Development of Toxic Gas Sensors Using 2D Materials: A First Principles Study

A

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Introduction

After the rigorous industrial growth and increment in global population, the world is facing problem of pollution (air, soil, water etc.)[1]. Globally, one of the main sources to fulfil the energy need is fossil fuel and its improper combustion of the fossil fuel in industries and vehicles is responsible for the generation of extremely hazardous gas pollutants like carbon monoxide (CO) and nitrogen monoxide (NO) in the environment. Both gases are colourless, odourless and tasteless, which make them untraceable ‘silent killers’[2][3]. While, the NO gas molecule is irritating to the skin, eyes and mucous membrane, the NO gas rapidly reacts with ozone or radicals in the atmosphere and forming NO_2. The ammonia (NH_3) another toxic gas which is also colorless but most abundant nitrogen containing compounds in the environment. It is building block for the synthesis of many pharmaceuticals. It is used in many cleaning products but its high concentrated form is very hazardous to human body which causes diseases of the lower airways and interstitial lung. Acute exposure to high level of NH_3 in our environment may be irritating to human skin, throat, eyes, and lungs and cause coughing and burns. Lung damage and death are also possible after exposure to very high concentration of NH_3.[4]Tracing of hazardous gases is a very important matter due to contamination of our environment and human life and therefore solid-state gas sensing technology is being demanded in daily life and different commercial industries[5].

In recent years, researchers have been increasingly concerned with the production and development of hazardous gas sensors and adsorbents from environmental sources. Various carbon allotropes, including fullerene (C_{60}), graphene, graphene nanoribbons, graphene quantum dots, and carbon nanotubes, have been investigated for their sensing abilities towards gases such as CO, NO, and NH_3[6][7]. Studies have shown that pristine forms of these carbon allotropes typically exhibit physisorption interactions with gas molecules[8]. But doping with elements like aluminum (Al), titanium (Ti), nitrogen (N), and others can alter the interaction nature to chemisorption, with the significant improvement in the adsorption performance. Functionalized carbon allotropes exhibit enhanced interactions with hazardous gases, leading to improved sensitivity[9]. Additionally, investigations into other materials like h-AlC, MoSSe, MoS_2 and PtS_2 monolayers have shown that after functionalization, their adsorption performances towards gas molecules are notably enhanced, making them suitable candidates for gas sensor applications[10][11][12]. Consequently, two dimensional materials exhibiting ideal adsorption characteristics; including optimal adsorption energy and distance, are crucial for the fabrication of high-performance toxic gas sensors[13][14].

Recently, Özdamar et.al found a family of stable 2D crystals[15] with chemical formula A_2B_2, where A = C, Si, Ge, Sn, Pb and B = N, P, As, Sb, Bi belong to groups IV and V, respectively. Two structural symmetries of hexagonal lattices $P\bar{6}m2$ (α-phase) and $P\bar{6}m1$ (β-phase) were dynamical stable with small cohesive energies. They found a wide range of band gap values between 0.35–5.14 eV[16][17] suggesting possibly application of these materials for gas sensing. To date, there has been limited exploration of this category of two-dimensional materials in the realm of toxic gas sensors[18]. With the efforts to bridge this gap, the present thesis explores the application of pristine and functionalized 2D α-CX (X=N, P) materials as a potential candidate in hazardous gas sensing or removal devices.

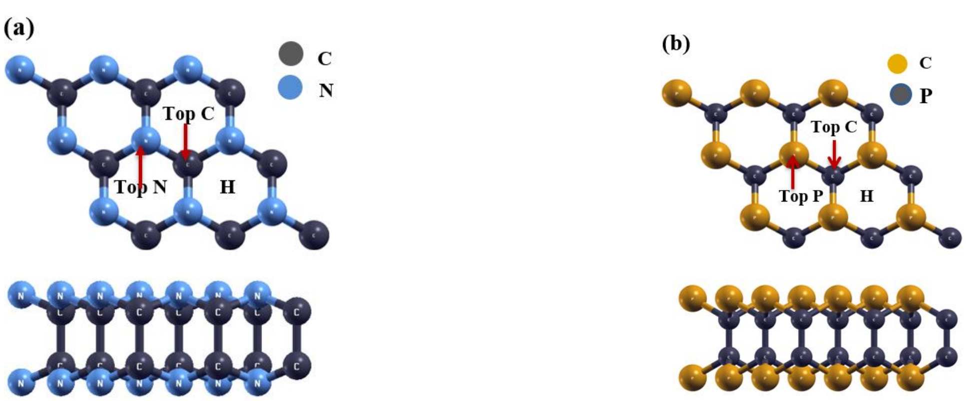

Figure 1: Top and side views of optimized geometries for pristine (a) α-CN (b) α-CP monolayers

Objectives

Our aim is to provide the better understanding of physical and chemical properties of α-CX monolayers that contain group IV and V elements and detailed study of the defect, impurity atom doping induced characteristic of it. The main focus of this work is to investigate the effect of tuning by various methods on structural and electronic properties to analyse the change in adsorption performance of toxic molecules on the monolayer of group IV and V elements. The primary objective of this thesis is to provide the understanding of enhancement of adsorption performance of hazardous gas before and after tuning properties of the selected 2D materials.

However, the specific objectives are:

1. To determine the ground state properties and dynamical stability of the selected 2D materials.
2. To study the interaction of toxic molecule at various possible sites of the monolayer.
3. To modulate electronic properties and surface phenomena of studied materials by doping or creating defect.
4. Determination of binding energy/formation energy of various impurity doped/defected monolayers to check its stability.
5. 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.
6. To analyze adsorption energy, recovery time, work function, electrical conductivity and etc. to understand effective gas sensing mechanism.

Summary of Research Work

The present thesis is organized in the following manner.

Chapter 1: Introduction

In this chapter, we explain the imperative need for hazardous gas sensing, highlighting the critical role it plays in safeguarding human health and environmental well-being. The chapter sets the stage by introducing the unique properties of two-dimensional materials, underscoring their immense potential in addressing contemporary challenges. Moreover, it explores the driving forces behind the quest for such innovative materials, emphasizing the pressing need for advanced sensing technologies. Additionally, the chapter briefly delves into the necessity of impurity doping, both through substitution and decoration techniques, to enhance the adsorption performance of 2D materials. Through this discussion, we lay the groundwork for understanding the properties of selected α-CX (X=N, P) monolayers, which serve as focal points in the thesis.

Chapter 2: Theoretical Framework

In this chapter, 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[19] and its practical implementation within the Quantum Espresso software package[20]. Our 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[21].

Chapter 3: Evaluation of Pristine α-CX (X = N, P) monolayers as Toxic as Sensors

In this chapter, 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 (X = N, P) to understand their adsorption mechanism. Our findings reveal that both CO and NO gas molecules exhibit physisorption tendencies towards α-CX (X = N, P) monolayers. However, further investigation unveils notable limitations: a considerable adsorption distance exceeding 3 Å alongside suboptimal adsorption energies. Moreover, the impractically short recovery time underscores the challenges associated with utilizing pristine α-CX (X = N, P) monolayers as effective candidates for toxic gas sensing application.

Chapter 4: Defected α-CX (X = N, P) Monolayers for Enhanced Adsorption

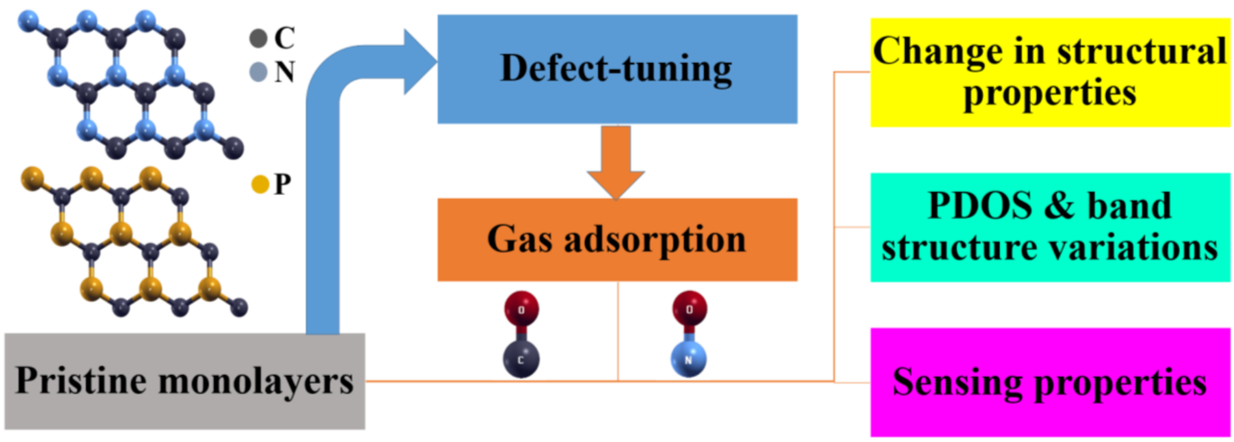

Figure 2: Schematic diagram for enhancement of adsorption performance upon defect-tuning

The previous chapter sheds light on the limitations encountered with pristine monolayers, prompting 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. A recent study by Ghambarian et al. underscores the potential of defect-tuning in phosphorene monolayers, showcasing remarkable improvements in CO and NO gas sensing capabilities[22]. Building upon this, in this chapter we examine the CO and NO adsorption, specifically over carbon-defected α-CX (X = N, P) monolayers. By scrutinizing the adsorption dynamics on these defect-tuned surfaces, the chapter elucidate the mechanisms underlying their enhanced gas sensing performance.

Chapter 5: Effect of Impurity-doping on Gas Adsorption

Doping stands as a pivotal mechanism in enhancing the gas adsorption performance of nanomaterials. This chapter focuses on a first principles study, exploring the structural, electronic, and sensing properties of 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.

Chapter 7: Summary and Future Scope

The last chapter of the thesis summarizes the entire work. It consists of a summary of results, conclusion, and future scope of the work.

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List of Publications related to Thesis

1. **<u>Heli Mistry</u>**, Darshil Chodvadiya, Shardul Vadalkar, Keyur N. Vyas, and Prafulla K. Jha. "Interaction study of CO and NO pollutant gases with pristine, defected and doped α-CX (X= N, P) monolayers using density functional theory." Surfaces and Interfaces 46 (2024): 103958.
2. **<u>Heli Mistry</u>**, Bhautik Dhori, Maitry Joshi, Keyur N. Vyas, and Prafulla K. Jha. "Hazardous CO, NO, NH_3 Gases over Boron and Beryllium Doped α-CN Monolayers: A First Principles Study for Sensing and Removal Applications." (Submitted).
3. **<u>Heli Mistry</u>**, Shardul Vadalkar, Keyur N. Vyas, and Prafulla K. Jha. "An ab-initio adsorption study of CO and NO gases over transition metal-decorated α-CN for sensing and removal applications" (manuscript under preparation).

List of Publications non-related to Thesis

1. Shardul Vadalkar, Darshil Chodvadiya, **<u>Heli Mistry</u>**, Narayn N. Som , Keyur N. Vyas, and Prafulla K. Jha. "Toxic Gas Removal using Transition Metal-decorated Cyclo[18]carbon: A First Principles Prevision" (submitted).

Place: Vadodara **Date: 13/04/2024**

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