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

EXECUTIVE SUMMARY OF THE THESIS

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1. INTRODUCTION

Toxic gas sensors play a critical role in mitigating the severe health and environmental risks associated with air pollution. Industrial emissions, vehicular exhaust, agricultural activities, and household practices release harmful gases like carbon monoxide (CO), nitrogen monoxide (NO), and ammonia (NH_3), which contribute to respiratory issues, cardiovascular diseases, and other severe health impacts.[1][2][3] Monitoring these gases is essential for preventing toxic exposure and ensuring public safety. The development of highly sensitive and accurate gas sensors is thus necessary to address these challenges.

The thesis begins by highlighting the significance of gas sensing technologies in mitigating these adverse effects. Gas sensors play a crucial role in detecting and monitoring harmful gases, enabling timely intervention and control measures to reduce exposure and prevent potential health hazards. The development of efficient and reliable gas sensors is therefore essential for ensuring air quality and safeguarding public health. In this context, the thesis emphasizes the role of carbon-based materials in enhancing the efficiency of gas adsorption and detection. Carbon materials, such as graphene[4], carbon nanotubes[5], and fullerene[6] derivatives, have been extensively studied for their unique properties, including high surface area, chemical stability, and exceptional electrical conductivity, making them ideal candidates for gas sensing applications. Among these, Group IV and V monolayers, specifically α-CN and α-CP, has garnered significant attention due to its distinct structural and electronic properties[7].

The 2D α-CX (X=N, P) structure is characterized by a hexagonal lattice with a high surface area, making it highly efficient for gas adsorption and catalysis. The thesis explores how the distinct characteristics of 2D α-CX (X=N, P) can be harnessed to develop advanced gas sensors with enhanced sensitivity and selectivity. The research caves into its functionalization with various dopants to improve its adsorption properties[8][9].This functionalization aims to optimize the adsorption energies, charge transfer, and recovery times, making two dimensional α-CX (X=N, P) highly effective for gas sensing applications.

2. THEORETICAL FRAMEWORK

Theoretical framework behind the computational methodology employed in this thesis centers around Density Functional Theory (DFT)[10] to study the interactions between toxic gases and 2D α-CX (X=N, P). Quantum Espresso package was used for simulations[11], employing the Generalized gradient approximation-based pseudo potentials[12].

Plane wave basis set was utilized for geometry optimizations and frequency calculations. This basis set strikes a balance between computational efficiency and accuracy, ensuring reliable predictions of molecular geometries and vibrational properties for pristine and functionalized 2D α-CX (X=N, P).

Initial geometries of pristine and functionalized 2D α-CX (X=N, P) as well as gas molecules were optimized to obtain stable structures with minimized energy. The optimization process involved adjusting the atomic positions to achieve the lowest possible total energy, ensuring that the structures were at their most stable configurations. The adsorption energies of gas molecules on the functionalized monolayer were calculated by optimizing the geometries of the adsorbed complexes and comparing the total energies before and after adsorption.

3. INTERACTION OF PRISTINE AND DEFECED α-CX (X=N,P) MONOLAYERS WITH TOXIC GASES

The adsorption performance of the gases CO and NO with pristine and defected 2D α-CX (X=N, P) has been examined using DFT calculations in this chapter. To understand the sensing behaviour, we have analyzed the structural, electrical, and sensing properties of pristine and defected 2D α-CX (X=N, P). The findings revealed that neither pristine α-CN nor α-CP yield optimal results for the adsorption of the hazardous CO and NO gases. This is perhaps due to the wide energy band gaps, the adsorption energy values falling within the range of physisorption, and the adsorption distances exceeding 3 Å. To overcome these shortcomings, we have done functionalization of pristine α-CN and α-CP by introducing a defect. Therefore, we have introduced a defect by removing one carbon atom, to amplify the adsorption performance of the pristine α-CX (X = N, P) monolayers. Following the creation of the defect, there has been a significant increase in the adsorption energy value in both cases. In case of functionalized α-CX, the adsorption energy order for CO gas goes as: E_{ads} (C-defected α-CN) > E_{ads} (C-defected α-CP). For NO adsorption, the energy order is: E_{ads} (C-defected α-CP) > E_{ads} (C-defected α-CN). Which implies that C-defected α-CN is most suitable for CO adsorption.

The computed recovery times are extremely long (exceeding several hours) in the best-case scenarios, this implies that C-defected α-CN and C defected α-CP are most suitable for CO and NO gas removal applications.[8]

4. ENHANCED GAS ADSORPTION IN BERYLLIUM, BORON AND ALUMINIUM DOPED α-CN

One of the most effective methods for enhancing the molecular adsorption performance of nanostructures is doping. In this chapter, we investigated the adsorption performance of Beryllium, Boron and Aluminium doped α-CN monolayers towards the gases CO, NO, and NH_3 using first-principles calculations. The structural, electronic, and sensing properties of Be, B, and Al doped α-CN monolayers were studied to understand their sensing behavior, employing the Quantum Espresso simulation package. The substitutional doping of Be, B and Al atoms, causes some geometrical and electronic structure variations in the pristine α-CN monolayer. α-CN with Boron doping at C site is unsuitable for CO adsorption due to the large adsorption distance exceeding 3 Å. However, it proves suitable for NO and NH_3 sensing, as evidenced by optimal adsorption energies and distances. Conversely, for B doping at the N site and Al doping at C site are more suitable for removal applications, owing to highly negative adsorption energies and prolonged recovery times. Similarly, for Be doping at the C-site, α-CN demonstrates efficacy in removing all three gas molecules. The recovery time for NO adsorption over B doped α-CN at C site is on the order of nanoseconds, which registers its candidature for an “ultra-fast” sensor. From the work function analysis, we can conclude that B-doped α-CN at C-site as well at N-site is most suitable for a ϕ-type sensor in the case of NH_3 adsorption[9].

5. ADSORPTION MECHANISM OF NICKEL DECORATED α-CN MONOLAYER TOWARDS CO, NO, AND NH_3 GASES

The adsorption performance of CO, NO, and NH_3 gases on Ni decorated α-CN monolayer was investigated again. Ni was chosen as impurity atom because its presence enhances adsorption due to orbital interactions and charge transfer from the transition metals' 3d orbitals to the 2p orbitals of oxygen atoms in CO and NO molecules and the 2p orbital of the nitrogen atom in NH_3. To replicate the structural and electronic properties of α-CN monolayer, *ab-initio* DFT calculations were conducted using the Quantum Espresso package[10],[11].The exchange-correlation interaction was handled using the generalized

gradient approximation-based pseudopotentials developed by Perdew-Burke-Ernzerhof [12]used for the calculations. Using the results from Quantum Espresso simulations, the electrical conductivity (σ_e/τ) was obtained through the BoltzTraP simulations[13]. Besides evaluating sensing properties, the study also examined the structural and electronic, properties of α-CN monolayers. Significant adsorption energies and long computed recovery times suggest chemisorption, indicating that Ni-decorated α-CN is suitable for removing CO, NO, and NH_3 gases from specific environments.

6. SUMMARY AND FUTURE PROSPECTS

The thesis investigates the adsorption capacities of pristine and functionalized α-CX (X = N, P) monolayers for toxic gas sensing, with a focus on enhancing performance through impurity doping and defect engineering. It emphasizes the importance of detecting hazardous gases like CO, NO, and NH_3 for human health and environmental safety. Using Density Functional Theory (DFT) calculations, the study analyzes the structural and electronic properties of α-CX monolayers, highlighting their limitations in pristine form due to weak physisorption. To address this, defect engineering and doping with elements like boron, aluminum, beryllium, and nickel were explored. The findings reveal that Ni-decorated α-CN and boron-doped α-CN significantly improve adsorption, making them suitable for toxic gas removal and sensing applications. The thesis underscores impurity doping and defect formation as effective strategies to enhance the sensitivity and selectivity of 2D materials for advanced gas detection technologies.

The future scope of this research involves exploring advanced functionalization techniques beyond traditional doping and decoration to enhance properties of two-dimensional material. The future of gas sensing holds significant potential with the advancements in 2D materials and heterostructures. The integration of materials like graphene, transition metal dichalcogenides (TMDs), boron nitride, black phosphorus, and MXenes promises improvements in sensor performance due to their exceptional electronic, thermal, and mechanical properties[14][15]. These materials can be further enhanced through doping and functionalization, allowing tailored surface properties for specific gas detection. The formation of heterostructures, including the attachment of C_n rings or stacking different monolayers, opens new avenues for designing interfaces with optimized adsorption properties. This ability to precisely control gas interactions with sensor materials suggests the development of highly selective, sensitive, and durable gas sensors. These innovations will play a crucial role in environmental monitoring, health safety, and industrial applications.

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