 DOI: 10.17344/acsi.2017.3826 *Acta Chim. Slov.* **2018,** *65,* 208–212

Scientific paper

The Cl Functionalized Aluminum Nitride (AlN) and Aluminum Phosphide (AlP) Nanocone Sheets as Hydrogen Selenide (H_2Se) Sensor: a Density Functional Investigation

Seyyed Milad Abrishamifar,[1] Negar Heidari,[2] Razieh Razavi,[3] Milad Janghorban Lariche[4,*] and Meysam Najafi[5,*]

[1] *Department of Chemical Engineering, New York International University of Technology and Management, New York, USA*

[2] *Department of Chemistry, Faculty of Science, Borujerd Branch, Islamic Azad University, Borujerd, Iran*

[3] *Department of Chemistry, Faculty of Science, University of Jiroft, Jiroft, Iran*

[4] *Abadan School of Medical Sciences, Abadan, IRAN*

[5] *Medical Biology Research Center, Kermanshah University of Medical Sciences, Kermanshah 67149-67346, Iran*

** Corresponding author: E-mail: janghorban@abadanums.ac.ir and meysamnajafi2016@gmail.com Phone: +98-8337243181 Fax: +98-8337243181*

Received: 06-09-2017

Abstract

The adsorption of H_2Se molecule on AlN-NCS and AlP-NCS surfaces were investigated by using of DFT calculations. The potentials of Cl-functionalized AlN-NCS and AlP-NCS for H_2Se adsorption were examined. All processes of H_2Se-adsorption on considered nanocone sheets were exothermic reactions. The calculated $|E_{ad}|$ amount of complex H_2Se with AlP-NCS was higher than AlN-NCS. The functionalization of considered nanocone sheets with Cl atom increase $|E_{ad}|$ amount of H_2Se. Results reveal that, obtained E_{ad} amounts of considered nanocone sheets have linear relationships with corresponding orbital energy amounts. Finally, the novel nanocone sheets with higher efficiency to adsorption of H_2Se can be proposed.

Keywords: DFT, nanocone, H_2Se, function, gas sensor

1. Introduction

Hydrogen selenide (H_2Se) as main toxic gas can be produced via reaction of selenium and hydrogen gas and it can be formed by reaction of acids with selenide. Some paths to H_2Se preparation in large and small scales have been investigated. The presence of H_2Se on exposed fur animals would result in relatively high oral doses resulting from preening and possibly skin permeation.[1–3]

H_2Se is the most toxic gases with a contact boundary of 0.05 ppm over an 8 hour cycle and H_2Se at really low concentrations is very infuriating smell resembling that of leaking gases.[1,2] Growth of H_2Se resultant from reticence of the Se methylation metabolism, the detoxification way of selenium, is found resulting frequent oral administration of toxic dose of selenocystine.[4–6]

Aluminum nitride nanocone sheet (AlN-NCS) have been synthesized and it has wide band gap and so it has various applications in optics, electronics and photoelectronics.[7] The previous studies shown that AlN-NCS and AlP-NCS were uniform and Al, P and N atoms on surface of AlN-NCS and AlP-NCS have 3-fold coordinate. The creation of unsaturated sites on Al, P and N atoms play main roles in gas adsorption and so AlN-NCS and AlP-NCS can be gas sensors with the highest performance.[8–12]

The adsorptions of toxic gases with various compounds to identify the suitable sensor are important works to solve the environmental problems. In previous studies, widely in chemical processes the various nanostructures because of their sensitivity and activity have been used and results have been shown that functionalization of na-

nostructure can improvement the capability of nanostructures to detect toxic gases.[13–17]

In previous papers the adsorption of various gases such as SO_2, H_2S, CO_2 and CO on surfaces of nanostructures have been investigated.[18–34] Zaboli and et al.[35] the adsorptions of the H_2S, H_2Se and SO_2 molecules on the surface of fullerene by the density functional theory investigated. Obtained results shown that, the adsorption energy amounts of gas molecule were short, so, the sensor were possess at short recovery times.[35] Also results shown that H_2Se molecule with adsorption energy of about –11.28 kJ/mol has the strongest adsorption on surface of fullerene.[35]

In previous study theoretical methods have been used to investigation influence of metal oxides on various polymers such as polyvinyl alcohol and polyaniline. Results show that, addition of metal oxides increase the total dipole moments of polymers and decrease the band gap energies of polymers. Results shown that predictable dipole moment of studied compounds reflects their potential to interact with their neighboring molecules and higher dipole moment of assumed structures was joint with the higher activity for various applications.[35–37]

Ibrahim and et al. used theoretical methods to study the dipole moment and geometrical structures of COOH. Their results show that increase of dipole moments are suitable pointer to ability of considered structures. Also they used DFT to study composite of divalent zinc and results show that obtained dipole moment was 23.4 Debye and band gap energy was 0.49 eV. Results shown that decorated CNT can form stable structures with increased molecular dimensions and decorated CNT can be a suitable sensor to volatile matter.[38–40]

In present work, the adsorptions of H_2Se molecule on surfaces of AlN-NCS and AlP-NCS were examined theoretically. The Cl-functionalized effects on ability of AlN -NCS and AlP-NCS to adsorption of H_2Se were calculated via theoretical method. The orbital energy amounts of considered nanocone sheets were calculated and relationships between orbital energy and E_{ad} amounts of considered nanocone sheets were examined. The initial points of this work are: (1) to find the ability of AlN-NCS and AlP -NCS to H_2Se-adsorption; (2) to categorize the influences of Cl functionalization of NCS on capability of AlN-NCS and AlP-NCS; (3) to discovery the linear relationships between adsorption and orbital energy NCS; (5) To propose the novel NCSs with the highest capacity to H_2Se-adsorption.

2. Computational Details

The geometry of AlN-NCS, AlP-NCS and their Cl functionalized derivatives were optimized via DFT method, B3LYP functional and 6-311G (d,p) basis set in GAMESS software.[41,42] The geometry of complexes of H_2Se molecule and considered AlN-NCSs and AlP-NCSs were optimized (obtained structures of considered complexes were reported in figure 1). In order to remove the border effects, termination atoms of considered AlN-NCSs and AlP-NCSs were sodden via hydrogen atoms. In this work, frequency calculations were done in order to confirm the structures were true minima.[43–46]

In this work, adsorption energy (E_{ad}) and free energy (G_{ad}) amounts of H_2Se molecule on considered AlN-NCSs and AlP-NCSs were obtained via equations 1 and 2, respectively:

$$E_{ad} = E\ (\text{nanocone sheet}/H_2Se) - E\ (\text{nanocone sheet}) - E\ (H_2Se) + E_{BSSE} \quad (1)$$

$$G_{ad} = G\ (\text{nanocone sheet}/H_2Se) - G\ (\text{nanocone sheet}) - G\ (H_2Se) \quad (2)$$

where E (nanocone sheet/H_2Se) is energy of complexes of H_2Se and considered nanostructures. The E (H_2Se) and E (nanocone sheet) are energies of H_2Se molecule and considered nanostructures, respectively. The negative amounts of E_{ad} and G_{ad} indicated that H_2Se molecule and AlN-NCSs and AlP-NCSs have exothermic interactions. In this work also the Basis set superposition error (BSSE) amounts of interactions of H_2Se-nanostructures were calculated.[47]

3. Results and Discussion

3. 1. E_{ad} and G_{ad} Amounts of H_2Se-nanocone Sheet

In this section E_{ad} and G_{ad} amounts of H_2Se adsorption on surface of AlN-NCS, AlP-NCS, Cl-AlN-NCS and Cl-AlP-NCS in table 1 were presented. In table 1 the E_{ad} and G_{ad} amounts of H_2Se-NCS and H_2Se-Cl-NCS were negative and so the interactions of H_2Se and considered nanocone sheets were exothermic reactions. The $|E_{ad}|$ and $|G_{ad}|$ amounts of H_2Se-AlP-NCS were higher than corresponding values of H_2Se-AlN-NCS ca 41.5 and 43.4 kJ/mol, respectively.

The $|E_{ad}|$ and $|G_{ad}|$ amounts of H_2Se-Cl-AlP-NCS were higher than corresponding values of H_2Se-Cl-AlN -NCS ca 18.3 and 18.2 kJ/mol, respectively. Also $|E_{ad}|$ and $|G_{ad}|$ amounts of H_2Se-Cl-AlP-NCS were higher than corresponding values of H_2Se-AlP-NCS ca 21.2 kJ/mol and 20.3 kJ/mol, respectively.

In table 1 the $|E_{ad}|$ and $|G_{ad}|$ amounts of H_2Se-NCS and H_2Se-Cl-NCS were decreased as follow: AlN-NCS < Cl-AlN-NCS < AlP-NCS < Cl-AlP-NCS. Data in table 1 consummated that Cl-AlP-NCS and AlN-NCS have the highest and the lowest performances to H_2Se-adsorption, respectively. Results in table 1 can be expounded that phosphor and chlorine atoms can stable the AlP-NCS, AlP -Cl-NCS and their H_2Se complexes; therefore the $|E_{ad}|$ and $|G_{ad}|$ amounts of AlP-NCS AlP-Cl-NCS were higher than corresponding values of AlN-NCS. [48]

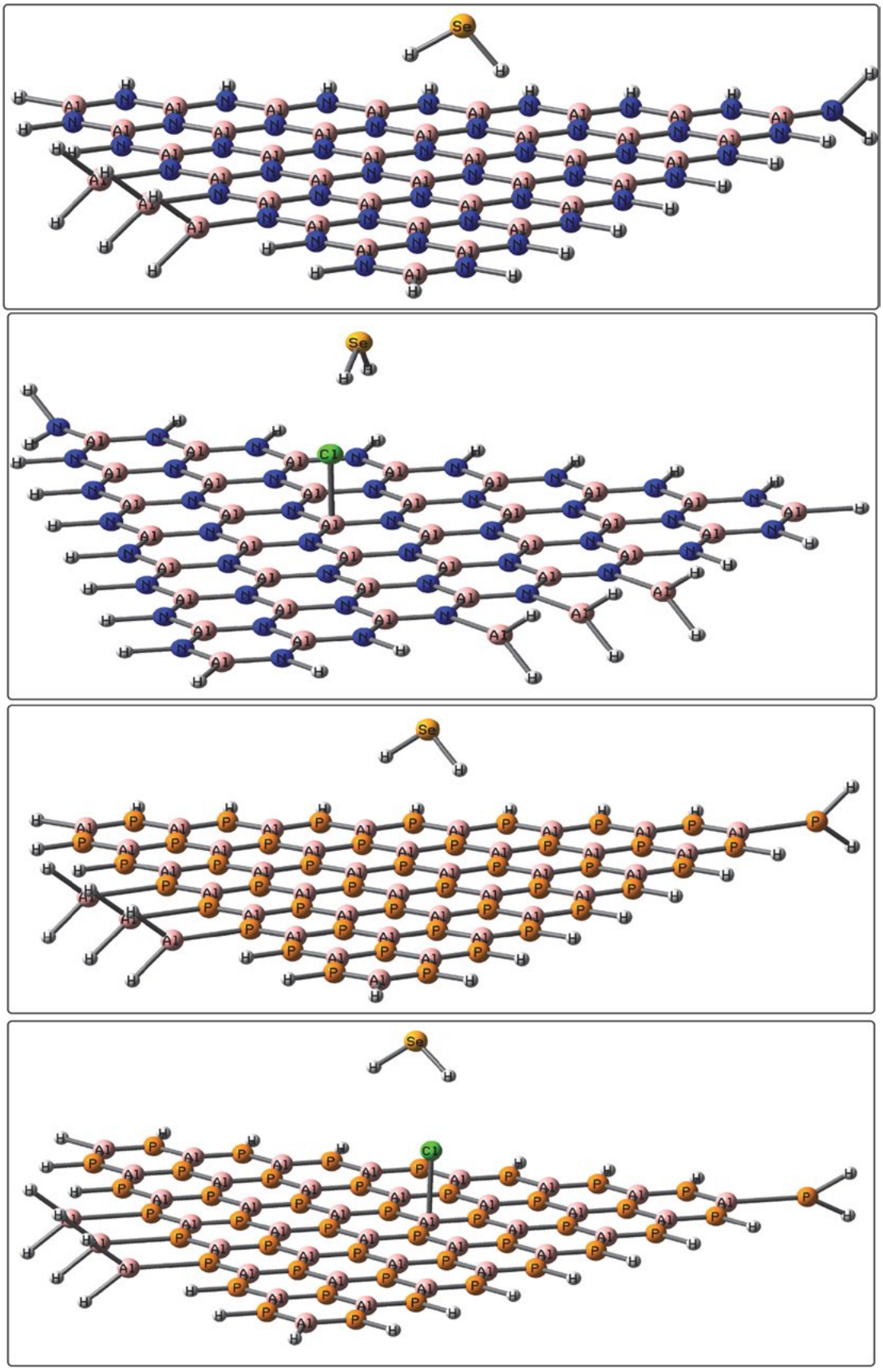

Figure 1. Complexes of H_2Se with AlN-NCS, AlP-NCS, Cl-AlN-NCS and Cl-AlP-NCS.

Table 1. Calculated E_{ad} and G_{ad} of H_2Se on AlN-NCS, AlP-NCS, Cl-AlN-NCS and Cl-AlP-NCS surfaces.

G_{ad} (kJ/mol)	E_{ad} (kJ/mol)	Nanostructure
−368.6	−377.3	AlN-NCS
−412.0	−418.8	AlP-NCS
−386.9	−395.6	Cl-AlN-NCS
−432.3	−440.0	Cl-AlP-NCS

Table 2. Calculated orbital energy amounts of AlN-NCS, AlP-NCS, Cl-AlN-NCS and Cl-AlP-NCS.

E_{HLG} (kJ/mol)	E_{LUMO} (kJ/mol)	E_{HOMO} (kJ/mol)	Nanostructure
222.0	−378.3	−600.2	AlN-NCS
193.0	−384.1	−577.1	AlP-NCS
173.7	−396.6	−570.3	Cl-AlN-NCS
136.1	−410.1	−546.2	Cl-AlP-NCS

3. 2. Orbital Energies of Considered Nanocone Sheets

In this section orbital energy amounts of AlN-NCS, AlP-NCS, AlN-NCS, AlP-NCS were calculated and obtained amounts were represented in table 2 and relationships of orbital energy amounts in table 2 and E_{ad} amounts in table 1 were examined. In table 2, AlN-NCS and Cl-AlP -NCS have the highest and the lowest amounts of $|E_{HOMO}|$, respectively.

Therefore in table 2 the Cl-AlP-NCS and AlN-NCS have the highest and the lowest inclination to lose an electron, respectively. In table 2, the $|E_{LUMO}|$ amounts of studied nanostructures were decrease as follow: AlN-NCS < Cl-AlN-NCS < AlP-NCS < Cl-AlP-NCS. In table 2, Cl -AlP-NCS and AlN-NCS have the highest and the lowest amounts of $|E_{LUMO}|$, respectively. Therefore in table 2 the Cl-AlP-NCS and AlN-NCS have the highest and the lowest capability to receive an electron, respectively.

In table 2, E_{HLG} amounts of considered nanocone sheets were decrease as follow: AlN-NCS > Cl-AlN-NCS > AlP-NCS > Cl-AlP-NCS. In table 2, Cl-AlP-NCS and AlN -NCS have the lowest and the highest amounts of E_{HLG}, respectively. So, in table 2 the Cl-AlP-NCS and AlN-NCS have the highest and the lowest reactivity. In table 2, AlP -NCS has higher $|E_{LUMO}|$ and lower $|E_{HOMO}|$ amounts than AlN-NCS. In table 2, Cl-AlN-NCS and Cl-AlP-NCS have higher $|E_{LUMO}|$ and lower $|E_{LUMO}|$ amounts than AlN-NCS and AlP-NCS. So, Cl functionalization increase the capability of AlN-NCS and AlP-NCS to H_2Se adsorption.

In this section, relationships between E_{ad} and orbital energy amounts of considered nanocone sheets were examined. The E_{ad} amounts of complexes of H_2Se-NCS in table 1 were modified against the orbital energy amounts of complexes of H_2Se-NCS in table 2. The equations 3-5 were calculated from these modifications as follow:

$$E_{ad} = -1.09 \times (E_{HOMO}) - 1032 \quad (3)$$

$$E_{ad} = 1.43 \times (E_{HOMO}) + 152 \quad (4)$$

$$E_{ad} = 0.63 \times (E_{HLG}) - 523 \quad (5)$$

The relationship constants of equations 3-5 were ca 0.994, 0.997 and 0.994, respectively and so there are linear relationship between E_{ad} and orbital energy amounts of complexes H_2Se-NCS.

In tables 1 and 2 the E_{ad} and orbital energy amounts of H_2Se-NCS complexes have similar trends and it can be established that ability of considered nanocone sheets to H_2Se-adsoprtion were decreased as follow: AlN-NCS < Cl -AlN-NCS < AlP-NCS < Cl-AlP-NCS. Finally, Cl-AlP-NCS and AlN-NCS have the highest and the lowest capacity to H_2Se-adsorption and also E_{ad} and orbital energy mounts were main factors to predicate of ability of NCS to H_2Se -adsorption.

4. Conclusion

The potentials of AlN-NCS, AlP-NCS, Cl-AlN-NCS and Cl-AlP-NCS to adsorption of H_2Se molecule via DFT method and B3LYP functional were examined. The interactions of H_2Se with considered nanocone sheets were exothermic processes and these interactions were possible theoretically. The $|E_{ad}|$ amount of H_2Se-AlP-NCS were higher than those of H_2Se-AlN-NCS. The considered Cl -AlP-NCS and Cl-AlN-NCS have higher $|E_{ad}|$ amounts than AlP-NCS and AlN-NCS, respectively. There were linear relationships between of E_{ad} and orbital energy amounts of considered NCSs. The E_{ad} and orbital energy amounts can be considers as main scale to predicate the ability of nanocone sheets to H_2Se-adsorption.

5. References

1. A. Afshar, M. Salami Hosseini, E. Behzadfar, *Sci. Iran. Trans. C* **2014**, *21*, 2107–2115. **DOI:**10.1016/j.snb.2011.04.070
2. T. Hübert, L. Boon-Brett, G. Black, U. Banach, *Sens. Actu. B: Chem.* **2011**, *157*, 329–352.
3. M. Ibrahim, E. Koglin, *Acta Chim. Slov.* **2005**, *52*, 159–163.
4. K. Nakamuro, T. Okuno, T. Hasegawa. *J. Heal Scie.* **2000**, *46*, 418–421. **DOI:**10.1248/jhs.46.418
5. A. Kiani, P. Haratipour, M. Ahmadi, R. Zare-Dorabei, A. Mahmoodi, *J. Water Supply. Res. T.* **2017**, *66*, 239-248.
6. K. Ho, W. Hung, *Sen. Actu. B: Chem.* **2001**, 79, 11–16. **DOI:**10.1016/S0925-4005(01)00782-1
7. M. Ari, M. L. Cohen, *Phys. Review B* **1997**, *56*, 6737–6741. **DOI:**10.1103/PhysRevB.56.6737
8. A. Aquila, *Opt. Express.* **2012**, *20*, 2706–2716. **DOI:**10.1364/OE.20.002706
9. J. C. Yang and P. K. Dutta, *Sen. Actu. B: Chem.* **2010**, *143*,

459–463. **DOI:**10.1016/j.snb.2009.09.023
10. Z. Parsaee, P. Haratipour, M. Janghorban Lariche, A. Vojood, *Ultrason. Sonochem.* **2018**, 41, 337–349. **DOI:**10.1016/j.ultsonch.2017.09.054
11. A. Khodadadi, A. M. Miri, *Sen. Actu. B: Chem.* **2001**, *80*, 267–271. **DOI:**10.1016/S0925-4005(01)00915-7
12. G. Korotcenkov, *Sen. Actu. B: Chem.* **2007**, *121*, 664–678. **DOI:**10.1016/j.snb.2006.04.092
13. M. Najafi, M. Najafi, H. Najafi, *J. Theor. Comput. Chem.* **2013**, *12*, 1250–116. **DOI:**10.1142/S0219633612501167
14. J. B. Halpern, A. Bello, J. Gilcrease, G. L. Harris, *Microelectron. J.* **2009**, *40*, 316–318. **DOI:**10.1016/j.mejo.2008.07.022
15. P. Haratipour, A. Baghban, A. H. Mohammadi, S. H. Hosseini Nazhad, A. Bahadori, *J. Mol. Liq.* **2017**, *242*, 146–159. **DOI:**10.1016/j.molliq.2017.06.123
16. A. Ahmadi, J. Beheshtian, M. Kamfiroozi, *J. Mol. Model.* **2012**, **18**, 1729–1734. **DOI:**10.1007/s00894-011-1202-5
17. J. Beheshtian, M. Kamfiroozi, Z. Bagheri, A. Ahmadi, *Comp. Mater. Sci.* **2012**, *54*, 115–118. **DOI:**10.1016/j.commatsci.2011.09.039
18. M. Zaboli, H. Raissi and F. Farzad, *Intern. J. Adva. Biotech. Rese.* **2016**, *7*, 1227–1232.
19. W. G. Liu, G. H. Chen, X. C. Huang, *J. Phys. Chem. C* **2012**, *116*, 4957–4964. **DOI:**10.1021/jp2124857
20. K. Rezouali, M. A. Belkhir, A. Houari, J. Bai, *Comput. Mater. Sci.* **2009**, *45*, 305–309. **DOI:**10.1016/j.commatsci.2008.10.004
21. D. Zhang, R. Q. Zhang, *Chem. Phys. Letters* **2003**, *371*, 426–432. **DOI:**10.1016/S0009-2614(03)00289-6
22. Y. F. Zhukovskii, N. Pugno, A. I. Popov, *J. Phys. Cond. Matter* **2007**, *19*, 395021–395038. **DOI:**10.1088/0953-8984/19/39/395021
23. M. Zhao, Y. Xia, Z. Tan, X. Liu, F. Li, *Chem. Phys. Letters* **2004**, *389*, 160–164. **DOI:**10.1016/j.cplett.2004.03.082
24. R. Thapa, B. Saha, N. S. Das, U. N. Maiti, *Appl. Sur. Sci.* **2010**, *256*, 3988–3992. **DOI:**10.1016/j.apsusc.2010.01.062
25. F. Li, C. Zhang, P. Wang, P. Li, *Appl. Sur. Sci.* **2012**, *258*, 6621–6626. **DOI:**10.1016/j.apsusc.2012.03.090
26. D. Tasis, N. Tagmatarchis, A. Bianco, M. Parto, *Chem. Rev.* **2006**, *106*, 1105–1136. **DOI:**10.1021/cr050569o
27. S. Y. Xie, W. Wang, K. A. S. Fernando, *Chem. Commun.* **2005**, *29*, 3670–3672. **DOI:**10.1039/b505330g
28. C. Y. Zhi, Y. Bando, C. C. Tang, *Angew. Chem. Int. Edit.* **2005**, *44*, 7929–7932. **DOI:**10.1002/anie.200502591
29. M. T. Baei, A. A. Peyghan, Z. Bagheri, *Superlattice Microst.* **2012**, *53*, 9–15. **DOI:**10.1016/j.spmi.2012.09.010
30. J. Andzelm, C. Kolmel, *J. Chem. Phys.* **1995**, *103*, 9312–9320. **DOI:**10.1063/1.469990
31. A. Warshel, *Israel J. Chem.* **1973**, *11*, 709–717. **DOI:**10.1002/ijch.197300067
32. A. Rahimi, M. Sepehr, M. J. Lariche, M. Mesbah, A. Kasaeipoor, E. H. Malekshah, *Physica E: Low Dimens. Syst. Nanostruct.* **2018***, 97*, 347–362. **DOI:**10.1016/j.physe.2017.12.003
33. A. Ahmadi, J. Beheshtian, N. L. Hadipour, *Physica E* **2011**, 43, 1717–1719. **DOI:**10.1016/j.physe.2011.05.029
34. A. Ahmadi, M. Kamfiroozi, J. Beheshtian, N. Hadipour, *Struct. Chem.* **2011**, *22*, 1261–1265. **DOI:**10.1007/s11224-011-9820-1
35. Y. Jiao, A. Du, Z. Zhu, V. Rudolph, S. C. Smith, *J. Mater. Chem.* **2010**, *20*, 10426–10430. **DOI:**10.1039/c0jm01416h
36. N. S. Alghunaim, A. Omar, H. Elhaes, M. Ibrahim, *J. Comput. Theor. Nanosci.* **2017**, *14*, 2838–2843. **DOI:**10.1166/jctn.2017.6583
37. A. M. F. Galal, E. M. Shalaby, A. Abouelsayed, M. A. Ibrahim, E. Al-Ashkar, A. G. Hanna *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2018**, *188*, 213–221. **DOI:**10.1016/j.saa.2017.06.068
38. A. Okasha, D. Atta, W. M. Badawy, M. V. Frontasyeva, H. Elhaes, M. Ibrahim, *J. Comput. Theor. Nanosci.* **2017**, *14*, 1357–1361. **DOI:**10.1166/jctn.2017.6457
39. M. Ibrahim, K. T. Kholmurodov, I. N. Fadeikina, S. V. Morzhuhina, E. S. Popova, H. Elhaes, A. A. Mahmoud, *J. Comput. Theor. Nanosci.* **2017**, *14*, 4133–4136. **DOI:**10.1166/jctn.2017.6797
40. H. Elhaes, A. Fakhry, M. Ibrahim, *Sensor Lett*. **2017**, *15*, 604-607. **DOI:**10.1166/sl.2017.3853
41. M. Schmidt, T. Windus, M. Dupuis, *J. Comput. Chem.* **1993**, *14*, 1347–1363. **DOI:**10.1002/jcc.540141112
42. S. Grimme, *J. Comput. Chem.* **2004**, *25*, 1463–1471. **DOI:**10.1002/jcc.20078
43. J. Andzelm, C. Kolmel, *J. Chem. Phys.* **1995**, *103*, 9312–9320. **DOI:**10.1063/1.469990
44. Z. Parsaee, P. Haratipour, M. J. Lariche, A. Vojood, *Ultrason. Sonochem.* **2018**, *41*, 337–349. **DOI:**10.1016/j.ultsonch.2017.09.054
45. M. H. Doranehgard, H. Samadyar, M. Mesbah, P. Haratipour, S. Samiezade, *Fuel,* 2017, *202*, 29–35. **DOI:**10.1016/j.fuel.2017.04.014
46. T. C. Dinadayalane, J. S. Murray, *J. Chem. Theory Comp.* **2010**, *6*, 1351–1357. **DOI:**10.1021/ct900669t
47. S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553–566. **DOI:**10.1080/00268977000101561
48. A. Baghban, J. Sasanipour, P. Haratipour, M. Alizad, M. Vafaee Ayouri, *Chem. Eng. Res. Des.* **2017**, *126*, 67–75. **DOI:**10.1016/j.cherd.2017.08.007

Povzetek

Z uporabo teorije gostotnega funkcionala (DFT) smo raziskovali adsorpcijo molekule H_2Se na površinah AlN-NCS in AlP-NCS nanostožcev. Preučili smo potenciale Cl-funkcionaliziranih AlN-NCS in AlP-NCS za adsorpcijo H2Se in ugotovili, da so vsi procesi adsorpcije H2Se na obravnavanih površinah nanostožcev eksotermne reakcije. Izračunana energija adsorpcije, |Ead| tvorbe kompleksa H_2Se z AlP-NCS je bila višja od | Ead| za nastanek kompleksa z AlN-NCS. Rezultati kažejo, da so dobljene vrednosti |Ead| linearno odvisne od orbitalnih energij. Proučevane površine nanostožcev bi bile primerne kot substrat z večjo učinkovitostjo adsorpcije H_2Se.