## Article preview




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# Single metal-doped silicon ($Si_{59}X$; X = Nb, Mo, Y, Zr) nanostructured as nanosensors for N-Nitrosodimethylamine (NDMA) pollutant: Intuition from computational study

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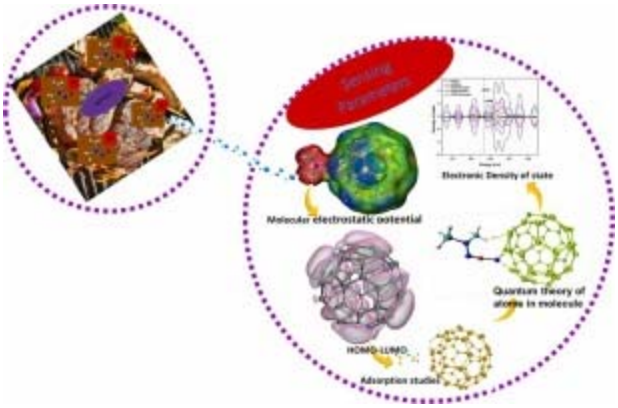
## Abstract

The present work examines the efficacy of metal-doped silicon ($Si_{59}X$; X = Nb, Mo, Y, Zr) nanocages as an efficient nanosensors for N-Nitrosodimethylamine (NDMA). A suitable computational approach employing the exchange-correlation functional (PBE) along the Lanl2DZ basis set was utilized to this end to investigate the potential of silicon nanostructure, doped transition metal as a detector for NDMA. To comprehend the nature of the interaction between the nanostructure and adsorbate (NDMA), diverse computational descriptors including the adsorption energy of interaction, electronic attributes of the surfaces, sensing mechanism and recovery time of the modelled nanostructures were examined. The results show that doping all $Si_{60}$ fullerene nanostructure with transition metals (Nb, Mo, Y, and Zr) enhanced the sensing attributes of the nanostructure towards NDMA. The average adsorption energy was calculated to be − 169.43 kcal/mol. The doped metals were also observed to influence the surface conductivity and binding affinity; the obtained adsorption energy was found to decrease with the doping of Zr metal whereas an increase was observed in the case of Nb doping. Other molecular descriptors also pointed out favourable results and affirmed the suitability of the surfaces to detect NDMA. Moreover, the recovery of NDMA from the surfaces was calculated to be in the milliseconds' range and therefore suggests the recyclability of the surfaces. Finally, classical MD simulations affirmed the stabilities of the surfaces and disclosed that adsorption the adsorbate does not result in considerable deformation of the modelled surfaces. It is, therefore,

concluded that the modelled surfaces could be further explored as potential candidates for the construction of amperometric nano-sensors.

## Graphical Abstract

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## Introduction

The nanotechnology domain, as a branch of science and engineering devoted to designing, producing, and using structures, devices, and systems by manipulating atoms and molecules at the nanoscale has grossly yielded applications at the submicroscopic levels [1]. Tentatively, this sphere of science has developed rapidly. Subsequently, the invention of nanoscale materials such as nanoclusters, nanowires, nanotubes, nanocages e.t.c., has equipped the field of nanotechnology with vast applications of these designed nanomaterials in the catalytic reaction processes, optical devices, adsorption, medicine, biological modeling, electronic, sonic devices, and as sensing materials [2]. Hence, these frameworks were laid by the invention of nanotube materials, specifically carbon nanoscale material. This discovery has, in turn, increased the insatiable demand for nanoscale materials, and has also laid a foundation for the rapid

development of nanomaterials [3]. Regardless of the frequent usage of nanotubes (carbon-based) and carbon allotrope framework ($C_{60}$ fullerene) in modern and advanced gadgets, substantial ground-breaking agitation towards the substitution of carbon-based nanomaterials and in the synthesis of nanocages, tubular, and cluster fullerene of varying non-carbon containing materials over the last decades has been the peak of scientific research [4]. It is pertinent to note that Silica, $XY_n$ materials (In the form of AlN, BN), metal carbides, metal nitride nanotubes, and subsequently axial cubic AlN-BN nanocomposites are the most embodied and highly emphasized examples in this regard [5]. Due to the atomically precise, crystalline nature of nanoclusters, which often pave way for their kinetic stability during the synthesis of macro materials, such as metallic nanocrystals, metalloids, and also their enclosed electronic shell system, nanoclusters have been long considered to play a crucial and pertinent role in the development of materials utilized in up-shooting technologies [6]. As such, nanoclusters have been the mainframe of recent and ongoing scientific investigations. More so, studies have revealed that inorganic nanomaterials have the most stable configuration of nanoclusters and nanocages. Nahali and coworkers reported diverse atomic geometries of $Si_4$ nanocluster. In their study via the density functional theory (DFT) approach, they concluded that the $Si_4$ nanocluster exhibited stable configuration with respect to their vibrational frequency and parametric adsorption when compared with other previously reported fullerene materials (Carbon based@$C_{60}$ and $C_{24}$). More so, these semiconductor-based nanoclusters ($(Si)_x$, $B_xN_x$, $Al_xN_x$, $GA_xAS_x$, $Ga_xN_x$, $Ga_xP_x$, $Si_xGe_x$) have also been found to have continuous applications in light emitting diode, batteries, and microelectronics, and having amazing physiochemical characteristics [7].

Silicon-based nanomaterials $(Si)_x$ have been spotlighted due to their cost-effectiveness, unique property, high sensitivity, thermal stability, large HOMO energy gap, and highly resistant to radiation and oxidation [8]. As such, instead of shrinking its marketplace, Silicon-based nanomaterials keep displacing competitive materials. Silicon-incorporated materials have grossly been looked upon as the cornerstone of the current era of electronic and sensing materials.

Recently, comparative studies of the adsorption of a well-known greenhouse gas (NO) have been understudied by Nahali et al. [9], utilizing the first principle theoretical approach, and employing the advanced hybrid-meta density functional theory method of Truhlar (MPW1B95), with MG3 semi-diffuse basis sets to study geometry, adsorption energy, Natural Population Analysis (NPA), Natural bond orbital (NBO) charge analysis, and vibrational frequency upon adsorption of Nitrogen(I)oxide (NO). Similar inter and intramolecular interactions existing between different molecules have also been studied with respect to utilizing Si-based nanomaterials. Li and coworkers [10] have also carried out a doping efficacy on a novel Ag-doped silicon-based nanosphere for effective sequestration and removal of radioactive iodide anions from solutions. In their study, they stated the relevance of doping, as a massive generation of highly specific binding sites, which were regarded as the strong binding centre of radioactive anion, and thus, a rapid adsorption process was achieved. Their results indicated that effective doping of silicon-based nanomaterials can find practical application in the field of toxic substance removal and recovery. More so, a recent theoretical density functional theory (DFT) study on high-capacity hydrogen adsorption over silicon-lithium binary nanocluster carried out by Jaiswal et al. [11] revealed that the $Si_4Li_n$ (n = 1–3) binary cluster can adsorb a maximum of 5–3 hydrogen molecules resulting in a high ascending order of gravimetric density. Their study further instituted and concludes that silicon-lithium binary clusters can be considered potent storage systems and sensing materials.

Profoundly, N-Nitrosodimethylamine (N-DMA), is a protonated amine bonded to a nitroso- group and an organic compound with the formula $(CH_3)_2NNO$, it is regarded as one of the unit members of a large class of N-nitrosamines [12]. This compound, has attracted attention as being highly hepatotoxic and carcinogenic. N-DMA can be produced by water treatment via chloramination or chlorination, it can further be leached during treatment of water by anion exchange resin. This hazardous compound can also be found in numerous items of human consumption, including processed (cured) meat, fish, and beer, as well as in tobacco products and in inhaling tobacco smoke [13]. More so, the high level of N-DMA existence in rocket fuel has been a

solicitude in the scientific community and the world at large. Exposure to this hepatotoxic compound has been shown to alter arginine biosynthesis, mitochondrial genome maintenance, and DNA damage repair in yeast and overall, in humans and other living organisms [13]. Consequently, it is pertinent and necessary to be in the sense of descry, detect, and expunge this hazardous organic compound from water bodies, human consumables, and ground-waters, even when present in minute concentrations. Thus, the adsorption of nitrosamine conformers on $C_{24}$, $B_{12}N_{12}$, $Be_{12}O_{12}$, and $Al_{12}P_{12}$ and the conversion of the conformers to basic nitrogen and water have been studied, employing the density functional theory (DFT) approach, the team reported that all their developed nanocages exhibited good catalytic ability in the conversion reaction of nitrosoamine to $N_2$ and water (toxic and non-toxic gases) [14]. Relatively, interaction studies of N-nitrosodimethyl on gamma phosphorene sheets emitted from rubber fumes have also been investigated, utilizing a first principle approach, reported by Nagarajan et al. [15], which revealed that the γ-phosphorene sheets can be used as a potent material for sensing N-DMA, even in a humid atmosphere.

Notwithstanding these technological advances, the adsorption of N-DMA on rare-earth metals (such as; Niobium, yttrium, molybdenum, and Zirconium) –doped pristine silicon nanocage ($Si_{60}$) has not yet been reported, presumably. More so, first row (early transition metals) and late transition metals bind with a less reasonable affinity with most nano-surfaces [16]. A recent report in the literature demonstrated that rare-earth metals bind effectively with semiconductor nanocages [17]. Moreover, rare-earth metals (of which Nb, Y, Mo, and Zr) are part, have been found to have a green future-dependent, superior magnetic character, and simulating ability [18]. Also, these rare-earth metals have the tendency to foster an adsorption process, and they have been found to have strong adsorbing abilities [19]. Thus, the efficacy of materials towards the adsorption of substances has been illustrated to be tuned by rare-earth metal doping [19].

Accordingly, all these findings motivated us to map out a system that can efficiently bind this hepatotoxic organic compound (N-DMA) by structural modification (that is, ‘doping of Nb, Y, Mo, Zr) rare-earth metals on $Si_{60}$ nanocage, which will aid in detecting, removing this

detrimental organic compound from human environment and consumables. The doping of the designed investigated nanostructures with rare-earth metals is much preferred here over the decoration of an atom of the Si-atom in the nanostructure endohedrally replaced with rare-earth atoms; Nb, Y, Mo, and Zr. Thus, this does not in any way perturb the intrinsic stability of the systems, as these rare-earth metal atoms can easily be detached from the pristine nanostructure as and when required. These interesting characteristics stimulated this explicit probe of the doping efficacy of rare-earth metals (such as; Nb, Y, Mo, and Zr) rather than decorating the $Si_{60}$ nanostructure with these rare-earth metal atoms.

For the course of this present study, the examination of N-DMA adsorption on pristine $Si_{60}$ and X-doped silicon nanocage (X = Nb, Y, Mo, and Zr) was investigated. Fundamentally, we surveyed the orientation (geometry) and electronic properties of the pristine $Si_{60}$ surface, and upon doping of the various rare-earth metals (Nb, Y, Mo, and Zr) through interaction energies (adsorption energies) assay, Natural population analysis (NPA), Natural bond orbital (NBO) charge analysis, frontier molecular orbital analysis (HOMO and LUMO), global reactivity descriptor study, density of states (DOS) analysis, solvation energy analysis, and other electronic parametric studies. Afterwards, the interaction of N-nitrosodimethylamine (N-DMA) with optimized designed structures of X-doped (X = Nb, Y, Mo, and Zr) silicon-based nanocage ($Si_{60}$) was explored.

## Section snippets

## Computational details

All computational analysis was performed by exhaustively employing density functional theory (DFT). Gaussian 16 and Gauss view 6.0.16 [20] were utilized to carryout ground state optimization using Lanl2DZ basis set, with exchange correction functional (PBE) by Perdew et al. [21], to accurately capture the inter and intra-atomic interactions, as this model has been reported to accurately capture the molecular orbital of Molybdenum, Oxygen, Hydrogen as well as other atoms respectively and provide

## Geometric optimization

Prior to the adsorption of N-Nitrosodimethylamine molecule (NDMA), using metal-doped engineered pristine ($Si_{60}$) surface, the systems were turned to their preferred and stable orientation and were assessed utilizing the DFT/PBE/Lanl2Dz theoretical level. The hollow studied compound, otherwise referred to as surface of interest ($Si_{60}$) incorporates a hexagonal morphology with surrounding silicon atoms, which embodies Si-Si bonds, extending from a given silicon atom to another within the hexagonal

## Conclusions

In order to investigate the sensing potency of designed silicon based nanosurface, the exchange correlation functional PBE with Lanl2Dz basis set was employed for this study. Below are highlight of our major findings:

- 1.
The semiconductor surface ($Si_{60}$) was doped, in attempt to improve the stability and sensing ability of $Si_{60}$ by intercalating selected rare earth metals of Nb, Mo, Zr and Y respectively. Detail insightful observations has been recorded and reported in this study. The overall

## CRediT authorship contribution statement

**Hitler Louis**: Validation, Supervision, reading, editing. **Ernest C. Agwamba**: Conceptualization, Software. **Kube T. Maxwell**: Formal analysis. **Gideon E. Mathias:** Investigation, Methodology, Writing – original draft. **Onyinye J. Ikenyirimba**: Investigation, Methodology, Writing – original draft. **Tomsmith O. Unimuke:** Project administration. **Eze F. Ahuekwe**: Project administration. **Dike Humphrey:** Data curation. **Innocent Benjamin**: Data curation. **Adedapo S. Adeyinka**: Resources.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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