REVIEW

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Synthesis, modification, and application of black phosphorus, few-layer black phosphorus (FLBP), and phosphorene: a detailed review

Nasrin Sultana, [iD] [ab] Annabelle Degg,[c] Samiran Upadhyaya, [iD] [a] Tom Nilges[c] and Neelotpal Sen Sarma [iD] *[a]

In the last few years, new two-dimensional (2-D) materials have garnered the scientific community's attention with the growing demand for functionalized materials for advanced electrical and biomedical applications. Among all the developed 2-D materials, black phosphorus and FLBP (few-layer black phosphorus), *i.e.*, phosphorene, has been in tremendous demand due to its unique electrical, optical, physical, and electrochemical properties. Its tunable bandgap enables the fabrication of sensing materials that could be utilized in various fields such as health care, batteries, transistors, photovoltaics (PV) and many more probable applications. However, properties like high conductivity, carrier mobility, tensile strength, and bio-safety make phosphorene an essential candidate for electrical and bio-medical applications. The present review highlights phosphorene's unique properties, potential applications, and prospects as an emerging 2-D single elemental material. A particular focus has been laid on the most recent studies on the synthetic approaches and modifications of phosphorene, mainly aimed at its functionalization and stabilization for prospective applications in different fields.

1. Introduction

Over the last decade, there has been a sharp growth in the use of 2-D nanomaterials in electronics, sensing, dye degradation, and different biomedical applications, including targeted drug delivery, hyperthermia induced photo-ablation therapy, bio-imaging, and bio-sensors.[1,2] In recent years, after the first isolation of graphene an enormous number of reports have been published related to 2-D layered materials ranging from protective coating to biochemical sensing. Until a few years ago, graphene was the only material comprising a single element that exhibited outstanding electronic and mechanical properties, and carrier transport, leading to restructuring in different technological areas. But the lack of a bandgap in graphene limited its use in electronic devices and their fabrication. With the efforts of researchers around the globe, phosphorene as a newly emerging 2-D material, also known as mono or few-layer black phosphorus (FLBP), was developed. Phosphorene is also a single-elemental 2-D material and can be synthesized from black phosphorus. The layers of BP are held together by the weak van der Waals forces which makes it a valuable source for

producing free-standing 2-D nanosheets. It can serve as a supporting substrate or an active sensing element in different fields, such as health care. In addition, it is also a favorable material for other applications, such as batteries, transistors, and photovoltaics (PV).[3] It is an emerging competitor to other 2-D materials, as it is a p-type semiconductor and can be used in optoelectronics and semiconductor-based devices.[4–17] The bandgap value of FLBP depends on the manifold stacking layers (*i.e.*, bulk ∼0.3 eV, bilayer ∼1.88 eV, and mono layer ∼2.0 eV), which could be functionalized and attuned to the desired application.[18] It has also attracted enormous interest because of its superior physical properties, such as high mechanical strength, desirable photo-electronic performance, and excellent biocompatibility. The most desirable advantage of phosphorene over other 2-D materials is its *in vivo* biodegradability, *i.e.*, it can be degraded inside the human body, making it a potential candidate for drug delivery.[19] Due to the tunable bandgap, broad absorption across the ultraviolet, visible light, and infra-red regions is possible. So, it can allow colorimetric and fluorescence detection of various types of bio-analytes like proteins, inorganic ions, and DNA. Phosphorene can be considered as one of the most ideal materials for device fabrication compared to other contemporary materials.

Recent studies have revealed the potential applications of phosphorene in various fields. Zhang *et al.* have theoretically shown that phosphorene can easily pass through the cell

[a] *Institute of Advanced Study in Science and Technology, Paschim Boragaon, Guwahati-35, Assam, India. E-mail: neelot@iasst.gov.in*

[b] *Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India*

[c] *Technical University of Muenchen, Lichtenbergstr.4, 85748 Garching, Germany*

membrane and extract many phospholipids from it, thereby inducing membrane degradation and reducing cell viability.[20] Dharani *et al.* demonstrated phosphorene as a sensing material to detect the presence of chronic obstructive pulmonary disease (COPD) biomarker volatiles.[21] Liang *et al.* developed a biosensor by synthesizing phosphorene stabilized with a coating of hexamethylenediamine (HMA), which exhibited a concentration-dependent response to 3,3′,4,4′-polychlorinated biphenyl (PCB77).[22] Qiu *et al.*, in their review, described the various aspects and applications of phosphorene in biomedical fields, such as bio-imaging, photothermal therapy (PTT), photodynamic therapy (PDT), and combination strategies.[18] Although the properties and application of phosphorene have been a topic of immense interest in recent times, minimal studies on its applications have been performed. Most of the recent reviews have been primarily focused on the structural aspects of phosphorene, but detailed analysis of the physico–chemical properties is of utmost importance[23–29] and is still awaited.

To understand the overall structural properties and explore potential future applications, detailed insight into the various aspects of phosphorene is necessary, including biological and electronic aspects. This review presents a detailed analysis of the recent advantages of 2-D materials in health care and bio-sensing applications ranging from neural interfacing to therapeutic to wearable devices. This review mainly focuses on (i) a comprehensive estimation of different properties over a wide range of 2-D systems, (ii) a comparison of biosensors based on 2-D materials, and (iii) mass production and commercialization.

2. Outline of 2-D phosphorene

2.1. Structural features and properties

Over the last few years, there has been growing interest in recognizing the comparative properties of BP for further experimental and theoretical research. After its first synthesis in 1914, the fundamental properties of BP such as density, specific heat capacity and electrical conductivity were determined subsequently. Hultgren and Gindrich specified the lattice and crystal structure parameters of BP.[30] After almost two decades, Keyes determined the electrical conductivity of BP up to 350 °C and 8000 kg cm^{-2} as a function of temperature and pressure.[31] According to the study, it was found that as an intrinsic

semiconductor, BP has a bandgap of about 0.33 eV at high temperatures. In the 1980s, researchers from Japan were able to form a large single crystal from melted red phosphorus under high pressure, using wedge-type cubic anvil apparatus, cooling down slowly under high pressure;[32] this paved the way for the study of the optical and electrical properties of BP. Large single crystals of BP up to 10 mm lateral size suitable for a top-down synthesis of phosphorene can be grown by short way transport.[33,34] Today, the majority of commercially available BP and phosphorene in a top-down fabrication process is still produced by this route despite various other top-down and bottom-up approaches.

The chemical properties of BP were initially predicted using quantum chemical calculations,[35–38] followed by multiple experiments. Scientists have been investigating different fascinating characteristics of BP such as mechanical stability,[38] optoelectronic features, electrical conductance,[39] anisotropic features, layer-dependent bandgap variation, *etc.*[40,41]

A detailed description of the research on the study of fundamental properties and phosphorene status is presented in the following sections.

2.1.1. Structural features. 2-D phosphorene is a layered material in which the layers are held together by van der Waals forces (Fig. 1a). The planes are made up of sp^3 hybridized P-atoms with distorted tetrahedral angles. Phosphorene has a puckered and bilayer configuration along the armchair direction (*c*-axis) and zig-zag direction (*a*-axis). With remarkable non-planarity in the shape of structural elevation, phosphorene has a honeycomb-like lattice structure. According to neoteric studies, lattice constants are $a = 4.52 \pm 0.05$ Å and $b = 3.31 \pm 0.03$ Å along the perpendicular directions (Fig. 1b), with the margin of error being dependent on the number of layers.[42–45] The number of layers can also influence the hinge angle (for bulk BP $\theta_1 = 96.16°$ and single-layer phosphorene $\theta_1 = 96°$) and the dihedral angle (for bulk BP $\theta_1 = 102.42°$ and single-layer phosphorene $\theta_1 = 103.51°$).[46]

2.1.2. Fundamental properties. Among all the other 2D materials explored over the past few years like graphene, hexagonal- boron nitride (h-BN), MoS$_2$, and WSe$_2$, phosphorene has been considered as one of the best 2-D materials due to its fascinating physical properties. However, graphene is still considered an ideal material with the highest thermal conductivity, charge mobility, stiffness, and zero bandgaps that lead to
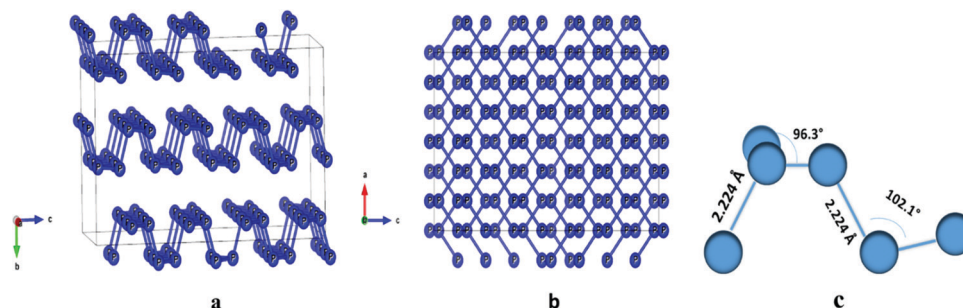

Fig. 1 (a) The crystal structure of BP; (b) crystal structure view along the *b*-axis; (c) bond length and bond angles of phosphorene.[47]

Table 1 Comparison between phosphorene and other 2-D materials based on their physical properties

2D materials	Band gap (eV)	Carrier mobility (cm^2 m^{-1} S^{-1})	ON/OFF ratio	Thermal conductance (W m^{-1} K^{-1})	Thermoelectric performance, ZT	Young's modulus (N m^{-2})	Features strain (%)	Conductance type
Phosphorene (semiconductor)[50–52,54–58]	0.3–0.2	~1000	10^3–10^5	10–36	1–2.5	35–166	24–32	p-Type
Graphene (semiconductor)[52,58,59–64]	0	~2 × 10^5	5.5–44	5 × 10^3	~0	1000	27–38	Ambipolar
MoS$_2$ (semiconductor)[52,58,65–70]	1.2–1.8	10–200	10^6–10^8	34.5–52	0.4	270 ± 100	25–33	n-Type
WSe$_2$ (semiconductor)[58,65,71–77]	1.2	140–500	10^4–10^6	9.7	0.91	75–195	26–37	Ambipolar
h-BN (insulator)[58,78–80]	1.7	—		250–360	—	220–880	24	—

a low ON/OFF ratio.[48] Other 2D materials such as MoS$_2$ and WSe$_2$ have extremely high ON/OFF ratios, owing to their high bandgap contrary to that of graphene, and are good candidates in the field of thermoelectric devices.[49] On the other hand, phosphorene is a promising candidate for optoelectronic device applications due to its physical, mechanical, and chemical properties. Phosphorene can be imperative in novel applications such as solar cells due to its high carrier mobility. It has a tunable carrier mobility of ~300 cm^2 m^{-1} S^{-1} at 120 K and at room temperature it is ~1000 cm^2 m^{-1} S^{-1}.[50–53]

Phosphorene as a field-effect transistor (FET) shows an ON/OFF ratio of about 10^3–10^5. However, the measured thermal conductivities of phosphorene for an infinite length zig-zag and armchair sheets are 36 W m^{-1} K^{-1} and 110 W m^{-1} K^{-1}, respectively,[54] which are lower than those of graphene. The properties of different 2-D materials are presented in Table 1.

Phosphorene's high electrical and low thermal conductivities make it a promising material for thermoelectric devices. Its optical absorption primarily depends on its structural orientation. He *et al.*, in their paper, suggested that the most significant absorption and diffusion coefficients of phosphorene are ~10 and ~16 times in the armchair direction, which are greater than those in any other direction.[81]

In a recent review, Rahman *et al.* predicted phosphorene as an ideal material for water splitting dynamics application and discussed the stability of the material when exposed to water, light, air, and temperature. Such distinctive properties of phosphorene make it a suitable material for the conversion processes of photo-energy, *i.e.*, solar cells and photo-catalysis applications.[82] Another unique feature of phosphorene is the high in-plane anisotropic band dispersion near the Fermi level in the Brillouin zone (BZ). Other 2-D materials do not usually possess in-plane anisotropy.[83–85] This unique feature distinguishes phosphorene significantly from other 2-D materials, leading to more than fifty percent direction-dependent optical and electronic properties.[86–88]

Kou *et al.* came up with a comprehensive colloquy on phosphorene and its anisotropic characteristics. Based on its directional anisotropy, the hole mobility of phosphorene is 16–38 times greater along the *y*-direction than in the *x*-direction,[83] resulting in a higher elastic modulus along the *y*-direction. Theoretical studies show that single-layer phosphorene withstands tensile strain up to 27% along the zig-zag direction, and along the armchair direction, it is 30%.[86] Due to its remarkable mechanical properties, it shows excellent flexibility and has been employed in nano-electronic resonators.[89]

The energy gap of phosphorene is the key parameter for its convenient electronic applications, including solar cells. Being a p-type semiconductor, phosphorene has a tunable bandgap ranging from 0.3–2.0 eV based on their interlayer stacking, which has not been seen for any other 2-D materials. This range of bandgap tunability is notably more remarkable than that of semi-metallic graphene and slightly better or equal to those of WSe$_2$ and MoS$_2$ (1.2–1.8 eV), which makes it suitable for application in different electronic devices.[50–53] As phosphorene has a direct bandgap, it attracts further interest because most 2-D semiconducting materials do not have a direct bandgap.[90,91]

Zhao *et al.* reported in their paper that if two or more layers of phosphorene are twisted against each other forming a Moiré pattern, the electronic structure of such materials can be tuned. The bandgap of bilayer phosphorene can be tuned from 1.73 eV (monolayer) to 0.83 eV by twisting it at an angle of 19° while the non-twisted bilayer shows a bandgap of 1.1 eV.[92]

3. Preparative methods

Preparative practices of 2-D nanostructured phosphorene can be classified into two types: top-down methods (mechanical exfoliation, liquid-phase exfoliation, plasma etching, *etc.*) and bottom-up methods (chemical deposition, hydrothermal synthesis, pulsed layer deposition, *etc.*).[93] Separation of the layers of BP is possible because they are held together only by weak van der Waals interlayer interactions.

Fig. 2 shows the different pathways for the synthesis of phosphorene.

3.1. Top-down methods

The top-down methods comprise synthetic processes such as liquid-phase exfoliation, mechanical exfoliation, and electrochemical exfoliation.

3.1.1. Liquid-based Exfoliation of BP. In this method, bulk BP is first suspended in a preferable solvent. The ionic species are intercalated into the BP interlayer space by applying ultrasonic voltage or energy. On applying high energy, bulk BP exfoliates into monolayer or few-layer phosphorene nanosheets with a wide or specific size range. The mostly used liquid-based exfoliation methods to prepare phosphorene nanosheets are ultra-sonication, bipolar electrochemical, and electrochemical anodic/cathodic techniques. Fig. 3(a–c) depict commonly used liquid-based exfoliation methods for BP. Other methods like microfluidics, microwave-associated, wet-jet milling, and
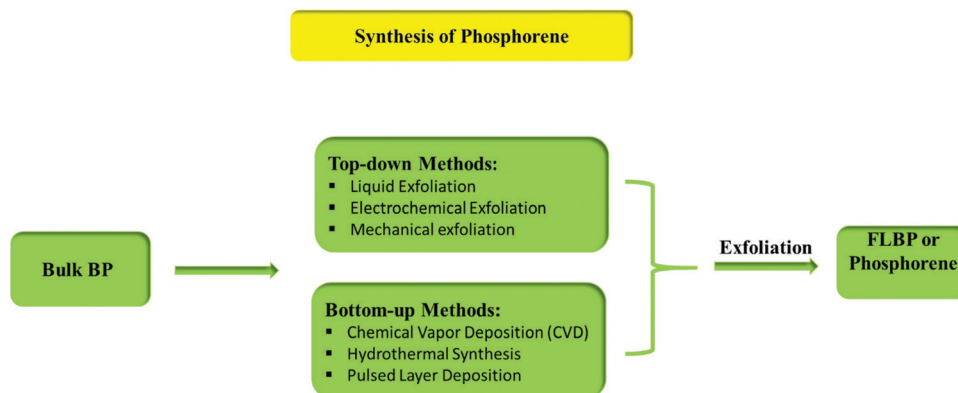
Synthesis of Phosphorene

Top-down Methods:
- Liquid Exfoliation
- Electrochemical Exfoliation
- Mechanical exfoliation

Bulk BP

Bottom-up Methods:
- Chemical Vapor Deposition (CVD)
- Hydrothermal Synthesis
- Pulsed Layer Deposition

Exfoliation

FLBP or Phosphorene

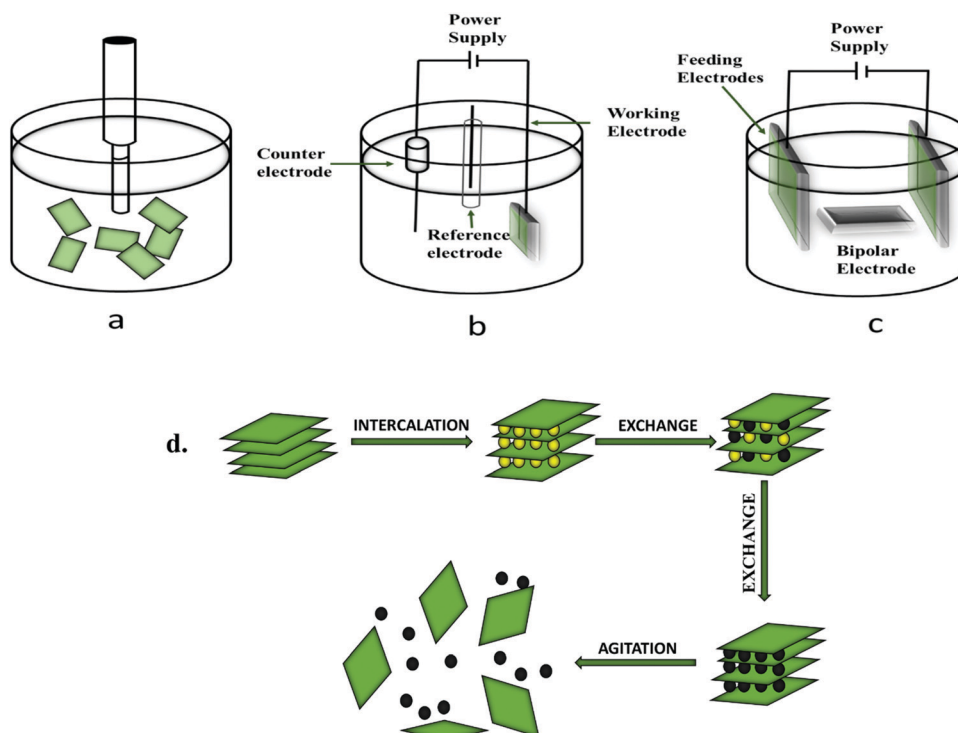Fig. 2 Different preparative methods of FLBP or phosphorene.[94]

Fig. 3 Schematic representation of liquid–based exfoliation, (a) ultra sonication, (b) electrochemical anodic or cathodic method, (c) bipolar electrochemical exfoliation method, and (d) schematic representation showing the exfoliation of BP nanosheets.

laser-assisted methods are also used for exfoliation. In this study, the effect of different parameters and conditions will also be briefly reviewed and discussed on the liquid-based exfoliation of BP to phosphorene.[23]

The exfoliation of BP *via* the ultra-sonication method involves dispersion in a preferable solvent followed by sonication, and then the exfoliated nanosheets are collected by the centrifugation method. At the time of sonication, due to the fluctuations and shear forces, micro-and nano-sized bubbles are produced. The solvent molecules, such as *N*-methyl pyrrolidone (NMP), DMSO, *etc.*, intercalate between the layers of BP and disperse the nanosheets within it, as depicted in Fig. 4. For the liquid-based exfoliation through the ultrasonic method,

selection of a favorable liquid solvent system for dispersion and exfoliation is necessary. The theoretical calculations of surface energy and surface tension provided information on the suitability of solvents for the exfoliation of 2-D materials. Previous studies confirmed that with the increase in surface tension of solvents, the exfoliation yield of BP increases. Unlike other 2-D materials, the production and large-scale exfoliation of phosphorene nanosheets should be anhydrous and free of oxygen because of the chemisorption of O-atoms by P-atoms present on the surface of BP nanosheets.[95–101]

3.1.2. Electrochemical exfoliation. Electrochemical exfoliation is a method in which a voltage is applied to expand and exfoliate the individual sheets of black phosphorus. It is a
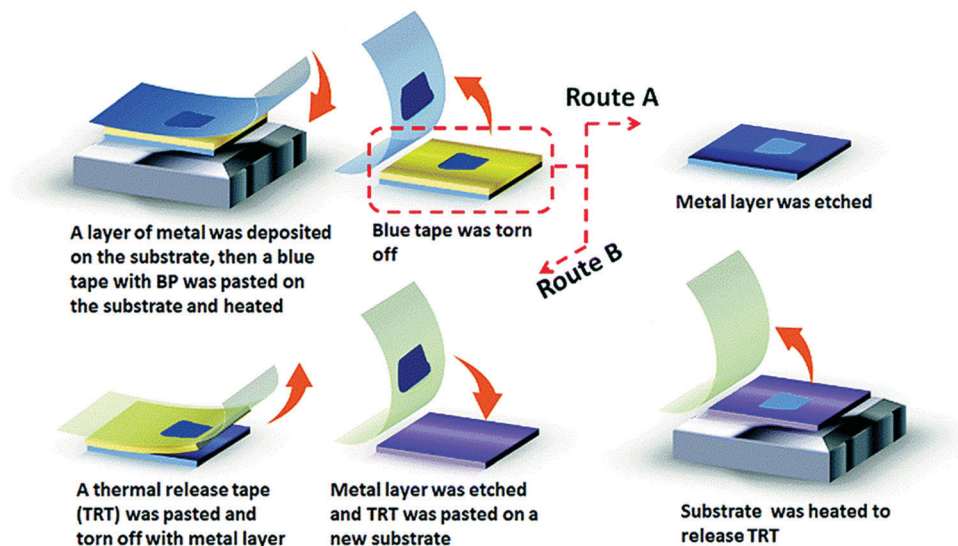
Fig. 4 Metal assisted exfoliation of FLBP[121] (reproduced with permission from ref. 121, published by Royal Society of Chemistry 2018).

simple, economic, and eco-friendly approach for the exfoliation of 2-D materials.[102–107] There are three classifications of electrochemical exfoliation: anodic, cathodic, and electrolytic electrochemical exfoliation.

3.1.2.1 Anodic electrochemical exfoliation. It is a simple method and the implementation is also easy. Among all the aqueous electrolytes for anodic exfoliation, sulfates are the most efficient negative ions for such types of exfoliations.[108] The first group to use anodic exfoliation to prepare BP nano sheets was Ernade and coworkers using Na_2SO_4 solution. Their work involves the use of BP and Pt wire as an anode and a counter electrode, respectively.[109] Since, their work does not provide any information regarding the nanosheets' morphology, yield, mechanism, and defects, they further studied and tried to prepare exfoliated BP with a yield of about 80% using an excellent mechanical approach. However, during exfoliation, Ph is prone to oxidation.[110] Ambrosi and co-workers evaluated the anodic exfoliation of BP in an acidic solution, *i.e.*, H_2SO_4, both in the presence and absence of an applied potential (3 V). The main advantage of anodic exfoliation is that it can work at a lower potential, which may lead to the low probability of oxidation of the BP nanosheets.[111]

3.1.2.2 Cathodic electrochemical exfoliation. This method involves the insertion of electrolytes and positive ions inside the nanosheets of BP by applying a negative potential. Cathodic exfoliation has more efficiency than the anodic one due to the low oxidation rate.[112] The used intercalating agent must have high solubility in the solvents to generate cations at high voltage.

Lingxin *et al.*, in their work, forward a highly efficient and simple method to synthesize and exfoliate BP through the electrochemical cathodic exfoliation process using ethylene imine polymer (PEI) as a solvent. This method does not involve any high temperature, pressure, or sonication. PEI, in this context, acts as an expanding agent to expand the layers of BP. This PEI-FLBP composite could prevent the newly peeled-off FLBP from accumulating and improve the compatibility between PEI-FLBP nanosheets and the waterborne polyurethane (WPU) matrix. This FLBP-PEI and WPU matrix has significantly increased the tensile stress.[113]

He *et al.* reported a cathodic electrochemical method for the exfoliation of bulky BP into FLBP. In general, the already established method for electrochemical exfoliation in an aqueous solution may result in the oxidation of the BP nanosheets.[112] Therefore, their group showed an appropriate and straightforward method that would exfoliate the crystals of BP into nanosheets and reduce the oxidation efficiency.[114]

3.1.2.3 Electrolytic electrochemical exfoliation. Bulk BP is necessary for anodic and cathodic electrochemical exfoliation. These materials are expensive and can hamper the application of electrochemical exfoliation in preparing the sheets of phosphorene. Baboukani *et al.* contrive high quality and orthorhombic crystal structured phosphorene through electrochemical exfoliation using deionized water.[115] This work does not involve any expensive bulk BP and Pt electrodes or any other organic solvents. This method is cost-effective and environmentally friendly and provides insight into future advances in the electrochemical exfoliation of BP into Ph nanosheets. In 2016, Mayorga-Martinez and co-workers synthesized BP nanoparticles using electrochemical exfoliation in Na_2SO_4 solution by applying opposite potentials.[116]

3.1.3. Mechanical exfoliation (the Scotch tape method). Another method used for the preparation of thin, layered materials is mechanical exfoliation. Exfoliation of BP can be easily carried out due to its weak interlayer van der Waals forces.[117] This type of exfoliation is also called the Scotch-tape delamination, which can be performed with the aid of adhesive tapes, like Scotch Magic tape™ or blue Nitro tape.[118] In this process, first a single layer BP nanosheet with a thickness of

0.85 nm is created with the help of the scotch tape.[119] These nanosheets of BP are then transferred onto a Si/SiO$_2$ substrate, which is then washed with acetone, isopropyl alcohol, and methanol in order to remove the scotch tape residue. After this, the remaining part is treated thermally until the removal of the solvent residues, and finally, the required nanosheets are obtained. The main drawback of using this method is the low yield and the difficulty in getting a large-sized monolayer or few-layered BP (FLBP).

Sha *et al.*, in their paper, found that a fine layer of Au or Ag on the Si/SiO$_2$ substrate can notably enhance the yield and the exfoliation of FLBP.[120] In this work, a layer of Ag or Au is first deposited on the surface of Si/SiO$_2$, Si water, or other substrates like PDMS using magnetron sputtering. BP is then pasted on the surface of the blue tap and put on the substrate, followed by heating. The blue tape is ripped off, and to keep the FLBP on the substrate, the metal layer on it to be removed. FLBP can also be transferred onto other preferred solvents using this technique. Fig. 4 shows the diagrammatic depiction of metal-assisted exfoliation of BP.

Commonly used metal-assisted exfoliation has disadvantages such as instability, low yield, and lack of control regarding size, thickness, and shape. To overcome these obstacles and obtain a high yield of nano BP, polydimethylsiloxane (PDMS) can be used as an additional layer on the substrate.[122] The transfer of BP *via* the PDMS substrate using the fully dry transfer technology can solve the problem of adhesive tape residue.[123] The metal-assisted mechanical exfoliation method was introduced to synthesize FLBP with a lateral size of >50 μm and a surface area larger than the one obtained from the typical scotch tape technique.[124] Although this process shows some positive results, the uncontrollable morphology and low yield of BP still need to be addressed.

3.2. Bottom-up method

Bottom-up methods include chemical vapor deposition (CVD), hydrothermal synthesis, and pulsed layer deposition. It can be said that to date there has been no promising method known for the large-scale synthesis of phosphorene. The main idea to synthesize phosphorene *via* the bottom-up process came from the approaches usually used for graphene and transition metal di-chalcogenides (TMD). However, CVD helps to grow graphene and monolayers of TMD but is not reliable for phosphorene because suitable non-toxic phosphorus-based precursors are absent. In the hydrothermal synthesis, the main problem is the instability of phosphorene as it is prone to oxidation. One can successfully synthesize phosphorene under oxygen-free conditions using wet chemical methods such as solvothermal synthesis, self-assembly, template-assisted growth; and hydrothermal processes.[125]

Tian *et al.*, in their paper, discussed the synthetic process for FLBP nanosheets in gram-scale quantities through the bottom-up approach. They have used white phosphorus as the raw material, which involves an ethylene diamine system of the direct solvothermal process operating in a temperature range of 60–140 °C, as shown in Fig. 6. The 2-D material has
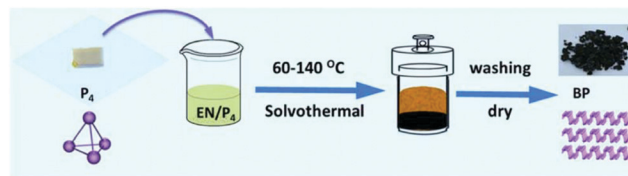

Fig. 5 Schematic representation of the synthesis of FLBP *via* the solvothermal process (reproduced from M. Pica and R. D'Amato, *Chemistry of Phosphorene: Synthesis, Functionalization and Biomedical Applications in an Update Review. Inorganics*, 2020, **8**(4), 29.; published by MDPI, Basel, Switzerland). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (https://doi.org/10.3390/inorganics8040029).

a 0.8–1.0 μm lateral size, where the thickness of flakes decreases with increasing temperature until 100 °C. However, a further increase in the temperature results in an increase in flake thickness. The thickness corresponding to 2–28 phosphorene atomic layers is about 1–15 nm. Even though the occurrence of oxidation was unavoidable in the sample, it was considered as an advantageous synthetic procedure for improving BP stability.[126]

The synthesis of FLBP *via* the solvothermal process has been depicted schematically in Fig. 5.

Gao *et al.* showed that the breaking of phosphorene sheets is initiated due to the strong interaction between phosphorus and the substrate, while the weak interaction is not much effective in stabilizing the 2-D sheets. An intermediate exchange per P-atom of about 0.35 eV is required for the proper growth of 2-D phosphorene. They also studied the effect of divergent substrate growth of phosphorene on Au (111), tellurium functionalized Au (111), and Cu (111). According to their investigation, the interaction of phosphorus with Cu (111) is strong, leading to random dispersion of phosphorus nanoclusters and single atoms. Au (111) functionalized tellurium (Te) can weaken the monolayer interaction between phosphorus and the substrate. The successful growth of a quasi, free-standing single-layer phosphorene on Te/Au (111) was observed with the help of low-temperature scanning tunneling microscopy (LT-STM), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT). Such successful quasi, free-standing films could further enable their application in fields of optoelectronic and electronic devices.[127]

There are reports which show the molecular beam epitaxy (MBE) growth of FLBP quantum dots (BPQD) on Si substrate using P_{white} as the precursor at a shallow temperature. According to the AFM analysis, the average radius and height were 27.5 ± 5 nm and 3.1 ± 0.6 nm, respectively, for BPQDs.[128]

Recently, the growth mechanism of phosphorene and BP from the gas phase was reported where SnI$_2$ acted as the important gas phase species to activate and transform white phosphorus into phosphorene.[129]

4. Functionalization of phosphorene

According to their specific applications, the functionalization of 2-D materials is carried out to tune their chemical, physical,

and electronic properties. Functionalization of phosphorene is usually aimed at improving stability as it is prone to oxidation when coming into contact with air and oxygen. On exposure to light, the degradation of phosphorene speeds up to form phosphate on the surface. The oxidation rate can be reduced by monitoring the thickness, light intensity, oxygen concentration, and energy gap.[130,131] However, the oxidative degradation of phosphorene is under investigation and not well understood yet. There are numerous blueprints to overcome such disadvantages and stabilize phosphorene through functionalization. The stabilization techniques include introducing a thin protection layer to prevent oxidation, lead to the formation of a heterostructure, and organic molecule passivation. Formation of such conjugates takes place *via* non-covalent interaction, encapsulation, transition metal acceptor fragments, or covering the surface with acidic chemical groups.[132] Covalent and non-covalent functionalization could enhance the intrinsic properties and circumvent the deterioration of the electronic structure of phosphorene. For instance, phosphorene can bind with soft materials, forming an advanced functionalized material.[133,134]

Kumar *et al.*, in their work, reported the functionalization of phosphorene with an artificial helical copolymer (a polypeptide). The composition of the biocompatible polypeptide with BP nanosheets could be suitable for biomedical devices for drug delivery and sensors. The main advantages of using such materials include (i) the passivation and encapsulation of BP nanosheets, (ii) their electronic interaction with BP nanosheets, (iii) the fabrication of BP in devices without sacrificing their inherent properties, and (iv) the protection of BP nanosheets from atmospheric oxygen.[133]

In another study, Pumera *et al.* reported the functionalization of BPSE (shear exfoliated BP) using non-covalent anthraquinone (AQ). In this process, BP and AQ were first exfoliated and then suspended in methanol, leading to the formation of a carbon-based layer in the BPSE-AQ sample with a lower oxidation rate which can be proven by XPS.[134]

Toffanin *et al.* studied the nature of physical and chemical interactions between 2-D BP and boronic acid or ester derivatives of pyrene. They showed the stability of 2-D BP on all the derivatives of boronic functionalities. This interaction leads to the limiting of the bandgap by around 0.10 eV of 2-D BP. According to them, modification of electronic structures can also increase the stability of such adduct. Such stabilizing interactions of 2-D BP and the conjugated organic molecules can be helpful in the synthesis of heterojunctions for optoelectronics, photonics, and chemical sensing applications.[135]

Wu *et al.* showed in their studies that the self-assembled monolayers of phosphorene with hexamethylenediamine (HMA) in chloroform encapsulated the surface of the material. First, a glove box was rigged to have definite oxygen and water levels, which would result in uniform hydroxylation. The introduction of – OH groups promotes the interaction with amino groups of HMA *via* hydrogen or ionic bonds to acquire a homogenous protective monolayer with a thickness of ~ 1.4 nm.[136]

Hair *et al.* developed a three-dimensional aptasensor for detecting norovirus using a BP–gold nanoparticle composite (BP–AuNCs). This composite has been prepared by *in situ* reduction of BP nanosheets with chloroauric acid. They have designed a movable working electrode that increases the ease of sampling and surface area and minimizes cross-contamination. The proposed aptasensor exhibits high selectivity, stability, and repeatability. This 3D aptasensor may provide a cost-effective, facile prototype for the detection of norovirus.[137]

Yanting and co-workers reported a new material for sensing based on phosphorene and a 2-D triazine polymer. These polymer sheets can prevent the opaque assemble of gas molecules on the surface of phosphorene, leading to a profuse pathway for the penetration and adsorption of gas molecules. Such nanocomposite evinces ambient selectivity, sensitivity, flexibility, and stability to detect gases like NO_2. This nanospacer intercalation blueprint can enlarge the 2-D nanomaterials for gas sensing. This outcome provides an ingenuity to improve more such 2-D polymer and nanomaterial composites for wearable electronics.[138]

5. Superiority over graphene and other 2-D materials

Following the discovery of graphene in 2004, 2-D materials have emerged as potential candidates in materials science and technology. 2-D materials, such as graphene, MoS_2, TMDs, *etc.*, have found applications in photovoltaics, photodetectors, and light emitters. Although graphene and other 2-D materials exhibit some excellent properties, their applications have been limited due to their large bandgap, resulting in optical absorptivity shrink. In addition, structural modification of these materials also could not tune their bandgap, and therefore a substitute to the existing 2-D materials was necessary.

The discovery of BP led to the foundation stone for developing materials with appreciable and tunable bandgaps, which was the primary concern towards using 2-D materials. Thus BP can be considered as one of the potential material for a wide range of areas including energy production and storage among the other 2-D materials. Although the bulk form was successfully synthesized about 100 years ago, its 2-D form was demonstrated only in 2014 by the mechanical exfoliation method. BP is a semiconductor with a direct bandgap in bulk and monolayer forms of about ~ 0.3 eV and ~ 2 eV, respectively, thereby bridging the gap between other 2-D semiconducting materials (TMDs ~ 1.29 eV to ~ 1.8 eV) and graphene (0 eV). The tunable bandgap of BP has made it a potential candidate for developing transistors, photodetectors, sensors, optical devices, solar cells, catalysts, thermoelectrics, triboelectric nanogenerators, supercapacitors, and batteries and in bioimaging. Although it has some fascinating properties which originated from its unique structural features, some intrinsic deficiencies are also observed. Several methods could resolve the inherent flaws, including surface passivation, deposition of protective layers,

and surface functionalization by chemical passivation for better stabilization and performance. Nevertheless, BP is currently the best material of choice for these wide range of applications.[139–170]

6. Application

Black phosphorus, a blueprint of phosphorene, has been known for more than 100 years. It is a candidate for various applications, including electronics, energy, photothermal devices, sensing, optoelectronics, photovoltaics, and batteries, demonstrated in multiple aspects.[171] The schematic representations showing various applications of phosphorene are depicted in Fig. 6.

6.1. BP for solar cells

The complete replacement of fossil fuels and nuclear energy has been a crucial issue in modern society and for the future. A genuinely sustainable alternative for such energy sources should be cheap, renewable, clean, and safe.[172] The radiation of the sun can be harnessed in all areas of the world; this idea has received considerable attention. Solar energy can be used to generate electricity (photovoltaics, PV) or for heating. However, the cost-effectiveness and low sunlight-to-electrical energy efficiency limit their applicability, and hence the replacement of Si solar cells is necessary.

In recent years, scientists have mainly focused on developing semiconducting materials, organic compounds, dye sensitizers, perovskite crystals, heterojunction interfaces, and quantum dots (QDs), which are cost-effective and exhibit high performance compared to Si solar cells.[173] Intriguingly, BP has a stellar set of properties that qualify it for application in solar cells, namely, carrier mobility, high ambipolar transport properties, and tunable bandgap.[174,175] BP and its derivatives have the potential to be used in developing high efficiency solar cells based on the grounds of theoretical and experimental results.

Fig. 6   Different applications of FLBP or phosphorene.

Zhang et al. reported a perovskite solar cell with high efficacy and stability. Thoughtful design and positioning of BP with tailored thickness as dual-functional nanomaterials enhance the carrier extraction at the perovskite/hole transport layer and electron transport layer/perovskite interface for highly stable and efficient perovskite solar cells. The combination of appreciative sequencing and collective cascade interfacial carrier extraction, rendered by concurrent positioning of BP, delivered a progressively enhanced power conversion efficiency from 16.95% to 19.83%. Further investigation revealed that BP incorporation through light absorption and reduced trap density can improve the performance of photovoltaic systems. This results in the pleading characteristics of the astute contrivance of BP as a dual-functional transport material for various sensors, light-emitting diodes, photodetectors, optoelectronic devices, etc.[176]

Zhiheng and co-workers developed a new phosphorene–polyimide and polyethylene glycol (PEG) aerogel composite to amplify the photo thermal energy. This aerogel composite leads to a remarkable increase in photo thermal energy and solar light absorption. The loading of PEG increases the volume capacity of the hybrid aerogel, obtained from the inception of Ph nanosheets. The hybrid polyimide–phosphorene and PEG exhibit photo thermal efficiency and latent heat capacity of 82.5% and 170 J g^{-1} respectively. This performance makes this hybrid composite effective for a broad range of solar energy storage and capture. This study also provides some encouraging blueprint for the development and design of high-performance hybrid materials for efficient utilization in the field of solar energy.[177]

Prabhat et al. investigated the effect of adsorption of atoms like K and Li based on the optical properties of BP using density functional theory (DFT). Their study reveals an enhancement of absorption of light for K and Li- atoms adsorbed on phosphorene in the visible range. Calculations suggested a negligible bandgap in the adsorbed structure than the pristine phosphorene. The peaks observed for the refractive index and dielectric constant are in accordance with the peaks in absorption. This high adsorption in the visible region suggested application in optoelectronic devices, including solar cells.[178]

Jian et al. in their work crossed linked BP and a hexagonal boron nitride graphene hybrid material rationally and calculated the high-power conversion efficiency of about 21.3% for excitonic solar cells (XSC). This heterojunction's excellent photo electronic conversion performance is due to the small conduction band offset, suitable bandgap (1.41 eV), and good visible light response. The boron nitride-graphene substrate with uneven interlayer charge transfer results in hole–electron puddle formation at the interfaces of the heterojunction. This will lead to a prototype of an optoelectronic device, which may be considered as a new direction for developing electronic energy storage devices in the near future.[179]

6.2. BP for biomedical application

Owing to the exceptional properties of 2-D materials, they have attracted a spectacular status in various technological and
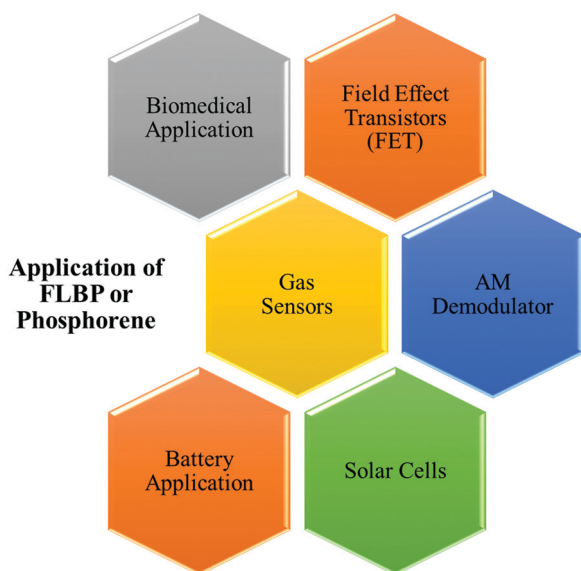
scientific disciplines. Compared to other 2-D materials, phosphorene or monolayer of BP has fascinating properties like excellent ON–OFF ratio, tunable bandgap, good carrier mobility, non-toxic biodegradability, and potent *in vivo* biocompatibility. For future biomedical technology, it is also a promising material. However, the practical approach is still highly challenging. Proper characterization and functionalization can make phosphorene a valuable material for future theranostic and biomedicine scenarios, regardless of such difficulties. However, 2-D materials like BP, MoS$_2$, graphene, hBN, WSe$_2$, *etc.* exhibit good biocompatibility based on the size of the material and concentration. When compared to other 2D materials, BP exhibits less cytotoxicity. Therefore, it is ideal for biomedical applications such as cancer therapy, biosensors, imaging and photothermal therapy, photoacoustic applications, drug delivery, photodynamic therapy, neural recognition, 3-D printing scaffold, *etc.* As it is a new material, there must be a proper investigation regarding the various inflammatory responses inside the systems and its effect on environmental exposure and reducing toxicity.[180]

BP is readily biodegradable inside the human body, producing non-toxic intermediates such as phosphates, phosphites, *etc.* It makes BP a suitable material for different *in vivo* biomedical applications.[181] However, other materials may accumulate inside the system, contributing to cytotoxicity and thus require essential functionalization with various surface coatings. It has both electron transferring and electron-donating capacities; combining these can enhance the reducibility of a catalyst in a reaction, improving biosensors' sensitivity. Therefore, easy degradation and stability-related issues become an advantage in biosensor applications. This advantage paved the way to enhance catalytic activity and possibility of constructing colorimetric biosensors for the first time. This work was performed using a hybrid BP–Au, synthesized by mixing FL-BP and Au precursor for about a few minutes at room temperature.[182] BP also has ambipolar nature, helpful for detecting positively and negatively charged species, making it suitable for biosensing applications. The non-toxic biodegradability of BP makes it ideal for cancer therapy. It can also be used for detecting various bio analytes (*e.g.*, immunoglobin (IgG) and myoglobin (Mb)) due to its tunable bandgap.[183]

Shabeer *et al.*, theoretically showed the ability of a carrier for thioguanine in drug delivery to treat diseases like cancer. Thioguanine is used for the treatment of leukemia. However, it is not biocompatible and has low aqueous solubility limiting its performance in cancer treatment. On the Ph surface, they have found three stable configurations of thioguanine with the absorption energy ranging from −76.99 kJ mol^{-1} to −38.69 kJ mol^{-1}, indicating physisorption of the drug on the phosphorene surface.[184]

6.3. Field effect transistors (FETs)

After the successful fabrication of FET using phosphorene in 2014 by Brien *et al.* and other groups, there have been many significant developments that have showcased phosphorene's novel properties for a variety of fields. These include engineering of electronic properties by strain, intrinsic electronic and transport properties, electric field, or doping of a transition metal; new phosphorene polymorphs with negligible molecular adsorption; gas sensors; low dimensional phosphorene derivatives; devices in electronics; and in photovoltaics.[185–210] Among all the applications of phosphorene, the most notable one is the fabrication of FETs. Conduction channels of a phosphorene-based FET can track the permitted light with different wavelengths. Therefore, it is a highly preferred material for near IR and night-vision imaging applications. Thus, researchers are making efforts to accomplish the performance of BP to construct PN junctions and solar cells.

For transistor applications, digital electronics takes huge advantage of the potential of semiconductors. The main criteria for achieving a great ON/OFF ratio are excellent charge mobility and adequate bandgap for high conductivity, low power consumption, and operational switching. In such cases, 2-D materials, especially phosphorene, with a controllable bandgap of 0.32 eV exhibited inclusive properties as a prospective transistor material. At room temperature, phosphorene has a high charge carrier mobility of about 600 cm^2 V^{-1} S^{-1}, leading to rationally rapid operation. The ability to tune the bandgap is notably valuable for electronic applications, specifically FETs. Due to adequate carrier mobility, it finds its uses in high voltage application with power gain. Phosphorene-based devices can be useful in high-frequency electronics because of their excellent current saturation properties. Thus, it is considered a prospective material for high-performance thin-film electronics applications at higher frequency. As phosphorene has a favorable bandgap and excellent mobility, it can also be used beyond transistors. It is used in semiconductor electronics, *i.e.*, amplitude modulated (AM) demodulators and circuits active for loudspeakers and radio receivers.[211]

6.4. Gas sensors

Among all the fascinating properties, the exceptional in-plane anisotropy of phosphorene influences its electrical, optical, mechanical, transport, and thermoelectric properties.

Liangzhi *et al.* calculated the adsorption of gas molecules like NO$_2$, CO$_2$, NO, CO, and NH$_3$ on the monolayer surface of phosphorene. According to their result, phosphorene's sensing performance transcends that of other 2D materials. They have determined the optimal adsorption of such gas molecules on the phosphorene surface, identified the molecular doping, and calculated the *I–V* relation using NEGF (non-equilibrium green's function formalism).[212]

Although there are numerous theoretical studies on phosphorene-based chemical sensors, a few experimental verifications are there for the introductory studies of this material. Ahmed *et al.* reported a chemical sensor using field-effect transistors based on BP. This BP-based gas sensor can detect NO$_2$ down to 5 ppb and is very sensitive. Its conductivity changes upon exposure to 5, 10, 15, 20, and 40 ppb, followed by the Langmuir isotherm for the adsorption on the surface. These results give an idea on the sensing and electronic

characteristics of BP, which can be of great importance in near future.[16] It is a material of choice and can easily replace current MoS_2 and graphene gas sensor materials. Far-reaching research has been performed to study the adsorption of gases like CO, CO_2, NH_3, and NO on single layers of graphene, MoS_2, and phosphorene. Among these materials, phosphorene shows better physisorption towards all the gaseous molecules due to its controllable electronic properties in optoelectronics and switching devices. Thus, it is one of the most suitable single-electron transistors (SET) for gas sensing applications. There are some reports regarding highly sensitive recognition of N-based molecules because of the stronger doping of phosphorene.[213,214]

Dian et al., in their work, substituted the P-atom of BP using Pt, Ag, and Au as dopants, which are more stable than the BP with only one substituted P-atom. They have shown the use of Ag-2P and Au-2P to detect NO gas. These dopants showed better catalytic activity toward the hydrogen evolution reaction than intact BP.[215]

6.5. Battery application

2D materials grab significant attention as anode materials in battery application due to their outstanding electronic properties and excellent surface-to-volume ratio. Current investigation and theoretical research have disclosed that phosphorene, with a high theoretical specific capacity of 2596 mA h g^{-1} and a potential of 0.4–1.2 V, can be a promising material for battery application. However, as an electrode, due to its good electrical conductivity, it possesses the potential to be used in rechargeable battery application in many industrial fields. At a 0.2 C current rate, the discharge capacity of phosphorene outperforms that of graphene by a factor of 7, which is higher than that of Li-ion batteries based on graphite, Ge, and Sn as anode materials. The reliability is demonstrated with a cycling life test, and it appears that the capacity retention of phosphorene after 100 cycles is 80%.[216]

There has been an extensive development of phosphorene-based Li-ion batteries as they have a reversible capacity and excellent cyclic continuance. The activity of such a battery is highly dependent on the capacity of Li and the cycling rate of anode materials. It has been confirmed that the binding of Li atoms with single-layered phosphorene is more robust than that with the bi-layered one. Therefore, monolayer phosphorene is appropriate as an anode material in Li-ion batteries, exhibiting larger capacity and lower open-circuit voltage. Calculations involving the ability of single-layer phosphorene show that it is superior as compared to other commercialized materials, which include graphite (372 mA h g^{-1}), TiO_2 polymorphs (200 mA h g^{-1}), and Ti_3C_2 (320 mA h g^{-1}).[217–219]

6.6. Amplitude-modulated (AM) demodulators

Amplitude-modulated (AM) demodulators are based on flexible BP, introduced recently to radio receivers, consisting of a single ambipolar BP transistor. The promoted mechanical robustness of BP transistors for uniaxial tensile strain and bending cycles is up to 2% and 5000, respectively. The fabrication method of flexible BP transistors on polyimide exhibited the most significant device mobility of almost 310 cm^2 V^{-1} s^{-1}, superior to the maximum TMD transistors' mobility. A study of BP-based AM modulator disclosed that it is the most appropriate layered semiconductor in terms of flexible nanoelectronics because of its remarkable properties, like ambipolar transport, excellent current saturation, and high mobility in an ambient environment.[220]

7. Conclusions and future prospects

The present review thoroughly explores the preparation, properties, functionalization, and applications of BP, FLBP or phosphorene in various fields. Due to their unique properties, phosphorene and its derivatives can be advanced materials for different applications in different areas, including electrical, energy storage, and optical applications. However, phosphorene is at the very early stage of development and has some issues which need to be resolved before its widespread practical application. As a relatively new member of the 2-D family, it displays exceptional properties over other materials like graphene and TMDCs. It combines a very desirable tunable bandgap with high charge mobility, which is indispensable for the recently demonstrated excellent performance of phosphorene-based devices such as the FETs. Extensive theoretical and experimental investigations have shown that phosphorene's novel electronic, mechanical, and transport properties exhibit intrinsic anisotropic behavior. Their electronic and transport properties are increasingly being investigated and understood, resulting in new opportunities for development and future research activities. Such unique characteristics make phosphorene an intriguing material among the burgeoning families of 2-D layered materials with significant applications in electronics and photovoltaics. Currently, most researchers focus on phosphorene's application and device demonstrations based on its tunable bandgap and high electron mobility.

Further work in phosphorene functionalization may reveal some superior properties and performance and other possible adjustments. However, challenges and opportunities coexist in studying and utilizing new materials. Degradation of phosphorene by oxidation and hydrophilicity are the significant hurdles that must be overcome for advanced future applications. Encapsulation and surface passivation techniques are some practical strategies that can ensure or even reduce structural and property degradation. Overall, its unique properties make it a promising material in materials science. The design and fabrication of advanced nanodevices and more fundamental and technological breakthroughs can be expected soon.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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