Nitrogen-Containing Gas Sensing Properties of 2-D Ti$_2$N and Its Derivative Nanosheets: Electronic Structures Insight

Hongni Zhang $^{1,2}$, Wenzheng Du $^1$, Jianjun Zhang $^1$, Rajeev Ahuja $^{3,4,*}$ and Zhao Qian $^{1,*}$

1. Introduction

Industrial pollutant emissions account for a large share of environmental pollution, and one of the most harmful is nitrogen-containing gas (NCGs), such as NO, NO$_2$, and NH$_3$. At the same time, the nitrogen-containing gases themselves are generally toxic and can damage the respiratory cells of humans and animals [1–4]. Therefore, there is an urgent need to explore efficient and alternative materials for the sensing or capturing of these gases. Although some current solid-state sensors can also detect toxic gases, there is still much room for improvement due to the increasingly high demand for sensitivity, selectivity, stability, and other factors [5,6]. Two-dimensional (2-D) materials have large contact areas with gas and special electronic properties; thus, their interactions with gas molecules have been studied in detail based on the quantum-mechanical Density Functional Theory (DFT) calculations. It is found that the interactions between pure Ti$_2$N and NCGs (including NO, NO$_2$, and NH$_3$) are very strong, in which NO and NO$_2$ can even be dissociated, and this would poison the substrate of Ti$_2$N monolayer and affect the stability of the sensing material. For the monolayer of Ti$_2$NT$_2$ (T=O, F, OH) that is terminated by functional groups on surface, the adsorption energies of NCGs are greatly reduced, and a large amount of charges are transferred to the functional group, which is beneficial to the reversibility of the sensing material. The significant changes in work function imply the good sensitivity of the above mentioned materials. In addition, the fast response time further consolidates the prospect of two-dimensional Ti$_2$NT$_2$ as efficient NCGs’ sensing materials. This theoretical study would supply physical insight into the NCGs’ sensing mechanism of Ti$_2$N based nanosheets and help experimentalists to design better 2-D materials for gas adsorption or sensing applications.

Keywords: atomic structure; electronic structure; Density Functional Theory (DFT); MXenes; two-dimensional materials

Abstract: In this work, the potentials of two-dimensional Ti$_2$N and its derivative nanosheets Ti$_2$NT$_2$ (T=O, F, OH) for some harmful nitrogen-containing gas (NCG) adsorption and sensing applications have been unveiled based on the quantum-mechanical Density Functional Theory calculations. It is found that the interactions between pure Ti$_2$N and NCGs (including NO, NO$_2$, and NH$_3$ in this study) are very strong, in which NO and NO$_2$ can even be dissociated, and this would poison the substrate of Ti$_2$N monolayer and affect the stability of the sensing material. For the monolayer of Ti$_2$NT$_2$ (T=O, F, OH) that is terminated by functional groups on surface, the adsorption energies of NCGs are greatly reduced, and a large amount of charges are transferred to the functional group, which is beneficial to the reversibility of the sensing material. The significant changes in work function imply the good sensitivity of the above mentioned materials. In addition, the fast response time further consolidates the prospect of two-dimensional Ti$_2$NT$_2$ as efficient NCGs’ sensing materials. This theoretical study would supply physical insight into the NCGs’ sensing mechanism of Ti$_2$N based nanosheets and help experimentalists to design better 2-D materials for gas adsorption or sensing applications.

1. Key Laboratory of Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Shandong University, Jinan 250061, China; niu810@126.com (H.Z.); 201813740@mail.sdu.edu.cn (W.D.);
2. College of Industry and Commerce, Shandong Management University, Jinan 250357, China;
3. Condensed Matter Theory, Department of Physics and Astronomy, Ångström Laboratory, Uppsala University, 75120 Uppsala, Sweden; rajeev.ahuja@physics.uu.se;
4. Department of Materials Science and Engineering, KTH Royal Institute of Technology, 10044 Stockholm, Sweden;
* Correspondence: qianzhao@sdu.edu.cn

Citation: Zhang, H.; Du, W.; Zhang, J.; Ahuja, R.; Qian, Z. Nitrogen-Containing Gas Sensing Properties of 2-D Ti$_2$N and Its Derivative Nanosheets: Electronic Structures Insight. Nanomaterials 2021, 11, 2459. https://doi.org/10.3390/nano11092459
material for optical sensors by adsorbing different small molecules [9]. Li et al. compared the structures and electronic properties of pure and two vacancy-defected MoS$_2$ nanosheets with NO adsorption. Defects can effectively improve the NO-sensing performance [10].

Transition metal carbide or nitride MXenes are also one family of promising gas-sensing materials [11,12], where M is a transition metal and X is carbon or nitrogen. The general formula of MXenes is written as $M_nX_{n-1}$. During the preparation process in an aqueous solution containing fluoride ions, there may be some O, F, and OH functional groups formed [13–15]. This type of MXene with functional groups is written as $M_nX_{n-1}T_n$ (T=O, F, OH). MXenes are also widely reported in energy storage, electrode materials, ion batteries, and the spintronic and optical devices, due to their unique structures and properties [16–24].

After our review of previous literature, we found that some carbide-based MXenes have the potential to be used as sensors for molecules, such as amino acids and nucleobase [25,26]. With less exfoliation energy compared with other types, the synthesizability of the nitride MXenes is good [27], while there are fewer studies on their use in sensing NCGs [28–32]. In order to obtain a theoretical understanding of the nitride MXenes in terms of their sensing or capturing performance towards nitrogen-containing gas (NCGs), in this work, we conducted a detailed computational study on the adsorption behaviors of NCGs (including NO, NO$_2$, and NH$_3$) of Ti$_2$N monolayer with bare surface and terminated with O, F, and OH functional groups. Density Functional Theory–based first-principles calculations were performed to unveil the adsorption structures, charge transfer, band structures, density of states, and work functions to stimulate and inspire the deep mechanism investigations.

2. Methods

DFT calculations were employed by using the projector augmented wave (PAW) pseudo-potentials in a Vienna Ab initio Simulation Package (VASP). For the exchange-correlation functional, we used the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA). Grimme’s DFT-D2 method was used to describe the van der Waals interactions. This method adds semi-empirical dispersion on the basis of conventional Kohn-Sham DFT energy. In calculations, Ti$_2$N and Ti$_2$NT$_2$ (T=O, F, OH) were constructed as $4 \times 4 \times 1$ supercells, and a 20 Å vacuum layer was added in Z-axis direction to eliminate the interlayer interaction. The energy cutoff of 520 eV was used for wave functions’ expansion. The Brillouin zone integration was sampled with $5 \times 5$ k-grid mesh for geometry optimizations and $15 \times 15$ k-grid mesh for electronic properties calculations to achieve high accuracy. Geometry optimizations were performed by using the conjugated gradient method, and the convergence criterion was set to be $0.02$ eV/Å on force and $1 \times 10^{-5}$ eV/atom on energy. The adsorption energy ($E_{\text{ads}}$) of nitrogen-containing gas (NCGs) on Ti$_2$N or Ti$_2$NT$_2$ (T=O, F, OH) is defined as follows:

$$E_{\text{ads}} = E_{\text{MXene + NCGs}} - E_{\text{NCGs}} - E_{\text{MXene}}$$

where $E_{\text{ads}}$, $E_{\text{MXene + NCGs}}$, $E_{\text{MXene}}$, and $E_{\text{NCGs}}$ stand for the adsorption energy, total energies of optimized Ti$_2$N or Ti$_2$NT$_2$ (T=O, F, OH) MXene with adsorbed NCGs molecules, energies of pure MXene, and isolated NCGs (NO, NO$_2$, and NH$_3$) molecules respectively.

3. Results and Discussion

First of all, the Ti$_2$N MXene has a hexagonal structure with three layers of atoms: the middle is N-atoms layer; and the upper (a) and lower (b) layers are Ti atoms, as is shown in Figure 1a. After structural optimizations, the Ti-N bond length is 2.07 Å, the bond angle of the same layer Ti and N (Ti–N–Ti) and N–Ti–N are both 92.4°, and the bond angle of different-layer Ti and N (Ti–N–Ti) is 87.6°. The lattice parameter of the $4 \times 4$ supercell is $a = b = 11.98$ Å. These parameters are very consistent with the results of Ti$_2$N studied in other works in the literature [37,38], indicating the reliability of the calculation results. The band structure and PDOS of the material are shown in Figure 1b; it can be seen that there...
are many electronic states available for occupation at the Fermi level, and Ti$_2$N exhibits metallic properties. The states near the Fermi level are occupied by Ti electrons, where N’s contribution is relatively small, meaning that low-energy carriers mainly originate from Ti.

**Figure 1.** (a) Top and side view of the optimized structures for Ti$_2$N monolayer (blue and silver balls represent Ti and N atoms, respectively). (b) Band structure and projected density of states of Ti$_2$N monolayer (Ti$d$-orbital uses top abscissa and other orbitals use bottom coordinate).

In order to study the most stable adsorption configurations of NCGs on Ti$_2$N MXene, the NO, NO$_2$, and NH$_3$ molecules were respectively placed at three different adsorption sites, namely on top of the Ti(a) atom shown in Figure 1a (site “a”), on top of the hollow Ti(b) atom (site “b”), or on top of the N atom (site “c”). The screened most stable configurations after adsorbing NCGs are shown in Figure 2. Both NO and NO$_2$ show dissociative adsorption. The adsorption energy is far greater than those of other two-dimensional materials [39–44]. When NO is adsorbed on Ti$_2$N, N and O atoms are adsorbed at the adjacent site “b” respectively. The distance between N and O is 3.07 Å, which is much larger than 1.15 Å of free NO gas molecule, indicating that the N–O bond is broken and NO dissociates. The dissociated N and O atoms form new bonds with Ti atoms in the upper layer of Ti$_2$N, with bond lengths of 1.93 and 1.97 Å, respectively. Ti atoms protrude slightly upwards from its binding, and the Ti–N bond length on the surrounding matrix increases by about 0.14 Å. It can be seen from Figure 3a that, after dissociation, the N 2$p$ and O 2$p$ in NO and the nearby Ti 3$d$-orbitals have similar peak positions and obvious $p$-$d$ hybridization in PDOS diagram. There is a strong bonding between NO and Ti$_2$N, and the adsorption energy is as high as $-9.809$ eV. At the same time, the band structure shows that the dissociative adsorption of NO on Ti$_2$N does not change the original metallic properties.

**Figure 2.** Top and side view of the optimized atomic structures for Ti$_2$N monolayer after adsorbing (a) NO, (b) NO$_2$, and (c) NH$_3$ (blue, silver, red, and pink balls represent Ti, N, O, and H atoms, respectively).
Figure 3. Band structures, PDOS and differential charge densities of Ti$_2$N after adsorbing (a,d) NO, (b,e) NO$_2$, and (c,f) NH$_3$ (Ti-$d$-orbital uses top abscissa and other orbitals use bottom coordinate; isovalue of NO and NO$_2$ is set to 0.01 e/Å$^3$, NH$_3$ is set to 0.005 e/Å$^3$).

When NO$_2$ interacts with Ti$_2$N, it is interesting that NO$_2$ will also dissociate similar to NO adsorption, and all the N and O atoms are adsorbed at the site “b”. One O-atom keeps the same shape adsorbed at adjacent position, while the another O-atom is adsorbed away from it. The N-O bond length in NO$_2$ is increased to 3.07 Å. The dissociative adsorption energy is up to $-14.336$ eV. As can be seen from the electronic structure in Figure 3b, the $p$-$d$ hybridization of N 2$p$-, O 2$p$-, and Ti 3$d$-orbitals corresponds with the strong bonding of Ti-N and Ti-O, respectively. The metallic behavior of Ti$_2$N remains after NO$_2$ dissociative adsorption. From the differential charge density in Figure 3d–f, it can be seen that the dissociation of NO and NO$_2$ is caused by the excessive charge transfer from Ti$_2$N MXene to the gas molecule. The Bader charge analysis shows that $2.57$ e$^-$ and $3.77$ e$^-$ charges were transferred from Ti$_2$N to NO and NO$_2$, respectively. The bulk of these transferred charges comes from the surrounding Ti atoms, and this is also the fundamental reason why the N-O bond is broken.

The adsorption of NH$_3$ is completely different from those of NO and NO$_2$. It is bound by associative adsorption with the binding distance of 2.2 Å and the $E_{ads}$ value of $-1.286$ eV. As shown in Figure 3c, NH$_3$ tends to be adsorbed at site “a” with N-atom below and three H-atoms evenly distributed above. The distance between the Ti atom at site “a” and the surrounding N atom is elongated to 2.14 Å, and the N-Ti-N bond angle is reduced to 88.3°. To figure out the binding and charge transfer mechanism between NH$_3$ molecule and Ti$_2$N monolayer, the band structure and PDOS were analyzed. It is difficult to find a pronounced overlap between N $p$ and Ti$d$ close to the Fermi level in Figure 3c. The amount of charge transfer is only 0.01 e$^-$, which is far less than those of NO and NO$_2$. The bonding between NH$_3$ and Ti$_2$N is very weak, and the band structure that is almost the same as the bare Ti$_2$N monolayer also confirms this.

For ideal gas sensing application, excessive adsorption energy is obviously not feasible. The dissociative adsorption of NO and NO$_2$ on Ti$_2$N monolayer will obviously poison the substrate and make it fail to work cyclically. The dissociation of gas molecules results from the strong interaction between the bare Ti$_2$N surface and O atoms. Thus, the pure Ti$_2$N monolayer can be used as a kind of gas-trapping material instead of highly efficient sensor for NO and NO$_2$. Compared with those two gases, the adsorption effect of NH$_3$
is satisfactory. The associative adsorption with lower energy will not cause chemical poisoning, which is beneficial to Ti$_2$N as a promising candidate material for reversible NH$_3$ sensors. In actual preparation process, some functional groups are usually introduced onto the Ti$_2$N monolayer, and these functional groups may have significant impacts on adsorption properties of the material. Considering this reality, in the following part, we recount how we studied the adsorption behaviors of the Ti$_2$N monolayer terminated by O, F, and OH towards NCGs.

We introduce O, F, and OH functional groups at three adsorption positions (site “a”, “b”, and “c”) of Ti$_2$N, of which OH only considers the vertical direction (O atom is close to the matrix). All the functional groups tend to adsorb at site “b” with the lowest energy, as shown in Figure 4a–c. After adsorbing different functional groups, the Ti–N bonds show different degrees of extension: 2.164, 2.052, and 2.065 Å for Ti$_2$NO$_2$, Ti$_2$NF$_2$, and Ti$_2$N(OH)$_2$, respectively, which is due to the bonding between Ti and functional groups. Gouveia et al. reported possible atomic-layer-stacking-phase transitions of some MXenes [41]; thus, we also carefully checked this point in our research. It is found that the material system maintains phase stability and stacking way after introduction of those functional groups. The Bader charge analysis shows that 1.1, 0.8, and 0.8 e$^-$ are respectively transferred to O, F, and OH from Ti$_2$N. It can also be observed in Figure 4d–f that there is a strong overlap between the Ti$d$-orbital and the T (O, F, or OH)$d$-orbitals.

After obtaining the stable configurations of Ti$_2$NT$_2$(T=O, F, OH), we placed various NCGs molecules at different adsorption sites (site “a”, “b”, and “c”), such as those in pure Ti$_2$N. It can be seen from the most stable adsorption structures after optimizations in Figure 5 that all NCGs have no dissociative adsorption on Ti$_2$NT$_2$(T=O, F, OH). The binding distance is defined as the shortest direct distance between the NCGs molecule and the matrix; hereby, the binding distances of NO, NO$_2$, and NH$_3$ on Ti$_2$NO$_2$ are 2.082, 1.824, and 2.172 Å, respectively. The bond lengths of NO and NH$_3$ after adsorption are the same as those of free gas molecules, while one of the N–O bonds of NO$_2$ is stretched to 1.530 Å.
The 2-D Ti$_2$NO$_2$ does not change significantly under NO environment, while the Ti atoms exposed to the adsorption positions of NO$_2$ and NH$_3$ are obviously dragged out. For NCGs adsorption on the surface of Ti$_2$NF$_2$, the molecular bond lengths and the matrix are almost unchanged with the adsorption distances of 2.951, 2.800, and 2.947 Å, respectively. It is surprising when NO is adsorbed on Ti$_2$N(OH)$_2$. The H atoms on the substrate bind with NO, where three H atoms combine with the N atom and one H atom combines with the O atom to form a hydroxyl lammonium-like product. The adsorption distances of NO$_2$ and NH$_3$ are 1.625 and 1.702 Å, which are measured from the nearest H atom; thus, they are shorter than those of other Ti$_2$NT$_2$(T=O, F). While, the adsorption is not strong, especially the NH$_3$ molecule has basically no change compared with the free molecule.

![Figure 5](image)

**Figure 5.** Top and side view of the optimized structures for Ti$_2$NO$_2$ after adsorbing (a) NO, (b) NO$_2$, and (c) NH$_3$; Ti$_2$NF$_2$ after adsorbing (d) NO, (e) NO$_2$, and (f) NH$_3$; and Ti$_2$N(OH)$_2$ after adsorbing (g) NO, (h) NO$_2$, and (i) NH$_3$ (blue, silver, red, pink, and yellow balls represent Ti, N, O, H, and F atoms, respectively).

We can clearly see that the absolute values of adsorption energy of NCGs on Ti$_2$NT$_2$(T=O, F, OH) decrease sharply compared with the pure substrate in Table 1, especially on the surface of Ti$_2$NF$_2$. Since the H atoms of the OH functional groups fall off the Ti$_2$N(OH)$_2$ substrate and bind with NO, their decrease is not that large. On the pure Ti$_2$N monolayer, a large amount of charge is transferred from Ti$_2$N to NO and NO$_2$. After the introduction of the functional group O, F, or OH, most of the charge transfer from Ti$_2$N is captured by these functional groups, which leaves a very small charge amount for exchange with NCGs.
In addition, one can see that the difference in adsorption energy of each NCG on substrate is obvious, indicating that the selectivity is good. As mentioned above, NO and NO$_2$ are dissociatively adsorbed on pure Ti$_2$N, which results in the poisoning of the Ti$_2$N surface. Similarly, NO binds with H atoms of Ti$_2$N(OH)$_2$ and destroys the surface integrity of the substrate, which is detrimental to the sensing material. Thus, Ti$_2$N(OH)$_2$ is not suitable for NO sensing. From the perspective of adsorption energy, those of NO on Ti$_2$NO$_2$, NO$_2$ on Ti$_2$NF$_2$, and NH$_3$ on Ti$_2$N(OH)$_2$ are between physisorption and chemisorption, which are important to make sensors work reversibly and increase their efficiency [45].

To better understand the effects of NCGs molecules on Ti$_2$NT$_2$ (T=O, F, OH), the band structure and PDOS of all the adsorption systems are calculated and shown in Figure 6. Regardless of the type of NCGs adsorption, the system retains metallic properties. Only when Ti$_2$NO$_2$ is exposed to NO$_2$, the Ti$d$-, O$p$-, and N$p$-orbitals show a certain degree of d-p hybridization, while the p- and d-orbitals in other PDOS do not overlap. When Ti$_2$NO$_2$ adsorbs NO, a flat band appears near the Fermi energy and indicates that the electrons are delocalized, which further proves that the interaction between NO and Ti$_2$NO$_2$ is not strong. This phenomenon is more obvious when NCGs are adsorbed on Ti$_2$NF$_2$ shown in Figure 6d–f. These results are consistent with the above discussion on energetics and charge-transfer profiles.

An ideal sensing material not only needs to possess excellent gas-binding capability but also has a requirement for good sensitivity. The conductivity of materials, especially two-dimensional materials, is closely related with work function. During adsorption, if the electron affinity of gas molecule surpasses the work function of substrate materials, the molecule will grab electrons from the surface of materials and the molecule would be charged negatively; in contrast, the adsorbed molecule would be charged positively. Both two cases would change the electronic structure, as well as conductivity of materials. The work function [46] is defined as the least energy required to free an electron from the Fermi energy, respectively. Figure 7 shows the change of work function of Ti$_2$N and Ti$_2$NT$_2$ (T=O, F, OH) before and after adsorption of various NCGs. “Bare” represents the bare system (before adsorption), and the names of NCGs in abscissa represent various systems after adsorption of different gases. The work functions of Ti$_2$NO$_2$ and Ti$_2$N(OH)$_2$ decrease obviously after adsorbing NO, while that of Ti$_2$NF$_2$ increases significantly after adsorbing NO$_2$. After adsorbing NH$_3$, the work functions of Ti$_2$N, Ti$_2$NF$_2$, and Ti$_2$NO$_2$ all decrease, and the change of Ti$_2$NO$_2$ is the most obvious. Because all the systems are metallic, even small changes in work function can cause large variation in conductivity [43]. Comprehensively considering the above results on adsorption structure and energy, Ti$_2$NO$_2$ can be used as a superior sensing candidate material for NO and NH$_3$, and Ti$_2$NF$_2$ can be utilized as that for NO$_2$. In addition, the potential of sensing properties of Ti$_2$N, Ti$_2$NF$_2$, and Ti$_2$N(OH)$_2$ towards NH$_3$ is also good.

### Table 1. Adsorption energy ($E_{ads}$) and charge-transfer profiles of NCGs adsorption on 2-D Ti$_2$N and Ti$_2$NT$_2$ (T=O, F, OH).

| NCGs     | Adsorption Energy (eV) | Charge Transfer (e$^-$) |
|----------|------------------------|-------------------------|
|          | Ti$_2$N                | Ti$_2$NO$_2$            | Ti$_2$NF$_2$ | Ti$_2$N(OH)$_2$ | Ti$_2$N   | Ti$_2$NO$_2$ | Ti$_2$NF$_2$ | Ti$_2$N(OH)$_2$ |
| NO       | −9.81                  | −0.68                   | −0.15        | −5.55     | 2.57        | −0.24       | −0.07        | 0.50          |
| NO$_2$   | −14.34                 | −2.38                   | −0.36        | −3.78     | 3.77        | 0.49        | 0.29         | 1.78          |
| NH$_3$   | −1.29                  | −1.16                   | −0.13        | −0.57     | 0.01        | −0.18       | −0.03        | 0.15          |
Finally, we discuss the recovery time ($\tau$). An ideal gas-sensing material needs appropriate adsorption energy, and a shorter recovery time is better. To make a gas sensor work efficiently, a short recovery time is required. It can be calculated through transition state theory, namely by the following relationship [47,48]:

$$\tau = \nu^{-1} \exp\left(-\frac{E_{\text{ads}}}{kT}\right)$$  \hspace{1cm} (3)
where $\nu$, $E_{\text{ads}}$, $k$, and $T$ are the attempt frequency, adsorption energy, Boltzmann’s constant ($8.62 \times 10^{-5}$ eV K$^{-1}$), and operational temperature, respectively. Under the same conditions, the increase in adsorption energy will lead to an exponential increase in recovery time; then the higher operating temperature compensation is required, which is detrimental to the sensor performance. In order to get a relatively reasonable value, we set the attempt frequency here to $10^{12}$ s$^{-1}$ based on traditional transition state theory [49–51]. The recovery time of NO on Ti$_2$NO$_2$ is calculated to be $2.16 \times 10^5$ us, and that of NO$_2$/Ti$_2$NF$_2$ and NH$_3$/Ti$_2$NF$_2$ is 1.29 and $1.71 \times 10^{-4}$ us, respectively. Here it can be seen in Figure 8 that the adsorption energy difference of less than 1 eV can be enlarged to several orders of magnitude in recovery time. Although NO on Ti$_2$NO$_2$ has the longest recovery time, the value is only 0.216 s. For the system of NH$_3$/Ti$_2$NF$_2$, it has the shortest recovery time, which shows that the MXene system in this research can be promising. Therefore, when other conditions are met, the candidate materials with appropriate gas adsorption energy and short response time should be selected.

4. Summary and Outlook

In this work, we used the first-principles DFT calculations to investigate the 2-D Ti$_2$N nanosheet and its Ti$_2$NT$_2$(T=O, F, OH) derivative materials for harmful nitrogen-containing gas (NGCs) adsorption and sensing applications. When NCGs are exposed on the surface of Ti$_2$N, the dissociative adsorption of NO and NO$_2$ occurs and destroys the stability of the nanosheet, which would make it hard to work reversibly, while NH$_3$ does not have this effect on Ti$_2$N. When studying the interaction mechanisms between NCGs and Ti$_2$NT$_2$(T=O, F, OH), it can be found that a large amount of charges accumulates at functional groups, thus greatly reducing the adsorption energy of NCGs in absolute value. The obvious change in work function, coupled with the metallic nature of the systems, would improve gas sensitivity. Appropriate gas adsorption energy can directly determine fast recovery time to ensure the efficiency and reversibility of sensors. This research gives the electronic structures origin and application prospect of Ti$_2$NT$_2$(T=O, F, OH) as efficient NCGs sensing materials and would inspire experimentalists to explore better 2-D candidates in the field.

Author Contributions: Formal analysis, H.Z., W.D., J.Z., R.A., and Z.Q.; project administration, Z.Q.; supervision, Z.Q.; writing—original draft, H.Z., W.D., and Z.Q.; writing—review and editing, H.Z. and Z.Q.; funding acquisition, Z.Q. All authors have read and agreed to the published version of the manuscript.

Funding: We are grateful for the support from the Natural Science Foundation of China (51801113 and 52171182), the Sino-German Center for Research Promotion and NSFC (GZ1673), the Natural
25. Gouveia, J.; Novell-Leruth, G.; Vines, F.; Illas, F.; Gomes, J. The Ti$_2$CO$_2$MXene as a nucleobase 2D sensor: A first-principles study. *Appl. Surf. Sci.* 2021, 544, 148946. [CrossRef]

26. Gouveia, J.; Novell-Leruth, G.; Reis, P.M.L.S.; Viñes, F.; Illas, F.; Gomes, J. First-principles calculations on the adsorption behavior of amino acids on a titanium carbide MXene. *ACS Appl. Bio. Mater.* 2020, 3, 5913–5921. [CrossRef]

27. Dolz, D.; Morales-García, A.; Vines, F.; Illas, F. Exfoliation energy as a descriptor of MXenes synthesizability and surface chemical activity. *Nanomaterials* 2021, 11, 127. [CrossRef] [PubMed]

28. Soundiraraju, B.; George, B.K. Two-dimensional Titanium Nitride (Ti2N) MXene: Synthesis, characterization, and potential application as surface-enhanced ramanscattering substrate. *ACS Nano* 2017, 11, 8892–8900. [CrossRef]

29. Li, Y.; Guo, Y.; Chen, W.; Jiao, Z.; Ma, S. Reversible hydrogen storage behaviors of Ti$_2$NMXenes predicted by first-principles calculations. *J. Mater. Sci.* 2018, 54, 493–505. [CrossRef]

30. Lin, H.; Yang, D.-D.; Lou, N.; Zhu, S.-G.; Li, H.-Z. Functionalized titanium nitride-based MXenes as promising host materials for lithium-sulfur batteries: A first principles study. *Ceram. Int.* 2018, 45, 1588–1594. [CrossRef]

31. Urbankowski, P.; Anasori, B.; Makaryan, T.; Er, D.; Kota, S.; Walsh, P.L.; Zhao, M.; Shenoy, V.B.; Barsoum, M.W.; Gogotsi, Y. Synthesis of two-dimensional titanium nitride Ti$_2$N$_2$(MXene). *Nanoscale* 2016, 8, 11385–11391. [CrossRef]

32. Xiao, X.; Yu, H.; Jin, H.; Wu, M.; Fang, Y.; Sun, J.; Hu, Z.; Li, T.; Wu, J.; Huang, L.; et al. Salt-templated synthesis of 2D metallic MoN and other nitrides. *ACS Nano* 2017, 11, 2180–2186. [CrossRef]

33. Bölöni, P.E. Projector augmented-wave method. *Phys. Rev. B* 1994, 50, 17953–17979. [CrossRef]

34. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* 1999, 59, 1758–1775. [CrossRef]

35. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996, 77, 3865–3868. [CrossRef]

36. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* 2006, 27, 1787–1799. [CrossRef]

37. Wang, D.; Gao, Y.; Liu, Y.; Jin, D.; Gogotsi, Y.; Meng, X.; Du, F.; Chen, G.; Wei, Y. First-principles calculations of Ti$_2$N and Ti$_2$NT$_2$ (T=O, F, OH) monolayers as potential anode materials for lithium-ion batteries and beyond. *J. Phys. Chem. C* 2017, 121, 13025–13034. [CrossRef]

38. Xie, Y.; Kent, P.R.C. Hybrid density functional study of structural and electronic properties of functionalized Ti$_{n+1}$X$_n$ (X=C, N) monolayers. *Phys. Rev. B* 2013, 87, 235441. [CrossRef]

39. Prasongkit, J.; Amorim, R.; Chakraborty, S.; Ahuja, R.; Scheicher, R.; Amorhim, V. Highly sensitive and selective gas detection based on silicene. *J. Phys. Chem. C* 2015, 119, 16934–16940. [CrossRef]

40. Leenaerts, O.; Partoens, B.; Peeters, F.M. Adsorption of H$_2$, H$_2$O, NH$_3$, CO, NO$_2$, and NO on graphene: A first-principles study. *Phys. Rev. B* 2008, 77, 125416. [CrossRef]

41. Gouveia, J.D.; Viñes, F.; Illas, F.; Gomes, J.R.B. MXenes atomic layer stacking phase transitions and their chemical activity consequences. *Phys. Rev. Mater.* 2020, 4, 054003. [CrossRef]

42. Ouyang, T.; Qian, Z.; Hao, X.; Ahuja, R.; Liu, X. Effect of defects on adsorption characteristics of AlN monolayer towards SO$_2$ and NO$_2$: Ab initio exposure. *Appl. Surf. Sci.* 2018, 462, 615–622. [CrossRef]

43. Kouv, L.; Frauenheim, T.; Chen, C. Phosphorene as a superior gas sensor: Selective adsorption and distinct I–V response. *J. Phys. Chem. Lett.* 2014, 5, 2675–2681. [CrossRef] [PubMed]

44. Yue, Q.; Shao, Z.; Chang, S.; Li, J. Adsorption of gas molecules on monolayer MoS$_2$ and effect of applied electric field. *Nanoscale Res. Lett.* 2013, 8, 425. [CrossRef] [PubMed]

45. Hussain, T.; Singh, D.; Gupta, S.K.; Karton, A.; Sonvane, Y.; Ahuja, R. Efficient and selective sensing of nitrogen-containing gases by Si$_2$BN nanosheets under pristine and pre-oxidized conditions. *Appl. Surf. Sci.* 2018, 469, 775–780. [CrossRef]

46. Gholizadeh, R.; Yu, Y.-X. Work functions of pristine and heteroatom-doped graphenes under different external electric fields: An ab initio DFT study. *J. Phys. Chem. C* 2014, 118, 28274–28282. [CrossRef]

47. Barsan, N.; Koziej, D.; Weimar, U. Metal oxide-based gas sensor research: How to? *Sens. Actuators B Chem.* 2007, 121, 18–35. [CrossRef]

48. Nagarajan, V.; Chandiramouli, R. Investigation of NH$_3$ adsorption behavior on graphdiyne nanosheet and nanotubes: A first-principles study. *J. Mol. Liq.* 2018, 249, 24–32. [CrossRef]

49. Eyring, H. The activated complex in chemical reactions. *J. Chem. Phys.* 1935, 3, 107–115. [CrossRef]

50. Hadipour, N.L.; Peyghan, A.A.; Soleymanabadi, H. Theoretical study on the Al-doped ZnO nanoclusters for CO chemical sensors. *J. Phys. Chem. C* 2015, 119, 6398–6404. [CrossRef]

51. Ahmadi, A.; Hadipour, N.L.; Kamfirooz, M.; Bagheri, Z. Theoretical study of aluminum nitride nanotubes for chemical sensing of formaldehyde. *Sens. Actuators B Chem.* 2012, 161, 1025–1029. [CrossRef]