First principle studies of the effects of alkali-metal intercalation on structural transition from black to blue phosphorene and the adsorption of N2H4 on WS2 layers.

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FIRST PRINCIPLE STUDIES OF THE EFFECTS OF ALKALI-METAL INTERCALATION ON STRUCTURAL TRANSITION FROM BLACK TO BLUE PHOSPHORENE AND THE ADSORPTION OF N₂H₄ ON WS₂ LAYERS

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A Dissertation
Submitted to the Faculty of the
College of Arts and Sciences of the University of Louisville
in Partial Fulfillment of the Requirements
for the Degree of

Doctor of Philosophy
in Physics

Department of Physics and Astronomy
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Louisville, Kentucky

December 2021
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FIRST PRINCIPLE STUDIES OF THE EFFECTS OF ALKALI-METAL INTERCALATION ON STRUCTURAL TRANSITION FROM BLACK TO BLUE PHOSPHORENE AND THE ADSORPTION OF N$_2$H$_4$ ON WS$_2$ LAYERS

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DEDICATION

This thesis work is dedicated to my parents. They have been a constant source of support and encouragement throughout my life.
ACKNOWLEDGMENTS

First and foremost, I want to convey my deepest gratitude to my supervisor, Dr. Ming Yu, for her constant guidance and encouragement. She became my ultimate role model with her patience, motivation, enthusiasm, and immense knowledge. I had the best supervisor anyone could ever ask for.

I want to thank Dr. Gamini Sumanasekera and Dr. Jacek Jasinski for giving me an excellent opportunity to collaborate with them. My journey would not be this smooth without their feedback, encouragement, and constant guidance.

I like to thank Dr. Shudun Liu and Dr. Badri Narayanan for being part of my thesis committee. Their expertise and invaluable suggestions greatly enriched this thesis.

I like to thank Dr. C. S. Jayanthi and Dr. Chris. L Davis, for arranging financial support and constant guidance. Maintaining good academic standing, performing TA duties, and continuing research all at the same time was incredibly hard, but their advice and support made it a lot easier.

It’s my pleasure to thank many people from the department of physics and astronomy of UofL who made this thesis possible, especially Ms. Mary Gayle Wrocklage and Missy Klotz. In addition, I like to thanks Dr. Lutz Haberzetttl and Dr. Harrison for their technical support, which was most critical for my research. I want to thank
everybody involved in running the "Cardinal Research Cluster (CRC)."

I am grateful to have incredibly helpful co-workers. Thanks to Congyan Zhang for providing me excellent initial guidance. I learned a lot from her, and her VASP manual helped me a lot. I like to thanks Dr. Manthila Rajapakse, Safia Alharbi, Dr. Bhupendra Karki, and Abu Usman for their incredible support and collaboration.

I would also like to say a heartfelt thank you to my parents and my younger brothers for always believing in me and encouraging me to follow my dreams. They were and will always be there for me.

Finally, I want to thank the greatest blessing of my life, my wife, Kazi Jannatul Tasnim, who has been by my side throughout this Ph.D. Thanks for making every minute of my life worth living for. I would like to thank her family for being very supportive till today.
ABSTRACT

FIRST PRINCIPLE STUDIES OF THE EFFECTS OF ALKALI-METAL INTERCALATION ON STRUCTURAL TRANSITION FROM BLACK TO BLUE PHOSPHORENE AND THE ADSORPTION OF N₂H₄ ON WS₂ LAYERS

Md Rajib Khan Musa
September 13, 2021

A comprehensive density functional theory calculation has been conducted to seek a potential structural transition from black to blue phosphorene layers, with a focus on the roles played by alkali-metal intercalation in black phosphorene/phosphorus. This study reveals that at sufficiently high Li concentration and specific, well-defined configurations, a phase transition from black to blue phosphorene can take place. The Li atoms intercalated in black phosphorene could act as a “catalyst” in the “reactive region” of the lone pair of P atoms, leading to a P-P bond breaking and, subsequently, a local structural transformation from an orthorhombic lattice to an assembly of parallel narrow nanoribbons with rhombohedra-like symmetry. During Li deintercalation, these nanoribbons are self-mended and form blue phosphorene layers with interlayer separation of 4.13 Å, indicating individual layer can be mechanically exfoliated. Besides Li, we studied intercalation of Sodium (Na), Potassium (K), and Cesium (Cs) in multilayer black phosphorene and found that only Li and Cs can induce stable black to blue phosphorene phase transition. We further extend our study by incorporating synergetic effect of pressure and Li intercalation on black to blue phosphorene phase transition. This study shows that pressure indeed can accelerate the phase transition process. We hope our study will guide future experiments in search of a phase transition from black to blue phosphorene.

Hydrazine gas adsorption on layered WS₂ has been systematically studied using first principle calculations. The hydrazine molecules were found to be exothermically physisorbed. The layer-dependent adsorption energy and interlayer separation induced by van der Waals interaction exerted by hydrazine molecules lead to the difficulty in desorbing hydrazine molecules from layered WS₂ as the number of layers increases. The emergence of localized impurity states below the Fermi level was discovered upon the hydrazine adsorption, which significantly alter the band structure and electrical transport properties of pristine WS₂. The existence of defects and the humidity, on the other hand, influences the sensitivity of layered WS₂ to the hydrazine adsorption. This study shows that a perfectly layered WS₂ could be a promising candidate for an efficient nano-sensor to detect hydrazine gas in dry environment.
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Raman shift of Cs intercalated BP

The relative stability (defined as $E_{coh} - <E_{coh}>$) as a function of concentration of phosphorous. The vertical dashed line indicates expected composition for $\alpha - \beta$ transition [153]

Structures of As$_x$P$_{1-x}$ for different values of x.

electron localization function of As$_x$P$_{1-x}$ for different values of x. Red color indicate highly localized electron where blue indicate delocalized electron
1 Introduction of 2D and layered materials

Successful exfoliation of graphene in 2004 by Andre Geim and Konstantin Novoselov [1–3] introduced a whole new class of materials, namely 2D materials, to the scientific world. The defining character of 2D materials is their large lateral dimensions varying from nanometer up to several micrometers, while they are only single to few atomic layers thick [4]. The nano-scaled thickness of 2D materials gave rise to unique properties due to the quantum size effect. These 2D materials show very distinctive electron distribution and transport, high surface-volume ratio, mechanical strength, absence of strong interlayer interactions compare to their 3D counterparts [5–8].

The most famous member of the 2D material family is graphene, which is a single layer of carbon atoms. Each sp² hybridized carbon atom, connected to three other sp² carbon atoms and formed flat honeycomb structure of graphene [9]. Graphene is undoubtedly a wonder material [10]; it is hundred times stronger than steel, conducts electricity better than copper [11], and completely flexible [12].

Beyond graphene, there exists a host of 2D materials with a wide range of different properties. One important group of post-graphene 2D materials is transition metal dichalcogenides (TMDs). Unlike graphene, they are three atomic layers thick, with one layer of transition metal (Mo or W) sandwiched between two layers of
chalcogenides (S, Se, or Te). Based on the coordination nature of transition metal (M) by chalcogen (X) TMDs can be two types, 1T-MX$_2$ has octahedral coordination whereas 2H-MX$_2$ has trigonal prismatic coordination \cite{13}. Monolayer TMDs are direct bandgap semiconductors, and their bandgap can be tuned by applying strain or by increasing the number of layers. TMDs potential for applications in areas such as lubrication, catalysis, electrochemical photocells, and battery systems made them a hot topic among materials scientists \cite{14–19}.

A single layer of silicon (silicene), germanium (germanene), and tin (stanine) are known as Xenes. They have graphene like honeycomb structures but are buckled to varying degrees. This class of materials are epitaxially grown on substrate. Xenes has potential applications from field-effect transistor to topological insulators \cite{20–23}.

Theoretical prediction of new 2D materials and improvement of 2D material synthesis are adding new members to the ever-growing list of 2D materials. Application of 2D materials and their functionalized form are revolutionizing solar energy research, battery, catalysis, chemical and bio-chemical sensor, superconductivity, and many other fields. As the demand for miniature electronic and opto-electronic device is rapidly increasing, 2D materials research will be more relevant in the coming days.

2 Introduction of black phosphorene and blue phosphorene

Black Phosphorous (BP) is a thermodynamically stable allotrope of Phosphorous at room temperature and pressure. BP consists of multiple layers of two-dimensional structures stacked vertically and bonded by weak Vander Walls (vdW) force. The individual layer of BP is known as black phosphorene, which exhibits a graphene-like honeycomb structure. However, due to sp$^3$ hybridization, phosphorene is not flat like graphene; instead, it has a puckered honeycomb structure consists of two layers of atoms \cite{25, 26}. The shortest distance between two phosphorous atoms ($d_1 = 2.224\text{Å}$) is in the zigzag direction, and the largest distance ($d_2 = 2.244\text{Å}$) is in the armchair
direction [see Fig. 2(a)]. Each phosphorus atom is bonded to three adjacent phosphorus atoms; therefore, each “p” orbital retains a lone pair of electrons. The crystalline structure of layered bulk BP is orthorhombic with space group Cmca (#64). Its structural and other properties have previously been discussed [27].

Since first experimental synthesis in 2014 [29–32], phosphorene gained a lot of interest from the research community. Because of its high carrier mobility, high optical and UV absorption, strong in-plane anisotropy, layer-dependent bandgap, and many other exciting properties, BP is of particular interest for electronics, optoelectronics, and energy storage applications [26, 28]. Phosphorene has an anisotropic structure,
Figure 2. (a) Side and top views of black phosphorene (b) Anisotropic properties of black phosphorene i) Band structure ii) Anisotropic change of electron mobility in arm-chair and zigzag direction iii) Poisson ratio of BP iv) Young modulus of BP [28] which leads to anisotropic mechanical, electrical, and thermal transport properties [33]. Fig. 2(b) shows band structure of monolayer phosphorene with a bandgap of $\sim 1.9$ eV at $\Gamma$ point. Interestingly, band structure in $\Gamma - X$ direction and $\Gamma - Y$ direction is anisotropic. Electrical conductance and electron mobility of phosphorene are also shown to be anisotropic [33]. As indicated in Fig. 2, electrical mobility along the armchair direction is three times bigger than the zigzag direction. Mechanical properties of phosphorene also show strong anisotropic behavior; for instance, Poisson’s ratio in the zigzag direction (0.703) is about four times higher than that in the armchair direction (0.175) [34], while Young’s modulus is 3.7 time bigger in the zigzag direction [35].

Blue phosphorene (BlueP) is theoretically predicted [37], stable two-dimensional allotropes of the phosphorous family. Structurally it resembles honeycomb like structure of graphene, with the exception of slight backlines. Its “zigzag” ridges are flatter than the deeper “armchair” ridges of black phosphorene. Energetically it is as stable as black phosphorene (with the binding energy difference $< 2$ meV/atom)
Figure 3. (a) Blue phosphorane monolayer structure (b) blue phosphorene band structure calculated using DFT. c) Density of state of blue phosphorene [36].

[37, 38]. Electronically blue phosphorene has bigger bandgap (>2eV) [see Fig. 3(b)] [37] compared to black phosphorene. It has a tunable bandgap depending on the number of layers, semiconducting-semimetal transition under strain, high carrier mobility, higher in-plane rigidity [39]. Layered blue phosphorene also shows metal intercalation induced superconductivity [40]. Blue phosphorene nanoribbons exhibit anisotropic quantum confinement nature on the bandgap [41]. Their electronic band structure and magnetic properties can be controlled by means of passivation [39, 42]. The blue phosphorene oxide, on the other hand, offers an intriguing platform for the exploration of fundamental properties of quantum phase transitions and novel emergent fermions. Blue phosphorous has great potential in important applications such as gas sensors, nanoelectronics devices, photocatalysts, and lithium-ion batteries.
3 Motivation of this study

For industry-scale applications, it is highly important to develop an efficient and cost-effective fabrication method for the mass production of high-quality blue phosphorene. Several group explored the possibility of growing a single-layered blue phosphorene via epitaxial growth [see Fig. 4(c)] on a proper catalytic substrate [e.g., tellurium functionalized Au(111), Cu(111), and GaN, etc.][43]. The problem associated with epitaxial growth is size and quality of BlueP strongly depend on the choice of the substrate due to the lattice mismatch and binding energy between blue phosphorene and the substrates [43]. Furthermore, epitaxially grown BlueP is hard to be isolated from substrate, and not suitable for growing free-standing single layer BlueP.

Another possible pathway to synthesis blue phosphorane is to apply high pressure
 (> 5GPa) on bulk black phosphorous [44] and then mechanically exfoliate blue phosphorene. However, the problem with this method is that blue phosphorous reverts to black phosphorous as soon as the pressure is released. Therefore, to date, direct growth of freestanding blue phosphorene remains a daunting challenge and seeking another possible pathway to obtain blue phosphorene is desired.

The crystalline structure of BP consists of armchair ridge puckering structure and rings of three connected P atoms in chair conformation sharing edges as in cis-decalin. The blue phosphorus, on the other hand, exhibits an arsenic-type (rhombohedral) structure, made of layers of six-membered rings linked in trans-decalin fashion. They can be accommodated in a common monoclinic subgroup \((P2_1/c)\) with P atoms on general Wyckoff positions \((4g)\). Under moderate compression (5 GPa), lone pair electrons are squeezed out of the interlayer van der Waals reservoir into the P-P bond scaffolding, leading to the formation of a Peierls intermediate along with the transformation from black to blue phosphorus. Such an atomistic mechanism provides a hint to find a possible alternative pathway in synthesizing blue phosphorene. For instance, instead of using pressure, one might consider incorporating foreign elements, such as Li, to induce the structural phase transition from black to blue phosphorus so that mechanical exfoliation becomes technically feasible.

4 Importance of this study

Intercalation has become one of the most widely used techniques to modify properties of 2D materials and has been applied as a means of exfoliating individual 2D layers from their bulk counterparts in large quantities. However, whether it can be effectively applied to induce phase transitions and the accompanying fundamental mechanism is not clear. Here, by applying first-principles approaches, we proposed to explore whether Li intercalation could induce the transition from black to blue
phosphorus so that mechanical exfoliation becomes technically feasible, and to reveal the atomistic mechanism of Li mediated phase transition from black to blue phosphorus [45]. We found that the fundamental mechanism of the bond to lone pair interconversion from black to blue phosphorus mediated by the pressure can also be realized via Li intercalation. We found that Li atoms could act as a “catalyst” that guides the structural transition. We identified the conditions for the Li distribution during intercalation and provided a fundamental guideline for the synthesis of the high-quality large size blue phosphorene. Our study prompts the idea that Li intercalation can drive the P atoms moving along specific directions, resulting in bond breaking and reforming, and subsequently reducing the energy barriers for structural phase transitions. This offers alternative pathways for the synthesis of blue phosphorene and creates an opportunity to explore novel physical phenomena in this and similar 2D systems.

5 A brief outline of this study

We will start with a detail discussion of fundamental theory behind computer simulation of 2D martials in chapter 2. We will discuss the main idea of density functional theory (DFT). In this chapter we will also discuss theory of common DFT data analysis technique (charge density difference, Bader charge analysis, Raman shift, and nudge elastic band calculation).

In chapter 3 we discussed the most important part of this dissertation, Li intercalation in black phosphorous. In this chapter we performed a systematic study of Li adsorption landscape, structural transition of phosphorene upon Li intercalation, identify specific condition for structural transition and mechanism of structural transition.
In chapter 4 we applied pressure on Li intercalated bulk BP and studied its structural changes. In chapter 5 we explored the possibility of Na intercalation induced phase transition.

In chapter 6 we focused on our 2nd project “Hydrazine gas adsorption on WS$_2$”. We discussed preferential N$_2$H$_4$ adsorption site on WS$_2$ surface and changes in electronic band structure of WS$_2$ upon hydrazine gas adsorption.

Our last chapter showcases an ongoing project, where we are going to study the mechanism of Cs intercalation in black phosphorous and exploring the possibility of structural phase transition of Black arsenic phosphorous.
CHAPTER 2
DENSITY FUNCTIONAL THEORY

1 Introduction to computational material design

Computational material design exploits the ever-increasing processing power of computers and powerful theoretical models to design and characterize new materials for diverse applications. Developing new materials in the laboratory with tailored physical and electrical properties is a long and expensive process. Computational material research can significantly accelerate this process and reduce the cost of experimental synthesis of novel materials. Computational simulation not only predicts new materials but also helps to understand the fundamental physics related to many phenomena.

Often computational modelling involves different length and time scale where different theoretical (see Fig. ??) model excels. Quantum mechanics-based first principal model (i.e., HF [46], DFT[47, 48], CC[49]) excel at the smallest time and length scale. First principle-based model is very accurate, transferable, and generalized but computationally very demanding. On the other hand, empirical models (i.e., KMC [50], FEM [51]) are fast and computationally cheap, but they are not as generalized as first principle-based methods. As the goal of this thesis was to provide a fundamental understanding of intercalation, adsorption properties layered materials, we used first principal density functional theory for our calculations.
2 Many-body Schrödinger equation

2.1 Many-body Hamiltonian

Quantum mechanical description of any material achieved by solving many-body Schrödinger equation (SE).

\[ \hat{H} \Psi(\{\vec{r}_k\}, \{\vec{R}_l\}) = E \Psi(\{\vec{r}_k\}, \{\vec{R}_l\}) \]  

(1)

Where \( \hat{H} \) is the many-body Hamiltonian of the system.

\[ \hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_i \sum_{l} \frac{Z_l e^2}{|\vec{r}_i - \vec{R}_l|} \]

\[ + \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + \sum_{I<J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \]

(2)

Here \( m_e \) and \( M_I \) are electron and nucleus mass. \( Z_I \) is charge associate with nucleus and \( R_I \) is atomic position.

As we can see \( \hat{H} \) consists of several parts.

\( \hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 \) and \( \hat{T}_N = -\frac{\hbar^2}{2M_i} \sum_i \nabla_i^2 \) are electronic and nuclear kinetic energies.

\( \hat{V}_{ext} = -\sum_i \sum_{N_{at}} \frac{Z_l e^2}{|\vec{r}_i - \vec{R}_l|} \) is the coulombic interaction between electrons and nuclei.

\( \hat{V}_{ee} = \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \) represents the electron-electron interaction via coulomb potential.

\( \hat{V}_{NN} = \sum_{I<J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \) is the nuclear-nuclear coulombic interaction.

So now we can write equation (2) as

\[ \hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{ext} + \hat{V}_{ee} + \hat{V}_{NN} \]

By solving Schrödinger equation, we can obtain many-body wave function \( \Psi(\{\vec{r}_i\}, \{\vec{R}_k\}) \).

In Quantum mechanics, wave-function \( \Psi \) plays the central role. Every information about a system is contained in the \( \Psi \). If we can solve the many-body equation and find \( \Psi \) somehow, we can obtain any observable using this \( \Psi \).

\[ <\hat{O}> = \int dr_1 \int dr_2 \ldots \int dr_N \Psi^*(r_1, r_2, \ldots r_{N_e}, R_1, R_2, \ldots R_{Nat}) \hat{O} \]

\[ \Psi(r_1, r_2, \ldots r_{N_e}, R_1, R_2, \ldots R_{Nat}) \]  

(3)
So, it turns out calculating any quantum mechanical properties of materials essentially becomes calculating $\Psi$.

2.2 Computational complexity of solving many-body Schrödinger equation

Schrödinger equation is one of the cornerstones of modern physics. Unfortunately, this equation is solvable only for the simplest system. The difficulty of solving SE arise from the many-body interaction present in this equation. As the Hamiltonian contains term like $\sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$ which is electron-electron interaction term, which means solution of Schrödinger equation $\Psi (r_1, r_2, \ldots r_{N_e}, R_1, R_2, \ldots R_{N_{at}})$ is a function of $3N_e + 3N_{at}$ coordinate where $N_e$ is the number of total electrons $N_{at}$ is total number of atoms. Even if we ignore nuclear position and only use electronic coordinates, $3N_e$ is a huge number for any practical condensed matter system. To solve many-body SE (eq. 1) for any decent size system, we have to untangle this many body interaction into single particle system. In the upcoming section, we will introduce several approximations to original Schrödinger Hamiltonian and then attempt to computationally solve it for moderate size system of practical value.

2.3 Born-Oppenheimer (BO) approximation [52]

In previous section we introduced wave function as the fundamental variable of quantum mechanics. $\Psi (r_1, r_2, \ldots r_{N_e}, R_1, R_2, \ldots R_{N_{at}})$ is a function of $3N_e$ electronic and $3N_{at}$ atomic coordinates. Nuclei is several thousand times heavier than electron, thus it is very slow compare to electron. At any instant electron respond immediately to the motion of nuclei. From electron’s point of view nucleus are practically motionless. Based on this fact, Born and Oppenheimer assumed that the motion of nuclei and electrons in a molecule can be separated. So, we can rewrite Schrödinger equation as,

$$\hat{H}\psi(\{\vec{r}_i\})\chi(\{R_k\}) = E\psi(\{\vec{r}_i\})\chi(\{R_k\})$$

(4)
Where, total wave function $\Psi$ become product of $\psi$ and $\chi$.

As electrons are very light and fast moving, we can solve electronic part of Schrödinger equation quantum mechanics and resort to Newtonian mechanics based molecular dynamics to simulate the dynamics of nucleus.

2.4 Hartree - Fock method

The main difficulty of the many-body problem is that we cannot replace it with $N$ number of equivalent single body problem with the original electron-electron interaction, which still presents in the Hamiltonian. So, in 1928 Hartree proposed that we can replace the electron-electron interaction with a static potential and eventually reduce the problem into a single body problem [53].

If we replace $\vec{V}_{ee}(\vec{r}) = \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$ by $\vec{V}_{ee}(\vec{r}) = \int \frac{dr'de^2}{|r-r'|} n(r')dr'$ where $n(r')$ is the density of electron at point $r'$

$$n(r) = \sum_i |\phi(r_i)|^2$$

then we can decompose N-body wave function in terms of the product of N single wavefunction.

$$\psi(r_1, r_2, \ldots r_{Ne}) = \phi(r_1) \phi(r_2) \phi(r_3) \ldots \phi(r_N)$$

Finally, we got the system of Hartree equation, which describe individual wavefunction of each electron

$$\left[-\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i} \frac{Z_i e^2}{|\vec{r}_i - \vec{R}_I|} + e^2 \sum_{i \neq j} \frac{\int |\phi(\vec{r}')|^2 dr'}{|\vec{r}_i - \vec{r}'|}\right] \phi_i = E_i \phi_i \quad (5)$$

Beauty of Hartree equation is instead of all electrons interacting with each other, each electron feels the average combined effect of all other electrons. One of the biggest drawbacks of Hartree equation is, it does not follow Pauli’s exclusion principle. To incorporate anti-symmetric behavior of electron, Fock later introduce staler determinant type wave function. In Fock formulation wave-function $\psi$ is replaced by,
Figure 5. Accuracy vs system size of several electron structure theory methods. DFT works with moderately large system size with acceptable accuracy.

\[
\psi(r_1, s_1, \ldots, r_{N_e}, s_{N_e}) = \frac{1}{\sqrt{N_e!}} \det \begin{bmatrix}
\phi_{n_1}(r_1, s_1) & \phi_{n_1}(r_2, s_2) & \cdots & \phi_{n_1}(r_{N_e}, s_{N_e}) \\
\phi_{n_2}(r_1, s_1) & \phi_{n_2}(r_2, s_2) & \cdots & \phi_{n_2}(r_{N_e}, s_{N_e}) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_{n_{N_e}}(r_1, s_1) & \phi_{n_{N_e}}(r_2, s_2) & \cdots & \phi_{n_{N_e}}(r_{N_e}, s_{N_e})
\end{bmatrix}
\]  

(6)

Where \( s_1, s_2, \ldots, s_{N_e} \) are spin of electron

2.5 From wave function to density

Wave function-based method like Hartree-Fock is very accurate, but solvable only for small molecular system. For large system it is still computationally unreachable.

Density Functional Theory (DFT) replaced 3\(N\) dimensional problem with 3 dimensional density of ground state electron, which dramatically reduced the computational cost and made quantum mechanical simulation of material a practical tool. DFT based simulations are accurate enough for many practical purposes and can simulate up to several thousand atoms (using Linear scale \(O(N)\) DFT [54, 55]), thus
become widely popular among material science communities.

2.6  Hohenberg – Khon theorem

The entire field of density functional theory is based on two mathematical theorems proved by Hohenberg and Khon and a set of equation derived by Khon and Sham. First Hohenberg–Kohn (HK) theorem states that the ground state energy of any interacting many particle quantum systems with a given fixed inter-atomic interaction is a unique functional of the ground state electron density $n(r)$.

Significance of this theorem is, there exists a one-to-one correspondence between ground state wave-function and ground state density. Thus, solving Schrödinger equation becomes finding a 3 dimensional density function, rather than a function of 3N variable.

The first HK theorem rigorously proved that ground state density exists, but it does not give any direction on how to calculate this density. Second theorem states that true ground state density minimizes the energy of the system. If we had a known “true” functional form, we could vary the electron density and minimizes the functional, thus found the ground state density.

2.7  Khon-Sham equation

Practical implementation of DFT start with Khon-Sham equition [48, 56], which is given by,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}} (r)\right] \psi_i (r) = \epsilon_i \psi_i (r)$$

(7)

where,

$$V_{\text{eff}} (r) = v_{\text{ext}} (r) + \int \left( \frac{n(r')}{|r - r'|} \right) dr' + v_{\text{xc}} (r)$$

(8)
$v_{xc}(r)$ is known as exchange-correlation potential and given by,

$$v_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)}$$

This equation is of the same form as Schrödinger equation, the difference is the effective potential part.

The energy is written as,

$$E = 2 \sum_{i}^{occ} \epsilon_i + E_{XC}[n(r)] - V_{XC}(r) \cdot n(r) dr - \frac{e^2}{2} \int \frac{n(r) n(r')}{|r-r'|} dr dr'$$

(10)

We need an approximation for exchange-correlation functional $E_{XC}[n(r)]$. The most used approximation for $E_{XC}[n(r)]$ are local density approximation (LDA) and generalized gradient approximation (GGA) [57].

2.8 Local density approximation

Local density approximation (LDA) assumes that the value of exchange-correlation functional at any point of space, solely depends on the value of electron density of that point. $E_{XC}^{LDA} = \int \epsilon_{xc}(n(r)) n(r) dr$ where, $\epsilon_{xc}$ is the exchange-correlation energy per-particle of a homogenous electron gas with local electron density of $n(r)$. LDA is accurate enough for system with slowly varying charge density. But for molecules, it overbinds the system and gives shorter bond length. LDA underestimates lattice constant by up to 5% in many cases. Some properties such as the dielectric and piezoelectric constant can be overestimated by 10%.

2.9 Generalized gradient approximation

LDA performed very poorly where electron density has rapid spatial variation, like molecular system. GGA [57] improved over LDA by incorporating gradient of electron density in addition to local electron density. $E_{XC}^{GGA} = E_{xc}[n(r), \nabla n(r)]$. The parameterization of LDA is unique but there many versions of GGA. Some GGA functional are parameterized by fitting experimental data (i.e., atomization energy),
some are derived from pure theoretical calculation. PW91, PBE, B3LYP are some examples of commonly used GGA functional.

GGA consistently give good estimate of structural properties for majority of the system with error range between 1% to 3%. It solves the over binding problem of LDA and gives a bigger lattice constant (unfortunately it slightly overestimates) and lower cohesive energies. GGA also underestimates band gap by 50% in many cases.

2.10 Solving Khon-sham equation

The Khon-Sham equation is solved iteratively. First, we guess an initial electron density \( n(r) \). This guess can be totally random or by combining atomic electron density. Then Khon-Sham Hamiltonian is formed using this electron density. Next by solving Khon-Sham equation we can obtain \( \psi_i \) which in turns gives \( n(r) \). This self-consistency loop breaks when magnitude of change of electron density is lower than a convergence criterion.

3 Calculating material properties using DFT

3.1 Structure optimization

Electronic energy of the system is obtained by solving Schrodinger equation

\[
H\psi_i = \epsilon_i \psi_i
\]

\[
E_{tot} = \sum_i f_i \epsilon_i + E_{ion}
\]

where \( f_i \) is the Fermi occupation function.

Then we can obtain force by applying Hellmann Feynman equation

\[
F = -\nabla_i E_{tot}
\]
Figure 6. Flow chart of solving Khon-Sham equation [58]
Based on this force acting on each atom, new atomic coordinates are determined by applying optimization algorithm like conjugate gradient or quasi-Newton method. When the energy difference and force of two consecutive MD step reach to the stopping criteria (i.e., $10^{-4}eV$ for energy and $10^{-3}eV/\AA$ for force), the system is fully relaxed.

Total energy and its derivative not only depend on the atomic coordinates but also depends on the cell volume, lattice constants, and cell shape. We can determine the equilibrium lattice constant by relaxing the system with a range of lattice constant value and then finding the lattice constant associate with minimum energy. Fig. 7 illustrates an example of this lattice constant optimization process, total energy of hcp Cu is calculated for different value of $c/a$ with a range of $a$ values. Minimum value of energy vs lattice constant $a$ curve gives the equilibrium value of both $c$ and $a$. As we can see in this example the equilibrium value of $c/a = 1.633$ and $a = 2.575\AA$.

This manual search of optimum lattice parameter is only doable, if the number of degrees of freedom is low. But in case of large number of degrees of freedom (i.e., lattice symmetry, lattice constant, and atomic positions), manual search over this whole parameter space is nearly impossible. In that case we must rely upon automated relaxation method. VASP provide a method (using ISIF =3 tag) to simultaneously optimize atomic position, lattice constant and lattice angle. In our study, Li intercalation induces local pressure, and to release that pressure we needed to change both cell volume and symmetry along with atomic position, so we used VASP automated cell volume and size relaxation method to find equilibrium structure of Li intercalated black phosphorous.

### 3.2 vdW correction

In layered materials Van der Waals interaction plays an important part. In VASP vdW interaction is modeled by a parametric function added as a correction to the
Figure 7. Total energy of hcp Cu structures for a range of c/a value [59]

Khon-Sham energy functional [60, 61]

\[ E_{DFT-vdW} = E_{KS-DFT} + E_{disp} \]  (14)

\( E_{disp} \) is the dispersion energy, \( E_{KS-DFT} \) is regular Khon-Sham energy. \( E_{disp} \) is calculated by various approximation methods. As an example DFT-D2 correction by Grimmes is expressed as

\[ E_{disp} = -\frac{1}{2} \sum_{i=1}^{N_{atom}} \sum_{j=1}^{N_{atom}} \sum_{L} C_{6ij} f_{d,6}(r_{ij}, L) \]  (15)

\( C_{6ij} \) is the dispersion coefficient for atom pair at \( ij \) where \( r_{ij} \) is the distance between them. \( f(r_{ij}) \) is the damping function which prevent energy going to \(-\infty\) at \( r = 0 \).

DFT-D3 model is slightly more complicated model

\[ E_{disp} = -\frac{1}{2} \sum_{i=1}^{N_{atom}} \sum_{j=1}^{N_{atom}} \sum_{L} \left( \frac{C_{6ij}}{r_{ij,L}^6} f_{d,6}(r_{ij}, L) + \frac{C_{8ij}}{r_{ij,L}^8} f_{d,8}(r_{ij}, L) \right) \]  (16)
In this model the parameters $C_6$ and $C_8$ depend on the coordination number of each atom, which makes it more accurate compare to DFT-D2 model.

The damping term in D3 model is given by

$$f_{d,n}(r_{ij}, L) = \frac{S_n}{1 + 6 \left( \frac{r_{ij}}{S_{R,n}R_{0,ij}} \right) - \alpha_n}$$  \hfill (17)

Where $R_{0,ij} = \sqrt{\frac{C_8}{C_6}}$ and the parameter $S_6, S_8, S_{R,6}$ are adjustable parameters whose value depends on the type of exchange-correlation function used.

Importance of Van der Waals correction is more evident in case of 2D and layered materials. As an example, Fig 8 shows interlayer separation of Si-C/Ge-C bi-layer changes significantly due to vdW correction. In fact, individual layers of multilayer 2D materials (i.e., Graphene) stick together with vdW force, for this reason they are also known as van der Waals materials.

![Figure 8. Relative energy with interlayer separation of Si-C/Ge-C bilayer with and without vdW correction [62]]
3.3 Nudged elastic band (NEB) method

Nudge elastic band \([65, 66]\) is a popular method to find the reaction pathways when the reactants and product is known. In context of solid-state physics, we are mostly concern about how the position of a group of atoms change from one stable configuration to another. For instance, in Fig. 9 blue color atom is moving from left side to right side and \(\Delta E^+\) is the height of the energy barrier. And the path taken by system to go from initial to final state is known as minimum energy path (MEP). The NEB works by first making a linear interpolation between initial and final state and make several intermediate configurations (known as image). These images are connected to each other by spring and NEB minimize the energy of these spring.

\[
\vec{F}_i^0 = -\vec{\nabla}V(\vec{R}_i)\bigg|_\perp + \vec{F}_i^s \cdot \hat{\tau}_\parallel \hat{\tau}_\parallel
\]  

where
\[
\vec{\nabla}V(\vec{R}_i)\bigg|_\perp = \vec{\nabla}V(\vec{R}) - \vec{\nabla}V(\vec{R}_i) \cdot \hat{\tau}_\parallel \hat{\tau}_\parallel
\]  

Here \(\hat{\tau}_\parallel\) is parallel unit vector of the path. And spring force is given by
\[
\vec{F}_i^s = k_{i+1} (\vec{R}_{i+1} - \vec{R}_i) - k_i (\vec{R}_i - \vec{R}_{i-1})
\]
Here $\vec{R}_i$ is the atomic coordinates of i’th image. This means that both the perpendicular component of the spring force and the parallel component of the true force are zero. This is known as nudging as this force pushes the image to the MEP.

3.4 Charge density difference

Charge density difference (CDC) is a powerful post processing method to understand electron distribution in different parts of the system. If system AB is made up of A and B than

$$\delta\rho_{AB} = \rho_{AB} - \rho_A - \rho_B$$  \hspace{1cm} (21)

This $\delta\rho_{AB}$ gives a qualitative idea how charge redistributed between subsystem A and B after they are combined.

Charge density difference can also show effect of external pressure or electric field on the charge density, for example

$$\delta\rho_{AB} = \rho(AB \text{ under pressure}) - \rho(AB)$$  \hspace{1cm} (22)

In analysis of catalysis, gas adsorption, surface reconstruction, doping, charge density difference analysis can provide very informative insight. Fig. 10 shows charge density difference of WS$_2$ surface after absorbing N$_2$H$_4$ molecule. Exact numerical value of transferred charge is calculated using Bader analysis.

3.5 Bader Analysis

Analyzing complex interaction of atomic electron density inside molecule or solid is a very complex task. Bader analysis [68, 69] is a powerful tool to partitioning charge into atomic contribution.

The idea behind the Bader analysis is to divide space within molecular system into atomic volume refer to as Bader volume. Each Bader volume contain a charge density maximum and the volume are separated by zero flux surface. Sum of charge enclosed
inside Bader volume is a good approximation of atomic charge. Bader analysis along with charge density difference can give insight into how electrons redistributed in a complex interface.

Fig. 11 shows grid-based Bader decomposition scheme. The input for Bader analysis is charge density mesh $\rho(i,j,k)$ where $\rho$ is charge density at the grid point denoted by $i, j, k$. This grid is need to be fine enough that linear interpolation between points is good approximation of real charge density in the bonding region. Steepest ascent algorithm is used to determine charge partition in Bader analysis. As in Fig. 11.A the first path start at point $(i_1, j_1, k_1)$ and after 4 step it reaches local maximum $m_1$. Second path start at $(i_2, j_2, k_2)$ and end up in a point already connected to path $m_1$, so this $(i_2, j_2, k_2)$ is also belong to maximum $m_1$. We can continue this process for every grid point and find all the maxima they belong to. Finally, we partition the space inside which all grid points belong to same maxima.

3.6 Phonon

Vibrational spectrum of crystalline structure provides plethora of information regarding the dynamic behavior of that material. Dynamic stability, thermal conductivity,
Figure 11. Algorithmic steps of bader analysis using charge grid [70]

thermal expansion, phase transition, superconductivity, and many other properties of material can be explained in terms of its phonon spectrum.

To obtain Phonon spectrum in harmonic approximation limit (small atomic displacement), second order force constant is given by

\[
\frac{\partial^2 \Phi}{\partial u_\alpha(lk)\partial u_\beta(l'k')} = -\frac{\partial F_\beta(l'k')}{\partial u_\alpha(lk)}
\]  

Dynamical properties of atom is obtained by solving eigenvalue equation of dynamical
matrix \( D(q) \)

\[
D(q) e_{qj} = \omega_{qj}^2 e_{qj}
\]  

(24)

\[
\sum_{\beta\kappa} D^{\alpha\beta}_{\kappa\kappa'}(q) e_{qj}^{\beta\kappa'} = \omega_{qj}^2 e_{qj}^{\alpha\kappa}
\]  

(25)

Dynamical matrix \( D(q) \) is a \( 3N \times 3N \) Hermitian matrix so its eigenvalues are real, here \( N \) is the number of atoms in the unit cell and there are \( 3N - 3 \) optical modes. After obtaining phonon frequencies over the Brillouin zone, we can calculate phonon energy

\[
E = \sum_{qj} \hbar \omega_{qj} \left[ \frac{1}{2} + \frac{1}{\exp\left(\frac{\hbar \omega_{qj}}{k_B T}\right) - 1} \right]
\]  

(26)

Where \( T \) is the temperature and \( k_B \) is Boltzmann constant. Using thermodynamic relation several important thermal quantities can be measured, like constant volume heat capacity \( C_v \), Helmholtz free energy \( F \), and Entropy \( S \)

\[
C_v = \sum_{qj} C_{qj}
\]

\[
= \sum_{qj} k_B \left( \frac{\hbar \omega_{qj}}{k_B T} \right)^2 \exp\left( \frac{\hbar \omega_{qj}}{k_B T} \right) \left[ \exp\left( \frac{\hbar \omega_{qj}}{k_B T} \right) - 1 \right]^2
\]  

(27)

Fig. 12 shows an example of phonon density of state of FCC Al and its thermal properties derived from phonon density of state.

Phonon frequency has major implication in determining the dynamical stability of the system. A system with imaginary phonon frequency is not stable and can lead to an alternative structure through continuous atomic displacements.

3.7 Raman spectrum

In harmonic approximation of crystal vibration, we found that, vibrational eigen-modes can be found by solving [72, 73]
\[ \sum_{k=1}^{3N} (H_{jk} - \lambda_i M_{jk}) X_{ki} = 0, \quad j = 1, \ldots, 3N, \quad \lambda_i = (2\pi\nu_i)^2 \quad (28) \]

Here \( H \) is the hessian matrix of the system and \( X_{ki} \) is the element of ith eigenvector. Atomic displacement in the direction of ith eigenvector is given by

\[ U_{ki} = Q_i X_{ki} \quad (29) \]

Here \( Q \) is the normal mode coordinate. Derivative of any properties in terms of normal mode coordinate is calculated using atomic cartesian coordinate as follows

\[ \frac{dA}{dQ_i} = \sum_{k=1}^{3N} \frac{\partial A}{\partial R_k} X_{ki} \quad (30) \]

Now Raman cross section for the ith eigen mode is given by

\[ \frac{d\sigma_i}{d\Omega} = \left( \frac{2\pi\nu_s}{c^4} \right)^4 \left| \hat{e}_s \frac{\partial \alpha}{\partial Q_i} \hat{e}_L \right|^2 \frac{h}{8\pi^2\nu_i} \left( n_i^b + 1 \right) \quad (31) \]

\[ n_i^b = \left[ \exp \left( \frac{\hbar \nu_i}{kT} \right) - 1 \right] \quad (32) \]

Here \( \nu_s \) is the frequency of scattered light and \( \hat{e}_s \) and \( \hat{e}_L \) are unit vector in the electric field direction of scattered and incident light.

From this we can have final expression for Raman cross section as
\[
\frac{d\sigma_i}{d\Omega} = \frac{(2\pi\nu_s)^4}{c^4} \frac{h \left(n_i^b + 1\right)}{8\pi^2 \nu_i} \frac{I_{Ram}}{45}
\]  
(33)

\[
I_{Ram} = 45 \left( \frac{d\alpha}{dQ_i} \right)^2 + 7 \left( \frac{d\beta}{dQ_i} \right)^2
\]  
(34)

Here \(I_{Ram}\) is the Raman Intensity for \(i\)th normal mode, and here \(\alpha\) is mean polarizability derivative and \(\beta\) the anisotropy of the polarizability tensor derivative.

In VASP this is done by first calculating Hessian matrix of the relaxed structure. Hessian calculations give \(3N_{atom} - 1\) normal modes frequency and eigen vector. Then derivative of macroscopic polarization vector in terms of normal mode is calculated. Finally, we calculated Raman intensity using equation (34).
CHAPTER 3
Li INTERCALATION IN BLACK PHOSPHOROUS

1 What is intercalation

Intercalation is a reversible process of inserting molecules, atoms, or ions inside layered materials [74]. It is one of the most widely used techniques to modify properties of layered materials and has been applied as a means of exfoliating individual 2D layers from their bulk counterparts in large quantities. Fig. 13 shows commonly used intercalation techniques [75]. As shown in Fig. 13a, electrochemical intercalation is driven by applying external voltage in an electrochemical cell setup, where anode and cathode play the roles of intercalant and host. Group I and Group II metals like Li, Na, Mg are well-known donor-type intercalants and are widely used with many-layered materials using the electrochemical intercalation method [76–79]. Electrochemical intercalation is popular due to its easy reversibility. Typically, deintercalation is achieved just by reversing the polarity of external voltage.

The vapor phase intercalation method is another widely used intercalation method (Fig. 13b). In this method, intercalant and host materials are heated together inside a sealed vessel. Then, depending on temperature gradient and vapor pressure gradient inside the tube, intercalant diffuse into host material structures. For example, several studies reported successful vapor phase intercalation of alkali (Na, K, and Cs) [80] and transition metals (Cu, Cd, and Hg) [81] into graphene and TMDs.

In the liquid phase intercalation method (Fig. 13c), host materials are submerged into intercalant solution [82–84] or molten intercalant [85, 86], then intercalant atoms
creeps into vdW gaps of host materials. The rate and amount of intercalation depend on the solvent type, temperature, intercalant concentration, and the size of the host lattice structure. This method is fundamentally different from electrochemical intercalation as this method doesn’t require any external current. For non conducting host material, this is a method of choice.

2 Intercalation as tools of property tuning

Intercalation is also a powerful tool for material synthesis and material property tuning[75]. Intercalation can be used for modifying interlayer interaction [87, 88], doping of 2D materials [89, 90], changing electronic properties, even creating new phases of material [91]. Intercalation is commonly used in large-scale exfoliation of 2d materials from their bulk counterparts. The main idea behind this process is intercalation increase the separation between individual layers and weakens the interlayer interaction, thus lower the barrier of the exfoliation. Exfoliation of TMDs using Li
Intercalation and deintercalation is the fundamental process responsible for Li-ion batteries [94]. In commercial Li-ion batteries, Li ion are intercalated into interlayer gaps of graphite anode. As the size of Li atom is very small compare to interlayer gaps of graphite, insertion, and extraction of Li from graphite anode does not alter the host structure in any considerable amount. Apart from exfoliation and energy storage, intercalation used in wide variety of property tuning process, reversible doping, band structure engineering for opto-electronic devices [95], induce magnetic phase transition [96, 97], doping induced superconductivity [98], modify thermal properties, and control electromagnetic wave absorption [99, 100].

3 Intercalation induced phase transition

Intercalation can drastically change the structure of 2D layered materials. Intercalation weakens the interlayer attractions; thus, layers can slide against each other and change stacking order. An experimentally observed example of this phenomenon is, changing of stacking order (AB to AC) of BP following Na intercalation [101]. Li intercalation induced, 2H to 1T/1T’ structural transition of TMDs, is a well-studied example of intercalation induced structural phase transition. During Li intercalation in MoS$_2$, the symmetry around the Mo atom changes, and the translation of atomic layers causes the formation of octahedral slabs of 1T-MoS$_2$ like in TiS$_2$ [102].

Now in our study, by applying first-principles approaches, we explored Li intercalation induced phase transition from black to blue phosphorus so that mechanical exfoliation becomes technically feasible and revealed the atomistic mechanism of Li mediated phase transition from black to blue phosphorus [103]. We found that the
fundamental mechanism of the bond to lone pair inter-conversion from black to blue phosphorus mediated by the pressure can also be realized via Li intercalation. We also found that Li atoms could act as a “catalyst” that guides the structural transition. We identified the conditions for the Li distribution during intercalation and provided a fundamental guideline for the synthesis of the high-quality, free-standing blue phosphorene. Our study prompts the idea that Li intercalation can drive the P atoms moving along specific directions, resulting in bond breaking and reforming and subsequently reducing the energy barriers for structural phase transitions. This offers alternative pathways for the synthesis of blue phosphorene and creates an opportunity to explore novel physical phenomena in this and similar 2D systems. Fig. 14 schematically illustrate our idea of synthesis blue phosphorene from black phosphorene using Li intercalation.
Computational Methods

We performed systematic first-principles calculations based on the density functional theory (DFT) [47, 48], implemented in the Vienna ab initio simulation package (VASP) [105]. The core-valence interaction was described by the frozen-core projector augmented wave (PAW) method [106] [i.e., considering one (s) valence electron on Li and five (two s and three p) valence electrons on P atoms]. The generalized gradient approximation (GGA) [57] of Perdew-Burke-Ernzerhof (GGA-PBE) [107] was adopted for the exchange-correlation functional. For the study of Li intercalation on monolayer and double-layer black phosphorene, a $2 \times 2$ planar supercell was chosen with a vertical vacuum space of 25 Å between adjacent layers to avoid any mirror interactions. For the study of Li intercalation in the black phosphorus, an orthorhombic unit cell was chosen. The Brillouin zone was sampled either by $16 \times 1 \times 12$ (for single- and double-layered systems) or by $9 \times 9 \times 9$ (for multilayered systems) gamma centered k-point meshes generated in accordance with the Monkhorst-Pack scheme [108] in the structural relaxation and charge distribution calculations. An energy cutoff of 300 eV was set for the plane-wave basis in all calculations. Energy and force convergence criteria were set to be $10^{-4}$ eV and $10^{-3}$ eV/Å, respectively. The systems were fully relaxed using the conjugate-gradient algorithm [109] implemented in VASP. The local strain introduced by the Li intercalation was fully released by allowing the free changes in the degrees of freedom on atomic positions, the unit cell shape, and cell volume (e.g., no restrictions on the atoms, the symmetry, and the volume) during the full relaxation process. The effect of vdW interactions was considered by employing the semiempirical correction scheme of Grimme [60, 61], implemented in the VASP package (i.e., referred as DFT-D3 in the VASP code). The charge transfer between Li and layered phosphorene was evaluated based on the Bader scheme [68, 69], which provides an intuitive way of separating the charge related to each atom using first-principles calculations. The charge redistribution in real space was evaluated by the
difference of electron charge density (DCD), defined as $\rho = \rho_{\text{total}} - \rho_P - \rho_{\text{Li}}$, where $\rho$ total is the total electron charge density of the combined system; $\rho_P$ and $\rho_{\text{Li}}$ are the electron charge densities associated with the layered phosphorene (or phosphorus) and Li atoms in the combined system, respectively. Namely, $\rho_P(\rho_{\text{Li}})$ was evaluated by removing Li (P) atoms from the relaxed combined system and calculating the density of states without further relaxation. Thus, the DCD tracks the charge transfer to get an idea of what is interacting with what in the system and how strongly they interact.

5 Preferential Li deposit position and Li distribution

To understand how Li atoms are distributed on monolayer black phosphorene, we calculated single Li atom adsorption energy landscape. We considered a $2 \times 2$ phosphorene supercell with 16 P atoms as our working system and classify bond $b_1 (~2.22\AA)$ as the zigzag bond and $b_2 (~2.31\AA)$ as the armchair bond, as indicated in Fig. 15a. Each side of phosphorene monolayer has several highly symmetric Li adsorption sites. Center of triangular region formed by three zigzag bonded P atoms marked as VH and TH, on Top of P atoms marked as TA sites, and on top of middle of zigzag bond marked as VB and TB. The results are shown in Fig. 15(a). It is found that positions of the Li atom with relatively low adsorption energies are along the valley in the zigzag direction, and the minimum energy is at the VH sites. The position of the Li atoms with relatively high energy is on top of ridge along the zigzag direction with maximum relative energy on the top of P atoms, referred to as TA sites. Based on our energy landscape, we found that Li atoms prefer to stay on top of VH site with optimized vertical distance of 2.53\AA, and shortest Li-P distance is $\sim 2.48\AA - 2.66\AA$ as shown in Fig. 15.(b), which is comparable with Li-P bond length of 2.6\AA [110]. Furthermore, diffusion barrier along the valley in zigzag direction is only $\sim 0.1eV$, which is several times smaller than that along the armchair direction.
Figure 15. (a) The adsorption energy landscape of a Li atom deposited on black phosphorene. The colors in the left-hand column scale the adsorption energy at an adsorption site relative to that at the VH site. The notations of VH, VB, TB, and TA represent the specific Li adsorption sites, as defined in the text. A schematic structure of the 2 × 2 phosphorene supercell is inserted to illustrate the Li adsorption positions. The zigzag and armchair bonds are indicated by $b_1$ and $b_2$, respectively. (b) Side view of Li atoms deposited on the top and bottom VH sites, and the numbers represent the shortest distances between Li and P atoms and the vertical distance. (c) Li$_8$P$_{16}$ with the first type of initial Li configuration, (d) Li$_8$P$_{16}$ with the second type of initial Li configuration, and (e) Li$_{16}$P$_{16}$ with the third type of initial Li configuration. The pink balls denote P atoms, and the light and dark gray balls represent Li atoms at top and bottom VH sites, respectively.
(~ 0.58eV – 0.78eV), (see the detailed discussion in Ref. [111]). Based on these we can conclude; Li prefers to move along valley of zigzag and adsorb on VH sites located in the valley in zigzag direction.

At higher concentration of Li, all VH positions will be filled and then metastable VB, TB sites will start to fill-up. Experimentally, Li intercalation is carried out, either by electrochemically or by means of vapor phase intercalation method. Depending on available thermal energy, various Li distribution on the adsorption energy landscape could happen during Li intercalation. We have systematically studied the Li diffusion/migration with various Li distributions on VH, VB, TB, and TA sites in our previous work [111] and found that those Li distributions can significantly increase the Li capacity for high performance of Li-ion batteries and have no influence on the structure of black phosphorene. In our study we mainly focused on the distribution of Li atoms on energetically lowest adsorption sites (VH position). We have examined how such low energy Li configurations, affected the structure of black phosphorene and, what role played by Li atoms during such Li intercalation.

We have conducted a systematical survey for all possible Li distributions on VH sites and found that the distribution of Li on those energetically preferential VH sites can be described in terms of the P-P armchair bond and clarified as three types of Li occupations. The first type of Li occupation corresponds to Li atoms deposited at one end of the armchair bonds, either at the top VH sites [such as the white dot shown at the top-left area of the 2 × 2 super cell in Fig. 15(a)] or at the bottom VH sites [such as the gray dot shown at the top-left area of the 2 × 2 super cell in Fig. 15(a)]. The second type of Li occupation corresponds to Li atoms deposited at two ends of the armchair bonds, one at the top VH site and the other at the bottom VH site, referred to as a Li pair [like the gray and white dots shown at the top-right area of the 2 × 2 super cell in Fig. 15(a)]. The third type of Li occupation corresponds to Li atoms deposited on top/bottom VH and top/bottom TH sites (the center of
Figure 16. Top views of initial Li configurations of LinL16. The indices in the parentheses indicate the specific Li configurations (distinguished by colors) for a given Li composition n. Note, for Li$_9$P$_{16}$, some initial Li configurations whose final energies are very close are denoted by the same color. The pink balls represent P atoms, and the grey and black balls represent the Li atoms on the top and bottom phosphorene, respectively.

The triangular region formed by P-P-P atoms on the ridge) which happens when the Li concentration is high (e.g., n=8 in Li$_n$P$_{16}$). Fig. 15(c)–15(e) illustrate these three types of Li occupation.

For example, in the first type (e.g., config. 1 in Li$_8$P$_{16}$ shown in Fig. 16), eight Li atoms are distributed alternatively at the top and bottom VH sites on one end of the armchair bonds along the zigzag valley [e.g., see the top and side views on Fig. 15(c)]. In the second type (e.g., config. 3 in Li$_8$P$_{16}$ shown in Fig. 16), eight Li atoms are distributed on both ends of the armchair bonds on the left bank of zigzag valleys; one is at the top VH site and the other is at the bottom VH site, forming a Li “pair” [e.g., see the top and side views on Fig. 15(d)]. In the third type (e.g., config. 1 in Li$_{16}$P$_{16}$ in Fig. 16), 16 Li atoms are distributed at all possible top and bottom VH and TH sites, as shown on the top and side views of Fig. 15(e). Noted that such configuration only exists at high Li concentrations. Other initial Li distributions are different kinds of the mixture of these three types of configurations (see Fig. 16).

6 Li intercalation on phosphorene (Li$_n$P$_{16}$)

To find all possible Li configuration that guide a transition from black phosphorene to blue phosphorene, we conducted a systematic study of all possible Li$_n$P$_{16}$ struc-
tures. For each Li concentration (i.e., for a given $n$ Li atoms) many Li configuration is possible. For an illustration, let’s distribute 8 Li atoms on top of VH sites in monolayer phosphorene. There are 16 VH sites and 8 Li atoms can be distributed in $\frac{16!}{8!(16 - 8)!} = 12870$ ways. This naive enumeration of every possible configuration and calculating energies for all of them will be a huge waste of computational resources. When we considered translation, mirror and rotational symmetry of Li decorated phosphorene monolayer, the number of unique Li arrangement drastically reduced. Another observation that helped us to reduce number of Li configuration by several folds is, two Li does not prefer to sit on adjacent VH sites along zigzag valley, when they are on the same side of the phosphorene. Li atoms become Li$^+$ and they try to maintain maximum possible distance from each other to reduce electrostatic repulsion. Considering these symmetry constraints, we studied all possible unique Li decorated phosphorene monolayer.

We performed full structural relaxation processes for each configuration using the conjugate-gradient algorithm [109] and allowed all atoms moving freely to reach their new equilibrium positions, without any restriction exerted on the shape and volume of the super-cell throughout the relaxation processes so that the local strains induced by intercalated Li atoms can be fully released. In this way, all the considered combined systems were fully relaxed and stabilized (e.g., Fig. 17). Depending on the initial distribution of Li, the $\text{Li}_n\text{P}_{16}$ ($6 \leq n \leq 16$) system may end up in one of the three possible stabilized structures: either with no structural transition (referred as no-transition), or with structural transition (referred to as transition), or with total or partial bonds breaking (referred to as bond-break). Significantly, among those stabilized combined systems, the most energetically preferential structures are found to be these with the structural transition (see each panel in Fig. 18). To illustrate how Li intercalation leads to three types of stabilized final structures, we presented in Fig. 18, the optimized structure of $\text{Li}_8\text{P}_{16}$ and $\text{Li}_{16}\text{P}_{16}$ which are fully relaxed from
We found that, Li intercalation with the first type of structure does not change the orthorhombic structure of the black phosphorene. Local strain induced by Li intercalation is very small and only slightly stretch the bond $b_1$ and $b_2$ by $0.05 - 0.1\,\text{Å}$.

The second type of Li configuration stabilized to structure with a series of six-membered rings linked in trans-decalin fashion [see Fig. 18(b)]. Interestingly, this stabilized structure is about $0.2eV/\text{atom}$ lower in energy than the stabilized first type Li configuration, indicating for a given concentration of Li atom (i.e., $n=8$ in $\text{Li}_n\text{P}_{16}$), second type Li distribution is the most energetically preferential structure. We consistently observed this trend in other $\text{Li}_n\text{P}_{16}$ ($6 \leq n \leq 16$) system, showing the robustness of our findings (see Fig. 17).

The third type of Li configuration as shown in Fig. 18(c), stabilized to an irregular structure with all of its armchair bond broken, forming a buckled zigzag chain. This
Figure 18. Three types of optimized structures indicated by the blue arrows and denoted as no-transition, transition, and bond-break, respectively. (a) Li$_8$P$_{16}$ with the first type of Li configuration, (b) Li$_8$P$_{16}$ with the second type of Li configuration, and (c) Li$_{16}$P$_{16}$ with the third type of Li configuration. The total energy per atom is presented in the parentheses and the side views of the final stabilized structures in (b, c) are guided by the arrows. The pink and light gray balls denote P and Li atoms, respectively.

Type of relaxed structure is energetically higher than the transition structure in the Li$_{16}$P$_{16}$ system. We observed another interesting phenomenon, such broken bonds can be self-reformed after removing Li atoms and Black phosphorene could self-recover (see Fig. 11 in ref [111]).

What attracts our attention in the above results is the optimized transition structure resulting from the second type of Li configuration. To understand the physics behind the formation of this type of structure, it is interesting to study whether we can reach to this transition structure starting from optimized Li$_8$P$_{16}$ with first type Li configuration, and what happens during this structural transition process. We applied climbing image nudged elastic band (cNEB) method [65, 66] to study this structural transition process, starting from optimized structure with no-transition [i.e., Fig. 18(a)] to the optimized structure with transition [i.e., Fig. 18(b)]. We
Figure 19. Structural transition process of $\text{Li}_8\text{P}_{16}$ starting from the optimized no transition structure to (a) the 2nd type of Li configuration and (b) the optimized transition structure, respectively. (c) and (b) are structural deformation processes of $\text{Li}_{16}\text{P}_{16}$ starting from the optimized no transition structures to (c) the 3rd type of Li configuration and (d) the optimized break structures. Inserts show the intermediate structures of the systems at different stages (indicated by the blue arrows).
Figure 20. The reaction energy per Li atom along the structural deformation/reaction path starting from the optimized Li$_8$P$_{16}$ with the first type of Li configuration [i.e., the structure shown at the bottom of Fig. 18(a)], and ending with the optimized transition structure of Li$_8$P$_{16}$ with the second type of Li configuration [i.e., the structure shown at the bottom of Fig. 18(b)]. The image shows the Li migration (indicated by a series of light gray balls) along the zigzag valley during the first half of the reaction path with the energy barrier of $\sim 0.1$ eV. The insets show the structures at stage 7 (top) and the final stage (bottom).

calculated transition barrier for several paths (see Fig. 19) and found the minimum energy path (as shown in Fig. 20) where Li atoms, starting from first configuration, moves along zigzag path and end up in second configuration in 7th stage. Then these Li atoms induce a structural deformation and finally leads to a series of six-membered rings linked in trans-decalin forms (shown in inset at bottom of Fig. 20). The estimated energy barrier is only $\sim 0.1$ eV/Li atom, which is equivalent to Li diffusion barrier along valley in the zigzag direction in phosphorane monolayer [111]. This low energy barrier indicates that such structural transition can be easily realized experimentally, mediated by Li intercalation.
We examined the structural transition along the minimum energy path (see Fig. 21(a)-21(d)) in detail and found that armchair bond with Li atoms pair located on both ends are broken in 8th step. This broken bond leads to separation of orthorhombic scaffolding structure into several pieces. Then Li atoms pulls edge P atoms in up and down direction, followed by vertical rotation and slow vibration. Finally, the structure stabilized to a series of parallel buckled rhombohedral-like stripes (referred to as buckled rhombohedral nanoribbons) with intercalated Li atoms floating in-between them.

At this stage Li atoms were removed from the structure and the “broken” black phosphorene structure were relaxed using periodic boundary conditions, surprisingly, few layers of blue phosphorene flakes emerge with a P-P bond length of 2.28–2.32 Å and buckling of 1.512 Å [Fig. 21(d)]. Our result indicate that Li atoms located both side of armchair bond can act as catalyst and create driving force to break armchair
bond of black phosphorene and subsequently the broken black phosphorene converted into layered blue phosphorene. Thus, Li intercalation can induce a phase transition from black phosphorene to blue phosphorene.

7 Transition mechanism under Li intercalation

The mechanism of the phase transition from orthorhombic black phosphorus to rhombohedra blue phosphorus under pressure has been pointed out to be an intrinsic reactivity given by lone pairs of P atoms leading to rapid PP bonds flipping sequences along the [001] direction [112]. It is expected that the lone pair rearrangement mechanisms and bond-flipping pattern are geared together, which allows for both the formation of a one-dimensional chain (called Peierls intermediate) and the conservation of lone pair identities.

The unique picture of structural transition mechanism induced by Li intercalation without pressure, on the other hand, is expected to be directly related to the interaction between Li and P atoms, or more specifically, hybridization between Li s electrons and P lone pairs. As we can see from the above results with the second type of Li configuration (Fig. 21), it took two processes to accomplish the phase transition from black to blue phosphorene: the lithiation and the delithiation processes. During the lithiation process, intercalated Li atoms at both ends of the armchair bonds (i.e., the Li pairs) act as catalysts and drive the P atoms connecting the armchair bonds to move oppositely, resulting in a bond breaking, and subsequently, an assembly of buckled rhombohedral nanoribbons is formed. In the second process, this assembly of buckled rhombohedral nanoribbons is self-mended, forming buckled rhombohedral layers, and a transition from black to blue phosphorene is reached. Therefore, the Li atoms should play a key role during the intercalation through interacting with P atoms. To better capture such transition mechanism, in particular, to understand how the s-like orbitals around Li and p-like orbitals around P atoms are hybridized, we
performed electronic charge distribution analysis, in terms of the net electron charge redistribution, especially at the “reactive centers,” and the charges transfer between Li and P atoms associated with the local structural changes during the Li intercalation process, since they are involved in the structural transition and are expected to play active roles during Li intercalation. The real space distribution of the electronic charge density of black phosphorene at the top valence band and the bottom of the conduction band is presented in Fig. 22. It is found that the charge density associated with the top valence band is around the lone pairs located outwards of P atoms, as shown in Fig. 22(a), which implies that those lone pairs are chemically active, tend to bond with Li atoms, and will act as reactive centers during Li intercalation. Such interaction/bonding process can be further confirmed from analyzing the net electron charge redistribution of combined Li$_n$P$_{16}$ systems during the Li intercalation from the difference of electron charge density (DCD) calculations.

Fig. 23 depicted some examples of the net electron charge redistribution (DCD) during Li intercalation for combined systems of Li$_8$P$_{16}$ and Li$_{16}$P$_{16}$ with three optimized structures, i.e., no transition, transition, and bond break, respectively, where the yellow represents the regions of the electron accumulation and the blue represents the regions of electron depletion, respectively. It is found that, for all three types of
Figure 23. Top views of initial configurations (top panels), DCD of initial states (middle panels), and DCD of final states (bottom panels) for (a) Li$_8$P$_{16}$ with the first type of initial Li configuration, (b) Li$_8$P$_{16}$ with the second type of initial Li configuration, and (c) Li$_{10}$P$_{16}$ with the third type of initial Li configuration. (d) The snapshots of DCD for Li$_8$P$_{16}$ (with the second type of Li configuration) during structural transition process as shown in Fig. 20 and 21. The electron accumulation and depletion (at the iso-surface of 0.004 e/Å$^3$) are represented by the yellow and blue colors, respectively. The red dashed circles indicate the hybridization between s-like orbitals located around the Li atoms and p-like orbitals around the lone pairs of P atoms. Black arrows point to the net electrons accumulate near lone pairs. Pink and light gray balls represent P and Li atoms, respectively.
Li distributions, most net electrons are accumulated between Li and nearby P atoms, and a few electrons are depleted in the regions of lone pairs of P atoms (see the yellow and blue regions in the middle panels of Figs. 23(a)–23(c)], demonstrating a strong hybridization between s-like orbitals around Li atoms and p-like orbitals associated with the lone pairs of nearby P atoms. Such hybridization pattern, however, depends on the type of Li distribution and results in different types of final stabilized states after full relaxation processes.

For the combined system with the first type of Li configuration [e.g., the top panel of Fig. 23(a)], net electrons initially accumulate between Li atoms and P atoms on one end of the armchair bonds [indicated by the red dashed circles in Fig. 23(a)], forming Li-P covalent bonds. Such accumulation pattern has no bond breaking effect on armchair bonds, and the black phosphorene in the combined system maintains its orthorhombic structure during such Li intercalation, which can be confirmed by comparing the DCD between the initial and the final stabilized states [i.e., the middle and the bottom panels of Fig. 23(a)].

For the combined system with the second type of Li configuration [e.g., the top panel of Fig. 23(b)], net electrons accumulate between Li and P atoms on both ends of alternative armchair bonds [indicated by the red dashed circles on the top and middle panels of Fig. 23(b)], forming two Li-P bonds at both ends of the P-P armchair bonds. Such accumulation pattern leads to a P-P bond breaking along the vertical direction, and the combined system is finally stabilized to a structure with buckled rhombohedral nanoribbons.

The combined system with the third type of Li configuration, on the other hand, for instance, Li_{16}P_{16} [see the top part of Fig. 23(c)], the results of DCD demonstrate that net electron density initially accumulates between all Li and P atoms, forming Li-P bonds [see the red circles on Fig. 23(c)] at both sides of all armchair bonds. Thus, the hybridization and the local strain induced by Li intercalation will generate
strong stretch on all armchair bonds and totally break them. The combined system is finally stabilized to a broken structure with a series of zigzag chains (formed by zigzag bonds) in parallel [see the bottom in Fig. 23(c)]. The net electrons finally accumulate between Li and zigzag chains [see the bottom panel of Fig. 23(c)].

To shed light onto the underlying physics of the P-P bond breaking and the structural transition in the second type of Li configuration, we further studied the redistribution of the net electrons accumulation (i.e., the DCD) during the structural transition process (as shown in Fig. 20) to track the charge transfer and to understand how Li atoms interact with P atoms in the combined system. The results were presented in Fig. 23(d), where a Li pair at the two ends of an armchair bond ($b_2$) is denoted by the numbers 1 and 2. We found that the electron accumulations between the Li pair and the lone pairs of the two P atoms (indicated by the red dashed circles at stage 7) start to spread, and simultaneously, some new accumulations appear at the other sides of the two P atoms of the armchair bonds (e.g., indicated by the black dashed circles at stage 8). Such redistribution of the net electron accumulations created a stretch in the armchair bonds in a very short time and led to armchair bonds broken (e.g., indicated by the red dashed line at stage 8). The black phosphorene layer was then broken down to pieces of nanoribbons. In the following reaction stages [see stage 10 and the final stage in Fig. 23(d)], the local strain associated with the bond breaking and the Li intercalation further drove the re-distributions of the net electron accumulations and the reorientation of the lone pairs, accompanied by the redistribution of the Li atoms (e.g., indicated by the red dashed circles and black arrows at stage 10 and the final stage), leading to a rotation of the nanoribbons, until the local strain was fully released. At the final stage, net electron density re-accumulates between Li atoms and new lone pairs of P atoms of adjacent buckled rhombohedral nanoribbons [indicated by the black dashed circles at the final stage in Fig. 23(d)].
Our Bader analysis pointed out that for the combined system of Li₈P₁₆ with the first type of Li configuration, the charge transfers between Li and P atoms keep 0.804 e/Li and -0.402 e/Li before and after the relaxation process, confirming that such Li distribution will not affect the structure of black phosphorene [as shown in Figs. 21(a) and 23(a)]. For the combined system of Li₈P₁₆ with the second type of Li configuration, the charge transfers between Li and P atoms are 0.798 e/Li and -0.399 e/Li at the initial state, and 0.824 e/Li and -0.412 e/Li at the final state. The increase in charge transfer during the relaxation process demonstrates that such Li distribution can affect the structure of black phosphorene and lead to a structure transformation via hybridization between s-like orbitals around Li atoms and p-like orbitals around lone pairs of P atoms [as shown in Figs. 21(b), 21(b), and 21(d)]. For the combined system of Li₁₆P₁₆ with the third type of Li configuration, on the other hand, the charge transfers between Li and P atoms keep a symmetric nature during the whole relaxation process, i.e., 0.544 e/Li and -0.544 e/P at the initial state, and 0.764 e/Li and -0.764 e/P at the final state. The change in charge transfer during such relaxation process shows that this Li distribution can break the structure of black phosphorene to a series of zigzag chains via hybridization. The distribution symmetry of the charge transfer also indicates that the interactions between all Li and P atoms are uniform [as shown in Figs. 21(c) and 23(c)].

From the above analyses of orbital hybridization and electron charge redistribution, we conclude that when a Li pair is intercalated at both ends of an armchair bond, the hybridization between the Li pair and lone pairs of P atoms of such armchair bond could induce the stretch on the bond and lead to such bond breaking and a decomposition of the black phosphorene. Local strain accompanied with intercalated Li atoms played the key role in stabilizing the decomposed system through the reorientation of the lone pairs and the rotation of the decomposed structures. As a result, an assembly of buckled rhombohedral nanoribbons is formed and a structure
transition is reached without the unstable Peierls intermediate found in the pressure-
induced phase transition [112]. Namely, the lone pairs of P atoms act as reactive
centers, and the Li pair acts as a catalyst triggering the armchair bonds breaking.
When such armchair bonds are on the same side of the zigzag valley, a series of buck-
led rhombohedral nanoribbons forms after the armchair bonds are broken, and these
buckled rhombohedral nanoribbons become the building block of blue phosphorene.
After removing Li atoms, those nanoribbons are self-mended, subsequently forming
a layered blue phosphorene. Thus, the Li intercalation can induce a structure transi-
tion from black to blue phosphorene, providing a possible route for synthesizing blue
phosphorene.

8 Identify specific conditions for structure transition

We made a comprehensive study of many Li$_n$P$_{16}$ structures to identify specific condi-
tions for intercalated Li atom induced phase transition from black to blue phospho-
rene. Various Li intercalation concentration and distribution with Li pairs located
at the reactive centers (i.e., both sides of the armchair bonds), were considered. All
the combined Li$_n$P$_{16}$ systems are fully relaxed and corresponding optimized struc-
tures were obtained (see Figs. 16 and 17 for details). The following combined Li$_n$P$_{16}$
systems have been identified which can possibly lead to a structural transition from
black to blue phosphorene: Li$_6$P$_{16}$ (with one possible configuration), Li$_7$P$_{16}$ (with one
possible configuration), Li$_8$P$_{16}$ (with five possible configurations), Li$_9$P$_{16}$ (with nine
possible configurations), Li$_{10}$P$_{16}$ (with two possible configuration), and Li$_{16}$P$_{16}$ (with
one possible configuration). Fig. 24 depicts the dynamic results of some examples for
Li$_6$P$_{16}$, Li$_{10}$P$_{16}$, and Li$_{16}$P$_{16}$. It was found that even though the degree of the “rota-
tion” of parallel-arranged buckled rhombohedral nanoribbons (see middle panels of
Fig. 24) driven by the local strain depends on the distribution of Li pairs (see left
panels of Fig. 24), they all can lead to a phase transition from black phosphorene to
Figure 24. Lithiation and delithiation processes of (a) Li₆P₁₆, (b) Li₁₀P₁₆, and (c) Li₁₆P₁₆. Pink and light gray balls represent P and Li atoms, respectively.

Figure 25. DCD at the initial states of (a) the double-layer Li₁₆P₃₂ with AA stacking and (c) the multilayer Li₃P₈ with AB stacking, respectively. (b), (d) are DCD at the final states of systems in (a), (c). The electron accumulation and depletion (at the iso-surface of 0.004 e/Å³) are represented by the yellow and blue colors, respectively. The pink and gray balls represent P and Li atoms, respectively.

layers of blue phosphorene after delithiation (right panels of Fig. 24).

9 Li intercalation on double-layer and multilayer black phosphorene

Li atoms will interact with P atoms at the bottom surface on the upper layers as well as the top surface of the bottom layers after they are intercalated between the black phosphorene layers. For example, the DCD analysis on the initial states of
double layered Li$_{16}$P$_{16}$ and multilayered Li$_3$P$_{16}$ [see Figs. 25(a) and 25(c)] provides evidence of this observation. The electron accumulation (the yellow color) appears between Li and P atoms at adjacent layers, mainly due to the orbital hybridization between Li atoms and P atoms at adjacent layers. Therefore, the numbers of Li atoms needed as catalysts to induce the structural transition from black to blue layered phosphorene could be reduced in the case of layered black phosphorene. Our systematic study has found that the required Li concentration window is 0.375 ≤ $x$ ≤ 1.0 (e.g., 6 ≤ $n$ ≤ 16 in Li$_n$P$_{16}$) for monolayer black phosphorene, while for double-layered black phosphorene, the required Li concentration window is around 0.5 ≤ $x$ ≤ 0.625 (e.g., 16 ≤ $n$ ≤ 20 in LinP32), and for multilayers or black phosphorus, the required Li concentration window is reduced to the range of 0.375 ≤ $x$ ≤ 0.5 (e.g., 3 ≤ $n$ ≤ 4 in Li$_n$P$_{16}$).

Two unique examples of the Li intercalation-induced structural transition processes for double-layered Li$_{16}$P$_{16}$ (or Li$_{0.5}$P) with AA stacking and multilayered Li$_8$P$_8$ (or Li$_{0.375}$P) with AB stacking are shown in Fig. 25. According to the atomistic model developed in Sec. 3.6, for both cases, all Li atoms are deposited at top and bottom VH sites, which are either on one side or both sides of armchair bonds [e.g., see top views in Figs. 26(a) and 26(d)]. Likewise, it became apparent that, during the lithiation process, Li atoms hybridize P atoms at both ends of the armchair bonds and induce breaking of the armchair bonds, and then an assembly of buckled rhombohedral nanoribbons is formed associated with the release of the local strain [e.g., see Figs. 26(b) and 26(e)]. Next, the assemblies of these nanoribbons are self-mended to release the local strains during the delithiation process (after the Li atoms were removed) and finally, form blue phosphorene layers [see Figs. 26(c) and 26(f)]. One of the most fascinating findings is that, induced by Li intercalation, the double-layered black phosphorene with AA stacking [see the top view of Fig. 26(a)] was converted to a layered blue phosphorene with AA stacking [see the top view of Fig. 26(c)],

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Figure 26. (a) Top (up) and side (bottom) views of double layered Li$_{16}$P$_{32}$ with initial Li configuration. (b) Two side views of stabilized double layered Li$_{16}$P$_{32}$ after full relaxation. (c) Two side views of stabilized blue phosphorene layers with AA stacking after delithiation. (d) Multilayered Li$_{0.375}$P with initial Li configuration (top and side views) undergoes (e) a structural transition induced by Li intercalation. After removing Li atoms, the system is finally stabilized to (f) blue phosphorus with ABC stacking. The notations of d and z are the interlayer distance and buckling, respectively.
while multilayered black phosphorene with AB stacking [see the top view of Fig. 26(d)] was converted to multilayered blue phosphorene with ABC stacking (see the right panel of Fig. 26(f), which was also found experimentally under high pressure [113]) since the Li intercalation leads to an antisymmetric distribution of buckled rhombohedral nanoribbons between layers [Fig. 26(e)]. The equilibrium interlayer distance \( (d) \) is found to be \( \sim 4.60\,\text{Å} \) for double-layer blue phosphorene with AA stacking and \( \sim 4.13\,\text{Å} \) for multilayer blue phosphorene with ABC stacking, indicating a stacking/layer dependent vdW weak interaction between layers. Thus, it is possible to peel out a monolayer by mechanical exfoliation. On top of that, the results confirm our assumption of with the increase of the numbers of layers, fewer Li atoms are required to trigger a structural transition. Therefore, to induce a transition from Black to Blue Phosphorus, the distribution of Li atoms will depend on the number of layers which leads to a fundamental guide for fabricating blue phosphorene by using this unique kinetic growth pathway.

10 Comparison with experimental result

We studied the off-resonance Raman activity of pristine and Li-intercalated bulk black phosphorus and compared with experimental data [45]. Fig 27(a) shows the Raman shifts for vibration modes \( A_{1g} \), \( B_{2g} \), and \( A_{2g} \), respectively. The theoretical calculations are presented by stars and experimental data are presented by circle. Both experimental and theoretical results show a redshift for all three Raman modes with an increasing lithiation, but the rate of redshift is much larger in theoretical results than in experimental results when Li density exceeds 25%. This discrepancy between theoretical and experimental result can be attributed to several factor. First, the experiment is done using electrochemical cell, so \( \text{Li}^+ \) is actually intercalated inside the BP host but in simulation we intercalated neutral Li atom. Our simulation indicates that s-orbital electron of Li atom plays the central role in breaking bond,
as Li in electro-chemical cell already lost its outer shell electron, it can not break the arm-chair bond of BP and thus can not make the transition structure as predicted by our DFT calculations. Another discrepancy originated from the fact that DFT calculation only consider zero temperature so the system prefer to remain in lowest energy structures but in real word experiment, finite temperature does not allow the system to be in the lowest possible energy configuration.

Figure 27. (a) Raman shift for $A_{1g}^1$, $B_{2g}$, and $A_{2g}^2$ modes as a function of Li density $x$. experimental data marked by solid circle and theoretical data is marked by star [45]
Evaluate the effects of Li PAW potentials and the periodicity constrain in the structural transitions mediated by Li intercalation

To prove robustness of our calculation we made some additional test calculation using different pseudopotential and extended boundary condition. VASP provide two types of PAW potentials for Li atom: one with energy cutoff of 140 eV and one s valence electron (i.e., frozen-core), and the other one with the energy cutoff of 499 eV and three s electrons (i.e., full-electrons). We performed full structural relaxation using both pseudopotentials, for two types of Li intercalated black phosphorene structure.

One is the Li intercalation on the monolayer of black phosphorene and the other is the Li intercalation in the multilayered black phosphorus. The results are shown in Fig. 28(a) and (b). We found that both types of PAW potentials result in the same optimized structures and clearly prove that the decisive role played in the structural transition induced by Li intercalation mainly comes from the interaction between the Li valence electron and phosphorene. Therefore, we choose the Li PAW potential with only one s-electron in our calculations. We also compares the optimized structures of the Li intercalation on black phosphorene with 2x2 and 4x4 supercells, respectively. The results (see Fig. 28 (c)) show that our findings for the structural transition under the Li intercalation is robust. Therefore, using 2x2 suercell is sufficient in our calculations.

Conclusion

We made a systematic study of Li intercalated mono-, double-, and multilayer black phosphorene with various Li distribution (over 50 configurations) and found that at sufficiently high Li concentration and certain arrangement, transition from black to blue phosphorene take place. We found that precise atomistic mechanism of the phase transition can be explained in terms of (1) the hybridization between s-like
(a) Li$_8$P$_{16}$

PAW potential for Li (frozen-core) (-4.4600 eV)  
PAW potential for Li (full-electrons) (-4.4683 eV)

(b) Li$_3$P$_6$

PAW potential for Li (frozen-core) (-4.8067 eV)  
PAW potential for Li (full-electrons) (-4.8079 eV)
Figure 28. (a) Optimized structure of the combined Li$_8$P$_{16}$ system using the Li PAW potential with a frozen-core (left) or full-electrons (right) calculations. (b) Optimized structure of the combined Li$_3$P$_8$ system using the Li PAW potential with a frozen core (left) or full-electrons (right) calculations. (c) The optimized structure of the combined Li$_8$P$_{16}$ system obtained using the 2x2 supercell (left) and the 4x4 supercell (right). The values in the parentheses are the total energy per atom.

orbitals located around Li atoms and p-like orbitals located around the lone pair of P atoms on both ends of the armchair bonds, leading to such bond breaking, and (2) the release of the local strains induced by Li intercalation and bond breaking, leading to the reorientation of the lone pairs and rearrangement of the decomposed system. Subsequently, the puckered orthorhombic structure of black phosphorene converts to an assembly of buckled rhombohedral nanoribbons. Thus, Li atoms located at these reactive centers (near the lone pairs of P atoms of P-P armchair bonds) act as catalysts to trigger the structural transition from black to layered blue phosphorene.

We also identified the required Li concentration is $0.375 \leq x \leq 1.0$ for monolayer phosphorene, $0.5 \leq x \leq 0.625$ for double layer phosphorene, and $0.375 \leq x \leq 0.5$ for black phosphorous. In this way, the insight into the fundamental information at the atomic level for fabricating/growing blue phosphorene was provided.

It should be noted that the orientation of the blue phosphorene nanoribbons with respect to the pristine black phosphorene depends on the local strain induced by Li
intercalation, and the effect of such local strain depends on the Li concentration, the Li distribution, and the number of black phosphorene layers (e.g., $\sim 90$ deg in Li$_8$L$_{16}$ and Li$_{16}$P$_{16}$ monolayer and Li$_{16}$P$_{32}$ bilayer, but $\sim 45$ deg in Li$_{10}$L$_{16}$ monolayer and Li$_3$P$_8$ in multilayer). As a result, the monolayer or bilayer black phosphorene could be transformed to an assembly of nanoribbons of blue phosphorene or flakes.

The size of the layered blue phosphorene flakes depends on the number of black phosphorene layers. The more the layers, the larger the size. In practical terms, multilayered black phosphorus is a good candidate to obtain layered blue phosphorus.

Pristine blue phosphorous can only exist in high pressure ($> 5GPa$) and converts back to black phosphorous as soon as the pressure is released. On the other hand, our theoretical study points out that, it is possible to induce a phase transition from black to blue phosphorene using Li interaction. In next chapter we will study the combined effect of pressure and Li intercalation in the phase transition of black phosphorous to blue phosphorous.
CHAPTER 4

Li-INTERCALATED BLACK PHOSPHOROUS UNDER HIGH-PRESSURE

1 Introduction

In previous chapter we explored the possibility of structural transition from black phosphorous to blue phosphorous through Li intercalation. In this chapter we focused on the combined effect of pressure and Li intercalation on the structure of black phosphorous. Several experimental studies found that pressure can induce two-step structural phase transition in black phosphorous: orthorhombic (A17) \textendash\textgreater rhombohedral (A7) under the pressure of \(\sim 5\) GPa and rhombohedral (A7) \textendash\textgreater\textgreater simple cubic under the pressure of \(\sim 10\) GPa. Interestingly, the A7 phase of black phosphorous reverts back to the regular black phosphorous (A17) structure as soon as the pressure is released (see schematic illustration in Fig 4(b)) [44].

Intercalation and high-pressure plays some sorts of opposite roles in structural changes in BP, as intercalation expands the structure, whereas pressure leads to compression of the structure. To complicate the matter further, intercalated Li atom transfer charge to the black phosphorous, affecting the bond strength and even leading to bond reconstruction. In this chapter we provided a first principle atomistic picture of combined effect of Li intercalation and high-pressure on black phosphorous structure.
2 Computational methods

The overall computational calculations in this study were mainly carried out by employing the DFT [47, 48] framework, as implemented in the VASP [105]. The electron–ion interactions were described by the Projector Augmented Wave (PAW) [106], while the electron exchange–correlation interactions were treated by the generalized gradient approximation (GGA) [57] in the scheme of Perdew Burke Ernzerhof (PBE) [57]. A primitive cell containing 8 phosphorus atoms (with optimized lattice constants $a = 3.326 \, \text{Å}, b = 11.18246 \, \text{Å},$ and $c = 4.5239 \, \text{Å}$) was chosen to study the behavior of black phosphorus under a certain pressure. Li atoms were intercalated at positions of the center of the triangular region formed by P-P-P atoms, which is the most energetically preferential position for Li adsorption (i.e., the VH sites on the adsorption energy landscape, as described in detail in [111]. The Brillouin zones (BZ) were sampled by $9 \times 9 \times 9$ k-point meshes generated in accordance with the Monkhorst–Pack scheme [108] in the calculations. The effect of vdW interactions was considered by employing the semiempirical correction scheme of Grimme [60, 61], implemented in the VASP package (i.e., referred as DFT-D3 in the VASP code). The full structural relaxation considering both the ionic and the cell degrees of freedom) was performed using the Congregate-Gradient algorithm [109] implemented in VASP. The energy cutoff was set to be 500 eV for the plane wave basis in all calculations, and the criteria for the convergences of energy and force in relaxation processes were set to be $10^{-4} \, \text{eV}$ and $10^{-3} \, \text{eVÅ}^{-1}$, respectively.

3 Effect of pressure on Li intercalated black phosphorous

For this study, 1 to 5 Li atoms were intercalated inside the BP unit cell containing 8 phosphorous atoms (i.e., Li$_n$P$_8$ where $n = 1 - 5$). To study the effect of the pressure on the structure of Li intercalated BP, a hydrostatic pressure was applied starting
Figure 29. Structural changes of Li intercalated BP (i.e., Li$_n$P$_8$ where $n = 1$ to 5) with applied hydrostatic pressure from 0 to 10 GPa.

First obvious observation from the Fig. 29 is that just Li interaction without any external pressure can make a substantial change in the structure of BP. For example, at 12.5% concentration of Li (i.e., Li$_{0.125}$P), the uneven distribution of Li slides the alternate layer (see Fig. 29 at 0 GPa) of BP and makes a mixture of AB and AA stacked layer. Adding one more Li atom breaks the orthorhombic symmetry of BP, and a rhombic shaped cell is formed. Further increase of Li atom concentration leads to P-P bonds breaking in armchair direction. In particular, a phase transition from black to blue phosphorene has been found at 37.5% of Li intercalation, as discussed in the section 8 of Chapter III. Unit cell volume and lattice constant (specially in b direction) expands with Li intercalation. At 62.5% Li concentration unit cell volume
Figure 30. Change of lattice constant $a, b, c$, lattice angle $\alpha, \beta, \gamma$ and unit cell volume with pressure in Li intercalated black phosphorous ($\text{Li}_n\text{P}_8$ where $n = 1$ to $5$ increases by 43% and lattice constant in $b$ direction increase by 30% (see Fig. 30 at 0 GPa).

Application of pressure on Li intercalated BP leads to some interesting phenomena, like bond breaking and bond reconstruction. In case of $\text{Li}_{0.0}\text{P}$, $\text{Li}_{0.125}\text{P}$, and $\text{Li}_{0.25}\text{P}$, the pressure (see Fig. 30) does not make or break any P-P bonding and unit cell volume and lattice constant monotonically decrease with pressure. Although Ex-
Experimental data indicates a sudden volume change (1.7 Å per atom) [44] at 5.5 GPa, but our DFT calculation doesn’t indicate any sudden volume change. The mixture of AB and AA stacking in Li$_{0.125}$P disappear starting from 1 GPa. But in case of Li$_{0.375}$P at pressure 3 GPa, broken armchair bonds reformed again (see Li$_{0.375}$P in Fig 29) under the pressure and keep intact up to 10 GPa pressure. Also, the unit cell volume of Li$_{0.375}$P drop sharply at pressure 2 and 3 GPa and then keep decreasing monotonically (see Fig. 30).

In terms of bond reconstruction, Li$_{0.625}$P shows some very interesting phenomena. This Li concentration of 0.625 is close to the Li$_{0.69}$P sample used in experiment done by our colleagues. We found a 43% of the volume expansion in Li$_{0.625}$P, where most of the P-P bonds between ridge and valley (i.e., along the AC direction) were broken, and P-P bonds along the zigzag (ZZ) direction were kept intact, forming ZZ chains (see bottom panel of Fig. 29 at zero pressure of Li$_{0.625}$P). The ratio of lattice constants $c/a$ increases from 1.33 Å to 1.57 Å at this Li concentration.

When the pressure is applied on the relaxed Li$_{0.625}$P, we found a notable change in the volume, lattice constants, and lattice angles, as shown on Fig. 31 and Fig 32. As shown in Fig. 32, the lattice angle between $a$ and $c$ axes (i.e., $\beta$) keeps unchanged under the pressure, while the lattice angles between $a$ and $b$ axes (i.e., $\gamma$) and between $b$ and $c$ axes (i.e., $\alpha$) suddenly drop in the range of 2–3 GPa, indicating a change in the cell shape. In the meantime, the lattice constant $b(c)$ increases (decreases) in this pressure range associated with the compression of the cell volume.

Compared to the volume compression of the pristine BP under the pressure (the black-dotted curve in Fig. 31), the volume of Li-intercalated BP (red-squared curve in Fig. 31) decreases linearly under the pressure with a steep drop in the range of 2–3 GPa. Such a drop is found to be associated with the structure change induced by the redistribution of intercalated Li atoms under the pressure, namely, breaking/re-bonding of P-P bonds at 2–3 GPa (indicated by the arrows/circles on the side views...
Figure 31. Cell volume as function of the pressure for the pristine BP (black-dotted curve) and Li-intercalated BP (red-squared curve), respectively.

Figure 32. a) Change of angles and c) lattice constant of BP and Li intercalated BP under pressure. b) The $1 \times 1 \times 1$ pristine black phosphorous cell and lattice vectors direction.
of the structures in the insets of Fig. 29(bottom panel). Furthermore, the clustering
due to bond formation is found at $8 - 10$ GPa.

After full relaxation under given pressure, various vibrational modes at gamma
point were calculated using the hessian matrix implemented in VASP code. Raman
active modes were then calculated using the derivative of macroscopic polarizability
with respect to normal modes coordinates [72, 73]. As shown in Fig. 33, calculated
Raman peaks for $A_1^g$ and $B_{2g}$ modes in Li-intercalated BP show a large downshift at 3
and 8 GPa, respectively. At the pressure of 2 and 8 GPa, a merge of Raman peaks was
found, which is indicative of a structural transition at those pressures. Fig. 32 also
shows both lattice constants and lattice angles suddenly change at these pressures.
Calculated Raman peak positions for Li-intercalated BP show a downshift at 3 GPa
for $A_1^g$, $B_{2g}$, and $A_2^g$ modes, and at 8 GPa, for $B_{2g}$ and $A_g^2$ modes, while an upshift
was found at a pressure above 3 GPa for $A_g^1$ mode. These trends of Raman peak
shifts under the pressure are consistent with our experimental observation (as shown
in Fig. 4 in our published paper [114]) except for slight differences in the pressure
regions.

4 De-lithiation after the effect of pressure on Li intercalated black phosphorous

After studying the effect of pressure on Li intercalated BP, we considered what would
happen when Li atoms are removed from the intercalated samples. We have studied
two different paths of Li deintercalations. In the first path, we removed the Li atoms
but kept the pressure unchanged, in the second path, we remove the Li atoms and at
the same time released the pressure. Some interesting results are found. In Li$_{0.375}$P,
broken P-P armchair bonds are reformed at 3 GPa and when we remove Li atom
but kept the pressure, we obtain a blue phosphorous like structure (see Fig.34 (a)).
While, for the same relaxed Li$_{0.375}$P structure, when we removed Li atoms and released
pressure at the same time, the structure went back to the black phosphorous structure.
**Figure 33.** a) Raman shift of pristine black phosphorous with pressure. b) Raman shift of Li intercalated black phosphorous (Li$_{0.625}$P). c) Raman shift of mode $A_{1g}, B_{2g}$ and $A'_{2g}$ with pressure for pristine and Li intercalated black phosphorous (Li$_{0.625}$P)
These results show that a phase transition from black to blue phosphorene could happen in BP when the Li intercalation is at the rate of 0.375 either without pressure or with the pressure if the de-lithiation is undergone under the pressure.

In the case of Li_{0.5}P, we found that the de-lithiation process with and without pressure lead to structures neither black nor blue phosphorous (see Fig. 34 (b). But
in the case of Li$_{0.625}$P, we found that the de-lithiation process with releasing pressure could lead to multilayer blue phosphorene (see Fig 34 (c)), while the structure under pressure shows a compressed blue phosphorus. These results clearly indicate that, in addition to the Li intercalation with 37.5\% of concentration, the Li intercalation with 62.5\% of concentration can also induce a phase transition from black to blue phosphorus with the help of pressure.

5 Conclusion

The combined effect of Li intercalation and pressure opens a new avenue for the study of the structures transition black phosphorous (\(A_{17}\)) to blue phosphorous (\(A_{7}\)). Li intercalation could lead to a symmetry change and a bond breaking process in BP and the pressure could lead to bonds reconstruction. De-lithiation process with/without pressure release revealed that a blue phosphorene like structure could be realized for some specific Li concentration. Based on this study we can conclude that, combined effect of pressure and Li intercalation can lead to a novel kinetic pathway to synthesis blue phosphorene from multilayer black phosphorene.
1 Intercalation of Na in monolayer and multilayer phosphorene

In chapter III we have discussed Li intercalation in monolayer and multilayer black phosphorene. In this chapter we focused on Na intercalation in monolayer and multilayer BP. For monolayer adsorption, we adopted the initial configurations of Li deposition on BP and replaced Li atoms by Na atoms. Depending on the distribution of Na atoms on monolayer BP surface, relaxed Na intercalated structures were found in three different types of structures (see Fig. 35). The first type is the puckered honeycomb-structured layer of black phosphorene (e.g., Config1 in Na$_6$P$_{16}$ of Fig.35). The second type is with a series of six-membered rings linked in trans-decalin-like fashion (e.g., Config1 in Na$_{12}$P$_{16}$ of Fig 35). The third type is with a series of six-membered rings linked in cis-decalin-like fashion (e.g., Config3 in Na$_6$P$_{16}$ of Fig 35).

At low concentration of Na (i.e. Na$_n$P$_{16}$, where n=1-5), the relaxed structure of BP keeps its original symmetry (i.e., the first type), and Na atoms prefers to sit on the top of the VH sites on BP (see example, the top panel in Fig. 35).

Furthermore, we found that by increasing number of Na atoms deposited on the black phosphorene, such Na intercalation leads to an armchair bond breaking on the black phosphorene leading to either type 2 or 3 structures (e.g., Config1 and Config4 in Na$_{13}$P$_{16}$ of Fig. 35). For example, in the cases of Na$_6$P$_{16}$ and Na$_8$P$_{16}$ we observed partial broken structures (see Fig. 35). These partial broken structures are energetically slightly more stable than unbroken structures. Increasing more Na
Figure 35. Intercalation of Na in monolayer black phosphorene. Pink color sphere denote P atom and grey spheres are Na atoms. The total energy per atom also shown.
atoms leads to more broken bonds. In the case of Na$_n$P$_{16}$ where $n$ is from 10 to 16, we found that some initial Na distributions leads to a series of six-membered rings linked in trans-decalin structure, just like Li intercalated BP. Most important observation is that these transition structures are more energetically stable than partially broken structures (see the total energy per-atom in Fig 35). Interesting finding is that in the case of Li$_{10}$P$_{16}$, when the Li distribution is in the same configuration 5 as in Na$_{10}$P$_{16}$, it could lead to a phase transition from black to blue phosphorene. However, it does not change the bone structure of black phosphorene under Na or K intercalation on the black phosphorene (see Fig.7 in [103]) Such results mostly come from their large atomic radius (K 2.27 Å; Na 1.86 Å) [115], which lead to their energetically preferential adsorption positions far away from the black phosphorene surface, as compared to Li atoms (e.g., calculated equilibrium distances are $\sim$ 3.36 Å for K-P and 3.00 Å for Na-P, much larger than that of Li-P ($\sim$ 2.48 – 2.66Å)). Our DCD calculations for these systems (Fig. 36) demonstrated that there are almost no orbital hybridization between K and P atoms (the right panel in Fig. 36), and very weak hybridization between Na and P atoms (the right panel in Fig. 36), as compared to Li and P atoms (the right panel in Fig. 36 (a)). These analyses, therefore, confirmed that at this particular configuration the attractive interactions between K (Na) and P atoms are not sufficiently enough to pull P atoms out to break the armchair bonds. But they can be used as good candidates for exfoliating black P.

For Na intercalated phosphorene monolayer, we further investigated, what will happen after removal of Na atoms. As an example, we removed Na from Na$_{13}$P$_{16}$ for all possible configuration. And we found that they all go back to their previous black phosphorous structure after desodiation (see Fig. 37), indicating that, unlike Li intercalation, Na intercalation could not induce the phase transition from black to blue phosphorene.

Next, we turned our focus to Na intercalation in bulk BP. As we can see in Fig. 38,
introducing Na atom first changes the stacking order of BP layer. For instance, in the case of Na$_1$P$_8$, Na is distributed at alternative layers. Based on the Na availability, BP’s layers slide and make a mixture of AA and AB stacked layers. In the case of Na$_2$P$_8$, Na atoms are evenly distributed between layers such that each layer slides against each other and make a perfect AB stacked BP. Introducing more Na atoms breaks P-P bonds in the arm-chair direction. When Na concentration reaches 50% (i.e., Na$_4$P$_8$) all P-P bonds in armchair direction are broken. Interestingly, further increase of Na atom leads to a reformation of some broken bonds.

We further investigate the stability of transformed BP structure after removal of Na. It was found that the intercalated BP (i.e., Na$_3$P$_8$) again goes back to its original BP structure after removal of Na (see Fig. 39), similar as we found in the
monolayer BP, which is quite opposite to Li interacted BP (see Fig. 26 (d)-(f)). Even at higher Na concentration (i.e., Na$_7$P$_8$) alternate layer of transformed structure goes back to BP after deintercalation (see bottom figure of 39). This means that Na intercalation and deintercalation cannot be used to make blue phosphorous from black phosphorous.

2 Intercalation of K, Cs in BP

We also check potassium (K) and Cesium (Cs) intercalation in multilayer BP. At lower concentration of K (i.e., K$_1$P$_8$, K$_2$P$_8$), we see similar behavior like Na intercalation. Intercalated K atoms induce a relative shift between layers and change the stacking of BP. Increasing K concentration leads to P-P armchair bond braking. Further increase of K leads to deformation of broken BP parts and formation of long chain in armchair direction (see K$_7$P$_8$ in Fig. 40).

The most interesting observation of our study in K intercalation into BP is, similar
to Na intercalated BP, K intercalated BP returns back to its original BP structures after de-intercalation (shown in Fig. 41).

In case of Cs intercalation, at lower concentration (i.e., Cs$_1$P$_8$, Cs$_2$P$_8$, Cs$_3$P$_8$) similar kind of layer sliding and staking order changes have been observed. At 50% concentration of Cs, all armchair bonds in BP are broken and further increase of Cs leads to formation of large cluster of Cs atom. This kind of large intercalant cluster formation was not observed in Li and K.

After de-intercalation of Cs from BP (Cs$_4$P$_8$), broken BP parts join and make a blue phosphorous like structure (see Fig. 43). We found both Cs$_4$P$_8$ and Cs$_6$P$_8$ structures transformed into blue phosphorene after Cs deintercalation. These blue
Figure 39. Deintercalation of Na from black phosphorous
Figure 40. K intercalation in multilayer BP
phosphorene like layers have layer separation of 3.23 Å, indicating that they can be separable into blue phosphorene monolayer by mechanical exfoliation.

3 Conclusion

Like Li atom, intercalation of both Na and K can break P-P arm-chair bonds of BP. For Na intercalation we had shown for both monolayer and multilayer BP, a bond-broken process takes place and after removal of Na atoms, broken BP structure goes back to same old BP structure. For K, we studied the K intercalation into multilayer black phosphorous. Similar to the case of Na, K intercalation can break armchair bonds but as soon as the K atoms are removed the structure goes back to its original BP structure.

Interestingly, Cs intercalation tells us a different story from those of K and Na intercalations. Intercalation of Cs at 50% and 0.75 % concentration can breaks all
the P-P armchair bonds, while, after removing Cs, all broken parts are self-mended and form a multilayer blue phosphorene structure. Thus, Cs intercalation into BP can provide a novel pathway to synthesis blue phosphorene from black phosphorene, just like Li intercalation.

In summary, the fundamental mechanism for the intercalation-induced transition from black to blue phosphorene should be a synergic effect of the orbital hybridization, charge transfer, and the strength of the electrostatic Coulomb interactions between alkali and P atoms. This finding is expected to be validated by experiments.
Figure 43. De-intercaltion of Cs intercalated BP
CHAPTER 6
HYDRAZINE GAS ADSORPTION ON LAYERED WS$_2$

1 Introduction

Sensing toxic gas molecules is crucial for monitoring industrial process, maintaining indoor and outdoor air quality, medical diagnosis, vehicle emission control, and detecting biohazard [116–119]. An ideal gas sensor should possess very high sensitivity, short recovery time, and at the same time should operate at room temperature and consume low electric power. It should also be less sensitive to humidity and resistive to degradation over time. Metal-oxide semiconductor [120], conducting polymers [121, 122], and carbon nanotubes [123] based gas sensors have been extensively studied. Among them metal-oxides (i.e SnO$_2$, WO$_3$, CeO$_2$, Nb$_2$O$_5$ and ZnO) are popular in commercial application, owing to their high sensitivity and low cost. But downside is their high operating temperature ($200^\circ C - 500^\circ C$), large power consumption, and low selectivity [124, 125]. Conducting polymers-based sensors can operate at room temperature but they are prone to environmental degradation and sensitive to humidity [126, 127]. Carbon nanotube-based sensors have excellent sensitivity and works at room temperature, but the long recovery time limits their application. In search of a better gas/chemical sensor material, two-dimensional (2D) materials are much more promising than their bulk counterparts.

2D materials have high surface to volume ratio, wide range of chemical compositions, and unique thickness-dependent properties [128, 129]. All of these properties made 2D materials ideal for sensor applications. Recent studies suggest that
2D material-based gas sensor possesses higher sensitivity, selectivity, speed (both in terms of the response and the recovery rate), and stability [130]. Among 2D materials classes, graphene and graphene derivatives like graphene oxide, reduced graphene oxide, and their functionalized derivatives have been extensively studied for gas-sensing applications. Graphene possesses high room-temperature carrier mobility (200,000 cm²V⁻¹s⁻¹) and a high carrier density of ~ 10¹² cm⁻². It also has low resistivity at room temperature and strong surface activity. A recent study by Schedin et al reported that a micrometer-sized graphene transistor can effectively detect very low concentration of gas molecule [119, 131]. Transition metal dichalcogenides (TMDs) have become a popular class of 2D materials for their outstanding electrochemical and optoelectrical properties [132, 133]. TMDs have layered structures where transition metal can have trigonal or octahedral coordination resulting in either hexagonal or rhombohedral structure symmetry. TMDs have large interlayer spacing and layers are held together via weak van der Waals (vdW) force. This large interlayer spacing allows intercalation of small gas molecule inside TMDs. TMDs show extreme sensitivity to various gas molecule as well as their layer dependence [120, 134, 135]. It has been found that MoS₂ is a promising gas sensor material from the TMD group. Monolayer MoS₂ can detect 1ppm for NH₃ and 20 bpm for NO₂ [136–138]. WS₂, on the other hand, has high thermal stability and wide operation temperature range. In fast fourier transform (FFT) type of applications, WS₂ can perform better than Si and some other 2D crystal [139, 140]. Recently, C. Zhou et al have theoretically studied the charge transfer and its impacts on Fermi-level pinning for gas molecules adsorbed on monolayer WS₂ [141, 142]. They found that most gas molecules (e.g. H₂, O₂, H₂O, NO, N₂O, and NH₃) are physisorbed on the surface of WS₂ monolayer. Except for NH₃ which donates charge to the WS₂, all other gas molecules accept a small amount of charge from WS₂ monolayer, indicating that WS₂ might be also a promised 2D materials for gas sensing applications. In this project, we focused on
understanding the mechanism of a hydrazine (N₂H₂) molecule absorbed on 2D WS₂ monolayer, double layer, and multilayers. N₂H₂ molecule is a colorless, toxic gas which can seriously damage the central nervous system. Every year 100000 tons of N₂H₂ are produced and used as rocket fuel, foaming agent etc. Detecting hydrazine with high sensitivity is crucial for many industries. Our recent experimental study [142] has found that the electrical resistance of 2D WS₂ layered materials decreases when they are exposed to hydrazine at varying pressures (i.e. varying N₂H₂ concentration). Interesting finding is that such change depends on the pressure of the hydrazine vapor and the number of layers of WS₂. For instance, two layers of WS₂ showed a complete reversibility upon pumping. While, 3-4 layers of WS₂ showed only partial recovery during desorption. In contrast, multi-layered WS₂ showed a little or no reversibility upon pumping [142]. To shed light into such interesting response behaviors of 2D WS₂ exposed to N₂H₂ gas molecule, we carried out a comprehensive study at the first principle level. We found that donor (n-type) like impurity states associated with the N₂H₂ molecule pin the Fermi level, which lead to a reduction on the energy gap and thereby reduce the resistance. The adsorption energy, on the other hand, increases with increasing the number of WS₂ layers, while the interlayer separation decreases as the number of WS₂ layers increases, and therefore, it becomes more difficult to pump N₂H₂ completely at multilayers of WS₂.

2 Computational details

In our first principle study, we adopted (DFT) [47, 48], implemented in the Vienna Ab-initio Simulation Package (VASP) [105]. The six outmost electrons for transition-metal (W element) and chalcogen (S element) were treated as valence electrons. The core-valence interaction was described by the frozen-core projector augmented wave method [106]. The generalized gradient approximation (GGA) [57] of Perdew–Burke–Ernzerhof (GGA-PBE) [57] was adopted for exchangecorrelation
functional. For the study of N\textsubscript{2}H\textsubscript{2} molecules adsorbed on the monolayer or the double layer WS\textsubscript{2}, a 3 \times 3 planar supercell was chosen with a vertical vacuum space of 20 Å between adjacent layers to avoid any mirror interactions. For the study of N\textsubscript{2}H\textsubscript{2} molecules adsorbed on the multilayer WS\textsubscript{2}, a supercell of 3 \times 3 \times 1 was chosen. The distance between two neighboring gas molecules on the surface of WS\textsubscript{2} layers was larger than 9 Å. The corresponding concentration of N\textsubscript{2}H\textsubscript{2} based on theoretical estimation is $\sim 10^{18} \text{m}^{-2}$, several orders lower than our estimated experimental concentration based on molecular collision theory with the assumption of perfect sticking coefficient of 1. This is obviously an overestimation of our experimentally estimated N\textsubscript{2}H\textsubscript{2} concentration on WS\textsubscript{2}. The Brillouin zone was sampled either by 3 \times 3 \times 1 (for single and double layered systems) or by 3 \times 3 \times 3 (for multilayered systems) Γ centered k-point meshes generated in accordance with the Monkhorst-Pack scheme [108] in the structural optimization and band structure calculations. An energy cut-off of 500 eV was set for the plane wave basis in all calculations. Energy and force convergence criteria were set to be $10^{-4}$ eV and $10^{-3}$ eV Å\textsuperscript{-1}, respectively. The combined adsorbate-adsorbent systems were fully relaxed using Conjugate-Gradient algorithm [109] implemented in VASP. The effect of vdW interactions between the N\textsubscript{2}H\textsubscript{2} molecules and layered WS\textsubscript{2} were considered by employing the semiempirical correction scheme of Grimme [60, 61], implemented in the VASP package (i.e. referred as DFT-D3 in VASP code). The adsorption energy $E_{\text{ad}}$ per N\textsubscript{2}H\textsubscript{2} molecule was determined by the formula, $E_{\text{ad}} = (E_{\text{total}} - E_{\text{WS2}} - NE_{\text{N2H4}})/N$, where $E_{\text{total}}$, $E_{\text{WS2}}$, and $E_{\text{N2H4}}$ are the total energy of the combined adsorbate-adsorbent system, the total energy of the pristine WS\textsubscript{2} layered system, and the energy of isolated N\textsubscript{2}H\textsubscript{2} molecule, respectively, and N is the number of N\textsubscript{2}H\textsubscript{2} molecules per supercell. The charge transfer between N\textsubscript{2}H\textsubscript{2} gas molecules and layered WS\textsubscript{2} was evaluated based on the Bader scheme [68, 69], which provides an intuitive way of separating the charge related to each atom using first-principles calculations. The charge redis-
tribution in real space is evaluated by the electron charge density difference, defined as \( \Delta \rho = \rho_{\text{total}} - \rho_{\text{WS}_2} - \rho_{\text{N}_2\text{H}_4} \), where \( \rho_{\text{total}} \) is the electron charge density of the combined system, \( \rho_{\text{WS}_2} \) is the electron charge density associated with the layered WS\(_2\) in the combined system, and \( \rho_{\text{N}_2\text{H}_4} \) is the electron charge density associated with N\(_2\)H\(_4\) molecules in the combined system, respectively. A benchmark for the pristine monolayer WS\(_2\) was established. Optimized lattice constant of 3.17 Å is in consistent with the experimental value of 3.15 Å [143] \((\sim 0.6\% \text{ underestimate})\). Calculated band structure with DFT-PBE potential shows a semiconductor nature with the direct band gap of 1.67 eV at K point, in consistent with other DFT calculations [144] and \(\sim 12\%\) underestimated as compared to the experimental value of 1.9 eV [145]. It is a typical underestimation for semiconductors in DFT-PBE potential, since such potential has unphysical self-interaction in the eigenstates, which reduces the bandgap. More sophisticated methods (such as GW [146, 147]) have been developed to correct the underestimated band gap issue in DFT. In this work, we mainly focus on the role played by the N\(_2\)H\(_2\) molecule on the electronic band structures of the layered WS\(_2\) (e.g. how the impurity states associated with N\(_2\)H\(_2\) molecule pinning in the Fermi level). Therefore, the DFT-PBE potential should be sufficient in our calculations.

3 Preferential adsorption sites and the adsorption energy

As shown in the planer projection of the relaxed structure of pristine monolayer WS\(_2\) (see Fig. 44(a)), it is a perfect hexagonal lattice of S atoms, with interleaved W atoms that are coordinated by S atoms in a trigonal prismatic arrangement. Three initial possible N\(_2\)H\(_2\) molecule absorption sites can be considered, based on this symmetry of WS\(_2\): (I) with the center of N–N bond either on the top of Tungsten atom (referred as W site), (II) on the top of Sulphur atom (referred as S site), (III) on the top of center of hexagon (referred as H site) as illustrated in Fig. 44(a). We examined several orientations of N\(_2\)H\(_2\) molecule with respect to the monolayer WS\(_2\) at these sites. It
Figure 44. (a) Schematic illustration of the three possible adsorption sites for N$_2$H$_2$ molecule on the top of WS$_2$ monolayer: the H site (on the top of center of hexagon), the W site (on the top of Tungsten atom), and the S site (on the top of Sulphur atom) marked with black dots on the top view of the monolayer WS$_2$. (b) The preferential orientation of N$_2$H$_2$ on the surface of the monolayer WS$_2$ and the vertical distance $h$ defined by the distance between the center of N–N bond and the top surface level of the monolayer WS$_2$. (c) The total energy as a function of the vertical distance $h$ for the N$_2$H$_2$ molecule stays either on the H site (left), or on the S site (middle), or on the W site (right) site, respectively. The insets in (c) are the top and side views of the optimized configurations of the combined systems. The yellow balls represent S atoms, green balls represent the W atoms, and the blue and white balls are N and H atoms, respectively.

was found that, N$_2$H$_2$ molecule prefers to stay on the top of WS$_2$ surface with N–N bond parallel to the surface, as illustrated on the side view in Fig. 44(b). To find the preferential positions of a N$_2$H$_2$ deposited on the monolayer WS$_2$, we proceeded with the following steps: First the vertical distance $h$, defined as the distance between the center of N–N bond and the top surface level of the monolayer WS$_2$ (see Fig. 44(b)) was optimized. Fig. 44(c) shows the total energy of the combined system as a function of the vertical distance $h$, where a N$_2$H$_2$ molecule is deposited either on the H site (left panel), or on the S site (middle panel), or on the W site (right panel). Next, A full atomic relaxation for the combined system is performed. It is found that the N$_2$H$_2$ molecule remains either at the H site, or at the W site, or at the S site, clearly indicating that these sites are energetically preferential adsorption positions.
Table 1. The adsorption energy per $N_2H_2$ molecule $E_{ad}$, the equilibrium adsorption vertical distance $h$ between the $N_2H_2$ molecule and the monolayer WS$_2$, and the shortest distance $d$ between the H atom of the $N_2H_2$ molecule and S atoms on the top surface of the monolayer WS$_2$ at different adsorption sites.

<table>
<thead>
<tr>
<th>Adsorption site</th>
<th>$E_{ad}$ (meV)</th>
<th>$h^*$</th>
<th>$d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H site</td>
<td>-220.0</td>
<td>3.37</td>
<td>2.95</td>
</tr>
<tr>
<td>W site</td>
<td>-207.0</td>
<td>3.78</td>
<td>3.09</td>
</tr>
<tr>
<td>S site</td>
<td>-207.9</td>
<td>3.78</td>
<td>3.19</td>
</tr>
</tbody>
</table>

In Table 1, the obtained adsorption energy $E_{ad}$ and the equilibrium vertical distance $h^*$ of a $N_2H_2$ molecule at these adsorption sites are listed. We can observe some interesting phenomena. First, the adsorption energies at these preferential adsorption sites attain negative values, clearly demonstrating that the adsorption of the $N_2H_2$ molecule on the surface of the monolayer WS$_2$ is a spontaneous and exothermic process, and these sites are energetically favorable (stable) adsorption positions for $N_2H_2$ molecules deposited on the monolayer WS$_2$. Second, we found that the lowest adsorption energy is at the H site ($-220.0$ meV), which confirms that, the H site is the mostly preferential adsorption position. We found similar results in the cases of combined systems for the double layer and multilayer WS$_2$ (see Fig. 45 and associated discussions). Third, the magnitude of the adsorption energy is less than 250 meV, indicating that the adsorption is a physisorption. This weak physical adsorption suggested that the $N_2H_2$ molecule might be easier for desorption as found in our experiment (e.g. desorb hydrazine gas by pumping, shown in Fig. 6(a) of [148]). Furthermore, the shortest distance $d$ between the H atom of the $N_2H_2$ molecule and the top S atoms of the WS$_2$ monolayer (see the 4th column in table 1) are about twice as large as the typical chemical bond length of H-S ($\sim 1.34$ Å [149]), indicating that the $N_2H_2$ molecule is vdW bonded with S atoms.

Our experimental measurements shows that the nature of resistance of layered WS$_2$ depends on the number of layers. Beginning with pumping only 1-2 layers, the resistance is completely reversible. For 3-4 layers WS$_2$ samples, the resistance is par-
Figure 45. Relaxation processes of (a) one hydrazine molecule inserted between two WS$_2$ layers, (b) two hydrazine molecules on top of each layer of bilayer WS$_2$, and (c) hydrazine molecules inserted between layers of multilayer WS$_2$. The insets show the side views of corresponding fully relaxed structure of the combined system with the optimized interlayer separation $z$ and the shortest distance $d$. The yellow balls represent S atoms, green balls represent W atoms, and the blue and white balls are N and H atoms, respectively.

Initially reversible. Upon pumping multilayer WS$_2$ samples, the resistance is little or no reversible. To examine this layer-dependent behavior, we studied structural stability and adsorption energy of double layer and multilayer WS$_2$ under hydrazine gas adsorption. For the double layer WS$_2$, we worked with two different configurations. The first configuration was a single hydrazine molecule sandwiched between two WS$_2$ layers while the second configurations was one hydrazine molecule on top of each layer of a bilayer WS$_2$. For both cases, first, the N$_2$H$_2$ molecules were initially placed at the highly preferential H sites, as obtained in the case of monolayer WS$_2$, then the optimized ground state structures of combined double layer systems were fully relaxed with different initial interlayer separations $z$ values and a vacuum space of 20 Å. The relaxation processes were performed using the conjugate gradient algorithm, and the criteria for force convergence between two successive steps was $10^{-3}$ eV Å$^{-1}$. Fig. 45(a) and 45(b) shows the total energy as a function of relaxation step for optimized double layer systems for both configurations respectively. The insets are side views of obtained combined systems with optimized interlayer separations $z*$ and the shortest distances $d$ between the H atom of N$_2$H$_2$ and the S atom of WS$_2$ layers. Similar
structural optimization for multilayered WS$_2$ with hydrazine molecules sandwiched in layers and initially located at the highly preferential H sites were performed. Fig. 45(c) shows the corresponding relaxation process and optimized structure. In comparison with the interlayer separation of the pristine bilayer ($\sim 5.584$ Å [150]) and multilayer WS$_2$ ($\sim 6.247$ Å [150]), it is found that the optimized interlayer distance is extended by $\sim 1.8 - 4.6$ Å when N$_2$H$_2$ molecules are inserted. Another interesting observation is, the optimized interlayer separation $z*$ decreases with increasing the number of layers, i.e. from 10.14 Å in the double layer with one N$_2$H$_2$ molecule, to 8.0 Å in the multilayer WS$_2$. This decrease is clearly induced by the week vdW force exerted by the hydrazine molecules to the WS$_2$ layers. With the increase of hydrazine molecule, the vdW interaction becomes stronger hence the shorter interlayer separation is obtained indicating that there is less free space for N$_2$H$_2$ molecules to move between the WS$_2$ layers, and therefore, it will become more difficult to desorb them from multilayered WS$_2$.

Table 2 shows the calculated adsorption energies for the N$_2$H$_2$ molecules adsorbed on the double layer and multilayer WS$_2$ along with the optimized interlayer separation $z$ and the shortest distance $d$. The adsorption energies in the double and multilayer cases are negative (i.e. exothermic process) and within the range of physical adsorption. The shortest distance $d$ is again larger than the H–S bond length (e.g. 3.21 Å in the double layer with one N$_2$H$_2$, 3.20 Å in the double layer with two N$_2$H$_2$, and 3.62 Å in the multilayers with N$_2$H$_2$ inserted between layers, respectively), indicating vdW bonding nature. On top of that, the adsorption energy per WS$_2$ layer increases.

<table>
<thead>
<tr>
<th>Combined system</th>
<th>$E_{ad}$ (meV)</th>
<th>$z$(Å)</th>
<th>$d$(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Double layer WS$_2$ exposed to one N$_2$H$_2$</td>
<td>-170</td>
<td>10.14</td>
<td>3.21</td>
</tr>
<tr>
<td>Double layer WS$_2$ exposed to two N$_2$H$_2$</td>
<td>-250</td>
<td>9.19</td>
<td>3.20</td>
</tr>
<tr>
<td>Multilayer WS$_2$ exposed to N$_2$H$_2$</td>
<td>-510</td>
<td>8.0</td>
<td>3.62</td>
</tr>
</tbody>
</table>
Figure 46. Electronic band structures of (a) the pristine $3 \times 3$ monolayer WS$_2$, (b) the combined system with one $N_2H_2$ molecule adsorbed on the monolayer WS$_2$, (c) the combined system with one $N_2H_2$ molecule adsorbed between two layers of WS$_2$, (d) the combined system with two $N_2H_2$ molecules adsorbed on the top of each layer of bilayer WS$_2$, and (e) the combined system with the $N_2H_2$ molecules adsorbed between layers of the multilayer WS$_2$, respectively. The red lines are impurity states associated with the $N_2H_2$ molecules, and the black-dashed lines are Fermi level. The inset in (a) is the Brillouin zone of the $3 \times 3$ supercell with three special $k$ points.

with increasing the number of layers (e.g. the adsorption energy in the combined multilayer WS$_2$ is almost as twice as that in the combined monolayer WS$_2$). This proves that each hydrazine molecule simultaneously interacts with neighbor layers and it might firmly stay between layers and becomes difficult to move out of the adsorbed multilayer WS$_2$. This again explains why the electrical resistance has only partially recovered or shown no reversibility upon pumping for the WS$_2$ samples with 3–4 layers or multilayers, observed in our experiment [148].
Electronic properties of adsorbed layered WS$_2$

We systematically studied the electronic properties of optimized combined systems for N$_2$H$_2$ molecules adsorbed on monolayer, double layer, and multilayer WS$_2$, respectively, to unravel the mechanism of the decrease in resistance when WS$_2$ exposed to N$_2$H$_2$, observed in our experimental measurements [148]. The band structure calculations were carried out within DFT PBE potentials (See Fig. 46 ). For the pristine 3 $\times$ 3 monolayer WS$_2$, the calculated band structure exhibits the semiconducting feature with the direct band gap of $\sim$ 1.67 eV at $\Gamma$ point (see Fig. 46(a), note that the $K$ point in the first Brillouin zone of the 1 $\times$ 1 unit cell merges to the $\Gamma$ point in the 3 $\times$ 3 supercell as the Brillouin zone is three folded). Although experiment suggest that WS$_2$ is a intrinsically n-type material [151] but our DFT calculation shows Conduction band minimum (CBM) above fermi level and our result is consistant with other theoretical results [152]. Calculated band structures of adsorbed systems are shown in Fig. 46(b)–(e). It is found that, even though WS$_2$ is exposed to N$_2$H$_2$ molecules, Compared with the pristine WS$_2$, the major features of the top valence band (VB) and the bottom of the conduction band (CB) are almost unaffected because of the weak vdW interaction between the hydrazine and WS$_2$ layers (Fig. 46(a)). Because the symmetry of the adsorbed system is lowered by introducing N$_2$H$_2$, only a slightly lifting on the band degeneracy was found, for instance, in the case of the double layer with one N$_2$H$_2$ (Fig. 46(c)). In fact, the significant effect on the band structures upon the N$_2$H$_2$ adsorption is the emergence of the flat impurity states associated with the N$_2$H$_2$ molecules (see red lines in Fig 46(b) – (e)). These impurity states are inside the band gap of the host layered WS$_2$ and pin below the Fermi energy, exhibiting an n-type like nature, irrespective of number of WS$_2$ layers. This implies that, as compared to electrons at the top VB band in the pristine WS$_2$, electrons occupying the impurity states can easily jump to the bottom of the empty CB, resulting in an increase of the charge carrier concentration. Thus when WS$_2$ samples are exposed
to N$_2$H$_2$ molecules, the emergence of the impurity states associated with the N$_2$H$_2$ below, the Fermi energy plays a key role in reducing the resistance of WS$_2$ samples, as observed in our experiment [148].

The effect of N$_2$H$_2$ on the electronic properties of layered WS$_2$ can be also found from the electronic densities of states (DOS) as shown in Fig. 47. For the pristine monolayer WS$_2$ (see Fig. 47(a)), since there is a big gap ($\sim$ 5.0 eV) between the deep band (below $-12.0$ eV) and the VB (between $-7.0$ and 0 eV), the major electronic properties of WS$_2$ will be dominated by the VB near the Fermi energy (indicated by the black dash line in Fig. 47). There is a clear energy gap ($\sim$ 1.67 eV) between VB and CB, exhibiting its semiconducting nature. The shape of the DOS almost
Figure 48. The side views of the isosurface plots of the electron charge density difference (DCD) for N\textsubscript{2}H\textsubscript{2} molecules (a) adsorbed on the monolayer WS\textsubscript{2}, (b) adsorbed on each layer of the double layer WS\textsubscript{2}, and (c) sandwiched in the multilayer WS\textsubscript{2}, respectively. The isosurface is taken as $6.0 \times 10^{-4}$ e Å\textsuperscript{-3}. The electron accumulation and depletion are represented by blue and pink colors respectively. The numbers, estimated from Bader analysis, indicate the charge transfer between the host WS\textsubscript{2} and the N\textsubscript{2}H\textsubscript{2} molecules. (d) The HOMO and LUMO of the isolated N\textsubscript{2}H\textsubscript{2} molecule (the isosurface is taken as $6.0 \times 10^{-3}$ e Å\textsuperscript{-3}).

maintains its original feature when the layered WS\textsubscript{2} is exposed to the N\textsubscript{2}H\textsubscript{2} molecules. But there are two more narrow bands or sharp peaks emerge, one is located below the VB (see the sharp peaks around $-8.0$ eV in Fig. 47(b)-(e)), and the other one is located above the top of the VB, closing to the Fermi energy (see the sharp peaks near the Fermi energy). Evidently, the sharp peak at the deep band will not affect the electronic properties of layered WS\textsubscript{2}. It is the sharp peak near the Fermi energy, narrowing the energy gap and affecting the nature of electronic properties of layered WS\textsubscript{2}. Later, it will enhanced its conductivity and reduce its electrical resistance. That is to say, layered WS\textsubscript{2} is highly sensitive to N\textsubscript{2}H\textsubscript{2} and can be considered as a
promising candidate to detect such a toxic gas.

5 Charge redistribution and charge transfer

As noted previously, the electronic properties of layered WS$_2$ are highly sensitive to N$_2$H$_2$ gas molecules. Specifically, the impacts on Fermi-level pinning due to the N$_2$H$_2$ gas adsorption are significant and play the role in reducing the electrical resistance. Therefore, it is also interesting to see how the electron charges are redistributed in the real space and how they are transferred between the adsorbed N$_2$H$_2$ molecules and underlying layered WS$_2$. To answer these questions, we performed differential charge density (DCD) calculations for the adsorbed systems to examine the net electron charge distribution after N$_2$H$_2$ molecules are stabilized on the layered WS$_2$. To estimate the charge transfer between the gas molecules and the sensing material, Bader charge analysis is also employed. The results are presented in Fig. 48. The blue and the pink colors represents the regions of the electron accumulation and depletion, respectively. We have found that, along with the polarization happens between N$_2$H$_2$ molecules and layered WS$_2$ due to the charge redistribution upon N$_2$H$_2$ adsorption, the S atoms on the layered WS$_2$ surface close to the N$_2$H$_2$ molecules are considerably polarized with more electron accumulation concentrated at one S atom and more electron depletion centered at another S atom. Likewise, on the N$_2$H$_2$ molecules, N atoms partially gain electrons and H atoms partially loss electrons. Such polarization is mainly attributed to the attractive electrostatic interaction. In addition to that, it is found that, in the case of monolayer WS$_2$, only S atoms on top surface are polarized, while, in the cases of double layer and multilayer WS$_2$, S atoms on both top and bottom surfaces of layers are polarized, and more electron accumulate (deplete) around S atoms as compared to the case of monolayer WS$_2$. Same tendency is also found in the N$_2$H$_2$ molecules. Although the N$_2$H$_2$ molecules are found to be vdw bonded with S atom on layered WS$_2$, there is still a small amount of charge
transfer, based on the Bader analysis, between N$_2$H$_2$ molecules and the layered WS$_2$. Namely, a 0.087 e, 0.114 e, and 0.162 e per N$_2$H$_2$ molecule are transferred from the monolayer, double layer, and multilayer WS$_2$ to N$_2$H$_2$ molecules, respectively (see the numbers on Fig. 48(a)–(c)). Such transfer increases with the increasing number of WS$_2$ layers. The calculated highest occupied molecule orbital (HOMO) and lowest unoccupied molecule orbital (LUMO) orbitals of an isolated N$_2$H$_2$ are shown in Fig. 48(d). By comparing them with the DCD of the adsorbed systems for monolayer, double layer, and multilayer WS$_2$ (i.e. Fig. 48(a)–(c)), it is clearly found that the DCD located around the adsorbate N$_2$H$_2$ molecules exhibit the nature of the LUMO of N$_2$H$_2$. Consequently, the small charge transfer from layered WS$_2$ to N$_2$H$_2$ molecules evaluated from Bader analysis comes from the hybridization of the N$_2$H$_2$ molecular LUMO with the substrate orbitals.

6 Effects of defects and humidity

The synthesis of layered WS$_2$ is usually followed by Defects. The vacancies associated with the absence of an atom at either the S atom site (referred as S vacancy) or the W atom site (referred as W vacancy) on the layered WS$_2$ lattice are two most possible defects. One interesting question is how such intrinsic defects qualitatively influence the N$_2$H$_2$ adsorption. Adsorption. To be specific, we want to understand the possible role of the defects on the electronic properties, and therefore on the sensitivity of layered WS$_2$ to the foreign gas molecules. As the vacancy has more chemically reactive locations to attract foreign molecules, it is anticipated that foreign molecules would easily bond to the layered WS$_2$ at such defect sites. In contrast, we found that when a N$_2$H$_2$ molecule was initially placed close to the vacancies within the bonding distance (e.g. $d \sim 1.78$ Å), it was ‘pushed’ away by the WS$_2$ layer during the adsorption process and eventually stabilized to a larger distance $d \sim 2.73$ Å (see the insets in Fig. 49(b) and (d)), indicating that the N$_2$H$_2$ molecule does not
Figure 49. Band structures of (a) monolayer WS\textsubscript{2} with a S vacancy, (b) N\textsubscript{2}H\textsubscript{2} on monolayer WS\textsubscript{2} located at the S vacancy, (c) monolayer WS\textsubscript{2} with a W vacancy, and (d) N\textsubscript{2}H\textsubscript{2} on monolayer WS\textsubscript{2} located at the W vacancy, respectively. The green curves are defect states associated with S (W) vacancy and the red lines are the impurity states associated with N\textsubscript{2}H\textsubscript{2} molecule. The black dashed vertical lines are used to guide the special k points, and the horizontal lines indicate the Fermi energy. The insets are top views of corresponding structures, where the red dashed circles indicate the defect locations, yellow balls represent S atoms, green balls represent W atoms, and blue and white balls are N and H atoms, respectively.

prefer to chemically bond with S atoms near the vacancy but weakly interacts with the WS\textsubscript{2} (e.g. calculated $E_{ad} \sim -200$ meV). The band structures of a monolayer WS\textsubscript{2} with a vacancy either at the S atom site or at the W atom site are shown in Fig. 49(a) and 49(c) respectively. We found that dangling bonds associated with the S vacancy introduce empty localized defect states below the CB (see the energy level in green color located above the Fermi energy in Fig. 49(a)), exhibiting a p-type like nature. On the other hand, dangling bonds associated with the W vacancy introduce defect states around the Fermi level, leading to a gap-less nature, as shown by the green curves in Fig. 49(c). The reason behind it is that, W vacancy is located between top and bottom S atoms and will induce local distortions inside the WS\textsubscript{2} layer (see the inset of Fig. 49(c)). In addition to that, the degeneracy in the VB of the pristine WS\textsubscript{2} was lifted by the S vacancy, and the dispersion of these bands was also reduced. The reduction of the dispersion indicates that these states are becoming
Figure 50. (a) The relaxation process of N$_2$H$_2$ molecules adsorbed on the monolayer WS$_2$ with a water film. Insets are top and side views of the combined system at the initial (left) and final (right) stage where yellow balls represent S atoms, green balls represent W atoms, red balls represent O atoms, and blue and white balls are N and H atoms, respectively. The red-dashed lines represent the hydrogen bonds. The values of 2.95 Å and 2.14 Å indicate the distance between the water film and the WS$_2$ layer and the hydrogen bond between N$_2$H$_2$ and water molecules, respectively.

(b) Band structures of a water film on the surface of monolayer WS$_2$ (left) and a N$_2$H$_2$ molecule adsorbed on monolayer WS$_2$ with a water film (right), respectively. The impurity states associated with N$_2$H$_2$ molecule are indicated by red color, and the degeneracy of the top VB is lifted which can be seen by the green and blue curves. The black dashed vertical lines are used to guide the special k points, and the horizontal lines indicate the Fermi energy.

more localized. N$_2$H$_2$ was trapped close to the vacancies (see the insets in Fig. 49(b) and (d)) after it was introduced to the monolayer WS$_2$ surface. By comparing the band structures of the WS$_2$ with vacancies (Fig. 49(a) and (c)), we found that the defect states associated with the vacancies are not affected by the introduction of the N$_2$H$_2$ molecule, instead, additional occupied impurity states associated with N$_2$H$_2$ molecule appear just below the Fermi energy, showing a n-type like nature (see the red lines in Fig. 49(b) and (d)). Electrons occupied on such localized n-type like states will be easily excited and trapped to the localized p-type like states near the vacancies. Hence, the defects states will influence the conductivity and the sensitivity of layered WS$_2$ to hydrazine gas.

Considering this fact that, the traces of moisture are inherent in experimental
observations, we also investigate theoretically the role of the humidity on the electronic structure of the monolayer WS$_2$ during N$_2$H$_2$ adsorption. A water film was introduced by adding water molecules one-by-one on the WS$_2$ surface in the chosen 3 × 3 unit cell. During this process, the distance and the orientation of water molecules were arranged such that hydrogen bonding nature (i.e. H–O bonds between neighboring water molecules) could always be maintained. A full relaxation process for this combined system was performed under the criteria of $10^{-3}$ eV Å$^{-1}$ for the force convergence (see Fig. 50(a)). The weak interactions between water film, the N$_2$H$_2$ molecule, and the WS$_2$ layer are considered by employing the semi-empirical correction scheme of Grimme. Fig. 50(a) shows the top and side views of optimized conformation for N$_2$H$_2$ molecules adsorbed on the monolayer WS$_2$ with a water film. It is found that, at this coverage, the hydrogen bonds between N$_2$H$_2$ and water molecules are $\sim 2.14$ Å, and the nearest neighbor distances between atoms in H$_2$O and those in WS$_2$ is $\sim 2.946$ Å, showing a weak interaction between the H$_2$O film and the WS$_2$. Similarly, the distance between the center of the N–N bond of the N$_2$H$_2$ and the surface of the WS$_2$ is $\sim 5.703$ Å, showing a weak interaction between the N$_2$H$_2$ and the WS$_2$. Electronic band structures corresponding to the WS$_2$ covered with the H$_2$O film and those corresponding to the combined N$_2$H$_2$/H$_2$O-film/WS$_2$ system are shown in Fig. 50(b) (left) and Fig. 50(b) (right), respectively. An interesting finding is that the additional states associated with water film are flat and embedded in the deep VB, the basic nature of top VB and bottom CB as well as the band gap of monolayer WS$_2$, on the other hand, maintains (as compared with the band structure of the pristine monolayer WS$_2$ shown in Fig 3(a)). In contrast to the cases of N$_2$H$_2$ adsorption without water film, when the N$_2$H$_2$ molecule is added to the WS$_2$ near the H$_2$O film, the impurity states associated with N$_2$H$_2$ on the water film move inside the VB (indicated by the red in the right panel of Fig. 50(b)), and therefore will have less effect on the resistance of WS$_2$. Additionally, the degeneracy of the top VB
band is also lifted due to the interaction between N$_2$H$_2$ and water molecules through hydrogen bonds between them (indicated by the green and blue in the right panel of Fig. 50(b)). These results indicate that the humidity plays a role to reduce the effect on the resistance of WS$_2$ upon the adsorption of the N$_2$H$_2$ gas.

7 Conclusion

We have systematically studied the N$_2$H$_2$ adsorption process on layered WS$_2$ on the basis of DFT calculations. The preferential absorption sites and the adsorption energy were determined through relaxation process. It is found that the adsorption of N$_2$H$_2$ gas molecules on layered WS$_2$ is an exothermic and energetically favorable process. N$_2$H$_2$ molecule are vdW bonded with S atoms on the surfaces of the layered WS$_2$, mostly located at the preferential sites on the top of the center of the hexagon. The hybridization between adsorbate and adsorbent is weak, and the adsorption energy is at the level of physical adsorption. Therefore, N$_2$H$_2$ molecules are easier to be desorbed. The level of the desorption will depend on the number of layers of the hosting layered WS$_2$, since the adsorption energy will become stronger and the interlayer separation will be shorter when the number of layers increases, which explained the layer-dependent of reversibility in electric resistance as observed in our experiment. The band structures and DOS of the combined adsorbate-adsorbent systems are calculated at the DFT-PBE level. The most interesting finding is the emergence of the flat impurity states pining below the Fermi energy on the band structure upon exposing to N$_2$H$_2$ molecules, irrespective of number of WS$_2$ layers. This induces a significant influence on the electronic properties of layered WS$_2$, in particular, on their conductance and subsequently on their resistance, which explains a drop of resistance of layered WS$_2$ under the N$_2$H$_2$ adsorption observed in our experiment. The electron charge density difference and Bader charge transfer analysis were performed. A layer-dependent small charge transfer ($\sim 0.087 \ e - 0.162 \ e$) between
N$_2$H$_2$ molecules and layered WS$_2$ was found which results in a charge redistribution in the real space, and leads to a considerable polarization between S atoms close to the N$_2$H$_2$ molecules, between N and H atoms in the molecule, and between the adsorbate and adsorbent, respectively. It is also found that the vacancies could trap the N$_2$H$_2$ and the moisture could reduce the sensitivity of WS$_2$. In conclusion, WS$_2$ is especially sensitive to the N$_2$H$_2$ gas and can be used to detect such flammable and toxic gases in dry environment.
1 Further study on Cs intercalation

We have already discussed in chapter 5.2 that Cs intercalation and subsequent de-intercalation lead to a phase transition from black phosphorous to blue phosphorous. We only discussed what happens when Cs is intercalated inside BP, but we have not provided any insight on how this transformation happens. So in future we need to further study this Cs intercalated BP to give a complete picture of Cs intercalation induced phase transition. We plan to find transition mechanism of Cs intercalation induced phase transition. We will study the charge density difference of the Cs intercalated structure and evolution of charge density during relaxation process. How charge redistribute during a phase transition will give vital insight into the mechanism of phase transition.

Our experimental collaborators are doing in-situ and ex-situ raman analysis of Cs intercalated BP. So we will theoretically simulate raman spectrum to understand whether theoretically predicted structure has been realized experimentally. Fig. 51 shows the density of the vibrational mode of Cs\textsubscript{1}P\textsubscript{8}, Cs\textsubscript{2}P\textsubscript{8} and Cs\textsubscript{3}P\textsubscript{8}. We will further calculate raman spectrum for Cs\textsubscript{n}P\textsubscript{8} where n=4, 5, 6, 7, and 8. Although our preliminary study shows that, Cs intercalation without any pressure is sufficient for black to blue phase transition, we will theoretically figure out whether pressure will help the phase transition.
Layered black arsenic-phosphorus alloy (b-As$_x$P$_{1-x}$) is an emerging material in optoelectronics and electronics applications. In addition to its anisotropic behavior, like black phosphorus (b-P), b-As$_x$P$_{1-x}$ exhibits a narrow bandgap and improves environmental stability. Pure phosphorus in ambient pressure prefers A17 phase, while pure arsenic prefers A7 phase. Alloying As into b-P is expected to induce a phase transition. A previous theoretical study on As$_x$P$_{1-x}$ monolayer found the coexistence of A17 and A7 phases at x=0.07 (see Fig. 52) [153]. Based on this finding, we proposed a hypothesis that there may also exist a transformation from the pure black phosphorous with A17 structure to layered As$_x$P$_{1-x}$ with A7 structure by substituting P with As. In this study, we will concentrate on alloying as a means of structural transition and then we will study the effect of pressure on this structural phase tran-
Figure 52. a) Black Phosphorous A17(αP) structure b) Arsenene A7 (βAs) structure c) The relative stability (defined as \( E_{coh} - <E_{coh}> \)) as a function of concentration of phosphorous. The vertical dashed line indicates expected composition for \( α \rightarrow β \) transition [153].

Figure 53. Structures of \( \text{As}_x\text{P}_{1-x} \) for different values of \( x \).

sition. To accomplish our goal, we thoroughly searched the large compositional space of \( b-\text{As}_x\text{P}_{1-x} \) alloy to find the critical composition for such phase transition.

We immediately see from our preliminary study of the structure relaxation (Fig 53) that same species of atoms prefer to bond along armchair direction, and different species of atoms prefer to bond along Zig-Zag direction. By far we have not found any phase transition. The electron Localization Function (ELF) also does not indicate any sign of phase transition (Fig. 54). The reason why we could not find the phase transition by alloying BP with As is probably the high energy barrier from A17 to
Figure 54. electron localization function of $\text{As}_x\text{P}_{1-x}$ for different values of $x$. Red color indicate highly localized electron where blue indicate delocalized electron.

A7 phase.

In future we will systematically study mechanism for alloying of black phosphorous and local change on the alloy system. We will apply an alternative alloying process by substituting As with P atoms from grey As (A7) and look the energetics of $\text{As}_x\text{P}_{1-x}$ alloys between black and grey phases. We will also study effect of pressure and Li intercalation in $\text{As}_x\text{P}_{1-x}$ phase transition.
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RESEARCH AREAS

Computational material design, Electronic structure theory, Computational method development, Gas sensor, Li intercalation, Cluster expansion, Monte Carlo simulation, High-throughput calculation, Machine learning in material science.

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- Li intercalation induced phase transition from layered black phosphorene to blue phosphorene using ab-initio DFT method as implemented in VASP.
- Theoretically calculate change in Raman peak position of Li-intercalated black phosphorous with Li concretion.
- Effect of high pressure in structural change of Li-intercalated black phosphorous.
- Effect of hydrazine gas adsorption on electronic structure of the WS2 monolayer and multilayer.
- Effect of Alloying and pressure in black arsenic phosphorous (AsxP1-x) structure using Cluster Expansion and Monte Carlo Simulation.

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- Static and dynamic properties of sodium-potassium (NaK) binary alloy using orbital-free Density Functional Theory (OF-DFT)

TECHNICAL SKILLS

- **DFT codes**: VASP, GPAW, Quantum espresso
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PUBLICATIONS

   https://doi.org/10.1088/1361-6528/abb337


POSTER AND ORAL PRESENTATIONS

1. Md Rajib khan Musa, Congyan Zhang, Adel Alruqi, Gamini Sumanasekera, Ming Yu, “The effect of the adsorption of the toxic hydrazine on the electronic structure of the WS2 monolayer: the first principle calculations”. Aps March Meeting,


9. Jacek B. Jasinski, Meysam Akhtar, Congyan Zhang, Manthila Rajapakse, **Md Rajib Khan Musa**, Ming Yu, Gamini Sumanasekera. ”High-pressure study of vibrational structure in phosphorene samples”, MRS Spring Meeting, Phoenix, AR, April 2019

10. Manthila Rajapaksa, **Md Rajib khan Musa**, Jacek B. Jasinski, Ming Yu, Gamini Sumanasekera. ”Vibrational Properties of Black Phosphorous under Intercalation High-pressure: An In-situ Study.” MRS Fall Meeting, Boston, MA, Nov. 2020
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Introduction to Physics I (PHYS 111):
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• Proctored exam and graded exam paper.

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• Insured lab safety and productive learning environment.

Atomic Nuclear Lab (PHYS 351):
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• Assisted student and insured lab safety.

PROFESSIONAL MEMBERSHIP

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