Titanium Carbide MXene as NH₃ Sensor: Realistic First-Principles Study

Pedram Khakbazar,† Milad Moshayedi,‡ Sajjad Hajian,‡ Maryam Soleimani,‡ Binu B. Narakathu,‡ Bradley J. Bazuin,‡ Mahdi Pourfath,§ and Massood Z. Atashbar†

†School of Electrical and Computer Engineering, College of Engineering, University of Tehran, Tehran 14395-515, Iran
‡Department of Electrical and Computer Engineering, Western Michigan University, Kalamazoo, Michigan 49008, United States
§Institute for Microelectronics, Technische Universität Wien, Vienna A-1040, Austria

ABSTRACT: This work presents a more realistic study on the potential of titanium carbide MXene (Ti₃C₂Tₓ) for gas sensing, by employing first-principle calculations. The effects of different ratios of different functional groups on the adsorption of NH₃, NO, NO₂, N₂O, CO, CO₂, CH₄, and H₂S gas molecules on Ti₃C₂Tₓ were analyzed. The results indicated that Ti₃C₂Tₓ is considerably more sensitive to NH₃ among the studied gas molecules, with a charge transfer of −0.098 e and an adsorption energy of −0.36 eV. By analyzing the electrostatic surface potential (ESP) and the projected density of states (PDOS), important physical and mechanical properties that determine the strength and nature of gas-substrate interactions were investigated, and also, the significant role of electrostatic effects on the charge transfer mechanism was revealed. Further, the Bader charge analysis for the closest oxygen and fluorine atoms to NH₃ molecule showed that oxygen atoms have 60% to 180% larger charge transfer than fluorine atoms, supporting that Ti₃C₂Tₓ substrate with a relatively lower ratio of fluorine surface terminations has a stronger interaction with NH₃ gas molecules. The calculations show that in the presence of water molecules, approximately 90% smaller charge transfer between NH₃ molecule and the Ti₃C₂Tₓ occurs. Ab initio molecular dynamics simulations (AIMD) were also carried out to evaluate the thermal stabilities of MXenes. The comprehensive study presented in this work provides insights and paves the way for realizing sensitive NH₃ sensors based on Ti₃C₂Tₓ that can be tuned by the ratio of surface termination groups.

INTRODUCTION

The development of novel gas sensors, with rapid and efficient gas concentration detection capabilities, has been a major research focus for applications including air pollution monitoring,¹ medical diagnostics,² food and beverage quality control,³ and explosives detection.⁴ Various materials, such as conductive polymer composites,⁵ carbon nanotubes,⁶ metal oxide semiconductors,⁷ graphene,⁸ and metal–organic frameworks⁹ have been used for the fabrication of gas sensors. Two-dimensional (2D) layered materials consist of atomic sheets with strongly bonded atoms, which are held together by weak interlayer Van der Waals forces. 2D layered materials have attracted growing interest in the development of room-temperature gas sensors with high sensitivity, due to their high surface-to-volume ratios.¹⁰ MXenes are a new family of 2D materials that have received significant attention for various applications, such as gas sensing,¹¹ biosensing,¹² catalysis,¹³ energy storage,¹⁴ hydrogen generation,¹⁵ and water purification.¹⁶ MXenes have layered structures and are typically formulated as MXₙ₋₁XₓTₓ (n = 1, 2, or 3), where M represents an early transition metal (e.g., Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, and Ta), X is carbon and/or nitrogen, with each X layer placed between two M layers, and Tₓ refers to surface terminations, such as fluorine (−F), oxygen (−O), or hydroxyl (−OH) groups. Naguib et al. have synthesized the first MXene, titanium carbide (Ti₃C₂Tₓ), by selective etching of aluminum (Al) from the Ti₃AlC₂ layered precursor.¹⁷ Surface terminations can significantly affect the gas sensing properties of MXenes.¹⁸ The mechanism of gas sensing is primarily dependent on the charge transfer (CT) between gas molecules and MXene, leading to conductivity modulation of these materials.¹⁹ Measurement of breath NH₃ has attracted considerable research interest in the biomedical field, since it can be used to predict kidney or liver malfunction or halitosis.²⁰ Considerable levels of NH₃ will be found in the human blood if a liver function disorder limits the conversion of NH₃ to urea. NH₃ gas is also present, at high concentrations, in the breath of uremic patients.²¹ Measurement of breath NH₃ levels can provide a fast and noninvasive method for the diagnosis of urea balance disturbance, which can be caused by kidney disorder or Helicobacter pylori bacterial infection.²² It is estimated that 5% of the worldwide population are affected by chronic kidney disease.²³ Thus, the development of sensitive, low-cost, and portable devices for monitoring breath NH₃ levels at home is of high importance.
The use of Ti$_3$C$_2$T$_x$ MXene (Figure 1) as a room-temperature flexible NH$_3$ sensor has been recently demonstrated. Yu et al. have employed density functional theory (DFT) to analyze monolayer Ti$_3$CO$_2$ for gas sensing. It was concluded that Ti$_3$CO$_2$ is more sensitive to NH$_3$ when compared to other gases assessed in their work. Xiao et al. investigated the adsorption behavior of NH$_3$ on different MXene materials usually have a combination of M$_2$CO$_2$ (M = Sc, Ti, Zr, and Hf), by using DFT calculations. They have predicted that the injection of a small number of electrons can alter the adsorption behavior of NH$_3$ on Ti$_3$CO$_2$ from chemisorption to physisorption, much larger than those reported for other M$_2$CO$_2$ MXenes (M = Sc, Zr, and Hf), implying that oxygen-terminated Ti$_3$CT$_x$ is the most suitable candidate among M$_2$CO$_2$ materials for NH$_3$ sensing.

Moreover, Ti$_3$C$_2$T$_x$ has been demonstrated as a base material for room-temperature NH$_3$ sensing. Therefore, optimizing the surface properties of the Ti$_3$C$_2$T$_x$ MXene, as a sensing layer, is essential for improving the sensitivity and selectivity of the breath NH$_3$ measurement systems, which is the sensing layer, is essential for improving the sensitivity and selectivity of the breath NH$_3$ measurement systems, which is addressed in this work. Even though Ti$_3$C$_2$T$_x$ MXenes have been successfully realized for NH$_3$ sensing, a comprehensive DFT study for the analysis and optimization of MXene’s NH$_3$ sensing is required. Previous DFT studies have focused on Ti$_3$CT$_x$ substrate and assumed only a single functional group for surface termination. However, synthesized Ti$_3$C$_2$T$_x$ MXene materials usually have a combination of −F, −O, and −OH as surface termination groups with ratios that highly depend on the synthesis method. For example, samples prepared by using 50 wt% hydrofluoric acid for the etching process have almost four times more −F termination groups compared to samples prepared by using a solution of lithium fluoride dissolved in 6 M hydrochloric acid for the etching process. As reported in our previous work, changing surface termination groups of titanium carbide MXene by controlling its synthesis method can significantly change gas sensing properties of the MXene.

In this work, electrostatic surface potential (ESP), projected density of states (PDOS) and thermal analysis were employed to further investigate the effect of different surface termination groups on NH$_3$ sensing of the Ti$_3$C$_2$T$_x$ from different aspects. Also, the effect of water molecules inherently present on the MXene substrate is taken into consideration in analyzing the gas sensing of the Ti$_3$C$_2$T$_x$. This study provides practical insights on tuning the NH$_3$ sensing of Ti$_3$C$_2$T$_x$ by using three configurations representing MXene samples that could result from different synthesis approaches: (a) Ti$_3$C$_2$(OH)$_{0.44}$F$_{0.88}$O$_{0.66}$ (S1) with relatively high-F surface functional groups; (b) Ti$_3$C$_2$(OH)$_{0.66}$F$_{0.22}$O$_{1.11}$ (S2) with relatively low-F surface groups; (c) Ti$_3$C$_2$(OH)$_{0.44}$F$_{0.88}$O$_{0.66}$(H$_2$O)$_{0.44}$ (S3) with relatively high-F surface functional groups as well as water molecules.

**APPRAOCH**

First-principle calculations were performed by DFT as it is implemented in the Vienna *ab initio* simulation package (VASP). Projector augmented-wave (PAW) pseudopotentials were employed to describe electron–ion interactions. The Perdew–Burke–Ernzerhof (PBE) version of the generalized gradient approximation (GGA) was applied for the exchange and correlation functional. A plane-wave energy cutoff of 700 eV and an energy convergence criterion of $10^{-6}$ eV was used for all calculations. Three $3 \times 3 \times 3$ supercells of Ti$_3$C$_2$T$_x$ (S1, S2, and S3) were analyzed. Initially, various gases including NH$_3$, NO, NO$_2$, N$_2$O, CO, CO$_2$, CH$_4$, and H$_2$S were placed on S1, considering several directions and different possible sites for the adsorption of the gas molecule on the substrate. On the basis of the calculated energy of the system, the most stable positions were eventually selected for the gas molecules. The Brillouin zone was sampled by a $3 \times 3 \times 3$ Monkhorst-Pack k-point grid for the relaxation calculations and a $4 \times 4 \times 1$ grid for the self-consistent procedures. The unit cell vectors and atom coordinates were relaxed until the forces on each atom became smaller than 0.01 eV/Å. The Van der Waals interactions were considered using Grimme’s semiempirical dispersion correction method (DFT-D3). A vacuum thickness larger than 25 Å was placed between the Ti$_3$C$_2$T$_x$ sheets to ensure the approximation of monolayer Ti$_3$C$_2$T$_x$. To analyze interactions between gas molecules and the substrates, the CT between gas molecules and the substrate was evaluated using Bader charge calculations, by differentiating the total charge of gas molecules before and after adsorption on the substrates.

Chemical bonding analyses were performed by means of the crystal orbital Hamilton population (COHP) method as implemented in the local-orbital basis suite toward electronic-structure reconstruction (LOBSTER) code. The adsorption energy ($E_{\text{ads}}$) is given by

$$E_{\text{ads}} = E_{\text{Ti}_3\text{C}_2\text{T}_x+\text{Gas}} - E_{\text{Ti}_3\text{C}_2\text{T}_x} - E_{\text{Gas}}$$

where $E_{\text{Ti}_3\text{C}_2\text{T}_x+\text{Gas}}$ is the total energy of the monolayer Ti$_3$C$_2$T$_x$ and the adsorbed gas molecule, $E_{\text{Gas}}$ is the energy of an isolated gas molecule, and $E_{\text{Ti}_3\text{C}_2\text{T}_x}$ is the energy of an isolated monolayer Ti$_3$C$_2$T$_x$. The recovery time (τ) is an important figure of merit for gas sensors that will be analyzed in the next
sections. The recovery time has an exponential relation with the adsorption energy as

$$\tau = \nu_0^{-1} e^{-E_0/k_B T}$$

(2)

where $\nu_0$ is the attempt frequency, $k_B$ is the Boltzmann’s constant, and $T$ is the temperature. It is assumed that NH$_3$ gas molecule has an attempt frequency equal to that of NO$_2$ ($\nu_0 = 10^{12}$ s$^{-1}$).47

In order to investigate the effect of the fluorine presence on hydrogen abstraction by NO$_2$, the Gibbs free energy should be calculated:48

$$\Delta G^H = G_{T_iC_2T_x-H} + G_{HNO_2} - G_{T_iC_2T_x} - G_{NO_3}$$

(3)

By assuming an ideal gas model, one can write

$$\Delta G^H(T) = \Delta E^H + \Delta E_{ZPE}^H + \int_0^T \Delta C_{vib}^H dT$$

$$- T \Delta S_{vib,rot}^H(T)$$

(4)

where $T$ is the temperature and $\Delta E^H$, $\Delta E_{ZPE}^H$, $\Delta C_{vib}^H$, and $\Delta S_{vib,rot}^H$ are the changes in the reaction chemisorption energy, the zero-point energy, vibrational heat capacity, and vibrational/rotational entropy, respectively. The rotational entropy is zero in solids implying that only vibrational entropy should be considered. In addition to static calculations, ab initio molecular dynamics (AIMD) simulations were performed to address the influence of thermal effects. The total energy convergence criterion is set to $10^{-4}$ eV for the AIMD simulations. The temperature of the systems during MD simulation is controlled by the Nose–Hoover thermostat.49

**RESULTS AND DISCUSSION**

**Gas Adsorption of Ti$_x$C$_2$T$_x$.** The most stable structures for the adsorption of NH$_3$, NO, NO$_2$, N$_2$O, CO, CO$_2$, CH$_4$, and H$_2$S gas molecules on S1 and the energy levels of their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are illustrated in Figures 2 and 3.

Figure 2. Most stable structures for the adsorption of various gas molecules on the S1: (a) NH$_3$, (b) NO, (c) N$_2$O, (d) NO$_2$, (e) CH$_4$, (f) CO, (g) CO$_2$, and (h) H$_2$S adsorption. Binding distances are in Å.

Figure 3. Energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the adsorption of gases on S1.

respectively. To determine the most stable gas orientation and adsorption site on the substrates, various initial structures for the gas molecule–substrate were considered and the system with the minimum energy was selected. The calculated $E_{ads}$, CT, and the nearest distances between the S1 and gas molecules ($D_{gas-substrate}$) are listed in Table 1. A positive CT value indicates electron transfer from the gas molecule to the substrate, while a negative CT value represents the reverse process.50

In the picture of a covalent Lewis base-acid interaction, a higher HOMO energy level of the gas molecules (Lewis base)
means strong adsorption energy with the surface (Lewis acid), which occurs when the HOMO gets closer to the unoccupied part of the surface and lower its energy. Lowering energy state leads to an effective charge transfer from the Lewis base to Lewis acid. On the basis of our calculations, the class of molecules with covalent Lewis acid–base interaction. As shown in Table 1 the NO2, N2O, CO, CO2, CH₄, and H₂S molecules are all physically adsorbed on the S1 with quite small adsorption energies and charge transfers, but NH₃ molecule with lowest adsorption energy (E_ads = −0.36 eV) and the highest CT (0.098 e) is the only gas molecule chemically adsorbed on the S1.

The isosurface representations of the total charge density for the adsorption of NH₃, H₂S, and CO₂ on S1 were investigated to visualize the interactions between Ti₃C₂Tₓ and gas molecules (Figure 4). For a reference charge density of 0.018 e/Å³, it was observed that a connection was established between the charge density isosurfaces of NH₃ and S1, while no connection was observed between the charge density isosurfaces of other gases and S1 that demonstrated a higher sensitivity of S1 to NH₃ compared to other studied gas molecules.

Remarkably, the addition of NO₂ to the S1 results in the formation of nitrous acid (HNO₂), where the oxygen atoms of NO₂ abstract hydrogen atoms from the S1. The presence of fluorine atoms in S1 reduces the electronegativity of oxygen atoms. Therefore, the O–H covalent bonds become relatively weak, so that oxygen atoms of NO2 can abstract hydrogen atoms from the S1, and new covalent bonds between hydrogen atoms and NO₂ molecules will form HNO₂. The Gibbs free energy (ΔG°) of hydrogen abstraction is considered to be an effective indicator of hydrogen-abstraction by the NO₂ molecule. Table 2 shows the thermodynamic quantities of this reaction. The calculated ΔG° for a hydrogen atom abstraction by NO₂ molecules from S1 and S2 are −1.10 and −0.69 eV respectively. This supports the fact that fluorine surface termination groups have a lower ΔG°, which can lead to a higher hydrogen-abstraction by NO₂ molecules and finally formation of more nitrous acid molecules on the Ti₃C₂Tₓ substrate.

**Surface Functional Groups.** The NH₃ sensing characteristics of Ti₃C₂Tₓ can be tuned by modifying the combination ratio of surface termination groups. The effect of surface termination groups and the presence of water molecules on the adsorption of NH₃ molecules on Ti₃C₂Tₓ MXene are investigated by analyzing three different substrates (S1, S2, and S3). Energy band diagrams for S1, S2, and S3 are shown in Figure 5. The density of states at the Fermi level, N(E₉), can be a representative of the material’s conductivity. Since the Fermi level is located at lower energies for S1 and S2, energy bands intersect the Fermi level at high-symmetry directions of the Brillouin zone. For S2, however, energy bands intersect the Fermi level mostly along the Γ–X and X–Γ directions, which results in a slight increase in N(E₉) compared to that of S1, whereas energy bands intersect the Fermi level along the X–M and M–Γ directions for S3 that results in the reduction of N(E₉) compared to that of S1.

The calculated adsorption parameters of the NH₃ on the three kinds of surfaces are shown in Table 3. The adsorption energies between the NH₃ gas molecule and S1, S2, and S3 are calculated as −0.36, −0.49, and −0.19 eV, respectively, which shows stronger adsorption of NH₃ on S2. For the adsorption energies of NH₃ on S1 and S2, the recovery times of the sensor at T = 298.15 K are 1.21 µs and 0.19 ms, respectively, which shows that Ti₃C₂Tₓ MXene is a suitable base material for reusable NH₃ gas sensors. Evidently, the relatively short recovery time reveals the rapid response of the S1 to NH₃ gas.

| Table 1. Adsorption Energies, Charge Transfers, and the Nearest Distances between S1 and Various Gas Molecules |
|----------------|----------------|----------------|
| Gas            | E_ads (eV)     | CT (e)         | D_gas-substrate (Å) |
| NH₃            | −0.36          | 0.098          | 2.54                |
| NO             | −0.16          | 0.068          | 2.32                |
| N₂O            | −0.23          | −0.006         | 2.89                |
| CO             | −0.20          | 0.003          | 3.16                |
| CO₂            | −0.08          | −0.011         | 2.75                |
| CH₄            | −0.16          | 0.000          | 3.17                |
| H₂S            | −0.16          | −0.010         | 2.18                |

| Table 2. Thermodynamic Quantities for NO₂, HNO₂, Ti₃C₂Tₓ, and Ti₃C₂Tₓ–H (S1 and S2) Species at T = 298.15 K |
|----------------|----------------|----------------|
| species        | E_ZPE (eV)     | −TS_rot (eV)   | −TS_def (eV)         |
| NO₂            | 0.23           | −0.003         | 0.23                |
| HNO₂           | 0.52           | −0.01          | 0.26                |
| Ti₃C₂Tₓ (S1)   | 5.98           | 0.00           | 2.82                |
| Ti₃C₂Tₓ–H (S1) | 5.69           | 0.00           | 2.79                |
| Ti₃C₂Tₓ (S2)   | 6.51           | 0.00           | 2.89                |
| Ti₃C₂Tₓ–H (S2) | 6.35           | 0.00           | 2.77                |

![Figure 4. Isosurface representations for total charge density of (a) NH₃, (b) H₂S, and (c) CO₂ on S1.](image-url)
The adsorption of the NH₃ gas molecule on Ti₃C₂Tₓ substrates. The NH₃ adsorption causes local structural deformation of both NH₃ molecules and the substrate. Titanium atom closest to the nitrogen atom is pulled outward from the layer, with its neighboring titanium—carbon (Ti—C) bonding length increasing from 2.06 to 2.23 Å for S1, and from 2.10 to 2.34 Å for S2. However, for S3, the titanium atom closest to the nitrogen atom is pushed inward to the layer, with its neighboring titanium—carbon (Ti—C) bonding length decreasing from 2.059 to 2.044 Å. For S1 and S2, there is a strong electrostatic attraction between the lone pair of oxygen atom on the substrate and the exposed positive parts of hydrogen atoms of NH₃ molecules, thus the created hydrogen bonds change the location of titanium atoms and configuration of NH₃ molecules, which results in the enhancement of CT between NH₃ and titanium. For S3, the oxygen atom of the H₂O molecule adsorbs the hydrogen atoms of NH₃ by hydrogen bonding. H₂O molecules stabilize NH₃ molecules on S3, but it could decrease the interaction strength between nitrogen and titanium atoms. It is worth mentioning that the bonding angles of NH₃ on S1 and S2 are larger than those of S3, which implies the repulsion of bond pair of NH₃ on S1 and S2 are smaller than that of single NH₃ molecule. As a result, the partially positive charge of hydrogen atoms and the electronegativity of the nitrogen atom of NH₃ molecule on S1 and S2 increase that might affect the CT from nitrogen to titanium.

The electrostatic surface potential (ESP) for the S1, S2, and S3 substrates and NH₃ gas are illustrated in Figure 7. The origin of the ESP is a strong local electrostatic potential on positive centers (titanium atoms) surrounded by negative centers (oxygen and fluorine atoms) of surfaces. The ESP can polarize the lone pair of NH₃ which in turn induces a dipole moment in the Ti₃C₂Tₓ MXene substrate. The induced dipole moment further polarizes NH₃ and leads to an electrostatic bonding between the substrate’s surface and the adsorbed NH₃ molecule. The strength of this interaction depends on the depth of the ESP well. As a result, for S1 and S2, there is a strong local ESP which stabilizes the occupied states of NH₃ and leads to forming of electrostatic bonds between nitrogen 2p lone pair and titanium 3d orbitals. For S2, the interaction and polarization of the NH₃ HOMO in the ESP well were enhanced by the outward movement of Ti from the layer. The results show the importance of electrostatic effects in addition to the covalent picture in determining the bonding mechanism, adsorption energies and CT trends.

The contribution of surface functional groups to charge transfer is studied by charge difference calculations. The isosurface representations of charge differences for NH₃ adsorption on S1, S2, and S3 for a reference charge density of 0.0028 e/Å³ are shown in Figure 8.

The accumulation or depletion of electrons between nitrogen and titanium atom sites is an indication of interaction strength between these atoms. Titanium atoms become partially negative due to the gain of electrons from NH₃ gas adsorption. According to Figure 8(d), the fluorine atom has a smaller contribution to CT than the oxygen atom. However, in the case of S2, due to the presence of more oxygen atoms and fewer fluorine atoms, the CT is larger than that of S1, as shown in Figure 8e. The difference in Bader charge of the nearest oxygen and fluorine atoms to NH₃ (before and after adsorption) for S1 and S2 were 0.005 e for fluorine atom and between 0.008 to 0.014 e for different oxygen atoms. The results support the fact that oxygen surface functional groups...
have a higher contribution in CT between the Ti₃C₂Tx substrate and the NH₃ gas molecule compared to fluorine surface functional groups. In the case of S₃, most of the charge from NH₃ is transferred to the Ti₃C₂Tx substrate and only a small portion is distributed over the water molecules. More precisely, the charge increments in water molecules are 0.0032 and 0.0008 e, respectively, that shows 33.61% of the CT was transferred to water molecules and the rest (66.39%) is transferred to the substrate.

To investigate the electronic properties of the three substrates, the projected density of states (PDOS) of valence electrons for different substrates are calculated and illustrated in Figure 9. The Fermi energy (\(E_F\)) is set to zero as a reference. The PDOS near the Fermi level is dominated by titanium 3d orbitals. For all the three Ti₃C₂Tx substrates, there is no energy gap at the Fermi level, which identifies the metallic nature of these materials. Figure 9a shows the total PDOS of a bare Ti₃C₂ for 3d orbitals of the titanium atom and 2p orbitals of the carbon atom. The valence and conduction bands near the Fermi level are mainly contributed by nonbonding titanium 3d orbitals of the surface (dangling bonds). In addition, there is a band at positive energies, which is originated from repulsive interactions between titanium atoms.

The strong bond of titanium 3d orbitals weakens after termination with −O, −F, and −OH surface functional groups. The titanium band at positive energies changes slightly, due to the interaction of nonbonding orbitals with surface termination groups. The Ti₃C₂ structure becomes stabilized by the saturation of nonbonding orbitals of valence electrons of titanium atoms at the surface by −O, −F, and −OH groups. Due to these bonding interactions, the PDOS curves shift toward more negative energies and pseudogaps around Fermi

Figure 7. Electrostatic surface potential (ESP) for the NH₃ gas molecule adsorption on (a) S1, (b) S2, and (c) S3.

Figure 8. Isosurface representations of charge difference for the adsorption of NH₃ on (a) S1, (b) S2, and (c) S3 and isosurfaces of charge difference for the oxygen (red), fluorine (green) and titanium (yellow) atoms nearest to NH₃ molecule, for (d) S1, (e) S2, and (f) S3. The accumulation and depletion of electrons are represented by the cyan and purple regions, respectively.

Figure 9. Projected density of states (PDOS) of (a) Ti–3Cₓ, (b) S1, (c) S2, (d) S3, and Ti atoms of the (e) S1. The PDOS of Ti atoms of the S1 are projected onto d_{xy}, d_{yz}, d_{x^2−y^2}, and d_{z^2} orbitals.
level are induced as shown in Figure 9b–d. The pseudogap appears between the bonding orbitals at negative energies and nonbonding orbitals at positive energies. It is worth mentioning that, for metallic structures, the width of the pseudogap represents the strength of the covalent bonding, which in turn, determines the stability of the structure. Therefore, it can be considered as a criterion for comparing the stability of substrates with various surface termination groups. For the S1, as shown in Figure 9b, the Fermi level can be divided into two maximum bands which are formed by hybridized titanium 3d–carbon 2p and titanium 3d–oxygen 2p orbitals between 0 and −5.3 eV (band A), and titanium 3d–fluorine 2p orbitals between −5.3 and −7 eV (band B). In addition, band C is formed below band B corresponding to the hybridization between titanium and functional groups. For the S2, which has fewer fluorine surface groups, after the surface groups are added to Ti3C2T, the Fermi level shifts toward lower energies and the DOS at the Fermi level decreases (a pseudogap occurs as shown in Figure 9c) due to the new induced energy states. The DOS related to bands A are increased by titanium 3d–oxygen 2p orbitals, whereas that of bands B are decreased. The DOS increases from 19.32 to 30.96 for oxygen atoms and decreases from 35.90 to 13.37 for fluorine atoms. For the S3, as shown in Figure 9d, after the addition of surface groups of −OH, −O, and −F, the Fermi level shifts downward in energy, and in the presence of H2O molecules a pseudogap appears. Figure 9e shows the PDOS for titanium atoms of the S1, which are projected onto dxy, dxz, d22, and d22 orbitals. Five titanium 3d orbitals split into three groups: (i) dxy, (ii) dxz, (iii) d22, and (iv) d22. The DOS at the Fermi level is dominated by the in plane dxy, d22, and d22 orbitals, and the d22 orbitals perpendicular to the substrate’s plane.

Figure 10 shows PDOS for the adsorption of NH3 molecule on S1, S2, and S3. It is worth mentioning that the conduction states of substrates are mainly contributed from titanium 3d orbitals. This implies that when an extra electron is introduced to the substrates, the electron will fill the titanium 3d unoccupied orbitals. Therefore, the adsorption of NH3 has a substantial effect near the Fermi level. NH3 molecules induce several distinct states at the carbon band in the energy range around −7.9 and −8.3 eV for S1 (Figure 10a) and S2 (Figure 10b), respectively. However, for S3, some states are induced around −6.2 and around −1.2 eV (near the Fermi level), as shown in Figure 10c. The results indicate that the orbital mixing in S2 is stronger when compared to S1 and S3, which leads to higher adsorption energy. Figure 11 shows the PDOS of nitrogen and titanium atoms when the NH3 molecule is adsorbed on the S1, S2, and S3. In parts a and b of Figure 11, the broadening of the adsorbed NH3 occupied states and an increased intermixing of nitrogen and titanium states can be observed, which shows a larger covalent contribution to the adsorption energy and CT. A gradual energy downshift of the center of the NH3 HOMO can be observed at PDOS plots in parts a and b of Figure 11 that reveals a HOMO in NH3 can be polarized more easily and responds better to the surface ESP well. The results indicate the importance of surface intrinsic electrostatic potential in the ligand to metal CT. The weak physical nature of NH3 adsorption on S3 is illustrated in Figure 11c.

To evaluate the N–T interaction at the surface, crystal orbital Hamilton population (COHP) calculations were performed. When an adsorbate binds to a solid surface, the overlap of their electronic states leads to the formation of bonding and antibonding states. The bonding states are positioned below the Fermi-energy and are fully occupied and the antibonding states are mostly positioned above the Fermi-level. The delocalized molecular orbitals of NH3 adsorbed on S1 and S2 interact with the titanium bands in about −6 to −2 eV energy zone and the antibonding surface–adsorbate states are partially filled. Compared to the case of NH3 adsorption on S1, the overlap region is wide in S2 and the antibonding occupancy is reduced. In addition, the bonding and antibonding interactions are getting smaller in S3 and the localized molecular orbitals of NH3 adsorbed on S3 weakly interact with the Ti bands at −1.2 eV. The results of the orbital analysis are consistent with the computed CT and adsorption energies of the three NH3–Mxene systems.

**Thermal Stability of NH3 Adsorption on Ti3C2T**

The thermal stability and NH3 adsorption on the surface were analyzed by performing AIMD. AIMDs up to 6 ps (1 ps equilibration) are simulated for three surfaces starting from the most stable structures obtained with static calculations. Figure 12 demonstrates that Ti3C2T substrates are stable systems in the presence of NH3 gas molecules at room temperature. Here, the total energy fluctuation is minimal for all the cases. Interestingly, the NH3 gas molecule is dissociated from the S1 and S2 at the early stage of the simulation, whereas for S3, the NH3 moves over the surface without more separation. These results show that cooperative hydrogen bond interactions and cooperative adsorption are key factors for determining the degree of dissociation of NH3 over the surface. From a computational point of view, considering the formation of a hydrogen bond between NH3 molecule and the nearest under-coordinated atom at the surface, as well as water–NH3 intrinsic interaction are of high importance for the fabrication of the Ti3C2T-based NH3 sensor.

**The Comparison with Other 2D Materials.** Phosphorene, MoS2, and boron-doped SWCNT have been proposed as promising materials for NH3 sensing. Adsorption energies and CTs related to the interaction between NH3 and these materials are compared in Figure 13. As illustrated in Figure...
13, the CT from NH$_3$ to MoS$_2$ and phosphorene is much smaller than that of Ti$_3$C$_2$T$_x$ MXenes.

Although boron-doped SWCNT has a higher CT, its relatively high adsorption energy ($-0.7$ eV) suggests this material as an NH$_3$ capturer which has a relatively long recovery time. Zr$_2$CO$_2$ and V$_2$CO$_2$ are MXene substrates that have higher CT compared to Ti$_3$C$_2$T$_x$ MXenes$^{30,32}$; however, similar to boron-doped SWCNT, their relatively high adsorption energy ($-0.81$ eV for both) leads to long recovery time. Ti$_3$C$_2$T$_x$ MXenes have a higher CT with NH$_3$ compared to phosphorene and MoS$_2$ and more appropriate adsorption energy which leads to a better sensor recovery time. Compared to ref 32, the configurations studied for Ti$_3$C$_2$T$_x$ MXenes are much similar to the reported synthesized samples$^{33,35}$ by choosing surface termination groups ratios closer to those of real samples, instead of using just one type of surface termination groups. The presented results in this work provide insights for understanding and performing optimization studies on Ti$_3$C$_2$T$_x$ for NH$_3$ sensing by controlling the synthesis process.

**CONCLUSION**

In this work, a first-principles study was successfully applied to investigate Ti$_3$C$_2$T$_x$ as an ammonia sensor. Since synthesized sample of Ti$_3$C$_2$T$_x$ have a combination of various surface termination groups, as well as water molecules, the impacts of different ratios of surface termination groups were analyzed, as well as the presence of water molecules on ammonia gas sensing behavior of Ti$_3$C$_2$T$_x$. DFT calculations for $E_{\text{ads}}$ and CT between various gases and S1 show a relatively high sensitivity of the substrate to NH$_3$ gas molecules compared to other gases with the highest CT (0.098 eV) and the lowest $E_{\text{ads}}$ ($-0.36$ eV). The calculated NH$_3$ adsorption energy for S2 was $-0.49$ eV, which is larger than those of S1 and S3. Isosurface representations of charge difference showed a smaller CT between fluorine atoms and NH$_3$ molecules compared to the CT between oxygen atoms and NH$_3$ molecules. At NH$_3$...
adsorption sites, the Bader charge difference of nearest oxygen atoms was 60% to 180% larger than that of the nearest fluorine atoms, demonstrating a stronger interaction of NH3 with the Ti3C2T1-based sensor with a lower ratio of fluorine surface terminations. PDOS curves shift toward energies that are more negative, and a pseudogap around the Fermi level appear, as surface termination groups are added to the Ti3C2 substrate. It shows that the orbital mixing of S3/NH3 is weaker compared to S1/NH3 and S2/NH3, which will lead to a smaller CT. Moreover, ESP and PDOS analyses for NH3 adsorption showed that the surface properties can dictate the strength and nature of bonding through a combination of covalent and electrostatic effects. The findings are related to the general Lewis acid–base interactions in the matter of molecular chemistry. AIMD simulations were also performed to confirm that all the structures in the presence of the NH3 gas molecule are thermally stable at room-temperature.

**AUTHOR INFORMATION**

Corresponding Author

* (M.P.) E-mail: pourfath@ut.ac.ir; pourfath@iue.tuwien.ac.at.

**ORCID**

Mahdi Pourfath: 0000-0002-8053-578X

**Notes**

The authors declare no competing financial interest.

**REFERENCES**


(22) Huang, K.; Li, Z.; Lin, J.; Han, G.; Huang, P. Correction: Two-dimensional transition metal carbides and nitrides (MXenes) for biomedical applications. Chem. Soc. Rev. 2018, 47, 6889−6889.


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