Investigation of the interaction of CO, NO, and HCN Gases with Transition Metal-Doped Ca₁₂O₁₂ Nanocages: Theoretical Study

H.O. Taha^{1,*}, A. M. El Mahdy¹

¹ Department of Physics, Faculty of Education, Ain Shams University, Roxy, 11575, Cairo, Egypt

Abstract

There are several uses for nanostructured gas sensors in environmental monitoring. Calcium oxide (Ca12O12) nanocages have significant surface area and unique structural characteristics, making them ideal for real-world sensing applications. Using dispersioncorrected density functional theory (DFT) computations, we examined the adsorption of carbon monoxide (CO), nitrogen oxide (NO), and hydrogen cyanide (HCN) gases on $(Ca_{12}O_{12})$ nanocages that are doped with transition metals (TM = Sc to Zn) and those that are pure. Charge transfer, as demonstrated by the analysis of dipole moments, adsorption energies, molecular electrostatic potential (MEP), thermodynamic characteristics (Gibbs free energy, ΔG , and enthalpy, ΔH), molecular dynamics (MD) simulations, non-covalent interaction (NCI), natural bonding orbitals (NBOs), and the quantum theory of atoms in molecules (QTAIM) were all considered. The ΔG values of all complexes, except for the NO/CuCa₁₁O₁₂, NO, and HCN on CoCa₁₁O₁₂, NO, CO, and HCN on ZnCa₁₁O₁₂ complexes, were negative, suggesting weak adsorption. For optimal geometries, the binding energy of TM-doped Ca₁₁O₁₂ falls between -5.728 and -6.023 eV. The CO, NO, and HCN adsorption energies in pure Ca₁₂O₁₂ nanocages are -0.404, -0.671, and -0.423 eV, respectively. On the other hand, the interaction energies for CO /TM-doped Ca₁₁O₁₂, ranged from -0.172 (Zn) to -2.616 (Cr) eV; for NO/TM-doped Ca₁₁O₁₂, ranged from -0.149 (Zn) to 4.072 (Cr); and for HCN/TM-doped Ca₁₁O₁₂, ranged from -0.055 (Zn) to -2.556 (Ti) eV, respectively. Ultimately, TM-doped Ca₁₁O₁₂ nanocages have the potential to improve the accuracy and reliability of hazardous substances, such as HCN, NO, and CO, detection in next-generation sensor technologies.

Keywords

DFT-D3; Ca₁₂O₁₂ nanocages; Gas Sensors ; QTAIM.

*: <u>hyamosman@edu.asu.edu.eg,</u> <u>drhotaha@hotmail.com</u>

Receive Date: 6-3-2025; Revise Date: 5-4-2025; Accept Date: 10 -4-2025; Publish: 13- 4-2025

1. Introduction

The increased industrialization and urbanization of recent years have resulted in a serious problem with air pollution. Nanomaterial-based gas monitors are growing increasingly important because of the release of harmful gases. A significant problem facing the semiconductor industry now is figuring out the critical factors that affect how these gas molecules interact with nanomaterials. [1–3]. Since poisonous gases including NO, CO, and HCN are easily found in the air and pose a serious threat to human health due to their introduction through fuel burning, automobiles, and industrial operations, they are regarded as the main gaseous pollutants [4–6].

Since CO is one of the most significant pollutants in the atmosphere, it has been extensively researched. Vehicles and industrial processes are the primary producers of this gas. CO can have harmful effects on both the human body and animal ecology. Most investigations have found CO gas in the 4–10 ppm range. There is no smell or color to this gas [7].

Cyanides are poisonous substances that can be naturally occurring or man-made. They are primarily found in automobile exhaust and smoke. Common poisonous cyanides include HCN, potassium cyanide KCN, and sodium cyanide NaCN. HCN is highly hazardous to human health, affecting oxygen utilization through various routes [8]. Cyanides are commonly used in manufacturing processes like dye synthesis, nitriles, resins, fibers, pigments, electroplating, chelating agents, and metal extraction. Detecting HCN's presence or discharge is crucial for human safety [9, 10]. HCN and cyanogen chloride (CNCl) are volatile and have low boiling points, necessitating sensitive sensors for their detection. Due to the extremely dangerous nature of HCN gas, which is released while burning nitrogen that contains living materials and from the smoke of various tobacco products, its detection is essential for both environmental preservation and human safety. Such sensors are needed for this purpose; their energy gap may be adjusted by adsorbing a small amount of dangerous gases that produce a detectable signal. Defective SWCNTs can be thought to be effective HCN sensors, as demonstrated by Zhou et al. [11]. Zhang et al. [12] found that SWCNTs doped with boron atoms exhibit strong reactivity to the deadly cyanide molecule. Yang et al. [13] found that SWCNTs doped with silicon to detect HCN are an especially promising sensing material. In their work, Shi et al. [14] examined the electronic characteristics and adsorption energies of graphene doped with Cr, Mn, and Fe in the presence and absence of HCN adsorption. The kinetic, geometrical, and electrical characteristics of Si and Al-doped graphene in response to hazardous HCN were investigated by Rastegar et al. [15] using DFT.

An extensive study on fullerenes has demonstrated that the spherical allotropes of carbon contain particularly fascinating features, ever since Kroto et al [16] discovered C_{60} fullerene in 1985. Extensive research is being conducted on novel nanoscale materials because of their unique properties and numerous possible uses [17–19]. Several research publications based on inorganic materials have recently been published that offer various forms of nanostructures that resemble fullerenes [20, 21]. These papers highlight the significance of inorganic nanocages, which have the generic formula (XY)n, where n is the total number of atoms in the structure. The nanocages (n = 12) are extremely stable [22–25]. This "magic number," [26], has not yet been satisfactorily explained, but what makes those nanocages (XY)₁₂ intriguing is the fact that they meet the tetragonal rule. Those nanocages (XY)₁₂ are made up of 6-squares and 8- hexagons. Within these cages, the most well-known nanostructures are B₁₂N₁₂ and Al₁₂N₁₂ [27, 28].

Many ways to produce exceptionally well nanostructured electronics with adjustable energy gaps (Eg) have been developed to enhance their semiconducting capabilities. One effective method for customizing the intrinsic characteristics of nano-cages is to dope them with metal atoms. Because of their varied characteristics over the whole periodic table, transition metals are intriguing dopants. Interesting features such as improved catalytic activity, electron retreating and donation ability, and light absorption spectrum tuning are obtained by doping transition metal (TM) on nanocages [29, 30]. Many investigations have found that materials with TM atoms on the surface, including metal oxide, graphene, phosphide, and metal nitride nanocages supply increased activity for gas detection and catalytic performance [31-35]. The 3D transition metal (TM) atoms adsorption onto monolayers has been investigated, revealing that the systems show significant promise potential 2D applications in spintronics and nanoelectronics [36, 37].

Because metal-oxide linkages are very ionic, $(XY)_{12}$ nanoclusters containing metal oxides, such as $Ca_{12}O_{12}$, have certain notable properties. As such, the aforementioned clusters' chemical and physical characteristics were thoroughly investigated [38–41]. CaO in the form of nanoparticles is highly desirable; these particles have been prepared with an average crystallite size of around 4 nm and 500 m² g⁻¹ greater surface areas [42]. Because of the enormous surface areas and significant surface reactivity, these materials are regarded as effective adsorbents [42]. There was theory behind the CaO nanoclusters. The adsorption of CaO nanostructures and their electrical and structural characteristics after interacting with single molecules have been the subject of numerous studies recently [43]. Oliveria et al.'s recent study [44] evaluated the Ca₁₂O₁₂ nanocage cluster using quantum chemical techniques.

According to their findings, these nanostructures have potential applications in adsorption procedures, gas sensors, catalysis, and chemical moieties storage.

Omidi et al. [45] showed that doping of Sc significantly improved the conductivity characteristics of Be₁₂O₁₂, Mg₁₂O₁₂, and Ca₁₂O₁₂. Recent research by Sajid et al. [46] showed that the trend $Ca_{12}O_{12} > Mg_{12}O_{12} > Be_{12}O_{12}$ was followed by various gaseous adsorption (N₂O, NO₂, NO, H₂S, SO₂, and SO₃) onto three chosen nanocages .S. A. Jasim et. al. [47] study the reactivity and sensitivity of a CaO nanocage to aluminum phosphide using density functional theory calculations. Results suggest CaO nanocages could be effective sensors for Air Pollution (AP) molecule detection. R. Kartika et. al. [48] demonstrate how the adsorption activity and mustard gas electrical sensitivity toward a Ca₁₂O₁₂ nanocage are revealed by the DFT simulations. Mustard molecule identification is made easier by the interaction of Ca atoms with mustard, which improves electrical conductivity. The electrical properties of the nano-cage are dependent on the solvent. H. Louis et. al. [49] study the efficient detection of phosgene using 3D nanomaterials Al₁₂N₁₂, Ca₁₂O₁₂, and Mg₁₂O₁₂, using density functional theory. Results show Ca₁₂O₁₂ is the best for phosgene gas adsorption due to stronger adsorptions and minimal energy gap. A.S. Rad et. al. [42] study water and hydrogen sulfide adsorption on $Ca_{12}O_{12}$ nanocages using DFT. Results illustrate that H_2S dissociates during adsorption, increasing electrical conductivity and softness, suggesting potential for selective sensor design. J.S. Al-Otaibi et. al. [50] study the thymine derivatives interaction with Ca₁₂O₁₂ and Be₁₂O₁₂ nanocages using DFT. Results showed adsorption energies of -43.16, -60.06, -29.62, -50.71, -45.95, -30.27 kcal/mol for thymine, 1-amino thymine, and thymine glycol, supporting drug adsorption. M. M. Kadhim et. al [51] they inspect the effects of the edifenphos molecule on the reactance and electrical sensitivity of pure (CaO) nanocage. They showed that the edifenphos molecule strongly adsorbs calcium oxide nanocage, causing a decrease in Eg of CaO and increased electrical conductance. This affects the work function of CaO nano-cage, affecting field emission electron current. The recovery time for edifenphos desorption is about 99 ms, making CaO nano-cage a suitable sensor.

As far as we know, the effect of adsorption of several poisonous gases such as CO, NO, and HCN on the electric characteristics of TM-doped calcium oxide nanoclusters (TM = Sc to Zn) has not been examined and requires more investigation. In the current investigation, a DFT approach was implemented to inspect the impacts of CO, NO, and HCN molecules adsorption on the electrical and geometrical features of pure $Ca_{12}O_{12}$ nanocages as well as doped TM- $Ca_{11}O_{12}$ (TM= Sc to Zn) nano-cages. The electrical characteristics, energy parameters, and geometric optimization of all structures were examined using NBOs, MD simulations ,QTAIM, and analysis of NCI. All of the geometry optimization calculations were conducted by DFT applying B3LYP-D3 functional and 6-311+G(d) basis set. The nature of the gas molecule's intermolecular interactions with the aforementioned nanocages was investigated.

2. Theory and Computation

All of the investigated compounds' geometry was optimized using the Gaussian 09 suite of algorithms, which did not impose any symmetry requirements. [52]. The third version of Grimme's atomic pair-wise dispersion correction (D3) [53], along with the exchangecorrelation functional of Becke-3-Lee- Yang-Parr (B3LYP) [54], was empirically used for optimized geometry. The geometries were optimized using the (6-311+G(d)) basis set in each case, and the same basis set was then used to calculate the single point energy that was corrected for basis set superposition error (BSSE) [55]. This combination is applicable to a wide range of chemical systems, including organic molecules, transition metals, and larger complexes, making it an ideal option for many research applications. To investigate the effect of the functional and basis set, calculations for CO, NO, and HCN molecules on the Ca₁₂O₁₂ nanocage are performed at three levels: B3LYP/6-31+g(d), B3LYP/6-311+g(d), and PBEPBE/6-311+g(d), as shown in Table S1 in the supplemental information (SI), the acquired results are somewhat similar. We took into consideration the following convergence criteria: (i) convergence on energy = 1.00D-06, (ii) convergence on MAX density matrix = 1.00D-06, and (iii) convergence on RMS density matrix = 1.00D-08 within 128 cycles. The optimized geometries for each structure under investigation, as well as the adsorption energies and electronic characteristics of NO, CO, and HCN gases on both pure Ca₁₂O₁₂ and doped with 3d Transition Metals (Sc to Zn) were calculated with the use of the Gauss View 5.0.8 software package [56]. MD simulations are used to investigate the Ca₁₂O₁₂ stability and TM- $Ca_{11}O_{12}$ clusters under investigation. The global reactivity parameters proposed by Koopmans and the systems frontier molecular orbitals (FMOs) were computed using Eg, lowest empty molecular orbitals (LUMOs) and highest occupied molecular orbitals (HOMOs) deduced from the FMOs studies. Following adsorption of the gaseous molecules, density of state (DOS) plots was used to investigate and validate the electronic mechanisms between the CO, NO, and HCN gaseous molecules and the pure Ca₁₂O₁₂ and doped Ca₁₁O₁₂ nanocage. The (NBOs) analysis was implemented [57]. The B3LYP-GD3/6-311+G(d) optimized geometries have been subjected to noncovalent interaction analysis and topological evaluation applying the QTAIM using version 3.7 of Multiwfn software [58]. To gain a comprehensive understanding of the nature of interatomic interactions. To visualize and produce isosurface maps, virtual molecular dynamics (VMD) software [59] has been utilized.

Equations (1) and (2) was used to get the average binding energy per atom (E_b) and the defect formation energy (E_{form}) for the TMCa₁₁O₁₂ nanocluster (TM = Sc to Zn).

$$E_{b} = \frac{1}{24} (E_{TMCa_{11}O_{12}} - E_{TM} - 11E_{Ca} - 12E_{O})$$
(1)
$$E_{form} = (E_{TMCa_{11}O_{12}} + E_{Ca}) - (E_{Ca_{11}O_{12}} + E_{TM})$$
(2)

Where, $E_{TMCa_{11}O_{12}}$ is the optimized TMCa_{11}O_{12} nanoclusters total energies, E_{TM} , E_{Ca} , and E_{O} are the TM, Ca, and O isolated single atoms energies, respectively.

The energies (E_{ads}) of adsorption for the gas on the Ca₁₂O₁₂ and TMCa₁₁O₁₂ nanoclusters were calculated using Eqs. (3) and (4) [55], respectively.

$$E_{ads} = E_{gas/Ca_{12}O_{12}} - (E_{Ca_{12}O_{12}} + E_{gas}) + E_{BSSE}$$
(3)
$$E_{ads} = E_{gas/TMCa_{11}O_{12}} - (E_{TMCa_{11}O_{12}} + E_{gas}) + E_{BSSE}$$
(4)

Where, $E_{gas/Ca_{12}O_{12}}$, $E_{gas/TMCa_{11}O_{12}}$, $E_{Ca_{12}O_{12}}$, $E_{TMCa_{11}O_{12}}$, E_{gas} and E_{BSSE} are the energies for the (gas/Ca_{12}O_{12}, gas/TMCa_{11}O_{12}) complexes, (Ca_{12}O_{12}, TMCa_{11}O_{12}) substrate, free gases, and basis set superposition error (BSSE), respectively. The (BSSE) was

taken into consideration while using the counterpoise method to correct the E_{ads} . The negativity of E_{ads} indicates an exothermic process, and its positivity indicates an endothermic process.

Global reactivity descriptions were taken into consideration using the extended Koopmans' theorem to further examine the stability and reactivity of the $Ca_{12}O_{12}$ nanocages, gases/ $Ca_{12}O_{12}$ nanocage, TM-doped $Ca_{11}O_{12}$ nanocage, and gases/TM-doped $Ca_{11}O_{12}$ nanocage. The electron affinity (EA) and ionization potential (IP) in Eqs. (5) and (6), respectively, are expressed using the generalized Koopman's theorem [60, 61]

$$EA = -E_{LUMO}$$
(5)
$$IP = -E_{HOMO}$$
(6)

The Fermi level (E_F) energies were estimated at T = 0 K [62,63]. Where is predicted as:

$$E_F = E_{HOMO} + (E_{LUMO} - E_{HOMO})/2$$
(7)

Chemical softness (*S*), chemical potential (μ), electrophilicity (ω), and chemical hardness (η) can also be calculated using equations 7, 8, 9, and 10 based on [64].

$$S = \frac{1}{2\eta} = \frac{1}{(IP - EA)} \tag{8}$$

$$\eta = \frac{1}{2} \left(IP - EA \right) \tag{9}$$

$$\mu = -\frac{(I+A)}{2} \tag{10}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{11}$$

The mean polarizability (α_0) and hyperpolarizability (β_0) are defined below [65-67].

$$\alpha_0 = \frac{1}{3} \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz} \right) \tag{12}$$

$$\beta_0 = [\beta_x^2 + \beta_y^2 + \beta_z^2]^{\overline{2}}$$
(13)

where $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$, $\beta_y = \beta_{yyy} + \beta_{yzz} + \beta_{yxx}$ and $\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}$ The total dipole moment μ_0 is obtained using the following equation:

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}}$$
(14)

Equations (15), (16), and (17) examine the thermodynamic parameters such as ΔG , ΔH , and entropy (ΔS) to better understand adsorbate-adsorbent interactions and ensure that all investigated configurations are matched to a minimum at the potential energy surface.

$$\Delta G = G_{Complex} - G_{TM-nanocage} - G_{gas} - H_{gas}$$
(15)

$$\Delta H = H_{Complex} - H_{TM-nanocage}$$
(16)
$$\Delta S = (\Delta H - \Delta G) / T$$
(17)

$$\Delta S = (\Delta H - \Delta G) / T$$

. . .

where in equation (15), $H_{Complex}$, $H_{TM-nanocage}$ and H_{gas} were represented as the sum of thermal and electronic enthalpies of complex structures, TM-Nano-cage, and gas molecules respectively. In equation (16), $G_{Complex}$, $G_{TM-nanocage}$ and G_{gas} were defined as the sum of thermal and electronic free energies of complex, gas and nanocage, respectively. The Gauss Sum software was utilized to determine the projected densities of states (PDOS) and sorbent clusters, gas-cluster complexes, and adsorbed gases densities (DOS) of states [68].

3. Results and Discussion

3.1. Structural Geometry

It was theoretically computed to use the B3LYP-GD3/6-311+G (d) to optimize the shape of the Ca₁₂O₁₂ nanocage and doped TM- Ca₁₁O₁₂ (TM=Sc to Zn) nanocage for sensing NO, CO, and HCN molecules. To satisfy the tetragonal rule, the nanocage under study is made up of 6-tetragonal and 8-hexagonal rings that collaborate to construct a nanocage Fig. 1(A). The optimized geometry configurations of pristine Ca₁₂O₁₂ were initially calculated. As depicted in Fig. 1(A), in Ca12O12 the oxygen and calcium bond that are shared between 6- and 6membered rings is 2.22 Å, 4- and 6-membered rings is 2.26 Å. The bond lengths are found to agree with previous computational results. [26,69-72]. The Eg value for $Ca_{12}O_{12}$ is 4.09 eV; the determined Eg agrees with earlier studies [69,70].

3.2. CO, NO, HCN Adsorption on the Pristine $Ca_{12}O_{12}$

Subsequently, Ca₁₂O₁₂ nanocages' adsorption structure and associated adsorption energies of NO, CO, and HCN were investigated. The optimized geometry configurations of these gases are depicted in Fig. 1(B-D). The corresponding energetic and structural characteristics of the optimized Ca₁₂O₁₂, CO, NO and HCN adsorbed on Ca₁₂O₁₂ nanocages are listed in Table 1, Fig. 2(A-C), and the atomic coordinates are listed in Table S2 in SI. The adsorption energies of the CO, NO, and HCN molecules on the Ca₁₂O₁₂ nanocage are -0.404, -0.671, and -0.423 eV, respectively, indicating the physical adsorption of the molecules onto the nanocluster. The negative binding energy values are indicative of the exothermic reaction. The adsorption energies indicate that this compound is weakly bound onto the Ca₁₂O₁₂ nanocage. The Ca₁₂O₁₂ nanocage was found to bind to NO, CO, and HCN molecules at distances of 2.79 Å, 2.83 Å, and 2.66 Å, in that order. To further recognize the electronic interactions between the NO, CO, and HCN molecules and the pure Ca₁₂O₁₂ nanocages, the (HOMOs) and (LUMOs) are assessed. The (E_{HOMO}), (E_{LUMO}), (E_F), and energy gap (Eg) values at the DFT/B3LYP-GD3 level are illustrated in Table 1. Figure 3 displays the (PDOS), (HOMOs) and (LUMOs) surfaces for the free NO, CO, and HCN gases; Figure 4 displays the same information for the CO/Ca₁₂O₁₂, NO/Ca₁₂O₁₂, and HCN/Ca₁₂O₁₂ complexes. While the HOMO is mostly found on the O atoms, the LUMO is split evenly between the O and Ca atoms. The pure $Ca_{12}O_{12}$'s (HOMO) and(LUMO) are found at -5.28 and -1.19 eV, respectively, according to Fig. 3a.



Fig. 1. Optimized structures of (A) Ca₁₂O₁₂ nanocage, (B) NO, (C) CO, and (D) HCN gases at (DFT/B3LYP-GD3/6-311+G (d) D3. Atoms are labelled as seen above

Table 1.

Structural and energetic parameters of the optimized, CO, NO, and HCN gases, Ca₁₂O₁₂, NO/ Ca₁₂O₁₂, CO/ Ca₁₂O₁₂, and HCN/ Ca₁₂O₁₂ hanocages. All distances (D, Å), adsorption energies ($E_{ads.}$, eV), and dipole moment (μ , Debye).

| System | E _{ads.} | D _(0 -X0) | $D_{(Ca-XO)}$ | D _(X-O) | μ |
|---------------------------------------|-------------------|----------------------|---------------|--------------------|--------|
| Ca ₁₂ O ₁₂ | - | - | - | 2.22 | 0.0004 |
| NO | - | - | - | 1.128 | 0.0983 |
| со | - | - | - | 1.148 | 0.0715 |
| HCN | - | - | - | 1.060,1.149 | 3.081 |
| NO/ Ca ₁₂ O ₁₂ | -0.671 | 2.686 | 2.792 | 1.182 | 2.816 |
| CO/ Ca ₁₂ O ₁₂ | -0.404 | 2.288 | 2.834 | 1.141 | 2.267 |
| HCN/ Ca ₁₂ O ₁₂ | -0.423 | 4.001 | 2.659 | 1.069,1.146 | 5.203 |
| (A) | | (B) | | (C) | |



Fig.2. Optimal structures of : (A) NO/Ca₁₂O₁₂, (B) CO/Ca₁₂O₁₂, and (C) HCN/Ca₁₂O₁₂. All distances are in Å.



Fig. 3. The (HOMO), (LUMO) and (PDOS) surfaces for relaxed structures of (a) $Ca_{12}O_{12}$, adsorbate gases: (b) free CO, (c) free NO and (d) free HCN at B3LYP/6-311+G(D)D3 level of



Fig. 4. (HOMO), and (LUMO) surfaces for $CO/Ca_{12}O_{12}$, $NO/Ca_{12}O_{12}$, and $HCN/Ca_{12}O_{12}$ and (PDOS) for (a) CO in $CO/Ca_{12}O_{12}$, (b) $Ca_{12}O_{12}$ in $CO/Ca_{12}O_{12}$, (c) NO in $NO/Ca_{12}O_{12}$, (d) $Ca_{12}O_{12}$ in $NO/Ca_{12}O_{12}$ (e) HCN in $HCN/Ca_{12}O_{12}$, (f) $Ca_{12}O_{12}$ in $HCN/Ca_{12}O_{12}$.

The two occupied states, -10.54 and -13.50 eV, which correspond to the free CO molecule are shown in Fig. 3(b). The CO interaction in the CO-Ca₁₂O₁₂ complex caused to relocate, as seen in Fig. 4(a) to -11.25 and -13.50 eV, respectively, in the CO/Ca₁₂O₁₂ complex. In contrast, Fig. 4(b) shows the LUMO and HOMO of Ca₁₂O₁₂ in CO/Ca₁₂O₁₂ to be at -5.28 and -1.19 eV, respectively. The CO molecule plays no part in the HOMO of CO/Ca₁₂O₁₂, which is (-5.28 eV) at the Ca₁₂O₁₂; the LUMO (-1.19 eV) is mostly localized to the CO molecule. For CO-Ca₁₂O₁₂, the HOMO is localized across the surface, whereas the LUMO is localized on CO. As can be seen in Figs. 3(c) and 4(c), where the LUMO and HOMO of NO in NO/Ca₁₂O₁₂ are found to be -4.61 and – 1.07 eV, respectively, because of adsorption The Ca₁₂O₁₂ DOS changes significantly , whereas the NO gas DOS changes just little. Furthermore, for NO/Ca₁₂O₁₂, the HOMO is -4.61 eV and is solely found in NO gas. In the NO/Ca₁₂O₁₂ system, the HOMO was localized on the NO surface exclusively, while the LUMO was unlocalized at both the NO and Ca₁₂O₁₂ surfaces. Moreover, there is a DOS significant variation before (Fig. 3d) and after (Fig. 4 e) for the interaction of HCN with

 $Ca_{12}O_{12}$. The LUMO and HOMO of $Ca_{12}O_{12}$ in HCN/ $Ca_{12}O_{12}$, which are situated at -1.19 and -5.28 eV, respectively, are likewise impacted by the interaction (Fig. 4f). In addition, the HCN/ $Ca_{12}O_{12}$ complex's HOMO surface is (-5.28 eV) related to the $Ca_{12}O_{12}$ states, meaning it is only located at the $Ca_{12}O_{12}$, where the LUMO is (-1.19 eV) for both the $Ca_{12}O_{12}$ and the HCN gas states, meaning it is less dispersed across the cluster surface. For HCN, HOMO is localized only on the $Ca_{12}O_{12}$ surface, while LUMO is unlocalized at both the HCN and $Ca_{12}O_{12}$ surfaces.

Due to its poor adsorption of CO, NO, and HCN, the $Ca_{12}O_{12}$ nanocage will be insufficient to capture or store the three hazardous gases. Table 3 provides the tabulated global reactivity descriptors, which simply offer the data needed to appropriately predict the reactivity and stability of all the structures under consideration. Great levels of global softness correlate to great stability with low reactivity, limited global hardness and ionization potential values indicate a system with limited stability and strong reactivity [73–76]. The calculated global reactivity for pristine $Ca_{12}O_{12}$ is like those previously reported [77]. Table 3 revealed the estimated values hardness, which were found to be 2.05, 4.69, 1.48, and 4.99 eV. Additionally, the ionization potential values for free pure $Ca_{12}O_{12}$, CO, NO, and HCN were determined to be 5.28, 10.54, 6.18, and 10.19 eV. The corresponding hardness and ionization potential values for $CO/Ca_{12}O_{12}$ (5.17 and 2.07 eV), $NO/Ca_{12}O_{12}$ (4.61 and 1.77 eV), and HCN/ $Ca_{12}O_{12}$ (4.83 and 1.94 eV) were found, however, following the adsorption of the CO, NO, and HCN on the nanocages. While $CO/Ca_{12}O_{12}$'s lowest values demonstrate its highest reactivity.

3.3. Transition Metals (TM=Sc to Zn) Doped Ca₁₂O₁₂

The Ca atoms were then substituted by Transition Metals (TM=Sc to Zn) in the Ca₁₂O₁₂ cages preparing TMCa₁₁O₁₂, the full optimization structures of which are illustrated in Fig. 5 and their electronic properties are listed in Tables 2 and 3. The spin multiplicity, electronic arrangement, spin state, electronic state, and total electronic energy of TM in the gas phase are shown in Table S3 in SI. As can be seen in Table 2, the Ca–O bond length in pristine Ca₁₂O₁₂ was 2.266 Å which decreases to 1.946, 1.835, 1.812, 1.825, 1.845, 1.856, 1.887, 1.853, 1.901, and 1.931 Å for the TM–O bond in TM Ca₁₁O₁₂ (TM=Sc to Zn), respectively. The findings demonstrate how doping influences the cluster shape, where the bond lengths of TM-O and TM-Ca are shorter than those of the corresponding Ca-O and Ca-Ca bonds. That is, local deformation in the clusters is caused by the doping of TM, and this could be because the doping TM atom is small in size. As illustrated in Table 2, the estimated E_b for Ca₁₂O₁₂ is

-5.82 eV, while the doping increases its values by 2.54%, 3.56%, 2.85%, 3.03%, 1.99%, and 1.15% for ScCa₁₁O₁₂ to FeCa₁₁O₁₂, respectively. Moreover, E_b values decreased to -0.40%, -0.10%, -1.48%, and -1.51%, from CoCa₁₁O₁₂ to ZnCa₁₁O₁₂, respectively. Following TM doping, the binding energy E_b exhibits a rising trend, as can be seen from the result in Table 2, TiCa₁₁O₁₂Ca₁₁O₁₂ > CrCa₁₁O₁₂ > VCa₁₁O₁₂ > ScCa₁₁O₁₂ > MnCa₁₁O₁₂ > FeCa₁₁O₁₂ >NiCa₁₁O₁₂ >CoCa₁₁O₁₂ >CuCa₁₁O₁₂ >ZnCa₁₁O₁₂. Based on the negative values of E_b , we conclude that all the systems that are being studied are stable.

Table 2.

Structural and energetic descriptors of the optimized TM dopped Ca₁₁O₁₂ nanocages. All distances (D) are given in Å, binding energy (E_b , eV), formation energy (E_{form} , eV), the atomic charges (Q, |e|), and dipole moment (μ , Debye).

| System | E _b | Eform | DTM-0 | D _{TM} -Ca | Q _{TM} (a.u) | Q ₀ (a.u) | Q _{Ca} (a.u) | μ |
|-------------------------------------|----------------|--------|----------------|------------------------|-----------------------|----------------------|-----------------------|--------|
| Ca12O12 | -5.816 | | DCa-0 2.266 | <u>Dса-са</u> 3.222 | | -1.633 | 1.633 | 0.0004 |
| $ScCa_{11}O_{12}$ | -5.964 | -3.561 | 1.946 | 3.061 | 1.180 | -1.408 | 1.437 | 5.182 |
| $TiCa_{11}O_{12}$ | -6.023 | -3.646 | 1.835 | 2.969 | 0.834 | -1.243 | 1.449 | 5.338 |
| $VCa_{11}O_{12}$ | -5.982 | -2.666 | 1.812 | 3.020 | 1.008 | -1.220 | 1.299 | 4.404 |
| CrCa ₁₁ O ₁₂ | -5.992 | -2.556 | 1.825 | 2.999 | 0.598 | -1.217 | 1.527 | 3.762 |
| $\mathbf{MnCa}_{11}\mathbf{O}_{12}$ | -5.932 | -1.536 | 1.845 | 2.952 | 0.891 | -1.309 | 1.518 | 3.257 |
| $FeCa_{11}O_{12}$ | -5.883 | -0.296 | 1.856 | 2.906 | 0.840 | 1.575 | -1.349 | 3.765 |
| $CoCa_{11}O_{12}$ | -5.790 | 1.909 | 1.887 | 2.906 | 0.962 | 1.591 | -1.399 | 3.115 |
| NiCa ₁₁ O ₁₂ | -5.810 | 1.452 | 1.853 | 2.929 | 0.863 | 1.593 | -1.364 | 2.921 |
| $CuCa_{11}O_{12}$ | -5.730 | 3.386 | 1.901 | 2.907 | 1.072 | 1.605 | -1.443 | 2.541 |
| $\mathbf{ZnCa_{11}O_{12}}$ | -5.728 | 3.436 | 1.931 | 2.876 | 1.337 | 1.608 | -1.538 | 2.174 |

Table 3.

(HOMOs) (E_H, eV), (LUMOs) (E_L, eV), (HOMO-LUMO) energy gap (Eg, eV), Fermi level (Ef, eV), electron affinity (EA, eV), Ionization potential (IP, eV), chemical hardness (η , eV), softness (S, eV⁻¹), chemical potential (μ , eV) and the electrophilic index (ω , eV) of Ca₁₂O₁₂, free gases, NO,CO,HCN/ Ca₁₂O₁₂

| System | EH | EL | Eg | EF | IP | EA | η | S | μ | ω |
|--------------|---------|--------|-------|---------|--------|--------|-------|-------|---------|-------|
| Ca12O12 | -5.282 | -1.189 | 4.093 | -3.236 | 5.282 | 1.189 | 2.047 | 0.244 | -3.236 | 2.558 |
| NO | -6.185 | -3.233 | 2.951 | -4.709 | 6.185 | 3.233 | 1.476 | 0.339 | -4.709 | 7.512 |
| со | -10.545 | -1.155 | 9.390 | -5.85 | 10.545 | 1.155 | 4.695 | 0.106 | -5.850 | 3.645 |
| HCN | -10.189 | -0.207 | 9.982 | -5.198 | 10.189 | 0.207 | 4.991 | 0.100 | -5.198 | 2.707 |
| NO/ Ca12O12 | -4.610 | -1.074 | 3.536 | -2.842 | 4.610 | 1.074 | 1.768 | 0.283 | -3.096 | 2.284 |
| CO/ Ca12O12 | -5.166 | -1.026 | 4.140 | -3.096 | 5.166 | 1.026 | 2.070 | 0.241 | -2.842 | 2.315 |
| HCN/ Ca12O12 | -4.833 | -0.956 | 3.877 | -2.8945 | 4.833 | 0.956 | 1.938 | 0.258 | -2.8945 | 2.161 |
| ScCa11O12 | -2.043 | -1.068 | 0.975 | -1.556 | 2.043 | 1.068 | 0.487 | 1.026 | -1.556 | 2.482 |
| TiCa11O12 | -2.251 | -1.140 | 1.111 | -1.696 | 2.251 | 1.1401 | 0.555 | 0.900 | -1.696 | 2.588 |
| VCa11O12 | -3.766 | -1.293 | 2.473 | -2.529 | 3.766 | 1.293 | 1.237 | 0.404 | -2.529 | 2.587 |
| CrCa11O12 | -2.618 | -1.041 | 1.577 | -1.829 | 2.618 | 1.041 | 0.788 | 0.634 | -1.829 | 2.123 |
| MnCa11O12 | -4.058 | -1.155 | 2.902 | -2.607 | 4.058 | 1.155 | 1.451 | 0.344 | -2.607 | 2.341 |
| FeCa11O12 | -3.136 | -1.062 | 2.073 | -2.099 | 3.136 | 1.062 | 1.037 | 0.482 | -2.099 | 2.125 |
| CoCa11O12 | -4.104 | -1.004 | 3.100 | -2.554 | 4.104 | 1.004 | 1.550 | 0.323 | -2.554 | 2.104 |
| NiCa11O12 | -3.986 | -1.034 | 2.952 | -2.510 | 3.986 | 1.034 | 1.476 | 0.339 | -2.510 | 2.134 |
| CuCa11O12 | -4.904 | -1.041 | 3.863 | -2.973 | 4.904 | 1.041 | 1.932 | 0.259 | -2.973 | 2.287 |
| ZnCa11O12 | -5.029 | -1.017 | 4.012 | -3.023 | 5.029 | 1.017 | 2.006 | 0.249 | -3.023 | 2.278 |



Fig.5. The optimized structures for $Ca_{12}O_{12}$ and $TMCa_{11}O_{12}$ (TM=Sc to Zn) computed at the B3LYP/6-311+G(D)D3 level of theory.

The NBO evaluation has been presented to determine the atomic charges for the inspected clusters. The positive charges on TM atoms, negative charges on the nearest O atoms and positive charges on the nearest Ca atoms. It was found that the TM atoms in TMCa₁₁O₁₂ (TM=Sc, Ti, V, Cr, and Mn) have +ve charges, while the nearest O atoms have -ve charges and the nearest Ca atoms have positive charges. It was discovered that the TM atoms in TMCa₁₁O₁₂ (TM=Fe, Co, Ni, Cu, and Zn) have +ve charges, the nearest O atoms have +ve charges while the nearest Ca atoms have negative charges. These findings validate charge transfer from TM to Ca₁₁O₁₂ and show that on Ca₁₁O₁₂, where the TM d orbitals overlap with the TM-O bonds sp4 orbitals to form the mixed sp4d hybridization and with the TM-Ca

bonds 4s2 orbitals to form the mixed 4p2d hybridization, the TM atoms donate electrons to the neighboring Ca and O atoms. Table 3 provides the tabulated global reactivity descriptors for TM Ca₁₁O₁₂ (TM=Sc to Zn). The estimated IP for Ca₁₁O₁₂ (5.282) lowered by 3.24, 3.03, 1.52, 2.66, 1.22, 2.15, 1.18, 1.30, 0.378, 0.253 from Sc Ca₁₂O₁₂ to Zn Ca₁₂O₁₂, respectively. Furthermore, EA (1.189) lowered by 0.12,0.05, -0.10, 0.15, 0.03, 0.13, 0.18, 0.15, 0.15, 0.17, respectively. In addition, η (2.047) lowered by 1.56, 1.49, 0.81, 1.26, 0.60, 1.01, 0.50, 0.57, 0.11, 0.04, respectively. While S increased by 0.78, 0.66, 0.16, 0.39, 0.10, 0.24, 0.08, 0.10, 0.02, 0.01, respectively. The preceding description indicates that all the structures under examination are stable.

We then looked at the impact of TM doping on the Ca₁₁O₁₂ nanocages electrical properties. For every nanocage that was considered, the (DOS) plots and the distribution of HOMO-LUMO are displayed in Figs (6,7). The energies of the HOMO and LUMO, as well as the ensuing energy gap (E_g), were calculated from the DOS spectra and are shown in Table 3. About 0.98 eV, 1.11 eV, 2.47 eV, 1.58 eV, 2.90 eV, 2.07 eV, 3.10 eV, 2.95 eV, 3.86 eV, and 4.01 eV are the E_g values of TM Ca₁₁O₁₂ (TM=Sc to Zn), in that order. Moreover, Table 3 clearly shows that doping TM atoms on nanocages significantly reduces the E_g . The largest E_g reduction occurs when titanium and scandium atoms doped on the nanocages (0.98 eV and 1.11 eV), but the minimum E_g reduction occurs when a zinc atom is doped (4.01 eV). This indicates that the kind of TM atom determines how much E_g is reduced. Therefore, the electrical conductance of all TM rises in the presence of the TM atom. The doping of TM atoms on Ca₁₁O₁₂, except for Cu and Zn, appears to release electron charge on the nanocluster and create a new HOMO level with a high energy level situated between the pure nanocage's LUMO and original HOMO, as depicted in Figs (6,7). This new HOMO level could be the cause of the notable decline in E_g values.

We employ, for instance, $Ca_{12}O_{12}$, Ti, Fe, and NO-Cr $Ca_{11}O_{12}$ to confirm the stability of the $Ca_{12}O_{12}$, TM- $Ca_{11}O_{12}$ and NO-Cr $Ca_{11}O_{12}$ nano-cages. To do this, we compute the potential energy fluctuation with time at 300 K using the atom-centered density matrix propagation molecular dynamics model (ADMP), as shown in Fig. 8. Additionally provided are the atomic configurations following 300 fs. The examined nano-cages are found to be stable, as evidenced by the lack of deformation in their atomic structures and the negligible potential energy variation over time.

An important factor in determining a material's electrical conductivity (σ) is the energy gap (E_g) value. The link between a material's E_g and σ may be represented mathematically as follows [78]:

$$\sigma \propto exp\left(\frac{-E_g}{2kT}\right) \tag{18}$$

where k and T are Boltzmann's constant and the temperature, respectively. According to equation Eq. (18), a smaller H-L gap value leads to higher σ at a given temperature T. The electric conductivity of the doped Sc/Ca₁₁O₁₂ to Zn/Ca₁₁O₁₂ structures is indicated that the σ for Sc/Ca₁₁O₁₂ to Zn/Ca₁₁O₁₂ clusters is higher than that of the Ca₁₂O₁₂ cluster.



Fig.6 the (HOMOs), (LUMOs) distribution and density of states (DOS) plots for all considered nanocages.

3.4 CO, NO, and HCN adsorption on doped TM Ca₁₁O₁₂ nanocages

For figuring out how much the CO, NO, and HCN molecules interact with the doped $TMCa_{11}O_{12}$ nanocages. The computation of the interaction energies was done using the optimized geometries at the B3LYP-GD3 /6-311+G(d) level. Tables 4-6 show the estimated adsorption energies (E_{ads}) for the molecules CO/TMCa₁₁O₁₂, NO/TMCa₁₁O₁₂, and

HCN/TMC $a_{11}O_{12}$, in that order. The corresponding optimized geometries are displayed in Figs. 9-11. It should be noted that the density functionals B3LYP were employed in the counterpoise.



The results of Table 4 indicate that the CO molecule's adsorption energies on $ScCa_{11}O_{12}$ to $ZnCa_{11}O_{12}$ vary from -0.172 to -2.616 eV. The estimated energy only slightly decreases when the BSSE-corrected values are detected within the same range. The BSSE-corrected energies are found to be between -0.158 and -2.614eV for $ScCa_{11}O_{12}$ to $ZnCa_{11}O_{12}$ surfaces. The observed minima and maxima values in the CO/TMCa_{11}O_{12} adsorption energies are explained by the specific effects caused by the various types of TM. The minima adsorption energy is observed in the case of CO/ZnCa_{11}O_{12}(-0.172 eV), the maxima adsorption energy is observed for $CrCa_{11}O_{12}$ (-2.616 eV). Doping improves adsorption by chemically adsorbing

CO on TMCa₁₁O₁₂ (TM=Sc-Cu) at 1.71Å to 2.28Å distances, whereas the ZnCa₁₁O₁₂ is physically bonded having values of $E_{ads} < -0.2 \text{ eV}$) [79] at distance 3.24Å.



Fig. 8. Potential energy fluctuations during MD simulation at 300 K and the atomic configuration after 300 fs of (a) $Ca_{12}O_{12}$, (b) Ti- $Ca_{11}O_{12}$, (c) Fe- $Ca_{11}O_{12}$, (d) Cr- $Ca_{11}O_{12}$.

Table 4.

Structural and energetic descriptors of the optimized CO adsorbed on TMCa₁₁O₁₂ nano-cages. All distances (D, Å), The adsorption energy ($\Delta E_{ads.}, eV$), (E_H, eV), (E_L, eV), (E_g, eV), NBO charges (Q, |e|) and dipole moment (μ , Debye). ($\Delta E_{ads.}$) calculated at the DFT/B3LYP-D3/6-311+G (d) level of theory

| System | $(E_{ads.})_{un}$ | $(E_{ads.})_{cor}$ | BSSE | D(TM-Ca) | D _(TM-O) | D(TM-CO) | D(C-0) | \mathbf{E}_{H} | EL | $\mathbf{E}_{\mathbf{g}}$ | Q_{TM} | μ |
|---------------------------------------|-------------------|--------------------|--------|----------|---------------------|----------|--------|---------------------------|--------|---------------------------|----------|-------|
| CO/ScCa11O12 | -0.953 | -0.925 | 0.028 | 3.089 | 2.007 | 2.280 | 1.176 | -1.891 | -1.240 | 0.651 | 1.109 | 9.334 |
| CO/TiCa11O12 | -1.055 | -1.020 | 0.035 | 3.060 | 1.943 | 2.045 | 1.176 | -1.827 | -1.304 | 0.523 | 0.710 | 9.008 |
| CO/VCa11O12 | -1.006 | -0.971 | 0.035 | 3.041 | 1.802 | 1.966 | 1.153 | -4.025 | -1.391 | 2.634 | 0.623 | 7.227 |
| CO/CrCa ₁₁ O ₁₂ | -2.616 | -2.614 | 0.002 | 2.945 | 1.880 | 1.771 | 1.181 | -2.659 | -1.240 | 1.419 | 0.381 | 9.274 |
| CO/MnCa ₁₁ O ₁₂ | -1.972 | -1.940 | 0.032 | 2.978 | 1.900 | 1.732 | 1.172 | -3.577 | -1.159 | 2.418 | 0.403 | 7.074 |
| CO/FeCa ₁₁ O ₁₂ | -1.440 | -1.396 | 0.044 | 3.006 | 1.926 | 1.710 | 1.161 | -2.681 | -0.807 | 1.874 | 0.385 | 5.468 |
| CO/CoCa11O12 | 0.908 | 0.850 | -0.059 | 2.957 | 2.180 | 1.820 | 1.145 | -3.155 | -1.083 | 2.072 | 0.633 | 3.873 |
| CO/NiCa11O12 | 4.852 | 4.852 | 0.097 | 2.752 | 1.890 | 1.837 | 1.217 | -2.474 | -1.148 | 1.326 | 0.495 | 8.593 |
| CO/CuCa11O12 | 3.665 | 3.760 | 0.095 | 2.816 | 1.950 | 1.954 | 1.213 | -2.672 | -0.983 | 1.689 | 0.721 | 8.564 |
| CO/ZnCa11O12 | -0.172 | -0.158 | 0.014 | 2.873 | 1.956 | 3.240 | 1.132 | -3.999 | -0.833 | 3.166 | 1.334 | 2.986 |
| | | | | | | | | | | | | |

The results of Table 5 indicate that the NO molecule's adsorption energies on ScCa₁₁O₁₂ to ZnCa₁₁O₁₂ vary from -0.149 to -4.072 eV. The estimated energy only slightly decreases when the BSSE-corrected values are detected within the same range. The BSSE-corrected energies are found to be between -0.138 and -4.060 eV for ScCa₁₁O₁₂ to ZnCa₁₁O₁₂ surfaces. The observed minima and maxima values in the NO-TMCa₁₁O₁₂ adsorption energies are explained by the specific effects caused by the various types of TM. The minima adsorption energy is observed in the case of NO/ZnCa₁₁O₁₂(-0.149 eV), the maxima adsorption energy is reported for CrCa₁₁O₁₂ (-4.072 eV). Doping improves adsorption by chemically adsorbing NO on TMCa₁₁O₁₂ (TM=Sc-Cu) at distance from 1.611Å to 2.111Å, whereas the ZnCa₁₁O₁₂ is physically adsorbed having E_{ads} values of -0.138 eV at distance 4.431Å.

Table 5.

Structural and energetic descriptors of the optimized NO adsorbed on TMCa₁₁O₁₂ nano-cages. All distances (D, Å), $(\Delta E_{ads.}, eV)$, (E_H, eV), (E_L, eV), (Eg, eV), NBO charges (Q, |e|) and dipole moment (μ , Debye). ($\Delta E_{ads.}$) calculated at the DFT/B3LYP-GD3/6-311+G (d) level of theory.

| System | $(E_{ads.})_{un}$ | $(E_{\it ads.})_{\it cor}$ | BSSE | D _(TM-Ca) | D _(TM-0) | D _(TM-NO) | D(N-0) | $\mathbf{E}_{\mathbf{H}}$ | EL | Eg | Q_{TM} | μ |
|----------------------|-------------------|----------------------------|--------|----------------------|---------------------|----------------------|--------|---------------------------|--------|-------|----------|--------|
| NO/ScCa11O12 | -1.577 | -1.537 | 0.040 | 3.089 | 2.021 | 2.111 | 1.207 | -2.659 | -1.239 | 1.420 | 1.252 | 9.381 |
| NO/TiCa11O12 | -2.642 | -2.601 | 0.041 | 3.083 | 1.815 | 1.969 | 1.205 | -4.704 | -1.455 | 3.249 | 1.043 | 8.901 |
| NO/VCa11O12 | -3.424 | -3.376 | 0.048 | 2.977 | 1.893 | 1.666 | 1.228 | -2.778 | -1.321 | 1.457 | 0.726 | 11.428 |
| NO/CrCa11O12 | -4.072 | -4.060 | 0.012 | 3.012 | 1.911 | 1.703 | 1.213 | -3.313 | -1.214 | 2.099 | 0.687 | 8.736 |
| NO/MnCa11O12 | -2.014 | -2.197 | -0.183 | 3.023 | 1.934 | 1.611 | 1.199 | -3.140 | -0.971 | 2.169 | 0.549 | 7.138 |
| $NO/FeCa_{11}O_{12}$ | -1.956 | -1.914 | 0.042 | 2.969 | 1.947 | 1.843 | 1.198 | -3.973 | -1.489 | 2.484 | 0.793 | 6.861 |
| NO/CoCa11O12 | -1.109 | -1.125 | -0.016 | 2.882 | 1.859 | 1.746 | 1.203 | -4.321 | -1.505 | 2.816 | 0.782 | 4.753 |
| NO/NiCa11O12 | -1.225 | -1.186 | 0.039 | 2.946 | 1.955 | 1.872 | 1.162 | -4.289 | -0.864 | 3.425 | 0.910 | 2.817 |
| $NO/CuCa_{11}O_{12}$ | 0.330 | 0.377 | 0.046 | 2.924 | 1.985 | 1.826 | 1.152 | -4.634 | -2.562 | 2.072 | 0.841 | 2.106 |
| NO/ZnCa11O12 | -0.149 | -0.138 | 0.011 | 2.880 | 1.957 | 4.431 | 1.150 | -5.053 | -3.628 | 1.424 | 1.338 | 1.953 |

Furthermore, the results of Table 6 show that the HCN molecule's adsorption energies on $ScCa_{11}O_{12}$ to $ZnCa_{11}O_{12}$ vary from -0.055 to -2.556 eV. The estimated energy only slightly decreases when the BSSE-corrected values are detected within the same range. The BSSE-corrected energies are found to be between -0.067 and -2.519 eV for $ScCa_{11}O_{12}$ to $ZnCa_{11}O_{12}$ surfaces. The observed minima and maxima values in the HCN-TMC $a_{11}O_{12}$ adsorption energies are explained by the specific effects caused by the various types of TM. The minima adsorption energy is observed in the case of HCN/ZnC $a_{11}O_{12}$ (-0.055 eV), however the maxima adsorption energy is reported for $CrCa_{11}O_{12}$ (TM=Sc-Cu) at distance from 1.782Å to 2.945Å, whereas the ZnC $a_{11}O_{12}$ is physically adsorbed having E_{ads} values of -0.055 eV at distance 2.693Å.

The results obviously disclosed that the $CrCa_{11}O_{12}$ has the strongest interactions with the CO and NO molecules at B3LYP, whereas HCN/TiCa_{11}O_{12} has the strongest interactions at

B3LYP functional. While $ZnCa_{11}O_{12}$ indicates the least interaction with the CO and NO at the B3LYP. Because of its strong redox characteristics and catalytic activity, chromium usually exceeds titanium in terms of sensitivity and response time, especially to a variety of gases such as CO and NO. However, Zn has lower catalytic activity than other transition metals. The inclusion of a doped TM in the nanocage wall may cause the $Ca_{12}O_{12}$ nanocages to become functionalized, according to all the results of the structural stability test, this makes it a viable material for nanodevice applications. These outcomes are explained by the following factors:

Table 6.

Structural and energetic descriptors of the optimized HCN adsorbed on TMCa₁₁O₁₂ nano-cages. All distances (D, Å), ($E_{ads.}, eV$), (E_{H_s}, eV), (E_{L_s}, eV), ($E_{$

| System | $(E_{ads.})_{un}$ | $(E_{ads.})_{cor}$ | BSSE | D _(TM-Ca) | D _(TM-O) | D(TM-HCN) | D _(C-N) | E _H | EL | Eg | Q_{TM} | μ |
|--|-------------------|--------------------|--------|----------------------|---------------------|-----------|--------------------|----------------|--------|-------|----------|-------|
| HCN/ScCal1O ₁₂ | -2.098 | -2.072 | 0.026 | 3.076 | 2.002 | 2.132 | 1.217 | -2.341 | -1.245 | 1.096 | 1.429 | 9.564 |
| HCN/TiCa ₁₁ O ₁₂ | -2.556 | -2.519 | 0.037 | 3.045 | 1.887 | 2.015 | 1.217 | -1.958 | -1.357 | 0.601 | 1.152 | 9.118 |
| HCN/VCa11O12 | -0.637 | -0.778 | -0.141 | 3.041 | 2.339 | 1.966 | 1.153 | -3.529 | -1.239 | 2.289 | 0.996 | 5.026 |
| HCN/CrCa11O12 | -2.232 | -2.148 | 0.084 | 2.980 | 1.890 | 1.783 | 1.210 | -2.488 | -1.198 | 1.290 | 0.827 | 7.721 |
| HCN/MnCa ₁₁ O ₁₂ | -0.621 | -0.635 | -0.014 | 2.982 | 1.926 | 1.799 | 1.172 | -3.073 | -1.020 | 2.053 | 0.806 | 2.264 |
| HCN/FeCa ₁₁ O ₁₂ | -0.419 | -0.394 | 0.025 | 3.001 | 1.945 | 1.782 | 1.161 | -3.012 | -0.969 | 2.043 | 0.754 | 0.205 |
| HCN/CoCa ₁₁ O ₁₂ | -0.156 | 0.179 | 0.335 | 2.953 | 1.982 | 1.978 | 1.152 | -3.854 | -0.922 | 2.932 | 0.839 | 1.543 |
| HCN/NiCa11O12 | -0.899 | -0.891 | 0.008 | 2.935 | 1.847 | 2.901 | 1.154 | -4.546 | -1.262 | 3.283 | 0.880 | 9.871 |
| HCN/CuCa ₁₁ O ₁₂ | -0.883 | -0.871 | 0.012 | 2.907 | 1.909 | 2.945 | 1.154 | -5.307 | -1.241 | 4.066 | 1.084 | 9.453 |
| HCN/ZnCa11O12 | -0.055 | -0.067 | -0.012 | 2.882 | 1.975 | 2.693 | 1.148 | -4.822 | -0.907 | 3.915 | 1.334 | 2.402 |
| | | | | | | | | | | | | |



Fig. 9 The optimal structures of the CO/TMCa₁₁O₁₂ (TM=Sc-Zn), at the B3LYP/6-311+G(D)D3 level of theory.



Fig. 10 The optimal structures of the NO/TMCa₁₁O₁₂ (TM=Sc-Zn) - at the B3LYP/6-311+G(D)D3 level of theory.



Fig. 11 The optimal structures of the HCN/TMCa₁₁O₁₂ (TM=Sc-Zn) - at the B3LYP/6-311+G(D)D3 level of theory.

3.4.1. The dipole moment of adsorbates and substrates

The strength of interactions inside complexes can be predicted thanks to molecular dipole moments [70,71]. The dipole moment (μ) of a molecule is a crucial factor in determining its reactivity with its surroundings. The dipole moments of the related systems were estimated using the optimized geometry of DFT/B3LYP-GD3. The results are displayed in Tables 1, 2 and 4-6. The findings show that pristine Ca₁₂O₁₂ is nonpolar, with a dipole moment of (0.0004D). This is because there is no charge separation and the Ca₁₂O₁₂

nanocluster is centrosymmetric, which invalidates the consequent dipole moment from negatively charged O atoms and positively charged Ca.

Table 1 displays the μ values for the molecules of NO, CO, and HCN, which are 0.098, 0.072, and 3.081 Debye, respectively. But since TM-doped nanocages are polar by nature, doping Ca₁₁O₁₂ led to a notable rise in the dipole moment. Following TM doping, the dipole moment increased from 2.174 to 5.338 Debye (Table 2), which is consistent with the significant dipole moments seen in TiCa₁₁O₁₂ complexes. It's interesting to note that, as Tables 4-6 make evident, the dipole moment for each complex greatly increased following the adsorption of the CO, NO, and HCN molecules on TMCa₁₁O₁₂. However, significant dipole moments were found in HCN/NiCa₁₁O₁₂ (9.871D), NO/V Ca₁₁O₁₂ (11.428 D), and CO/ScCa₁₁O₁₂ (9.334 D). In conclusion, the obtained results indicate that doping affects the dipole moment, which can change the molecular species' electrical properties.

3.4.2. The analysis of natural bond orbital (NBO) charge

Table S4 in SI shows the outcomes of the (NBO) investigation, which was done to find out the adsorbed gases atomic charges and the exact adsorbing site of the $C_{12}O_{12}$. The charges for the CO molecule are (0.478, - 0.478), for the NO molecule are (0.186, -0.186), and for HCN are (0.217, 0.095, -0.312) |e|, respectively. The E_{ads} values follow a sequence NO > HCN > CO for $Ca_{12}O_{12}$ (Table 1). The average charges of the TM (Table 2) for TM- $C_{11}O_{12}$ systems were altered from 0.598 to 1.337|e|. Therefore, the doped $Ca_{12}O_{12}$ has larger Eads than the non-doped Ca₁₂O₁₂. In addition to the CO/TMCa₁₁O₁₂, NO/TMCa₁₁O₁₂, and HCN/TMC₁₁O₁₂ complexes, investigating the electronic arrangements of TM atoms in the TM-Ca₁₁O₁₂ is intriguing. Table S5 in SI illustrates the electronic configurations of the CO-TM-Ca₁₁O₁₂, NO-TM-Ca₁₁O₁₂, and HCN-TM-Ca₁₁O₁₂. The 4s and 3d orbitals hybridization, with a minor 4p and 5p contribution, provides the most obvious changes in the electronic configurations compared to the configurations of free atom. This is noticeable from the results in Table S5 in SI, which have been computed applying the outcomes of an examination of the (NBOs) [80-82]. This study found that the electronic configurations of free metal differed significantly from that of adsorbed metal. Charge transfer is visible in the metal's 4s and 3d orbitals. This is also compatible with the bonds that exist between the TM atom and its normal sites, which are dominated by the transition metal's polarization generated by the existence of $Ca_{12}O_{12}$.

3.4.3. Frontier orbitals and DOS

Figs. S1, S2 and S3 in SI provide an additional investigation of the impact of adsorbed gases on the adsorbent complexes by displaying the LUMOs and HOMOs surfaces for

CO/TMCa₁₁O₁₂, NO/TMCa₁₁O₁₂, and HCN/TMCa₁₁O₁₂ nanocage (TM = Sc to Zn), while Fig. S4 and S5 in SI shows the corresponding DOS. As shown in Fig. S1 in SI the HOMOs are strongly localized on both CO and TM (Sc, V, Cr, Mn, Fe, Cu and Zn). While there is strong delocalization of the LUMOs on both CO and TM (Sc, V, Cr, Mn, Fe, Cu and Zn). HOMO and LUMO are strongly localized on both CO and Co and Ni atoms. In CO-TMCa₁₁O₁₂ systems(Table 4), the HOMOs move by (0.15,0.42, -0.26,-0.04,0.48,0.45, 0.95, 1.51, 2.23, 1.03 eV), respectively, while the LUMOs move by (-0.17, -0.16, -0.10, -0.20,-0.05, -0.25, -0.08, -0.11, 0.06, 0.18 eV), respectively, the E_g values changed by (-33.2%, -55.9%, 6.5%,-10.0%, -16.7%, -9.6%, -33.2%, -55.1%, -56.3%, -21.1%), respectively.

As shown in Fig. S2 in SI the HOMOs are strongly localized and LUMOs are strong delocalization on both NO and TM (Sc, Ti, V, Cr, Mn), While there is strong localization of the HOMO and the LUMOs on both NO and TM (Fe, Co, Ni, and Cu). Additionally, in NO/ZnCa₁₁O₁₂ the HOMOs are strongly localized on the surface of nanocage and strong delocalization on NO gas, while there is strong localization of the LUMOs only on NO gas and strong delocalization on ZnCa₁₁O₁₂. In NO-TMCa₁₁O₁₂ systems (Table 5) the HOMOs move by (-0.62, -2.45, 0.99, -0.70,-0.92, -0.84, -0.22, -0.30, 0.27, -0.02 eV), respectively, while the LUMOs move by (-0.17, -0.32, -0.03, -0.17, 0.18, -0.43, -0.50, 0.17, -1.52, -2.61 eV), respectively, the E_g values changed by (45.6%, 192.4%, -41.1%, 33.1%, -25.3%, 19.8%, -9.2%, 16.0%, -46.4%, -64.5%), respectively.

As shown in Fig. S3 in SI the LUMOs are strong delocalization on both HCN and all TMCa₁₁O₁₂ except TiCa₁₁O₁₂ and NiCa₁₁O₁₂, while there is strong localization of the HOMO on both HCN and all TMCa₁₁O₁₂ except ZnCa₁₁O₁₂. HOMO and LOMO are strong delocalization on HCN gas. In HCN-TMCa₁₁O₁₂ systems (Table 6), the HOMOs move by (-0.30, 0.29, 0.24, ,0.13, 0.98, 0.12, 0.25, -0.56, -0.40, 0.21 eV), respectively, while the LUMOs move by (-0.18, -0.22, 0.05, -0.16, 0.14, 009, 0.08, -0.23, -0.20, 0.11 eV), respectively, the E_g values changed by (12.4%, -45.9%, -7.4%, -18.2%, -29.3%, -1.4%, -5.4%, 11.2%, -5.2%, -2.4%), respectively.

3.4.4. Thermodynamic parameters

Then, we include the interaction Gibbs-free energies (G), enthalpies (H), and interaction entropies (S) in our study of interaction energies. Thermodynamic descriptors (defined as Gibbs-free energy change, Δ G), enthalpy change, and entropy change, Δ S) were measured at 298.15 K and P=1 atm for the adsorbed gases CO, NO, and HCN on TM-doped Ca₁₁O₁₂. Table 7 indicates that the Gibbs-free energies are negative, indicating spontaneous adsorption of gas molecules on the TM-doped Ca₁₁O₁₂. A larger Δ G value indicates a significant connection between the gas molecule and substrate. It is deemed to have stabilized when the values of enthalpy changes are greater than the values of the Gibbs-free energy. Numerically, ΔG , ΔH , and ΔS parameters for the CO/CuCa₁₁O₁₂ complex were found to be -60.780, -71.559, and -0.036 kcal/ mol, respectively. While for the NO/ScCa₁₁O₁₂ complex were found to be -66.793, -79.810, and -0.043 kcal/ mol, respectively. In addition, for the HNC/CrCa₁₁O₁₂ complex were found to be -42.336, -53.493, and -0.037 kcal/ mol, respectively. Positive value of ΔG indicates weak adsorption for NO/CoCa₁₁O₁₂, NO/CuCa₁₁O₁₂, NO/ZnCa₁₁O₁₂, CO/ZnCa₁₁O₁₂, HCN/CoCa₁₁O₁₂, and HCN/ZnCa₁₁O₁₂ complexes.

| T | 1.00 | L | т | - | - |
|-----|------|---|---|---|---|
| - E | а | n | | ρ | 1 |
| _ | | | - | ~ | |

| | Ľ1 | hermody | vnamic | analysis | of the | gases adsorbed | 1 on | TMCa ₁₁ C |)12 | nano-cage |
|--|----|---------|--------|----------|--------|----------------|------|----------------------|-----|-----------|
|--|----|---------|--------|----------|--------|----------------|------|----------------------|-----|-----------|

| System | ΔG (Kcal/mole) | $\Delta H(Kcal/mole)$ | ΔS(Cal/mole-K) |
|--|--|--|--|
| CO/ScCa11O12 | -34.468 | -40.290 | -19.529 |
| CO/TiCa11012 | -11.833 | -22.050 | -34.268 |
| CO/VCa11O12 | -20.675 | -30.718 | -30.841 |
| CO/CrCa11O12 | -51.652 | -63.426 | -39.492 |
| CO/MuCa ₁₁ O ₁₂ | -34.408 | -45.186 | -36.151 |
| CO/FeCanOn | -25.331 | -36.921 | -38.874 |
| CO/CoCa+O+ | -4.699 | -15 462 | -36,100 |
| CO/NiCanOn | -56,787 | -67.022 | -34.326 |
| CO/CuCanOn | -60.780 | -71.559 | -36,153 |
| CO/ZnCa11O12 | 5.113 | -3.950 | -30.397 |
| NO/ScCa ₁₁ O ₁₂ NO/TiCa ₁₁ O ₁₂ NO/VCa ₁₁ O ₁₂ NO/CrCa ₁₁ O ₁₂ NO/MnCa ₁₁ O ₁₂ NO/MnCa ₁₁ O ₁₂ NO/FeCa ₁₁ O ₁₂ NO/CoCa ₁₁ O ₁₂ NO/NCa ₁₂ O ₁₂ NO/NCa ₁₂ O ₁₂ NO/CuCa ₁₁ O ₁₂ | -66.793 -24.861 -31.203 -65.665 -42.158 -31.540 4.314 -54.862 5.957 6.399 | -79.810 -37.114 -43.953 -78.671 -53.079 -43.536 -5.051 -65.155 -6.795 -7.057 | -43.658 -41.096 -42.765 -43.623 -36.630 -40.236 -31.413 -34.521 -42.772 -38.425 |
| HCN/ScCa ₁₁ O ₁₂ HCN/TiCa ₁₁ O ₁₂ HCN/VCa ₁₁ O ₁₂ HCN/CrCa ₁₁ O ₁₂ HCN/ErCa ₁₁ O ₁₂ HCN/FeCa ₁₁ O ₁₂ HCN/FeCa ₁₁ O ₁₂ HCN/CoCa ₁₁ O ₁₂ HCN/CoCa ₁₁ O ₁₂ HCN/CuCa ₁₁ O ₁₂ | -36.979 -24.256 -28.898 -42.336 -8.985 -2.748 2.922 -11.785 -11.229 3.274 | -47.396 -36.514 -25.458 -53.493 -18.233 -11.204 -6.845 -17.473 -17.742 -1.286 | -34.939 -41.113 -16.842 -37.421 -31.017 -28.361 -32.759 -18.912 -21.843 -15.295 |

3.4.5. Optical properties

Table 8 shows the polarizability (α) and hyperpolarizability (β_0) based on assessments of the nonlinear optical characteristics. According to Table 8, the values for Ca₁₂O₁₂ first hyperpolarizability (β_0) and polarizability (α) were around 0.156 and 358.259 au (atomic units), respectively. The findings suggested that doping Ca₁₂O₁₂ with transition metal atoms increases the cluster's first hyperpolarizability (β_0). The following findings were reached after careful observation: In the case of NO-TMCa₁₁O₁₂, NO/TiCa₁₁O₁₂ has the greatest polarizability (α) and dominates by the α_{yy}, whereas NO/ZnCa₁₁O₁₂ has a minimal dipole moment value and dominates by the μ_x. Conversely NO/CrCa₁₁O₁₂ dominates by the β_{xxx} and has the largest average hyperpolarizability (β).

• Out of all the CO/TMCa₁₁O₁₂, CO/VCa₁₁O₁₂ has the greatest polarizability (α) value, dominates by the α_{ZZ} . However, CO/ZnCa₁₁O₁₂, which dominates by the μ_y , has the minimal dipole moment. Conversely, the structure of the β_{XXX} dominates CO/VCa₁₁O₁₂ and has the biggest (β).

• Regarding HCN/TMCa₁₁O₁₂, the structure HCN/VCa₁₁O₁₂ has the largest average hyperpolarizability terms $\langle \beta \rangle$ and highest polarizability (α), with α_{yy} and β_{zzz} terms predominating. The term dominates the structure with the lowest dipole moment value, HCN/FeCa₁₁O₁₂.

Table 8.

The dipole moment (μ_{01} (Debye), polarizability (α_0)(au) and first hyperpolarizability (β_0) (au) values for the doped Ca₁₂O₁₂, NO-TMCa₁₁O₁₂, CO-TMCa₁₁O₁₂, and HCN-TM-Ca₁₁O₁₂ nano-cages.

| | | TMCa ₁₁ | O ₁₂ | | NO/TMCa11O12 | | | CO/TMCa | 11012 | HCN/TMCa11O12 | | |
|---------|--------|--------------------|-----------------|-------|--------------|------------|----------------|----------|------------|---------------|----------|-----------|
| System | μ | α | βο | μ | αο | βo | μ ₀ | αο | βο | μο | α | βο |
| Ca12O12 | 0.0002 | 358.259 | 0.156 | 0.878 | 350.324 | 1997.108 | 0.230 | 377.794 | 2286.069 | 2.045 | 363.319 | 90.543 |
| Sc | 1.829 | 1026.80 | 348292.134 | 2.918 | 381.531 | 56369.777 | 3.906 | 437.594 | 139067.474 | 3.688 | 367.378 | 14978.409 |
| Ti | 1.8475 | 830.357 | 101061.965 | 2.304 | 1158.811 | 346979.195 | 3.105 | 1008.696 | 466781.310 | 1.814 | 1245.779 | 390226.73 |
| v | 1.602 | 1383.42 | 425992.191 | 4.061 | 371.864 | 6965.473 | 2.447 | 1361.332 | 659920.048 | 1.931 | 1511.946 | 704782.45 |
| Cr | 1.472 | 458.763 | 33044.997 | 2.871 | 907.856 | 453363.534 | 3.569 | 369.339 | 13003.737 | 2.938 | 433.734 | 39849.864 |
| Mn | 1.284 | 589.213 | 114162.599 | 2.792 | 390.926 | 15209.424 | 2.738 | 359.301 | 3663.082 | 2.738 | 359.301 | 3647.504 |
| Fe | 1.355 | 360.040 | 4784.981 | 2.011 | 380.845 | 7152.332 | 2.021 | 355.447 | 5302.648 | 0.090 | 392.752 | 11676.705 |
| Co | 1.214 | 349.757 | 1703.825 | 1.746 | 349.160 | 2358.561 | 1.374 | 351.397 | 1906.253 | 0.771 | 371.494 | 3067.013 |
| Ni | 1.086 | 333.920 | 1747.965 | 1.132 | 360.705 | 637.926 | 3.163 | 351.435 | 2640.457 | 3.811 | 349.192 | 2565.055 |
| Cu | 0.930 | 337.661 | 845.356 | 0.825 | 370.067 | 1631.548 | 3.220 | 364.631 | 2293.850 | 3.524 | 346.213 | 1997.595 |
| Zn | 0.750 | 333.749 | 481.554 | 0.614 | 348.265 | 8464.808 | 0.903 | 332.954 | 872.950 | 1.086 | 353.312 | 732.2004 |

3.4.6 Molecular electrostatic potentials (MEPs)

Determining Molecular Electrostatic (MEPs) Potentials contours is a vital advance concerning greater comprehending and anticipating molecular activities [83]. It serves as an efficient instrument for researching electrophilic and nucleophilic reactions, particularly "recognition" of one molecule by another [84]. In the study of (SWCNT) sensors, electrostatic interactions are important [85, 86]. Numerous investigations have demonstrated that, despite applications of diverse theoretical techniques, flaws in SWCNTs are significantly more active than defect-free locations [87-89]. Nevertheless, there hasn't been much theoretical focus on $Ca_{12}O_{12}$ in this scenario. MEPs can be (-ve) or low potentials that are also reactive to electrons and nucleophiles, or (+ve) high potentials that are reactive to electrons and nucleophiles. The former is denoted by deep blue, whereas the latter is indicated by deep red. Figs.12 (a, b, c, and d) show the MEP contours for the bure $Ca_{12}O_{12}$, free CO, NO, HCN molecules. As shown in Fig

12a, the free Ca₁₂O₁₂ nanocage possesses symmetrical potential due to the symmetrical structure: Ca atoms have positive potential and O atoms have negative potential. Even though the o atom has -ve charge, and the C atom should be charged positively, it is evident that the CO molecule has a negative MEP surrounding each of them, with the negative MEP surrounding the (C) atom being greater than the one surrounding the (O) atom, as shown in Fig 12b. In accordance with earlier research, this indicates that (C) atom has a significant nucleophilic nature [90, 91]. Thus, the CO molecule uses its C head to engage with the clusters. As shown in Fig. 12c, for NO, where (N) atom is positively charged and has surrounded by a -ve MEP larger than the one around the (O) with -ve charge, a similar tendency was noted. Because the N atom is nucleophilic, (NO) acts on the cluster through its head is N. As can be shown in Fig. 12d, the H and N atoms have the highest and lowest MEP (Vmax and Vmin) of the HCN molecule, respectively. Consequently, in the interaction with nanocages, the H and N atoms of HCN can function as an electron donor and acceptor, respectively. Figs. 12(e-g) illustrate the MEP contours for CO/Ca₁₂O₁₂, NO/Ca₁₂O₁₂, HCN/Ca₁₂O₁₂, and Figs. 12(h-j) show the MEP contours for the CO/MnCa₁₁O₁₂, NO/MnCa₁₁O₁₂, and HCN/MnCa₁₁O₁₂ clusters as examples, respectively. The rest of the MEP plots for gases / $TMCa_{11}O_{12}$ are shown in Fig. S6 and S7 in SI.

It is shown that the intensity of the contours is enhanced by the adsorption of gas molecules and the addition of TM atoms. Positive and negative MEP contours of gases- $Ca_{12}O_{12}$, and gases- $TMCa_{11}O_{12}$ differ significantly from one to another. On the other hand, the MEP outlines surrounding the TM atoms and gas molecules. There are differences between the MEPs of CO/TMCa_{11}O_{12}, NO/TMCa_{11}O_{12}, and HCN/TMCa_{11}O_{12}. Nevertheless, the outcomes additionally demonstrate that a molecule's electrostatic potential could potentially describe the systems CO/TMCa_{11}O_{12}, NO/TMCa_{11}O_{12}, and HCN/TMCa_{11}O_{12}, which represent gases and doped $Ca_{11}O_{12}$ interactions.



Fig.12 Molecular electrostatic (MEP) potential contours for (a) pure $Ca_{12}O_{12}$, (b) free CO, (c) free NO, (d) free HCN, (e) $CO/Ca_{12}O_{12}$, (f) NO/ $Ca_{12}O_{12}$, (g) HCN/ $Ca_{12}O_{12}$, (h) $CO/MnCa_{11}O_{12}$, (i) NO/MnCa₁₁O₁₂, and (j) HCN/MnCa₁₁O₁₂ at the B3LYP/6-311+G(D)D3 level of theory.

3.4.7. QTAIM analysis

QTAIM, which was suggested by Bader's hypothesis [92,93], aids in comprehending the bonds type and through-space interaction for NO, CO, and HCN molecules and the doped TM-Ca₁₁O₁₂ (TM=Sc to Zn) complex. The theory of QTAIM illustrates the bonds path connecting the cooperating atoms nuclei under investigation for the topological (3, -1) point in space with zero value for the Laplacian electron density, $\nabla^2 \rho(\mathbf{r}) = 0$. The topological investigations were used the potential (V(r)) electron energy density, $\nabla^2 \rho(\mathbf{r})$, G(r) (Lagrangian kinetic energy), H(r) (total electron energy density), eigenvalues (λ_1, λ_2 , and λ_3) of the Hessian matrix, and the bond ellipticity, ε [94], and electron density $\rho(\mathbf{r})$. Table 9 displays the obtained values, whereas Fig 13(A, B, C) depicts the topological graphs as an example for NO,CO, and HCN molecule adsorption on CrCa₁₁O₁₂. The rest of the topological graphs for gases / TMCa₁₁O₁₂ are shown in Fig. S8 in SI. A stronger covalent nature is indicated by a greater values of ρ (r) ($\rho > 0.1$ au), while a weaker non-covalent interaction (NCI) is indicated by a lower values of ρ (r) ($\rho < 0.1$ au). These predictions can be made using the electron density values, ρ (r). Syzgantseva et. al [95], state that although negative values of H(r) signify a covalent interaction, positive ones show an electrostatic one.

From Table 9, for NO/ TM-Ca₁₁O₁₂ (TM=Sc to Zn) the highest $\rho(r)$ value of (0.225, and 0.191 a.u) is observed in the NO/MnCa₁₁O₁₂ and NO/VCa₁₁O₁₂ complex, which indicates a strong covalent bonding interaction between doped MnCa₁₁O₁₂, VCa₁₁O₁₂ and NO. Additional $\rho(\mathbf{r})$ values fall between 0.010 and 0.252 a.u. While positive $\nabla^2(\mathbf{r})$ and negative values of H(r) imply medium interaction (partially covalent), the negativity of these two parameters suggest strong covalent interactions. Furthermore, they exhibit weak (noncovalent) interactions when both $\nabla^2(\mathbf{r})$ and H(r) are positive [59]. The table shows that all interacting bonds were found to be positive $\nabla^2(r)$ and negativity of H(r) supporting the partially covalent (medium interactions) and being consistent with the electron density. Furthermore, the NCI analysis indicates a repulsive force by displaying more blue colors. $\nabla^2 \rho(\mathbf{r})$ has positive values for most of the bond pathways, suggesting that interactions of closed-shell predominate in the structures. A highly polar covalent interaction is also demonstrated by the H(r) with +ve and -ve values in practically all structures. The values of G(r) and V(r) divulge the nature of intermolecular interaction; as a result, the ratio (G(r)/|V|(r)) can be used as an adequate index for link categorization. G(r)/|V|(r) < 0.5, indicates a covalent interaction, while G(r)/|V|(r) > 1.0 indicates a non-covalent interaction. Conversely, a high elliptical bond (ε) value denotes an instability and is associated with the ratio of the Hessian matrix's eigenvalues (λ_1 , λ_2 , etc.) [96]. Additionally, stable interactions

are indicated by $\varepsilon < 1$ value at the BCP. When compared to other systems, NO/MnCa₁₁O₁₂, NO/VCa₁₁O₁₂, NO/CoCa₁₁O₁₂, and NO/CrCa₁₁O₁₂, were found to have the highest values of electron density, which is supported by their good global descriptors and electronic properties; such systems are appropriate sensors for NO detection. Fig. S8 in SI shows a schematic representation of the bond crucial locations between nanocages

and gas.

Table 9: topological QTAIM descriptors for electron density $\rho(r)$, Laplacian of electron density $\nabla^2 \rho(r)$, Lagrangian kinetic energy G(r), potential electron density V(r), total electron energy density H(r), eigenvalues of Hessian matrix (λ), and bond ellipticity index (ϵ) at the BCPs of the NO,CO, and HCN with TM-Ca₁₁O₁₂ (TM=Sc to Zn). All parameters were calculated at the B3LYP-D3/6-311+G(d) level of theory.

| Structure | Bonds | $\rho(r)$ | $\nabla^2 \rho$ | G(r) | K(r) | V(r) | H(r) | G(r)/ V (r) | λ1 | λ_2 | λ_3 | ε |
|---------------------------------------|-------|-----------|-----------------|--------|---------|---------|---------|-------------|---------|-------------|-------------|--------|
| NO/ScCa11O12 | N-Sc | 0.0655 | 0.3194 | 0.0836 | 0.0037 | -0.0873 | -0.0037 | 0.9540 | -0.0619 | -0.1000 | 0.4813 | 0.6170 |
| NO/TiCa11O12 | N-Ti | 0.0926 | 0.4293 | 0.1252 | 0.0179 | -0.1431 | -0.0179 | 0.8741 | -0.1254 | -0.1257 | 0.6804 | 0.0020 |
| NO/VCa11O12 | N-V | 0.1905 | 0.3294 | 0.3689 | 0.0919 | -0.4608 | -0.0919 | 0.8004 | -0.1633 | -0.1717 | 1.4419 | 0.0580 |
| NO/CrCa ₁₁ O ₁₂ | N-Cr | 0.1702 | 0.9239 | 0.3071 | 0.0761 | -0.3832 | -0.0761 | 0.8016 | -0.1731 | -0.1769 | 1.2739 | 0.0217 |
| NO/MnCa11O12 | N-Mn | 0.2248 | 0.9400 | 0.3742 | 0.1392 | -0.5134 | -0.1392 | 0.7290 | -0.3125 | -0.3580 | 1.6104 | 0.1453 |
| NO/FeCa11O12 | N-Fe | 0.1295 | 0.5065 | 0.1672 | 0.0406 | -0.2078 | -0.0406 | 0.8068 | -0.1698 | -0.2056 | 0.8819 | 0.2110 |
| NO/CoCa11O12 | N-Co | 0.1791 | 0.5276 | 0.2155 | 0.0836 | -0.2991 | -0.0836 | 0.7191 | -0.2837 | -0.3069 | 1.1183 | 0.0817 |
| NO/NiCa11O12 | N-Ni | 0.1168 | 0.4845 | 0.1500 | 0.0288 | -0.1788 | -0.0288 | 0.8380 | -0.1611 | -0.1733 | 0.8189 | 0.0753 |
| NO/CuCa ₁₁ O ₁₂ | N-Cu | 0.1328 | 0.4260 | 0.1460 | 0.0395 | -0.1855 | -0.0395 | 0.7892 | -0.2066 | -0.2337 | 0.8663 | 0.1311 |
| NO/ZnCa11O12 | N-Zn | 0.0106 | 0.0575 | 0.0115 | -0.0029 | -0.0086 | 0.0029 | 1.3750 | -0.0099 | -0.1043 | 0.0778 | 0.0550 |
| CO/ScCa11O12 | C-Sc | 0.0531 | 0.1853 | 0.0510 | 0.0047 | -0.0558 | -0.0047 | 0.9107 | -0.0484 | -0.0698 | 0.3035 | 0.4408 |
| CO/TiCa11012 | C-Ti | 0.0876 | 0.3178 | 0.1007 | 0.0212 | -0.1219 | -0.0212 | 0.8279 | -0.0438 | -0.1381 | 0.4998 | 2.1527 |
| CO/VCa11O12 | C-V | 0.1021 | 0.3940 | 0.1277 | 0.0292 | -0.1569 | -0.0292 | 0.8153 | -0.1012 | -0.1027 | 0.5979 | 0.0148 |
| CO/CrCa11O12 | C-Cr | 0.1518 | 0.6726 | 0.2353 | 0.0672 | -0.3025 | -0.0672 | 0.7781 | -0.9715 | -0.9763 | 0.8673 | 0.0049 |
| CO/MnCa11O12 | C-Mn | 0.1651 | 0.6872 | 0.2515 | 0.0797 | -0.3313 | -0.0797 | 0.7583 | -0.1261 | -0.1275 | 0.9408 | 0.0109 |
| CO/FeCa11O12 | C-Fe | 0.1740 | 0.6413 | 0.2481 | 0.8782 | -0.3360 | -0.8782 | 0.7381 | -0.1734 | -0.1779 | 0.9926 | 0.0259 |
| CO/CoCa11O12 | C-Co | 0.1300 | 0.5969 | 0.1921 | 0.0429 | -0.2350 | -0.0429 | 0.8170 | -0.1277 | -0.1281 | 0.8528 | 0.0031 |
| CO/NiCa11O12 | C-Ni | 0.1515 | 0.2175 | 0.1194 | 0.0651 | -0.1845 | -0.0651 | 0.6467 | -0.2012 | -0.2316 | 0.6503 | 0.1512 |
| CO/CuCa11O12 | C-Cu | 0.1138 | 0.2179 | 0.0950 | 0.4060 | -0.1356 | -0.4060 | 0.6985 | -0.1409 | -0.1575 | 0.5163 | 0.1180 |
| CO/ZnCa ₁₁ O ₁₂ | C-Zn | 0.0132 | 0.0384 | 0.0087 | -0.0009 | -0.0077 | 0.0009 | 1.1250 | -0.0776 | -0.0102 | 0.0563 | 0.3123 |
| HCN/ScCauOn | N-Sc | 0.0691 | 0.2868 | 0.0784 | 0.0067 | -0.0852 | -0.0067 | 0.9176 | -0.0877 | -0.0990 | 0.4735 | 0.1294 |
| HCN/TiCanO12 | N-Ti | 0.0900 | 0.3706 | 0.1105 | 0.1787 | -0.1284 | -0.1787 | 0.8594 | -0.1425 | -0.9899 | 0.6121 | 0.4398 |
| HCN/VCanO12 | N-V | 0.0879 | 0.4919 | 0.1357 | 0.0127 | -0.1485 | -0.0127 | 0.9189 | -0.8979 | -0.9079 | 0.6725 | 0.0111 |
| HCN/CrCa11O12 | N-Cr | 0.1474 | 0.7043 | 0.2344 | 0.5836 | -0.2928 | -0.5836 | 0.7986 | -0.1536 | -0.1930 | 1.0509 | 0.2568 |
| HCN/MnCa11O12 | N-Mn | 0.1281 | 0.8490 | 0.2482 | 0.0359 | -0.2841 | -0.0359 | 0.8732 | -0.0748 | -0.0869 | 1.0107 | 0.1618 |
| HCN/FeCanO12 | N-Fe | 0.1315 | 0.8370 | 0.2473 | 0.0381 | -0.2854 | -0.0381 | 0.8667 | -0.0961 | -0.1079 | 1.0411 | 0.1226 |
| HCN/CoCa11O12 | N-Co | 0.0800 | 0.4608 | 0.1232 | 0.0080 | -0.1313 | -0.0080 | 0.9389 | -0.0735 | -0.0972 | 0.6314 | 0.3221 |
| HCN/NiCanOn | N-Ni | 0.0518 | 0.1475 | 0.0434 | 0.0065 | -0.0500 | -0.0065 | 0.8600 | -0.0849 | -0.0857 | 0.3181 | 0.0090 |
| HCN/CuCa11O12 | N-Cu | 0.0531 | 0.1489 | 0.0443 | 0.0071 | -0.0514 | -0.0071 | 0.8461 | -0.0876 | -0.0879 | 0.3243 | 0.0032 |
| HCN/ZnCa11O12 | N-Zn | 0.0167 | 0.0622 | 0.0150 | -0.0006 | -0.0143 | 0.0006 | 1.0714 | -0.0145 | -0.0148 | 0.0915 | 0.0175 |

While for CO/ TM-Ca₁₁O₁₂ (TM=Sc to Zn) (Table 9), the CO/FeCa11O12 and CO/MnCa₁₁O₁₂ complexes have the highest values of $\rho(r)$ (0.174, and 0.165 a.u), respectively, which indicates a strong covalent bonding interaction between the doped FeCa₁₁O₁₂, MnCa₁₁O₁₂ and NO molecule. The other $\rho(r)$ values range from 0.013 to 0.174 a.u. The table shows that all interacting bonds were found to be positive $\nabla^2(r)$ and negative H(r) supporting the medium interactions (partially covalent) and being consistent with the electron density. For CO/TiCa₁₁O₁₂ with 2.153 au, with $\varepsilon > 1$; this implies instability. When compared to other systems, CO/FeCa₁₁O₁₂ , CO/MnCa₁₁O₁₂, CO/CrCa₁₁O₁₂, and CO/NiCa₁₁O₁₂ were found to possess the greatest $\rho(r)$, which is supported by their good electronic and global descriptors; these structures are appropriate sensors for CO detection.

Furthermore, the results of Table 9, for HCN/ TM-Ca₁₁O₁₂ (TM=Sc to Zn) the highest $\rho(r)$ value of (0.147, and 0.131 a.u) is observed in the HCN/CrCa₁₁O₁₂ and HCN/FeCa₁₁O₁₂

complex, which indicates a strong covalent bonding interaction between doped $CrCa_{11}O_{12}$ FeCa₁₁O₁₂, and HCN. Additional $\rho(r)$ values fell between 0.017 to 0.147 a.u. Stability is generally shown by $\varepsilon < 1$ in all interactions.

3.4.8. Noncovalent Interaction (NCI) Analysis

By using the NCI analysis [42], the weak interactions nature between the TM-Ca₁₁O₁₂ surfaces and NO, CO and HCN molecules was further clarified. In a graph made for these studies using the VMD tool, the reduced density gradient (RDG) was plotted against the electron density Hessian matrix second eigenvalue (λ_2) and the $\rho(a.u)$ (RDG against sign $\lambda_2(r)\rho(r)$).

Fig 13(D-F) and Fig 13(G-I) depict the NCI molecular graphs, and RDG scatter maps as examples for NO,CO, and HCN molecule adsorption on $CrCa_{11}O_{12}$. The rest of the NCI molecular graphs, and RDG scatter maps for gases / TMCa₁₁O₁₂ are provided in Fig. S9 and Fig S10 -S12 in SI. The green, blue, and red index scale are used to interpret weak interactions. The red zone with (sign $(\lambda_2) \rho > 0$) implies a great repulsive contact, such as the electron density ρ depletion, and steric effect. Conversely, green zone (sign (λ_2) $\rho \approx 0$) indicates rather weak interactions of van der Waal (vdW). In the blue zone, positive values (sign (λ_2) $\rho < 0$) denote high electron density and strong interactions (like hydrogen bonds) [47,97]. As demonstrated in Fig S10 -S12 in SI, sign($\lambda 2$) ρ rises for red regions, indicating significant steric repulsions within the nanocage, while sign($\lambda 2$) ρ falls for blue regions. Van der Waals interactions are represented by the green regions between the complex's constituents that are becoming closer to zero. The geometric approach, which takes weak interactions into account, supports this conclusion. Blue and green blended spikes were observed at higher electron densities with sign (λ_2) $\rho < 0$, which shows that the NO/ CrCa₁₁O₁₂, CO/ CrCa₁₁O₁₂, and HCN/ TiCa₁₁O₁₂ complexes have developed partial covalent interactions. As seen in Figs. S10 - S12 in SI, the partial covalent link showed the green and blue regions among gases and nanocages, along with the intermolecular contact. Because of the partial covalent contacts between the NO, CO, and HCN molecules and the $CrCa_{11}O_{12}$ and TiCa₁₁O₁₂ nanocages in the graph of RDG versus sign(λ_2) ρ , higher interaction intensities were observed for the NO/CrCa₁₁O₁₂, CO/CrCa₁₁O₁₂, and HCN/TiCa₁₁O₁₂ configurations.

3.5. Analysis of recovery time

The recovery of sensors from adsorbed gases is essential. We can evaluate the recovery time (τ) by heating adsorbents to higher temperatures or exposing them to UV light [98]. We can deduce τ using transition theory as follows:

$$\tau = \frac{1}{\nu} \left[\exp\left(\frac{-AE}{kT}\right) \right] \tag{19}$$

Where v is the attempt frequency, T assigns the temperature, and k assigns the Boltzmann constant (~8.31 × 10– 3 kJ mol– 1.K). For carbon nanotube recovery at ambient temperature [63], an attempt frequency of roughly 10^{12} s⁻¹ is utilized, τ are 187 ms, 6 μ s, and 12 μ s for NO, CO, and HCN in complexes NO/ Ca₁₂O₁₂, CO/ Ca₁₂O₁₂, and HCN/ Ca₁₂O₁₂, respectively. This demonstrates the quick recovery time of the Ca₁₂O₁₂ nanocage as a sensor.



Fig 13. QTAIM, NCI molecular graphs, and RDG scatter maps for the optimized (A,D,G) for NO, (B,E,H) for CO, and (C,F,I) for HCN molecule adsorption on $CrCa_{11}O_{12}$ complexes.

3.6. The impact of solvent

To find out the solvent impact upon the adsorption strength between the (CO, NO, and HCN) molecules and CaO nanocage, the simulations are carried out for the water solution. In the aqueous phase, the solvent had insignificant impact upon the electronic and structural characteristics of the nanocluster. According to the DFT results in Table 10, the E_g values of

the structures under study in the aqueous phase are higher compared to those of the gas phase by approximately 0.341, 0.304, 0.562 eV, respectively. Nonetheless, the solvent's effect on the electric: **Table 10:** Calculated HOMO (E_{HOMO}/eV), LUMO (E_{LUMO}/eV) energies, and HOMO-LUMO gnal. energy gap (E_z/eV), for Ca₁₂O₁₂, NO/Ca₁₂O₁₂, CO/Ca₁₂O₁₂, and HCN/Ca₁₂O₁₂ nanocages.

| SYSTEM | E _H | EL | E _{G-GAS} | E _{G-SOLV} |
|--------------|----------------|--------|--------------------|---------------------|
| CA12O12 | -5.282 | -1.189 | 4.093 | 4.388 |
| NO/ CA12O12 | -4.610 | -1.074 | 3.536 | (4.090)* 3.840 |
| CO/ CA12O12 | -5.166 | -1.026 | • 4.140 | 4.481 |
| HCN/ CA12O12 | -4.833 | -0.956 | 3.877 | 4.439 |

Ref [99] B3LYP-D3 functional and 6-31G basis set

4. Conclusions

Using dispersion corrected (DFT) calculations, interaction studies were carried out using the calcium oxide (Ca₁₁O₁₂)-nanocage doped with TM (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) metals to function as a sensor for sensing CO, NO, and HCN. The geometrical parameters, E_{ads}, (µ), (NBOs), (FMOs), (DOS), global reactivity descriptors, thermodynamic properties (ΔG and ΔH),molecular electrostatic potential, topological investigation (NCI), and (QTAIM) were applied to assess the modeled nanoclusters suitability as adsorbents for the elimination of harmful gases such as CO, NO, and HCN. Weak interactions were found in $NO/CuCa_{11}O_{12}$, $NO/CoCa_{11}O_{12}$, $HCN/CoCa_{11}O_{12}$, $NO/ZnCa_{11}O_{12}$, $CO/ZnCa_{11}O_{12}$, and HCN/ZnCa₁₁O₁₂ in the BSSE-corrected adsorption energy mechanism approach. In contrast, Chemical adsorption in interactions involving CO/CrCa₁₁O₁₂, CO/MnCa₁₁O₁₂, NO/VCa₁₁O₁₂, NO/CrCa₁₁O₁₂, HCN/TiCa₁₁O₁₂, and HCN/CrCa₁₁O₁₂ was extremely favorable. This indicates that CO has a covalent bond NO/CuCa₁₁O₁₂, NO, HCN/CoCa₁₁O₁₂, NO, CO, and HCN/ZnCa₁₁O₁₂, which have positive values indicating weak adsorption, all complexes have negative Gibbs-free energy changes (ΔG). By using molecular dynamics (MD) calculations, the stability of the structures under analysis is examined. Following the adsorption of NO, CO, and HCN on TM-Ca₁₁O₁₂ nanocages and TM doping on Ca₁₂O₁₂, the energy gaps decreased. To validate the covalent interactions in the systems, (QTAIM and NCI) investigations were implemented; it was confirmed in the high Laplacian and densities of all electrons showed in the systems. Based on the findings of these theoretical investigations, Ca₁₁O₁₂ doped with TM nano-cages served as promising materials for the removing of CO, NO, and HCN poisonous gases.

Declaration of Conflicting Interests

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Supplementary material

See the electronic supplementary information for the obtained xyz coordinates for all studied systems, the electronic configuration, orbital diagram, spin multiplicity and total electronic energy of free TM in the low-pin state and TMCa₁₁O₁₂, NBO charges, the NBO analysis, HOMO-LUMO plot, density of states (DOS), MEPs contours, QTAIM, NCI analysis graphs, and RDG scatter maps for all systems.

References

[1] S. Patel, P. Patel, D. Chodvadiya, N.N. Som, P.K. Jha, Adsorption performance of C_{12} , B_6N_6 and Al_6N_6 nanoclusters towards hazardous gas molecules: A DFT investigation for gas sensing and removal application, J. Mol. Liq., **352** (2022)118702.

https://doi.org/10.1016/j.molliq.2022.118702.

[2] S. Dolmaseven, N. Yuksel, M.F. Fellah, Au, Ag and Cu Doped BNNT for ethylene oxide gas detection: A density functional theory study, Sensors Actuators A Phys, 350(2023)114109. <u>https://doi.org/10.1016/j.sna.2022.114109</u>.

[3] M. Liangruksa, P. Sukpoonprom, A. Junkaew, W. Photaram, C. Siriwong, Gas sensing properties of palladium-modified zinc oxide nanofilms: A DFT study, Appl. Surf. Sci., 544(2021)148868. <u>https://doi.org/10.1016/j.apsusc.2020.148868.</u>

[4] Z.Y. Deng, J.M. Zhang, K.W. Xu, First-principles study of SO₂ molecule adsorption on the pristine and Mn-doped boron nitride nanotubes, Appl. Surf. Sci., **347**(2015)485–490.

https://doi.org/10.1016/j.apsusc.2015.04.116

[5] W. Ruoxi, Z. Dongju, L. Yongjun, L. Chengbu, A theoretical study of silicon-doped boron nitride nanotubes serving as a potential chemical sensor for hydrogen cyanide, Nanotechnology, 20 (2009)21264,. <u>https://doi.org/10.1088/0957-4484/20/50/505704</u>
[6] X. Zhang, Z. Lu, Y. Tang, Z. Fu, D. Ma, Z. Yang, A density function theory study on the NO reduction on nitrogen doped graphene, Phys. Chem. Chem. Phys., 16(2014)20561–20569. <u>https://doi.org/10.1039/C4CP02873B</u>

[7] Y. Xie, Y. P. Huo, J. M. Zhang, First-principles study of CO and NO adsorption on transition metals doped (8,0) boron nitride nanotube, Applied Surface Science,
258(2012)6391–6397. https://doi.org/10.1016/j.apsusc.2012.03.048

[8] J. Ma, P.K. Das gupta, Recent developments in cyanide detection: A review, Anal. Chim.
Acta, 673(2010)117–125. https://doi.org/10.1016/j.aca.2010.05.042

[9] T.L. Porter, T.L. Vail, M.P. Eastman, R. Stewart, J. Reed, R. Venedam, W. Delinger, A solid-state sensor platform for the detection of hydrogen cyanide gas, Sens. Actuators B, **123** (2007)313-317. https://doi.org/10.1016/j.snb.2006.08.025

 [10] Z. Xu, X. Chen, H.N. Kim, J. Yoon, Sensors for the optical detection of cyanide ion Chem. Soc. Rev. 39(2010)127–137. <u>https://doi.org/10.1039/B907368J</u>

[11] X. Zhou, W.Q. Tian, Sensitivity of (5,5) SWSiCNTs and SWSiCNTs with Stone–Wales Defects toward Hazardous Molecules, J. Phys. Chem. C, **115** (2011)11493–11499.

https://doi.org/10.1021/jp2029196

[12] Z. Zhang, Z. Zhang, Liu, Novel Chemical Sensor for Cyanides: Boron-Doped Carbon Nanotubes, Phys. Chem. B, **110**(2006)4671–4674.

https://doi.org/10.1021/jp0602272

[13] R.Q. Wu, M. Yang, Y.H. Lu, Y.P. Feng, Z.G. Huang, Q.Y. Wu, Silicon Carbide

Nanotubes As Potential Gas Sensors for CO and HCN Detection, J. Phys. Chem. C,

112(2008)15985–15988. <u>https://doi.org/10.1021/jp804727c</u>

[14] L.B. Shi, Y.P. Wang, H.K. Dong, First-principle study of structural, electronic,

vibrational and magnetic properties of HCN adsorbed graphene doped with Cr, Mn and Fe,

Appl. Surf. Sci., **329**(2015)330–336. https://doi.org/10.1016/j.apsusc.2014.12.172

[15] S.F. Rastegar, A.A. Peyghan, N.L. Hadipour, Response of Si- and Al-doped graphenes

toward HCN: A computational study, Appl. Surf. Sci. **265**(2013)412–417. http://dx.doi.org/10.1016/j.apsusc.2012.11.021

[16] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, C60 Buckminsterfullerene, Nature, **318**(1985)162–163. <u>https://doi.org/10.1038/318162a0</u>

[17] N. V. Sibirev, V. G. Dubrovskii, A. V. Matetskiy, L. V. Bondarenko, D. V. Gruznev, A.

V. Zotov and A. A. Saranin, Size distributions of fullerene surface clusters, Appl. Surf. Sci., **307**(2014)46–51. <u>https://doi.org/10.1016/j.apsusc.2014.03.132</u>

[18] A. F. Jalbout, Endohedral metallo [80] fullerene interactions with small polar molecules, Comput. Mater. Sci., 44(2009)1065–1070.

https://doi.org/10.1016/j.commatsci.2008.07.038.

[19] J. H. Lee, B. S. Lee, F. T. K. Au, J. Zhang and Y. Zeng, Vibrational and dynamic

analysis of C_{60} and C_{30} fullerenes using FEM, Comput. Mater. Sci., **56**(2012)131–140. https://doi.org/10.1016/j.commatsci.2012.01.019.

[20] Y. Li, G. Zhou, J. Li, B.-L. Gu and W. Duan, Alkali-Metal-Doped B80 as High-Capacity Hydrogen Storage Media, J. Phys. Chem. C, **112**(2008)19268–19271.

https://doi.org/10.1021/jp807156g.

[21] M. Moradi, A. A. Peyghan and Z. Bagheri, Tuning the electronic properties of C30B15N15 fullerene via encapsulation of alkali and alkali earth metals, Synth. Met., 177(2013)94–99. https://doi.org/10.1016/j.synthmet.2013.06.018.

[22] M. Kazemi and A. S. Rad, Sulfur mustard gas adsorption on ZnO fullerene-like nanocage: Quantum chemical calculations, Superlattices Microstruct., 106(2017)122–128. https://doi.org/10.1016/j.spmi.2017.03.046.

[23] J. Beheshtian, Z. Bagheri, M. Kamfiroozi and A. Ahmadi, A comparative study on the

B₁₂N₁₂, Al₁₂N₁₂, B₁₂P₁₂ and Al₁₂P₁₂ fullerene-like cages, J. Mol. Model., **18**(2012)2653–2658. <u>https://doi.org/10.1007/s00894-011-1286-y</u>.

[24] J. Kakemam and A. A. Peyghan, Electronic, energetic, and structural properties of Cand Si-doped Mg₁₂O₁₂ nano-cages, Comput. Mater. Sci., **79**(2013)352–355.

https://doi.org/10.1016/j.commatsci.2013.06.036

[25] W.-M. Sun, X.-H. Li, D. Wu, Y. Li, H.-M. He, Z.-R. Li, J.-H. Chen and C.-Y. Li, A theoretical study on super alkali-doped nanocages: unique inorganic electrides with high stability, deep-ultraviolet transparency, and a considerable nonlinear optical response, Dalton Trans., **45**(2016)7500–7509. <u>https://doi.org/10.1039/C6DT00342G</u>

[26] O. V. de Oliveira, J. M. Pires, A. C. Neto and J. Divino dos Santos, Computational studies of the $Ca_{12}O_{12}$, $Ti_{12}O_{12}$, $Fe_{12}O_{12}$ and $Zn_{12}O_{12}$ nanocage clusters, Chem. Phys. Lett., **634**(2015)25–28. <u>https://doi.org/10.1016/j.cplett.2015.05.069</u>

[27] M. Niu, G. Yu, G. Yang, W. Chen, X. Zhao and X. Huang, Doping the Alkali Atom: An Effective Strategy to Improve the Electronic and Nonlinear Optical Properties of the Inorganic $Al_{12}N_{12}$ Nanocage, Inorg. Chem., **53**(2014)349–358. https://doi.org/10.1021/ic4022917

[28] Maria, J. Iqbal and K. Ayub, Enhanced electronic and non-linear optical properties of alkali metal (Li, Na, K) doped boron nitride nano-cages, J. Alloys Compd., 687(2016)976–983. https://doi.org/10.1016/j.jallcom.2016.06.121

[29] A.S. Rad, K. Ayub, Change in the electronic and nonlinear optical properties of Fullerene through its incorporation with Sc-, Fe-, Cu-, and Zn transition metals, Appl. Phys.

A, 125(2019)430. <u>https://doi.org/10.1007/s00339-019-2721-7</u>

 [30] D. Paul, J. Deb, B. Bhattacharya, U. Sarkar, The Influence of the Substitution of Transition Metals on Pristine C₂₀: A DFT Study, Int. J. Nano sci., 17(2018)1760026. https://doi.org/10.1142/S0219581X17600262

[31] D. Ma, W. Ju, T. Li, X. Zhang, C. He, B. Ma, Z. Yang, The adsorption of CO and NO on the MoS₂ monolayer doped with Au, Pt, Pd, or Ni: A first-principles study, Appl. Surface Sci. **383**(2016)98–105. <u>https://doi.org/10.1016/j.apsusc.2016.04.171</u>

[32] Y. Arshad, S. Khan, M.A. Hashmi, K. Ayub, Transition metal doping: a new and effective approach for remarkably high nonlinear optical response in aluminum nitride nanocages, New J. Chem. 42(2018) 6976–6989. <u>https://doi.org/10.1039/C7NJ04971D</u>
[33] Y. Hu, H. Zhang, P. Wu, H. Zhang, B. Zhou, C. Cai, Bimetallic Pt–Au nanocatalysts electrochemically deposited on graphene and their electrocatalytic characteristics towards oxygen reduction and methanol oxidation, Phys. Chem. Chem. Phys., 13(2011)4083–4094.

https://doi.org/10.1039/C0CP01998D

[34] S. Hussain, S.A.S. Chatha, A.I. Hussain, R. Hussain, M.Y. Mehboob, S. Muhammad, K. Ayub, Zinc-Doped Boron Phosphide Nanocluster as Efficient Sensor for SO₂, J. Chem., (2020)12. <u>https://doi.org/10.1155/2020/2629596</u>

[35] X. Zhang, L. Yu, X. Wu, W. Hu, Experimental Sensing and Density Functional Theory Study of H₂S and SOF₂ Adsorption on Au-Modified Graphene, Adv. Sci., **2**(2015). <u>https://doi.org/10.1002/advs.201500101</u>

[36] D. Wang, J. Weiwei, T. Li, Q. Zhou, Z. Gao, Y. Zhang, H. Li, Electronic and magnetic properties of MoS₂ monolayers with antisite defects, J. Phys. Chem. Solids 131(2019) 119–124. https://doi.org/10.1016/j.jpcs.2019.03.028

[37] J. Weiwei, T. Li, Q. Zhou, H. Li, X. Li, D. Ma., Adsorption of 3*d* transition-metal atom on InSe monolayer: A first-principles study, Comput. Mater. Sci., **150**(2018)33–41.

https://doi.org/10.1016/j.commatsci.2018.03.067

[38] J. Guo, C Zhu, Y. Zhao, H. Wang, Y. Hu, X. He, D. Cai LAMP: label augmented multimodal pretraining. arXiv, (2020). <u>https://doi.org/10.48550/arXiv.2012.04446</u>

[39] M. Wang, C. Jiang, S. Zhang, X. Song, Y. Tang, H-M. Cheng, Reversible calcium alloying enables a practical room-temperature rechargeable calcium-ion battery with a high discharge voltage, Nat. Chem. **10**(2018)667–672.https://doi.org/10.1038/s41557-018-0045-4

[40] L. Chen, G-Q. Zhou, C. Xu, T. Zhou, Y. Huo, Structural and electronic properties of hydrated MgO nanotube clusters. J Mol Struct THEOCHEM **900**(2009)33–36.

https://doi.org/10.1016/j.theochem.2008.12.019

[41] H. Wang, T. Song, Z. Li, J. Qiu, Y. Zhao, H. Zhang, Exceptional high and reversible ammonia uptake by two dimension few-layer Bil₃ nanosheets. ACS Appl. Mater. Interfaces, 13(2021)25918–25925. <u>https://doi.org/10.1021/acsami.1c03261</u>

[42] A.S. Rad, S.M. Aghaei, H. Pazoki, E. Binaeian, M. Mirzaei, Surface interaction of H2O and H_2S onto $Ca_{12}O_{12}$ nanocluster: quantum-chemical analyses. Surf. Interface Anal. **50**(2018)411–419. <u>https://doi.org/10.1002/sia.6382</u>

[43] A. Ahsan, S. Khan, M.A. Gilani, K. Ayub, Endohedral metallofullerene electrides of $Ca_{12}O_{12}$ with remarkable nonlinear optical response. RSC Adv. **11**(2021)1569–1580.

https://doi.org/10.1039/D0RA08571E

[44] S. Yang, X. Wan, K. Wei, W. Ma, Z. Wang, Silicon recycling and iron, nickel removal from diamond wire saw silicon powder waste: synergistic chlorination with CaO smelting treatment. Miner. Eng., **169**(2021)106966. <u>https://doi.org/10.1016/j.mineng.2021.106966</u>

[45] M. Omidi, H.R. Shamlouei, M. Noormohammadbeigi, The influence of Sc doping on structural, electronic and optical properties of $Be_{12}O_{12}$, $Mg_{12}O_{12}$ and $Ca_{12}O_{12}$ nanocages: a DFT study. J. Mol. Model., **23**(2017) 82. https://doi.org/10.1007/s00894-017-3243-x

[46] H. Sajid, S. A. Siddique, E. Ahmed, M., Arshad, M. A. Gilani, A. Rauf, M. Imran, T. Mahmood, DFT outcome for comparative analysis of $Be_{12}O_{12}$, $Mg_{12}O_{12}$ and $Ca_{12}O_{12}$ nanocages toward sensing of N₂O, NO₂, NO, H₂S, SO₂ and SO₃ gases, Computational and Theoretical Chemistry, **1211**(2022)113694. <u>https://doi.org/10.1016/j.comptc.2022.113694</u>

[47] S. A. Jasim, M. S Maashi, M. M. Kadhim, L. Thangavelu, B. S. Bashar, Y. Riadi, A.

Mohamad, retracted: application of $Ca_{12}O_{12}$ nanocage for detection of aluminum phosphide molecule: First-principles investigation, Computational and Theoretical Chemistry, **1209**(2022)113615. <u>https://doi.org/10.1016/j.comptc.2022.113615</u>

[48] R. Kartika, F H. Alsultany, A T. Jalil, M. Z. Mahmoud, M. N. Fenjan, H. Rajabzadeh, $Ca_{12}O_{12}$ nanocluster as highly sensitive material for the detection of hazardous mustard gas: Density-functional theory, Inorganic Chemistry Communications, **137**(2022)109174.

https://doi.org/10.1016/j.inoche.2021.109174

[49] H. Louis, I. O. Amodu, T. O. Unimuke , T. E. Gber , B.B. Isang , A. S. Adeyinka, Modeling of $Ca_{12}O_{12}$, $Mg_{12}O_{12}$, and $Al_{12}N_{12}$ nanostructured materials as sensors for phosgene (Cl₂CO), Materials Today Communications **32**(2022)103946.

https://doi.org/10.1016/j.mtcomm.2022.103946

[50] J. S. Al-Otaibi, Y. Sheena Mary, Y. Shyma Mary, A. Mondal, N. Acharjee, D. S. R. Nair, Investigation of the interaction of thymine drugs with $Be_{12}O_{12}$ and $Ca_{12}O_{12}$ nanocages: A quantum chemical study, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **308**(2024)123728. <u>https://doi.org/10.1016/j.saa.2023.123728</u>

[51] M. M. Kadhim, T. Z. Taban, R. F. Obaid, H A. Almashhadani, M. H. Shadhar, G. S. Bustani, A. M. Rheima, A. Mohamadi, A computational study on the potential application of $Ca_{12}O_{12}$ cluster for sensing of fungicide molecule, Brazilian Journal of Chemical Engineering **40**(2023)789–795. <u>https://doi.org/10.1007/s43153-022-00262-2</u>

[52] M.J. Frisch, et al., Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT, 2009.

[53] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio

parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-

Pu, Journal of Chemical physics 132(2010)154104. https://doi.org/ 10.1063/1.3382344.

[54] A. D. Becke, A new mixing of Hartree–Fock and local density functional theories. J. Chem. Phys., 98(1993)1372–1377. https://doi.org/10.1063/1.464304

[55] S.F. Boys, F. Bernardi, The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors, Molecular Physics, 19(1970) 553-566. <u>https://doi.org/10.1080/00268977000101561</u>

[56] R. Dennington, T. Keith, J. Millam, GaussView, Version 5.0.8.: Semichem Inc., Shawnee Mission KS; 2009.

[57] E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, NBO version 3.1, 2003.

[58] T. Lu,; F. Chen, Multiwfn: a multifunctional wavefunction analyzer. J. Comput. Chem.,
33(2012)580–592. <u>https://doi.org/10.1002/jcc.22885</u>

[59] W. Humphrey, A. Dalke, K. Schulten, VMD: visual molecular dynamics. J. Mol.

Graphics, **14**(1996) 33–38. <u>https://doi.org/10.1080/00268977000101561</u>

[60] S. Larki, E. Shakerzadeh, E.C. Anota, R. Behjatmanesh-Ardakani, The Al, Ga and Sc dopants effect on the adsorption performance of $B_{12}N_{12}$ nanocluster toward pnictogen hydrides, Chemical Physics, **526**(2019)110424.

https://doi.org/ 10.1016/j.chemphys.2019.110424.

[61] D.R. Roy, E.V. Shah, S.M. Roy, Optical activity of Co-porphyrin in the light of IR and Raman spectroscopy: A critical DFT investigation, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, **190**(2018)121–128.

https://doi.org/ 10.1016/j.saa.2017.08.069.

[62] M. Ernzerhof, Validity of the extended Koopmans' theorem. J. Chem. Theory Comput., 5(2009)793–797. <u>https://doi.org/10.1021/ct800552k</u>

[63] N. Islam, D. C. Ghosh, The electronegativity, and the global hardness are periodic properties of atoms. J. Quantum Inf. Sci., **1**(2011)135–141.

https://doi.org/10.4236/jqis.2011.13019

[64] P.K. Chattaraj, D.R. Roy, Update 1 of: electrophilicity index, Chem. Rev., 107(2007)46–
79. <u>https://doi.org/10.1021/cr078014b.</u>

[65] H. O. Taha, M.A. Ramadan, A.M. El Mahdy, Influence of point defects on the hydrogen storage in nickel decorated GeC and SnC nanotubes, Computational and Theoretical Chemistry, **1212**(2022)113691. <u>https://doi.org/10.1016/j.comptc.2022.113691.</u>

[66] H.O. Taha, A.M. El Mahdy, H.I. Lebda, Adsorption of gases on doped graphene quantum dots with (TM = Ni, Pd, and Pt): DFT and TD-DFT investigation, Physica B: Condensed Matter, 676(2024)415667. <u>https://doi.org/10.1016/j.physb.2024.415667</u>

[67] H.O. Taha, M.A. Tarek, Axial deformation effects on hydrogen storage of Ni decorated
(8, 0) zigzag single-walled boron nitride nanotubes: a DFT study, Mol. Phys. **119**(2021)
1937738. <u>https://doi.org/10.1080/00268976.2021.1937738</u>

 [68] N. M. O'Boyle, A.L. Tenderholt, K.M. Langner, cclib: Journal of Computational Chemistry, 29(2008)839–845. <u>https://doi.org/10.1002/jcc.20823</u>.

[69] M. D. Mohammadi, H. Y. Abdullah, Suvitha, A. The adsorption of 1-chloro-1, 2, 2, 2-tetrafluoroethane onto the pristine, Al-, and Ga-doped boron nitride nanosheet. Iran. J. Sci. Technol., Trans. A: Sci., 45(2021) 1287–1300. <u>https://doi.org/10.1007/s40995-021-01117-0</u>
[70] W. Emori, G. J. Ogunwale, H. Louis, E. C. Agwamba, K. Wei, T. O. Unimuke, C. Cheng, E. U. Ejiofor, F. C. Asogwa, A. S. Adeyinka, Spectroscopic (UV–vis, FT-IR, FT-Raman, and NMR) analysis, structural benchmarking, molecular properties, and the in-silico cerebral anti-ischemic activity of 2 amino-6-ethoxybenzothiazole. J. Mol. Struct., 1265(2022)133318.

https://doi.org/10.1016/j.molstruc.2022.133318

[71] Y. Zhihong, Y. Ye, A. Pejhan, A. Nasr, N. Nourbakhsh, R. Tayebee, A theoretical study on the pure and doped ZnO nanoclusters as effective nanobiosensors for 5-fluorouracil anticancer druadsorption. Appl. Organomet. Chem., **34**(2020)No. e5534.

https://doi.org/10.1002/aoc.5534

[72] E. E. Hodgkin, W. G. Richards, Molecular similarity based on electrostatic potential and electric field. Int. J. Quantum Chem., **32**(1987)105–110.

https://doi.org/10.1002/qua.560320814

[73] P. L. A. Popelier, Quantum molecular similarity. 1. BCP space. J. Phys. Chem. A, 103(1999)883–2890. <u>https://doi.org/10.1021/jp984735q</u>

[74] C. F. Matta, Hydrogen–Hydrogen Bonding: The Non-Electrostatic Limit of Closed-Shell Interaction between Two Hydro. In "Hydrogen Bonding New Insights"; Springer: Dordrecht, 3(2006)337–375. <u>https://doi.org/10.1007/978-1-4020-4853-1_9</u>

[75] T. O. Unimuke, H. Louis, W. Emori, P. S. Idante, E. C. Agwamba, I. C. Nwobodo, K. Wei, C. R. Cheng, S. A. Adalikwu, V. M. Bassey, C. A. Anyama, Spectroscopic and molecular electronic property investigation of 2-phenylpyrimidine-4, 6-diamine via 1HNMR, UV–vis, FT-Raman, FT-IR, and DFT approach. J. Mol. Struct., **1263**(2022)133195.

https://doi.org/10.1016/j.molstruc.2022.133195

[76] H. Louis, T. E. Gber, F. C. Asogwa, E. A. Eno, T. O. Unimuke, V. M. Bassey, B. I. Ita, Understanding the lithiation mechanisms of pyrenetetrone-based carbonyl compound as cathode material for lithium-ion battery: Insight from first principle density functional theory. Mater. Chem. Phys. **278**(2022)125518.

https://doi.org/10.1016/j.matchemphys.2021.125518

[77] G. J. Ogunwale, H. Louis, T. O. Unimuke, G. E. Mathias, A. Owen, H. O. Edet, O. C. Enudi, E.O. Oluwasanmi, A. S. Adeyinka, and M. D. Mohammadi, Interaction of 5-Fluorouracil on the Surfaces of Pristine and Functionalized $Ca_{12}O_{12}$ Nanocages: An Intuition from DFT, ACS Omega, 8, **15**(2023)13551-13568.

https://doi.org/10.1021/acsomega.2c03635

[78] S. Li, "Semiconductor Physical Electronics", second ed., Springer, USA, 2006.

[79] A.S. Shalabi, S. Abdel Aal, M.A. Kamel, H.O. Taha, H.Y. Ammar, W.S. Abdel Halim, The role of oxidation states in FA1 Tln+ (n = 1, 3) lasers and CO interactions at the (1 0 0) surface of NaCl: An ab initio study, Chem. Phys., **328**(2006)8–16.

https://doi.org/10.1016/j.chemphys.2006.06.009.

[80] A.E. Read, F. Weinhold, Natural bond orbital analysis of near-Hartree–Fock water dimer,

J. Chem. Phys. **78**(1983) 4066. <u>https://doi.org/10.1063/1.445134</u>

[81] J.E. Carpenter, F. Weinhold, Analysis of the geometry of the hydroxymethyl radical by the "different hybrids for different spins" natural bond orbital procedure, J. Mol. Struc. Theochem. **169**(1988)41. <u>https://doi.org/10.1016/0166-1280(88)80248-3.</u>

[82] A.E. Read, L.A.F. Weinhold, Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint, Chem. Rev. **88**(1988) 899. <u>https://doi.org/10.1021/cr00088a005.</u>

[83] D.L. Wang, H.T. Shen, H.M. Gu, Y.C. Zhai, Ab initio studies on the molecular electrostatic potential of C_{50} , J. Mol. Struct. **776**(2006)47–51.

https://doi:10.101 6/j.theochem.2006.08.025.

[84] G. Naray-Szabo and G.G. Ferenczy, Molecular Electrostatics, Click to copy article link Chem. Rev. **95**(1995)829–847. https://doi:10.1021/cr00036a002.

[85] X.-X. Wang, X.-Y. Li, H.-N. Li, First principles study of Eu doped carbon nanotubes, Phys. Lett. **37**(2008)6677–6680. <u>https://doi:10.1016/j.physleta.2008.09.011.</u>

[86] K. Parikth, K. Cattanatch, R. Rao, D.S. Suh, A. Wu, S.K. Manohar, Flexible vapour sensors using single walled carbon nanotubes, Sens. Actuators, B 113(2006)55. https://doi:10.1016/j.snb.2005.02.021.

[87] D. Wang, X. Sun, G. Xin, D. Hou, Ab initio and density functional study on the molecular electrostatic potential of C_{32} , Physica B, **405**(2010)2745–2748.

https:// Doi: 10.1016/j.physb.2010.03.065.

[88] K. Raghavachari, B. Zhang, J.A. Pople, B.G. Johnson, P.M.W. Gill, Isomers of C_{24} . Density functional studies including gradient corrections, Chem. Phys. Lett. **220**(1994)385. <u>https://doi.org/10.1016/0009-2614(94)00192-8.</u> [89] P. Politzer, D.G. Truhlar, Chemical Applications of Atomic and Molecular Electrostatic Potentials, Plenum, New York, 1981. <u>https://doi.org/10.1007/978-1- 4757-9634-6</u>.

[90] P. Politzer, C.W. Kammeyer, J. Bauer, W.L. Hedges, Polar Properties of Carbon Monoxide, Journal of Physical Chemistry **85**(1981)4057–4060,

https://doi.org/ 10.1021/j150626a021.

[91] G. Frenking, C. Loschen, A. Krapp, S. Fau, S.H. Strauss, Electronic structure of CO—An exercise in modern chemical bonding theory, Journal of computational Chemistry **28**(2006) 117–126. <u>https://doi.org/10.1002/jcc.20477.</u>

[92] Bader, R. F. W. A "Quantum Theory"; Clarendon: Oxford, U.K., 1990.

[93] T. A. Keith, R. F. W. Bader, Y. Aray, Structural homeomorphism between the electron density and the virial field. Int. J. Quant. Chem., **57**(1996)183–198.

https://doi.org/10.1002/(SICI)1097-461X(1996)57:2%3C183::AID-QUA4%3E3.0.CO;2-U

[94] N. Bokka, V. Adepu, A. Tiwari, S. Kanungo, P. A Sahatiya, detailed comparative performance analysis of the Transition Metal Di-chalcogenides (TMDs) based strain sensors through experimental realisations and first principle calculations. FlatChem, **32**(2022)100344. <u>https://doi.org/10.1016/j.flatc.2022.100344</u>

[95] O. A. Syzgantseva, V. Tognetti, L. Joubert, On the physical nature of halogen bonds: A
 QTAIM study. J. Phys. Chem. A, 117(2013) 8969. https://doi.org/10.1021/jp4059774

[96] H.J. Bohorquez, 'R.J. Boyd, C.F. Matta, Molecular model with quantum mechanical bonding information, J. Phys. Chem. A **115**(2011) 12991–12997.

https://doi:10.1021/jp204100z

[97] A. U. Agobi, H. Louis, A. Ekpunobi, T. O. Unimuke, A. I. Ikeuba, A. M. S. Pembere, C. N. Ozoemena, Theoretical investigation of the structural, optoelectronic, and the application of waste graphen oxide/polymer nanocomposite as a photosensitizer. Mater. Res. Express, 9(2022) 065301. <u>https://doi: 10.1088/2053-1591/ac7300</u>

[98] O. Moradi & K. Zare, Adsorption of Pb(II), Cd(II) and Cu(II) Ions in Aqueous Solution on SWCNTs and SWCNT –COOH Surfaces: Kinetics Studies. Fullerenes, Nanotubes and Carbon Nanostructures, 19(2011), 628–652. <u>https://doi.org/10.1080/1536383X.2010.504955</u>
[99] R. Kartika, F. H. Alsultany, A. T. Jalil, M. Z. Mahmoud, M. N. Fenjan, H. Rajabzadeh,

 $Ca_{12}O_{12}$ nanocluster as highly sensitive material for the detection of hazardous mustard gas: Density-functional theory, Inorganic Chemistry Communications, **137**(2022)109174.

https://doi.org/10.1016/j.inoche.2021.109174.