Experimental and Theoretical Advances in MXene-Based Gas Sensors

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ABSTRACT: MXenes, two-dimensional (2D) transition metal carbides and nitrides, have been arousing interest lately in the field of gas sensing thanks to their remarkable features such as graphene-like morphology, metal-comparable conductivity, large surface-to-volume ratio, mechanical flexibility, and great hydrophilic surface functionalities. With tunable etching and synthesis methods, the morphology of the MXenes, the interlayer structures, and functional group ratios on their surfaces were effectively harnessed, enhancing the efficiency of MXene-based gas-sensing devices. MXenes also efficiently form nanohybrids with other nanomaterials, as a practical approach to revamp the sensing performance of the MXene sensors. This Mini-Review summarizes the recent experimental and theoretical reports on the gas-sensing applications of MXenes and their hybrids. It also discusses the challenges and provides probable solutions that can accentuate the future perspective of MXenes in gas sensors.

INTRODUCTION

Since the discovery of MXenes as novel two-dimensional (2D) compounds in 2011 by Gogotsi et al.,¹ they have gained increasing interest thanks to their exceptional properties such as graphene-like morphology, metallic conductivity, mechanical flexibility, tunable energy bandgap, and strong hydrophilicity.¹ MAX phases, MXene’s precursors, are layered ternary carbides or nitrides with a general formula of Mₙ₋₁AXₙ (n = 1–3), where M is an early transition metal (Sc, Ti, V, Cr, Zr, Hf, Nb, Mo, Ta, and W); A is a IIIA and IVA group element (Al, Si, P, Ga, Ge, As, In, Sn, and Pb); and X represents N or C (Figure 1a). MXenes with a general formula of Mₙ₋₁XₙTₓ are synthesized by selectively etching the A element from MAX phases using solutions containing fluoride ions, yielding multilayered MXene sheets which can then be delaminated into single or few-layered sheets (Figure 1b). Depending on the etching process, MXenes are separated by terminal groups such as hydroxyl (−OH), oxygen (−O), fluoride (−F), and/or chloride (−Cl) ions located on their surfaces (called T), resulting in surface hydrophilicity.²

Gas sensing is crucial to diagnose disease, monitor air pollution, detect explosives, and control chemical processes. Among different gas-sensing methods, chemiresistive gas sensors have drawn substantial interest because of their superior performance and low cost. However, they suffer from high operating temperature, high power consumption, and limited selectivity.³ Thanks to the large surface-to-volume ratio, excellent surface conductivity, and surface-terminated functionality and on top of all hydrophilicity, MXenes are promising candidates for chemiresistive gas sensor applications.² It should be mentioned that while hydrophilic gas molecules (known as polar molecules) may be absorbed satisfactorily by hydrophilic absorbents such as MXenes the applicability of MXenes for detection of hydrophobic gas molecules (known as nonpolar molecules) could be limited.

The objective of this Mini-Review is to provide a short and concise survey of scientific literature, the most recent progress, and prospects in sensing of gases by MXenes. To this end, we discuss both experimental and theoretical studies that have been reported so far.

EXPERIMENTAL PERSPECTIVE

Following the successful synthesis of 2D titanium carbide MXene,¹ its gas-sensing applications have been investigated. Lee et al.⁴ reported the first demonstration of MXene as a gas sensor by evaluating the gas-sensing properties of drop-casted Ti₃C₂Tₓ on Pt-interdigitated electrodes fabricated on a flexible polyimide substrate under ambient atmosphere (Figure 2a). They observed the random functionalization of the surface of the MXene with different terminal groups like −O, −OH, and −F, with the first two dominating (Figure 2a). The sensor indicated p-type semiconductor behavior, and its resistance enhanced after adsorption of ammonia, acetone, methanol, and ethanol gases (Figure 2b). The electron transfer from the gas molecules to the dominant surface terminal groups reduces the MXene film’s

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majority carrier (holes) by electron−hole recombination, increasing the resistance. The lowest response was achieved for acetone, while the sensor presented its highest response to ammonia with a theoretical limit of detection (LoD) of 9.27 ppm. Kim et al.\textsuperscript{5} further investigated the volatile organic compound (VOCs) sensing performance of Ti$_3$C$_2$T$_x$ by fabrication of a metallic sensor with an exceptionally high signal-to-noise ratio (SNR). The sensor was exposed to acetone, ethanol, ammonia, nitrogen dioxide, sulfur dioxide, and carbon dioxide, while its electrical resistance was monitored (Figure 2c). Due to metallic conductivity and full termination of the surface with −OH and −O functional groups, the sensitivity of the sensor exceeded the conventional sensors with semiconductor channel materials, offering a LoD of 50−100 ppb for VOCs at room temperature. Regardless of being oxidative or reductive, all the gases caused a resistance enhancement after exposure, ascribed to the metallic conductivity of the channel material in which the gas molecule adsorption limits its charge carrier transport. Additionally, the SNR of Ti$_3$C$_2$T$_x$ sensors was 2 orders of magnitude larger than those reported for other 2D materials, which is highly desirable for gas-sensing utilizations.

The influence of Ti$_3$C$_2$T$_x$ MXene precursors (Ti$_3$AlC$_2$) on the MXene’s gas-sensing performance was studied by Shuck et al.\textsuperscript{6} The Ti$_3$AlC$_2$ precursor (MAX phase) was synthesized by using different carbon sources (graphite, titanium carbide, and carbon lampblack) (Figure 2d). A minimal intensive layer delamination (MILD)-like process which involves etching in HCl and LiF was employed to convert MAX phase crystals into Ti$_3$C$_2$T$_x$ MXene flakes (Figure 2d). The MXene flakes produced from graphite, titanium carbide, and carbon lampblack had an average size of 4.2, 2.6, and 0.5 μm, respectively (Figure 2d). It was discovered that the highest gas response to acetone, ethanol, and ammonia is attributed to MXene-derived titanium carbide, followed by graphite and carbon lampblack, revealing that the MXene precursor has a key role in the performance of its sensor (Figure 2e). The lower response of carbon lampblack based MXene can be related to its lower electrical conductivity (1020 S/cm) in comparison with graphite-based (4400 S/cm) and TiC-based (3480 S/cm) MXene.

The gas-sensing properties of sensors based on 2D Ti$_3$C$_2$T$_x$ MXenes could be enhanced by engineering the structure and surface chemistry. Yuan et al.\textsuperscript{7} reported the fabrication of a flexible and high-performance VOC sensor based on a three-dimensional (3D) Ti$_3$C$_2$T$_x$ MXene framework. A 3D polymer (PVA/PEI mixture) framework containing cross-linked fibers was synthesized using an electrospinning process, transferred on Au-interdigitated electrodes, and then immersed into the MXene dispersion. Because of electrostatic interactions between the negatively charged MXene (caused by functional groups) and positively charged 3D polymer framework (originated from the PEI component), the surface of the fibers was functionalized by self-assembly (Figure 3a). Thanks to the highly interconnected porous structure, the sensor offered higher sensitivity toward VOCs, such as acetone, methanol, and ethanol in ppb level in comparison with pure MXene (Figure 3b−d). The sensor also showed a lower response toward polar inorganic gas molecules (NO$_2$, NH$_3$, and H$_2$O) and almost no response to hydrocarbons (toluene and cyclohexane). The functional groups of MXene (mostly −OH and −F) interact with VOCs and polar inorganic gas molecules by forming hydrogen bonds, resulting in
charge transfer. The amplitude of the gas response can be related to the strength of the formed hydrogen bond. Interestingly, the resistance of the sensor increased regardless of the type of the molecule as a result of the metallic conductivity of the MXene. Yang et al.\textsuperscript{8} improved the sensing properties of the Ti$_3$C$_2$T$_x$ MXene by increasing the surface oxygen—fluorine ratio and alkali metal ion (Na$^+$) intercalation. After HF acid etching of Ti$_3$AlC$_2$, the produced organ-like Ti$_3$C$_2$T$_x$ was added into 5 M NaOH under magnetic stirring at room temperature for 2 h for the purpose of Na$^+$ intercalation. The fabricated alkalized Ti$_3$C$_2$T$_x$ sensor was found to be very selective to ammonia with 28.87% response at 100 ppm, almost two times higher than bare Ti$_3$C$_2$T$_x$ (Figure 3e). Unlike bare Ti$_3$C$_2$T$_x$, alkalized Ti$_3$C$_2$T$_x$ showed a negative gas response to NH$_3$ associated with change in the carrier type after oxygen functionalization brought by alkaline treatment (Figure 3f,g).

The gas-sensing mechanism in metallic MXenes is more complicated than the surface adsorption and typical charge transfer in conventional 2D materials. For stacked layered structures such as MXenes, interlayer swelling is also responsible for conductivity change and gas response.\textsuperscript{9} Koh et al. investigated the impact of interlayer swelling on the gas detection performance of Ti$_3$C$_2$T$_x$ MXene sensors.\textsuperscript{9} Followed by the preparation of Ti$_3$C$_2$T$_x$ MXene powders by etching Ti$_3$AlC$_2$ in LiF and HCl, few single Ti$_3$C$_2$T$_x$ flakes were produced by sonication. A continuous film was formed on an anodized aluminum oxide (AAO) filter through vacuum filtration and was transferred onto SiO$_2$/Si substrates. The filter was then etched away using NaOH solutions at different concentrations (0.03, 0.3, 5, and 100 mM), followed by washing using DI water and drying in a vacuum chamber, resulting in the occupation of the interlayer spacing with Na$^+$ ions and water molecules (Figure 3h). The degree of Na$^+$ ion intercalation was controlled by NaOH concentration. Using in situ X-ray diffraction (XRD), the dynamic change in interlayer distance of the MXene films ($d$-spacing) upon exposure to gas molecules was monitored (Figure 3h). The free interlayer spacing of Ti$_3$C$_2$T$_x$ thin film was obtained to be 4.3 Å, associated with the trapped water molecules. A decrease in the interlayer distance of 0.84 Å after N$_2$ purging of intercalated Ti$_3$C$_2$T$_x$ MXene suggested that water and adsorbents were eliminated. While the interlayer distance of intercalated Ti$_3$C$_2$T$_x$ MXene remained constant upon exposure to CO$_2$, it significantly
enlarged after interaction with ethanol (Figure 3i) and returned to almost its original value after N₂ purge. It was reported that the degree of swelling because of ion intercalation corresponds well with the intensity of the gas response. Treatment of Ti₃C₂Tx MXene with 0.3 mM NaOH resulted in the maximum swelling as well as the largest gas selectivity to ethanol over CO₂ (Figure 3j).

Gas-sensing improvement of MXene-based devices can also be achieved through their hybridization with other nanomaterials. Chen et al. reported the fabrication of a flexible nanohybrid room-temperature sensor composed of MXene (Ti₃C₂Tx) and TMD (WSe₂) via liquid-phase exfoliation and inject printing. The MXene scaffolds with a typical size of 300 nm were uniformly decorated by WSe₂ flakes with a typical size of less than 30 nm, creating numerous heterojunction interfaces (Figure 4a). The sensitivity of Ti₃C₂Tx toward gas molecules was increased after its hybridization with WSe₂ (Figure 4b). Selective and sensitive detection of O-containing VOCs (ethanol, methanol, and acetone) was achieved by a Ti₃C₂Tx/WSe₂ sensor, while the detection of hydrocarbons was limited (Figure 4c). Specifically, the sensitivity of Ti₃C₂Tx/WSe₂ toward ethanol was 12 times larger than that of Ti₃C₂Tx. Moreover, unlike a pure MXene sensor, the gas response of the MXene/TMD sensor did not reach saturation at 40 ppm of ethanol, suggesting the capability of the sensor for wide-range detection of ethanol (Figure 4c).

The fabrication of a room-temperature ammonia sensor composed of Ti₃C₂Tx MXene and reduced graphene oxide (rGO) sheets was presented by Lee et al. Through a scalable one-step wet-spinning process, the MXene/rGO hybrid fibers with superior mechanical and electronic properties were prepared (Figure 4d). The hybrid fibers showed an extremely high response of 6.77% to NH₃ (7.9 and 4.7 times greater than those of MXene film and rGO fiber, respectively) (Figure 4e) but had a low response of almost 1% to H₂S, SO₂, acetone, ethanol, xylene, and benzene (Figure 4f). The enhanced ammonia response of the hybrid fibers was attributed to the three times increase in active sites of the MXene (Ti−O) after its hybridization with graphene.

Sun et al. reported that the homogeneous distribution of the W₁₈O₄₉ nanorods on the surface of Ti₃C₂Tx significantly improves the acetone-sensing performance toward LoD of 170 ppb at 300 °C (Figure 5a). The high response (11.6) of the W₁₈O₄₉/Ti₃C₂Tx sensor to 20 ppm of acetone and low response (less than 2) to ammonia, formaldehyde, acetone, and ethanol confirmed its selectivity toward acetone (Figure 5b). The W₁₈O₄₉/Ti₃C₂Tx sensor’s gas response was also investigated in terms of the weight percent of MXene within the composite. For less than 2 wt % of MXene, the response was enhanced with

Figure 3. (a) SEM image of a 3D Ti₃C₂Tx MXene. (Adapted with permission from ref 7. Copyright 2018 Royal Society of Chemistry.) Resistance changes of the 3D MXene sensor and MXene sensor with exposure to 5 ppm of (b) acetone, (c) methanol, and (d) ethanol. (Adapted with permission from ref 7. Copyright 2018 Royal Society of Chemistry.) (e) Response of the sensors based on Ti₃C₂Tx and alkalized Ti₃C₂Tx to 100 ppm of different gases. (Adapted with permission from ref 8. Copyright 2019 American Chemical Society.) Response curve of the sensors based on (f) Ti₃C₂Tx, and (g) alkalized Ti₃C₂Tx to the NH₃ at different concentrations. (Adapted with permission from ref 8. Copyright 2019 American Chemical Society.) (h) In situ XRD characterization of Ti₃C₂Tx films and schematic view of the interlayer structure of Ti₃C₂Tx MXene nanosheets with intercalated water molecules and Na⁺ ions. (Adapted with permission from ref 9. Copyright 2019 American Chemical Society.) (i) Change in d-spacing of Ti₃C₂Tx films upon CO₂ and ethanol exposure. (Adapted with permission from ref 9. Copyright 2019 American Chemical Society.) (j) Ethanol response of gas sensors over the CO₂ response versus NaOH concentration. (Adapted with permission from ref 9. Copyright 2019 American Chemical Society.)
increasing MXene content, attributing to the removal of $\text{−F}$ groups after the solvothermal process and synergistic interfacial interactions between two components. The response of the $\text{W}_{18}\text{O}_{49}/\text{Ti}_3\text{C}_2\text{T}_x$ sensor with more than 2 wt % of MXene decayed due to the presence of $\text{−F}$ functional groups that were not fully eliminated after the solvothermal process, indicating the deteriorating effect of the $\text{−F}$ functional group on the gas-sensing performance of MXene-based sensors. Due to the nonpolar structure of C-containing gas molecules such as toluene, MXenes do not show a good response to them.7,10,13 Hermawan et al.13

**Figure 4.** (a) Low-magnification TEM image of a single Ti$_3$C$_2$T$_x$/WSe$_2$ nanohybrid (scale bar, 100 nm). (Adapted with permission from ref 10. Copyright 2020 Springer Nature.) (b) Selectivity of the Ti$_3$C$_2$T$_x$ and Ti$_3$C$_2$T$_x$/WSe$_2$ sensors upon exposure to various VOCs at 40 ppm. (Adapted with permission from ref 10. Copyright 2020 Springer Nature.) (c) Ethanol response as a function of gas concentrations for Ti$_3$C$_2$T$_x$ and Ti$_3$C$_2$T$_x$/WSe$_2$ sensors. (Adapted with permission from ref 10. Copyright 2020 Springer Nature.) (d) Schematic view of the spinning process for a MXene/GO hybrid fiber. (Adapted with permission from ref 11. Copyright 2020 American Chemical Society.) (e) Comparison of the gas response of MXene film, rGO fiber, and MXene/rGO hybrid fiber. (Adapted with permission from ref 11. Copyright 2020 American Chemical Society.) (f) The gas selectivity comparison of rGO fiber and MXene/rGO hybrid fiber to various testing gases. (Adapted with permission from ref 11. Copyright 2020 American Chemical Society.)

**Figure 5.** Response of different $\text{W}_{18}\text{O}_{49}/\text{Ti}_3\text{C}_2\text{T}_x$ sensors to (a) various concentrations of acetone and (b) 20 ppm of ammonia, formaldehyde, acetone, and ethanol. (Adapted with permission from ref 12. Copyright 2020 Elsevier.) (c) SEM image of CuO/Ti$_3$C$_2$T$_x$. (Adapted with permission from ref 13. Copyright 2020 American Chemical Society.) (d) Toluene response of CuO/Ti$_3$C$_2$T$_x$, Ti$_3$C$_2$T$_x$, MXene, and CuO with respect to temperature. (Adapted with permission from ref 13. Copyright 2020 American Chemical Society.) (e) Response of CuO/Ti$_3$C$_2$T$_x$ to 50 ppm of different gases. (Adapted with permission from ref 13. Copyright 2020 American Chemical Society.) (f) Toluene response of CuO/Ti$_3$C$_2$T$_x$, CuO/MoS$_2$, and CuO/rGO. (Adapted with permission from ref 13. Copyright 2020 American Chemical Society.)
described the fabrication of hybrid heterostructures of CuO nanoparticles/Ti3C2T x MXene via electrostatic self-assembly. It was reported that CuO nanoparticles have an average size of 7 nm and were uniformly distributed over the interlayers and surface of Ti3C2T x MXene (Figure 5c). Although bare Ti3C2T x exhibited a trivial response to 50 ppm of toluene at 250 °C, the CuO/Ti3C2T x showed a 5-fold increase in toluene response at the same condition compared to pristine CuO (Figure 5d). The reason behind this is that the metallic MXene as the support layer for p-type semiconductor CuO nanoparticles plays a key role in improvement of the gas response and recovery time of the CuO nanoparticles by enhancing the charge carrier mobility. The CuO/Ti3C2T x sensor also presented an adequate selectivity toward toluene in the presence of VOCs and hydrogen gas (Figure 5e); moreover, it showed higher response in comparison with CuO/MoS2 and CuO/rGO sensors toward toluene (Figure 5f).

There are very few reports on the gas-sensing applications of other MXenes beyond Ti3C2T x. The performance of V2CT x for detection of nonpolar and polar gases was reported by Lee et al.14 By selectively etching Al atoms from the V2AlC MAX phase using HF acid, multilayered V2CT x MXene was produced, followed by intercalating with tetra n-butyl ammonium ions (TBA+) to facilitate the delamination process (Figure 6a). They discovered that the contents of −O and −OH functionals on the surface of V2CT x MXene are much more than the undesirable −F terminal group. Due to the presence of −O atoms on the surface of V2CT x MXene, the sensor showed excellent room-temperature sensitivity to both polar gases such as acetone and nonpolar gases such as hydrogen with a theoretical LoD of 11.16 and 1.735 ppm, respectively (Figure 6bc). In comparison with their previous report on Ti3C2T x MXene5 in which under the same experimental conditions ammonia gained the highest response, V2CT x MXene is very selective to hydrogen owing to the presence of V atoms, suggesting that the selectivity of the MXenes can be engineered by replacing the transition metal atoms. Molybdenum carbide is another MXene structure for which the gas-sensing properties were evaluated. Guo et al. studied the VOC sensing performance of Mo2CT x MXene sensors.15 By selective etching of Ga layers from the Mo2Ga2C precursor using HF, multilayer Mo2CT x MXenes were produced. The concentration of the MXene (0.066 mg/mL) and the sonication time (8 h) were optimized in order to achieve a higher VOCs sensitivity. The optimized Mo2CT x sensor offered an excellent selectivity toward toluene against the other VOCs with sensitivity of 0.0366 Ω/ppm at 140 ppm and a LOD of 220 ppb. Cho et al. also reported the synthesis of two phases of pure molybdenum carbide materials (α-MoC1−x and β-Mo2C) with structures similar to MXenes (without the expression Tx in the chemical formula) via a temperature-programmed reduction technique.16 While both phases show metallic behavior, α-MoC1−x MXene (200−400 ohm) has higher resistance compared to β-Mo2C (tens of ohm) (Figure 6d). Due to the excellent catalytic properties and high electrical conductivity, the molybdenum carbide-based sensors showed great sensing performance as well as ultrahigh SNR. The sensors were exposed to various gases like acetone, ethanol, propanal, hexane, toluene, NO2, SO2, and NH3. Irrespective of the gases’ reducing or oxidizing characteristics, the β-Mo2C sensor presented a positive response (Figure 6e). This phenomenon is correlated to the highly metallic properties and delocalized density of states (DOS) of β-Mo2C in which the flowing electrons are impeded by charge clouds formed by adsorbed gases (Figure 6f). However, α-MoC1−x with a higher resistance than β-Mo2C revealed p-type
| MXene sensor fabrication details (source, synthesis, and deposition) | concentration (ppm) | response (%) | recovery time (min) | LoD (ppb) | ref |
|---|---|---|---|---|---|
| Ti\(_3\)C\(_2\)T\(_x\) powder; LiF−HCl etching; drop coating on flexible polyimide films | 100 | 21 | NR | NR | 4 |
| Ti\(_3\)AlC\(_2\) powder; LiF−HCl etching; vacuum filtration on SiO\(_2\) substrates | 100 | 0.88 | NR | NR | 5 |
| Ti\(_3\)AlC\(_2\) powder; LiF−HCl etching; spin coating on SiO\(_2\)/Si substrates | 10000 | 0.1 | NR | NR | |
| Ti\(_3\)AlC\(_2\) powder; HF etching + alkaline treatment (Na\(^+\) intercalation); drop coating on Al\(_2\)O\(_3\) ceramic substrate | 100 | 2 | NR | NR | 8 |
| Ti\(_3\)AlC\(_2\) powder; HF etching + mixing into CTA\(^+\)−WSe\(_2\) solution; inkjet printing on polyimide substrates | 40 | 9.4 | NR | NR | 10 |
| Ti\(_3\)AlC\(_2\) powder; HF etching + mixing into CuO nanoparticles dispersed in ethanol; brush coating on silicate glass | 50 | 2.5 | 10 s to 50 ppm | NR | 13 |
| V\(_2\)C\(_2\) powder; HF etching; drop casting on flexible polyimide films | 100 | 0.05 | 7 min to hydrogen and 5.5 min to CH\(_4\) | 3504 | 14 |
| Mo\(_2\)C\(_2\) powder; HF etching; drop coating on SiO\(_2\)/Si substrates | 140 | 0.97 | NR | NR | 15 |
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sensing characteristics and various responses to different gases due to localized DOS (Figure 6e,f). Moreover, the gas response of the $\alpha$-MoC$_{1-x}$ sensor is dramatically larger than that of $\beta$-Mo$_2$C. The fabricated $\alpha$-MoC$_{1-x}$ sensor was able to detect ppb–ppt levels of NO$_2$ with outstanding stability of half-year (Figure 6g).

Table 1 summarized the gas-sensing performance of MXene-based sensors.

| MXene sensors’ fabrication details (source, synthesis, and deposition) | concentration (ppm) | response (%) | recovery time | LoD (ppb) | ref |
|---|---|---|---|---|---|
| acetone | 140 | 0.14 | NR | |

Figure 7. (a) Optimized configurations for gas molecule adsorption on Ti$_2$CO$_2$. (Adapted with permission from ref 17. Copyright 2015 American Chemical Society.) (b) $I$–$V$ curve of Ti$_2$CO$_2$ MXene, MoS$_2$, and phosphorene before and after exposure to NH$_3$. Inset shows a schematic view of the Ti$_2$CO$_2$ MXene sensor for NH$_3$ molecule detection. (Adapted with permission from ref 17. Copyright 2015 American Chemical Society.) (c). Optimized configurations for adsorbed acetone and ammonia on Ti$_3$C$_2$(OH)$_2$. (Adapted with permission from ref 5. Copyright 2018 American Chemical Society.) (d) Binding energies of adsorbed acetone and ammonia on various 2D materials. (Adapted with permission from ref 5. Copyright 2018 American Chemical Society.)

The complexity of the sensing mechanism of the MXene sensors renders its experimental tuning challenging. Thus, there is a need for atomic-level modeling (density functional theory (DFT) and molecular dynamics (MD)) to complement the experimental data and deepen our insights into MXene and gas analyte interactions. The first theoretical study was done by Yu et al. They investigated the interaction behavior of H$_2$, CO$_2$, O$_2$, NH$_3$, CO, N$_2$, NO$_2$, and CH$_4$ gas molecules on the semiconductor Ti$_2$CO$_2$ (Figure 7a). Among all considered gases, only NH$_3$ is chemisorbed on the surface of Ti$_2$CO$_2$ MXene by donating a relatively large charge of 0.174 e and forming a N–Ti bond. The adsorption energy of NH$_3$ on Ti$_2$CO$_2$ ($-0.37$ eV) was found to be less than Ti$_3$C(OH)$_2$ ($-0.48$ eV) and V$_2$CO$_2$ ($-0.81$ eV) and comparable to Ti$_3$C$_2$O$_2$ ($-0.34$). The superior sensitivity of Ti$_2$CO$_2$ toward NH$_3$ in comparison with phosphorene and MoS$_2$ was demonstrated by calculating current–voltage curves before and after adsorption of the gas (Figure 7b). It was also revealed that NH$_3$–Ti$_2$CO$_2$ interactions could be further reinforced under strains. Under 3% biaxial strain, the energy of adsorption for NH$_3$ on Ti$_2$CO$_2$ became $-0.51$ eV, while the adsorption energies of other gases were slightly changed. Interestingly, the NH$_3$ capture was a reversible process due to the escape of the gas molecule from the MXene surface after the removal of the strain. In a different study, Xia et al. probed the interactions of H$_2$, NO, CO, CO$_2$, N$_2$, O$_2$, and CH$_4$ on Zr$_2$CO$_2$ MXene, finding that NH$_3$ is strongly chemisorbed due to an apparent charge transfer ($0.188$ e) and large adsorption energy ($-0.81$ eV), while other gases are only physisorbed. The authors expected the same behavior for M$_2$CO$_2$ (M = Sc, Ti, Zr, and Hf) owing to their similar atomic and electronic structures. It was also discovered that chemisorption to physisorption transition in the adsorption of NH$_3$ on Zr$_2$CO$_2$ happens when two extra electrons are introduced into the MXene sheet, providing a practical way to release the gas molecule. Wang et al. further analyzed the performance of the Hf$_2$CO$_2$ for sensing multiple gases like H$_2$, O$_2$, CO, NO$_2$, N$_2$, O$_2$, NH$_3$, HCN, and H$_2$S. As expected from ref 18, Hf$_2$CO$_2$ is greatly sensitive and selective to NH$_3$ with the adsorption energy of $-0.834$ eV and an outstanding charge transfer of 0.146 e. It was also revealed that preadsorption of the MXene surface with H$_2$O, SO$_2$, and CO$_2$ molecules could significantly increase the adsorption of NH$_3$ due to the formation of hydrogen bonds.
To complement their experimental studies, Kim et al. scrutinized the influence of the functional groups of Ti$_3$C$_2$Tx MXene on its sensing performance. Using the DFT method, the interactions of acetone and NH$_3$ on the −OH, −O−, and −F− terminated Ti$_3$C$_2$T$_x$ were investigated. They concluded that Ti$_3$C$_2$(OH)$_2$ showed higher binding energy toward acetone and NH$_3$ compared to Ti$_3$C$_2$O$_2$ and Ti$_3$C$_2$F$_2$ MXenes (Figure 7c). In addition to that, the binding energies between these gases and Ti$_3$C$_2$(OH)$_2$ are more than twice the corresponding energies obtained for these gases on other 2D materials such as MoS$_2$, graphene, and black phosphorus (Figure 7d). Hajian et al. analyzed the effect of the ratio of functional groups on NH$_3$ detection of Ti$_3$C$_2$T$_x$ MXene. Considering two different ratios of −F functional groups in the form of Ti$_3$C$_2$(OH)$_{0.44}$F$_{0.88}$O$_{0.66}$ and Ti$_3$C$_2$(OH)$_{0.66}$F$_{0.22}$O$_{0.11}$, they found that low ratios of −F result in stronger ammonia adsorption. This can be attributed to the smaller charge transfer between ammonia and fluorine in comparison with ammonia and oxygen. Hence, the synthesis method and the type of MAX phase etchant which determine the ratios of functional group are important factors for the gas-sensing performance of the MXene sensors.

Apart from NH$_3$ and VOCs, the MXene-based sensor showed great promise for detecting other inorganic gases. Zhang et al. investigated the formaldehyde capture efficiency of Ti$_3$C$_2$O$_2$ nanosheets around room temperature. The moderate adsorption energy of 0.45 eV, as well as an adsorption capacity of greater than 6 mmol/g, suggested the potential of Ti$_3$C$_2$O$_2$ MXene for indoor formaldehyde removal. Ma et al. considered M$_2$CO$_2$ (M = Sc, Ti, Zr, and Hf) MXenes to find the best toxic SO$_2$ detection platforms. A strong chemical bond between SO$_2$ and Sc$_2$CO$_2$ accompanied by adsorption energy of −0.646 and charge transfer of 0.453 e implied that monolayer Sc$_2$CO$_2$ is a desirable material for sensing SO$_2$. Interestingly, the SO$_2$ molecules were only physisorbed on M$_2$CO$_2$ MXenes (Figure 8a). The reason behind this is the orbital hybridization of SO$_2$ and Sc$_2$CO$_2$ around the Fermi level in projected DOS (PDOS) (Figure 8b), which results in metallic behavior and consequently more charge transfer in the system. Due to a sharp increase in the conductance upon exposure to SO$_2$ and low adsorption energies obtained for N$_2$, CO, CO$_2$, CH$_4$, H$_2$, H$_2$S, and H$_2$O, Sc$_2$CO$_2$ MXene is a highly sensitive and selective material to SO$_2$. Besides that, the adsorption strength of SO$_2$ on the monolayer could be strengthened or reduced by exerting the negative electric field or controlling the tensile strength. M$_2$CO$_2$ (M = Sc, Ti, Zr, and Hf) MXenes were also evaluated for other toxic gases such as NO and CO detection. For NO, the strongest interactions took place between the molecule and Sc$_2$CO$_2$, which can be related to the orbital hybridization between MXene and the gas molecule around the Fermi level. The large charge transfer of 0.303 e and moderate adsorption energy of −0.47 eV proved that Sc$_2$CO$_2$ is highly suitable for NO sensing. On the other hand, CO was only physisorbed on Sc$_2$CO$_2$ MXene, and a small charge 0.017 e was transferred. However, the sensing performance of the Sc$_2$CO$_2$ MXene to CO was improved by introducing Mn dopants in the structure, leading to charge transfer of 0.199 e and strong adsorption energy of −0.85 eV.

Nitride MXenes were also inspected for gas-sensing applications. Naqvi et al. analyzed M$_2$NS$_2$ (M = V, Ti) MXenes for detection of H$_2$S, SO$_2$, NH$_3$, NO, NO$_2$, CH$_4$, CO, and CO$_2$. It was found that gas molecules are mostly physisorbed (C-containing molecules) or weakly chemisorbed (N- and S-containing molecules) on MXene (Figure 8c), promising a reversible N- and S-containing molecule adsorption/desorption process. While both Ti$_3$NS$_2$ and V$_2$NS$_2$ MXenes could be utilized...
as platforms for NO₂ and NO sensing, the latter exhibited higher sensitivity (Figure 8d).

The potential of double transition metal MXene in gas sensing was also studied. Khaleddialidusti et al. examined Mo₂TiC₂O₂ MXene terminated with specific surface functional groups of fluorine, oxygen, or hydroxide for CO₂ capture, while pristine and O-terminated MXenes are metallic, F-terminated, and OH-terminated MXenes that exhibit semiconducting behavior. The CO₂ molecule is weakly physisorbed on the surface of perfect O-terminated MXenes are metallic, F-terminated, and OH-terminated MXenes with a nonspontaneous and endothermic process with reaction energy of 0.21 eV. To address this limitation, the impact of atomic vacancy defects on the capture efficiency of MXene was explored. It was discovered that the O-terminated MXene requires more energy than the F- and OH-terminated MXenes, showing that the surface terminations have a key role in defect formation. Moreover, defect formation was likely to occur in the outer Mo layers than in the inner Ti layer. CO₂ adsorption energy was significantly enhanced to ~0.11 and ~0.35 eV by trapping in the defects formed in Mo₂TiC₂O₂ MXene.

### SUMMARY AND OUTLOOK

In this Mini-Review, we highlighted the state-of-the-art use of MXenes and their hybrids in advanced gas sensors from experimental and theoretical perspectives. MXenes have grabbed enormous attention for their gas-sensing applications due to their fascinating properties such as metal-comparable conductivity, graphene-like morphology, large surface-to-volume ratio, strong hydrophilicity, mechanical flexibility, and rich elemental compositions and surface terminations. Recent studies have shown that the morphology, the surface functional groups, the precursor, and the interlayer structures of MXenes could be tuned in order to enhance the gas-sensing performance of the MXene-based devices. Numerous MXenes have been introduced theoretically, among which around 20 distinct MXenes have been experimentally synthesized. To date, most of the experimental works on MXene-based gas sensors refer to titanium carbide, the first discovered MXene. However, few works appear in the literature showing the gas-sensing potential of vanadium carbide and molybdenum carbide. Ergo, it would be advantageous to explore the possibility of other synthesized MXenes for gas-sensing and VOC applications.

The hydrophilicity of the MXenes which originates from their hydroxyl or oxygen-terminated surfaces is an important property that ensures their high sensitivity and selectivity in unfavorable environments. Observations from theoretical studies revealed that fluorine functional groups have a deteriorating effect on gas-sensing performance; therefore, controlling the synthesis method and the type of MAX phase etchant, which determine the functional groups’ ratios, is of crucial significance to keeping the fluorine content low. Fabrication of high-quality MXenes with fewer defects, large lateral dimensions, and uniform terminations with only a single type of functional group is highly desirable to develop sensors with excellent performance. Incorporating MXenes with 2D nanomaterials, gold nanoparticles, nanotubes, metal oxides, polymers, etc., could also be considered a strategy to improve the gas sensors’ efficiency. The modulation of heterojunction interfaces and underlying gas-sensing mechanisms needs to be intensively explored.

The modulation of Debye length/the depth of the space charge layer on the flakes’ size and their gas-sensing performance need to be comprehensively studied. The frequency dependence of electrical conductivity and the gas-sensing aspects need further exploration. Current flake sizes using atomic force microscopy (AFM) revealed a thickness of ~70 nm for gas-sensing applications. This is larger than 10 atomic layers and cannot be called a 2D solid in strict definition, as anything above 10 layers is considered 3D. Thus, the gas-sensing properties reported are from a 3D nanostucture. Unlike graphene, which is straightforward to make single layers, the current methods of making MXenes are not straightforward, utilizing strong acids that are not conducive for the environment. New processing methods that enable a more benign environmental footprint are highly necessary to fully realize MXenes as 2D nanomaterials, which presents significant opportunities in the processing area.

The mechanism of gas sensing in metallic MXenes is more complex than the surface adsorption and typical charge transfer in conventional 2D materials. Regardless of being oxidative and reductive, it was observed that all the adsorbed gas molecules cause an enhancement or decrement in the resistance with a high signal-to-noise ratio. The high signal-to-noise ratio is attributed to the metallic conductivity. Interestingly, for highly metallic MXenes, the gas response was trivial, attributed to the difficulty of flowing electrons by charge clouds formed by adsorbed gases. Moreover, for stacked layered structures such as MXenes, interlayer swelling makes a significant contribution to conductivity change and gas response. Hence, computational assessments should be employed to deepen the understanding of MXene and gas–molecule interactions.

Finally, MXene research is still only in its infancy. As a 2D nanomaterial, MXenes present a fundamental building block on which exotic nanostructures can be constructed. Experimental data should be combined with computational material predictions to investigate the structure, process, and property relationships for sensor applications. With the choice of a 60 plus group of layered ternary carbides and nitrides available, MXenes as 2D material present tantalizing opportunities to enable new scientific discoveries that are yet to be realized.

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REFERENCES

1. Naguib, M.; Kurtoglu, M.; Presser, V.; Lu, J.; Niu, J.; Heon, M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-dimensional nanocrystals produced by exfoliation of Ti3AlC2. Adv. Mater. 2011, 23 (37), 4248–4253.
2. Gogotsi, Y.; Asanori, B. The rise of MXenes. ACS Nano 2019, 13 (8), 8491–8494.
3. Sun, Y.-F.; Liu, S.-B.; Meng, F.-L.; Liu, J.-Y.; Jin, Z.; Kong, L.-T.; Liu, J.-H. Metal oxide nanostructures and their gas sensing properties: a review. Sensors 2012, 12 (3), 2610–2631.
4. Lee, E.; VahidMohammadi, A.; Prorok, B. C.; Yoon, Y. S.; Beidaghi, M.; Kim, D.-J. Room temperature gas sensing of two-dimensional titanium carbide (MXene). ACS Appl. Mater. Interfaces 2017, 9 (42), 37184–37190.
5. Kim, S. J.; Koh, H.-J.; Ren, C. E.; Kwon, O.; Maleski, K.; Cho, S.-Y.; Asanori, B.; Kim, C.-K.; Choi, Y.-K.; Kim, J.; Gogotsi, Y.; Jung, H.-T. Metallic Ti3C2Tx x MXene gas sensors with ultrahigh signal-to-noise ratio. ACS Nano 2018, 12 (2), 986–993.
6. Shuck, C. E.; Han, M.; Maleski, K.; Hantanasirisakul, K.; Kim, S. J.; Choi, J.; Reil, W. E.; Gogotsi, Y. Effect of Ti3AlC2 MAX Phase on Structure and Properties of Resultant Ti3C2Tx MXene. ACS Appl. Nano Mater. 2019, 2 (6), 3368–3376.
7. 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. J. Mater. Chem. A 2018, 6 (37), 18116–18124.
8. Yang, Z.; Liu, A.; Wang, C.; Liu, F.; He, J.; Li, S.; Wang, J.; You, R.; Yan, X.; Sun, P.; Duan, Y.; Lu, G. Improvement of gas and humidity sensing properties of organ-like MXene by alkaline treatment. ACS Sens. 2019, 4 (5), 1261–1269.
9. Koh, H.-J.; Kim, S. J.; Maleski, K.; Cho, S.-Y.; Kim, Y.-J.; Ahn, C. W.; Gogotsi, Y.; Jung, H.-T. Enhanced selectivity of MXene gas sensors through metal ion intercalation: in situ X-ray diffraction study. ACS Sens. 2019, 4 (5), 1365–1372.
10. Chen, W. Y.; Jiang, X.; Lai, S.-N.; Peroulis, D.; Stanciu, L. Nanohybrids of a MXene and transition metal dichalcogenide for selective detection of volatile organic compounds. Nat. Commun. 2020, 11 (1), 1–10.
11. Lee, S. H.; Eom, W.; Shin, H.; Ambade, R. B.; Bang, J. H.; Kim, H. W.; Han, T. H. Room-Temperature, Highly Durable Ti3C2Tx MXene/Graphene Hybrid Fibers for NH3 Gas Sensing. ACS Appl. Mater. Interfaces 2020, 12 (9), 10434–10442.
12. Sun, S.; Wang, M.; Chang, X.; Jiang, Y.; Zhang, D.; Wang, D.; Zhang, Y.; Lei, Y.; W18O49/Ti3C2Tx Mxene nanocomposites for highly sensitive acetone gas sensor with low detection limit. Sens. Actuators, B 2020, 304, 127274.
13. Hermawan, A.; Zhang, B.; Taufik, A.; Asakura, Y.; Hasegawa, T.; Zhu, J.; Shi, P.; Yin, S. CuO Nanoparticles/Ti3C2Tx MXene Hybrid Nanocomposites for Detection of Toluene Gas. ACS Appl. Nano Mater. 2020, 3 (5), 4755–4766.
14. Lee, E.; VahidMohammadi, A.; Yoon, Y. S.; Beidaghi, M.; Kim, D.-J. Two-dimensional vanadium carbide MXene for gas sensors with ultrahigh sensitivity toward nonpolar gases. ACS Sens. 2019, 4 (6), 1603–1611.
15. Guo, W.; Surya, S. G.; Babar, V.; Ming, F.; Sharma, S.; Alshareef, H. N.; Schwingenschlögl, U.; Salama, K. N. Selective Toluene Detection with MoO5CT, MXene at Room Temperature. ACS Appl. Mater. Interfaces 2020, 12, 57218.
16. Cho, S.-Y.; Kim, J. Y.; Kwon, O.; Kim, J.; Jung, H.-T. Molybdenum carbide chemical sensors with ultrahigh signal-to-noise ratios and ambient stability. J. Mater. Chem. A 2018, 6 (46), 23408–23416.
(17) Yu, X.-f.; Li, Y.-c.; Cheng, J.-b.; Liu, Z.-b.; Li, Q.-z.; Li, W.-z.; Yang, X.; Xiao, B. Monolayer Ti$_2$CO$_2$: a promising candidate for NH$_3$ sensor or capturer with high sensitivity and selectivity. *ACS Appl. Mater. Interfaces* **2015**, *7*(24), 13707–13713.

(18) Xiao, B.; Li, Y.-c.; Yu, X.-f.; Cheng, J.-b. MXenes: Reusable materials for NH$_3$ sensor or capturer by controlling the charge injection. *Sens. Actuators, B* **2016**, *235*, 103–109.

(19) Wang, Y.; Ma, S.; Wang, L.; Jiao, Z. A novel highly selective and sensitive NH$_3$ gas sensor based on monolayer Hf$_2$CO$_2$. *Appl. Surf. Sci.* **2019**, *492*, 116–124.

(20) Hajian, S.; Khakhbaz, P.; Moshayed, M.; Maddipatla, D.; Narakathu, B. B.; Turkani, V. S.; Bazuin, B. J.; Pourfath, M.; Atashbar, M. Z. Impact of Different Ratios of Fluorine, Oxygen, and Hydroxyl Surface Terminations on Ti$_3$C$_2$T$_x$ MXene as Ammonia Sensor: A First-Principles Study. *2018 IEEE Sens. 2018*, *1*, 1–4.

(21) Zhang, Y.; Zhou, Z.; Lan, J.; Zhang, P. Prediction of Ti$_3$C$_2$O$_2$ MXene as an effective capturer of formaldehyde. *Appl. Surf. Sci.* **2019**, *469*, 770–774.

(22) Ma, S.; Yuan, D.; Jiao, Z.; Wang, T.; Dai, X. Monolayer Sc$_2$CO$_2$: a promising candidate as a SO$_2$ gas sensor or capturer. *J. Phys. Chem. C* **2017**, *121*(43), 24077–24084.

(23) Yang, D.; Fan, X.; Zhao, D.; An, Y.; Hu, Y.; Luo, Z. Sc$_2$CO$_2$ and Mn-doped Sc$_2$CO$_2$ as gas sensor materials to NO and CO: A first-principles study. *Phys. E* **2019**, *111*, 84–90.

(24) Naqvi, S. R.; Shukla, V.; Jena, N. K.; Luo, W.; Ahuja, R. Exploring two-dimensional M$_2$NS$_2$ (M= Ti, V) MXenes based gas sensors for air pollutants. *Appl. Mater. Today* **2020**, *19*, 100574.

(25) Khaledialidusti, R.; Mishra, A. K.; Barnoush, A. Atomic defects in monolayer ordered double transition metal carbide (Mo$_2$TiC$_2$T$_x$) MXene and CO$_2$ adsorption. *J. Mater. Chem. C* **2020**, *8*(14), 4771–4779.