INVESTIGATION OF ELECTRONIC, OPTICAL, AND SURFACE ADSORPTION PROPERTIES IN ENGINEERED BLACK PHOSPHORENE AND ITS ISOSTRUCTURAL TIN SULFIDE SYSTEMS

A thesis submitted in partial fulfilment of the requirements
for award of the degree of

Doctor of Philosophy

Dhanjit Talukdar

Registration No.TZ24003131 of 2024

DEPARTMENT OF PHYSICS
SCHOOL OF SCIENCES
TEZPUR UNIVERSITY
TEZPUR-784028
ASSAM, INDIA
MAY, 2025

Chapter 7:

Conclusions and future prospects

7.1 Concluding remarks

This thesis presents a comprehensive theoretical investigation into the anisotropic structural, electronic, optical, and surface adsorption properties of two orthorhombic layered materials, BP and its isostructural counterpart, SnS. It emphasizes the role of defect and heterostructure engineering in tailoring their physicochemical behaviours, aiming to expand their applicability in next-generation sensing and optoelectronic devices. We began by contextualizing the significance of low-dimensional materials through the lens of quantum confinement effects and the evolution of 2D materials, starting with the successful exfoliation of graphene. This set the stage for a discussion on the unique properties of 2D materials such as TMDCs, BP, and SnS, highlighting their potential across various application domains. The key findings and contributions of this thesis are summarized below.

Chapter 3 focuses on the defect engineering of BP, motivated by its higher susceptibility to defects compared to SnS. In this chapter, a novel strategy involving the incorporation of a compound defect was proposed and systematically investigated for the BP monolayer. First-principles calculations demonstrated that such defects can be energetically favourable and chemically stable, as evidenced by the formation energy, binding energy, and cohesive energy values. In particular, nitrogen was found to preferentially occupy a phosphorus vacancy site, forming the compound defect system BP_{v}^{N}, which remains thermally stable at both room temperature (300 K) and elevated temperatures up to 600 K. This defect configuration not only introduces localized electronic states but also significantly alters the fundamental band structure of BP. Moreover, the introduction of uniaxial strain along the armchair and zigzag directions further tunes the electronic characteristics of the BP_{v}^{N} system, influencing both the band gap size and the transition between direct and indirect band gap behaviour. Importantly, this strain-induced tunability preserves the intrinsic anisotropic response of pristine BP, reinforcing the effectiveness of combining defect and strain engineering for tailored electronic behaviour.

In Chapter 4, in continuation of the compound defect BP system, we investigate its surface adsorption properties to assess its potential for gas sensing and storage applications. The surface reactivity of BP was systematically analysed by evaluating its interaction with hazardous gas molecules, with a particular focus on the role of defects. The presence of a compound defect in the monolayer significantly enhances its chemical reactivity, especially towards NO_2 molecules. This enhanced interaction leads to strong chemisorption, characterized by high adsorption energy, substantial charge transfer, and a remarkable ability of the monolayer to break the N-O bond and capture the detached oxygen atom. These effects collectively result in an extraordinarily long desorption or recovery time (on the order of ~7.57×10^{82} s), positioning BP_V^N as a highly promising candidate for NO_2 storage applications. Additionally, while monolayers with single point defect (BP_V and BP^N) show inadequate sensitivity to SO_2, the BP_V^N system exhibits a unique synergistic effect of dopant and vacancy that enhances its responsiveness. This makes the compound-defected BP not only suitable for NO_2 capture but also a viable, sensitive, and selective sensor for SO_2 molecules. These findings emphasize the critical role of compound defects in tuning the surface chemistry of BP, broadening its applicability in environmental sensing and gas storage applications.

Chapter 5 introduces the novel concept of mixed-phase or anisotropic/isotropic heterostructures by investigating the 2D/2D SnS/*h*-BN system through comprehensive first-principles DFT and GW+BSE analysis. Stacking SnS with *h*-BN not only enhances the thermal and structural stability of the system but also preserves the intrinsic optoelectronic properties of the SnS monolayer. The heterostructure exhibits a type-I (straddling) band alignment, ensuring that both the conduction band minimum and valence band maximum remain localized within the SnS layer, an essential feature for efficient light emission and absorption in SnS. Importantly, non-uniform charge dynamics at the interface generate intrinsic intralayer electric fields within the SnS, which effectively reduce the exciton binding energies of both A_{SnS} and B_{SnS}. This reduction leads to improved exciton recombination lifetimes, a critical factor for enhancing the performance of optoelectronic devices. These intrinsic field-induced excitonic modifications underscore the potential of SnS/*h*-BN heterostructure for use in next-generation photovoltaics and other optoelectronic devices.

In Chapter 6, the unconventional and novel idea of mixed-dimensional heterostructure was explored through the investigation of SnS/BNNT systems, offering valuable insights into the effects dimensionality and curvature in tailoring electronic and optical properties. These heterostructures are found to be stable at room temperature and exhibit type-I band alignment at the quasiparticle GW level. A key feature of these systems is the radius-dependent modulation of band gaps, which leads to a systematic blue-shift in optical (excitonic) transitions, as the BNNT radius increases. Notably, in the SnS/(5,0) BNNT heterostructure, a localised type-II band alignment emerges, wherein the electron becomes confined within the 1D nanotube while the hole remains localized on the 2D SnS surface. This spatial charge separation gives rise to an IDE with a strong binding energy of 0.71 eV, driven by the strong confinement and high effective mass of the electron. Furthermore, the application of uniaxial tensile strain to the SnS/(5,0) BNNT system expands the localised type-II direct gap, enabling the formation of additional IDE transitions and enhancing the tunability of the excitonic landscape. Overall, SnS/BNNT heterostructures serve as a unique model system for investigating 2D/1D interdimensional interactions, offering exciting opportunities for the development of next-generation quantum optoelectronic devices.

In conclusion, this thesis presents a multi-faceted approach to understanding and engineering the structural, electronic, and functional properties of BP and SnS monolayers. By employing strategies such as compound defect formation and heterostructure design, we demonstrate new pathways to enhance the performance of these materials for practical applications. The synergy between intrinsic anisotropy, defect-induced modulation, and interlayer interactions paves the way for future exploration of 2D and mixed-dimensional materials in advanced sensing, energy conversion, and quantum technologies.

7.2 Future scope of the research work

The findings presented in this thesis pave the way for several promising avenues of future research, particularly in the realm of low-dimensional material engineering via defect modulation and heterostructure design.

The demonstration of enhanced chemical reactivity in BP via compound defect incorporation suggests that further exploration of defect engineering, by tuning the type, concentration, and spatial arrangement of vacancies and dopants, could yield a wide range of tailored properties. Such engineered BP systems hold immense potential not only for the selective detection and storage of toxic gas molecules but also for broader applications in electronics, optoelectronics, energy storage, and even in the emerging fields of magnetism and spintronics. Specifically, introducing magnetic dopants or complex vacancy clusters may enable BP to exhibit tunable magnetic ordering or spin-dependent transport properties, making it a strong candidate for future spintronic devices.

In parallel, the work on SnS-based heterostructures highlights the versatility of monochalcogenides when integrated with stable, wide-bandgap 2D materials like *h*-BN. Moving forward, the concept of mixed-phase heterostructure engineering can be extended to other monochalcogenides (e.g., SnSe, GeS, GeSe) and layered semiconductors such as TMDCs. Such combinations may lead to emergent phenomena such as charge transfer excitons, moiré superlattices, and interfacial ferroelectricity, each holding unique implications for quantum devices and optoelectronics.

Moreover, the demonstrated potential of mixed-dimensional heterostructures, particularly SnS/BNNT systems, opens up avenues for exploring novel excitonic and interfacial charge phenomena in 2D/1D architectures. Expanding this approach to include other dimensional hybrids, such as 2D materials interfaced with nanoribbons, quantum dots, or nanowires, could enable tunable quantum confinement effects, enhanced light-matter interactions, and new regimes of exciton dynamics. These platforms may serve as the basis for highly integrated and nanoscale devices in future quantum computing, sensing, and photonic circuits.

Overall, the strategies developed in this thesis establish a foundational framework for manipulating the structural, electronic, optical, and surface properties of 2D materials and their hybrids. Future research in this direction holds significant potential for uncovering emergent quantum phenomena, enabling novel functionalities across diverse fields of nanotechnology and materials science. Finally, collaboration with experimental groups will be essential to verify these theoretical predictions, particularly for SnS/*h*-BN and SnS/BNNT heterostructures. Experimental synthesis, coupled with advanced spectroscopic and transport characterization, will provide critical feedback for refining theoretical models and accelerating the transition of these materials into practical device fabrication.