Biointerface Research in Applied Chemistry
Platinum Open Access Journal (ISSN: 2069-5837)

Article
Volume 12, Issue 1, 2022, 359 - 365
https://doi.org/10.33263/BRIAC121.359365

BN Nanoflake for Hazardous SO_2 Gas Capturing: DFT Study

Mahmoud Mirzaei [1,*], Elnaz Karimi [2], Mohammad Yousefi [2]

[1] Department of Biomaterials, Nanotechnology and Tissue Engineering, School of Advanced Technologies in Medicine, Isfahan University of Medical Sciences, Isfahan, Iran; mdmirzaei@pharm.mui.ac.ir (M.M.);
[2] Department of Chemistry, Faculty of Pharmaceutical Chemistry, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran; elnazkarimi64@yahoo.com (E.K.); myousefi50@hotmail.com (M.Y.);
* Correspondence: mdmirzaei@pharm.mui.ac.ir;

Scopus Author ID 13204227300

Received: 23.02.2021; Revised: 28.02.2021; Accepted: 5.04.2021; Published: 20.04.2021

Abstract: Density functional theory (DFT) calculations were performed to investigate an idea of employing boron nitride (BN) nanoflake for hazardous SO_2 gas capturing process regarding the gas pollutant problems of environmental issues. To do this, a representative model of hydrogen capped B12N12 coronene-like surface was considered for such a gas capturing process. Two starting positions were chosen for SO_2 gas, once perpendicularly locating the S side of SO_2 towards the BN surface to form the S@BN model and once more perpendicularly locating the O side of SO_2 towards the BN surface to form the O@BN model. All singular and complex models were optimized to achieve the minimized energy structures, which were all confirmed by avoiding imaginary frequencies. Subsequently, molecular descriptors were achieved to discuss the problem of this work. The results indicated significant impacts of SO_2@BN complex formation on the molecular properties, in which the levels energies of molecular orbitals were detected such impacts. Total energies and adsorption energies were meaningful for both complex formations with better O@BN model formation than S@BN one. Consequently, the investigated SO_2@BN complex system could be proposed for further investigating such activities of pollutant gas sensing and removal regarding the environmental issues.

Keywords: boron nitride; nanoflake; sulfur dioxide; gas capturing; DFT.

© 2021 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Gas pollutants have been almost the unavoidable issues of modern industrial cities, which cause several harmful effects on the health of people living in such an environment [1]. Therefore, exploring efficient procedures for removing such gas pollutants has always been an important task of research and development divisions of the industries or related agencies [2]. To this aim, novel materials have been expected to work for such gas removal purposes to capture such pollutants in two ways of sensing in the environment or removing them [3]. Considerable works have been dedicated to such a strategy to show the advantage of such novel materials, including nanostructures for the expected purposes [4-6]. The currently known nanostructures were first initiated by the pioneering work of Iijima, in which they have been widely spread in the world of science and technology research very soon after the first innovation [7-10]. In addition to carbon nanotube (CNT), several other nanostructures have been introduced in various shapes and components for specified purposes, among which boron nitride (BN) nanostructures have been seen as suitable materials in stability and electronic

properties comparing with carbon nanostructures [11-16]. Nanoflake is a single standing piece of the nanostructure, in which coronene has been already reported as a nanoflake [17]. As mentioned for advantages of non-carbon-based nanostructures, formations and properties of BN nanoflake have also been reported by earlier works to show the benefit of performing further investigations on such systems [18-21]. To this point, a coronene-like BN nanoflake (Figure 1) was investigated in this work for hazardous SO_2 gas capturing regarding pollutant sensing and removal purposes. Unfortunately, SO_2 gas could be easily released into the air in the industrial environment, and it is really important to make an efficient procedure for its removal to save the health of people from the harmful effects of this hazardous gas [22-25]. In this case, several other attempts have been dedicated to doing such sensing and removal purposes by innovating new ways of SO_2 capturing, but the story has not been completed yet [26]. Nanostructures are important for such adsorption processes because of their activated surfaces for such purposes in addition to their components [27-31]. Therefore, it could be an advantage to explore further nano-assisted surfaces for capturing such gases regarding the environmental safety aspects.

A representative model of BN nanoflake (Figure 1) was investigated for SO2 gas capturing (Figure 2) through quantum mechanical calculations within this work. One of the important points about BN nanostructures is their semi-ionic B-N bonds characterizing them as somehow ionic-surface nanostructures. To achieve this work's purpose, such ionic-surface BN nanoflake was explored to see its advantage for the SO_2 gas capturing process to reach SO_2@BN complex formation. The models were optimized to prepare stable surfaces for such gas capturing, which were examined next by additional optimization processes on bi-molecular systems. The advantage of computer-based research performed this work works providing insightful information about the matters at the lowest molecular, atomic, and even sub-atomic unit scales [32-36].

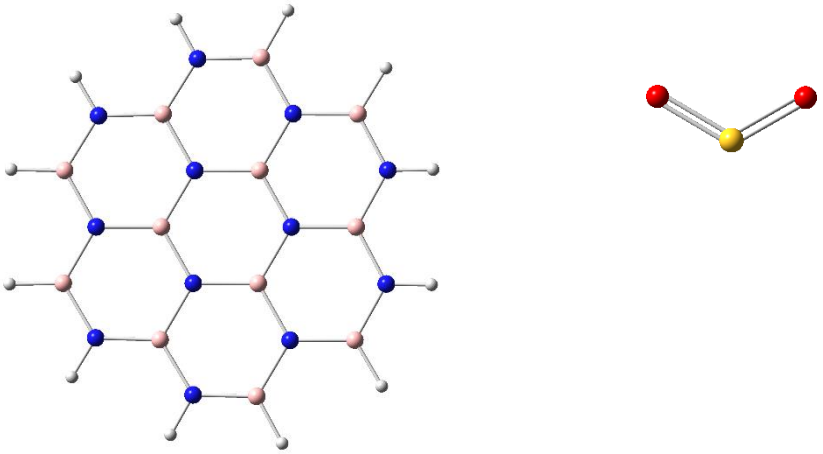

Figure 1. Models of singular BN nanoflake and SO_2 gas.

2. Materials and Methods

Density functional theory (DFT) calculations were performed using the B3LYP exchange-correlation functional and the 6-31G* basis set using the Gaussian program to obtain the required results of this work [37]. The singular models, including BN nanoflake ($B_{12}N_{12}H_{12}$) and SO_2 gas (Figure 1), were first optimized to achieve the energy-minimized structures. Next, bimolecular SO_2@BN complexes were composed of already optimized singular structures in two starting models of locating the S side and O side of SO_2 versus the BN surface designated by S@BN and O@BN models (Figure 2). To make sure about the

validity of calculations, dispersion correction effects were included by IOp=(3/124=3) for bi-molecular optimization processes and the basis set superposition errors (BSSE) were evaluated for the optimized bimolecular systems. The optimized structures were also confirmed by the vibrational calculations avoiding the existence of any imaginary frequencies. At this moment, the models were ready for further investigating regarding the evaluation of molecular descriptors. Values of the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) were obtained and listed in Table 1 in addition to their distribution patterns representations in Figure 3. Additional descriptors including energy gap (EG) (eq. 1), Fermi energy (FE) (eq. 2), total energy (TE), adsorption energy (AE) (eq. 3), BSSE, volume (V), dipole moment (DM), and interacting distance (ID) were all obtained for the investigated systems, and they were listed in Table 1.

$$EG = LUMO - HOMO \quad (1)$$

$$FE = ½ (HOMO + LUMO) \quad (2)$$

$$AE = TE_{SO2@BN} - TE_{SO2} - TE_{BN} \quad (3)$$

Table 1. Evaluated molecular descriptors.*

Property	BN	SO_2	S@BN	O@BN
HOMO eV	-6.731	-8.984	-6.825	-6.766
LUMO eV	0.198	-3.617	-3.190	-3.214
EG eV	6.929	5.367	3.635	3.552
FE eV	-3.226	-6.301	-5.008	-4.991
TE eV	-26225.126	-14928.162	-41155.204	-41155.218
AE eV	N/A	N/A	-1.916	-1.929
BSSE eV	N/A	N/A	0.179	0.184
V cm^3/mol	225.361	39.442	247.718	241.041
DM Debye	1.002	1.776	1.506	1.447
ID Å	N/A	N/A	3.046	3.022

*See Figures 1-3 for the models.

3. Results and Discussion

Within this work, a model pollutant gas capturing by nanoflake was investigated using DFT calculations. SO_2 gas is one of the common hazardous pollutants in an industrial environment, in which its sensing and removal are very much important for the health of those people in the condition of direct exposure to it. Therefore, a representative BN nanoflake was employed in this work to explore SO_2 gas capturing with the purpose of such gas pollutants sensing and removal from the environment (Figures 1 and 2). The singular molecules of BN and SO_2 were first optimized to reach the minimum energy structures. Afterward, the complex systems of SO_2@BN were composed of the already optimized structures, and they were optimized again to achieve the best localization of SO_2 at the BN surface. To do this, two starting positions of SO_2 were first considered, in which the S side of SO_2 was perpendicularly located towards the BN surface in the S@BN model, and the O side of SO_2 was perpendicularly located towards the BN surface in the O@BN model. It was very much interesting that the starting localization of SO_2 molecule was converted to parallel to the BN surface in both models after performing the optimization processes (Figure 2). However, the obtained descriptors from calculations were not identical for both of them, and deviations were found regarding the starting localization of molecular forms. Moreover, careful analyses of the content of Table 1 could reveal what was happened inside the systems at the molecular scale calculations to describe the problem as much as possible for reaching a possible solution for the purpose of this work.

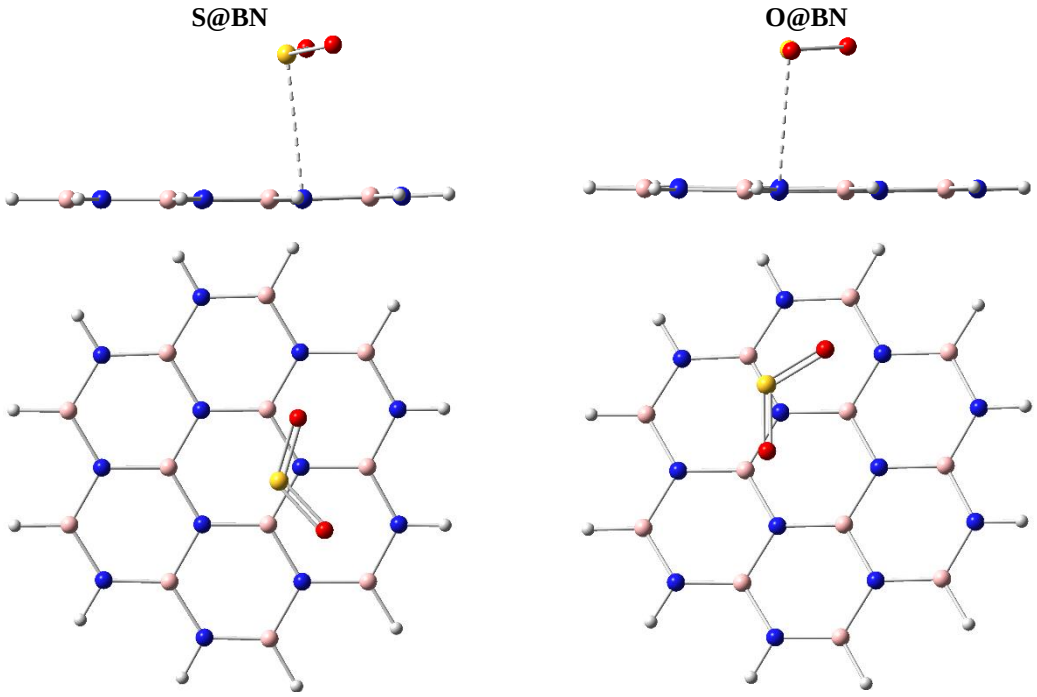

Figure 2. Models of S@BN and O@BN of SO_2@BN complexes. In both models, dash lines (S…N) are shown for the interacting position of S and N with distances of 3.046 and 3.022 Å for models, respectively.

Herein, the energy levels of HOMO and LUMO could show that such gas-nanoflake complex formation had a significant impact on the system. The level of LUMO was changed to a value close to that of singular SO_2 in both of S@BN and O@BN models. The changes in HOMO levels in complex models were close to that of the singular BN model. Moreover, such changes impact the values of EG and FE, changing both of them in significant ways. Looking at Figure 3 could visually show the achievement, in which the localization of HOMO was remained at the BN surface, whereas those of LUMO were moved to the SO_2 molecule. A good agreement of quantitative values and qualitative representations as obtained here regarding the HOMO and LUMO conditions of complex systems and singular molecules. Further analyses of TE could show that the stability of the O@BN complex model was slightly better than that of the S@BN model, in which the values approved the trend of AE showing a more favorable adsorption process of SO_2 at the BN surface for the O@BN model rather than such process for S@BN model. The obtained values of -1.916 and -1.929 eV were meaningful for the adsorption process revealing the benefit of such nanoflake for the SO_2 capturing purpose. Moreover, the calculated values of BSSE indicated that such type of error was almost negligible for the adsorption strength of both complexes. As a consequence, the idea of employing BN nanoflake for SO_2 gas capturing was somehow approved with such achievements. Looking again at both Figures 2 and 3 could reveal that the surface size was wide enough for such gas capturing, in which the gas molecule was located almost at the internal part of the surface, even far from the surface edges. Hence, all the obtained results up to now could show the complex formation possibility of the SO_2@BN complex in each of the S and O model systems. The interacting systems were driven by forming a type of S…N physical interaction between gas and nanoflake with a slightly shorter distance for the O@BN model than the S@BN model. Volumes were almost similar for both complexes and the values of dipole moment showed deviations of such electric charge distribution systems of complexes from that of the singular BN model. Indeed, this work's achievements showed the advantage of employing such BN nanoflake for the SO_2 gas capturing process. The results yielded such favorability of SO_2@BN complex formation

based on obtained molecular descriptors in quantitative and qualitative representations. Consequently, such a system could be proposed for further investigation regarding the environmental pollutant removal issues.

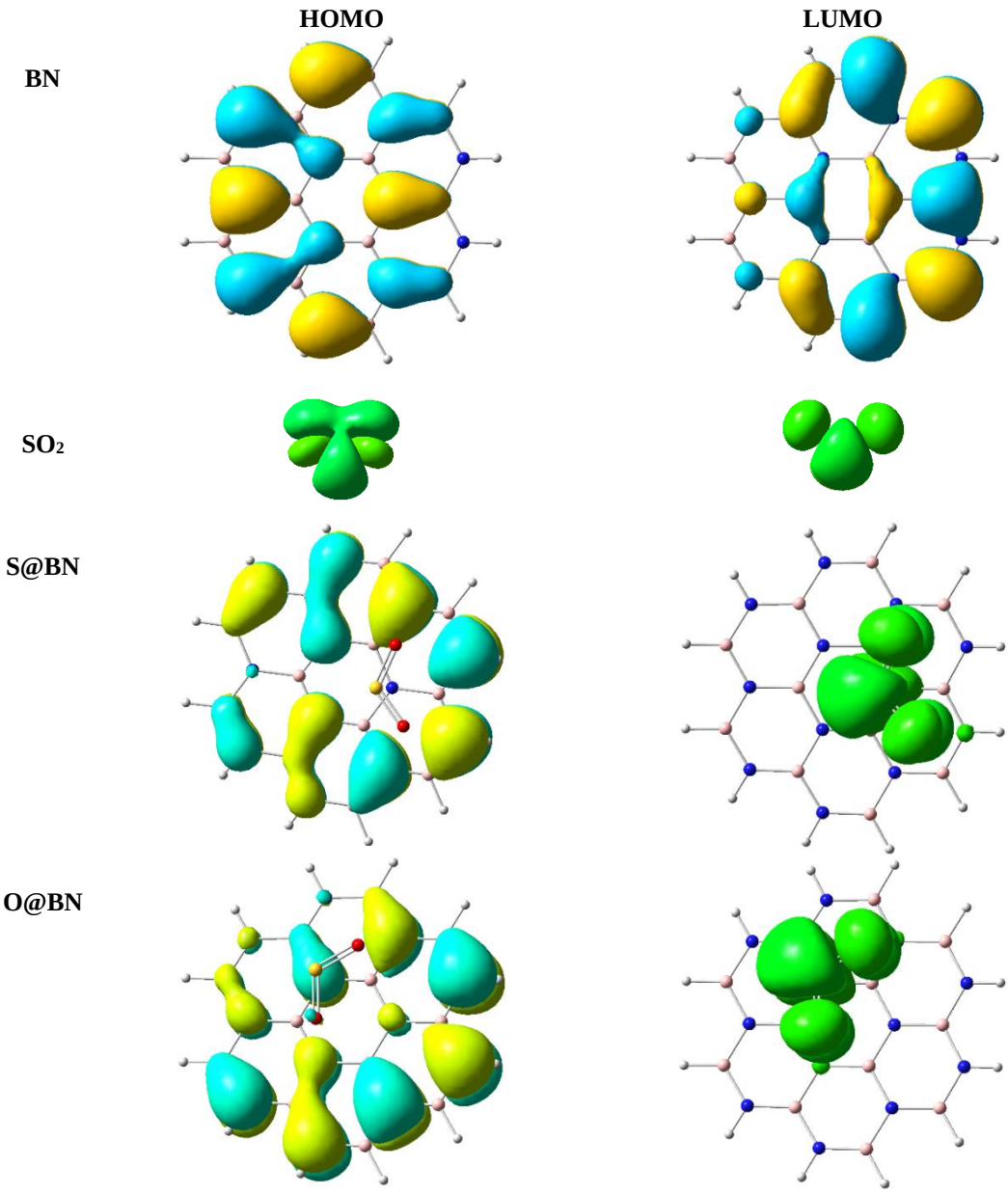

Figure 3. HOMO and LUMO distribution patterns.

4. Conclusions

The idea of employing BN nanoflake for hazardous SO_2 gas capturing was investigated by the DFT calculated results within the work. After optimizing the required structure and confirming them, molecular descriptors were evaluated for achieving the purpose. The results indicated that the most favorable locations of the SO_2 molecule were somehow parallel to the BN surface, neglecting the starting position. In such a case, the gas molecule was located almost at the middle of the surface, approving the appropriate size of surface for such molecular adsorption process. HOMO and LUMO distribution patterns also approved such a trend, in which the major localization was achieved at the middle area. Furthermore, the LUMO of complexes' energy levels was significantly changed to that of the singular SO2 molecule. The distribution pattern also approved it. The values of HOMO of complexes were almost similar

to that of singular BN surface. Based on total energies and adsorption energies, the formation of the O@BN model was slightly more favorable than the S@BN model, in which the models were already defined regarding the starting localization of each of S and O atoms of SO_2 towards the BN surface. Furthermore, adsorption's strength was meaningful for complex model systems for efficient SO_2 capturing at the BN nanoflake surface. As a final remark, such SO_2@BN model system could be proposed for further investigations regarding the importance of pollutant gas sensing and removal of environmental issues.

Funding

This research received no external funding.

Acknowledgments

This work was evaluated from a part of the master thesis of E. Karimi supported by the research council of Tehran Medical Sciences, Islamic Azad University, which is acknowledged.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Al-Kindi, S.G.; Brook, R.D.; Biswal, S.; Rajagopalan, S. Environmental determinants of cardiovascular disease: lessons learned from air pollution. *Nature Reviews Cardiology* **2020**, *17*, 656-672, https://doi.org/10.1038/s41569-020-0371-2.
2. Lv, S.W.; Liu, J.M.; Wang, Z.H.; Ma, H.; Li, C.Y.; Zhao, N.; Wang, S. Recent advances on porous organic frameworks for the adsorptive removal of hazardous materials. *Journal of Environmental Sciences* **2019**, *80*, 169-185, https://doi.org/10.1016/j.jes.2018.12.010.
3. Zhang, Y.N.; Niu, Q.; Gu, X.; Yang, N.; Zhao, G. Recent progress on carbon nanomaterials for the electrochemical detection and removal of environmental pollutants. *Nanoscale* **2019**, *11*, 11992-12014, https://doi.org/10.1039/C9NR02935D.
4. Zahedi, H.; Yousefi, M.; Mirzaei, M. DFT investigation of AlP-doped BN nanotube for CO gas capturing. *Lab-in-Silico* **2020**, *1*, 38-43.
5. Ariaei, S. DFT approach on arsine and phosphine gases adsorption at the surface of B16C16 nanocluster. *Lab-in-Silico* **2020**, *1*, 44-49.
6. Ariaei, S.; Basiri, H.; Ramezani, M. Selective adsorption function of $B_{16}C_{16}$ nano-cage for H_2O, CO, CH_4 and NO_2. *Advanced Journal of Chemistry - Section B* **2020**, *2*, 18-25, https://doi.org/10.33945/SAMI/AJCB.2020.1.4.
7. Iijima S. Carbon nanotubes: past, present, and future. *Physica B* **2002**, *323*, 1-5, https://doi.org/10.1016/S0921-4526(02)00869-4.
8. Tahmasebi, E.; Shakerzadeh, E. Potential application of B_{40} fullerene as an innovative anode material for Ca-ion batteries: In silico investigation. *Lab-in-Silico* **2020**, *1*, 16-20.
9. Ozkendir, O.M. Temperature dependent XAFS study of $CrFe_2O_4$. *Lab-in-Silico* **2020**, *1*, 33-37.
10. Harismah, K.; Ozkendir, O.M.; Mirzaei, M. Lithium adsorption at the C_{20} fullerene-like cage: DFT approach. *Advanced Journal of Science and Engineering* **2020**, *1*, 74-79, https://doi.org/10.22034/AJSE2013074.
11. Zhi, C.; Bando, Y.; Tang, C.; Honda, S.; Kuwahara, H.; Golberg, D. Boron nitride nanotubes/polystyrene composites. *Journal of Materials Research* **2006**, *21*, 2794-2800, https://doi.org/10.1557/jmr.2006.0340.
12. Mirzaei, M.; Mirzaei, M. Sulfur doping at the tips of (6, 0) boron nitride nanotube: A DFT study. *Physica E* **2010**, *42*, 2147-2150, https://doi.org/10.1016/j.physe.2010.04.014.
13. Mirzaei, M.; Hadipour, N.L.; Abolhassani, M.R. Influence of C-doping on the B-11 and N-14 quadrupole coupling constants in boron-nitride nanotubes: A DFT study. *Zeitschrift für Naturforschung A* **2007**, *62*, 56-60, https://doi.org/10.1515/zna-2007-1-208.
14. Mirzaei, M. Calculation of chemical shielding in C-doped zigzag BN nanotubes. *Monatshefte für Chemie* **2009**, *140*, 1275-1278, https://doi.org/10.1007/s00706-009-0195-6.
15. Mirzaei, M.; Mirzaei, M. An electronic structure study of O-terminated zigzag BN nanotubes: Density functional calculations of the quadrupole coupling constants. *Solid State Communications* **2010**, *150*, 1238-1240, https://doi.org/10.1016/j.ssc.2010.04.012.

16. Faramarzi, R.; Falahati, M.; Mirzaei, M. Interactions of fluorouracil by CNT and BNNT: DFT analyses. *Advanced Journal of Science and Engineering* **2020**, *1*, 62-66, https://doi.org/10.22034/AJSE.2012062.
17. Prodhan, S.; Mazumdar, S.; Ramasesha, S. Correlated electronic properties of a graphene nanoflake: coronene. *Molecules* **2019**, *24*, https://doi.org/10.3390/molecules24040730.
18. Wang, B.B.; Qu, X.L.; Zheng, K.; Levchenko, I.; Keidar, M.; Zhu, M.K.; Xu, S.; Ostrikov, K. C and O doped BN nanoflake and nanowire hybrid structures for tuneable photoluminescence. *Journal of Alloys and Compounds* **2017**, *705*, 691-699, https://doi.org/10.1016/j.jallcom.2017.02.168.
19. Petrushenko, I.K.; Tikhonov, N.I.; Petrushenko, K.B. Graphene-BN-organic nanoflake complexes: DFT, IGM and SAPT0 insights. *Diamond and Related Materials* **2020**, *107*, https://doi.org/10.1016/j.diamond.2020.107905.
20. Hu, R.; Zhang, Z.H.; Fan, Z.Q. BN nanoflake quantum-dot arrays: structural stability, and electronic and half-metallic properties. *Physical Chemistry Chemical Physics* **2017**, *19*, 20137-20146, https://doi.org/10.1039/C7CP02391J.
21. Yamanaka, A.; Okada, S. Energetics and electronic structure of h-BN nanoflakes. *Scientific Reports* **2016**, *6*, 1-9, https://doi.org/10.1038/srep30653.
22. Zhu, H.; Lin, W.; Li, Q.; Hu, Y.; Guo, S.; Wang, C.; Yan, F. Bipyridinium-based ionic covalent triazine frameworks for CO_2, SO_2, and NO capture. *ACS Applied Materials & Interfaces*. **2020**, *12*, 8614-8621, https://doi.org/10.1021/acsami.9b15903.
23. Martínez-Ahumada, E.; López-Olvera, A.; Jancik, V.; Sánchez-Bautista, J.E.; González-Zamora, E.; Martis, V.; Williams, D.R.; Ibarra, I.A. MOF materials for the capture of highly toxic H_2S and SO_2. *Organometallics* **2020**, *39*, 883-915, https://doi.org/10.1021/acs.organomet.9b00735.
24. An, X.C.; Li, Z.M.; Zhou, Y.; Zhu, W.; Tao, D.J. Rapid capture and efficient removal of low-concentration SO_2 in simulated flue gas by hypercrosslinked hollow nanotube ionic polymers. *Chemical Engineering Journal* **2020**, *394*, https://doi.org/10.1016/j.cej.2020.124859.
25. Hong, Q.; Xu, H.; Yuan, Y.; Shen, Y.; Wang, Y.; Huang, W.; Qu, Z.; Yan, N. Gaseous mercury capture using supported CuSx on layered double hydroxides from SO_2-rich flue gas. *Chemical Engineering Journal* **2020**, *400*, https://doi.org/10.1016/j.cej.2020.125963.
26. Yan, S.; Han, F.; Hou, Q.; Zhang, S.; Ai, S. Recent advances in ionic liquid-mediated SO_2 capture. *Industrial & Engineering Chemistry Research* **2019**, *58*, 13804-13818, https://doi.org/10.1021/acs.iecr.9b01959.
27. Chen, Z.; Wang, X.; Cao, R.; Idrees. K.B.; Liu, X.; Wasson, M.C.; Farha, O.K. Water-based synthesis of a stable iron-based metal-organic framework for capturing toxic gases. *ACS Materials Letters* **2020**, *2*, 1129-1134, https://doi.org/10.1021/acsmaterialslett.0c00264.
28. Rad, A.S.; Mirabi, A.; Peyravi, M.; Mirzaei, M. Nickel-decorated $B_{12}P_{12}$ nanoclusters as a strong adsorbent for SO_2 adsorption: Quantum chemical calculations. *Canadian Journal of Physics* **2017**, *95*, 958-962, https://doi.org/10.1139/cjp-2017-0119.
29. Lee, J.; Lee, K.; Kim, J. Fiber-based gas filter assembled via in situ synthesis of ZIF-8 metal organic frameworks for an optimal adsorption of SO_2: experimental and theoretical approaches. *ACS Applied Materials & Interfaces* **2021**, *13*, 1620-1631, https://doi.org/10.1021/acsami.0c19957.
30. Shen, H.; Wang, H.; Shen, C.; Wu, J.; Zhu, Y.; Shi, W.; Zhang, X.; Ying, Z. Effect of atmosphere of SO_2 coexisted with oxidizing gas on mercury removal under oxy-fuel condition. *Chemosphere* **2020**, *259*, https://doi.org/10.1016/j.chemosphere.2020.127525.
31. Li, D.; Kang, Y. Significantly promoted SO_2 uptake by the mixture of N-methylated ethylene imine polymer and 1-ethyl-3-methylimidazolium tetrazolate. *Journal of Hazardous Materials* **2021**, *404*, https://doi.org/10.1016/j.jhazmat.2020.124101.
32. Mirzaei, M. Making sense the ideas in silico. *Lab-in-Silico* **2020**, *1*, 31-32.
33. Mirzaei, M. Science and engineering in silico. *Advanced Journal of Science and Engineering* **2020**, *1*, 1-2, https://doi.org/10.22034/AJSE2011001.
34. Samadi, Z.; Mirzaei, M.; Hadipour, N.L.; Khorami, S.A. Density functional calculations of oxygen, nitrogen and hydrogen electric field gradient and chemical shielding tensors to study hydrogen bonding properties of peptide group (OC–NH) in crystalline acetamide. *Journal of Molecular Graphics and Modelling* **2008**, *26*, 977-981, https://doi.org/10.1016/j.jmgm.2007.08.003.
35. Mirzaei, M. A computational NMR study of boron phosphide nanotubes. *Zeitschrift für Naturforschung A* **2010**, *65*, 844-848, https://doi.org/10.1515/zna-2010-1010.
36. Mirzaei, M.; Mirzaei, M. The C-doped AlP nanotubes: a computational study. *Solid State Sciences* **2011**, *13*, 244-250, https://doi.org/10.1016/j.solidstatesciences.2010.11.022.
37. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.J.I.W. Gaussian 09 program. Gaussian Inc., Wallingford, CT. **2009**.