REVIEW ARTICLE

Phosphorene: Current status, challenges and opportunities

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Abstract   The field of 2-dimensional (2D) materials has witnessed a sharp growth since its inception and can majorly be attributed to the substantial technical and scientific developments, leading to significant improvements in their syntheses, characterization and applications. In the list of 2D materials, the relatively newer addition is phosphorene, which ideally consists of a single layer of black phosphorous. Keeping in mind the past, and ongoing research activities, this short account offers a brief overview of the present status and the associated challenges in the field of phosphorene-related research, with special emphasis on their syntheses, properties, applications and future opportunities.

1   Introduction

It is undeniable that the current energy concerns call for both scientific and industrial developments specifically related to the current manufacturing processes and the materials for energy-intensive applications [1,2]. To make the processes more efficient, selective and environmentally friendly, the development of different materials and fundamental understanding of their properties are essential. In this regard, nanomaterials (the materials, size of which falls between 10 to 100 nm), by virtue of their unique size and shape-dependent properties, have come a long way since Feynman first proposed the concept [3–5]. One of most recent albeit important class among the different types of nanomaterials is 2-dimensional (2D) nanomater-

ials, which comprise of a single layer with the thickness of one or two atom(s) [6]. Historically, graphene (or graphene-related systems) gained popularity as 2D nano-materials because of their exceptional electrical, thermal, mechanical properties, leading to various applications. However, in recent past, in parallel to the growth of graphene-related research, several 2D nanomaterials like TMDs (Transition Metal Dichalcogenides, MX_2, M = Mo, W, etc., X = S, Se, etc.) [7], germenes, silicenes are reported to overcome the challenges related to graphene [8]. In that list, probably the newest addition is single layer black phosphorous (BP) or popularly known as phosphorene (Fig. 1) [9].

Despite the first synthetic report of black phosphorus by Bridgman in 1914 [10], the research related to it did not flourish as anticipated mainly because of it's not-so-trivial high-pressure synthetic procedures and the limited knowledge about it's properties and applications. The field was rejuvenated when Park et al. utilized BP as anode materials in lithium-ion battery [11]. Subsequently, several reports identified the potential of BP as an active component in various energy-related devices [12]. In addition to the advancement in synthetic and technological tools, this revival can also be attributed to the researchers' quest to identify novel 2D nanomaterials, especially to resolve some of the issues related to graphene-based systems. The reclaimed fame of BP essentially originates from the 2D variations of BP and their corresponding layer-dependent properties [13]. Technically, only a single layer (in a more stringent definition of the term) of BP should fall under this category. But from a single layer to few layers (< 5) of BP can also be included in this category. Nonetheless, irrespective of the initial dispute regarding the nomenclature, they all are termed as "phosphorene" in order to establish its resemblance with graphene [14].

Among the reported allotropes of phosphorous, BP, the thermodynamically most stable allotrope, was first synthesized from white phosphorous using high pressure and
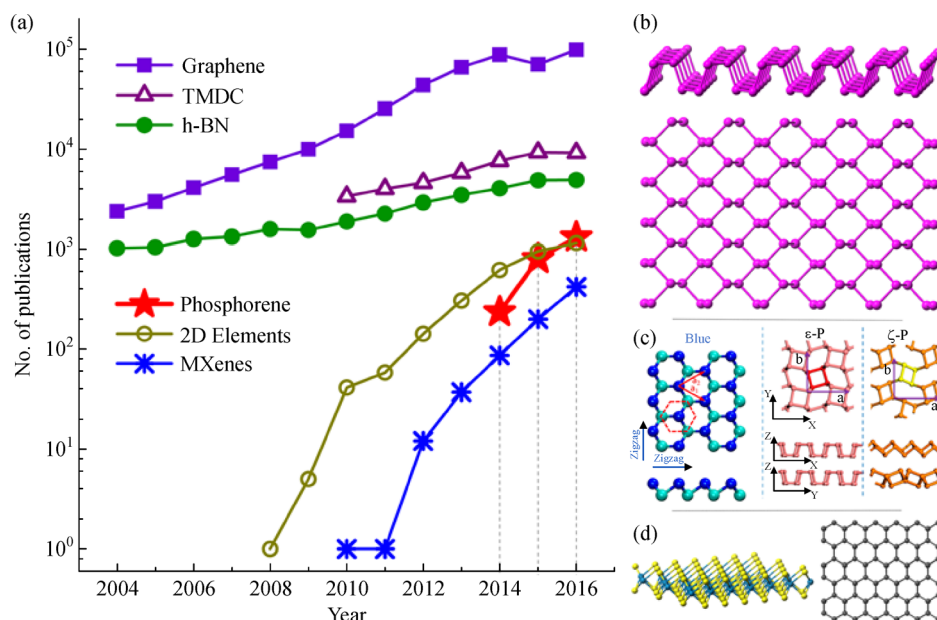
Fig. 1 (a) Comparison of the 2D materials in terms of number of published articles during a decade (The vertical axis is in log scale. Key words: graphene, hexagonal boron nitride, phosphorene, mxenes, MoS_2 or WS_2 or $MoSe_2$ or WSe_2 or $MoTe_2$, silicene or germanene; Search engine: Google Scholar); (b) Crystal structure of phosphorene (side and top view); (c) Structures of three predicted polymorphs of phosphorene; (d) Crystal structures of monolayer of MoS_2 (left) and graphene (right). Images c adapted with permission from the ref. [15] Copyright 2015 Nature Publishing Group, and the ref. [16]. Copyright 2015 American Chemical Society

temperature [10]. In its bulk form, it consists of vertically stacked 2D sheets, each of which is called phosphorene [17]. The crystallographic and other characterization evidences (vide infra) suggest a puckered configuration of phosphorene where each sp^3 hybridized phosphorous atom forms bonds with three neighboring phosphorous, leaving a lone-pair of electrons on them (Fig. 2). Because of this sp^3 hybridization, the phosphorene single layer does not form a single sheet-like graphene. Every single layer contains two atomic layers, which leads to two distinct distances among the neighboring phosphorous atoms: one with the neighboring atom in the same layer (2.224 Å) and the other one is between the two layers (2.244 Å) [17,18]. In case of BP, each of the single layers of phosphorene is connected via weak interlayer van der Walls interaction (inter-layer spacing of ~0.53 nm as compared to 0.33 nm spacing in graphene) and can easily be disrupted to yield a single layer of phosphorene [13,19]. Due to the presence of two atomic layers in a single layer of phosphorene, originating from the unique bonding patterns of phosphorous, both "zigzag" and "arm-chair" structural features are observed, which in turn display the anisotropic behavior of phosphorene along the two directions [13,15].

2 Current status

In view of the current scientific progress on phosphorene and/or BP, the following sub-sections attempt to summarize the highlights of synthesis, characterization/properties

and applications of phosphorene. In addition to the available reviews and primary literatures on phosphorene, the following subsections have been described based on the recent review by Rumeli and co-workers [20] as it aims to cover broad areas of research on phosphorene.

2.1 Characterization and properties

The investigation of mechanical, photonic, electrical, optical properties of phosphorene has been of great interest in recent times due to significant advancement of instrumental techniques. In the current section, detailed discussion on properties related to specific applications is omitted to avoid possible overlap with the application sections (vide infra).

The microscopic techniques has definitely emerged as a powerful technique in order to understand the morphology as well as crystal stacking of the phosphorene [21]. Along with the high resolution transmission electron microscopy (HRTEM), which is in good agreement with the crystallographic evidence, the selected area electron diffraction (SAED) images show characteristic (101), (002) and (200) crystal planes, thereby offering a combination of methods to recognize a single crystal of phosphorene (Fig. 2) [21,22]. For example, the intensity ratio of (101) and (002) planes provides an indirect estimation of no. of layers in BP: 2.6 for single layer, 0.3 for bilayer, 0.3 for trilayer, etc. Additionally, based on these microscopic evidence (including atomic force microscopy, AFM), a non-single crystal of black phosphorus as well as different kinds of
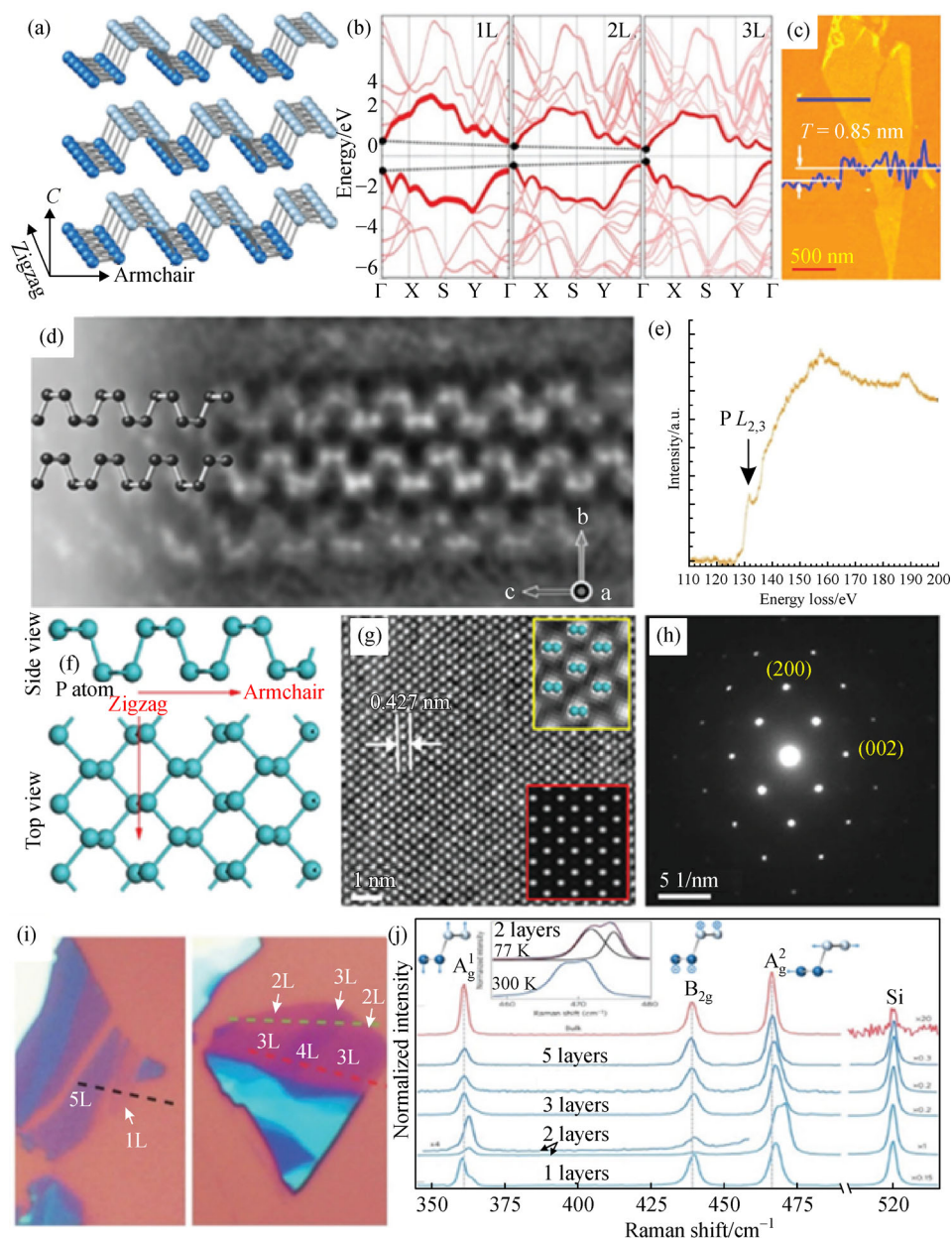
Fig. 2 Phosphorene: (a) Crystal structure, (b) electronic band structure, (c) AFM image, HR-TEM of (d) side view and (g) top view, (e) electron energy loss spectroscopy spectrum, (f) side view and top view of atomic structure, (h) SAED, (i) optical micrograph, and (j) Raman spectra. (a) Reproduced with permission from the ref. [25], Copyright 2017, American Chemical Society. (b) Reproduced with permission from Copyright 2015, American Chemical Society. (c) Reproduced with permission from the ref. [14], Copyright 2014, American Chemical Society. (d) Reproduced with permission from the ref. [21], Copyright 2015, AIP Publishing LLC. (e–h) Reproduced with permission from the ref. [20], Copyright 2016, IOP Science. (i) Reproduced with permission from the ref. [26], Copyright 2017, Macmillan Publishers limited. (j) Reproduced with permission from the ref. [27], Copyright 2015, Macmillan Publishers limited

stacking for multilayer phosphorene, can be identified [23,24].

The fact that the direct band gap of a single layer phosphorene is 2.05 eV (which falls under visible light region) opens up newer opportunities in the photovoltaic applications of phosphorene [28]. As opposed to graphene where valence and conduction bands are composed of mainly p orbitals, in case of phosphorene, both s and p

orbitals contribute to the orbital hybridization in its valence and conduction band, dictating the band-gap properties [29,30]. Additionally, both theoretical and experimental studies strongly support an inverse correlation between the number of layers of phosphorene and its band-gap [30,31].

One of the important factors that influence the electron-hole transport in 2D materials is the mobility of the charge-carriers and generally a reciprocal relationship between the

charge career mobility and effective mass is observed. For phosphorene, the theoretical studies showed that the effective masses as well as the mobility of electron and holes are different in x and y directions, suggesting an asymmetric and anisotropic behavior [31]. In spite of having a high effective mass, extremely small deformational potential predicts a hole-dominant transport, which allows charge-separation and subsequent transport of electrons and holes in different directions [32].

The optical properties of phosphorene can often be extracted from their band-gap properties. In case of phosphorene, strong absorption peaks in the ultraviolet region (236–240 nm) can vary depending on the nos. of layers, surface modification, tensile-strain [33–35]. In fact, such modifications often bring out specific properties required for particular applications. For instance, while armchair phosphorene nanoribbons exhibit direct optical band gap, no optical activity can be seen in case of zigzag orientation [36]. Due to the difference in optical property along the two directions, armchair direction aids better photon diffusion process, enhancing the photo(electro) catalytic properties along that direction [36]. Though, this direction-oriented control of optical properties indeed helps to implement phosphorene in various applications such as solar fuel production, hydrogen evolution, water splitting etc., the fundamental understanding of the directional optical properties is yet to be fully developed.

In addition to crystallographic and microscopic data, vibrational spectroscopies such as infra-red (IR) and Raman also provide very useful structural and physico-chemical information including crystal orientation [37], layer numbers [38], strain-based deformation [18], etc. IR spectroscopy is normally used to obtain details information about the presence/absence of functional groups. For example, as compared to pristine phosphorene, the presence of surface-oxidized species (like P–O, P = O, etc.) as well as heteroatom doping (P–N, P–F, etc.) can be easily identified using this technique [39,40]. In addition to IR, Raman spectroscopic techniques have also been widely used for the characterization of phosphorene. Recent improvements in the sophistication of Raman spectroscopy allow performing experiments in a non-destructive way. For phosphorene, these experiments provide essential information, which can be correlated with the information obtained from other characterization techniques. In general, 3 vibrational modes namely A_g^1, B_g^2 and A_g^2 are observed for phosphorene at 362, 439 and 471 cm^{-1}, respectively [41,42]. It is shown that the peak position (and also full width half maxima) of A_g^2 mode depends strongly on the number of layers [43,44]. For bilayer, trilayer and bulk phosphorene, the peaks corresponding to A_g^2 mode appear as red-shifted (470, 469 and 468 cm^{-1} respectively) [44]. Both theoretical and experimental findings continue to shed light on the origin of different modes as well their shifting pattern [27,45]. Recently the advanced low-frequency Raman techniques (acquisition mode < 100 cm^{-1}) have been utilized to specifically determine the numbers of layers only to find a good agreement among other techniques [46–48]. Additionally, interlayer breathing corresponding to A_g^3, A_g^4 and other vibrational modes of BP can also be identified using this technique and significant works, are being carried out for further consideration of this technique for phosphorene and other 2D nanomaterials [49–51].

In spite of having various interesting directional and layer-dependent properties of phosphorene, it's stability is one of the major concerns for it's future developments in various applications [27]. Since, without the proper knowledge about the nature of interactions among phosphorene (and/or BP) with air, water and other environmental entities, it is almost impossible to develop specific protection strategies; the current research has been devoted to understand such interactions as well as the possible degradation pathways of phosphorene [52]. For an example, Castro-Neto and co-workers studied the oxidation of mechanically exfoliated phosphorene upon exposure to air to understand possible active sites of degradation as well as the stability of surface oxide layer [53]. Several protection strategies have been developed based on the available information (vide infra) to enhance the stability of phosphorene but it surely requires better understanding of the nature of the interactions.

In addition to above-mentioned properties, other application-driven properties such as non-linear optical property, magnetism, spintronics, biocompatibility, etc. are also currently being explored. While the efforts have just continued to expand, these studies are expected to bring out positive outcome with newer opportunities for novel applications.

2.2 Preparation

The synthesis of phosphorene (2D form of BP) can be linked to the preparation of BP itself, as most of the preparations involve BP as a precursor. For the synthesis of BP, a mineralized-assisted heating process was reported to convert red phosphorous to BP in presence of SnI_4/Sn in a sealed tube [54]. Different variants of this method (commonly known as "chemical-vapor-transport") along with some recently developed large-scale synthetic strategies have been adopted mostly for the synthesis of BP (rather than phosphorene) [55,56]. For the fabrication of monolayer or few layers of phosphorene (mainly in the form of thin films), both "top-down" and "bottom-up" approaches have been considered (Fig. 3), adopting the synthetic methods from its predecessor 2D materials, graphene [57,58]. In particular, the "top-down" approach for the synthesis of phosphorene, primarily refers to the exfoliation of bulk BP by breaking of the weak van der Walls interaction between the two monolayers [57]. On the
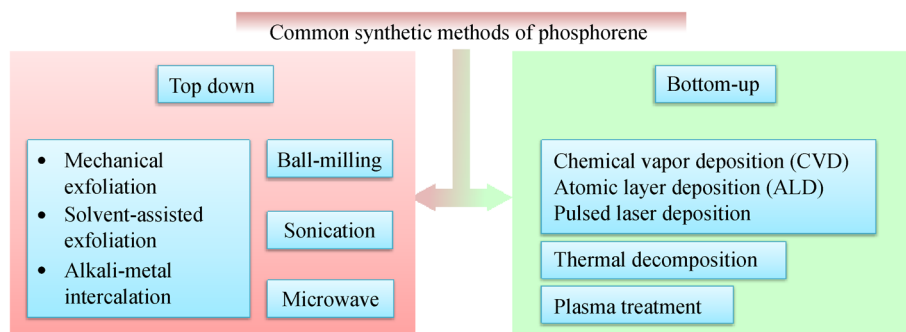
Fig. 3 Common synthetic methods for the preparation of phosphorene

other hand, the "bottom-up" method involves the synthesis of phosphorene from molecular precursors [59]. Despite the prevalence of both the methods in the literature, the "top-down" approach gains the popularity predominantly because of the ease of the synthesis as compared to the other one.

The exfoliation strategies for the conversion of BP to monolayer phosphorene, closely resembles to those of graphite [60,61], TMDs [62], hexagonal boron nitride (h-BN) [63], etc. to their respective 2D counterparts. Among several exfoliation strategies, one of the popular exfoliation strategies involves the isolation of monolayer phosphorene using a "scotch-tape" [14,64], which was originally developed for the preparation of graphene from graphite. This type of mechanical exfoliation generally follows additional cleaning steps to remove organic and other impurities. However, despite wide use of this method at laboratory scale, the concerns regarding reproducibility, cleaning, characterization steps (after each exfoliation) limit the large-scale synthesis of phosphorene and alternative approaches have been pursued.

Excluding mechanical exfoliation, there are mainly two major exfoliation procedures that are currently being exploited for the synthesis of phosphorene: Liquid-assisted exfoliation and alkali-metal-intercalation. In the first case, mostly organic solvents such as N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), isopropanol etc. are used to disrupt the weak interlayer van der Waals interaction [65]. Additionally, pre-exfoliation protocols like grinding, sonication etc. also contribute significantly to the success of this procedure. The encapsulation of phosphorene especially by organic solvents increases the stability of the materials by protecting the material from the environment [65]. Recently, simple-sonication-based exfoliation strategy [66] has also been employed utilizing water as a green solvent and this type of protocol is expected to be widely applicable in near future.

Among the other substances, which aids the exfoliation process, alkali metals such as lithium, sodium etc. are also capable of weakening inter-layer interaction, as exemplified in case of TMDs [67]. In case of phosphorene, at first,

the alkali metals are used to intercalate between the layers of phosphorene, which normally follows a subsequent washing treatment with water to form a homogeneous dispersion of 2D phosphorene [68,69]. Additional sonication treatment sometimes helps to control the numbers of layers as well as the particle size. A relatively newer method utilizes chemical surfactants to isolate the phosphorene sheets. The surfactants like sodium dodecyl sulfate (SDS), etc. have been used to synthesize exfoliated phosphorene for various optical and photoluminescent applications [70]. These "top-down" approaches offer advantages for the synthesis and isolation procedures but more efforts are needed to have a better control over the shape, size and thickness of phosphorene.

The "bottom-up" approach is normally preferred when precursor molecules/reagents, as well as the instruments (if required) are readily accessible. For the synthesis of phosphorene, various types of "chemical vapor deposition (CVD)" are routinely used [71]. For instance, the thermal conversion of red phosphorous to BP using "chemical-vapor-transport" process (a variant of CVD) was reported [54]. Following the same trend, different modified protocols of CVD technique have already been established for the deposition of BP from red phosphorous onto specific substrates (including flexible ones) [55,56]. Apart from red phosphorous as a precursor, various phosphorenes/BP have also been explored to fabricate phosphorene on Si [72], Au (111) [73], GaN (111) [74] surfaces. Since most of the reported CVD techniques do not always focus on the mechanistic understanding of the procedures, ongoing research efforts are focused to address both thermodynamic and kinetic concerns regarding the growth of phosphorene on different surfaces. As far as the deposition of 2D phosphorene films on a particular surface is concerned, generally three steps are considered: nucleation of the smallest unit, expansion of the smallest unit to larger deposition sites and the subsequent formation of the phosphorene layer on the surface. At atomistic level, such formation procedure can be a combination of several processes among which the dissociation of the precursor, adsorption of the dissociated species on the surface, attachment of different units to obtain a film [75] are

considered to be the important ones. However, irrespective of the strategies, it is important to understand various nuances of different methods to have a better control of the deposition processes as well as the quality of materials. For instance, recently, P_2 (two phosphorous atom atoms joined together) dimer was claimed to be the smallest unit of for the sublimation of phosphorene on the BP surface [76], corroborating well with the growth of graphene where C_2 was also considered to be the smallest unit [77,78]. The present understanding of the mechanism along with recent advancement in both CVD instruments as well as corresponding characterization techniques is expected to provide breakthroughs in large-scale synthesis of phosphorene [20].

For long-term use of phosphorene, the stability of phosphorene in presence of heat, air, water and environment is crucial and a proper understanding of degradation pathways including their thermodynamic and kinetic parameters, characterization of the degradation products etc. becomes imperative. Several groups have indeed started looking into these areas and significant progress has been observed within a short time. For example, mechanically exfoliated phosphorene undergoes oxidation in presence of air, resulting in a decrease of their electrical properties [53]. The presence of lone-pair of electrons on phosphorous atoms has been claimed to be responsible for the inherent instability of phosphorene [79]. Since these damages clearly have raised some concerns regarding the long-term use of the materials, some passivation strategies have also been developed to minimize such adverse environmental effects. The encapsulation of phosphorene between two layers of other 2D materials (e.g., h-BN, graphene) [80], organic liquid exfoliation strategies, the formation of particular protective layer (e.g., AlO_x, etc.) [52] over phosphorene sheets etc. are some of the protocols that are currently being employed to improve the stability of the materials for the long-term use. However, more efforts are needed to understand the inherent chemistry that are essential for the development of large-scale synthetic procedures of phosphorene with long-term stability.

2.3   Applications

The advent of phosphorene is directly proportional to its potential to be employed in various important applications. Till date, researchers mainly focus on the electronic and optical properties and their related applications [13,20], leaving a vast pool of other applications to be explored.

Rechargeable Li-ion batteries are among the new classes of secondary batteries, which gained popularity due to their cycling stability, high storage capacity, high energy density and they are currently available as power sources in smartphones, tablets, laptops, etc. [81,82]. The Li-ion battery mainly consists of two electrodes (anode and cathode), an electrolyte and a separating membrane. Generally, graphite acts as anode and lithium metal oxides play the role of cathode material. The mobility of Li^+ ion through the membrane plays an important role in deciding the final performance. Moreover, for a better utilization of space, the modification of anode materials as compared to cathode materials is preferred because of the fixed amount of Li in lithium metal oxides [81]. Though graphite is by far the most widely used anode material, its limited specific energy calls for the development of better anode materials [83].

Due to having high power density and long cycle life, BP and phosphorene have attracted a great deal of attention in recent years for battery-related applications [84]. In most cases, instead of pure phosphorene, a composite of phosphorene/BP and carbon nanomaterials (to increase the electrical conductivity) is used as anode material in Li-ion battery [11]. While such combinations provide improvements in charge and discharge capacities, high reversibility of BP and Li_3P (starting material and the end product of cathodic discharge reaction respectively) is expected to offer a longer lifetime of the batteries [84]. Though there still remains concerns and challenges regarding the stability of BP and phosphorene, volume-change associated with periodic lithiation and delithiation etc., efforts such as the development of passivation and protection strategies (e.g., thermal annealing, P–C bond formation, etc.) are currently being pursued to overcome those challenges [85].

A newly developed Li-based battery, Li-S battery is also considered to be a promising battery alternative because of specific capacities of lithium and sulfur, normally used as a Li-S cathode [86,87]. However, low electrical and ionic conductivities of S, stability and dissolution of S, high volume expansion upon lithiation pose some hurdles, which need to be overcome for successful commercialization of Li-S battery [88,89]. Though as alternative solutions, various carbon-based composites of sulfur have been reported [90,91], the immobilization of sulfur still remains an area of concern. In this respect, phosphorene shows promises because of its ability to form more stable P–S bonds [92]. Additionally, phosphorene in similar cathode matrix was reported to reduce polarizations, increase the efficiency of redox reactions and also activate polysulfides, thereby providing a better efficiency as compared to non-phosphorene-based Li-S batteries [93].

In the list of rechargeable batteries, another class of battery that shows huge promises as a potential replacement for Li-ion battery is Na-ion battery because of the low cost and high abundance of Na [94,95]. Similar to Li-ion battery, the graphene-phosphorene composite has already been recognized as potential anode materials [96]. While graphene increases the electron transport, stacking of phosphorene layers helps to accommodate the volume expansion due to it's intercalation with sodium [91]. Apart from Na-ion battery, Mg-ion batteries, selenium batteries are also emerging as potential replacements for Li-ion
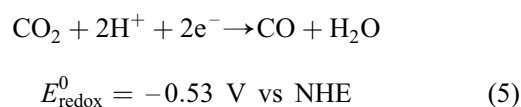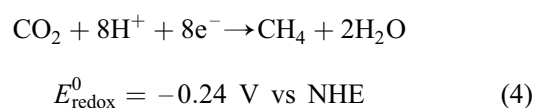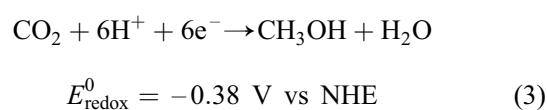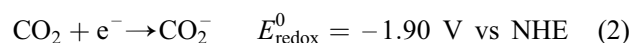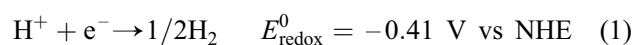
batteries and in most cases, phosphorene and/or phosphorous-based composites/alloys have also started to be employed for better performance [97,98].

Supercapacitors are indeed becoming one of the major fields of modern-day research in electronics [99,100]. Materials with high specific surface area like graphene have been reported as major contributors for the development of double electrode supercapacitors with high capacitance [101]. Recently, as an alternative to graphene, phosphorene films, deposited on polyethylene terephthalate (PET) surface, has been utilized as supercapacitors to obtain a capacitance value of 12.75 $F \cdot cm^{-1}$ at a scanning rate of 0.01 $V \cdot s^{-1}$ [101]. In future, the development in phosphorene fabrication and stabilization techniques is expected to improve properties such as flexibility, high power density, long cycle life, fast charge/discharge rate, etc. [102] and offer significant advantages for the progress in supercapacitor field.

One of the most important components in a photovoltaic cell (or more specifically a solar cell) is a semiconductor material, which generates electron-hole pairs when light with a particular wavelength corresponding to its band gap, falls on it. Once the electron-hole pair is generated, the charges move to respective electrodes depending on the external potential [103]. Since the first report of commercialized solar cell made of mono or polycrystalline Si, the field has witnessed a sharp growth leading to the fabrication of next-generation solar cell (e.g., perovskite solar cell, organic solar cell, etc.) [104–108]. In that list, because of controllable band-gap as well as high electrical conductivity, phosphorene has been recently included [109–112]. In most cases, phosphorene is employed either as composite materials or as an integral component of the system (to bridge photoactive layer as well as electron transport layer) [113]. In the latter case, it's worthmentioning that the thickness of a phosphorene layer dictates the performance of the solar cell. Due to favorable compatibility of phosphorene with different components of a solar cell, phosphorene is also considered (both theoretically and experimentally) as an active constituent for various types of solar cell like dye-sensitized solar cell, perovskite solar cell, etc. [114]. Various combinations of composites such as phosphorene/h-BN heterostructures, TMDs/phosphorene nanostructure, Si/SiO$_2$-phosphorene, graphene-phosphorene materials are either predicted or employed for better performance of solar cell [115–118]. Though some challenges regarding the stability of phosphorene as well as an understanding of detailed mechanistic insights, still remain to be resolved, the future of phosphorene-based systems for photovoltaic applications indeed looks brighter for the development of a sustainable efficient solar cell with long-term stability.

The formation of electron-hole pair upon shining light of a particular wavelength corresponding to the band-gap of semiconductor opens up an enormous opportunity for photocatalytic transformations [119,120]. Whereas the photogenerated electrons in the conduction band can be used for reducing different species, the holes normally accept the electrons from the reagent, resulting into oxidation of the starting materials. Depending on the redox potential of a reaction and the band-gap of semiconductor material, a particular scheme can be designed to afford various reaction products from simple starting materials. In case of phosphorene, four classes of reactions are thus far reported depending on the substrates and the efficiency of the catalysts: hydrogen evolution, carbon-di-oxide reduction, hydrogenation and removal of pollutant [20].

$$H^+ + e^- \rightarrow 1/2H_2 \qquad E^0_{redox} = -0.41 \text{ V vs NHE} \quad (1)$$

$$CO_2 + e^- \rightarrow CO_2^- \qquad E^0_{redox} = -1.90 \text{ V vs NHE} \quad (2)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$$

$$E^0_{redox} = -0.38 \text{ V vs NHE} \qquad (3)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$$

$$E^0_{redox} = -0.24 \text{ V vs NHE} \qquad (4)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$$

$$E^0_{redox} = -0.53 \text{ V vs NHE} \qquad (5)$$

Equations (1–5) are representative photo(electro) chemical reactions (reproduced with permission from the ref [20], Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

Since the overall water splitting (i.e., generation of hydrogen and oxygen from water) require relatively large energy, the photocatalytic generation of hydrogen from water has long been considered as one of the sustainable solutions for the current and imminent upcoming energy crisis primarily because of high-energy capacity (143 $MJ \cdot kg^{-1}$) of hydrogen and environmentally safe reaction [121]. Though for such catalytic process, TiO$_2$ (or a combination of TiO$_2$ with other nanomaterials) is probably the most popular one, several challenges such band-gap mismatching, inefficient utilization of total electromagnetic spectrum, possibility of electron-hole recombination etc. often limit the wider applications [122]. In this respect, phosphorene showed promises as potential choices as compared to other materials [123]. Because of its unique wider band-gap position, it often allows better electron reduction ability and also decreases the electron-hole recombination [124,125]. Future works are still needed to understand and correlate a better structure-activity relationship but the progress seems promising.

One of the ways to control CO$_2$ in the atmosphere is to convert it to different fuels or value-added products [126]. The chemistry behind the conversion of CO$_2$ to fuels majorly involves the reduction of CO$_2$. However, for

practical purposes, the complex combinations of proton-coupled-electron-transfer (PCET) reactions, as well as the efficiency and selectivity of the employed catalysts govern the final products of the reactions (Eqs. (1–5)) [127,128]. Semiconductor materials (such as TMDs, MXenes, graphitic–C_3N_4) with specific band-gap energies have been investigated theoretically and experimentally for conversion of carbon-di-oxide into different fuel molecules [129–131]. Because of comparable band minina of phosphorene and graphitic-C_3N_4, the former (or its precursor black/red phosphorous) is also expected to catalyze these PCET reactions with high efficiency and selectivity [132]. Recently, a combination of red phosphorous and BP demonstrated comparable activity than that of cadmium sulfide quantum dots [133]. Though the determination of active site and origin of catalysis are yet to be conclusively confirmed, these studies show the prospect of phosphorene materials as catalysts for such transformations.

The generation and the fate of electron-hole pair along with the choice of reaction, corresponding to the band-gap of the photoactive materials dictate the overall photocatalytic performance. Similar to the reduction of CO_2, phosphorene can also be envisioned as a photocatalyst for other reactions. Corroborating with that thought, several theoretical studies have already been performed for the hydrogenation (i.e., addition of hydrogen to unsaturated bonds) of olefin [134,135]. These studies also shed light on the effect of electron-deficient dopants like B, Al, etc. for the generation of frustrated Lewis-pair as well as their subsequent catalytic cycles [135]. These studies are yet to be confirmed by experiments but a latest study on catalytic hydrogenation of Ni-phosphorene has clearly shown the path on which the future studies can be performed [136].

The photocatalytic materials have often been utilized for effective degradation of toxic organic chemicals from the environment and in that regard, TiO_2 and other photoactive materials have already been reported [137,138]. However, most of the materials suffer from challenges such as partial utilization of entire solar spectrum, recombination of electron-hole pair etc. As a newer addition to that class, phosphorene nanosheets have been explored as photosensitizers with a high quantum yield for the effective generation of singlet oxygen upon irradiation of UV-visible light, leading to decomposition of 1,3-diphenylisobenzofuran and methyl orange [139]. This particular report along with previous reports opens up the opportunity for the use of 2D semiconducting materials for photodynamic therapy, which need to be explored for the removal of toxic materials from the environment.

Phosphorene has also been explored as an electrocatalyst because of its conducive electrical conductivity, high surface area, leading to better activity. Among the electrocatalytic reactions, electrocatalytic activity of phosphorene and BP was explored for very important yet quite challenging oxygen evolution reaction (OER) [140,141].

Presently, noble-metal-based nanomaterials are being used as electrocatalysts for OER (or its reverse reaction, i.e., oxygen reduction reaction or ORR) and hence, efforts are being focused to find a sustainable alternative for such catalysts. In this case, phosphorene nanosheets or BP (either as pure or as nanocomposite with other materials) has been used to electrocatalyze the OER process and their activity and stability often resemble the current state-of-the-art catalysts. For instance, while Zhang and co-workers investigated the activity and the stability of few layers of phosphorene for OER, BP (or phosphorene or their doped variants) nanocomposites such as BP on Ti foil, phosphorene on graphene, etc. were studied for OER [141]. Though the active sites and other mechanistic studies still remain elusive, the current progress is clearly indicative of better prospect.

Owing to the unique thermal and electrical properties of phosphorene (especially the anisotropic behavior), phosphorene (or BP) emerged as a strong candidate for thermoelectric applications where high electrical conductance but low thermal conductivity (i.e., high figure of merit) is required [142]. BP nanoribbons exhibited high Seebeck coefficient and the anisotropic behavior of BP can be observed from the differences in Seebeck coefficients, electrical and thermal conductivities of the BP in arm-chair and zig-zag directions [143,144]. Theoretical and experimental studies on phosphorene have also revealed that this behavior of BP could also be extended in case of phosphorene [144,145]. Additionally, concepts have already been proposed to utilize these properties for the development of the industrial (exhaust-gas-treatment, [146]) and the household items (nanogenerator, [147]) and based on the preliminary reports, the future opportunities of phosphorene being utilized in different industrial and household sectors seem endless.

3 Conclusions and future directions

In this current review, a brief development of phosphorene including their synthesis, characterization and properties and the applications is presented. The past and ongoing research efforts clearly suggest that the potential of phosphorene for various applications is enormous (Fig. 4). Despite knowing the existence of BP since 1914, the prospect of the 2D variant of BP, i.e., phosphorene actually started to resurface as a quest for finding an alternative to existing 2D materials to eliminate or minimize their associated challenges. The fundamental knowledge regarding the preparation, characterization and applications is still in its infancy and more efforts are genuinely needed to identify the challenges as well as the possible solutions.

Due to the advancements in several instrumental techniques, the synthetic tools for the synthesis of phosphorene seem to explode. However, in reality, most of the procedures indeed lack detailed theoretical and
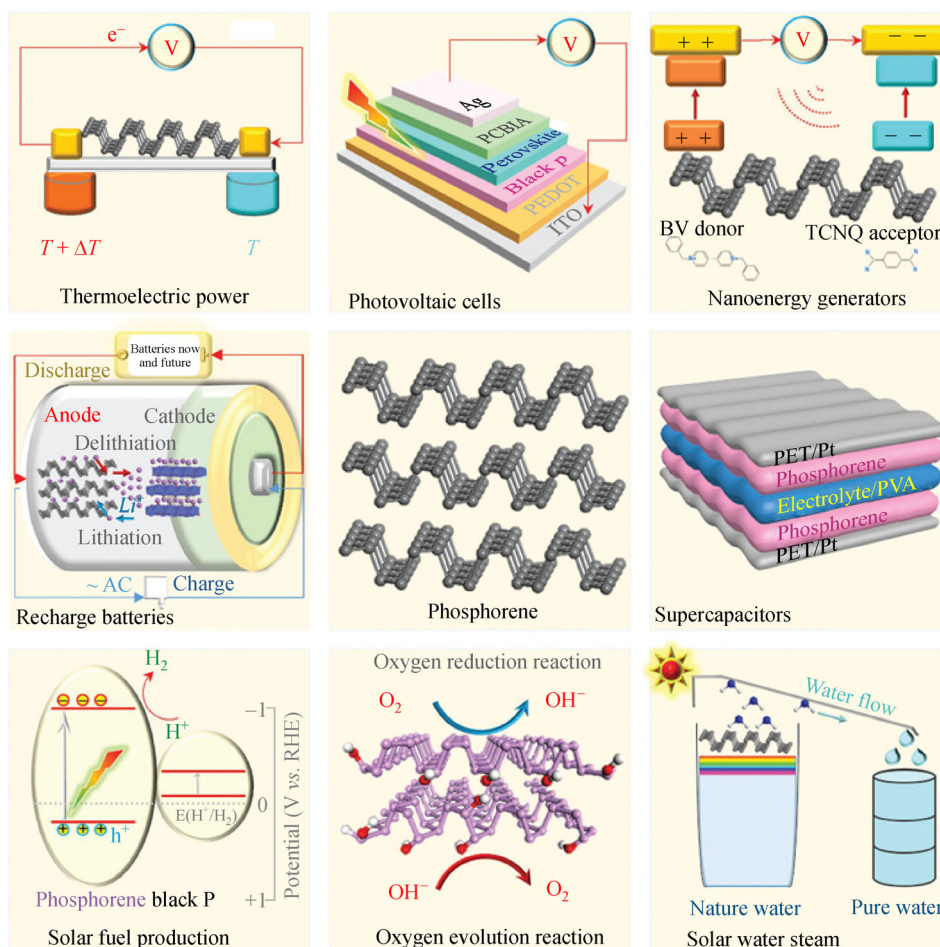
Fig. 4 Schematic of diverse applications of phosphorene. Reproduced with permission from the ref. [20], Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

experimental investigation about their fundamental processes at the atomic level and without understanding them, the breakthroughs in synthetic methods (especially at the large scale) appear to be challenging. In addition to synthesizing phosphorene and BP, post-synthetic modifications offer significant advantages to tune the properties of the materials. However, this seemingly simple idea is often found to be a daunting task because of the lack of compatibility between the phosphorene and the attached moieties and due to the stability of phosphorene in different conditions. Hence, the development of such post-synthetic process along with their fundamental understanding and the stability of the phosphorene upon exposure to different environments become imperative.

In terms of the characterization of properties of phosphorene, the anisotropic nature of phosphorene separates it from the other 2D materials. Though the origin of anisotropy still remains controversial for some properties, this directional behavior of phosphorene encourages the researcher to utilize it for different applications [13,118,148]. Though, morphology, layer numbers, band-gap properties and thermal and electrical

properties of phosphorene are routinely being carried out, several other properties such magnetism, non-linear optics, biocompatibility etc. are still not explored primarily due to lack of proper vision towards possible applications.

Despite the interest regarding the potential applications of phosphorene, without the active participation from different interdisciplinary branches of research, the progress can be sluggish. Since, the stability of phosphorene still remains a major concern, the long-term applications utilizing the semiconducting, catalytic, mechanical properties of phosphorene have been limited. The fabrication of phosphorene on different substrates for the development of devices is also restricted by the lack of fundamental knowledge of fabrication techniques. Additionally, even for the current applications (e.g., photo and electrocatalysis), the identification of the reaction pathway as well as the interpretation of technical parameters often remains dubious. Though the applications regarding the materials' aspect of phosphorene have been a part of active investigations, the biological activity, toxicity and biocompatibility of phosphorene still remain relatively unexplored.

The aforementioned challenges regarding synthesis, characterization and applications of phosphorene somehow restrict the utilization of its full potential. However, given the responses from different research fields (based on the number of research papers published) [13], it is evident that the research community is actively putting its best efforts to tackle such problems, as a result of which , an overall sharper growth is expected in near future regarding the preparation, characterization and applications of phosphorene.

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