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An Ab-initio Study of the C_{18} nanocluster for Hazardous Gas Sensor Application

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Understanding the interaction mechanism of CO, NO, and NH_3 gas molecules with cyclo[18]carbon (C_{18} nanocluster) is important in developing C_{18} nanocluster based sensors for hazardous gas detection. In this work, the adsorption performance of these gases with C_{18} nanocluster was investigated using density functional theory (DFT) calculation. We have analyzed structural, electronic and sensing properties of C_{18} along with Raman spectra to understand the sensing behaviour. We observed that the CO and NO molecules show chemisorption whereas NH_3 molecule shows physisorption towards C_{18} nanocluster. The decrement of HOMO-LUMO gap after adsorption shows increment in conductivity, which is a good sign for sensor application. The fast recovery time of C_{18} nanocluster (nanosecond to femtosecond) for CO and NO adsorption makes it portable and its abundance in nature as low-cost gas sensors. In a nutshell, the analysis of adsorption and electronic properties suggest that the C_{18} nanocluster can be used as the ultrafast hazardous gas sensor.

Introduction

After the rigorous industrial growth and increment in global population, the world is facing the problem of pollution (air, soil, water etc.).[1] Globally, one of the main sources to fulfil the energy need is a 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.[2,3] 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, it rapidly reacts with ozone or radicals in the atmosphere and forming NO_2.[2,3] whereas continuous exposure of CO leads to loss of consciousness with heart irregularity and breathing difficulties which may cause fatality. 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.[3-4] 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.[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 highly demanded in daily life and different commercial industries.[3–16]

From past few years, production and development of hazardous gas sensors and adsorbents from environment are major concerns of the researchers and scientists.[3–16] The various carbon allotropes such as fullerene (C_{60}), graphene, graphene nanoribbons, graphene quantum dots and carbon nanotubes have been examined towards the hazardous gases such as CO, NO and NH_3 sensing.[5–16] Wang et al. studied the sensing ability of graphene towards CO gas molecule and found that the CO gas molecule shows physisorption interaction with graphene with 0.01 eV and 3.85 Å adsorption energy and adsorption distance, respectively.[5] However, aluminium (Al) doping changes the interaction nature from physisorption to chemisorption with modified adsorption energy and adsorption distance (-2.69 eV and 2.06 Å).[5] Zhang et al. reported that the adsorption of NO gas on the pristine and Ti or N-doped graphene sheets is physisorption and chemisorption respectively.[6] Density functional theory (DFT) investigation also demonstrates that the adsorption performance of the NH_3 gas is quite poor on the pure graphene surface similar towards CO and NO gases.[7] The CO, NO and NH_3 adsorption performances on the pristine carbon nanotube shows physisorption interaction with negligible adsorption energy and large adsorption distance but the adsorption

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Adsorption of HCN on pristine and Al/Si/P decorated C_{18} nanocluster: A first principles study

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ABSTRACT

Hydrogen cyanide (HCN) is a poisonous compound that is likely to be found in a gaseous form due to its high volatility. Therefore, its tracing is necessary. Here, we have studied adsorption properties of C_{18} nanocluster towards HCN molecule. Pristine C_{18} towards HCN yields negligible adsorption energy and large adsorption distance. For enhancement of interaction between HCN and C_{18}, we have decorated Al, Si, P atoms on C_{18} nanocluster. After the decoration, we found that C_{18}Al nanocluster is most suitable candidate for HCN sensor due to optimal adsorption energy (-0.61 eV), adsorption distance (2.11 Å), and recovery time (17.7 ms).

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1. Introduction

Hydrogen cyanide (or HCN) is a toxic compound, which is widely used in the places of fumigation, electroplating, mining, chemical synthesis, and the production of synthetic fibers, plastics, dyes, and pesticides [1–3]. Because of its volatility and low boiling point (25.6 °C) [4], HCN is most likely to be found in the gaseous form at the room temperature, and workers from the above-mentioned places, may inhale this toxic gas. Such exposure to HCN can cause fatal harm to the brain, heart, blood vessels and lungs as it tampers cellular respiration [5–7]. Therefore, tracing of HCN is very important to prevent the contamination of the environment. In the past, researchers have used carbon-based materials such as pristine or functionalized graphene, carbon nanotubes, graphyne, graphitic carbon nitrides, graphene nanoribbon, silicon carbide nanotube for HCN sensing [8–17]. Novel materials are always coveted for sensing, as optimum adsorption behavior with suitable adsorption energy and adsorption distance is needed for a good gas sensor.

Cyclo[18]carbon (or C_{18} nanocluster) contains 18 carbon atoms in the form of a circular ring, which is also an allotrope of carbon like graphite, diamonds, and graphene.[18] From past few years, researchers have been doing significant studies on this new carbon allotrope. While some theoretical studies show that the C_{18} nanocluster is characterized by carbon–carbon double bonds i.e cumulenic structure, other theoretical studies shows that it has alternating carbon–carbon triple and single bonds i.e. polyynic structure [19–22]. The polyynic structure of the C_{18} nanocluster was successfully synthesized for the first time in august 2019 by experiment [20] and it acted as a semiconductor [21,22]. The study of Stasyuk et al. demonstrates that the C_{18} nanocluster has strong electron acceptor properties similar to C_{60} [23]. To our best knowledge, C_{18} nanocluster is used as a toxic gas sensor only by us in the previous work. Wherein, we have studied the structural, electronic and sensing properties of C_{18} nanocluster (or cyclo[18]carbon) towards the gases CO, NO and NH_3 [24].

In this work, we have studied the structural, electronic, and sensing properties of C_{18} nanocluster towards the hydrogen cyanide gas molecule (HCN). The pristine C_{18} nanocluster shows physisorption interaction towards HCN molecule with negligible adsorption energy and large adsorption distance. To overcome this and use C_{18} nanocluster as a sensing material, we have decorated Al (aluminium), Si (silicon) and P (phosphorous) atoms at different possible sites, for enhancement of interaction between HCN molecule and C_{18} nanocluster.

2. Computational methodology

We have performed first principles based density functional theory (DFT) calculations using Gaussian 09 package [25]. We have chosen to use the range-separated hybrid ωB97XD for the

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Cyclo[18]carbon as a Hazardous Gas Scavenger: Effect of Boron and Nitrogen Doping on Molecular Adsorption

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Doping is one of the most important mechanisms to enhance the molecular adsorption performance of bulk and nanostructures. Here, we have investigated the adsorption performance of Boron and Nitrogen doped C_{18} nanocluster (or $C_{17}X$: X=B,N) towards the gases CO, NO and NH_3 by means of first principles calculations. The structural, electronic, and sensing properties of $C_{17}X$ nanoclusters are studied to understand their sensing behavior, using gaussian 09 package. The interaction of $C_{17}B$ nanocluster with CO, NO and NH_3 molecules results into chemical adsorption with order of adsorption energies as: CO (−1.41 eV) > NH_3 (−1.81 eV) > NO (−2 eV). However, in case of $C_{17}N$, the interaction with CO and NH_3 results into physisorption, and chemisorption is observed only for its interaction with NO gas molecule. The adsorption energy order goes as: CO (−0.15 eV) > NH_3 (−0.25 eV) > NO (−1.32 eV). The long recovery time in case of $C_{17}B$ nanocluster after the adsorption, makes it suitable for removal application, whereas shorter recovery time (in case of $C_{17}N$ nanocluster for CO and NH_3 adsorption), is suitable for sensor application.

Introduction

On account of its allotropy, carbon has grabbed the interest of many researchers. Allotropes range from diamond to graphite, with physical, chemical, electronic, and reactive properties that differ.[1,2] Almost every carbon allotrope has three or four-fold coordination and is either sp^2-hybridized or mixed (sp-sp^2). Graphene, fullerene, carbon nanotube, and other carbon allotropes are among the most widely used. The electrical, thermal, optical, and mechanical characteristics of these materials are well-known.[3–5] These distinct features have led to research in a variety of domains, including energy storage,[6] optoelectronics, catalysis, medicine,[7] as well as gas separation and sensing.[8] Other carbon allotropes, such as graphdiyne with mixed hybridization (sp^2-sp) and carbon rings with hybridization (sp or sp^2), are also being studied for diverse applications.[9,10] C_n nanoclusters have risen in the rankings because of their involvement in the formation of nanotubes, fullerenes, thin solid diamond films, and conducting polymers, in addition to carbon clusters. These clusters are prominent for their contribution as either stable or intermediate reagents in the celestial chemistry of carbon-intensive stars.

Nonetheless, a complete understanding of complex cluster formations and their fundamental properties in comparison to smaller ones is still lacking. From carbon atom chains to ring-like structures, from nano-cages to tubes, the properties of carbon clusters vary depending on their configurations and dimensions.[8] Following that, the synthesis of various carbon clusters and isomers becomes a prominent area for low-cost applications. Among the carbon allotropes, the newest one, an 18 carbon sp-hybridized ring, was added in 2019. Kaiser et al. successfully synthesized cyclo[18]carbon, or C_{18}, in the year 2019.[11] It is sp-hybridized with two-fold coordination, unlike the other allotropes.[11–13] It has received a lot of attention since its synthesis. Since the C_{18} is the tiniest all-carbon electron acceptor,[13] it is expected to have excellent sensing properties. In the past, researchers have stayed in the course to develop carbon-based sensors that are cost-effective and sensitive to certain gases as well.[14,15]

Following the world's rapid industrialization and population growth, a new problem of pollution (air, soil, water, and so on) has arisen. Arguably, the most significant energy sources in use today is fossil fuel. Its combustion releases harmful gases namely carbon monoxide (CO) and nitric oxide (NO) into the atmosphere, which drastically alters the composition of the atmosphere. CO and NO gases are severely harmful to human health as well as the earth's ecology. The formation of highly toxic gas CO is caused by the incomplete burning of fossil fuels in industries and vehicles. It is colourless, odourless, and tasteless, making it untraceable 'silent killers'.[16] Nitric Oxide is likewise a transparent, odourless gas that irritates the skin, eyes, and mucous membranes. NO_2 is formed when NO interacts quickly with ozone or radicals in the environment.[17] Another toxic gas, ammonia (NH_3), is colourless and is the most prevalent nitrogen-containing substance in the atmosphere. It is a key component in the production of several medications. It is found in a variety of cleansing agents, but its high-concentration phase is extremely harmful to humans, causing illnesses of the lower airways and interstitial lung.[18]

Researchers are motivated to concentrate on the development of gas sensors and sensing materials due to the lethality of these poisonous gases on the living organisms. For CO, NO,

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