A Comparative study of SCN- adsorption on the $Al_{12}N_{12}$, $Al_{12}P_{12}$, and Siand Ge - doped $Al_{12}N_{12}$ nano-cages to remove from the environment

Mahshad Vakili[a]∗ , Vahideh Bahramzadeh[a], Mahshid Vakili[b]

[a] Young Researchers and Elite club, Miyaneh Branch, Islamic Azad University, Miyaneh, Iran
[b] Department of Chemistry, Payame Noor University, Tehran, Iran

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ABSTRACT

The geometry, electronic structure, and catalytic properties of $Al_{12}N_{12}$ and $Al_{12}P_{12}$ nano-cages are investigated by density functional theory calculations. The results express that toxic gas SCN⁻adsorption upon the Al atom of $Al_{12}N_{12}$ is stronger than that of isolated $Al_{12}P_{12}$ nano-cage. The adsorption value is about -192.74 kJ mol^{-1}, which is reason via the chemisorptions of SCN anion. The computed density of states (DOS) indicates that a notable orbital hybridization take place between SCN⁻ and $Al_{12}N_{12}$ nano-cage in adsorption process. Finally, the $Al_{12}N_{12}$ nano-cage can be used to design as useful sensor for nanodevice applications.
Hence, we concluded that the Si-doped $Al_{11}N_{12}$ nano-cage can be served as a reliable material for SCN⁻ adsorption.

1. Introduction

Environmental pollution is one of the most important problems that human beings face and due to the increase in population and the expansion of industries, the importance of controlling environmental pollution and preventing its exponential growth, is felt more than ever. Problems caused by the presence of pollutants that are not biologically eliminated, have led humans to identify different ways to reduce or eliminate them. For a long time, various processes have been implemented to remove harmful environmental pollutants from water, wastewater and air, which have not had a very good efficiency. In recent years, nanotechnology has played a significant role in green chemistry and the use of nanoparticles in the removal of environmental pollutants is considered as one of the newest methods of removing pollutants in the world. These materials have a very good performance in controlling environmental pollution due to their high surface-to-volume ratio and excellent chemical activity and production of harmless products. This article introduces some of the most important nanoparticles and their application in the removal of environmental pollutants.
Thiocyanate is the anion (SCN⁻). Due to the high level of the importance of thiocyanate anion detection in both

atmospheric and environmental sciences, a wide variety of investigations have been done upon the adsorption of this molecule both theoretically and experimentally [1–11]. SCN⁻ anion is the product of reaction between CS_2 and NH_2-species and also reaction between $CH_3SCN + e^-$ SCN$^-$ +CH$_3$• and it can be found in interstellar ice and dust clouds. Quite fadeaway or reducing SCN⁻ in human body is highly important regarding the human host defense system. It may happen via biosynthesis of hypothiocyanite by a lactoperoxidase. Moreover, the photoelectron spectrum of thiocyanate anion has been studied reporting the adiabatic electron affinity of SCN⁻ radical [8,14]. The SCN⁻ can play notable roles in determining the structure of polymeric transition-metal complexes. The SCN⁻ anion is a very adaptable ambidentate ligand with two donor atoms [9–13]. In thiocyanates, the organic group (or metal ion) is attached to sulfur: R−S−C≡N has a S-C single bond and a C≡N triple bond [15]. In isothiocyanates, the substituent is attached to nitrogen: R−N=C=S has a S=C double bond and a C=N double bond.
Also The dangerous reaction between thiocyanate anion and acids, it is possible to release highly toxic gases. Nanotechnology can act as a green technology in the destruction and transformation of various environmental pollutants. The most prominent feature of this

∗ Corresponding author. Tel.: +989113381994; e-mail: nikpassand@iaurasht.ac.ir

nanotechnology is that it can be used to remove many toxic and dangerous pollutants. They are not easily removed without producing dangerous by-products. Elimination of nanomaterials that are used as catalysts, adsorbents, membranes, etc., have high activity and sensitivity and therefore better performance, and due to their high specific surface area, less of them are needed to perform the process.

$Al_{12}N_{12}$ and $Al_{12}P_{12}$ nano-cages have also represented to be such a promising candidate for the sensing applications [16,17]. In particular, the aluminum nitrides (AlN) nanocages and nanotubes have been extensively investigated due their high temperature stability, low dielectric constant, large thermal conductivity, ultra-violet light emission and oxidation resistance [18–21]. AlN nanostructures have been successfully synthesized from the non-layered structure [22,23]. Wu et al. [24] have studied the structure and energy of $(AlN)_n$ nanocages (n = 2–41), theoretically, showing that the $Al_{12}N_{12}$ is energetically the most stable cluster in this family and would thus be an ideal inorganic fullerene-like cage. Ahmadi Peyghan et al. [25] have reported the chemical adsorption of one or two H atoms on an aluminum phosphide nanocluster by density functional theory calculations. The $Al_{12}N_{12}$ and $Al_{12}P_{12}$ nano-cages are made of eight hexagonal rings and six tetragonal rings. In These nano-cages due to the significant charge separation between the aluminum and nitrogen phosphide atoms, the aluminum atom (electron deficient) and nitrogen and phosphide atoms (electron rich) can be viewed as Lewis acid and base, respectively. Therefore, AlN and AlP nanostructures can be considered as a desirable non-metal catalyst with Lewis acid–base pairs.

Correct description of molecular interactions with cluster surfaces is important for catalysis as well as for the development of cluster-based materials. In the present study, the adsorption of thiocyanate anion (SCN⁻) on the $Al_{12}N_{12}$, $Al_{12}P_{12}$, and doping metals AlN nano-cages is investigated. Density functional theory (DFT) calculations are performed to elucidate the strength and nature the interaction of SCN⁻ with the $Al_{12}N_{12}$, $Al_{12}P_{12}$, and doping metals $Al_{12}N_{12}$, respectively, in the complexes.

2. Computational details

Geometry optimizations, density of states (DOS) [26], frontier molecular orbital (FMO), and natural bond orbital (NBO) analyses were carried out with the GAMESS quantum chemistry software package [27-29]. All calculations are based upon the density functional theory (DFT) at the M06 method with the standard 6-31G* basis set [30,31]. The standard 6-311+G* and CC-PVDZ basis sets were used for the applied systems [32,33]. The M06 is indicated to be a dependable and usually applied functional in the study of different nanostructures [16,34]. We have performed the

exchange–correlation functional parameterized by Becke, Three-parameters, Lee-Yang-Parr (B3LYP) in the hybride [35,36]. The adsorption energies (E_{ad}) of SCN⁻ upon the $Al_{12}N_{12}$ and $Al_{12}P_{12}$ and doping metals AlN nano-cages are represented by:

$$E_{ad} = E_{\text{cage-Molecule}} - \left(E_{\text{cage}} + E_{\text{Molecule}} \right)$$

$$E_{ad} = E_{\text{M-cage-Molecule}} - \left(E_{\text{M-cage}} + E_{\text{Molecule}} \right)$$

where E_{cage} is the adsorption energies of the pristine $Al_{12}N_{12}$ and $Al_{12}P_{12}$ nano-cages. $E_{\text{cage-Molecule}}$ and $E_{\text{M-cage-Molecule}}$ are the adsorption energies of SCN⁻ interacted with the pristine, Si and Ge-doped $Al_{12}N_{12}$ and E_{Molecule} representing the energy of an isolated SCN⁻ molecule.

µ is defined according to the following equation [37]:

$$\mu = \frac{-(E_{\text{HOMO}} + E_{\text{LUMO}})}{2} \tag{4}$$

where EHOMO is the energy of the Fermi level and ELUMO is the first given value of the valance band.

3. Results and discussion

3-1- Adsorption of SCN⁻ upon the $Al_{12}N_{12}$ and $Al_{12}P_{12}$ nano-cage

Scheme 1 displays optimized structures of the perfect $Al_{12}N_{12}$ and $Al_{12}P_{12}$ in interaction with the SCN⁻ at the M06/6-31G* level of calculations. We exhibit two adsorption states with the nitrogen atom of SCN⁻ for the most stable configurations via its expected active sites (N-side) directed downward toward the Al atom in $Al_{12}N_{12}$ and $Al_{12}P_{12}$ surfaces. In the SCN⁻ adsorbed systems, the Al–N and Al–P bonds in the $Al_{12}N_{12}$ and $Al_{12}P_{12}$ nano-cages are elongated by about 1.84 and 2.33 Å, while the N–C and C–S bonds in $Al_{12}N_{12}$ are 1.19 and 1.59 Å and are 1.19 and 1.58 Å in $Al_{12}P_{12}$ nano-cage, respectively (see Table 1). The binding energy for the most stable chemisorbed configurations (N-side) of SCN⁻ on $Al_{12}N_{12}$ and $Al_{12}P_{12}$ are about -192.74 and -177.77 kJ mol⁻¹ respectively. The separation distances between the $Al_{12}N_{12}$ and $Al_{12}P_{12}$ and the SCN⁻ are 1.82 and 1.84 Å, respectively. Ahmadi Peyghan et al. [16] have shown the theoretical results of the NH_3 adsorption upon the $Al_{12}N_{12}$ and $Al_{12}P_{12}$ nano-cages, indicated that the bond lengths of Al–N and Al–P are 2.03 and 2.06 Å and with the binding energy are -37.5 and -32.8 kcal/mol, respectively. Hadipour et al. [36] introduced the strong interaction between the NH_3 molecule and AlN nano-tubes is mainly electrostatic rather than covalent because of the high heteropolar nature of Al–N bonds. The NBO analysis

demonstrated a change in the hybridization of the Al atom from sp^2 to sp^3 together with a charge transfer from the lone pair of N atom of SCN⁻ to the anti-bonding orbitals of Al–N and Al–P bonds around Al site. This analysis shows that in these formations 0.67 and 0.69 el charge transferred from SCN⁻ to the $Al_{12}N_{12}$ and $Al_{12}P_{12}$ surfaces. Thus, we believed that the nature of this interaction can be mainly covalent.
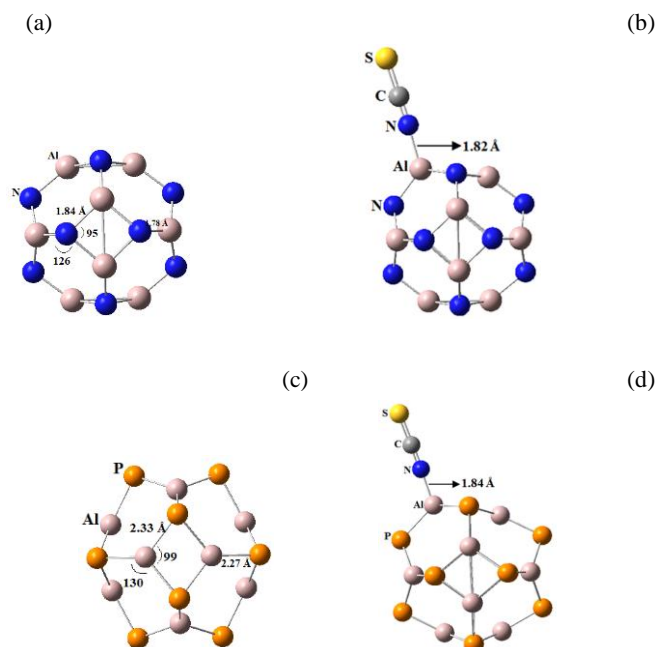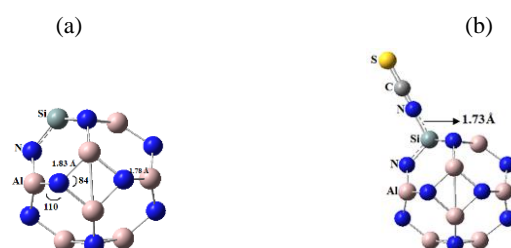

Scheme 1. Geometrical parameters of optimized structures of the (a) $Al_{12}N_{12}$, (b) $Al_{12}P_{12}$, (c) SCN⁻/$Al_{12}N_{12}$ and (d) SCN⁻/$Al_{12}P_{12}$ nano-cages (distances and angels are in angstrom and degree, respectively).
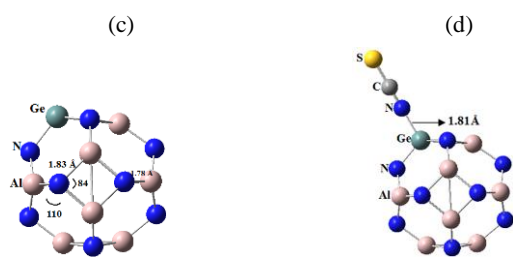
Table 1. Calculated LUMO energy (E_{LUMO}) and HOMO energy (E_{HOMO}), DM (Debye), energy gap (E_g), binding energy (eV), for SCN⁻ adsorbed on the $Al_{12}N_{12}$ and $Al_{12}P_{12}$ nano-cages at the M06/6-31G* method. Energies are in eV.

Property	SCN⁻	$Al_{12}N_{12}$	$Al_{12}P_{12}$	SCN⁻/ $Al_{12}N_{12}$	SCN⁻/ $Al_{12}P_{12}$
l_{Al-N}	–	1.84	–	1.82	–
l_{Al-P}	–	–	2.33	–	2.35
l_{N-C}	1.18	–	–	1.19	1.19
l_{C-S}	1.66	–	–	1.59	1.58
Θ_{N-C-S}	180.00	–	–	179.97	179.91
Θ_{Al-N-C}	–	–	–	178.63	178.63
E_{ad} (ev)	–	–	–	−192.74	-177.77
E_{HOMO} (ev)	-0.69	-6.78	-6.82	-6.57	-6.73
E_{LUMO} (ev)	7.60	-2.27	-3.61	-2.54	-3.56
E_g (ev)	8.30	4.51	3.21	4.03	3.17
D (Debey)μ	1.38	0.00	0.00	7.68	5.39

3-2- Adsorption of SCN⁻ upon the Si and Ge -doped $Al_{11}N_{12}$ nano-cage

We randomly substituted one aluminum atom by randomly replacing with one Si and Ge atoms from four-membered rings of $Al_{12}N_{12}$ nano-cage. It is found that the geometric structures of the Si and Ge $Al_{11}N_{12}$ changes dramatically. As shown in Table 2, the Si and Ge doping result in elongation of the bond length (l) at the doping sites from l_{Al-N} = 1.84 Å to l_{Si-N} = 1.79 and l_{Ge-N} = 1.91, respectively. Upon the adsorption processes, the bond lengths are decreased to l_{Si-N}= 1.76 and l_{Ge-N}= 1.86, respectively, owing to structural deformation of all configurations. They reveal that these bonds have become stronger and shorter than the Al–N bonds. We examine the interaction of SCN⁻ adsorbed upon the Si and Ge$Al_{11}N_{12}$ nano-cages in order to find the adsorption energies of complexes that are shown in Scheme 2. The binding energies of SCN⁻ from its N head adsorbed on the Si and Ge $Al_{11}N_{12}$ nano-cages are computed to be -454.32 and -401.61 kJ mol⁻¹ with the distances of 1.73 and 1.81 Å, respectively, which reveals that SCN⁻ experiences a strong chemical adsorption upon the exterior surfaces of metal doping such as Si and Ge atoms (see Scheme 2). These results for Si atom of nano-cages interacted with N atom of molecule as expected, are very strong interaction in comparison with Ge atom of nano-cage. It shows that the Si atom is energetically notable for adsorption of SCN⁻. For the above configurations, the largest charges transferred from 0.610 and 0.635 electrons take place for the adsorption of SCN⁻ on the Si and Ge-doped $Al_{11}N_{12}$ nano-cages, respectively. Locally structural deformations at the interaction sites are observed after the adsorption of SCN⁻ upon metals doping, where the adsorbing Si and Ge atoms are slightly pulled out of the walls of $Al_{11}N_{12}$ nano-cage. Therefore, the elongation of Si–N and Ge–N bonds is expected upon the adsorption process. For the most stable configuration ($SiAl_{11}N_{12}$), we examined the interaction of SCN⁻ with different sites of the nano-cage.

Scheme 2. Geometrical parameters of optimized structures of the (a) SiAl₁₁N₁₂, (b) SCN⁻/SiAl₁₁N₁₂, (c) GeAl₁₁N₁₂ and (d) SCN⁻/GeAl₁₁N₁₂ nano-cages (distances and angels are in angstrom and degree, respectively).

Table 2. Calculated LUMO energy (E_{LUMO}) and HOMO energy (E_{HOMO}), MD (Debye), energy gap (E_g), binding energy (eV), for SCN− adsorbed on the Si- and Ge-doped Al₁₁N₁₂ nano-cages at the M06/6-31G* method. Energies are in eV.

Property	SiAl₁₁N₁₂	GeAl₁₁N₁₂	SCN⁻/SiAl₁₁N₁₂	SCN⁻/GeAl₁₁N₁₂
l_{Si-N}	1.79	–	1.73	–
l_{Ge-N}	–	1.91	–	1.81
l_{N-C}	–	–	1.19	1.18
l_{C-S}	–	–	1.58	1.5
Θ_{N-C-S}	–	–	179.96	179.98
Θ_{Si-N-C}	–	–	179.73	179.96
E_{ad} (ev)	–	–	-454.32	-401.61
E_{HOMO} (ev)	-6.72	-6.75	-4.64	-5.24
E_{LUMO} (ev)	-2.45	-2.52	-2.30	-2.26
E_g (ev)	4.26	4.23	2.33	2.97
μ D (Debey)	5.70	6.14	1.38	1.40

3-3- The effect of basis set in the interaction of SCN⁻ with the pristine and the Si-doped Al₁₁N₁₂ nano-cage
In the next stage, we have explored the effect of basis set for the most stable adsorption site in the interaction of SCN⁻ with the pristine and the Si-doped Al₁₁N₁₂ nano-cage at the M06 method with 6-311+G* basis set. The computed values of the E_{ad} and interaction distance for SCN⁻ close to Al₁₂N₁₂ nano-cage computed in this study are -221.24 kJ mol⁻¹ and 1.88 Å, respectively. This result is presented in Table 3, revealing that the adsorption value of M06/6-311+G* method is somewhat more negative than that of the m06/6-31G* method. The E_{ad} and interaction distance values for SCN⁻ from its N head close to the Si atom of Al₁₁N₁₂ , are about -486.62 kJ mol⁻¹ and 1.76 Å, respectively. As we explored earlier, the adsorption energy is not changed significantly in going from the 6-31G* to 6-311+G* basis set. In contrast with the above results, we investigated the interaction of SCN⁻ from its N head with the pristine Al₁₂N₁₂ nano-cage at the M06 method with CC-PVDZ basis set. The computed adsorption energy is -213.01 kJ mol⁻¹ and the equilibrium distance between the N atom of molecule and the Al atom of nano-cage is 1.89 Å in the SCN⁻/Al₁₂N₁₂ system. In contrast with the Si-doped Al₁₁N₁₂ is strongly chemisorbed on the pristine Al₁₂N₁₂, the SCN⁻ molecule nano-cage at the M06 method with CC-PVDZ basis set. Whereas its adsorption energy and interaction distance are -439.86 kJ mol⁻¹ and 1.78 Å, respectively.

Table 3. Calculated LUMO energy (E_{LUMO}) and HOMO energy (E_{HOMO}), MD (Debye), energy gap (E_g), binding energy (eV), for SCN⁻ adsorbed on the pure and Si-doped Al₁₂N₁₂ nano-cages at the m06 method using 6-311+G* and CC-PVDZ basis sets. Energies are in eV.

Property	6-311+G* Al₁₂N₁₂	SCN⁻/Al₁₂N₁₂	SiAl₁₁N₁₂	SCN⁻/SiAl₁₁N₁₂
l_{Al-N}	1.84	1.88	–	–
l_{Si-N}	–	–	1.78	1.76
l_{N-C}	–	1.18	–	1.18
Θ_{N-C-S}	–	179.94	–	179.91
Θ_{Al-N-C}	–	178.98	–	–
Θ_{Si-N-C}	–	–	–	178.00
E_{ad} (ev)	–	-221.24	–	-486.62
E_{HOMO} (ev)	-6.79	-6.59	-6.74	-4.66
E_{LUMO} (ev)	-2.43	-2.65	-2.59	-2.51
E_g (ev)	4.36	3.93	4.14	2.15
μ D (Debey)	0.00	7.72	1.54	5.71

CC-PVDZ			
$Al_{12}N_{12}$	$SCN^-/$ $Al_{12}N_{12}$	$SiAl_{11}N_{12}$	$SCN^-/$ $SiAl_{11}N_{12}$
1.85	1.89	–	–
–	–	1.81	1.78
–	1.19	–	1.19
–	179.98	–	179.99
–	177.13	–	–
–	–	–	179.55
–	-213.01	–	-439.86
-6.74	-6.52	-4.71	-6.69
-2.30	-2.60	-2.26	-2.49
4.44	3.91	2.45	4.20
0.00	7.92	1.47	5.84

3-4- Density of states (DOS)

Computed DOS maps (see Scheme. 3) represent that the $Al_{12}N_{12}$ and $Al_{12}P_{12}$ nano-cages are semiconductors with the energy gaps of 4.51 and 3.21 eV at the M06/6-31G* method, respectively. There is a direct relationship between the stability and HOMO–LUMO energy gap (E_g) of the clusters, i.e. greater E_g leads to more stability [38]. The relative order magnitudes of E_g are $Al_{12}N_{12} > Al_{12}P_{12}$. The $Al_{12}P_{12}$ nano-cages has the smallest E_g; therefore, it is the most electrically conductive cluster. The energy gaps of the Si and Ge-doped $Al_{11}N_{12}$ are calculated with the values of 4.26 and 4.23 eV at the M06/6-31G* method, respectively. E. Shakerzadeh et al. [39] performed a comparative theoretical study on the structural, electronic and nonlinear optical features of $B_{12}N_{12}$ and $Al_{12}N_{12}$ nanoclusters with the groups III, IV and V dopants nanoclusters. As seen in Tables 1 and 2, the values of HOMO, LUMO and E_g of SCN^- interacting with the $Al_{12}P_{12}$, $Al_{12}N_{12}$ and doping metals $Al_{12}N_{12}$ nano-cages were investigated. The E_g in $Al_{12}P_{12}$ and $Al_{12}N_{12}$ nano-cages are significantly reduced to 4.03 and 3.17 eV, respectively. DOS maps of the SCN^- adsorbed towards the Si and Ge-doped $Al_{11}N_{12}$ nano-cages reveal that the E_g values are obviously increased to 2.33 and 2.97 eV, respectively, during the adsorption processes. Results is presented in Table 3, revealing the effect of basis set for the E_g in the interaction of SCN^- with the pristine and the Si-doped $Al_{11}N_{12}$ nano-cage of M06/6-311+G* and M06/CC-PVDZ methods. Results is presented in Table 3, revealing that the E_g values at the M06 method with 6-311+G* and CC-PVDZ basis sets. The E_g in the pristine and the Si-doped $Al_{11}N_{12}$ nano-cage are significantly reduced and increased, respectively. We applied at the B3LYP with the 6-31 G* basis sets.
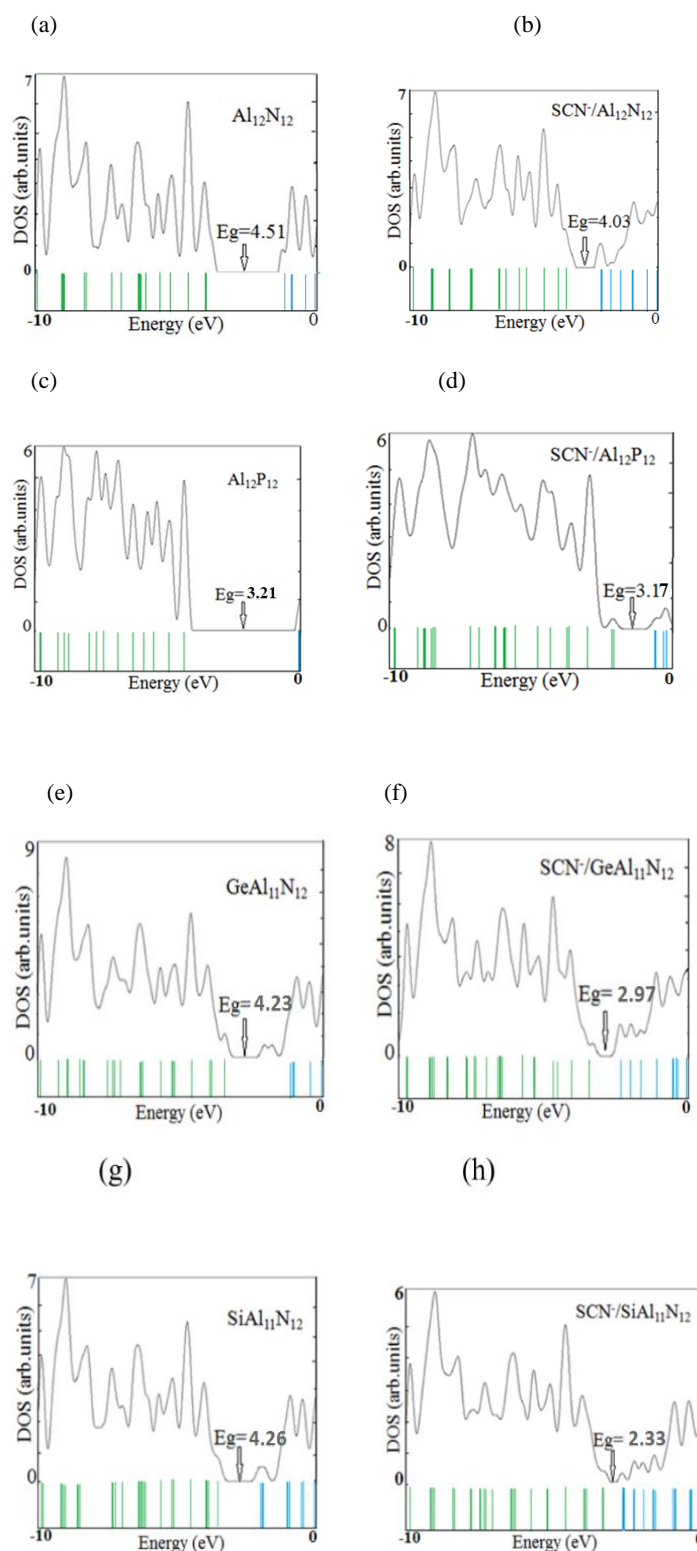
Scheme 3. Computed density of states (DOS) for (a) $Al_{12}N_{12}$, (b) $SCN^-/Al_{12}N_{12}$, (c) $Al_{12}P_{12}$, (d) $SCN^-/Al_{12}P_{12}$, (e) $SiAl_{11}N_{12}$, (f) $SCN^-/SiAl_{11}N_{12}$, (g) $GeAl_{11}N_{12}$ and (h) $SCN^-/GeAl_{11}N_{12}$ nano-cages.

4. Conclusion

The adsorption phenomena and electronic properties of SCN⁻ on the pristine $Al_{12}N_{12}$, $Al_{12}P_{12}$, and Si and Ge-doped $Al_{11}N_{12}$ nano-cages were investigated via DFT calculations with the M06 and B3LYP methods. It was found that the energy gap of $Al_{12}N_{12}$ interacted with SCN⁻ has the largest in comparison with $Al_{12}P_{12}$. The pure $Al_{12}N_{12}$ can more strongly absorb the SCN⁻ upon adsorption of up to -192.74 kJ mol^{-1} than that of the $Al_{12}P_{12}$ (-177.77 kJ mol^{-1}). The result indicates that the SCN⁻ is strongly adsorbed upon the wall of Si-doped $Al_{11}N_{12}$ nano-cage compared to Ge atom and this interaction leads to significant change in the electronic properties of nano-cage. The reduction of energy gaps, ionization potential, and global hardness along with increase of the chemical reactivity also lead to the lowering of stability during the adsorption process of SCN⁻ upon the pure and the Si-doped $Al_{11}N_{12}$ nano-cages surface that indicates the capacity of these materials as promising candidates for SCN⁻ detection.

Acknowledgements

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