Abstract

Low-dimensional materials, classified as zero-dimensional (0D), one-dimensional (1D), and two-dimensional (2D), exhibit distinct physical and chemical properties due to quantum confinement and reduced dimensionality. As dimensionality decreases, phenomena such as discrete energy levels, anisotropic charge transport, and enhanced surface reactivity emerge, making these materials fundamentally different from their bulk counterparts. Following the discovery of graphene, which revealed extraordinary electrical, mechanical, and thermal properties in a single atomic layer, 2D materials have garnered exceptional attention among low-dimensional systems. This breakthrough catalysed the exploration of a wide range of 2D systems, including transition metal dichalcogenides (TMDCs), transition metal monochalcogenides (TMMCs), and other layered compounds.

The exceptional optical, electronic, and surface properties of 2D materials can be further tuned through techniques such as defect engineering and heterostructure engineering. Defect engineering, involving controlled introduction of vacancies, dopants, or substitutions, allows modulation of the aforementioned properties by altering the local atomic environment. Heterostructure engineering, on the other hand, enables the stacking or lateral integration of 2D materials with other low-dimensional materials to form van der Waals heterostructures with novel interfacial interactions and emergent functionalities. These strategies provide powerful means to tailor band alignment, charge transfer dynamics, and surface reactivity, making them highly effective for optimizing performance in a broad range of electronic, optoelectronic, nano sensing, and energy-related devices.

In this thesis, we employ defect and heterostructure engineering strategies to investigate and modify the electronic, optical, and surface adsorption properties of two key 2D materials: black phosphorene (BP) and tin(II) sulfide (SnS). The following chapters present a comprehensive overview of the research conducted, highlighting the methodologies used and the core findings that contribute to advancing the understanding and application of these materials.

Chapter 1 provides an introduction to low-dimensional materials, with a focus on the intriguing and unique properties of 2D materials and their heterojunctions. Special

attention is given to BP and its isostructural orthorhombic counterpart, SnS, which belongs to the family of TMMCs. Following the introduction of these materials, the chapter highlights the motivation behind the thesis, emphasizing gaps in the existing literature. The chapter concludes by outlining the primary objectives of the research.

Chapter 2 presents a detailed theoretical background of the methodologies employed in the thesis. It introduces and discusses the formalism of density functional theory (DFT), which serves as the primary tool for achieving the objectives of the thesis. Additionally, the chapter discusses the concept of many-body perturbation theory (MBPT), including advanced computational approaches such as the Green's function 'G' combined with the screened Coulomb potential 'W' (GW). This methodology is specifically used in Chapter 5 and Chapter 6 in conjunction with the Bethe-Salpeter equation (BSE) to analyse excitonic phenomena.

Chapter 3 investigates the formation and stability of a compound defect in BP, specifically focusing on a configuration featuring a phosphorus vacancy with a substitutionally doped nitrogen atom (BP_V^N). Compound defects refer to the coexistence of two or more distinct point defects within a material. The structural and chemical stability of BP_V^N is evaluated through calculations of vacancy formation energy, binding energy, and cohesive energy. Thermal stability across different temperatures is further confirmed using ab initio molecular dynamics (AIMD) simulations. Additionally, the impact of uniaxial compressive and tensile strain on the electronic properties of BP_V^N is systematically explored.

Chapter 4 extends the investigation of stability of compound defect in BP, by examining the surface adsorption properties of BP_V^N with five environmentally hazardous gas molecules: NO_2, SO_2, CO, CO_2, and NH_3. The adsorption behaviour is systematically characterized using metrics such as adsorption energy, distance of separation, charge density difference, recovery time, electron localization function, electrostatic potential, and electronic properties including a density of states (DOS), projected DOS, and band structure.

Chapter 5 explores the optoelectronic properties of an orthorhombic SnS monolayer stacked with a hexagonal boron nitride (*h*-BN) monolayer, forming a mixed-phase heterostructure. The high interfacial binding energy, along with AIMD simulations at

elevated temperatures, confirms the structural stability of the heterostructure. The non-uniform charge redistribution at the interface gives rise to an out-of-plane intralayer electric field within the SnS layer. The impact of this proximity-induced electric field on the behaviour of SnS bound excitons, is examined in detail.

Chapter 6 expands upon the mixed-phase SnS/*h*-BN (2D/2D) heterostructure and its excitonic dynamics discussed in Chapter 5. It explores the optoelectronic properties of a mixed-dimensional SnS/BNNT (2D/1D) heterostructure, where an orthorhombic SnS monolayer is stacked with a one-dimensional boron nitride nanotube (BNNT). The combination of different confinement effects arising from the mismatch in dimensionalities, and their influence on optical transitions from a 2D state to a 1D state, is discussed in detail. The chapter further explores the evolution of the interdimensional exciton (IDE) under the influence of uniaxial strain.

Chapter 7 provides a summary of the key findings, concluding remarks from all chapters, and an outlook on the future scope of this work.