STUDY AND TECHNICAL REVIEW ON PROPERTIES AND APPLICATIONS OF 2D VA MATERIAL - PHOSPHORENE

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Abstract - *Black phosphorus (BP) is known to human beings for almost a century. It started receiving more attention of scientists and researchers worldwide in recent years, with its ability to exist in two-dimensional (2D) form, popularly known as Phosphorene. In the post-Graphene-discovery period, Phosphorene is probably receiving most attention, owing to its excellent and fascinating Band Structures, Carrier Transport ,Optical, Thermal and Mechanical properties. In this article, first, the fundamentals properties of Phosphorene, are briefly introduced, along with their structures, properties, and synthesis methods. In addition, the article also focuses on opportunities in Field-effect transistors, Photodetectors and Solar cells, Gas sensors, Energy Storage, Thermo Electric Applications, Light Emitting Devices sensors etc arising from Phosphorene's remarkable properties.*

*Key Words***:** Phosphorene, 2D-Materials, Mono Layer, Few Layer

1. INTRODUCTION

This document Phosphorus is the 15 element of the periodic table and is classed as a reactive non-metal. Depending on environmental conditions and how it is processed, elemental phosphorus can take several forms (allotropes). These allotropes are generally referred to by their physical appearance; white (or yellow) phosphorus, red phosphorus, violet phosphorus, and black phosphorus. Black phosphorus was first synthesised in 1914 by Percy W Bridgman by heating white phosphorus at high pressures. It is the most stable known allotrope of phosphorus and is currently of intense interest to the scientific community. It consists of 2-dimensional layers of phosphorus (termed 'Phosphorene') held together by weak van der Waals interaction, in the same way that graphite is made up of many layers of Graphene the black phosphorus (BP) has the most stable crystal structure at ambient pressure among the several allotropes of phosphorus.

In 2014, Liu et al. extracted monolayer Phosphorene from the layered BP crystal by employing the mechanical exfoliation technique, and demonstrated its semiconducting transport properties. It is formed by alternative stacking of Phosphorene layers, in which phosphorus atoms form a puckered honeycomb lattice. A huge amount of research has been performed on its properties and applications.

2. STUCTURES OF PHOSPHORENE

Before Group-VA layered bulk materials show a structural variety, being their typical allotropes. Significantly, phosphorus has white, red, black phosphorus and other several amorphous forms [1,2].Black phosphorus is the most thermodynamically stable allotropic form under ambient conditions. It crystallizes in a layered orthorhombic structure with space group Cmca, consisting of parallel puckered double-floor atomic layers. Within the individual atomic layer, each phosphorus atom has five valence electrons from the 3s and 3p orbitals, which hybridize to form three covalent bonds with neighboring atoms. Among them, two covalent bonds lie parallel with the atomic plane while the third one is nearly perpendicular to that and plays an important role in bridge connection of phosphorus atoms from upper and lower layers, forming a unique puckered structure (α phase) as shown in Fig. 1(a). Bulk black phosphorus exhibits a band gap of 0.3 eV, a high carrier mobility of 103 $cm^2V^{-1}s^{-1}$ and a highly anisotropic layered structure[3,4] .Under approximately 5 GPa, black phosphorus transforms into a semimetallic β phase with space group R$\bar{3}$m as shown in Fig.1(b)[5]. The β phase is crystallized in a layered rhombohedral structure, which adopts a double-layered structure consisting of many interlocked, ruffled and six-membered rings.
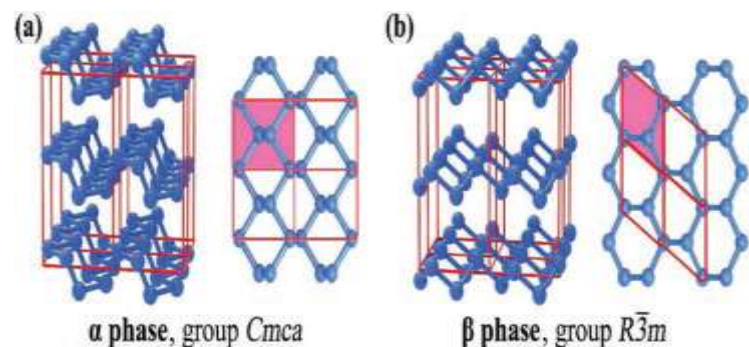

Fig.1(a): Consisted of parallel puckered layers with space group Cmca (α phase).
Fig.1(b): Consisted of parallel buckled layers with space group R$\bar{3}$m (β phase).

Many Phosphorene allotropes with compacted honeycomb or nonhoneycomb nanosheets have been designed and studied from first-principles calculations [6]. The puckered (α-Phosphorene) and buckled (β-Phosphorene) monolayers are the most common allotropes, which have a structure corresponding to the individual atomic layer of black phosphorus (α phase) and blue phosphorus (β phase) crystals. Systematically it was predicted a class of group-VA monolayers with five typical honeycomb (α,β,γ ,δ ,ε) and four non-honeycomb (ζ ,η ,θ ,ι) structures, as illustrated in Fig. 2(a)[7] .The average binding energy for group-VA monolayer configurations, as presented in Fig. 2(b).

For Phosphorene, among the five honeycomb α, β, γ ,δ ,ε monolayers and four non-honeycomb ζ ,η ,θ ,ι monolayers, α -Phosphorene with the puckered form is the most stable. The counterpart bulk material of α-Phosphorene monolayer is black phosphorus, which is the most stable form of the allotropic bulk crystals under standard conditions

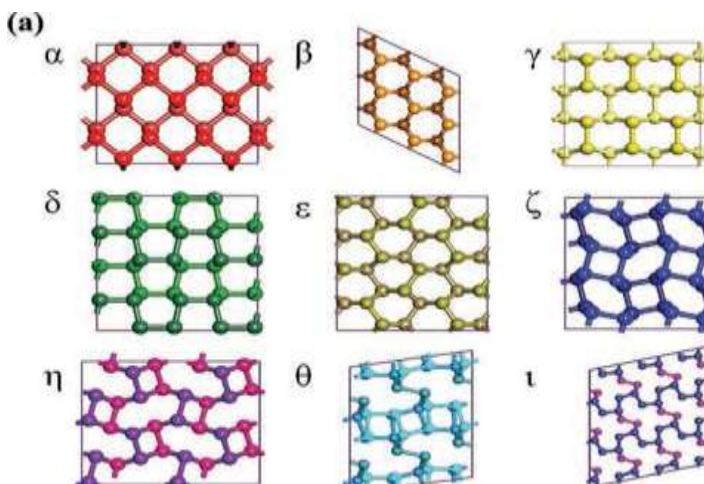Fig.2(a): Top view of the relaxed group-VA monolayer allotropes with five typical honeycomb structures (α, β,γ ,δ ,ε) and four non-honeycomb structures (ζ ,η ,θ ,ι).
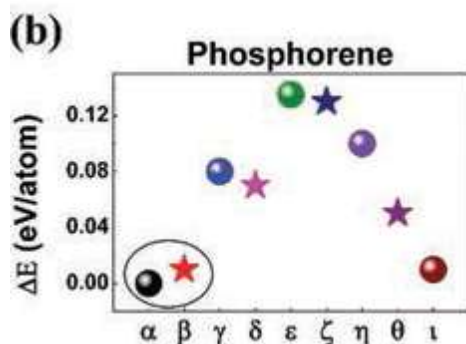

Fig.2(b): calculated average binding energies of VA monolayer allotropes, which show energetic stability for α and β phases of group-VA monolayers.

3. FUNDAMENTAL PROPERTIES
3.1. Band structures

Black phosphorous is a typical direct-band-gap semiconductor. When thinned to few-layer and monolayer, it still retains a direct band gap, as shown in Fig. 3(a). Promisingly, the band gap of Phosphorene depends sensitively on the number of layers (Fig. 3(b)[8]. The fundamental band gap of semiconductor is dominated by the electron–electron interaction, which can be accurately described by HSE06 or the GW method.
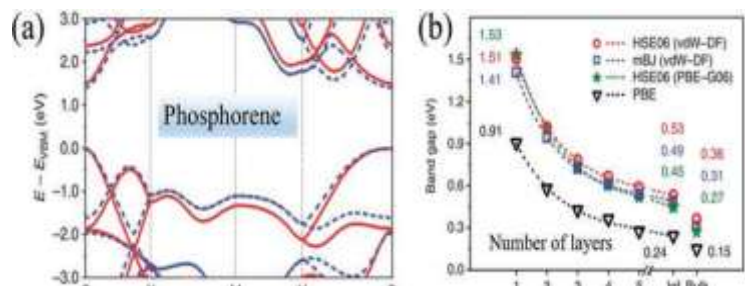

Fig.3(a): Band structures of black Phosphorene monolayer calculated with the HSE06 functional (red solid lines) and the mBJ potential (blue dashed lines), respectively[8].
Fig.3(b): Evolution of the direct bandgaps as a function of the sample thickness. Functional used for structural optimization are shown in parentheses [8].

3.2. Carrier transport

2D group-VA semiconductors exhibit superior carrier transport properties, leading to their promising application in electronic and optoelectronic devices. It is known that carrier transport properties are evaluated based on the calculation of mobility. In theory, the carrier mobility of 2D materials is defined by the following expression [8].

$$\mu_{2D} = \frac{2e\hbar^3 C_{2D}}{3k_B T |m^*|^2 E_1^2}$$

where $\hbar$ - the reduced Planck constant
k_B - Boltzmann constant and
T - Temperature, respectively.
The term m^* is the effective mass along the transport direction and
C_{2D} means the elastic modulus.
E_1 represents the deformation potential constant of the valence-band minimum (hole) or conduction-band maximum (electron) along the transport direction.

3.3. Optical properties

 2D group-VA materials present unique optical properties. The calculated absorption spectrum is anisotropic, for

light linearly polarized in the armchair and zigzag directions. The band edge of the first absorption peak is found at the bandgap and falls quickly with increasing layer thickness in the armchair direction, while the peak is found at 3.14 eV in the monolayer and falls slightly with thickness in the zigzag direction. This in-plane linear dichroism allows optical determination of the crystalline orientation and optical activation of the anisotropic transport properties [9].
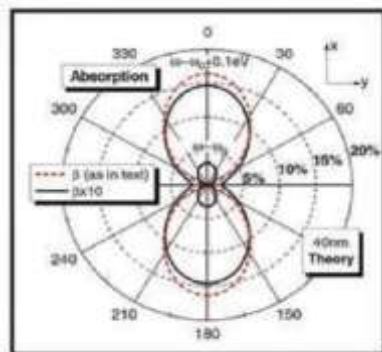

Fig.4: Polar representation of the absorption coefficient A(x) for a 40 nm intrinsic black phosphorus film for normal incident light with excitation energies at the band gap ω_0, and larger. α is the light polarization angle. A(x) is plotted for two values of interbasnd coupling strengths [10].

The Phosphorene monolayer absorbs light between 1.1 and 2.8 eV along the armchair direction and is transparent to light in the same energy range along the zigzag direction, covering the infrared and a part of the visible light regime of broad interest [10].

3.4. Thermal properties

Thermal properties of 2D group-VA materials have been widely studied by theoretical and experimental methods [11,12,13,14]. It is predicted that the linear thermal expansion coefficients of black Phosphorene along the zig-zag and armchair directions are highly anisotropic (up to 20%) [13]. The thermal conductivities in Black Phosphorene are highly anisotropic because of orientation dependent group velocities and phonon relaxation times [15]. The electronic conductivity along the armchair direction is much larger than that along the zigzag direction [16].
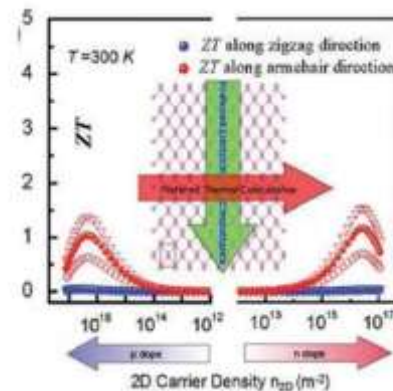

Fig.5: The thermoelectric figure of merit according to the doping density at T = 300 K. Different long-wave relaxation times of phonons are included. The unit of the doping density is m-²[16].

3.5. Mechanical properties

Due to the puckered and buckled structures, 2D group-VA materials exhibit distinctive mechanical properties. Black Phosphorene has special and anisotropic mechanical properties, as depicted in Fig. 6[17,18,19].Wei et al [18] used first-principles calculations to find that the maximal Young's modulus of 166 GPa is along the zigzag direction and the minimal value of 44 GPa is along the armchair direction Fig.(6). Along the armchair direction Black Phosphorene can suffer a strain of up to 30%. In particular, Jiang et al.[17] reported a negative Poisson's ratio in the out-of-plane direction during the deformation of Phosphorene in its zigzag direction, originating from its puckered structure. This fantastic property endows Phosphorene with great potential to be an auxetic material.
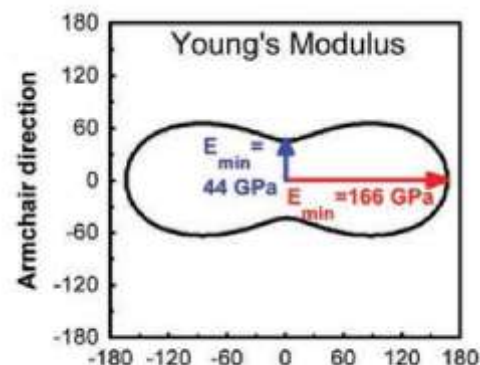

Fig.6: Direction dependence of Young's modulus of Phosphorene[18].

4. TUNABLE ELECTRONIC PROPERTIES

The tunability of the material properties in such 2D group-VA nanosheets offers a charming prospect of engineering versatile applications. Various strategies such as strain, electric field, doping, defect, chemical functionalization, heterostructure have been theoretically proposed to effectively tune their fundamental properties.

4.1. Strain/electric field

It is well known that ultra thin 2D materials often hold high mechanical stretch ability, and can reversibly withstand extreme structural deformation. Therefore, strain has been considered as an effective method to modulate electronic properties of 2D materials, and can further extend their applications[20,21,22]. Peng et al. investigated the band gap of Phosphorene under external strain [22].The value of band gap decreases with the increase of strain. Intriguingly, the value of band gap increases to a maximum with critical tensile strain (4%) in the zig-zag direction and then decreases with increasing strain.The effective mass of Phosphorene also causes the dramatic transformation under external strain. Fei and Yang found that the favorable direction of electron transport can be switched by the applied biaxial strain [23].Dai and Zeng studied the band gap of few-layer Phosphorene under an external electric field [24].The band gap decreases (from 0.78 to 0.56 eV) with increasing electric field while monolayer Phosphorene only has a tiny change (from 0.86 to 0.78 eV).

4.2. Defect

Theoretical calculations have revealed that defects can effectively affect the electronic properties of 2D group-VA materials and produce magnetism in nonmagnetic pristine Phosphorene [25,26]. Hong et al [27] studied the electronic band structures and bias dependent transport properties of various defective Phosphorene systems. They found that the band gap closes in single vacancy Phosphorene but reappears in the divacancy system. Moreover, the vacancy defects can greatly increase the Phosphorene-based device current. Hu et al.[28] studied ten kinds of point defects in Phosphorene, including Stone–Wales defects, single vacancies (SV) and double vacancies (DV).

4.3. Surface functionalization

Surface functionalization is an effective strategy to modify intrinsic properties of 2D group-VA materials through physical adsorption and chemical functionalization. Tunable electronic properties have been realized in Phosphorene by external adsorption doping. Using means of selective doping, one can transform the semiconducting α-Phosphorene into a half-metal, even a metal, or

transform a spin-non-polarized semiconductor into a spin polarized semiconductor. For example, adsorption of B, C, N, F,Li, Na, K, Al and Cr on Phosphorene induces a fermi level shift and produces metallic electronic structures[29,30,31].Both NO and NO2 adsorption result in a magnetic moment of 1µB. In addition, the NH3 (NO) adsorption on Phosphorene can alter the resistance and lead to the increase (decrease) of the current by transport calculations. Wang et al. studied the physical and chemical properties of Phosphorene oxides [32]. Its phonon spectrum shows that Phosphorene oxides are stable under ambient conditions. They found that the degree of O-functionalization of Phosphorene can influence its band gap. Furthermore, the band gap of Phosphorene oxide can be tuned effectively by external strain or an electric field. Lately, Zhu et al. proposed a new stable 2D blue Phosphorene oxide (BPO)[33]. First-principles calculations indicate that BPO is found to be a narrow bandgap semiconductor and it can be subjected to a semiconductor-to-semimetal quantum phase transition under strain. Moreover, they pointed out exotic effects via building effective models characterizing the phase transition and novel emergent fermions. BPO will make contributions to explore fundamental properties of quantum phase transitions and fermions, and it can be a candidate for Nano device applications.

4.4. Heterostructures.

Many studies have focused on van der Waals heterostructures (vdWHs) A typical vdWH is composed of two different monolayers free of dangling bonds, such as Graphene/BN, Graphene/TMDCs, Graphene/Phosphorene, BN/TMDCs, BN/Phosphorene, TMDCs/Phosphorene, and TMDCs/MXenes. A great number of research studies have demonstrated that these vdWHs present many novel electronic and optical properties to fabricate ideal electronic and optoelectronic devices. As the novel 2D group-VA family members, Phosphorene,[34,35] provide potential building blocks for vdWHs. In the Phosphorene based heterostructure, Guo et al. investigated the heterobilayers of Phosphorene with a TMDC monolayer which possess properties of a semiconductor, and found that their bandgaps can be reduced by a vertical electric field [36]. The power conversion efficiency for the Phosphorene/MoS2 heterobilayer can be up to 17.5%. Besides, Wang et al. investigated a Graphene/Phosphorene/Graphene heterostructure [37]. Based on their computational results, vdWHs have two advantages: (1) the thermionic transport barriers can be tuned by changing the number of layers; (2) thermal conductance across these noncovalent structures is weak. It is widely believed that layered van der Waals structures have potential to be a candidate for solidstate energy-conversion devices. Afterwards, Yu et al. examined the physical properties of a Phosphorene van der Waals p–n heterostructure and found that the heterostructure holds

a type-II band alignment and indirect band gap. Through external strain, interesting indirect–direct and insulator–metal transitions can be achieved. Besides, they found spontaneous electron–hole charge separation, and thus, the GeSe/Phosphorene heterostructure has the potential to be applied in optoelectronic devices.

5. FABRICATION OF PHOSPHORENE

Different methods are used for synthesis process to prepare 2D group-VA material Phosphorene and their thicknesses are listed below.

Table -1:

S.no	Synthesis method	Thickness
1	Mechanical Exfoliation	Mono to Multilayer
2	Liquid Phase Exfoliation	Mono to Multilayer
3	Plasma-Assisted/Treatment	Monolayer, 4–50 nm
4	Pulsed Laser Deposition	2–10 nm
5	Electrochemical Exfoliation	Few-layer
6	Chemical Vapour Deposition	3.4 nm

6. APPLICATIONS OF PHOSPHORENE

Phosphorene is still a newcomer in the field of 2D devices. Below are some potential applications being investigated.

6.1. Field-effect transistors.

FETs are the most studied of Phosphorene's potential applications, with many theoretical and experimental studies carried out over the last few years. This stems from the attractive FET characteristics of relatively high on/off ratio and good charge carrier mobility, which should ensure fast switching with high efficiency and error-free logic.

In 2014, Liu et al.[67] and Li et al.[38] firstly reported Phosphorene field-effects transistors based on few-layer Phosphorene Fig. (7). The drain current modulation of the transistor is on the order of 105 at room temperature, four orders of magnitude larger than that in Graphene. The highest value of charge carrier mobility is up to ~1000 cm^2 V^{-1} s^{-1} superior to that of commercial silicon-based devices. Li et al. also pointed out that optimizing the gate dielectric could improve the existing low on-state current and high subthreshold swing in the future[38]. Chen et al. reported fabrication of a FET device made of sandwiched Heterostructures by encapsulating few-layer Phosphorene

between hexagonal boron nitride layers to realize ultra-clean interfaces[65]. This electronic device allowed a higher mobility of up to ~1350 cm^2 V^{-1} s^{-1} at room temperature and on–off ratios exceeding 10^5.

Based on theoretical and experimental studies, it is shown that the carrier mobilities of black Phosphorene are highly direction dependent, because of the structural anisotropy. The lower effective masses along the armchair direction lead to higher drive current at the same biasing. At the same time, the higher degree of anisotropy improves the performance of p-type devices[66].
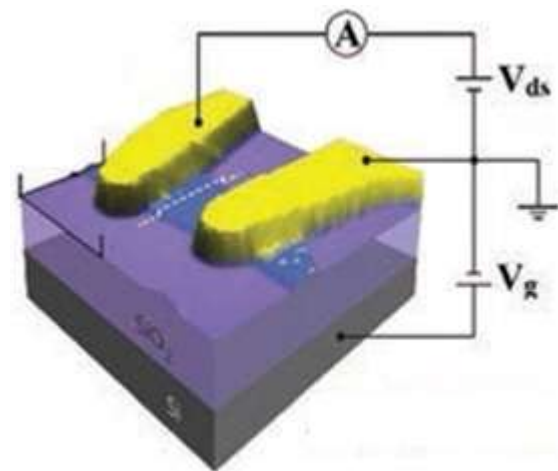

Fig.7: Schematic of the device structure of a few-layer Phosphorene FET[38].

6.2. Photodetectors and Solar cells. Phosphorene's direct bandgap is tunable (between 0.3eV to 1.88eV) by changing the number of stacked layers. This makes it optically active in the red to NIR spectrum and has allowed the fabrication of visible to NIR photodetectors [39,40,41]. This region of the spectrum is important for optical fibre networks and suggests that Phosphorene could play a role in future communication networks. The photovoltaic effect has been observed in few-layer black phosphorus [42]. With thicker samples having a bandgap smaller than that of silicon, it could be used to harvest the NIR-IR region of the solar spectrum that silicon cannot access. While the observed external quantum efficiencies observed so far are small (<1%), it has been predicted that a modified Phosphorene structure could reach efficiencies of 20% [43].

6.3. Gas sensors.

Phosphorene is an interesting prospect for chemical sensing due to its large surface-to-volume ratio and the presence of a lone electron pair on each atom. A NO2 sensor has been demonstrated with a sensitivity of 20 parts per billion in air [44]. A theoretical study has

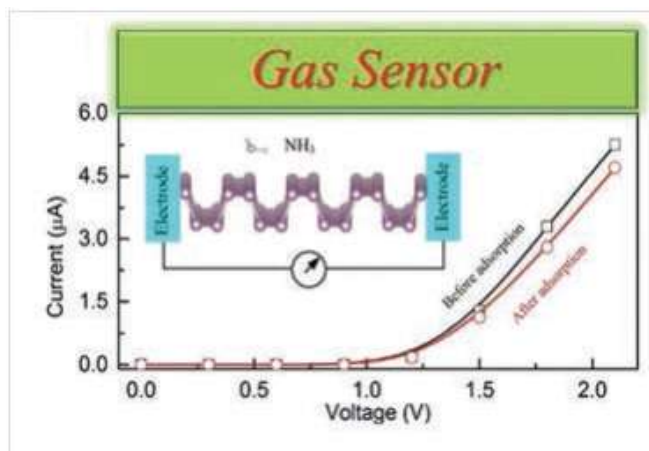suggested that single molecule sensing may be possible with such sensors [45].

Fig.8:.Phosphorene as a superior gas sensor: selective adsorption and distinct I–V response [46].

Phosphorene exhibits stronger adsorption of gas molecules with high sensitivity and selectivity than Graphene and MoS2, tending to be a more efficient sensor. Furthermore, Phosphorene is found to be more sensitive to gas molecules containing nitrogen atoms,such as NO and NO2. Moreover, the transport feature exhibits distinct responses with a dramatic change of the I–V relation before and after gas molecule adsorption on Phosphorene. In view of the theoretical studies, Abbas et al. firstly reported on the sensing of NO2 gas on FETs fabricated based on fewlayer Phosphorene[47]. They found that no apparent change in the peak before and after targeted gas adsorption can be obtained by using the Raman spectroscopy technology, suggesting the good stability of the NO2 adsorbed multilayer Phosphorene system.

Phosphorene sensors exhibit excellent sensitivity for detection of NO2 concentration down to 5 ppb. Moreover, the conductance of devices shows good recovery after flushing the devices with Ar, indicating reversible adsorption and desorption of NO2. Cho et al. accurately compared the sensing performances of Phosphorene, Graphene and MoS2[48] The electrical sensing measurement results show that the sensitivity of Phosphorene is about 20 times higher than those of Graphene and MoS2, which corroborates with the theoretical DFT simulations by Kou et al[46]. Response/recovery time, selectivity, molar response factor and adsorption behavior all support the fact that Phosphorene is a superior gas sensing material. In addition to NO2, Phosphorene is also sensitive to methanol [49].The device based on Phosphorene is very selective in the presence of other vapors for methanol detection and has long-term stability.

6.4. Energy Storage.

Phosphorene has been proposed as an anode material for Li-ion batteries, with lithium diffusion expected to be orders of magnitude faster than in other 2D materials [50]. Structural engineering, incorporation into heterostructures with other 2D materials, and addition of defect states is expected to further improve properties (including lithium diffusion rates and binding energies). Few-layer Phosphorene may also find application in future sodium ion batteries (the expected replacement for lithium ion) [51]. The large interlayer spacing allows for the diffusion of the large sodium ions, in contrast to current graphite anodes. Experimental works concerning Phosphorene as the anode for Li and Na ion batteries have also been presented[52,53]. Sun et al. experimentally studied few-layer Phosphorene sandwiched between Graphene layers used as a high-capacity anode for Na ion batteries[54]. They found that the hybrid Phosphorene–Graphene material possesses a specific capacity of 2440 mA h g-1 at a current density of 0.05 A g-1 and 83% capacity retention after 100 cycles while operating between 0 and 1.5 V.The superior electrochemical properties of the sandwiched hybrid structure could render a suitable anode material for sodium-ion batteries.

6.5. Thermo Electric Applications

Theoretical works indicate that 2D group-VA materials have great potential in thermoelectric applications [55,14,56,57]. Due to the anisotropic puckered structures, group-VA crystals exhibit strong anisotropy in electrical and thermal conductivities, where the value of ZT along the armchair direction is much larger than that along the zig-zag direction[58,59,60]. Fei et al. predicted that depending on the p or n doping and orthogonal electric field, the thermoelectric performance of Phosphorene can be strongly enhanced. Its figure of merit ZT can reach ∼1.5 along the armchair direction at room temperature [16].Additionally, some groups studied the effect of the applied strain on the thermoelectric effect of black phosphorus[61,56,57]. When the zig-zag direction strain is applied, the Seebeck coefficient and electrical conductivity in the zig-zag direction can be greatly enhanced at a strain of 5%.When the armchair direction strain of 8% is applied, the room temperature ZT value can reach 2.12 in the armchair direction of Phosphorene [57]. By nano-structure engineering (cutting a monolayer Phosphorene along armchair or zigzag directions), Zhang et al. showed that very good thermoelectric performance of Phosphorene can be obtained[62].The ZT value of Phosphorene nanoribbons with armchair edges can be optimized to as high as 6.4 at room temperature, which suggests that Phosphorene nanoribbons could be very promising candidates for high performance thermoelectric applications. Promisingly, Sandonas et al. explored the thermoelectric performance of the puckered Phosphorene

6.6. Light Emitting Devies

Phosphorene is an atomically-thin optical material with direct exciton emission, and its wavelength is tunable by controlling the number of layers. Zhang et al. investigated the photoluminescence (PL) spectra of few-layer Phosphorene exfoliated on a silicon substrate, obtaining a strong and highly layer-dependent PL in few-layer Phosphorene Fig. 9(a) [63]. Strong PL peaks of Phosphorene at 961, 1268, 1413, and 1558 nm have been observed in 2–5 layers, which correspond to energy peaks of 1.29, 0.98, 0.88, and 0.80 eV, respectively. The PL peaks are attributed to the nature of excitons, which represent lower bounds on the fundamental band gap values in few-layer Phosphorene. The measured PL spectra provide very useful information to investigate the exciton nature and the electronic structures in Phosphorene. Li et al. studied the PL spectra of monolayer, bilayer, and trilayer Phosphorene at 77 K under unpolarized photoexcitation at 2.33 eV Fig. 9(b) and 9(c) [64]. They have observed strong polarization dependence in monolayer, bilayer and trilayer Phosphorene. The PL peak energy can match well with that in the absorption spectra, which confirms the direct bandgap nature of Phosphorene.
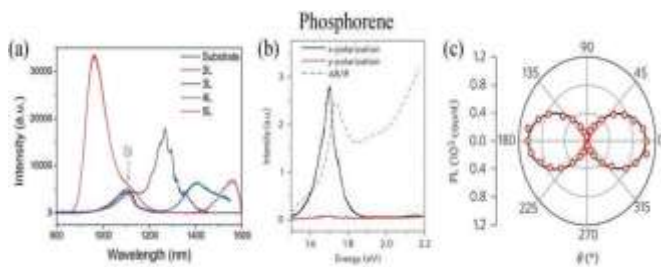

Fig.9(a): Photoluminescence spectra of 2L, 3L, 4L and 5L Phosphorene [63].
Fig.9(b):Photoluminescence spectra of monolayer Phosphorene recorded at 77 K with unpolarized photoexcitation at 2.33 eV.
Fig.9(c): Intensity of the PL at peak energy as a function of polarization angle y. Data taken on monolayer Phosphorene are shown by the red circles. All angular dependences show a nearly perfect cos 2y pattern (black solid curves), consistent with the fact that optical transitions along the y direction are forbidden by symmetry. (b and c) [64].

7. CONCLUSION

The 2D group-VA materials, from Phosphorene, offer a new platform to study emerging device physics in these atomically thin 2D systems and create new concepts for nanodevices. This review article aims at establishing a well-defined impression of 2D group-VA materials, from their atomic structures, fundamental properties, electronic modulations, synthesis methods, to various potential applications. We hope that this review will inspire more exciting discoveries and applications in this growing family of 2D group-VA materials.

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