

Interaction study of CO and NO pollutant gases with pristine, defected and doped α -CX (X=N, P) monolayers using density functional theory

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ABSTRACT

CO and NO are two of the most pollutant gases that exist in the environment, which makes their tracing highly crucial. In this problem, we have investigated the adsorption performances of highly toxic CO and NO gases over pristine, defect-tuned, and Aluminium (Al)-doped α -CX (X=N, P) monolayers. In addition to the adsorption properties, we have calculated electronic properties such as band structure, projected density of states (PDOS) and charge transfer, sensing properties such as work function and recovery time for pristine, defect-tuned, and Al-doped α -CX before and after the gas adsorption process. Given the poor adsorption energies and large adsorption distances, pristine α -CX monolayers are not suitable candidates for the toxic gas sensors. In case of functionalized α -CX, the adsorption energy is highest in case of C-defected α -CN for CO gas adsorption. For interaction of NO gas molecule with functionalized α -CX, Al-doped α -CN is deemed to be best candidate for adsorption. The computed recovery times are extremely long (exceeding several hours) in the best-case scenarios, this implies that C-defected α -CN and Al-doped α -CN are most suitable for CO and NO gas removal applications.

1. Introduction

Pollution originates from various human activities, including industrial processes, transportation, agriculture and inadequate waste disposal. These activities disrupt ecosystems and have detrimental effects on organisms, posing significant harm to both human health and the environment [1]. Carbon monoxide (CO) and nitrogen monoxide (NO) are major pollutants with notable environmental impacts [2]. The CO primarily originates from vehicle and industrial emissions, along with faulty heating systems indoors [3]. On the other hand, NO largely emanates from vehicle engines, industries burning fossil fuels, agricultural activities (including fertilizer use and waste), as well as natural events such as lightning and volcanic activity [4]. The health implications of CO encompass headaches, dizziness, oxygen deprivation and even fatality, as it has the ability to bind with haemoglobin [5]. NO, on the other hand, contributes to smog, acid rain, ecosystem degradation and urban air pollution by giving rise to nitrogen dioxide (NO₂) and fine particulates [4]. To counter these threats, toxic gas sensors are crucial for safeguarding health, preventing accidents and maintaining a healthy environment [6–8]. They offer early alerts that empower individuals, systems and organizations to effectively respond to toxic gas exposure risks [9].

The detection of pollutant gases is crucial for the environment, and ongoing research in environmental applications implicitly lays groundwork for gas adsorption mechanisms. Recent study by Kuang et al. [10], explores impact of interface engineering in interaction process, while Wang et al. [11], investigate how nano-biomaterial modifications affect membrane properties. A work by Zhao et al. [12], on the infiltration process for MgB₂ pellet preparation showcases the versatility of nanomaterial applications. Highlighting their low or non-toxic nature [13,14], 2D monolayers like g-C₃N₄ are pivotal for toxic gas sensing, where a non-toxic substrate is essential. Hence, the attraction of 2D materials extends beyond surface properties, making them highly coveted for gas adsorption mechanisms [15].

After the successful synthesis of two-dimensional (2D) carbon allotrope graphene, various other 2D materials have gained significant recognition in the field of pollutant gases sensing [16]. This is attributed to their high surface-to-volume ratio, numerous potential interaction sites and material sensitivity [15,17]. Graphene, a versatile 2D material, was analysed using density functional theory (DFT) to detect CO molecule, revealing a physisorption type (weak) interaction between them [18]. However, the introduction of substitutional doping of Al atom into the graphene improved the interaction between graphene and CO molecule. Furthermore, the research carried out by Dai et al. improved

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Hazardous CO, NO, NH₃ gases over boron and beryllium doped α -CN monolayers: A *first principles* study for sensing and removal applications

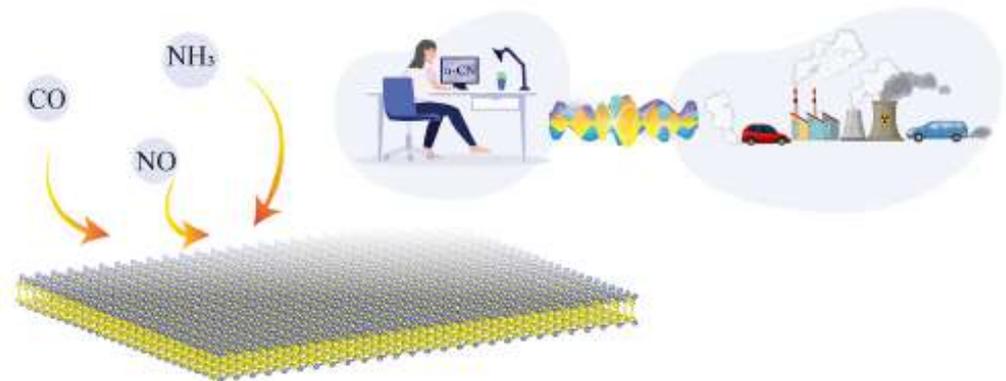
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HIGHLIGHTS

- α -CN is a novel 2D hexagonal lattice which is to be studied for hazardous gas adsorption.
- Pristine α -CN lattice exhibits weak interaction towards CO, NO, and NH₃ gas molecules.
- Substitutional doping is done by replacing either carbon or nitrogen of α -CN by boron and beryllium atoms.
- The doped α -CN lattice shows enhanced adsorption performance towards the aforementioned gases.

GRAPHICAL ABSTRACT



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ABSTRACT

The exploration of two-dimensional (2D) honeycomb layered structure (HLS) has garnered significant attention due to their multifunctional properties, with diverse applications emerging in various fields. Motivated by the challenges posed by hazardous gases such as CO, NO, NH₃ and inspired by the unique properties of 2D HLS this first principles study digs into the structural, electronic, and sensing properties of Boron and Beryllium doped α -CN monolayers. Rendering the structural and electronic variations induced by B and Be doping, our analysis reveals distinct functionalities for α -CN monolayers. Boron doping at the C-site exhibits promise for NO and NH₃ sensing (with 73 % and 77 % increment in adsorption energies), 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, the ultra-fast response (2.31×10^{-8} s) observed for NO adsorption over B-doped α -CN highlights its potential as a rapid sensor. Additionally, work function analysis suggests the suitability of B-doped α -CN for φ -type sensing in NH₃ adsorption. These findings underscore the applicability of doped α -CN monolayers in gas sensing mechanisms.

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Adsorption mechanism of Ni decorated α -CN monolayer towards CO, NO, and NH₃ gases: Insights from DFT and semi-classical studies

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ABSTRACT

Toxic gases such as carbon monoxide (CO), nitric oxide (NO) and ammonia (NH₃) 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. Among these, α -CN has been identified as a potential candidate for gas adsorption mechanisms. This study investigates the adsorption performance α -CN surface with the decoration of nickel (Ni)-atom for CO, NO, and NH₃ 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, computed using semi-classical methods, have been evaluated to validate the effectiveness of the material.

1. Introduction

Industrial incinerations and incomplete combustions are major sources of toxic gases, mainly carbon monoxide (CO) and nitric oxide (NO). These gases, being colorless and odorless, pose grave threats to human health and the environment [1]. In recent times, CO poisonings from radiators have emerged as a pertinent issue. When inhaled, CO combines with hemoglobin to form carboxy-hemoglobin, reducing the blood's oxygen-carrying capacity. This leads to oxygen displacement in the blood, starving vital organs and causing suffocation and loss of consciousness [2]. Similarly, exposure to nitrogen oxides primarily occurs through inhalation, though systemic effects can result from exposure via any route. Nitrogen oxides irritate the eyes, skin, mucous membranes, and respiratory tract [3]. Despite its role in green hydrogen production, the potential hazards of ammonia (NH₃) cannot be disregarded due to its corrosive nature [4]. The severity of health effects depends on exposure route, dose, and duration. High concentrations of airborne ammonia cause immediate burning of the eyes, nose, throat, and respiratory tract, potentially resulting in blindness, lung damage, or death [5]. While monitors for toxic gases such as carbon monoxide are

available in the market [6], their high price range relative to the purchasing power parity (PPP) in countries like India presents a challenge [7]. Hence, the quest for novel and cost-effective materials for toxic gas sensing devices remains relentless.

Two-dimensional materials such as Graphene [8], have been explored for multi-faceted applications. This is attributed to the high surface-to-volume ratio, numerous potential interaction sites and material sensitivity of the said materials [9,10]. When it comes to the toxic gas adsorption mechanisms, 2D materials have indeed undergone thorough examination for their potential applications [11]. However, the adsorption mechanisms of pristine monolayers possess some challenges. For example, density functional theory (DFT) analysis of graphene, unveiled its capability in detecting toxic gas molecules, showcasing a weak interaction (physisorption) between them [12]. Nevertheless, with the introduction of transition metals such as Ni, Pd, and Pt as decoration, the gas adsorption experiences substantial enhancement [13]. Hexagonal boron nitride (h-BN) stands out as another prominent 2D material investigated for its adsorption mechanisms. One notable instance involves the utilization of Ni-decoration on h-BN, which serves to catalyze the adsorption of hydrogen [14]. In

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Toxic gas removal using transition metal-decorated Cyclo[18]carbon: A first principles prevision

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ABSTRACT

Carbon monoxide (CO), nitric oxide (NO), and ammonia (NH₃) are highly toxic gases that are hazardous to human health and the environment. This study dives into the examination of interaction mechanism between transition metal-decorated Cyclo[18]carbon or C₁₈TM (TM = Ni, Pd, Pt) nanoclusters and aforementioned gas molecules. The analysis of structural, electronic, topological, spectroscopic, and sensing properties, uncovers significant findings. The computed adsorption energies exhibit highly negative values. Notably, a substantial sensing response is observed, particularly in the context of NO adsorption over C₁₈Ni and CO adsorption over C₁₈Pd nanoclusters. Employing the Quantum Theory of Atoms in Molecules (QTAIM), we discern the strength of each interaction. Raman spectra analyses provide additional details regarding the vibrational aspects of these interactions. Our Non-Covalent Interaction (NCI) study effectively elucidates the mechanisms underlying van der Waals interactions. Evidently, the longer recovery times observed in our calculations, owing to the highly negative adsorption energies with -2.31 eV being the most negative value for CO molecule over C₁₈Pt nanocluster and -1.09 eV value for NO over C₁₈Pd being the least, suggest that C₁₈TM nanoclusters are better suited for gas removal applications rather than rapid-response sensors.

1. Introduction

Carbon, with its diverse allotropy, encompasses a wide range of physical, chemical, electrical, and reactive properties, ranging from diamond's unyielding brightness to graphite's layered adaptability [1]. Because of their outstanding electrical, thermal, optical, and mechanical capabilities, carbon allotropes such as graphene, fullerene, carbon nanotubes, and numerous developing forms have emerged as important materials. Ongoing research looks into other carbon allotropes, such as hybridised carbon rings and the interesting sp²-sp hybridised graphdiyne, which have promising applications [2]. C_n nanoclusters [3] have attracted interest in this expanded carbon landscape for their critical role in the fabrication of conducting polymers, thin solid diamond sheets, nanotubes, fullerenes, and various carbon clusters, all of which are contingent upon their intricate arrangements and dimensions [4]. Among these, the 2019 synthesis of C₁₈ nanocluster, an 18-carbon sp²-hybridized ring by Kaiser et al., has captured significant interest, primarily attributed to its remarkable reactivity [5,6].

In the wake of incomplete fossil fuel combustion, the presence of toxic gases, including the insidious carbon monoxide (CO) and the skin-irritating nitric oxide (NO), presents an imminent and potentially life-threatening threat [7]. CO, known for its odorless and colorless properties, can silently infiltrate indoor spaces, leading to carbon monoxide poisoning—a deadly condition that can cause headaches, dizziness, and even fatalities [8]. Similarly, nitric oxide (NO), poses severe health risks, irritating the skin, eyes, and mucous membranes and contributing to respiratory problems [9]. Therefore, there has been an escalating demand for gas sensors that are not only cost-effective but also highly sensitive, capable of swiftly detecting these hazardous gases. Consequently, a wealth of research has been dedicated to exploring various nanostructures, such as C₆₀ [10], graphene [11], graphene nanoribbons [12], carbon dots [13], nanotubes [14], and nano-rings [15,16], Pt_nBe clusters [17] for their potential in detecting CO, NO, and ammonia (NH₃). Furthermore, the quest for advanced gas-sensing materials has led to the investigation of carbon oxide quantum dots [18], boron nitride nanotubes [19], and boron nitride nanosheets [20], carbon pnictide

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