Free-standing and supported phosphorene nanoflakes: Shape- and size-dependent properties

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Abstract
The ultra-small sized nanomaterials are important for basic functional com-
ponents of future nanoelectronics, spintronics and sensor devices. In this study, based on first-principles density functional theory, the free-standing and supported nanoflakes of bare and hydrogen saturated black and blue phosphorene of diverse size and shape have been investigated. Cohesion, formation energy, thermal stability and electronic structure of these nanoflakes have been revealed. For nanoflakes supported by specific substrates, such as phosphorene, graphene and MoS$_2$ monolayers, in possible device applications, the equilibrium configuration and the binding energy of the flakes, as well as the effects of substrate on the electronic structure have been investigated. While the cohesive and formation energies and HOMO-LUMO gaps of nanoflakes with their edges passivated by hydrogen display clear size, shape and edge geometry dependencies, they are rather dispersed in bare nanoflakes. The binding of phosphorene nanoflakes to two-dimensional (2D) phosphorene, graphene and MoS$_2$ monolayers is generally weak and originate from van der Waals interaction. Accordingly, when supported by these monolayers, the electronic structure of free-standing nanoflakes can be preserved for critical applications.

Keywords: Black phosphorene, blue phosphorene, nano flakes, surface interaction, density functional theory

1. Introduction

Strictly 2D monolayers of diverse elements and compounds have been brought into focus after the synthesis of graphene[1]. These are monolayers of group-IV elements,[2, 3, 4, 5] group III-V and group II-VI compounds,[2, 6, 7, 8, 9, 10, 11, 12] and transition metal dichalcogenides.[13, 14, 15, 16, 17, 18, 19, 20] More recently, the synthesis of ultrathin, 2D black phosphorus from its layered bulk counterparts, has brought the free-standing 2D monolayers and multilayers of group-VA elements (pnictogens) into focus.[21, 22] Later, Liu et al.[23] have revealed the 2D counterpart of black phosphorus, called phosphorene, as a p-type semiconducting material in which phosphorus atoms are $sp^3$-like hybridized forming a puckered structure like silicene and germanene. Additionally, theoretical studies have predicted free-standing monolayers of group-VA elements, such as nitrogen,[24] blue phosphorene having buckled honeycomb structure,[25] arsenene,[26, 27, 28] antimonene,[29, 30] bismuthene.[31, 32]. It was shown that these systems are thermally and dynamically stable and suitable for applications at room temperature and
above. 2D monolayers and few-layer of black phosphorus, i.e. black phosphor-
rene in symmetric washboard structure (sw-P or α-P) has been successfully
isolated by mechanical exfoliation method from black phosphorus which is
the most stable three-dimensional (3D) layered form of phosphorus with a
weak van der Waals interlayer interactions like graphite [33, 34]. Recently, a
phosphorene sheet on Au(111) substrate has been synthesized by molecular
beam epitaxy technique and the grown structure identified as a blue phospho-
rene (also named as β-P) sheet [35, 36]. The thermal stability and flexibil-
ity of α- and β-P have also been studied theoretically;[37] it is suggested that
the α-phase is slightly more stable than the β-phase. Nonetheless, since the
energy barrier between β- and α-phase is small, the transformation of one
phase to the other can be realized without difficulty.[37] Later, various stud-
ies unveiled anisotropic thermal, mechanical, and electronic properties of α-P
and its nanoribbons.[38, 39, 40, 41]

The structural, electronic and optical properties of 2D black phosphorene
and its applications have been investigated in recent review articles compre-
prehensively [42, 43, 44]. The effects of defects and doping on electronic prop-
erties of phosphorene together with possible phosphorene-based devices have
been reviewed by Carvalho et al.[42]. Phosphorene and its structural deriva-
tives, like nanoribbons, nanotubes, fulleranes, and heterostructures have also
been reviewed by Sorkin et al.[43] who draw a perspective for opportunities
and experimental challenges in phosphorene studies. The properties, fabrica-
tion and applications of phosphorene have been discussed by Kou et al.[44],
who described the latest developments of more sophisticated design concepts
and implementation schemes by addressing some of the challenges in phos-
phorene research. Additional background related with phosphorene can be
acquired from these review articles[42, 43, 44].

While 2D monolayers have been treated within the periodic boundary
conditions, their finite sheets are actually relevant for various applications.
For example, a nanoflake of a 2D monolayer situated on another extended
2D monolayer can be considered as the simplest heterostructure. Nanoflakes
can also behave as nanomechanical devices on the surfaces. The nanometer-
size flakes of 2D materials on 2D sheets, like graphene flake on graphene
[45, 46] display crucial dynamical behaviors. It was shown that the trans-
lational and rotational displacements of the flakes on graphene surface can
generate restoring forces which can lead to a harmonic motion with a char-
acteristic frequency. Due to weak interaction between nanoflake and a 2D
monolayer or very thin substrate, low energy barriers involved in the rota-
tional and translational dynamics of nanoflakes keep promises of nearly frictionless motion.\cite{47, 48, 49} Consequently, the nanoflakes of 2D monolayers, in particular those of phosphorene have gained importance recently.

In fact, nanoflakes of $\alpha$-P and $\beta$-P, which are essential for diverse nanoelectronic application, display critical geometry and quantum size effects.\cite{50, 51} Earlier, the electronic and dielectric properties of only six specific blue phosphorene nanoflakes ($\beta$-PNF) have been studied and the possible usage in optoelectronic device applications has been discussed.\cite{52} Zhou et al.\cite{53} studied 12 parallelogram and rectangular nanoflakes of $\alpha$- and $\beta$-PNF. Heterojunctions of nanoflakes of black phosphorene ($\alpha$-PNF) have been proposed for solar cell applications, since phosphorene has superior properties compared to graphene and MoS$_2$.\cite{54} $\alpha$-P has also thickness dependent direct gap ranging between 0.3 eV (bulk) and 1.5 eV (monolayer). Hu et al.\cite{54} report that electronic structure of $\alpha$-PNFs depends on edge passivation by hydrogen and fluorine. Since devices of phosphorene nanoflakes can be fabricated on substrates, substrate-nanoflake interaction is essential. In a theoretical study, Gao et al.\cite{55} investigated the role of substrate, such as Cu(111) and h-BN, on the stabilization of $\alpha$-PNF nanoflakes. No extensive substrate-phosphorene nanoflake interactions and their effects on the electronic structure are available yet.

In this study, we consider 52 nanoflake systems of black and blue phosphorene of diverse geometry (i.e. triangular (t), coronene (c), and parallelogram (p)) and size with bare and hydrogen passivated zigzag and armchair edges and reveal their structural parameters, cohesion and electronic structures. In this respect, most of the nanoflake systems are studied in this paper for the first time. Since the nanoflakes have to be supported by selected substrates in various applications, the nanoflake-substrate interaction is crucial for whether the initial configuration and electronic properties of the free-standing nanoflake will be maintained on the substrate. Important conclusions of our study are summarized as: (i) bare nanoflakes are prone to instability and edge reconstruction; their properties usually do not show well-defined trends. (ii) Bare nanoflakes of phosphorene can attain stability and durability through the saturation of their edges. Their cohesion, formation energy and HOMO-LUMO gaps display well-defined trends with respect to the number of their phosphorus atoms or size, and their geometrical shape or type. The energy gap decreases with $n_P$, and approaches to the band gap of their parent 2D monolayers. Nanoflakes with zigzag edges saturated with hydrogen have consistently higher cohesion than its corresponding armchair
counterparts. Coronene geometry appears to be most favorable energetically for a given number of P atoms and edge geometry. (iii) The interaction between nanoflakes and supporting 2D monolayer substrates like graphene, phosphorene and MoS$_2$ is weak, so that the electronic energy structure of free-standing nanoflakes can be maintained when supported.

2. Computational Methodology

Calculations are performed within the framework of spin-polarized density functional theory (DFT) using plane-wave basis sets and projector augmented wave (PAW) [56] potentials as implemented in the Vienna ab-initio simulation package (VASP)[57]. The exchange correlation potential is approximated with generalized gradient approximation (GGA) using Perdew-Burke-Ernzerhof (PBE) [58] parametrization including van der Waals (vdW) correction. The kinetic energy cut-off for the plane-wave expansion is set to 450 eV. The $\mathbf{k}$-point mesh of $1 \times 1 \times 1$ and $3 \times 3 \times 1$ are used for flakes and flake+substrate systems, respectively. Tests for the convergence of the total energy with respect to the $\mathbf{k}$-mesh and cut-off energy are carried out. We employ following supercells for substrate+flake systems: The $12 \times 12$ supercell for graphene, $9 \times 6$ for $\alpha$-P, $10 \times 10$ for $\beta$-P, $7 \times 7$ for MoS$_2$. Extensive tests of the energy convergence with respect to the $\mathbf{k}$-point mesh and energy cut-off values to be used in the calculations have been carried out. The electronic and geometric relaxation of the structures are performed using rhombic flakes (supercell geometry) with a vacuum distance about 15 Å in all directions, which is large enough to avoid interactions between two adjacent flakes in the periodic arrangement of the supercell method. Atomic positions are optimized using the conjugate gradient (CG) method, where all the atomic coordinates are fully relaxed until the Hellman-Feynman force on each atom is less than 0.001 eV/Å. The energy convergence criteria of the electronic self-consistency was taken as $10^{-5}$ eV between two successive iterations. Gaussian type Fermi-level smearing method is used with a smearing width 0.01 eV. In order to indicate the stability of PNFs, we have calculated the average cohesive and formation energies. The average cohesive energy (per atom) of a nanoflake, which is edge-passivated by H is calculated as:

$$E_c = \frac{E_{PNFH} - n_P E_P - n_H E_H}{n_P + n_H}$$  \hspace{1cm} (1)

where $E_{PNFH}$ is the calculated total energy of a given edge-passivated nanoflake saturated by H atoms, $E_P$ is the calculated total energy of an
isolated P atom, and $E_H$ is that of the isolated hydrogen atom, $n_P$ and $n_H$ are the total number of P and H atoms of the nanoflake, respectively. For the nanoflakes with bare edge (unsaturated) $n_H=0$. $E_c < 0$ indicates that the formation of a nanoflake is favorable relative to free constituent atoms. Hence, the lower $E_c$ the stronger is the cohesion. The average formation energy (per atom) is calculated as:

$$E_f = (E_{PNFH} - n_P(E_{SL}/n) - n_H(E_{H_2}/2))/(n_P + n_H)$$  \hspace{1cm} (2)$$

$n_P$ and $n_H$ are number of P and H atoms in nanoflake, respectively. $E_{PNFH}$ is the total energy of edge passivated nanoflake, $E_{SL}$ is the total ground state energy of 2D monolayer sheet, $n$ is the number of P atoms in the unit cell of monolayer, and $E_{H_2}$ is the energy of $H_2$ molecule. For the nanoflakes with bare edge (unpassivated) $n_H=0$. According to this definition, $E_f > 0$ indicates that formation of a flake from the parent 2D phosphorene phases (and $H_2$ molecule, if the edges are saturated by H atoms) is not favored energetically. Then, a stable nanoflake with $E_f > 0$ corresponds to local minimum on the Born-Oppenheimer surface. The binding energy and of a specific, edge-passivated nanoflake placed on a monolayer substrate is calculated as:

$$E_b = E_{Sub+PNFH} - E_{PNFH} - E_{Sub}$$  \hspace{1cm} (3)$$

where $E_{Sub+PNFH}$ and $E_{Sub}$ are the total energies of substrate+hydrogen saturated nanoflake and bare substrate, respectively. $E_b < 0$ indicates that there is an attractive interaction between the substrate and the nanoflake providing the binding interaction between them.

We performed charge density analysis and calculated atomic charges by using Bader analysis which presents a good approximation to total charge of an atom [59]. By subtracting the free atom charges from the Bader charges we obtained the charge transfer to the edge passivating hydrogen atoms.

3. Results and discussion

We first calculate the optimized structure, cohesive energy and the fundamental band gap of 2D $\alpha$-P and $\beta$-P monolayers for the sake of comparison with the flakes. The optimized structure of $\alpha$-P and $\beta$-P have cohesive energy, $E_c=-3.49$ eV and -3.45 eV, respectively. Earlier, Guo et al.[60] calculated these cohesive energies as -3.30 eV/atom and -3.29 eV/atom, respectively.
Minute differences between present values and those of Guo et al.\textsuperscript{[60]} are due to different pseudopotentials used in the present and previous calculations. Both $\alpha$-P and $\beta$-P monolayers are semiconductors with fundamental band gap of $E_g=0.88$ eV (direct) and 1.88 eV (indirect), respectively. Our results related with the fundamental band gap are in good agreement with previously calculated data \textsuperscript{[23, 25, 61]}.

We now consider a series of bare and hydrogenated $\alpha$-PNFs and $\beta$-PNFs for two commonly known edge structures, i.e. zigzag (zz) and armchair (ac), to investigate the structural stability and electronic properties. We consider three different shapes for nanoflakes; these are triangular (t), coronene (c), and parallelogram (p) structures with zz and ac edge geometries. Edge passivation is usually required for the mechanical and chemical stabilization of a nanoflake. Different kind of atoms can be used to passivate the edges of a nanoflake.\textsuperscript{[37]} Here we passivate zz- and ac-edges by hydrogen atom, while other atoms, e.g. fluorine, can also be used for various purposes like decoration and functionalization.\textsuperscript{[54]}

### 3.1. Bare Phosphorene Nano flakes, PNF

The triangular nanoflakes of $\alpha$-PNF and $\beta$-PNF with zigzag edges are modelled by flakes consisting of 13,22,33,46,61,78 P atoms as seen in Fig.1 (a), while their armchair counterparts are modelled by 18,36,60 P atoms. Coronene nanoflakes with armchair edge are formed by 16,24,54,96 P atoms and zigzag ones with 26,42,84,114 P atoms. As for parallelogram nanoflakes, zigzag versions are constructed by 16,22,28,30,46 P atoms and armchair variants by 24,36,48,72 P atoms. In Table 1, we list the values of $E_c$, $E_f$, $E_{H-L}$ calculated for bare phosphorene nanoflakes, namely $\beta$-PNF and $\alpha$-PNF, in diverse shapes and sizes. Both phases have average P-P bond length ranging between 2.17 Å and 2.34 Å.

In Fig. 2, we illustrate the variation of calculated cohesive energy, formation energy and HOMO-LUMO gap of bare $\alpha$-PNF and $\beta$-PNF with number of P atoms, $n_p$, to reveal possible trends. As a result of the structural irregularity, variation of $E_c$, $E_f$, and $E_{H-L}$ exhibit irregular behavior without a well-defined trend in size-dependency. Here we point out the general trends unveiled from the plots. The cohesion of bare nanoflakes generally increase (i.e. $E_c$ is lowered) with size or with increasing $n_p$. The formation energy of flakes (per atom) are small but positive, indicating the fact that the formation of a flake from 2D phosphorene is unfavorable. The general trend displayed by Fig. 2 is that the formation energy per atom decreases with
increasing \( n_P \); namely the formation of large nanoflakes become less unfavorable. A few cases of parallelogram nanoflakes go beyond this trend due to their shape and relatively lower coordination number of edge atoms.

Nanoflakes with limited number of \( n_p \) are finite size systems and have discrete electronic states instead of bands. The level spacing increases with decreasing \( n_P \) due to the confinement of electronic wave function. Also an energy gap occurs between HOMO and LUMO. This gap can be wider with decreasing \( n_p \), as a natural consequence of quantum confinement effect. For bare nanoflakes here, \( \Delta E_{\text{H-L}} \) displays practically a random variation with \( n_P \). Depending on the the type (t,c,p), edge geometry (zz,ac) and the parent phase (\( \alpha, \beta \)) the energy gap can vary in the range from 0.1 eV to 2.2 eV due to the dangling bonds states of reconstructed atoms.

It was reported that unpassivated atoms of nanoflake systems can lead to edge reconstruction, whereby the 2D nature of flakes can be destroyed as shown earlier in graphene flakes.\cite{62} Earlier, edge reconstruction and stability of black phosphorene nanoribbons have been investigated both theoretically and experimentally.\cite{63, 64, 65, 66} Edge reconstruction is an exothermic process, where the energy of a nanoflake is lowered and hence the structure reconstructs to attain a structure, which is more stable energetically relative to the ideal structure. Thus, the structural configuration in bare nanoflakes cannot be preserved properly upon reconstruction. In the next section, we will compare the average cohesive energies of bare-reconstructed and hydrogen passivated nanoflakes. It is clearly seen that an edge reconstruction occurs at both armchair and zigzag regions for \( \alpha \)- and \( \beta \)-PNFs. The edge reconstruction is very remarkable in small nanoflakes yielding rather asymmetrical structures, so that shapes of these systems are completely destroyed for all triangular, coronene, and parallelogram geometries. Nonetheless, ideal geometry and shape set before the structural optimization are preserved to a large extent for systems with larger than \( \approx 50 \) atoms. As an extreme case, \( \beta \)-PNF with coronene shape consisting of 26 P atoms is disassociated into two pieces. In this study, we also note that the corner regions with low coordination number are reconstructed as shown in Fig. 1. Accordingly, bare phosphorene nanoflakes are prone to instability, which are undesirable in diverse applications. Under this circumstances, the edges and corners can be passivated by adatoms for a stable and durable configuration, which eventually becomes resistant to structural and electronic changes.
3.2. Hydrogen Passivated Phosphorene Nanofoakes, PNFH

When phosphorene nanoflakes are obtained using mechanical exfoliation, unpassivated structures are stabilized by hydrogen termination of the edge atoms. This way their ideal like configuration are maintained. The edge induced bond strain can have remarkable effects on the structural and electronic properties of small nanoflake systems. It was reported that different passivation groups, e.g. O, H, OH, can induce different effects on electronic structure.[67] We consider H atom for edge passivation, since H-passivation has little influence on the edge morphology, ideal structure and electronic properties. In Fig. 3, we present the atomic configurations of hydrogen passivated phosphorene nanoflakes, α- and β-PNFH of diverse shape, size and edge-geometry. In Table 2, we present the optimized cohesive and formation energies, as well as the HOMO-LUMO gap of these nanoflakes. The average lengths of P-P and P-H bonds in diverse β-PNFH are rather uniform and are stabilized at the value of \( \bar{d}_{P-P} = 2.25 \text{ - } 2.26 \text{ Å} \) and \( \bar{d}_{P-H} = 1.44 \text{ Å} \), respectively. While the average length of P-H bonds marks the same value, \( \bar{d}_{P-H} = 1.44\text{Å} \) in α-PNFHs, the average length of P-P bonds is smaller and occurs at \( \bar{d}_{P-P} = 2.23 \text{ Å} \). The average electronic charge transferred from nanoflake to each passivating H atoms is calculated to be \( \rho_F \sim -1.34 \text{ e} \).

In Fig. 4, we present the overall behavior and trends depending on the shape, size and edge geometry of H-passivated nanoflakes, α-PNFH and β-PNFH as revealed from the data in Table 2. First, it is seen that the cohesion in terms of average \( E_c \) increases gradually with the number of atoms \( n_P \) for all nanoflakes; namely for three types of nanoflakes, for two edge geometries and for both α-PNFH and β-PNFH. In view of the fact that the cohesive energies of 2D α-P and β-P are -3.49 eV and -3.45 eV, respectively, the limiting values of \( E_c \) can be estimated as \( n_P \to \infty \). This is an indication that the cohesion may increase with increasing flake size. However, it was reported that the stability of larger nanoflakes are more sensitive to temperature [37], so that flake size should be optimized for a given temperature for use in possible applications. Perhaps, this argument stemmed from the large size oscillation (wiggles) on the surface of flakes.

If we compare the calculated average cohesive energies, \( E_c \) of bare and edge-passivated nanoflakes as given in Table 1 and 2, bare and reconstructed nanoflakes appear to have stronger cohesive energy per atom. The difference in average cohesive energies between bare and edge-passivated flakes decreases with flake size. We note however, that the total cohesive energy of a hydrogen-passivated nanoflake, \( E_{T,c} = E_{PNFH} - n_P E_P - n_H E_H \), is lower
(more energetic) than that of the bare and reconstructed nanoflake, $E_{T,c} = E_{PNF} - n_P E_P$. For example, $\alpha$-PNFH ($\beta$-PNFH) of type t-zz/33P+15H has $E_{T,c} = -151.735 \text{ eV}$ ($-150.660 \text{ eV}$). Whereas, bare and reconstructed $\alpha$-PNF ($\beta$-PNF) of the same type t-zz/33P has $E_{T,c} = -110.014 \text{ eV}$ ($-106.192 \text{ eV}$). This confirms that nanoflakes gain higher stability through hydrogen passivation as compared the reconstruction of bare nanoflakes.

Nanoflakes with zigzag edges have consistently higher cohesion than its corresponding armchair counterparts. $\alpha$-PNFHs with zigzag edges are the flakes with highest cohesion among the similar type of nanoflakes, except one case. Generally, for a given $n_P$ the cohesion is higher in coronene nanoflakes, and cohesive energies are ordered as $E_c[p] > E_c[t] > E_c[c]$. Hence, coronene shape (or type) appears to be most favorable energetically for a given $n_P$ and edge geometry. Notably, the energy difference between $\alpha$-PNFH and $\beta$-PNFH is generally small for any $n_P$, type and edge geometry, like that of their 2D parent monolayers. Hence, the structural transitions from $\alpha$-phase to $\beta$-phase or vice versa can take place by thermal excitation at elevated temperatures, if the energy barrier between them is not high. On the other hand, all the formation energies are positive which means flake structures cannot spontaneously be formed from a phosphorene sheet and $H_2$ molecule. Formation energies follow a trend that the formation of a H-passivated nanoflake becomes less unfavorable as $n_P$ increases. Our calculations predict that armchair as well as zigzag edged coronene $\beta$-PNFHs become energetically least unfavorable as $n_P$ increases.

Average bond length between P atoms $d_{P-P} = 2.26 \text{ Å}$ and $2.23 \text{ Å}$ for $\beta$-PNFH and $\alpha$-PNFH, respectively. The average length of P-H bonds, $d_{P-H} \approx 1.44 \text{ Å}$ for almost all nanoflakes. These values are consistent with previous studies, where bond lengths of P-P bonds in black phosphorus were reported as $2.22$ and $2.24 \text{ Å}$ for two different bonds at two layers [68].

Hydrogen atom is more electronegative than P atom; hence it receives always charge from phosphorene atoms at the edges behaving as an acceptor material. This is consistent with previous studies [54]. The effects of passivation of edge atoms by hydrogen on charge distribution of nanoflakes are different for $\beta$- and $\alpha$-phases. While the calculated average charge density of hydrogen atom, $\bar{\rho} \approx 1.34 \text{ e}$ and distributes rather uniformly among passivating H atoms of the former, it ranges between $-1.33 \text{ e}$ and $-1.72 \text{ e}$ in $\alpha$-PNFH nanoflakes. For example, triangular $\alpha$-PNFH receives more charge as compared to other nanoflakes and hence they become electrically more polarized. This behavior can single out one specific nanoflake from others.
under external electric field.

The level spacings, as well energy gaps, $E_{H-L}$, of nanoflakes decrease with increasing $n_P$, and eventually the band formation of discrete electronic energy states starts to form as the size of the nanoflakes increases, which is also consistent with the previous study investigating phosphorene nanoflakes with larger dimension\[54\]. Conversely, the level spacing, as well as $E_{H-L}$ increase with decreasing $n_P$ as a manifestation of the quantum confinement effect. The overall variations of $E_{H-L}$ with $n_P$ or with size in the plots in Fig. 4 comply with the above arguments based on quantum confinement effect. For small size ($n_P \sim 15$), triangular, α-PNFH and β-PNFH, the calculated values of $E_{H-L} \approx 3.1 \text{ eV}$. The larger $E_{H-L}$ values can be attributed to the chemical hardness of the flake corresponding to larger chemical stability. Chemical hardness is also a measure of the rigidity of electron clouds to deformations\[69\]. However, as $n_P$ increases, this wide energy gap starts to decrease and starts to distinguish β-PNFH from α-PNFH. Notably, the energy gap values of zz and ac edge geometries in each phase coincide. The energy gap of α-PNFH attains values lower than that of the β-PNFH; the difference between them is $\sim 0.6 \text{ eV}$ for $n_P \sim 80$, but increases with increasing $n_P$ to attain a value of $\sim 1.0 \text{ eV}$ as $n_P \rightarrow \infty$. The similar trend is also seen for the coronene type nanoflakes. While the overall behavior of the parallelogram complies with the trends of the triangular and coronene types, their non-uniform geometries and relatively smaller size prevent them to show exactly similar trends. It appears that the bulk like behavior of these flakes can be realized only for $n_P > 200$. Nonetheless, each flake being passivated or unpassivated and having specific type, size, edge geometry and phase can be considered as a unique molecule with well-defined level spacing, $E_{H-L}$. However, as their sizes increase, all these nanoflakes tend to be similar to either one of the 2D monolayer phases with their well-defined energy band gap.

Earlier, Bhatia et al.\[52\] have studied optical and electronic properties of β-PNFHs, and reported 2.77 eV, 2.50 eV, and 2.56 eV $E_{H-L}$ values, for hydrogen-passivated t-zz/33P, p-zz/46P, and c-zz/54P. Our corresponding values for similar flakes are 2.62 eV, 1.96 eV, and 2.40 eV. The results are in reasonable agreement. In another work, Hu et al. have studied larger flake systems and they give an approximate gap value as a function of flake length; $E_g = 0.89 + 4.93/L$ for H-passivated flakes. That means for very large flakes $E_g$ converges to 0.89 eV, which is very close to our calculated value of 0.88 eV for α-P sheet \[54\]. $E_{H-L}$ values of hydrogen passivated black- and blue-
phosphorus quantum dots (PQD) with size \( n_P = 22 \rightarrow 178 \) P atoms have been reported also in a previous study [53]. They report \( E_{H-L} \) values 2.52 to 1.36 eV for \( \alpha \)-PQDs and 2.85 to 2.14 eV for \( \beta \)-PQDs within the studied range of size. These values are consistent with the present values. Small differences originate from different potentials and methods used in the calculations.

3.3. Supported and Hydrogen Passivated Phosphorene Nano flakes

Since nano flakes are normally placed on specific substrates to construct heterostructures, nanomechanical device and mediums for superlow frictions, the nature of interaction between the nanoflake and the substrate becomes crucial. This interaction becomes also critical for the growth of flakes or monolayers on substrates, as well as for the stabilization of nano flakes. A strong interaction can influence the atomic and electronic structure of nanoflake+substrate system. Under these circumstances the electronic structure of a nanoflake can be also substrate-specific. Strong interaction between substrate atoms and phosphorus atoms of the nano flakes can lead to destabilization, which results in massive structural reconstruction and clustering. In fact, Gao et al. have theoretically studied the role of substrate on the stabilization of \( \alpha \)-PNF nano flakes[55]. They reported that \( \alpha \)-PNF is disassociated on Cu(111) substrate due to strong interaction, while the interaction with h-BN surface is so weak to stabilize \( \alpha \)-PNFs. They conclude that a moderate interface interaction is needed to stabilize \( \alpha \)-P and also to grow \( \alpha \)-P epitaxially. Conversely, a weak interactions, like vdW attraction between nanoflake and substrate is usually desired to attain libration motion with low angular frequencies to construct detectors. Also, weak interaction leads to low energy barriers in rotational and translational dynamics of nano flakes on substrate, which is essential for nearly frictionless motion. For reason discussed above, the study of the interaction between nanoflake and substrate has been one of our prime objectives.

To unveil the substrate-nanoflake interaction, we investigated specific nano flakes placed on the selected substrates, namely \( \alpha \)-PNFH on graphene, \( \alpha \)-P and MoS\(_2\) monolayer substrates; \( \beta \)-PNFHs on graphene, \( \beta \)-P, and MoS\(_2\) monolayer substrates. All the flakes are edge passivated by hydrogen atoms with increased chemical and thermal stability. It was shown that quasi-planar structure of edge passivated free-standing phosphorene nano flakes are preserved up to 500 K, although flakes have mechanical flexibility [37]. The size of the flakes is varied from 13 P atoms to 36 P atoms (e.g. 13P+9H, 36P+18H). The equilibrium configuration corresponding to the minimum
(lowest) total energy of a nanoflake+substrate system is obtained by the optimization process explained in computational details, which starts from diverse positions and heights of a nanoflake relative to the selected substrates and minimizes the total energy and atomic forces.

In Fig. 5, we show three typical equilibrium positions of two different flakes on three different substrates. AA, AB, and AC type stacking geometries are considered for flakes on related substrates. Flakes are usually attained the equilibrium height \( h \), of \( \sim 3 \) Å from the substrate, which is significantly larger than the P-P bond distance. The wide spacing between the flake and the substrate indicates weak interaction. Equilibrium stacking (or minimum total energy) configuration depends on flake size, since flakes with larger \( n_p \) are exposed to larger body forces. Hence, the larger the flake size, the stronger is the binding. All the \( \alpha \)-PNFHs are stabilized on \( \alpha \)-P substrate in AB-type stacking. However, \( \alpha \)-PNFHs on MoS\(_2\) are settled in AC configuration. Same nanoflakes (for \( n_p > 13 \)) are anchored to graphene surface in AA stacking. In Table 3, we present the optimized values, such as the equilibrium stacking, the binding energy \( E_b \), and spacing \( h \), calculated for selected nanoflakes-substrate pairs.

Both \( \alpha \)- and \( \beta \)-PNFHs are stabilized on graphene at higher distances compared to their 2D parent sheets. However, the binding energies show different trends. \( \beta \)-PNFHs are adhered to graphene surface more strongly than to \( \beta \)-P and MoS\(_2\) monolayers. As an example, for t-\( zz/33P+15H \) and c-\( zz/24P+12H \) types, the strength of the binding, i.e. the magnitude of \( E_b \), is highest on graphene, but lowest on \( \beta \)-P. The binding is, however, intermediate on MoS\(_2\). As for \( \alpha \)-PNFHs, their binding to different substrates displays a size and shape dependent behavior and can deviate from the order given above for \( \beta \)-PNFHs. All the binding energies per phosphorus atom are less than \( \approx 100 \) meV. This is really a weak binding generated from the weak Van der Waals interaction. Accordingly, we can conclude that, based on these findings, the electronic structures of free-standing nanoflakes presented in Table 1 and 2 can be preserved even if they are supported by specific substrates in Table 3. Notably, not all substrates couple weakly with phosphorene nanoflakes, but some substrates like Cu(111) interact strongly to dissociate the phosphorene nanoflakes[55].

Since the interactions of the hydrogen passivated phosphorene nanoflakes with the specific substrates are weak and hence the spacings between them are wide, the libration frequency of these flakes on these substrates is expected to be low as predicted earlier for graphene nanoflakes[70]. Moreover,
this libration frequency can be affected by a biological molecule, which can be adsorbed to the flake. Hence, the tunable dynamics of the weakly bound phosphorene nanoflakes, which are known to be a biologically important materials, can lead to important biological sensor applications.

4. Conclusions

A large class of phosphorene nanoflakes of diverse type, size and edge geometry with bare and hydrogen passivated edges have been investigated. All nanoflakes considered in this study have cohesion and hence are favorable relative to their free constituent atoms. However, the formations of all nanoflakes are energetically unfavorable relative to the 2D phosphorene phases. The bare (unpassivated) nanoflakes are prone to instability and edge reconstruction. They do not display a well-defined trends with size, due to the edge atoms having small coordination number prone to the reconstruction. Significant amount of electronic charge is transferred from phosphorus atoms to hydrogen atoms when the dangling bonds at the edges are saturated. Consequently the surface of the nanoflake becomes polarized. The flakes, by themselves, attain structural and chemical stability and display well-defined physical properties through passivation by H atoms, and can sustain applications in ambient conditions. Cohesive and formation energies of H-saturated nanoflakes exhibit clear trends depending on their types, sizes, edge geometries and phases. While their cohesion increases with increasing number of phosphorus atoms of the flake, their formation relative to parent 2D phosphorene and H$_2$ molecule becomes less unfavorable. This means that these nanoflakes (passivated or unpassivated) cannot form spontaneously from the parent 2D phosphorene phases. But they can sustain as a local minimum of the energy once they formed following well-defined kinetic paths. Incidentally, hydrogen passivated nanoflakes in coronene geometry appear to be most favorable energetically for a given number of P atoms and edge geometry. The level spacing and the HOMO-LUMO gap of the nanoflake depend on whether the dangling bonds at the bare edge are saturated by H atoms. Hydrogen passivated nanoflakes of both black and blue phosphorene display well-defined trends with respect to their size or the number of phosphorus atoms. In particular, the HOMO-LUMO gaps of hydrogen passivated nanoflakes decrease with the increasing size of the flake in compliance with the quantum confinement effects and eventually converge to the band gaps of the 2D phosphorene phases for large number of phosphorus
atoms.

Even if the interaction of these nanoflakes with some supporting substrates was shown to be strong and led to its dissociation, we showed that their bindings to specific supporting substrates, like graphene, parent phosphorene and MoS$_2$ monolayers are weak. Hence, the properties of nanoflakes determined for free-standing state are maintained even when they are supported by these substrates for specific technological applications. Accordingly, each hydrogen passivated nanoflake having a robust atomic and electronic structure can be considered as a unique molecule having specific energy level spacing and HOMO-LUMO energy gap to function as a specific nanodevice or sensor. Therefore, each phosphorene nanoflake offers wide ranges of options for various technological applications. Additionally, their properties can be functionalized and multiplied by doping of magnetic and non-magnetic adatoms, by forming junctions, composite flakes, and insulator-metal-insulator heterostructures for novel devices and sensors.

5. Acknowledgement

Computing resources used in this work were provided by the TUBITAK ULAKBIM, High Performance and Grid Computing Center (Tr-Grid e-Infrastructure). This research was supported by the TUBITAK under Project No. 116F059. SC acknowledges the financial support of Academy of Science of Turkey, TÜBA for financial Support.
Figure 1: Atomic structures of bare phosphorene nanoflakes considered in this study. Red: $\alpha$-PNF and Blue: $\beta$-PNF. (a) Triangular-zigzag (t-zz); (b) triangular-armchair (t-ac); (c) coronene-zigzag (c-zz); (d) coronene-armchair (c-ac); (e)-(f) 2-atom and 3-atom based parallelogram-zigzag (p-zz); (g) parallelogram-armchair (p-ac).
Table 1: Optimized values of bare (unpassivated) phosphorene nanoflakes of different types calculated by using PBE: Type of $\beta$-PNF; formation energy $E_f$ (meV per P atom); cohesive energy $E_c$ (eV per P atom); HOMO-LUMO gap $E_{H-L}$ (eV); type of $\alpha$-PNF; formation energy $E_f$ (meV per P atom); cohesive energy $E_c$ (eV per P atom); HOMO-LUMO gap $E_{H-L}$ (eV). Here t-ac/18P, as an example, indicates an armchair edged and bare triangular flake comprising 18 P.

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Figure 2: Variation of the cohesive energy $E_c$ (eV per P atom), the formation energy, $E_f$ (meV per P atom), and HOMO-LUMO energy gap $E_{H-L}$ (eV), with number of P atoms, $n_P$ for bare $\alpha$-PNF and $\beta$-PNF with zigzag (zz) and armchair (ac) edge geometries. From left to right: bare triangular (t), bare coronene (c), and bare parallelogram (p), nanoflakes.
Figure 3: Atomic structures of edge-passivated, phosphorene nanoflakes considered in this study. Red: α-PNFH and Blue: β-PNFH. (a) Triangular-zigzag (t-zz); (b) triangular-armchair (t-ac); (c) coronene-zigzag (c-zz); (d) coronene-armchair (c-ac); (e)-(f) 2-atom and 3-atom based parallelogram-zigzag (p-zz); (g) parallelogram-armchair (p-ac).
Figure 4: Variation of optimized values calculated for edge-passivated nano flakes, α-PNFH and β-PNFH with the number of P atoms, n_P. Cohesive energy, $E_c$ (eV/per atom); formation energy $E_f$ (meV/per atom); HOMO-LUMO band gap $E_{H-L}$ (eV). Nano flakes have either zigzag (zz) or armchair (ac) edge geometry. From left to right: bare triangular (t), bare coronene (c), and bare parallelogram (p), type nano flakes.
Table 2: Optimized values of hydrogen passivated phosphorene nanoflakes of different types calculated by using PBE: Type of β-PNFH; formation energy, $E_f$ (meV per atom); cohesive energy, $E_c$ (eV/per atom); HOMO-LUMO gap $E_{H-L}$ (eV); type of α-PNFH; formation energy, $E_f$ (meV per atom); cohesive energy, $E_c$ (eV/per atom); HOMO-LUMO gap $E_{H-L}$ (eV). Here t-ac/18P+12H indicates an armchair edged and H passivated triangular flake comprising 18 P and 12 H atoms.

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Table 3: Equilibrium configuration of edge-passivated phosphorene nanoflakes on various monolayer substrates. Type of α-PNFH; monolayer substrate, Subs; equilibrium site; minimum spacing h (Å); the binding energy $E_b$ (eV). Same listing for β-PNFH flakes. Here, t-zz/13P+9H indicates a zigzag edged and H passivated triangular flake comprising 13 P and 9 H atoms.

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Figure 5: Top and side views of the atomic configurations corresponding to three different stacking geometry for the supported, triangular phosphorene nanoflakes on different substrate monolayers: (a) AA stacking of a triangular, zigzag edged nanoflake, $\beta$-PNFH on 2D blue phosphorene ($\beta$-P) monolayer substrate. (b) AB stacking of a triangular, zigzag edged nanoflake, $\alpha$-PNFH on 2D black phosphorene ($\alpha$-P) monolayer substrate. (c) AC stacking of a triangular, zigzag edged nanoflake $\alpha$-PNFH on 2D MoS$_2$ monolayer substrate. $h$ indicates the minimum spacing between the nanoflake and the monolayers substrate.


