CHAPTER 1
INTRODUCTION

1.1. Need for Toxic Gas Sensors

Millions of people around the world suffer from the imperative environmental issue of air pollution. It is triggered by the emission of toxic gases into the atmosphere, which poses serious risks to ecosystems, human health, and the global climate. The causes of air pollution include industrial emissions, modes of transportation such as cars, buses, and trucks, agricultural activities such as the use of fertilizers, pesticides, and burning of crop residues, household activities such as cooking with fossil fuels and using heating appliances, as well as the presence of indoor pollutants like tobacco smoke[1]. Additionally, natural events such as volcanic eruptions, wildfires, and dust storms release natural pollutants into the air. As mentioned earlier, the air pollution causes the release of multiple toxic gases[2]. Some of these gases are described below.

Carbon monoxide (CO) is a highly toxic gas produced through incomplete combustion of carbon-containing fuels like gasoline, natural gas, and coal[3]. It poses significant health risks, especially in indoor environments with inadequate ventilation. CO accumulation in radiators can lead to severe health risks, as it interferes with the body's ability to transport oxygen[4]. Symptoms of CO poisoning vary depending on the concentration and duration of exposure, with initial symptoms being mild headaches, dizziness, and nausea. With higher concentrations or prolonged exposure, symptoms can escalate to severe poisoning, confusion, loss of consciousness, and potentially fatal outcomes[5]. Chronic exposure to lower levels of CO can have long-term health effects, particularly on the cardiovascular and neurological systems. Accurate detection and monitoring of CO are crucial due to its toxic nature and high potential for accidental exposure. CO detectors and alarms can alert individuals to dangerous levels of CO before severe symptoms occur. Proper maintenance of fuel-burning appliances and adequate ventilation are essential preventative measures. Public awareness and education about CO dangers can significantly enhance safety and prevent CO poisoning incidents[6].

Nitrogen monoxide (NO), also known as nitric oxide, is a colorless gas produced through combustion processes in vehicle engines, power plants, and industrial operations[7]. It is a significant component of air pollution and is released into the atmosphere, where it plays a crucial role in chemical reactions. NOx, a compound of NO and NO_2, contributes to the formation of ground-level ozone (O_3), a major component of smog and poses serious health risks, including respiratory problems, cardiovascular issues, and increased mortality rates. High concentrations of NO can cause immediate respiratory irritation and inflammation, leading to

symptoms such as coughing, wheezing, shortness of breath, and chest pain[8]. Chronic exposure to lower levels can result in long-term lung damage, decreased lung function, and exacerbation of pre-existing respiratory conditions like asthma and bronchitis. NO also plays a role in the formation of fine particulate matter ($PM_{2.5}$), which is associated with serious health problems, including heart disease, stroke, and lung cancer. Monitoring and controlling NO emissions is essential to minimize air pollution and protect human health[9].

Ammonia (NH_3) is a toxic and colorless gas with a strong, pungent odor, produced naturally by decomposition processes and used in various industrial applications, including the green hydrogen procuction[10]. It is commonly encountered in agricultural settings, particularly on livestock farms, where it is released from animal waste and nitrogen-based fertilizers. High concentrations of ammonia contribute to poor air quality, posing risks to farm workers and animals. Ammonia emissions from agriculture are a significant source of atmospheric NH_3, leading to the formation of fine particulate matter ($PM_{2.5}$)[11]. High concentrations of ammonia in water can cause significant harm to aquatic life, leading to decreased biodiversity and disrupted ecosystems. Exposure to high concentrations of ammonia gas can cause immediate health effects in humans, including respiratory distress and lung damage. Effective monitoring and control of NH_3 emissions are crucial for reducing health and environmental impacts. Strategies in agricultural settings include improving manure management practices, optimizing fertilizer application, and using technologies like anaerobic digesters. In industrial contexts, emission control technologies and regulatory measures are implemented to limit the release of NH_3 into the atmosphere. Public awareness and education about the sources and risks of ammonia exposure are essential for promoting safer practices and reducing emissions[12].

In a nutshell, toxic gas sensing devices are crucial apparatus for protecting human health and the environment by detecting potential risks. Utilizing sensors, helps identify potential risks, enabling timely interventions, and promoting a safer living environment. By providing real-time data, it helps prevent accidents and minimize toxic exposure, ensuring a sustainable future.

1.2. Two Dimensional (2D) Materials

Solid materials in their bulk phase are referred as three-dimensional (3D) materials. When their dimensions are reduced, they become low-dimensional materials, which are
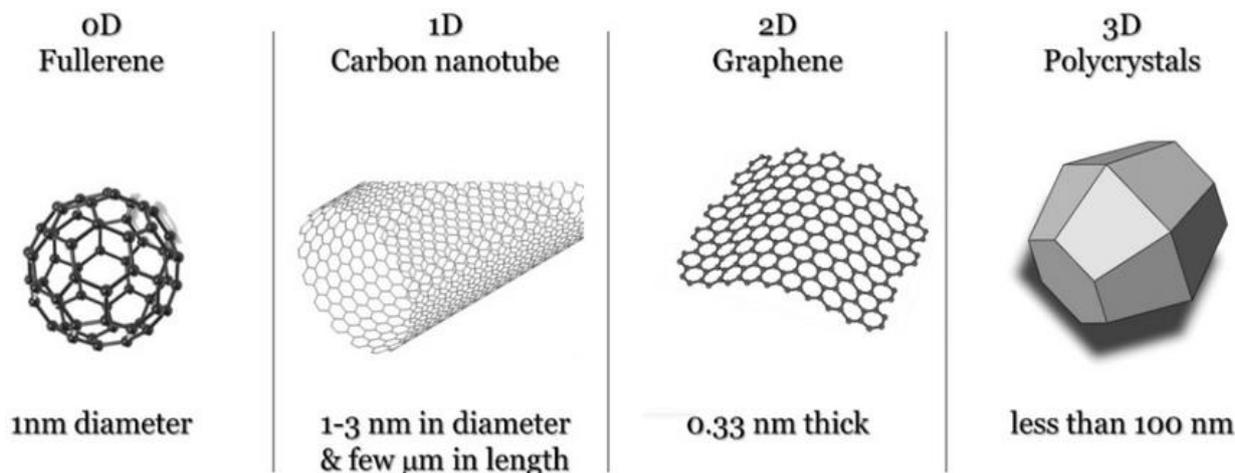
0D Fullerene	1D Carbon nanotube	2D Graphene	3D Polycrystals
1nm diameter	1-3 nm in diameter & few μm in length	0.33 nm thick	less than 100 nm

Figure 1.1: Schematic illustration of zero-, one-, two- and three-dimensional nanostructured materials

classified based on their dimensional confinement. Two-dimensional (2D) materials have length and width but minimal thickness. One-dimensional (1D) materials, such as nanowires, have length but minimal width and thickness[13]. Zero-dimensional (0D) materials, like nanoparticles, have minimal dimensions in all directions[14].

Since the discovery of graphene, a single layer of graphite with carbon atoms arranged in a hexagonal lattice, the field of two-dimensional (2D) materials has experienced remarkable growth[15]. The groundbreaking properties of graphene such as exceptional electrical conductivity, mechanical strength, and thermal conductivity—have spurred extensive research into other 2D materials and their diverse applications. Despite its extraordinary properties, the zero band-gap nature limits the use of graphene in semiconductor applications[16]. Researchers have focused on band-gap engineering and suitable substrates to enhance its electronic properties. Hexagonal boron nitride (h-BN) has emerged as a promising substrate due to its wide band-gap and its ability to improve electron mobility in heterostructures. Often referred to as "white graphene," h-BN is an excellent electrical insulator with high thermal conductivity and chemical stability[17]. It provides a dielectric environment and reduces charge point defects, making it an ideal substrate for graphene and other 2D materials. Graphitic carbon nitride (g-C_3N_4), composed of carbon and nitrogen, is known for its photocatalytic properties, making it highly suitable for solar energy conversion and environmental remediation[18].

Mono-elemental monolayers include silicene and borophene. Silicene, a silicon-based analogue of graphene, features a honeycomb structure and promising electronic properties, though it is less stable under ambient conditions[7]. Borophene, composed of boron atoms, exhibits remarkable strength, flexibility, and conductivity, although its synthesis and stabilization present significant challenges[19]. MXenes, a class of transition metal carbides, nitrides, or carbonitrides, exhibit high electrical conductivity and hold potential for applications in energy storage, sensors, and electromagnetic interference shielding[20]. The pnictide group includes materials such as phosphorene, a single layer of black phosphorus characterized by high carrier mobility and a direct bandgap, making it an excellent candidate for applications in transistors and photodetectors[21]. Transition metal dichalcogenides (TMDs) like MoS_2 possess semiconducting properties with bandgaps ranging from 1 to 3 eV, making them suitable for various electronic and optoelectronic applications[22]. However, some TMDs exhibit indirect bandgaps, which limit their efficiency in certain applications[23].
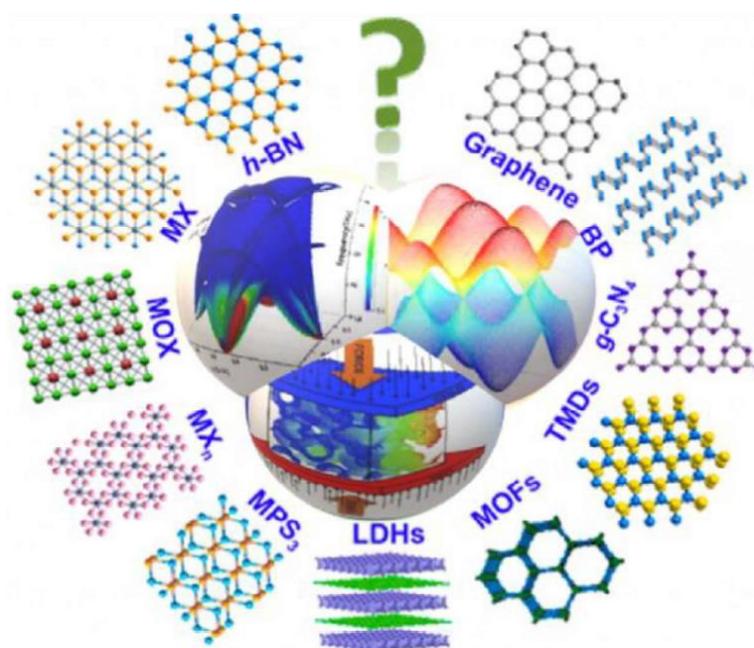

Figure 1.2: Illustration for various categories of 2D materials, highlighting the electronic, mechanical, and dynamic properties with graphene positioned at the centre

Despite significant progress, numerous challenges persist in the field of 2D materials. Graphene's lack of a band-gap poses a limitation for its application in semiconductor electronics, as it cannot easily switch between conducting and non-conducting states necessary for transistor operations. Moreover, its low sensitivity and poor interaction with gas molecules hinder its effectiveness in sensing applications, where precise detection capabilities are crucial. MoS_2, another widely studied 2D material, faces issues with low electron mobility, which limits

its performance in high-speed electronic devices requiring rapid charge transport. To address these challenges, researchers are actively engaged in the synthesis of novel materials and optimization of existing ones[24]. These efforts aim to enhance the properties of 2D materials for diverse applications across electronics, optoelectronics, sensing, and beyond.

1.3. Prediction of Novel 2D Materials

A novel 2D material is typically predicted or modeled after already synthesized ones. For example, graphyne was predicted following the successful synthesis of graphene. Graphyne is a class of two-dimensional carbon allotropes structurally related to graphene but featuring a mixture of single and triple carbon-carbon bonds within their lattice. Due to this unique bonding pattern, graphyne is sometimes referred to as "extended graphene" because of its similar structure but with additional connectivity between carbon atoms. Notably, graphyne was successfully synthesized in its γ phase in the year 2022[25].

Another approach to discovering novel 2D materials involves modeling the 2D monolayer based on existing bulk materials. For instance, in 2020, Tikhomirova et al. studied the properties of the NaCl lattice in its 2D hexagonal form, which is originally known as a face-centered cubic (FCC) crystal. By utilizing a combination of the ab initio evolutionary algorithm USPEX and advanced experimental techniques, they crystallized exotic hexagonal NaCl thin films on (110) diamond surfaces. This innovative study revealed unexpected complexities arising from the strong chemical interaction between the NaCl film and the diamond substrate[26].

Predicting the structure of novel 2D materials is typically followed by an extensive exploration of their electronic properties. This process includes constructing band diagrams to understand the electronic band structure and evaluating dynamical stability through phonon dispersion curves[24]. Additionally, researchers calculate other relevant properties such as optical, mechanical, and thermal characteristics to fully characterize the potential of these materials. For instance, band structure calculations help determine whether the material is a metal, semiconductor, or insulator by revealing the presence of band gaps. Phonon dispersion curves are essential for assessing the vibrational properties of the lattice, which directly relate to the material's thermal stability and transport properties. These comprehensive studies enable

scientists to predict the feasibility and potential applications of the novel 2D materials, paving the way for future experimental validations and technological advancements.

1.4. Single-layer hexagonal crystals of group IV and V elements

In 2018, Özdamar et al. used first-principles density functional theory (DFT) calculations to investigate a family of stable two-dimensional crystals with the chemical formula A_2B_2, where A and B belong to groups IV and V, respectively (A = C, Si, Ge, Sn, Pb; B = N, P, As, Sb, Bi), focusing on their structural, vibrational, and electronic properties[27]. They demonstrated that two structural symmetries of hexagonal lattices, named α- and β-phases, are dynamically stable. The study highlighted numerous potential applications for these A_2B_2 monolayers. For example, structures like CN and SiAs were identified as promising candidates for water splitting, indicating their potential in sustainable energy applications. Materials with quartic band edges are expected to be efficient for thermoelectric applications, which is crucial for energy conversion technologies. Additionally, the wide band gaps of certain materials make them suitable for optoelectronic applications, enhancing their utility in technological advancements. Specifically, the α-phase of C_2N_2 (α-CN) is predicted to be suitable for adsorption mechanisms such as hydrogen evolution, among other potential applications. Monolayers like α-CP are projected to have applications in optoelectronics due to their wide band gaps.

Expanding on Özdamar's predictions, researchers utilized Density Functional Theory (DFT) to explore how strain affects the band structure of α-CN monolayers. Their investigation extended to potential applications of α-CN monolayers in UV light detection and photodetectors, specifically under conditions of 6-12% tensile strain[28]. Subsequently, they examined the viability of α-CN monolayers for catalyzing the water splitting reaction, encompassing both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)[29]. The study revealed that pristine α-CN monolayers exhibit low efficiency in these reactions, but this was notably enhanced by substituting P and B atoms, respectively. Furthermore, detailed DFT calculations were conducted to assess the thermoelectric properties of α-CN and α-CP monolayers, underscoring their potential role in improving the thermal management of electronic devices[21]. In another study, Paras et al. explored the energy storage capabilities of α-CN and α-CP monolayers as anode materials in rechargeable Li-ion batteries, highlighting the exceptional electrochemical performance of α-CP monolayers suitable for anode applications[30]. Recently, He et al. investigated the interaction of various pollutant

gases—CO_2, CO, NO_2, H_2, NH_3, N_2, O_2, CH_4, and SO_2—with α-CN (α-C_2N_2) monolayers[31]. Their findings indicated weak interactions initially, but by manipulating the structural and electronic properties of the monolayer with an applied electric field, they significantly enhanced the interaction strength, particularly with NH_3 gas molecules, surpassing interactions with other gases.

1.5. Definition and Approach to the Problem

The development of chemical and toxic gas sensors using 2D materials has garnered significant research interest due to the sensitivity of these materials' physical and electronic properties to external environments. This study focuses on investigating the sensing behavior of monolayers composed of Group IV and V elements in response to selected toxic molecules. Additionally, we will conduct a detailed investigation into enhancing the reactivity of these monolayers through surface modifications such as functionalization, metal doping, introducing defects, and applying strain. These surface modifications are expected to alter the electronic properties of the Group IV and V monolayers. By examining the electronic properties of both pristine and modified monolayers, we aim to identify the most suitable monolayer configurations for Group IV and V element-based sensors.
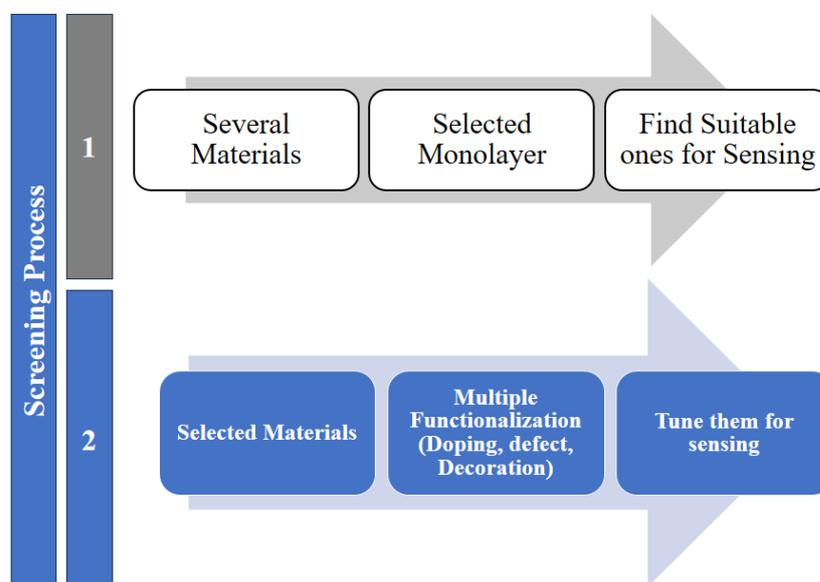

Figure 1.3: Two approaches for toxic gas sensor material exploration: broad screening of monolayers vs. targeted functionalization of selected materials

There are primarily two approaches for exploring materials for toxic gas sensor applications. The first approach involves screening a wide range of materials, selecting specific monolayers from among them, and then evaluating their suitability for sensing applications

based on their inherent properties. This method can be time-consuming and may not always yield the most promising candidates for specific applications. In our research, we have adopted the second approach, which is more targeted and systematic. Instead of broadly screening many materials, we have chosen to focus on particular materials—specifically, α-CN and α-CP monolayers from the Group IV and Group V elemental 2D crystals. These materials were selected based on their promising preliminary properties and potential for modification. We then employed a variety of functionalization techniques to enhance their sensing capabilities. These techniques include doping, where we substitute different atoms to alter the electronic properties; defect-tuning, where we create defects within the monolayer to affect its reactivity and interaction with gas molecules; and decoration, which involves adding impurity atoms to the surface to improve sensitivity and selectivity. By systematically applying these modifications, we aim to tune the α-CN and α-CP monolayers to maximize their effectiveness in detecting toxic gases.

1.6. Specific Objectives

i. To determine the ground state properties and dynamical stability of the selected 2D materials.

ii. To study the interaction of toxic molecule at various possible sites of the monolayer.

iii. To modulate electronic properties and surface phenomena of studied materials by doping, decoration, or creating defect.

iv. Determination of binding energy/formation energy of various metals/defected monolayers to check its stability.

v. To understand effect of creation of vacancies, metal decoration and substitution of impurity atoms on monolayers through density of states (DOS), band structure analysis and charge transfer.

vi. To calculate cohesive energy for the determination of stability and non-clustering property of decorated metal atoms.

vii. To analyze adsorption energy, recovery time, work function, electrical conductivity and etc. to understand effective gas sensing mechanism.

1.7. Structure of the Thesis

In the **chapter 2**, we provide a comprehensive theoretical description of the computational methodology employed throughout our study. We begin with the formalism of Density Functional Theory (DFT), getting into the foundational Kohn-Sham equation[32] and its practical implementation within the Quantum Espresso software package. The discussion extends to crucial aspects such as exchange-correlation functionals and basis sets, pointing out their significance in accurately capturing the electronic structure and properties of materials under investigation. Furthermore, we explore advanced theoretical concepts and their practical applications, including conductivity analysis and Bader's theory of charge transfer.

In the **chapter 3**, we examine the adsorption performance of carbon monoxide (CO) and nitrogen monoxide (NO) gases on pristine α-CX (X = N, P) monolayers through Density Functional Theory (DFT) calculations. Our analysis consists of an in-depth examination of the structural, electronic, and sensing properties of α-CX to understand their adsorption mechanism. Our findings reveal that both CO and NO gas molecules exhibit physisorption tendencies towards α-CX monolayers. However, further investigation unveils notable limitations: a considerable adsorption distance exceeding 3 Å alongside suboptimal adsorption energies[33]. Moreover, the impractically short recovery time underscores the challenges associated with utilizing pristine α-CX monolayers as effective candidates for toxic gas sensing application. The limitations encountered with pristine monolayers, prompt researchers to explore alternative avenues. Such as, introduction of defects into two-dimensional (2D) monolayers. This defect-tuning strategy has emerged as a potent means to enhance the performance of these materials in detecting hazardous gases[34]. Therefore we examine the CO and NO adsorption, specifically over carbon-defected α-CX monolayers. By scrutinizing the adsorption dynamics on these defect-tuned surfaces, the chapters elucidates the mechanisms underlying their enhanced gas sensing performance.

Doping stands as a pivotal mechanism in enhancing the gas adsorption performance of nanomaterials[35]. The **chapter 4** focuses on a first principles study, exploring the structural, electronic, and sensing properties of Aluminium, Boron, and Beryllium doped α-CN monolayers. Our investigation unveils the structural and electronic transformations induced by impurity doping, illuminating distinct functionalities for α-CN monolayers. Boron doping at the C-site emerges as particularly promising for NO and NH_3 sensing, while B-doping at the N-site enhances suitability for gas removal applications. Similarly, Be-doping demonstrates effectiveness in gas removal across both C and N sites. Notably, our study reveals an ultra-fast

response observed for NO adsorption over B-doped α-CN, highlighting its potential as a rapid sensor. Furthermore, work function analysis suggests the suitability of B-doped α-CN for φ-type sensing in NH$_3$ adsorption.

Toxic gases such as carbon monoxide (CO), nitric oxide (NO) and ammonia (NH$_3$) pose serious health and environmental risks. While existing toxic gas monitors are costly, two-dimensional (2D) materials have shown promise for gas sensing applications due to their high surface-to-volume ratios and sensitivity[36]. Among these, α-CN has been identified as a potential candidate for gas adsorption mechanisms. The **chapter 5** investigates the adsorption performance α-CN surface with the decoration of nickel (Ni)-atom for CO, NO, and NH$_3$ toxic gases using state of art density functional theory (DFT) based first principles calculations. The results indicate that the Ni-decoration significantly enhances the adsorption performance of α-CN, as evidenced by highly negative adsorption energies. Therefore, the calculated recovery times are extremely long, suggesting that Ni-decorated α-CN is more suitable for the removal of these toxic gases rather than as a sensor. The structural and electronic properties, including projected density of states (PDOS), band structure, charge density diagrams and transfer mechanisms, have been thoroughly analyzed. Additionally, sensing properties such as work function and electrical conductivity have been computed to validate the effectiveness of the material.

The final chapter of the thesis (**chapter 6**) summarises the entire work. It includes a summary of the results, the conclusion, and the future scope of the research.

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