

A THEORETICAL STUDY OF Y-MODIFIED B₁₂N₁₂ NANOCAGE AS A SENSOR FOR N₂O GAS SELECTIVE DETECTION

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ABSTRACT

The emission of toxic gases into the atmosphere has caused alarming effects to humanity, such as the case of N₂O gas, which contributes to the destruction of the ozone layer. To mitigate the environmental effects of N₂O, actions to reduce its emissions are necessary. B₁₂N₁₂ nanocages can contribute to the efficient detection of N₂O in the atmosphere. In this context, this work performed DFT-D3 calculations using B3LYP and Lanl2DZ basis set to investigate the geometric, electrical and energetic parameters of N₂O gas adsorption on pure and Y-modified B₁₂N₁₂ nanocages. The electronic sensitivity of the systems to N₂O adsorption was analyzed and Y@b₆₆ showed the highest sensitivity ($\Delta E_{\text{gap}} = 38.7\%$) of the studied cages. The results show that N₂O physically adsorbs on the B₁₂N₁₂ cage ($E_{\text{ads}} = -0.16$ eV). On the other hand, N₂O interacts moderately with the Y@b₆₆ nanocage ($E_{\text{ads}} = -1.07$ eV) and presents a good recovery time ($\tau = 120.54$ s). Furthermore, the cage is able to selectively differentiate N₂O gas from interferents (H₂, CH₄ and CO). Finally, the Y@b₆₆ nanocage shows potential as a material for application as a N₂O gas sensor.

Keywords: *B₁₂N₁₂ nanocage, adsorption, N₂O, sensor.*

INTRODUCTION

The mission of scientists to find materials capable of detecting or eliminating harmful gases present in the atmosphere has not been an easy task. In recent decades, studies have intensified for the development of chemical sensors capable of rapid and efficient detection of these gases [1,2]. Nanometric materials have been investigated as an alternative for application as sensors, due to their small size, good precision and excellent reactivity properties. Among these materials, we have boron nitride (BN)_n nanocages, which have gained prominence due to their excellent properties, such as oxidation resistance, high sensitivity and low recovery time [3].

Even with their excellent properties, some gases, such as COCl₂, H₂S, NO tend not to be spontaneously adsorbed on the surface of the B₁₂N₁₂ nanocage [4]. In this context, recent studies have investigated the structural modification of this nanomaterial using transition metals; in order to overcome this limitation, as well as improve their adsorption properties [5, 6]. Among the second-row transition metals, yttrium (Y) has gained prominence in studies as a modifier of nanomaterials for application as a sensor of atmospheric gases [7, 8]. Agwamba et al. [9] investigated the adsorption of metal-doped silicon nanocages (Si₅₉X; X = Nb, Mo, Y, Zr) as N-Nitrosodimethylamine (NDMA) gas nanosensors using correlation-exchange functional (PBE) and Lanl2DZ basis set. The results reported that doping with transition metals (Nb, Mo, Y, Zr)

in the Si₆₀ fullerene nanostructure significantly improved the interaction with NDMA. Other molecular descriptors also indicated positive results, confirming the suitability of the surfaces for NDMA detection.

The objective of this study was to explore, using DFT calculations, the adsorption behavior of N₂O gas on Y-modified B₁₂N₁₂ nanocages, along with the interfering gases H₂, CH₄, and CO, to assess the potential of this material as an environmental sensor for toxic gases.

MATERIALS AND METHODS

DFT calculations were performed using the ORCA 5.0 program [10]. The pure and Y-modified B₁₂N₁₂ nanocages were optimized using the B3LYP-D3[11] functional and the Lanl2DZ basis set. Frequency analysis was performed to confirm the global minima of the optimized structures. The modification of B₁₂N₁₂ with Y resulted in five optimized structures [12]: doped (YB₁₁N₁₂ and B₁₂N₁₁Y, with substitution of a boron atom and a nitrogen atom for a Y atom in the nanocage, respectively); decorated (Y@b₆₄ and Y@b₆₆, with a Y atom positioned above the atomic bond between the tetragonal and hexagonal rings and above the atomic bond between two hexagonal rings, respectively) and the encapsulated structure (Y@B₁₂N₁₂, in which a Y atom is positioned inside the B₁₂N₁₂ nanocage).

The structures were calculated as neutral, and their stability was investigated through the cohesive energy (E_{coh}), which was calculated according to the following equation [13]:

$$E_{\text{coh}} = \frac{1}{N} (E_{\text{nanocage}} - xE_{\text{B}} - yE_{\text{N}} - zE_{\text{Y}}) \quad (1)$$

where E_{nanocage} is the total energy of the nanocage (either pure or yttrium-modified); E_{B} , E_{N} and E_{Y} are the energies of the B, N, and Y atoms, respectively; x , y , and z represent the quantities of each atom (B, N, and Y, respectively) in the structure; and N is the total number of atoms in the nanocage.

Given the energy gap E_{gap} , defined as the difference between the LUMO (E_{LUMO}) and HOMO (E_{HOMO}) energies, we determine the value of electronic sensitivity (ΔE_{gap}) for the interaction between the H₂ molecule and the pure or Y-modified B₁₂N₁₂ nanocages according to equation 2, below:

$$\Delta E_{\text{gap}} = \left[\frac{(E_{\text{gap(nanocage-N}_2\text{O)}} - E_{\text{gap(nanocage)}})}{E_{\text{gap(nanocage)}}} \right] * 100 \quad (2)$$

where $E_{\text{gap(nanocage-N}_2\text{O)}}$ is the energy gap for the interaction of N₂O with pure and modified B₁₂N₁₂ nanocages, and $E_{\text{gap(nanocage)}}$ is the energy gap for pure or Y-modified B₁₂N₁₂.

The E_{ads} value for the interaction between N₂O and B₁₂N₁₂ or Y-B₁₂N₁₂ was calculated according to equation 3:

$$E_{\text{ads}} = E_{(\text{nanocage-N}_2\text{O})} - (E_{(\text{nanocage})} + E_{(\text{N}_2\text{O})}) + E_{\text{BSSE}} \quad (3)$$

where $E_{(\text{nanocage-N}_2\text{O})}$ is the energy of the B₁₂N₁₂ or Y-B₁₂N₁₂ nanocage bound to N₂O, $E_{(\text{nanocage})}$ is the energy of the pure B₁₂N₁₂ or Y-modified B₁₂N₁₂ nanocages, $E_{(\text{N}_2\text{O})}$ is the energy of the N₂O molecule, and E_{BSSE} is the basis set superposition error (BSSE) [13].

The recovery time (τ), which is exponentially related to the system E_{ads} , can be calculated by equation 4 [14]:

$$\tau = v_0^{-1} e^{-E_{\text{ads}}/k_{\text{B}}T} \quad (4)$$

where v_0 is the attempt frequency ($10^{12} v_0 \text{ s}^{-1}$), k_{B} is the Boltzmann constant ($8.62 \times 10^{-5} \text{ eV K}^{-1}$), and T is the thermodynamic temperature (K).

The yttrium-modified nanocage that showed the best result for N₂O detection was subjected to interaction with other gases considered interferents (H₂, CH₄ and CO) to investigate its selectivity for N₂O adsorption in comparison with these gases. The selectivity was evaluated by calculating the sensor response (S) and the selectivity coefficient (κ) using the following equations [15]:

$$S = \left| \left(\frac{\sigma_{\text{pure}}}{\sigma_{\text{gas}}} \right) - 1 \right| = e^{|\Delta E_{\text{gl}}|/2k_B T} - 1 \quad (5)$$

$$\kappa_{\text{gas-int}} = \frac{S_{\text{cage/gas}}}{S_{\text{cage/int}}} \quad (6)$$

where σ_{gas} represents the conductivity of the gas adsorbed on the surface of the nanocage, σ_{pure} is the conductance of the isolated nanocage.

RESULTS AND DISCUSSION

The optimized structures of B₁₂N₁₂ and Y-modified nanocages are shown in Fig. 1 a), and their electronic properties are presented in Table 1. The interaction of N₂O gas is presented in Fig. 1 b). The results show that for B₁₂N₁₂ nanocages, the B-N bond lengths of 1.485 and 1.437 Å are in agreement with previous studies [16, 17].

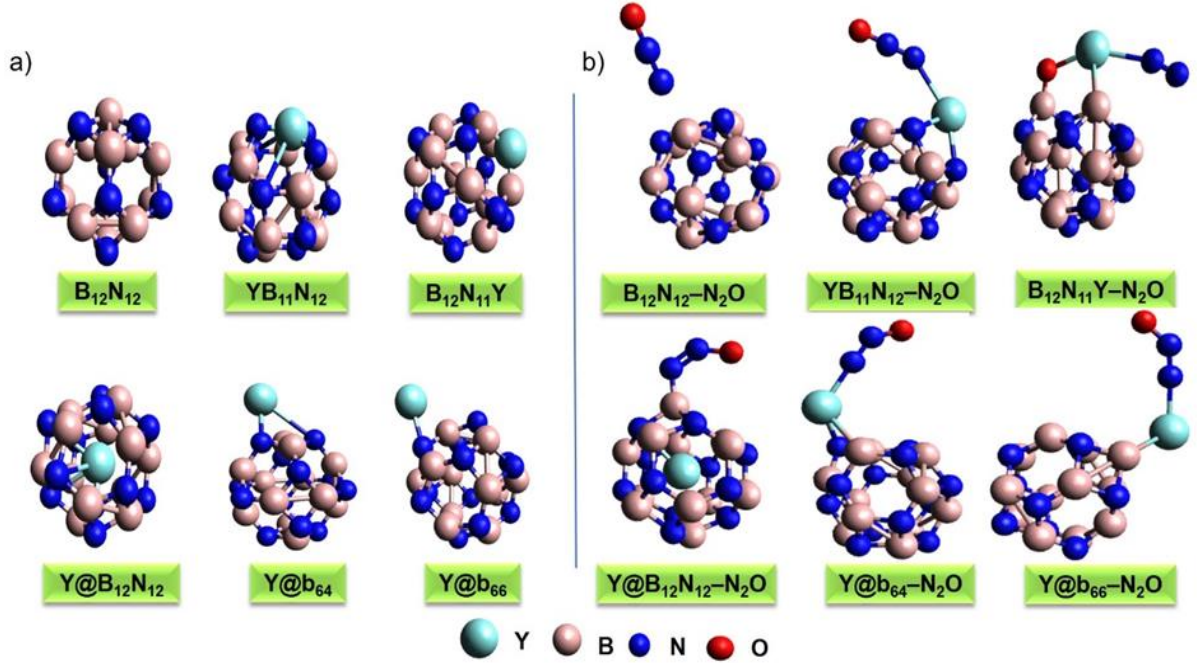


Fig. 1 – Optimized structures for pristine and Y-modified B₁₂N₁₂ nanocages a), interaction of N₂O molecule gas with isolated and Y-modified B₁₂N₁₂ nanocages b).

As seen in Fig. 1 a), the modification with Y atom causes a local deformation in the nanocages and this may be due to their large atomic radius. After the optimization of the geometry of the modified cages, it is observed that there was an increase in the bond length; in the case of the encapsulated structure, the metal projected to the center of the nanocage. Fig. 1 b) shows that N₂O presents a nonlinear geometry when interacting with Y in the decorated nanocages, binding through the N atom and not through O as occurs in other analyzed systems. Table 1 shows the cohesion energy (E_{coh}), dipole moment (DM) and charge transfer (Q) for the pure and Y-modified B₁₂N₁₂ structures. The B₁₂N₁₂ nanocage showed a dipole moment equal to zero [18]. The highest dipole moment value was for B₁₁N₁₂Y DM = 10.18 Debye, while the lowest was for Y@B₁₂N₁₂ DM = 1.63 Debye, indicating a lower charge partition in the encapsulated cage (-0.37 |e|). The largest charge shift from Y to the cage is seen in the Y@b₆₄

system (+0.45 |e|), where the metal replaces a B atom in B₁₂N₁₂. The E_{coh} analysis provides information about the affinity of the nanocage with the metal, exploring in detail the stability of the cage/metal systems. The results show that the lower E_{coh} values (less negative) for the modified nanocages prove that all structures are less stable than pure B₁₂N₁₂ [12]. In addition, YB₁₁N₁₂ stands out as the most unstable among the studied nanocages, with E_{coh} = -6.81 eV.

Table 1 - Calculated values of cohesive energy (E_{coh}), dipole moment (DM) and the Y atomic charges (Q) for isolated systems.

System	E _{coh} / eV	DM / Debye	Q / e
B ₁₂ N ₁₂	- 6.82	0.00	-
YB ₁₁ N ₁₂	- 6.81	10.18	+0.63
B ₁₂ N ₁₁ Y	- 6.49	9.71	+0.05
Y@b ₆₄	- 6.64	6.93	+0.45
Y@b ₆₆	- 6.63	7.21	+0.33
Y@B ₁₂ N ₁₂	- 6.27	1.63	-0.37

The parameters of the isolated and modified systems for N₂O gas adsorption: HOMO energy (E_H / eV), LUMO energy (E_L / eV), HOMO-LUMO gap (E_{gap} / eV), sensitivity (ΔE_{gap} / %) are shown in Table 2. It is noted that the energies of the HOMO and LUMO orbitals of B₁₂N₁₂ underwent changes after the interaction with N₂O, this change directly reflected in the variation of E_{gap}.

Table 2 – Calculated values of the parameters: HOMO energy (E_H), LUMO energy (E_L), energy gap (E_{gap}), electronic sensitivity (ΔE_{gap}) and adsorption energy (E_{ads}) of the isolated cages and interaction with N₂O.

System	S	Isolated			With N ₂ O adsorbed				
		E _H (eV)	E _L (eV)	E _{gap} (eV)	E _H (eV)	E _L (eV)	E _{gap} (eV)	ΔE _{gap} (%)	E _{ads} (eV)
B ₁₂ N ₁₂		-7.77	-1.84	5.93	-7.61	-2.43	5.18	12.54	-0.16
YB ₁₁ N ₁₂	α	-6.71	-2.78	3.93	-6.60	-3.33	3.27	16.87	-0.46
B ₁₂ N ₁₁ Y	α	-5.48	-2.79	2.69	-5.65	-3.16	2.49	7.42	-0.55
Y@b ₆₄	α	-4.53	-2.19	2.34	-5.99	-2.91	3.08	31.44	-0.63
	β	-5.70	-2.63	3.07	-5.99	-3.35	2.64	14.12	
Y@b ₆₆	α	-4.57	-2.20	2.37	-6.16	-2.87	3.29	38.70	-1.07
	β	-5.33	-2.72	2.61	-6.47	-3.32	3.15	20.53	
Y@B ₁₂ N ₁₂	α	-4.88	-2.89	1.99	-4.87	-3.33	1.54	22.21	-0.49
	β	-5.00	-2.85	2.15	-5.19	-3.34	1.85	14.19	

α – spin up – (alpha); β – spin down – (beta)

The bandgap of B₁₂N₁₂ decreased from 5.93 eV to 5.18 eV after adsorption, indicating weak interaction with N₂O gas. The sensitivity of a system is determined by the change in the bandgap before and after gas adsorption (see Equation 2) [19]. In this context, modifying the nanocage with yttrium increases its sensitivity to the gas [20]. For the pure B₁₂N₁₂ system, the sensitivity to N₂O adsorption was (ΔE_{gap} = 12.54 %). These data are confirmed by the low

adsorption energy obtained for the system ($E_{\text{ads}} = -0.16$ eV), characterizing a physisorption ($E_{\text{ads}} > -0.3$ eV) [21] with Van der Waals-type interaction. Among the metal-modified cages, $\text{B}_{12}\text{N}_{11}\text{Y}$ showed the lowest sensitivity ($\Delta E_{\text{gap}} = 7.42\%$) with adsorption energy ($E_{\text{ads}} = -0.55$ eV). In the case of the Y@b_{66} (α - spin up) system, the energy was ($E_{\text{ads}} = -1.07$ eV), a value considered moderate for a chemisorption process. Furthermore, it showed good sensitivity ($\Delta E_{\text{gap}} = 38.70\%$) with satisfactory recovery time at a temperature of 298 K ($\tau = 120.54$ s), making it suitable as a material for application as a sensor. To assess the selectivity of the Y@b_{66} nanocage for N_2O gas detection, the adsorption of other gases, including H_2 , CH_4 , and CO , was examined using the same calculation methods. The optimized structures are presented in Fig. 2.

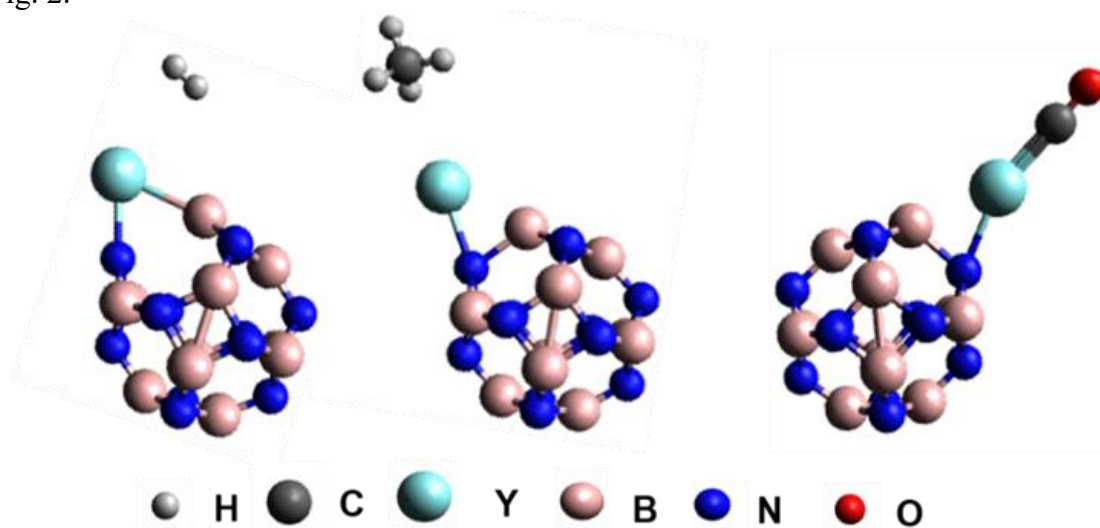


Fig. 2 – Optimized structures of the adsorption of Y@b_{66} nanocage with interfering gases H_2 , CH_4 and CO .

Table 3 presents the results for HOMO-LUMO (E_{gap}), distance (d), adsorption energy (E_{ads}) and sensitivity (ΔE_{gap}) for the adsorption of H_2 , CH_4 and CO gases (considered interfering gases) on the surface of the Y@b_{66} nanocage. The FMO data show that the nanocage is more sensitive to nitrous oxide compared to the other gases studied ($\Delta E_{\text{gap}} = 38.70\%$), indicating that N_2O is preferentially detected by the Y@b_{66} system. Regarding the adsorption distances of the interfering gases on the nanocage, it is noted that CH_4 has the largest interaction distance ($d = 3.44$ Å), while the smallest was observed for N_2O gas ($d = 2.16$ Å). The adsorption energies indicate that H_2 , CH_4 and CO gases undergo physical adsorption on the surface of the Y@b_{66} cage [22]. For nitrous oxide gas adsorption, the resulting adsorption energy ($E_{\text{ads}} = -1.07$ eV) characterizes a chemisorption process. Regarding the recovery time of the interfering gases, the values obtained were high, making them unfavorable for adsorption on the Y@b_{66} surface. In contrast, the recovery time for the interaction between the nanocage and N_2O gas ($\tau = 120.54$ s) is considered satisfactory at room temperature.

To analyze the interaction of Y@b_{66} with N_2O and interfering gases, the sensitivity (S) and selectivity (κ) were calculated using the same methodology as in previous studies. These parameters assess the system's effectiveness in gas detection and its ability to distinguish a specific gas in the atmosphere. Overall, the results indicate that the Y@b_{66} nanocage exhibits higher sensitivity to N_2O compared to other gases and can effectively differentiate it from interfering gases, showing the highest selectivity coefficient for the $\text{N}_2\text{O}/\text{CH}_4$ pair. These findings suggest that the Y@b_{66} nanocage holds potential as a sensor with strong sensitivity and selectivity for N_2O detection.

Table 3 – Values of gap HOMO-LUMO (E_{gap}), cage/gas distance (d), adsorption energy (E_{ads}), electronic sensitivity (ΔE_{gap}), recovery time (τ), and also the sensitivity (S) and selectivity coefficient (κ) calculated for the interaction of H_2 , CH_4 and CO gases with the Y@b_{66} cage.

System	E_{gap} (eV)	d (Å)	E_{ads} (eV)	ΔE_{gap} (%)	τ	S	κ
$\text{Y@b}_{66} - \text{N}_2\text{O}$	3.29	2.16	-1.07	38.70	120.54 s	5.93×10^7	—
$\text{Y@b}_{66} - \text{H}_2$	2.30	3.01	-0.19	3.04	1.13×10^{12} s	2.90	2.05×10^7
$\text{Y@b}_{66} - \text{CH}_4$	2.38	3.44	-0.04	0.34	1.24×10^{19} s	0.22	2.69×10^8
$\text{Y@b}_{66} - \text{CO}$	1.79	2.09	-0.60	24.54	5.15×10^5 s	7.95×10^4	7.46×10^2

CONCLUSIONS

DFT-D3 level calculations with B3LYP functional and Lanl2DZ basis set were employed in this work to explore the geometrical and energetic properties of N_2O -adsorbed on pristine and Y-modified $\text{B}_{12}\text{N}_{12}$ nanocages. The results indicate a weak adsorption interaction of N_2O gas on pure $\text{B}_{12}\text{N}_{12}$, $\text{YB}_{11}\text{N}_{12}$, $\text{B}_{12}\text{N}_{11}\text{Y}$, Y@b_{64} and $\text{Y@B}_{12}\text{N}_{12}$ nanocages, characterizing a physical adsorption ($E_{\text{ads}} > -0.3$ eV). However, N_2O gas is adsorbed, by a chemisorption process, on the surface of the Y@b_{66} nanocage ($E_{\text{ads}} = -1.07$ eV) with recovery time ($\tau = 120.54$ s) at room temperature. The electronic sensitivity of Y@b_{66} was ($\Delta E_{\text{gap}} = 38.70$ %) of the interaction with the N_2O molecule, which is considered the best compared to other modified systems. Furthermore, the nanocage demonstrated the ability to selectively differentiate N_2O molecules from interfering gases (H_2 , CH_4 , and CO). In summary, the Y-modified nanocages exhibited better results than the $\text{B}_{12}\text{N}_{12}$ nanocage alone for N_2O gas adsorption. The Y@b_{66} nanocage shows potential for application as a sensor in the selective detection of N_2O gas molecules in the environment.

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REFERENCES

- [1] YOOSEFIAN, M. Powerful greenhouse gas nitrous oxide adsorption onto intrinsic and Pd doped Single walled carbon nanotube, *Applied Surface Science* 392, p. 225–230, 2017.
- [2] RAD, A. S. First principles study of Al-doped graphene as nanostructure adsorbent for NO_2 and N_2O : DFT calculations, *Applied Surface Science* 357, p. 1217–1224, 2015.
- [3] DING, S.; GU, W. Evaluate the potential utilization of $\text{B}_{24}\text{N}_{24}$ fullerene in the recognition of COS , H_2S , SO_2 , and CS_2 gases (environmental pollution). *J. Mol. Liq.* 345, 117041, 2022.
- [4] SILVA, A.L.P.; SOUSA, N.S.; VARELA, J.J.G. Theoretical studies with $\text{B}_{12}\text{N}_{12}$ as a toxic gas sensor: a review. *J Nanopart Research* 25, 22, 2023.
- [5] QADIR, K.W.; MOHAMMADI, M.D.; RIDHA, N.J.; ABDULLAH, H.Y. Determining the binding mechanism of $\text{B}_{12}\text{N}_{12}(\text{Zn})$ with CH_4 , CO , CO_2 , H_2O , N_2 , NH_3 , NO , NO_2 , O_2 , and SO_2 gases. *Microp Mesop Mater* 379, 113289, 2024.

- [6] SOUSA, N.S.; NASCIMENTO, W.C.L.; SILVA, A.L.P.; VARELA, J.J.G. DFT study of TM (Sc-Zn) modified B₁₂N₁₂ nanocage as sensor for N₂O gas selective detection. *Sens Actuat A* 378, 115841, 2024.
- [7] WANG, T.; TIAN, Z. Yttrium-decorated C₄₈B₁₂ as hydrogen storage media: A DFT study. *Int J Hydrog Energy* 45, 24895–24901, 2020.
- [8] ESRAFILI, M.D.; Sadeghi S. Y decorated all-boron B₃₈ nanocluster for reversible molecular hydrogen storage: A first-principles investigation, *Int J Hydrog Energy* 47, 11611–11621, 2022.
- [9] AGWAMBA, E.C.; MATHIAS, G.E.; LOUIS, H.; IKENYIRIMBA, O.; UNIMUKE, T.O.; AHUEKWE et al. Single metal-doped silicon (Si₅₉X; X = Nb, Mo, Y, Zr) nanostructured as nanosensors for N-Nitrosodimethylamine (NDMA) pollutant: Intuition from computational study, *Materials Today Communications*, 35, 106173, 2023.
- [10] NEESE, F. Software update: The ORCA program system–Version 5.0. *WIREs Comput Mol Sci* 12:e1606, 2022.
- [11] GRIMME, S. Density functional theory with London dispersion corrections. *WIREs Comput Mol Sci* 1, 211–228, 2011.
- [12] SILVA, A.L.P.; VARELA, J.J.G. Density Functional Theory Study of Cu-Modified B₁₂N₁₂ Nanocage as a Chemical Sensor for Carbon Monoxide Gas. *Inorg Chem* 62, 1926–1934, 2023.
- [13] SILVA, A.L.P.; VARELA, J.J.G. MB₁₁N₁₂ (M = Fe–Zn) Nanocages for Cyanogen Chloride Detection: A DFT Study. *J Inorg Organom Polym Mat* 34, 302–312, 2024.
- [14] KOETTGEN, J.; ZACHERLE, T.; GRIESHAMMER, S.; MARTIN, M. Ab initio calculation of the attempt frequency of oxygen diffusion in pure and samarium doped ceria. *Phys. Chem. Chem. Phys.* 19, 9957-9973, 2017.
- [15] CUI, H.; JIA, P.; PENG, X.; LI, P. Adsorption and sensing of CO and C₂H₂ by S-defected SnS₂ monolayer for DGA in transformer oil: A DFT study. *Mater. Chem. Phys.* 249, 123006, 2020.
- [16] RAD, A.S.; and AYUB, K. O₃ and SO₂ sensing concept on extended surface of B₁₂N₁₂ nanocages modified by Nickel decoration: A comprehensive DFT study. *Solid State Sci.* 69, 22–30, 2017.
- [17] MA, S.; LI, D.; RAO, X.; XIA, X.; SU, Y.; LU, Y. Pd-doped h-BN monolayer: a promising gas scavenger for SF₆ insulation devices. *Adsorption*. 26, 619-626, 2020.
- [18] ESCOBEDO-MORALES, A.; TEPECH-CARRILLO, L.; BAUTISTA-HERNÁNDEZ, A.; CAMACHO-GARCÍA, J.H.; CORTES-ARRIAGADA, D.; CHIGO-ANOTA, E. Effect of Chemical Order in the Structural Stability and Physicochemical Properties of B₁₂N₁₂ Fullerenes. *Sci. Rep.* 9, 16521, 2019.
- [19] BAEI, M.T. Si-Doped B₁₂N₁₂ Nanocage as an Adsorbent for Dissociation of N₂O to N₂ Molecule. *Heteroatom Chemistry* 24, 476-481, 2013.
- [20] NASCIMENTO, W.C.L.; SOUSA, N.S.; MARTINS, J. DOS S.; MACIEL, A.P. Estudo a Nível DFT do B₁₂N₁₂ Puro e Modificado com Y para Adsorção do Gás Hidrogênio. *Anais do Congresso Brasileiro de Química - CBQ 63º edição*, 2024.
- [21] HADIPOUR, N.L.; PEYGHAN, A.A.; SOLEYMANABADI, H. Theoretical Study on the Al-Doped ZnO Nanoclusters for CO Chemical Sensors. *J Phys Chem C* 119, 6398–6404, 2015.
- [22] CHOIR, A.A.; AMELIA, S.R.; MARTOPRAWIRO, M.A.; KUSUMAWATI, Y.; IVANSYAH, A.L. Insight into the adsorption properties of CO₂ and H₂ gas on the B₁₂Y₁₂ (Y - N, P, As, Sb) nanocages from host-guest interaction perspective. *Int J Hydrog Energy* 2024, 53:780–791.