CHAPTER 6
SUMMARY AND FUTURE SCOPE

6.1. THESIS IN A NUTSHELL

The present thesis dived into the adsorption capacities of pristine and functionalized α-CX (X = N, P) monolayers concerning toxic gases. The first chapter explored the critical importance of detecting hazardous gases, underscoring its pivotal role in safeguarding human health and environmental well-being. This chapter introduced the unique attributes of two-dimensional materials, highlighting their potential to address contemporary challenges. It also enlightened the motivations driving the search for innovative materials, emphasizing the urgent need for advanced sensing technologies. Furthermore, the chapter discussed the necessity and methods of impurity doping, including substitution and decoration techniques, aimed at enhancing the adsorption performance of 2D materials. This groundwork provided a comprehensive understanding of the properties of selected α-CX monolayers, which serve as central elements in the thesis.

In the subsequent chapter, we presented a thorough theoretical overview of the computational methodology utilized in our study. We commenced with an explanation of Density Functional Theory (DFT), beginning with the foundational Kohn-Sham equation and its practical implementation using the Quantum Espresso software package. The discussion encompassed critical components such as exchange-correlation functionals and basis sets, emphasizing their crucial role in precisely modelling the electronic structure and characteristics of the materials under examination. Additionally, we delved into advanced theoretical concepts and their practical applications, including the analysis of conductivity using the BoltzTraP code.

In the third chapter, we investigated the adsorption performance of carbon monoxide (CO) and nitrogen monoxide (NO) gases on pristine α-CX (X = N, P) monolayers using Density Functional Theory (DFT) calculations. Our study involved a comprehensive analysis of the structural, electronic, and sensing characteristics of α-CX to unravel their adsorption mechanisms. Our findings indicated that both CO and NO gas molecules predominantly undergo physisorption on α-CX monolayers. However, our examination revealed significant drawbacks, including a notable adsorption distance exceeding 3 Å and suboptimal adsorption energies. Moreover, impractically short recovery times underscored the challenges of utilizing pristine α-CX monolayers effectively for toxic gas sensing applications. These limitations prompted us to explore alternative approaches, such as introducing defects into two-dimensional (2D) monolayers. This defect engineering strategy has emerged as a promising

method to enhance the performance of these materials in detecting hazardous gases. Therefore, we specifically examined CO and NO adsorption on carbon-defected α-CX monolayers. By scrutinizing the adsorption dynamics on these defect-engineered surfaces, the chapter elucidated the mechanisms responsible for their improved gas sensing capabilities.

Doping plays a crucial role in enhancing the gas adsorption capabilities of nanomaterials. Fourth chapter of the thesis focused on a first principles investigation into the structural, electronic, and sensing properties of α-CN monolayers doped with Aluminum, Boron, and Beryllium. Our research uncovered significant structural and electronic modifications induced by impurity doping, revealing distinct functionalities for α-CN monolayers. Specifically, Boron doping at the C-site emerged as highly promising for NO and NH_3 sensing applications, while B-doping at the N-site enhanced suitability for gas removal purposes. Similarly, Be-doping exhibited effectiveness in gas removal at both C and N sites. Importantly, our study identified an exceptionally rapid response for NO adsorption over B-doped α-CN, underscoring its potential as a swift sensor. Additionally, analysis of the work function suggested that B-doped α-CN is well-suited for φ-type sensing in NH_3 adsorption scenarios.

Toxic gases such as carbon monoxide (CO), nitric oxide (NO), and ammonia (NH_3) pose significant health and environmental risks. Current toxic gas monitors are expensive, prompting exploration into two-dimensional (2D) materials for their potential in gas sensing applications, leveraging their high surface-to-volume ratios and sensitivity. Among these materials, α-CN has emerged as a promising candidate for gas adsorption mechanisms. Chapter five of this thesis investigated the adsorption performance of α-CN surfaces decorated with nickel (Ni) atoms for CO, NO, and NH_3 toxic gases using advanced Density Functional Theory (DFT) based first principles calculations. The findings highlighted that Ni-decoration markedly improves the adsorption capability of α-CN, evident from highly negative adsorption energies. Consequently, the calculated recovery times were exceptionally long, indicating that Ni-decorated α-CN is more suitable for the removal of these toxic gases rather than as a sensor. The study extensively analyzed the structural and electronic properties, including projected density of states (PDOS), band structure, charge density diagrams, and charge transfer mechanisms. Additionally, sensing properties such as work function and electrical conductivity were computed to validate the material's effectiveness in gas detection applications.

Table 6.1: Adsorption properties of the α-CX monolayers, both before and after the process of doping and decoration

System	CO adsorption		NO adsorption		NH_3 adsorption	
	E_{ads} (eV)	τ (s)	E_{ads} (eV)	τ (s)	E_{ads} (eV)	τ (s)
Pristine α-CN	-0.08	22.9×10^{-12}	-0.07	18.1×10^{-12}	-0.10	47.8×10^{-12}
Pristine α-CP	-0.06	10.5×10^{-12}	-0.09	32.5×10^{-12}	-	-
sC defected α-CN	-3.63	01.2×10^{49}	-1.90	01.05×10^{22}	-	-
C defected α-CP	-1.33	02.6×10^{10}	-1.98	02.26×10^{21}	-	-
Al (at C) doped α-CN	-0.88	06.30×10^{2}	-1.89	8.11×10^{19}	-1.24	6.78×10^{8}
B (at C) doped α-CN	-0.10	47.8×10^{-12}	-0.26	2.31×10^{-8}	-0.43	1.6×10^{-5}
B (at N) doped α-CN	-1.79	1.1×10^{18}	-1.75	2.4×10^{17}	-2.89	3.5×10^{36}
Be (at C) doped α-CN	-0.49	1.7×10^{-4}	-0.32	2.3×10^{-7}	-1.23	4.6×10^{8}
Be (at N) doped α-CN	-1.38	1.5×10^{11}	-1.48	7.3×10^{12}	-2.18	4.1×10^{24}
Ni decorated α-CN	-3.11	1.77×10^{40}	-3.15	8.31×10^{40}	-2.07	2.25×10^{32}

Table 6.1 provides a comprehensive overview of the adsorption properties of α-CN and α-CP materials under various doping and defect configurations, focusing on their interaction with CO, NO, and NH_3 gases. Starting with pristine α-CN and α-CP materials, the table establishes baseline adsorption energies (Eads) and recovery times (τ) for each gas, which are crucial for establishing comparative benchmarks. Introducing carbon defects into α-CN and α-CP significantly alters their adsorption behaviors, resulting in drastically lower adsorption energies and varied recovery times across all gases. For instance, C defected α-CN shows a CO

adsorption energy of -3.63 eV with an extremely long recovery time of 1.2×10^{49} seconds, indicating a very strong interaction with CO molecules, making it more suitable for toxic gas removal applications rather than rapid response sensors. Similarly, C defected α-CP exhibits a NO adsorption energy of -1.98 eV and a recovery time of 2.26×10^{21} seconds.

For the doped configurations, we explore the effects of aluminum (Al), boron (B), beryllium (Be), and nickel (Ni) on the adsorption characteristics of α-CN. Notably, Ni-decorated α-CN emerges as highly effective for both CO and NO adsorption, with substantial adsorption energies of -3.11 eV and -3.15 eV, respectively, and extremely long recovery times, suggesting very strong interactions with these gases. These longer recovery times suggest that Ni-decorated α-CN is more suitable for toxic gas removal applications rather than rapid response sensors, due to its enhanced ability to retain adsorbed gases over extended periods. Similarly, boron doping at nitrogen sites (B (at N) doped α-CN) shows significant NO and NH_3 adsorption energies of -1.75 eV and -2.89 eV, respectively, indicating its efficacy in NO and NH_3 sensing applications. For NH_3 adsorption, the table highlights the effectiveness of boron doping at carbon sites (B (at C) doped α-CN), which has a moderate NH_3 adsorption energy of -0.43 eV, indicating a favorable interaction with NH_3 molecules. Additionally, beryllium doping at nitrogen sites (Be (at N) doped α-CN) and carbon sites (Be (at C) doped α-CN) also demonstrate substantial NH_3 adsorption energies, reinforcing their potential in tailored sensor designs.

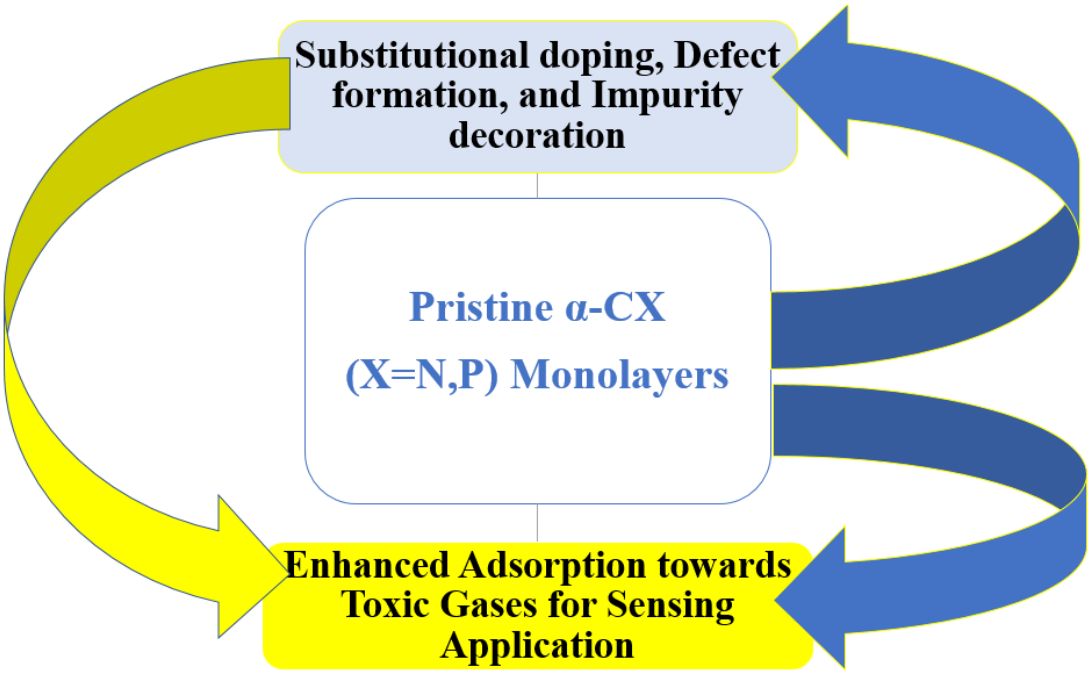

Figure 6.1: Conceptual framework for improving gas adsorption in materials

Fig. 6.1 illustrates the achieved objectives in enhancing gas sensing materials through a systematic approach. It begins with the concept of impurity doping and defect formation, where intentional introduction of impurities like nitrogen or phosphorus and creation of defects in alpha-phase carbon nitride or phosphide monolayers are employed. These modifications are aimed at enhancing the structural and electronic properties of the materials. From there, the flow moves to the pristine α-phase carbon nitride or phosphide monolayers, which serve as the starting point for further enhancement. The process highlights the evolution towards improved adsorption capabilities of these materials, specifically targeting toxic gases for sensing applications. By leveraging impurity doping and defect engineering, the flowchart demonstrates a pathway to achieve heightened selectivity and sensitivity in gas sensing, crucial for applications in environmental monitoring and health safety.

6.2. ADVANCED PROPERTIES

6.2.1. Current-Voltage (I-V) Characteristics:

These characteristics would illustrate how the current through the sensor varies with the applied voltage when exposed to different concentrations of toxic gases like CO, NO, and NH_3. By plotting these characteristics, researchers can analyze how sensitive the sensors are to changes in gas concentration, understand their response times, and assess their overall efficiency and reliability in detecting and quantifying toxic gases[1]. This analysis is crucial for optimizing sensor design and ensuring accurate and responsive gas sensing capabilities.

6.2.2. Selectivity:

Selectivity in gas sensors is a crucial aspect that determines their ability to accurately detect and distinguish between different gases, especially in complex and varied environments. Achieving high selectivity ensures that the sensor can reliably identify a target gas even when other gases are present simultaneously. Monte Carlo methods play a significant role in enhancing selectivity by simulating the probabilistic interactions between gases and the sensor material[2]. Unlike deterministic methods, Monte Carlo simulations consider the statistical distribution of gas molecules and their behaviors, allowing researchers to explore a wide range of conditions and configurations. This approach enables the optimization of sensor parameters such as material composition, surface morphology, and operating conditions to maximize the sensor's sensitivity to specific gases while minimizing interference from others.

6.3. 2D MATERIALS BEYOND α-CX AND HETEROSTRUCTURES

6.3.1. 2D Materials Beyond α-CX Monolayers

Beyond α-CX (X = N, P) monolayers, the realm of two-dimensional (2D) materials unfolds with a rich tapestry of structures and compositions that promise diverse applications across multiple fields. Graphene, celebrated as the archetype of 2D materials, stands out for its remarkable electrical conductivity, mechanical robustness, and superior thermal properties. Its single-layer carbon lattice configuration makes it indispensable in advanced electronics, photonics, and composite materials, driving innovations in flexible devices and high-performance coatings.

Transition metal dichalcogenides (TMDs) like MoS_2 and WS_2 represent another pivotal class of 2D materials with inherent semiconducting characteristics, positioning them at the forefront of optoelectronic applications and catalytic processes[3]. Emerging alongside are boron nitride (BN) nanosheets, distinguished by their exceptional thermal conductivity and chemical resilience, making them ideal for applications in thermal management and protective coatings. Black phosphorus (BP), known for its tunable band-gap and potential in nanoelectronics, underscores the versatility of 2D materials in enabling next-generation electronic devices and sensors[4].

MXenes are a rapidly growing family of 2D transition metal carbides, nitrides, and carbonitrides that have gained significant attention in recent years[5]. They exhibit excellent electrical conductivity due to the presence of metallic transition metals, making them suitable for applications in energy storage devices such as supercapacitors and batteries. They have a hydrophilic nature and their surfaces can be easily functionalized with various groups (e.g., -OH, -O, -F), which enhances their dispersibility in aqueous solutions and allows for tailored surface properties. MXenes are known for their impressive mechanical strength and flexibility, which can be leveraged in applications requiring durable yet flexible materials, such as flexible electronics and coatings. Depending on the transition metal and surface termination, MXenes can exhibit excellent chemical stability, making them suitable for harsh environments.

The ongoing exploration and discovery of new 2D materials and hybrid structures continue to expand this diverse family, each offering unique properties that researchers harness for advancements in energy storage, biomedical sensing technologies, and environmental monitoring systems.

6.3.2. Heterostructure Formation

The process of forming heterostructures involves attaching or depositing C_n (cyclo[n]carbon) rings onto 2D monolayers like α-CN or other alternative 2D materials. This process has the potential to induce substantial changes in the surface chemistry and structural composition of these monolayers. By exploring the detailed interactions between C_n nanoclusters and the 2D substrate, there is an opportunity to engineer interfaces with precise control. These interfaces can exhibit a range of adjustable adsorption properties tailored for specific gas molecules, thus enabling the creation of surfaces optimized for targeted gas adsorption applications. Additionally, heterostructures can also be formed by stacking two different monolayers, such as α-CN and α-CP, which further expands the potential for creating novel material combinations with enhanced properties for diverse applications.

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"Life is not easy for any of us. But what of that? We must have perseverance and above all confidence in ourselves. We must believe that we are gifted for something, and that this thing, at whatever cost, must be attained."

-Marie Skłodowska Curie