J Nanostruct 13(3): 777-782, Summer 2023

RESEARCH PAPER

Reactive Molecular Dynamics Study of the Ti_2C Monolayer and Nanotube: Promising Candidates for CO and CO_2 Gas Sensors

Maryam Malmir

Department of Physics, Faculty of Basic Sciences, Lorestan University, Khorramabad, Lorestan, Iran

ARTICLE INFO

Article History:
Received 19 March 2023
Accepted 20 June 2023
Published 01 July 2023

Keywords:
CO and CO_2 gas sensor
MXenes
Ti_2C monolayer
Ti_2C nanotube

ABSTRACT

Gas sensors are essential for protecting humans against hazardous gases such as flammable and toxic gases. Unlike traditional gas sensors, MXenes gas sensors act at room temperature, Which is a good advantage. In this work Reactive molecular dynamics simulation calculations were run through the canonical ensemble calculation method with the Nosé Hoover thermostat temperature controller at T=298 K and the dynamic condition of the simulation was based on the popular Verlet algorithm with a time step of 0.01 fs and conducted MD simulation for 0.3 ns. the ReaxFF force field allowed atoms to break and form bonds with other atoms during the simulation, So it is a powerful force field. Adsorption of the CO and CO_2 pollution gas molecules by Ti_2C monolayer and nanotube was investigated and adsorption weight percentages were reported. Results show that Ti_2C monolayer, and nanotube, have more adsorbed weight percentage against CO_2 pollution gas molecules than CO one, and two gases have more affinity to the Ti_2C monolayer than Ti_2C nanotube.

How to cite this article
Malmir M. Reactive Molecular Dynamics Study of the Ti_2C Monolayer and Nanotube: Promising Candidates for CO and CO_2 Gas Sensors. J Nanostruct, 2023; 13(3):777-782. DOI: 10.22052/JNS.2023.03.018

INTRODUCTION

Gas sensors are essential for protecting human beings against hazardous gases such as flammable and toxic gases [1-4]. Traditional gas sensors based on semiconductor oxide materials display high sensitivity and operate at undesired high temperatures, i.e., 200-600 ˚C [5], so scientists have tried to produce one- and two-dimensional nano-materials gas sensors that operate at room temperature [5, 6].

In this regard, one-dimensional materials such as carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs) due to their electronic and mechanical properties, high thermal conductivity [7], chemical stability [8, 9], high surface-to-volume rate, and hollow structure, have been different applications such as gas storage, gas sensors, etc. Also, two-dimensional (2D) materials such as graphene, transition metal dichalcogenides, phosphorene, etc. have been used as suitable candidates for sensors in different applications due to their large surface area, thermal and electrical conductivity, high mechanical strength, and electron transfer rates [10-13]. Ref. 14 concluded that graphene functionalized with vanadium pentoxide (V_2O_5) using laser ablation technique is suitable for highly sensitive NH3 sensors [14]. Chen and coworkers have produced a Li+/CNT film that operates as an excellent sensor of the CH4 gas molecules [15].

Unfortunately, some 2D materials such as graphene and transition-metal dichalcogenides

* *Corresponding Author Email: malmir.m@lu.ac.ir*

(TMDs) show low-temperature gas sensors [16, 17]. To overcome this restriction, a new family of 2D transition metal carbides and nitrides (named MXenes) have been studied for room-temperature (RT) gas-sensing applications [18-20]. MXenes are synthesized by selective etching of metal atoms from the structure of MAX phases, a large group of ternary carbides and nitrides with a hexagonal layered structure, with the chemical composition: $M_{n+1}AX_n$, where n = 1, 2, or 3, "M" is an early transition metal, "A" is an A group (groups 13 and 14) element, an "X" is carbon, nitrogen, or both [21]. Previous studies showed that the surface of MXenes is randomly terminated by oxygen, hydroxyl, and/or fluorine where these ratios are mainly dependent on synthesis methods [22]. The unique chemistry of MXenes allows particular applications such as energy storage, water purification, gas sensors, catalysis, etc [23]. The first computational study on MXenes as gas sensors showed chemisorption of NH_3 on Ti_2CO_2 monolayer while other gas molecules (H_2, CH_4, CO, CO_2, N_2, NO_2, and O_2) showed much lower interaction [24]. Also, the first experimental report elaborated that, $Ti_3C_2T_x$, where T_x is a random combination of terminations present at the MXenes surfaces, showed p-type sensing behavior to methanol, ethanol, ammonia, and acetone gases [18]. Vanadium carbide (V_2CT_x) and molybdenum carbide (Mo_2C) also have been studied as gas sensors [25].

In addition, experimental and theoretical studies demonstrated that MXenes can be rolled as nanotubes [26]. Despite the potential applications of MXenes as gas sensors, there are very limited studies in this area. Interestingly, gas sensor MXene nanotubes have not been studied yet, so in this study, we investigate gas sensor properties of monolayer (Ti_2C-ML) and for the report, nanotube (Ti_2C-NT) of the Ti_2C for adsorption of CO_2 and CO gas molecules.

SIMULATION METHOD AND SYSTEM

In the present work, we investigated the adsorption of Co and CO_2 gas molecules on Ti_2C monolayer and nanotube by a reactive MD simulation method using the reactive force field (ReaxFF) developed by van Duin et al. [27], which is integrated with the "Large-scale Atomic/Molecular Massively Parallelized Simulator" (LAMMPs) code [28].

The ReaxFF force field used bond orders instead of the specific atomic connectivity, which allowed atoms to break and form bonds with other atoms during the simulation. The bond order is obtained from interatomic distances empirically. The system's total energy consists of various partial energy contributions, the bonded and non-bonded interactions (van der Waals, Coulomb). ReaxFF describes non-bonded interactions between all atoms, irrespective of connectivity. Unlike the fixed partial charges on atoms in classical MD, in ReaxFF MD, they are dynamically approximated in a charge equilibration procedure by minimizing the Coulomb energy using Electron Equilibration Method (EEM) when the atomic coordinates are

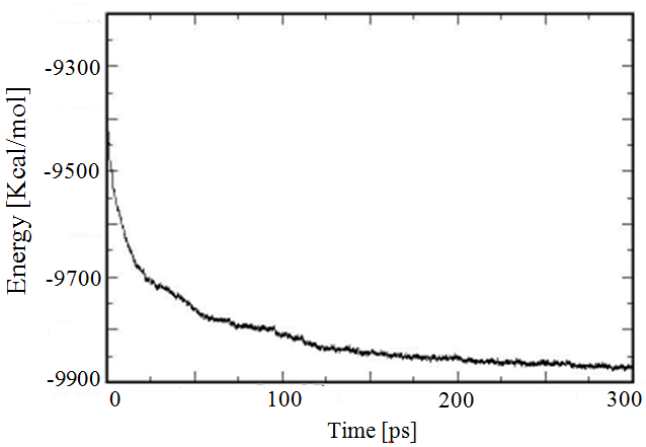

Fig. 1. Fluctuation of total energy versus the simulation steps for the Ti_2C-ML@CO system. After 2×107 steps, the magnitude of the fluctuation is less than 0.2% compared with the shown values by the vertical axes. The total energy is about -98770 kcal.

updated at each time step [29].

Indeed, the Ti_2C nanotube is made of atomic coaxial cylinders whose walls include Ti@C@Ti coaxial cylinders. The simulation box had sides of 60×60×22 Å3 for monolayer and 40×40×50 Å3 for the nanotube systems that include Ti2C nanotube or monolayer in the box center and 172 CO or 109 CO_2 gas molecules, the amount of the gas molecule was chosen proportional to the volume of the boxes. The simulation ran through the canonical ensemble (NVT) calculation method with the Nosé Hoover thermostat temperature controller at T=298 K. the dynamic condition of the simulation was based on the popular Verlet algorithm. The time step and total time of the simulation were 0.01 fs and 0.3 ns, respectively. Approaching the steady states was checked by setting the total energy fluctuations to be less than 0.2%. Fig. 1 shows it against the simulation's steps for the Ti_2C-ML@ CO as a sample.

RESULTS AND DISCUSSION

Fig. 2 and 3 show the interaction between Ti_2C monolayer and nanotube with CO and CO_2 gas molecules during simulation. As you can see in Figs. 2 and 3 at the final step, the interaction of gas molecules with Ti_2C-NTs distorts the tube cross-section. To better understand the behavior of sensing characteristics, binding energies, and charge transfer between Ti_2C-ML, Ti_2C-NT, and toxic gases, i.e., CO, and CO_2, have been calculated by the following relation and reported in the Table. 1,

$$E_b = \left[E_{ML/NT@gas} - E_{ML/NT} - E_{gas}\right]/N_{gas} \quad (1)$$

Where $E_{ML/NT@gas}$, $E_{ML/NT}$, and Egas represent the total energy of the Ti_2C-ML or Ti_2C-NT with gas molecules, pristine Ti_2C-ML or Ti_2C-NT, and isolated gas molecules, respectively, divided by the whole number of the adsorbed gas molecules, Ngas. According to Table. 1, negative values of the binding energies show that the adsorption process is energetically favorable and the gas molecules are strongly bonded to the Ti_2C-ML and Ti_2C-NT.After interactions, toxic gas molecules gain 0.518 and 0.554 e^{-1} on the Ti_2C-ML and Ti_2C-NT, respectively. These charges are 0.469 and 0.551 e^{-1} for CO_2 gas molecules on the Ti_2C-ML and Ti_2C-NT.

The weight percentage of the adsorbed gas molecules was calculated by Eq. 2 to find out the desired type of adsorption.

$$E_b = \left[E_{ML/NT@gas} - E_{ML/NT} - E_{gas}\right]/N_{gas} \quad (2)$$

Where Ng: was the number of the adsorbed gas molecules, NTi and NC: were the number of the titanium and carbon atoms of the ML- Ti_2C or NT-Ti_2C, and W was the molecular or atomic weight. Table. 1, shows the simulation results for the

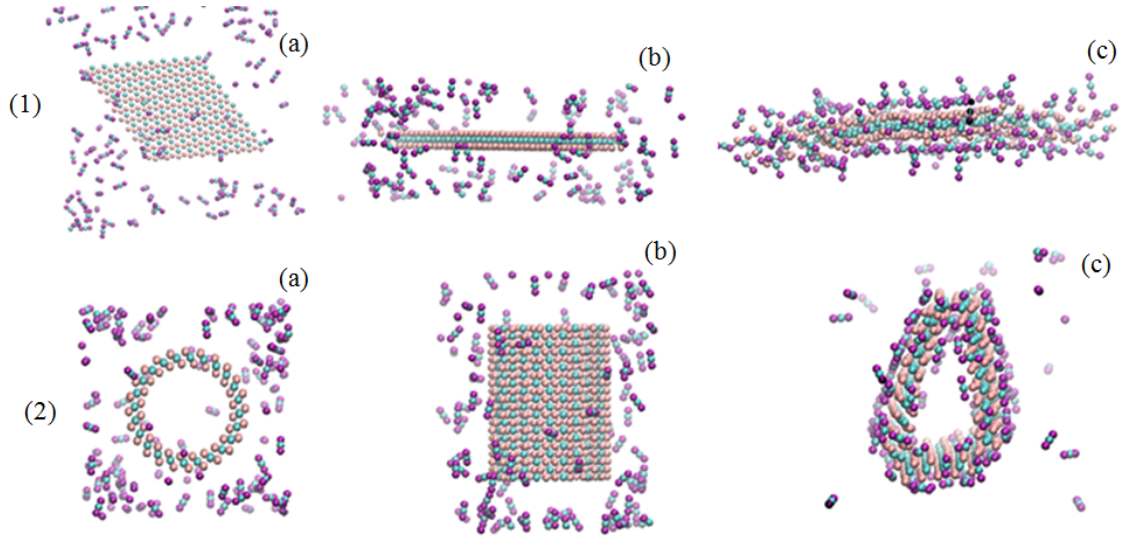

Fig. 2. Interaction between Ti_2C monolayer (1-a,b,c) and nanotube (2-a,b,c) with CO_2 gas molecules during simulation steps. a,b show the first steps in up and side view, and c is the final step.

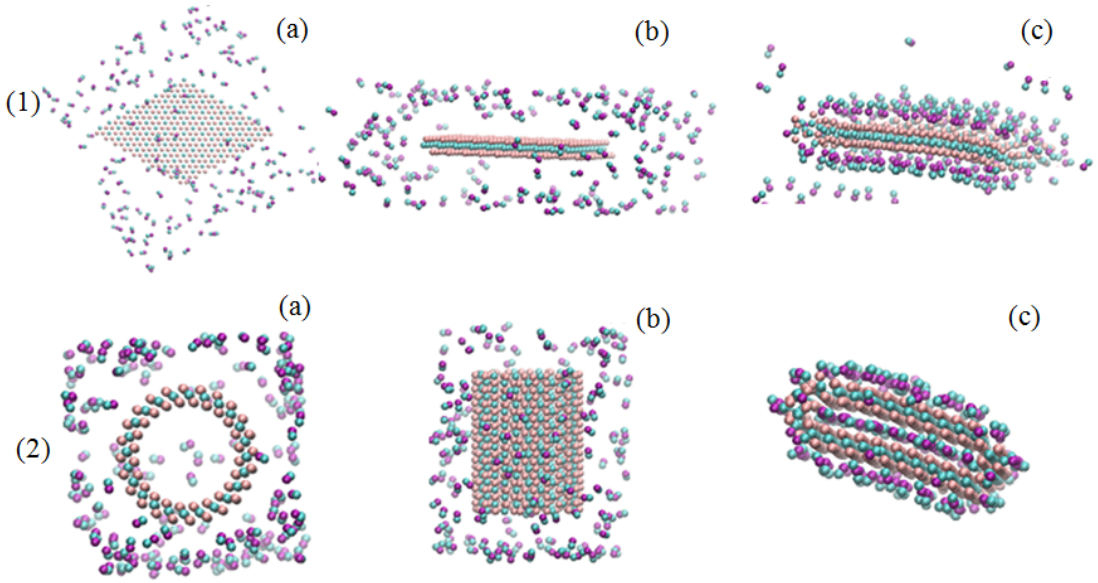

Fig. 3. Interaction between Ti_2C monolayer (1-a,b,c) and nanotube (2-a,b,c) with CO gas molecules during simulation steps. a,b show the first steps in up and side view and, c is the final step.

Table 1. binding energy (Eb), average charge transfer to gas molecules (Q), the weight percentage of the chemical (nch), and physical (nphy) adsorption of the gas molecules.

	E_b[Kj/mol]	Q[e^{-1}]	n_{ch}	n_{phy}
Ti_2C-ML@CO_2	-336.39	-0.469	13.11	27.74
Ti_2C-ML@CO	-352.22	-0.518	5.7	14.98
Ti_2C-NT@CO_2	-391.23	-0.551	7.70	14.87
Ti_2C-NT@CO	-457.63	-0.554	2.3	9.52

chemical and physical adsorbed gas molecules by the structures. According to Table. 1, it seems that Ti_2C-ML has more sensitivity than Ti_2C- NT against CO and CO_2 toxic gas molecules. Also, physical adsorption is more probable than chemical ones. The most physical and chemical weight percentages are 27.74% and 13.11% for Ti_2C-ML against CO_2 gas molecules, and both structures have more physical and chemical adsorption weight percentages for CO_2 gas molecules than CO.

Variation of distance densities (DDEN), which were the average number of equidistant adsorbed CO and CO2 gas molecules on two surfaces of the Ti_2C-ML and the walls of the Ti_2C-NT up to 10 Å, is shown in Fig. 4. This figure shows that dominant adsorption of CO and CO_2 gas molecules is the distance of 2 up to 6 Å from structure surfaces of ML and walls of the NT, so physical adsorption is the likely scenario as mentioned previously. DDENs of the ML and NT for CO_2 gas molecules are comparable, and gas molecules have nearly the same distribution around these structures. Also, the adsorption of CO molecules on NT is more than twice, about 2.8 Å from the walls, and comparable with ML at other distances. The sharp peaks in Fig. 4 show the most accumulation around surfaces or walls of the structures.

Table. 2, compares this work with other works. For example, higher sensitivity to CO_2 gas molecules showed by the NbSeTe monolayer on the Te side, which operates like the Ti2C monolayer in our study [30]. In Ref. 31, the sensitivity of Ti_2CTx to CO_2 gas molecules is 0.1 %, which is

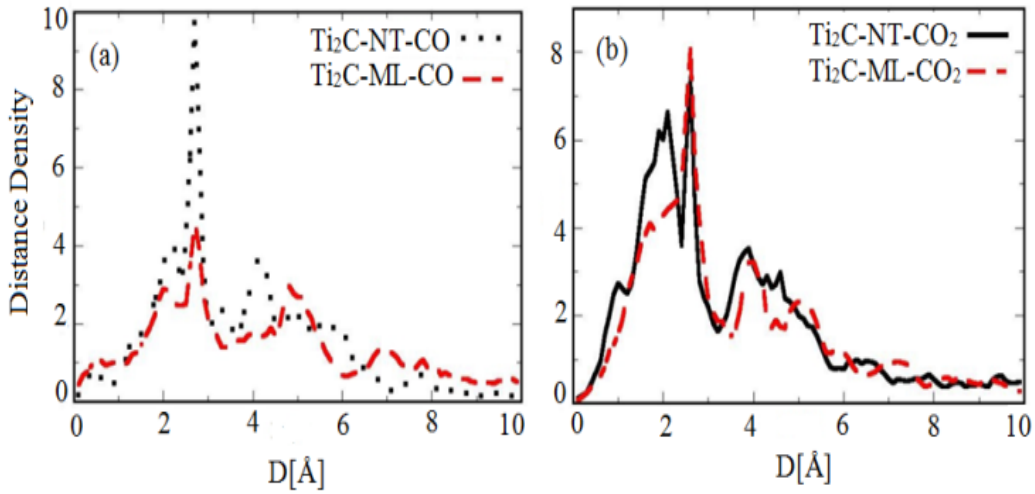

Fig. 4. Variation of the distance densities (DDEN) versus distance from the surface of the Ti_2C-ML or Ti_2C-NT.

Table 2. Other reported study, adsorption energy, E_{ad} (eV) and sensitivity, S.

	CO	CO_2
NbSeTe monolayer [30]	0.11 S	0.88 S
Ti_2CT_x monolayer [31]	-----	0.1 S
$Ti_3C_2T_x$ monolayer[32]	-0.2 E_{ad}	-0.08 Ead
SnSe monolayer [33]	-0.44 E_{ad}	-0.25 Ead
SiC Bilayer [34]	-0.12 E_{ad}	-0.13 Ead

very smaller than our result [31]. Khakbaz et.al reported that Ti_3C_2Tx MXene monolayer has more negative adsorption energy for CO gas molecules than CO_2 ones, in addition, physisorption is the dominant adsorption type, like our work [32]. in addition, these results have introduced about SnSe monolayer [33]. Also, SiC Bilayer adsorped CO and CO2 physically, as in our work, and they have nearly adsorption energy [34].

CONCLUSION

In this study, the adsorption of the CO and CO_2 toxic gas molecules on Ti_2C-ML and NT has been presented, and we can conclude that two phases of the Ti_2C (ML and NT) have different behavior against these gases. The adsorption is energetically favorable. Physical adsorption is dominant, and the most physical and chemical adsorption is for CO_2 toxic gas molecules on Ti_2C-ML as well the least one is for CO toxic gas molecules on Ti_2C-NT. Results show that Ti_2C-ML and Ti_2C-NT can be used as CO and CO_2 toxic and polluted gas sensors.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

1. Janata J. Chemical sensors. Anal Chem. 1992;64(12):196-219.
2. Lee E, Lee D, Yoon J, Yin Y, Lee Y, Uprety S, et al. Enhanced Gas-Sensing Performance of GO/TiO_2 Composite by Photocatalysis. Sensors. 2018;18(10):3334.
3. Al-Mohammad A, Darwich R, Rukiah M, Abo Shaker S, Kakhia M. ZnO Nanopowders as Chemical Sensor to Malathion Vapor. Acta Phys Pol, A. 2014;125(1):131-134.
4. Struk P, Pustelny T, Gołaszewska K, Borysiewicz MA, Piotrowska A. Gas Sensors Based on ZnO Structures. Acta Phys Pol, A. 2013;124(3):567-569.
5. Afzal A, Cioffi N, Sabbatini L, Torsi L. NO sensors based on semiconducting metal oxide nanostructures: Progress and perspectives. Sensors Actuators B: Chem. 2012;171-172:25-42.
6. Chang CW, Fennimore AM, Afanasiev A, Okawa D, Ikuno T,

Garcia H, et al. Isotope Effect on the Thermal Conductivity of Boron Nitride Nanotubes. Phys Rev Lett. 2006;97(8).
7. Shin H, Guan J, Zgierski MZ, Kim KS, Kingston CT, Simard B. Covalent Functionalization of Boron Nitride Nanotubes via Reduction Chemistry. ACS Nano. 2015;9(12):12573-12582.
8. Fan G-h, Zhu S, Li X-k, Ni K, Xu H. Ab initio investigation of pristine and doped single-walled boron nitride nanotubes as acetone sensor. Computational and Theoretical Chemistry. 2017;1115:208-216.
9. Blase X, Rubio A, Louie SG, Cohen ML. Stability and Band Gap Constancy of Boron Nitride Nanotubes. Europhysics Letters (EPL). 1994;28(5):335-340.
10. Chen X, Pu H, Fu Z, Sui X, Chang J, Chen J, et al. Real-time and selective detection of nitrates in water using graphene-based field-effect transistor sensors. Environmental Science: Nano. 2018;5(8):1990-1999.
11. Liu S, Wu T, Li F, Zhang Q, Dong X, Niu L. Disposable graphene sensor with an internal reference electrode for stripping analysis of heavy metals. Analytical Methods. 2018;10(17):1986-1992.
12. Lezi N, Economopoulos S, Prodromidis M, Economou A, Tagmatarchis N. Fabrication of a “Green” and Low–Cost Screen–Printed Graphene Sensor and Its Application to the Determination of Caffeine by Adsorptive Stripping Voltammetry. International Journal of Electrochemical Science. 2017;12(7):6054-6067.
13. Leng X, Wang F. Modified graphene oxide/Nafion composite humidity sensor and its linear response to the relative humidity. 2017 IEEE SENSORS; 2017/10: IEEE; 2017.
14. Kodu M, Berholts A, Kahro T, Kook M, Ritslaid P, Seemen H, et al. Graphene functionalised by laser-ablated V_2O_5 for a highly sensitive NH_3 sensor. Beilstein Journal of Nanotechnology. 2017;8:571-578.
15. Chen X, Huang Z, Li J, Wu C, Wang Z, Cui Y. Methane gas sensing behavior of lithium ion doped carbon nanotubes sensor. Vacuum. 2018;154:120-128.
16. Varghese SS, Lonkar S, Singh KK, Swaminathan S, Abdala A. Recent advances in graphene based gas sensors. Sensors Actuators B: Chem. 2015;218:160-183.
17. Choi W, Choudhary N, Han GH, Park J, Akinwande D, Lee YH. Recent development of two-dimensional transition metal dichalcogenides and their applications. Mater Today. 2017;20(3):116-130.
18. Lee E, VahidMohammadi A, Prorok BC, Yoon YS, Beidaghi M, Kim D-J. Room Temperature Gas Sensing of Two-Dimensional Titanium Carbide (MXene). ACS Applied Materials & Interfaces. 2017;9(42):37184-37190.
19. Kim SJ, Koh H-J, Ren CE, Kwon O, Maleski K, Cho S-Y, et al. Metallic Ti_3C_2Tx MXene Gas Sensors with Ultrahigh Signal-to-Noise Ratio. ACS Nano. 2018;12(2):986-993.
20. Yuan W, Yang K, Peng H, Li F, Yin F. A flexible VOCs sensor based on a 3D Mxene framework with a high sensing performance. Journal of Materials Chemistry A. 2018;6(37):18116-18124.
21. Naguib M, Mashtalir O, Carle J, Presser V, Lu J, Hultman L, et al. Two-Dimensional Transition Metal Carbides. ACS Nano. 2012;6(2):1322-1331.
22. Hope MA, Forse AC, Griffith KJ, Lukatskaya MR, Ghidiu M, Gogotsi Y, et al. NMR reveals the surface functionalisation of Ti_3C_2 MXene. Physical Chemistry Chemical Physics. 2016;18(7):5099-5102.
23. Anasori B, Lukatskaya MR, Gogotsi Y. 2D metal carbides and nitrides (MXenes) for energy storage. Nature Reviews Materials. 2017;2(2).
24. Yu X-f, Li Y-c, Cheng J-b, Liu Z-b, Li Q-z, Li W-z, et al. Monolayer Ti_2CO_2: A Promising Candidate for NH_3 Sensor or Capturer with High Sensitivity and Selectivity. ACS Applied Materials & Interfaces. 2015;7(24):13707-13713.
25. Lee E, VahidMohammadi A, Yoon YS, Beidaghi M, Kim D-J. Two-Dimensional Vanadium Carbide MXene for Gas Sensors with Ultrahigh Sensitivity Toward Nonpolar Gases. ACS Sensors. 2019;4(6):1603-1611.
26. Enyashin AN, Ivanovskii AL. Structural and electronic properties of the TiC nanotubes: Density functional-based tight binding calculations. Physica E: Low-dimensional Systems and Nanostructures. 2005;30(1-2):164-168.
27. van Duin A, Verners O, Shin Y-K. REACTIVE FORCE FIELDS: CONCEPTS OF REAXFF AND APPLICATIONS TO HIGH-ENERGY MATERIALS. International Journal of Energetic Materials and Chemical Propulsion. 2013;12(2):95-118.
28. Plimpton S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. J Comput Phys. 1995;117(1):1-19.
29. Mortier WJ, Ghosh SK, Shankar S. Electronegativity-equalization method for the calculation of atomic charges in molecules. Journal of the American Chemical Society. 1986;108(15):4315-4320.
30. Singh D, Ahuja R. Highly Sensitive Gas Sensing Material for Environmentally Toxic Gases Based on Janus NbSeTe Monolayer. Nanomaterials. 2020;10(12):2554.
31. Joon Kim S, Koh H-J, Ren CE, Kwon O, Maleski K, Cho S-Y, et al. Metallic Ti_3C_2Tx MXene Gas Sensors with Ultrahigh Signal-to-Noise Ratio. MXenes: Jenny Stanford Publishing; 2023. p. 971-992.
32. Khakbaz P, Moshayedi M, Hajian S, Soleimani M, Narakathu BB, Bazuin BJ, et al. Titanium Carbide MXene as NH_3 Sensor: Realistic First-Principles Study. The Journal of Physical Chemistry C. 2019;123(49):29794-29803.
33. Zhao Z, Yong Y, Zhou Q, Kuang Y, Li X. Gas-Sensing Properties of the SiC Monolayer and Bilayer: A Density Functional Theory Study. ACS Omega. 2020;5(21):12364-12373.
34. Wang X, Yong Y, Yang W, Zhang A, Xie X, Zhu P, et al. Adsorption, Gas-Sensing, and Optical Properties of Molecules on a Diazine Monolayer: A First-Principles Study. ACS Omega. 2021;6(17):11418-11426.