP in an RP/Sn/I₂ system, serving as a heterogeneous nucleation site for BP nucleation and growth. Accordingly, a step-by-step phase-induced nucleation and growth mechanism was proposed for the RP/Sn/I₂ CVT reaction system, as shown in figure 2.

2.2. High energy mechanical milling (HEMM)

The practical implementation of BP requires the development of a high-volume synthesis technique. In this manner, the high-energy ball-milling technique has been demonstrated to be a promising method due to its relatively simple operation at low pressure/temperature conditions. During the HEMM process, the temperature can be increased to above 200 °C and the pressure can be of the order of 6 GPa, which will induce the phase transformation of precursors inside a steel vessel under inert atmosphere. Compared to the CVT method, HEMM requires no catalyst and is favorable in the interest of alleviating potential safety hazards.

Park et al prepared the BP powder with an average size of 3.3 μm using the RP powder (high-purity chemicals, >99%, average size: 15 μm) as precursors \([63]\). The RP was subjected to 54 h of high-energy mechanical milling technique at ambient temperature and pressure under Ar atmosphere. The amorphous nature of RP was confirmed by the XRD pattern. After the HEMM process, the corresponding sample
Figure 2. Schematic diagram of the nucleation and growth mechanism during the process of RP to BP phase transition. (a) The initial state. (b) Solid tin phosphide iodide and tin phosphide were adsorbed on the solid HP surface. (c) The solid HP transformed into the crystalline HP. (d) The crystalline HP acted as a heterogeneous nucleation site for BP nucleation. (e) The BP single crystal growth. (f) The obtained bulk highly crystalline BP single crystals. Reproduced from [62] with permission of The Royal Society of Chemistry.

Figure 3. Characterization of the mechanochemical conversion of RP to BP. (a) Optical image of bulk powders revealing the color change during the increasing milling time via high-energy ball milling (scale bar is 1 cm). (b) Powder XRD patterns of RP during conversion to BP showing an increase in the intensity of the main BP (040) and (111) peaks with increasing milling time. Reproduced from [49]. CC BY 4.0.

became black, which was identified as orthorhombic BP based on the XRD pattern and high-resolution transmission electron microscopy (HR-TEM).

Although the HEMM method demonstrates the successful transformation of RP to BP, it is still a black-box process, during which little is known with regard to detailed mechanism. Very recently, Pedersen et al achieved a high conversion yield of ~90% for ~5 g of bulk BP powder using the high-energy planetary ball milling [49]. With the increase in milling time, the powder gradually changes from a burnt umber red to a dull black (figure 3(a)). The successful transformation from RP to orthorhombic BP was monitored by XRD measurements (figure 3(b)). They investigated the milling conversion kinetics of the BP phase transformation by monitoring the process via ex-situ XRD, manifesting a sigmoidal behavior best described by the Arrami rate model with each impact of sufficient energy (>25 mK) producing BP nuclei. However, it was demonstrated that the overall process is limited by the grain growth, leading to the small size of produced BP. Therefore, it is still a challenge for the HEMM technique to enhance the grain growth during the phase transformation. Furthermore, as detected by TEM and selected area electron diffraction (SAED), the crystalline BP domains were found to be embedded into an amorphous matrix, demonstrating its insufficient crystallinity. Furthermore, the Raman spectra reveal the presence of residual RP in BP, although the optimal experimental conditions were utilized. Therefore, as an extension, this method was used to
prepare black–red phosphorus heterostructures. However, for the purpose of preparing high-quality BP crystals, improvements regarding crystallinity, size and purity are still necessary for the HEMM method.

2.3. Wet-chemical method
In addition to the two typical methods discussed above, wet-chemical synthesis has been very recently reported as a low-cost synthetic strategy. Recently, Wang et al demonstrated the synthesis of micrometer-sized BP on a gram-scale directly from RP in the ethylenediamine medium via a one-step hydrothermal method at a low temperature of 120 °C–200 °C [64]. The crystallinity of the produced BP increases as the reaction temperature increases, as evidenced by the increased intensity of XRD peaks. A crystallization mechanism from RP to BP was also proposed based on Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), and DFT calculation. It was demonstrated that ethylenediamine as a medium can activate the basic unit P_4 cluster of RP and provide the electron to P_4 molecule. When two activated P_4 molecules are coupled, a table P_8 basic unit is formed in a symmetrical way, which serves as the template for further growth. Since the short P–P bond takes precedence along the x-axis spatial orientation, the coupling basic unit will grow via extension along the y-axis. Finally, the growth will take place along the x-axis under van der Waals force, giving rise to the formation of BP.

3. Preparation of black phosphorus quantum dots (0D)
Zero-dimensional BP quantum dots (BPQDs) were for the first time reported by Zhang et al [65]. In just a few years, BPQDs have been emerging as a functional material due to their unique properties and potential wide applications including photovoltaics, fluorescence sensing, cancer therapy, and optoelectronic devices [66, 67]. To date, there have been various synthetic methods for preparing BPQDs, including ultrasonic liquid-phase exfoliation, solvothermal treatment, high-energy ball milling, microwave-assisted method, and pulsed laser irradiation, among others.

3.1. Ultrasonic liquid-phase exfoliation
During the ultrasonic liquid-phase exfoliation process, bulk BP crystals are directly used as the starting materials, together with proper exfoliation solvents (e.g., N-methyl pyrrolidone, isopropanol, dimethyl formamide, etc). The mixture is further sonicated to downsize the bulk BP into nanostructures.

As a pioneering study, Zhang et al were the first to prepare BPQDs via ultrasonic liquid-phase exfoliation [65]. For the experimental details, the micro-sized bulk BP crystals prepared under high pressure and high temperature were mixed with N-methyl pyrrolidone (NMP) and then ground in a mortar, followed by an ice-bath sonication at a power of 200 W. The obtained solution was further centrifuged for 20 min at a speed of 7000 rpm to remove the large particles and the supernatant containing BPQDs was decanted gently. Noted that the experiments except the sonication and centrifugation processes were conducted in a glove box to avoid the oxidation of BPQDs. The combination of grinding and sonication is expected to increase the yield while narrowing the size distribution of BPQDs. As shown in figures 4(a)–(e), the average size of the as-obtained BPQDs is 4.9 ± 1.6 nm with clear lattice fringes observed in TEM, demonstrating the preserved crystallinity. Statistical atomic force microscopy (AFM) analysis (figures 4(f)–(i)) shows an average thickness of 1.9 ± 0.9 nm, corresponding to 4 ± 2 layers of BP. Although the exposure to air was prevented in the best possible way, the oxidation of BPQDs was still detected with the obvious presence of O signal in the XPS. This can be ascribed to the air instability of BP, especially for the ultrasmall QDs, which can readily react with the minor oxygen or water molecules in the surroundings. Instead of using grinding, Sun et al utilized a more reproducible probe sonication method to downsize BP crystals at the beginning, followed by the ice-bath sonication. The operations were performed under ambient conditions, and the BPQDs were dispersed in an aqueous solution; thus, some surface oxidation was also detected. Evidently, it is a challenging task to prepare BPQDs with improved air stability.

During the ultrasonication process, small polar molecules containing hydroxyl and/or phosphorus have been demonstrated as efficient additives in the exfoliation solvents since they can easily interact with polar BP, thus increasing their solubility and leading to ultimate effective exfoliation. For example, phytic acid (C_{37}H_{18}O_{24}P_{6}) with six phosphate carboxyl groups and 12 hydroxyl groups was used as the assisting reagent of NMP [68]. The mixture of ground BP powder, NMP, and phytic acid was sealed and sonicated in a bath sonicator at 50 kHz frequency for 10 h. As characterized by TEM and AFM, the produced BPQDs are ~3.4 nm in lateral size and 1.9 ± 1.0 nm in thickness. This work enlightens researchers to explore effective additives in the exfoliation solvent to shorten the sonication time and improve the efficiency. It can also be favorable to prevent the degradation of produced BPQDs.
3.2. Solvothermal method
Recently, BPQDs have been also prepared from BP powders via a solvothermal method. For example, Xu et al prepared ultrasmall BPQDs on a large scale using this method, as schematically illustrated in figure 5(a) [69]. In brief, the BP powders were first ground, and then added into a flask with a saturated NaOH/NMP solution, which has been verified to be beneficial in improving the stability of nanostructured BP. After vigorous stirring for 6 h at 140 °C under the protection of nitrogen, the ultrasmall and uniform BPQDs with an average size of 2.1 ± 0.9 nm were synthesized (figures 5(b)–(e)). Compared with previously reported liquid-phase exfoliation methods, this solvothermal synthesis is relatively simple and controllable, making it highly promising for large-scale BPQD production. Three typical peaks corresponding to the out-of-plane vibration mode $A_{g1}$, the in-plane vibration mode $B_{2g}$ and $A_{g2}$, respectively, can be observed in the Raman spectra of the bulk BP and BPQDs (figure 5(f)). After being calibrated by the silicon peak as a standard, it was found that the three Raman peaks of BPQDs were blue-shifted relative to those of bulk BP. Figure 4(g) shows the linear absorption spectrum of the as-obtained BPQD suspension.

3.3. High-energy ball-milling method
A high-energy ball-milling method has also been reported for the synthesis of BPQDs. Different from the case of bulk BP prepared from RP via HEMM method, the bulk BP crystals were directly used as the precursor, followed by subjecting to the milling process for 6 h with ethanol as the solvent [70]. Subsequently, the dispersion was centrifuged at 10000 rpm for 20 min and the supernatant containing BPQDs was gently decanted. The resulting BPQD suspension was brown and translucent, with a concentration of 30 μg ml⁻¹ (determined by inductively coupled plasma-mass spectrometry). As characterized by TEM and AFM, the average size of BPQDs was 6.5 ± 3 nm with height from 3 to 8 nm.

3.4. Microwave-assisted method
A microwave-assisted method was recently reported as a simple and efficient approach to produce high-quality BPQDs. Compared to the commonly used ultrasonication technique and the other methods
discussed above, the microwave-assisted liquid-phase exfoliation requires very short processing time for the successful synthesis of BPQDs. In a typical synthesis process, BP crystals were ground and added into NMP solvent, followed by heating in a commercial microwave system. Then, the supernatant was centrifuged at 6000 rpm for 30 min. It was demonstrated that the BP crystals gradually evolved into BP nanosheets and further into BPQDs with the increasing treatment time from 10 to 30 min. The TEM image shows the produced ultrasmall BPQDs with a lateral size of 2.95 ± 0.59 nm, confirming the uniform production of BPQDs. Both SAED and Fast Fourier transform demonstrated the high crystallinity of the BPQDs. However, the P 2p spectrum shows a peak located at around 132.9 eV, corresponding to the highly oxidized state (P–O). Explicitly, this method still suffers from a common challenge with other methods, although it takes a short time for the synthetic process.

3.5. Pulsed laser ablation
Pulsed laser ablation is the process of removing material from a solid surface by irradiating it with a laser beam. It has been considered as a clean and orientable technique for preparing nanomaterials by treating the solid precursors (including metal, semiconductive, and carbon-based nanomaterials) in liquid. The BP crystals were placed at the bottom of a cuvette filled with N\textsubscript{2} saturated isopropyl ether solvent [71]. During the ablation process, a pulsed laser beam was focused on the BP crystals by continuously adjusting the x–y–z directions, as a purpose of ablating the BP crystals. As a result, a light-yellow supernatant containing BPQDs was obtained. The as-obtained BPQDs were about 6 nm in average diameter and about 1.1 nm in height.
4. Preparation of phosphorene (2D) and nano/micro belts (1D)

The 2D structure of bulk BP made of perpendicular stacked layers via weak van der Waals force (151 meV per atom, theoretically) makes it possible to split into atomically thin BP nanosheets (phosphorene). Since its introduction in 2014, phosphorene has become a rising star in the field of 2D nanomaterials due to its tunable bandgap, high charge mobility, high surface area, and anisotropic structure [72]. Apart from this extensively studied phosphorene, research on few-layered BP nano/micro belts (or ribbons) with high length-to-width ratio has also been a major focus in recent years due to its combined advantages of the planar layer structure and the high orientation of 1D materials with fascinating properties. Considering the similarities of their preparation methods, we combine these two parts and refer to those BP ribbons/nanobelts as ‘1DBP’. Their synthesis methods can be classified into top-down and bottom-up, which are elaborated in detail below.

4.1. Top-down approach

Inspired by the success of graphene, mono- and few-layered BPs were also first prepared via scotch-tape mechanical exfoliation [17, 72]. Jin and co-workers successfully prepared phosphorene via mechanical cleavage, followed by thinning and stabilizing process by argon plasma [73]. The phosphorene retains its crystallinity without any transformation to RP or WP in a dry environment for a few months, even when annealed at 200 °C under relatively low vacuum. In addition to argon plasma, a number of advanced thinning methods have also been reported. Some of the notable ones are laser pruning, thermal thinning, focused ion beam cutting, photochemical etching, and wet chemical thinning [74–77]. Remarkably, under ambient conditions, Lu et al successfully prepared the laser-induced micropatterned few-layered phosphorene with unique optical and fluorescence properties [78]. Later, layer-by-layer thinning to single-layer BP was also realized by ozone etching [76]. Unfortunately, the generated O3 partially oxidized BP to form P2O5-like oxides; hence, the additional step of oxide removal by water was needed to obtain the self-protecting phosphorene with oxygen functional groups. Though this mechanical exfoliation method followed by thinning processes is an effective way to prepare a single quality phosphorene, which can be used for lab-level studies; the uncontrollable lateral size, tedious transfer process from the scotch tape to certain substrates and poor yield discourage researchers from in-depth investigations [72, 73].

Liquid-phase exfoliation, which has shown success in exfoliating many-layered materials, has been considered as a simple, scalable and controllable approach. In this method, suitable solvents, which are used to weaken the van der Waals forces between interlayers, should be anhydrous and oxygen-free since oxygen preferred to chemisorbed onto a lone pair of phosphorus atoms resulting in phosphoric acid or oxide mixtures [72, 79, 80]. By virtue of these criteria, N-methyl-2-pyrrolidone (NMP) was the first solvent of choice to prepare few-layered phosphorene with oxygen functional groups. Though this mechanical exfoliation method followed by thinning processes is an effective way to prepare a single quality phosphorene, which can be used for lab-level studies; the uncontrollable lateral size, tedious transfer process from the scotch tape to certain substrates and poor yield discourage researchers from in-depth investigations [72, 73].

Later, various organic solvents that are inert and polarized including dimethylformamide (DMF), dimethyl sulfoxide, isopropyl alcohol (IPA), N-cyclohexyl-2-pyrrolidone (CHP) can also be used to prepare single-layer phosphorene with high resistance to degradation [82–84]. Zhang et al demonstrated that formamide with high surface tension showed the highest yield of phosphorene among several commonly used solvents [15]. In the case of CHP, the high stability was explained by the solvation shell, which can isolate phosphorene from external oxygen [83]. In addition, their theoretical predictions combined with experimental results indicate that the oxidation of prepared phosphorene only happens at the edges (no basal plane oxidized) with the rate/extent dependent on oxygen content (figures 6(a)–(c)). As shown in figures 6(d)–(h), SEM, HRTEM and statistical TEM results confirmed the crystalline nature of the BP nanosheets with lateral size of ~1 mm [83]. To further improve the scalability of this method, a mixture of NaOH and NMP was proposed as a solvent by Guo et al, which results in size-controlled and water-stable phosphorene with a controlled number of layers [20]. Herein, the obtained phosphorene at 12 000 rpm is 5–12 layers (5.3 ± 2.0 nm) with an average lateral size of 670 nm. The number of layers of lateral size drop to 2–7 (68% are 2–4) and 210, respectively, when the centrifugation speed increases to 18 000 rpm.

Compared to the bath-sonication method, the probe sonicator has higher power, enabling the preparation of highly concentrated electronic-grade phosphorene suspension [85]. Other than organic solvent, environmentally friendly non-volatility recyclable ionic liquids were also reported to be prepared in high-purity, stable, crystalline, and highly dispersed phosphorene suspension. When 1-hydroxyethyl-3-methylimidazolium trifluoromethansulfonate ([HOEMIM]-[TfO]) was used to exfoliate bulk BP, no sign
of sedimentation or aggregation was seen after 30 d, demonstrating the excellent stability of the as-prepared phosphorene [86]. Although liquid exfoliation presents itself as a more scalable option compared to mechanical ones, the small lateral size of the BP sheets and defects caused by long-term sonication might hamper its use in electronic applications; not to mention, the use of toxic organic solvents and their adsorption on the surface during the exfoliating process. In this regard, several works have reported on the electrochemical exfoliation of BP [14, 87, 88]. One of the first was Pumera et al, who reported the preparation of phosphorene within a few micrometers in lateral size BP through the electrochemical exfoliation in aqueous solution [72]. The process was done in just 2 h at a relatively low voltage and current of 3 V and 0.25 A, respectively, in aqueous 0.5 M H\textsubscript{2}SO\textsubscript{4} solution.

From another aspect, shaping these exfoliated 2D phosphorenes into nanobelts or nanoribbons is also attractive due to its potential application for 1D nanoelectronics. Drndic and co-workers demonstrated the \textit{in-situ} TEM drilling and scanning TEM (STEM) nanosculpting of DMF-exfoliated BP to fabricate few-layered sub-10 nm width armchair and zigzag BP nanoribbons [89]. Interestingly, Howard et al presented an approach to prepare high-quality single-crystal atomically thin BP nanoribbons oriented along the zigzag crystal via lithium-intercalated intermediate [90]. This top-down method results in predominantly 4–50 nm width nanoribbons with length-to-width ratio of up to 1000. However, the process is time-demanding and a low temperature of −50 °C is required. Recently, Cheetham and colleagues

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**Figure 6.** (a)–(c) Reactivity of solvent-stabilized BP with water: (a) edge selective degradation model for BP exposed to pure neutral water (green, red and white balls represent P, O and H atoms, respectively). (b) Experimental data for amount of reacted phosphorus and water, respectively, as a function of time for std-BP GB in CHP after addition of 3 vol% of water. (c) Molar ratio of water/BP as a function of time measured for a std-BP GB dispersion in CHP after addition of 3 and 10 vol% of water. (d), (e) Low-resolution TEM images of exfoliated FL-BP (scale bars in (d) and (e) are 100 and 500 nm). (f) Bright-field STEM image and (g) Butterworth-filtered high-angle annular dark field STEM image of phosphorene exfoliated in IPA (scale bars in (f) and (g) are 2 and 1 nm). (h) Nanosheet length histogram of the exfoliated FL-BP obtained from TEM (sample size of 239). Reprinted by permission from Springer Nature Customer Service Centre GmbH: Nature, Nature Communications [83]. Hanlon D, Backes C, Doherty E et al Liquid exfoliation of solvent-stabilized few-layer black phosphorus for applications beyond electronics. © 2015.
Figure 7. (a) Mechanism of preparation of zig-zag BP nanobelt from bulk BP. (b) TEM image of a single BP nanobelt with the zigzag directions. (c) corresponding HRTEM image; (d) corresponding SAED pattern (inset: intensity of (200) and (101) fast Fourier transform patterns). (e) Low-magnification TEM image of an individual BP nanobelt. (f) Aspect ratio of the TEM images statistics on 73 BP nanobelt. (g) Thickness distribution from AFM images of BP nanobelt (inset: AFM image of two typical nanobelts). Reprinted by permission from Springer Nature Customer Service Centre GmbH: Nature, Nature Communications [91]. Z Liu, Y Sun, H Cao, D Xie, W Li, J Wang and A K Cheetham. Unzipping of black phosphorus to form zigzag-phosphorene nanobelts. © 2020.

electrochemically unzipped single-crystal BP into zigzag-oriented BP nanobelts (figures 7(a)–(d)) via the novel oxygen-driven mechanism [91]. Their theoretical simulation, combined with experimental characterizations, suggested that the critical intermediate species enabling the process were interstitial oxygen pairs. As can be seen in figures 7(e)–(g), the resulting nanobelts are 1–8 layers (>90% are \(\sim 2.7 \pm 1.7 \text{ nm} \)) in thickness), flexible, highly crystalline with aspect ratio over 10. Although some degree of oxidation of BP was seen, lengthwise cutting was not found. Through this mechanism, BP
quantum dots and nanosheets could be prepared as well. This scalable, low-cost, and incredibly fast approach opens wide the door to commercialization once surface oxidation can be controlled.

4.2. Bottom-up methods
In contrast to top-down methods, bottom-up methods including wet chemical self-assembly (hydrothermal/solvolothermal, templated synthesis) and chemical vapor deposition (CVD) have received far more attention from the academic community due to their scalable potential and versatility. With regard to CVD, Lau et al were the first to employ BP crystals as a target to produce 2 nm thick phosphorene on wafer as the substrate by KrF pulsed laser ($\lambda = 248$ nm) deposition with 5 Hz repetition rate at a very low temperature of 150 °C. However, the produced phosphorene is limited by the highly disordered form [11]. Meanwhile, starting from RP instead of BP, Ji’s group demonstrated an in-situ CVD approach to prepare four-layered BP with a large area of over 3 $\mu$m$^2$. In their synthesis, the pristine RP was first heated at 600 °C to form an amorphous film, which was then heated at a high temperature of 900 °C and high pressure of 27.2 atm with Sn/SnI$_4$ as mineralizer [92]. Notably, Xia and colleagues have successfully prepared a thin film of BP (~40 nm in thickness) with a lateral size of up to 4000 $\mu$m on a flexible polyester substrate. The process starts with an RP powder thermally deposited on the substrate, followed by intensive pressurization of over 8 GPa in a multi-anvil cell at 400 °C. Controllable thicknesses can be obtained by changing the process duration [93]. Similarly, at a much lower pressure of 1.5 GPa but a higher temperature of 700 °C, phosphorene on sapphire with 5 nm thickness was also reported, which is polycrystalline and has a crystal domain size of 40–70 $\mu$m revealed by infrared extinction spectroscopy and Raman mapping [94]. Despite these significant progresses, the lack of nucleation sites on the substrate and the uncontrollable phosphorus concentration during growth have hindered the preparation of electronic-grade nanofilms by the CVD method. Moreover, the efficiency of CVD growth is rather low, and the majority of phosphorus gas is transformed into the poisonous and non-flammable WP. Until very recently, Xu et al, by epitaxial nucleation design and a subsequent lateral growth control, have successfully grown crystaline millimeter-sized BP films with tunable thicknesses on Si substrates. The as-prepared BP films displayed comparable electrical properties to the one exfoliated from bulk BP [95].

As another bottom-up approach, hydrothermal/solvolothermal methods have recently received increasing attention due to the advantage of uniform size, controllable thickness, and most importantly, being easily scalable [72]. Using the solvolothermal method in ethylenediamine solvent, Tian et al successfully prepared few-layered phosphorene from WP [96, 97]. In this synthesis, ethylenediamine holds a crucial role which transmits into the interlaminar spacing of RP, increasing the interlayer spacing and weakening the van der Waals’ force [98]. Thereby, under solvolothermal conditions, RP is then exfoliated while being transformed to BP. A similar mechanism was also observed in the formation of mono-layered Co(OH)$_2$ nanosheets from Co(OH)$_2$ nanocones, which is well adopted here [99]. Also, by varying the solvolothermal temperature, the number of layers can be conveniently tuned. Interestingly, Yan et al reported a sublimation-induced solvolothermal synthesis of few-layered thick BP from bulk RP. A mechanism was also proposed in which continuous vaporization and condensation promote solid–vapor–solid transformation, followed by bottom-up assembly growth. Unfortunately, phosphorus oxide was also found in the final product [100]. In a more environmentally friendly manner, Zhao and co-workers further improved the aqueous-based hydrothermal synthesis by employing ammonium fluoride to lower the surface activation energy of the formed mono- and few-layered phosphorene [101]. The process is done with an RP microsphere precursor (figure 8(a)) and far excess amount of ammonium fluoride at 200 °C for 16 h. The as-obtained sample with sheet-like morphology was confirmed as phosphorene by TEM and XRD pattern (figures 8(b), (c) and (f)). Their polycrystalline nature was further evidenced by numerous structural distortions and clear contraction folds due to sp$^3$ hybridization (figures 8(d) and (e)).

With regard to bottom-up synthesis for 1D BP, no effort has been spared. Notably, Wang et al reported a low-cost, high-yield bottom-up synthesis of BP microribbons, which can be exfoliated easily due to the large area of the cleavage plane [58]. This synthesis does not require a temperature difference between the RP precursor zone and BP growth zone; therefore, a simple box furnace can be used instead of a space-limited tube furnace to significantly enhance the scale of the process. A reaction mechanism was also proposed on the basis of a series of controlled experiments. First, during the heating process up to 673 K, iodine and tin sublime/evaporate and react with each other to form tin iodide (SnI$_2$) which later serves as a mineralizer to enhance the crystallization of meta-stable/stable phases. From 673 to 863 K, RP sublimates and reacts with SnI$_2$ and gaseous Sn to form a P-Sn-I compound. The final stage starts when the temperature is cooled down and the gaseous P-Sn-I deposits play the role of nucleation sites and catalysts for BP microribbon growth.
The authors suggested that by tuning growth conditions, BP microbelts and few-layered nanobelts could also be formed.

Using the CVT method, single-crystal BP nanoribbons were grown with zigzag direction being the preferred growth (indicated by HRTEM and angle-resolved Raman spectroscopy) due to the replacement of Sn by Pb in the synthesis [102]. With Pb, much fewer metal clusters were in contact with BP nuclei, resulting in the favored addition of P$_4$ clusters along the zigzag direction of BP. Accordingly, BP nanoribbons with high length (tens of microns) to width (400 nm) ratio were obtained. However, to better study the in-plane anisotropic thermal transport of BP, 400 nm in width is not good enough; at least 200 nm-wide nanoribbons are required [103]. Recognizing that need, by a top-down reactive ion etching method, Ang et al have realized both armchair-oriented and zigzag-oriented nanoribbons with a much lower controllable width of 60 nm [104].

Instead of the commonly used highly toxic WP, RP was used to synthesize BP nanobelts with thicknesses of 73 nm via a simple single-step solid–liquid–solid reaction under atmospheric pressure [41]. Using bismuth particles as catalysts, the nanobelt growth mechanism was proposed to be similar to those of carbon nanotubes and other 1D nanomaterials.

5. Preparation of black phosphorus sponge (3D)

Although 1D and 2D phosphorene seems compelling for electronic applications, they tend to undergo restacking, leading to limited active sites, poor ionic transport among re-stacked sheets, and blocked electron transport [105]. Therefore, constructing 3D BPs with 1D/2D ribbons/nanosheets as building blocks could alleviate those shortcomings by higher surface-to-volume ratio and abundant pores/channels for ion/electron transport.

From bulk layered BP, Yu et al electrochemically prepared 3D BP sponges consisting of large BP sheets [42]. The synthesis was done in barely 3 min in a two-electrode configuration with an electrolyte comprising 0.05 M tetrabutylphosphonium bromide in DMF and Pt as the anode (figure 9(a)). Tetrabutylphosphonium was chosen as an intercalated ion due to its much larger diameter of 0.884 nm compared to the interplanar spacing of BP, which justifies the sponge-like BP formation. In addition, by virtue of the choice of electrolyte, there are no gas bubbles during the process, preventing any chance of shattering the sponge (figure 9(b)). The prepared BP sponge is highly crystalline and has numerous pores/channels, which was shown to be very beneficial compared to bulk BP or phosphorene for energy storage applications, such as supercapacitors and batteries (figures 9(c)–(e)). A table summarizing the synthesis methods and representative structural features for different BP nanostructures is provided in table 1.
Figure 9. (a), (b) Synthesis of BP sponge. (a) Schematic illustration of bulk BP. (b) Photographs taken at different times during synthesis. (c), (d) SEM images and (e) HRTEM image of BP sponge. Reproduced from [42]. CC BY 4.0.

Table 1. A summary of production methods and representative structural features for different BP nanostructures.

| Samples          | Methods                          | Features                                                  | Ref.  |
|------------------|----------------------------------|-----------------------------------------------------------|-------|
| BP crystals      | Chemical vapor transport         | High crystallinity with possible by-products               | [59]  |
|                  | High energy mechanical milling   | Small size; insufficient crystallinity                     | [49]  |
|                  | Wet-chemical method              | Micrometer size                                           | [64]  |
| 0D BP (QDs)      | Ultrasonic liquid-phase exfoliation | 4.9 ± 1.6 nm in lateral size; 1.9 ± 0.9 nm in thickness    | [65]  |
|                  | Solvothermal method              | 2.1 ± 0.9 nm in lateral size                              | [69]  |
|                  | High-energy ball-milling method  | 6.5 ± 3 nm in lateral size; 3–8 nm in thickness           | [70]  |
|                  | Pulsed laser ablation            | 6 nm in lateral size and about 1.1 nm in thickness         | [71]  |
| 2D BP (phosphorene) | Top-down methods              | Single quality phosphorene                                 | [12]  |
|                  | Mechanical exfoliation           | 670 nm in lateral size and 5.3 ± 2.0 nm in thickness       | [20]  |
|                  | Liquid-phase exfoliation         |                                                           |       |
|                  | Bottom-up methods               | Electrochemical exfoliation                                | [72]  |
|                  | Chemical vapor deposition        | Few micrometres in lateral size                            | [95]  |
|                  | Hydrothermal/                    | Polycrystalline phase; micrometer sized; 3 nm in thickness | [101] |
|                  | solvothermal method              |                                                           |       |
| 1D BP (belts)    | Top-down methods                | Reactive ion etching                                       | [104] |
|                  |                                  | 60 nm in width with both armchair and zigzag orientation  |       |
|                  | Bottom-up methods               | Chemical vapor transport                                   | [102] |
|                  |                                  | Tens of micron in length and 400 nm in width              |       |
| 3D BP (sponges)  | Electrochemical exfoliation      | High crystallinity with numerous pores/channels            | [41]  |
|                  |                                  |                                                           | [42]  |
6. Conclusions and outlook

The emerging nanostructured BP with distinguished nature has presented itself as a promising multi-functional material for a wide range of applications. In this review, we have summarized the recent advances in the synthesis of BP and its nanostructures ranging from 0D to 3D. Enormous efforts have been devoted to the synthesis of bulk BP and its nanostructured counterparts with desired properties. However, some critical challenges remain to be overcome before their practical implementation. First and foremost, the stability of nanostructured BP under ambient conditions needs to be addressed. So far, coating aluminum oxide or boron nitride on the surface of phosphorene has been demonstrated as an effective passivation way through preventing the oxygen permeation [93]. However, it is currently limited to a single piece of phosphorene and some voids remain between these physical passivation nanoparticles. Meanwhile, the impact of passivation layers on the electronic and electrochemical properties needs to be also considered. Therefore, it could be a promising method through inactivating the surface phosphorus at atomic level via occupying its lone electron pair by exfoliation agents.

Second, the synthesis of bulk BP is still at a low yield (e.g., several grams per batch) due to the lack of in-depth understanding of the growth mechanism. In addition, the majority of research work regarding the preparation of nanostructured BP is based on the top-down method from bulk BP crystals, making the synthesis far less productive. In this regard, the less-developed bottom-up approaches need much more attention, which could hold great potential for realizing controllable and high-yield production. In addition, the development of reliable and reproducible synthetic means the possibility of wafer-scale phosphorene for electronic applications is still exciting since great achievements in producing wafer-scale graphene and transition metal dichalcogenides by CVD have been demonstrated to be effective.

Finally, the synthesis of 3D BP is rather less fruitful despite being highly rewarding for electrocatalytic applications due to abundant active sites and good ionic/electron transport along channels. Currently, to our knowledge, electrochemical methods have been reported as the only way to prepare 3D BP. Other promising approaches, which have been known for their success in converting 2D materials into 3D, such as template-assisted, electrospinning, and hydrothermal strategies, could also be adopted. Overall, although BP and its nanostructures have demonstrated their unique feasibility in a wide range of applications, the development of their synthetic methods, which is of primary concern, is still in its infancy and the exciting achievements are still on the way.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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