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MXene-based chemical gas sensors: Recent developments and challenges

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ABSTRACT

The long-running Covid-19 pandemic has forced researchers across the globe to develop novel sensors and sensor materials for detecting minute quantities of biogenic viruses with high accuracy in a short period. In this context, MXene galleries comprising carbon/nitride two-dimensional nanolayered materials have emerged as excellent host materials in chemical gas sensors owing to their multiple advantages, including high surface area, high electrical conductivity, good thermal/chemical conductivity and chemical stability, composition diversity, and layer-spacing tunability; furthermore, they are popular in clinical, medical, food production, and chemical industries. This review summarizes recent advances in the synthesis, structure, and gas-sensing properties of MXene materials. Current opportunities and future challenges for obtaining MXene-based chemical gas sensors with high sensitivity, selectivity, response/recovery time, and chemical durability are addressed. This review provides a rational and in-depth understanding of the relationship between the gas-sensing properties of MXenes and structure/components, which will promote the further development of two-dimensional MXene-based gas sensors for technical device fabrication and industrial processing applications.

1. Introduction

After the emergence of graphene and graphene-like materials, research on the development of new structures and properties in the field of material science has attracted considerable research attention. Graphene is a traditional two-dimensional (2D) material, the research directions of which have diversified over time. In the past decade, MXene, a 2D layered material with a graphene-like structure, has attracted significant scientific and technological interest [1]. Typically, 2D materials contain strong intracrystalline covalent bonds and weak interlayer van der Waals forces and exhibit almost all physical and chemical properties of insulators, semiconductors, metals, and superconductors. MXene galleries are 2D materials with a crystal structure similar to that of graphene. The chemical formula of MXenes is \( M_{n-1}X_n \) \((n \geq 1, 2, 3)\) where M is an early transition metal element and X is carbon or nitrogen. MXenes are generally obtained by ablating MAX, a ternary layered compound with the chemical formula \( M_{n-1}AX_n \) where A is a main group element. This process involves the removal of the metal element A in the MAX phase by using a hydrofluoric acid solution at \( \sim 25^\circ C \) [2–4]. MXenes demonstrate excellent electron migration properties, high specific surface area, and high thermal as well as chemical stabilities [5–10], which render them suitable for various applications in several fields, such as catalysis, hydrogen production, adsorption, and energy storage [11–16]. In addition, as gas sensors, MXenes exhibit high sensitivity and selectivity to certain gases [17–21]. Although different types of gas sensors are available, such as semiconductor, catalytic combustion, electrochemical, optical, and thermal conductivity gas sensors, they suffer from significant limitations, such as high working temperature, poor gas selectivity, short stability, and long response time. Considering the serious risk posed to human health by toxic and harmful gases, such as ammonia, ozone, nitrogen dioxide, sulfur dioxide, carbon monoxide, carbon dioxide, and hydrogen sulfide, which are emitted from various sources, the development of chemical gas sensors with better selectivity, sensitivity, and response/recovery time for the detection of these gases at an early stage has become an unrelenting and urgent task.

Herein, the preparation methods, physicochemical properties, and sensing applications of MXene are comprehensively reviewed. In
particular, the latest research findings on MXene-based gas sensors, the principles of the device design, the underlying sensing mechanisms, and insightful prospects for future endeavors are addressed.

2. Synthesis of MXenes

Many different MXenes including Ti$_3$C$_2$, Ti$_2$C, Ta$_4$C$_3$, TiNbC, V$_2$C, Nb$_2$C, Mo$_2$C, and Ti$_4$N$_3$ have been prepared thus far [22–28]. Currently, MXene synthesis is still at the laboratory stage. The lack of a large-scale industrial production technology substantially limits their practical applications. Therefore, improving MXene synthesis methods has become a critical research topic. MXene is a layered material that is obtained by selectively removing the A phase in MAX, affording an accordion-like multilayer structure [29]. In the resulting MXene, which is usually called multilayered MXene, the layers are mainly connected by van der Waals forces. Although the most commonly used methods for the synthesis of graphene, transition metal disulfides, transition metal oxides, and hexagonal boron nitrides are mechanical exfoliation methods [30–33], most of the synthesis methods for 2D MXenes are top–down wet chemical etching methods such as hydrofluoric acid (HF), hydrochloric acid (HCl), and lithium fluoride (LiF) mixed solution etching and fluoride-free etching [34] (Table 1). Moreover, bottom–up synthesis methods have also been developed, as summarized below and in Fig. 1.

2.1. Wet chemical etching methods

2.1.1. HF acid etching

To obtain a multilayered MXene material, the MAX phase material is treated with an etchant to selectively remove the main group element A. In 2011, Gogotsi et al. used HF as an etchant for the first time to etch the MAX material Ti$_3$AlC$_2$ at room temperature (~25 °C), producing the MXene material Ti$_3$C$_2$[26]. Feng et al. used ultrasonic-assisted HF acid etching to considerably reduce the time required for the etching process [35], as shown in Fig. 2a. The HF acid etching process can be described through the following reactions.

$$\text{Ti}_3\text{AlC}_2 + 3\text{HF} \rightarrow \text{AlF}_3 + 3/2\text{H}_2 + \text{Ti}_3\text{C}_2 \quad (1)$$

$$\text{Ti}_3\text{C}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ti}_3\text{C}_2(\text{OH})_2 + \text{H}_2 \quad (2)$$

$$\text{Ti}_3\text{C}_2 + 2\text{HF} \rightarrow \text{Ti}_3\text{C}_2\text{F}_2 + \text{H}_2 \quad (3)$$

Currently, this method is widely applied to the preparation of Ti$_3$C$_2$.

Table 1

| Etching method                      | Procedure conditions | Advantages                                         | Disadvantages                                                                 |
|------------------------------------|----------------------|----------------------------------------------------|-------------------------------------------------------------------------------|
| 40 % HF                            | Etching at room temperature | Simple operation                                  | Highly toxic reactant, the etching range is wide, and the product has many impurity functional groups |
| LiF + HCl                          | Exfoliation at 60 °C-180 °C | The operation process is simple, the reactants are nontoxic, and the etching range is wide | The resulting product is often incomplete                                      |
| Dilute hydrochloric acid           | Electrochemically etched porous Ti$_3$AlC$_2$ electrode | The reactants are nontoxic, and the conditions are mild, with a low risk factor | The reaction process is slow                                                  |
| Molten fluoride salt/ high temperature etching | The mixture of fluoride salt and Ti$_3$AlN$_3$ powder under the Ar atmosphere | The reaction conditions are harsher, the operation is complex and dangerous | N-based MXene can be obtained, and the resulting product is relatively pure |
| Generic Lewis acid etching         | Generic Lewis acid mixed with MAX phases with different A elements (Al, Zn, Si, Ga, etc.) NH$_4$HF$_2$ (1 mol/L) as an etchant at room temperature | Wide etching range and as-obtained MXenes with good electrochemical performance | The purity of the resulting product is not high |
| NH$_4$HF$_2$ (1 mol/L)             | NH$_4$HF$_2$ (1 mol/L) as an etchant at room temperature | Mild conditions, nontoxic and harmless | The product contains several by-products, resulting in a low product purity |

Fig. 1. Timeline of MXenes from Ti$_3$C$_2$ discovery to the current development [10,19,26,28,106,107].
and other MXene materials. Li et al. prepared Ti$_3$C$_2$ by impregnating maximum-phase MAX with 40 % or 49 % HF at 0 °C, 15 °C, and 60 °C, respectively, where Ti$_3$C$_2$ synthesized without pressure exhibited higher orientation than that obtained via the hot pressing method [36]. However, HF etching for MXene preparation suffers from a series of limitations. Etching with 40 %–50 % (wt., mass fraction) HF solution introduces diverse functional groups, such as F and OH, on the MXene crystal surface, and excessive F-containing functional groups may change the properties of the material, thus affecting its performance [37]. The morphology of Ti$_3$C$_2$ depends on the etching time, etching temperature, and ball milling time of the precursor [34]. In addition, HF is highly corrosive and toxic, rendering the process cumbersome and dangerous. Thus, HF etching is not the ultimate method for MXene preparation.

2.1.2. HCl and LiF mixed solution etching

In 2014, Zhang et al. [38] successfully prepared Ti$_3$C$_2$ using a mixture of HCl and LiF as the etchant (Fig. 2b) according to the following reactions.

\[ \text{Ti}_3\text{ALC} + 6\text{LiF} + 3\text{HCl} \rightarrow \text{Ti}_3\text{C} + \text{Li}_3\text{AlF}_6 + 3\text{LiCl} + 3/2\text{H}_2 \]  
\[ \text{Ti}_3\text{C} + 2\text{H}_2\text{O} \rightarrow \text{Ti}_3\text{C(OH)}_3 + \text{H}_2 \]  
\[ \text{Ti}_3\text{C} + 2\text{LiF} + 2\text{HCl} \rightarrow \text{Ti}_3\text{CF}_2 + 2\text{LiCl} + \text{H}_2 \]

This synthesis method presents a lower risk and is simpler than previous preparation methods [26,28]. The obtained MXene material is thinner, which results in an improved capacitance in the presence of Li$^+$. Using this method, Cao et al. [39] prepared Ti$_3$C$_2$ nanosheets via an ultrasonic treatment. Yazdanparast et al. used a mixture of LiF and HCl (1.9 M LiF + 12 M HCl) to etch the TiAlC$_2$ MAX phase and successfully synthesized TiVC-solid solution MXenes [40]. The obtained product contained a higher concentration of = O and F groups for an improved energy storage performance. Although the preparation of delaminated MXenes using this route is relatively mild, the resulting MXenes usually contain incompletely etched MAX phases. To prepare MXenes with high quality and yield, continuously optimizing the conditions of each reaction step [41–43] is necessary; however, this limits the applicability of the method.

2.1.3. Other wet chemical etching processes

Currently, HF or LiF/HCl mixtures are generally used as the etchant in MXene preparation via etching processes. To obtain more efficient and safer etchant materials, several novel methods have been developed. Sun et al. [44] reported for the first time the etching of a MAX phase using a fluoride-free solution. Specifically, they electrochemically etched porous Ti$_3$AlC using dilute HCl solution to obtain a single-layer Ti$_3$CT$_x$ MXene. In 2016, Urbankowsk et al. obtained for the first time the 2D layered transition metal nitride Ti$_3$N$_2$ via a high-temperature molten fluoride salt method [45]. Shang et al. successfully prepared Ti$_3$C$_2$Tx free from F-containing functional groups using an alkali-assisted hydrothermal method in the presence of 27.5 mol/L NaOH at 270 °C [46]. Pang et al. proposed a nontoxic and HF-free route for MXene synthesis through a thermally assisted electrochemical etching method [47], which was extended to prepare Ti$_2$CT$_x$, Cr$_2$CT$_x$, and V$_2$CT$_x$. Huang et al. adopted a generic Lewis acid etching route for the preparation of various MXenes using a large family of MAX phases with different A elements as substrates, including Al, Zn, Si, and Ga. The obtained MXenes exhibited excellent electrochemical and energy storage performances [5]. Halim et al. used NH$_4$HF$_2$ (1 mol/L) to etch a Ti$_3$AlC$_2$ film at 25 °C, affording Ti$_3$CT$_x$ with uniform morphology [48] but accompanied by several byproducts, resulting in low product purity. These wet chemical etching methods suffer from a series of drawbacks, including the formation of many byproducts, the presence of significant...
amounts of unetched MAX phases in the final products, and insufficient purity of the products.

2.2. Non-wet chemical etching method

Apart from the commonly used wet chemical etching methods, other approaches have been explored for MXene preparation, such as mechanical lift-off and bottom–up synthesis methods. Examples of bottom–up synthesis methods are chemical vapor deposition, template and plasma deposition, and enhanced pulsed laser deposition. As the presence of van der Waals forces between the multiple layers of MXenes hinders their preparation via mechanical peeling [49], other peeling methods are currently adopted, i.e., ultrasonic treatment and intercalation. Wang et al. successfully obtained a single piece of Ti$_3$C$_2$ by subjecting Ti$_3$C$_2$ MXene to ultrasonic treatment [50]. Common intercalation etchants include tetrabutylammonium hydroxide, dimethylsulfoxide, and dimethylamide. When using top–down synthesis methods, chemical vapor deposition produces MXene crystals with better quality [51]. Additionally, these methods can be used for the synthesis of 2D transition metal carbides and nitrides that cannot be obtained via selective etching processes [52]. Unfortunately, non-wet chemical etching methods are expensive, cumbersome, and difficult to control.

As described in this section, wet chemical etching is the most common synthesis method for MXene preparation owing to its simplicity, low cost, and ability to produce a single or few layers of MXenes. However, the introduction of functional groups, such as $-\text{O}$, $-\text{OH}$, and $-\text{F}$ on the surface of the MXene is unavoidable and negatively affects the gas-sensing properties of the product. Therefore, extensive research is ongoing on eliminating the influence of functional groups on MXene performance. The shape of the MXene sheets endows the resulting material with an accordion-like structure, which alleviates the MXene stacking and volume expansion of the active material, thereby improving the gas adsorption of the sensors. The surface functional groups of MXenes can be fully utilized in the in situ preparation of composites, which can contribute to improving the overall performance of MXene-based chemical gas sensors.

3. Structure of MXenes

MXene is a graphene-like 2D layered metal transition carbide or nitride. The SEM microstructure pictures of some MXenes (Ti$_3$C$_2$T$x$, Ti$_5$CT$_x$, Ta$_4$C$_3$T$_x$, TiNbCT$_x$, and Ti$_3$CNT$_x$) are shown in Fig. 3a-f. Ti$_3$C$_2$T$_x$ is currently the most widely studied MXene material; 70 % of the
research in this field focuses on Ti$_3$C$_2$T$_x$. By stripping the metal in Ti$_2$AlC$_2$, Ti$_2$C$_2$T$_x$ with empty layers is formed. The empty layer spacing changes with the etching conditions, which yields Ti$_3$C$_2$T$_x$ materials with different physical and chemical properties [34].

In electrocatalysis research, Ti$_3$C$_2$T$_x$ has been widely regarded as a good electrocatalyst or electrocatalytic promoter owing to its conductive metal core and abundant surface functional groups. Moreover, Ti$_3$C$_2$T$_x$ can be integrated with other materials, and its properties can be tuned. For instance, Du et al. successfully embedded MoS$_2$ in Ti$_2$C$_2$T$_x$ via a hydrothermal reaction [53]. The growth of MoS$_2$ atoms on the surface and between the layers of Ti$_3$C$_2$T$_x$ formed a three-dimensional (3D) structure with good hydrogen evolution reaction activity and long-term stability, which demonstrates that the electrocatalytic ability can be improved by modifying the Ti$_3$C$_2$T$_x$ surface groups.

4. Properties of MXenes

4.1. Thermal conductivity

MXenes inherit the high thermal conductivity of the parent MXA phase materials, resulting in higher thermal conductivity than that of most metal and low-dimensional semiconductor materials such as MoS$_2$ and phosphorus heterocycles. At room temperature, 5-μm-thick armchair-type Sc$_2$C$_2$F$_2$ has a thermal conductivity of 472 W m$^{-1}$ K$^{-1}$, which is higher than the corresponding value of the best traditional conductor, silver. Moreover, the thermal conductivity of zigzag-type Sc$_2$C$_2$F$_2$ is 178 W m$^{-1}$ K$^{-1}$, and that of Sc$_2$CO$_2$ is considerably lower. At room temperature, the thermal conductivity of armchair-type and zigzag-type Sc$_2$C$_2$F$_2$ are 173 and 107 W m$^{-1}$ K$^{-1}$, respectively. Considering their excellent thermal conductivity and electron mobility, MXene materials are deemed potential candidates for next-generation electronic devices [54].

4.2. Mechanical properties

Compared with other 2D materials, MXenes exhibit better mechanical properties, comparable to those of graphene in some respects. In 2012, Kurtoglu et al. used the density functional theory to perform mechanical calculations on TiC$_2$, Ti$_3$C$_2$, Ti$_2$C$_2$, Cr$_2$C, Zr$_2$C, Hf$_2$C, Ta$_2$C, Ta$_2$C$_2$, V$_2$C, and Ta$_4$C$_3$ [55], and they found that the elastic modulus of these MXene materials is very high when stretched along the base surface. Using first-principle calculations, Chakraborty et al. predicted the influence of doping B and V at the Ti and C sites of TiC$_2$, respectively, on the mechanical properties of MXenes [56]. B doping was found to effectively improve the elastic properties of MXenes, especially with regard to withstanding high critical strain. Zha et al. noted that under biaxial strain, the elastic modulus of Mo$_2$C was 312 ± 10 GPa. For a critical strain of 0.086, this material exhibits a good mechanical strength of 20.8 GPa. Hu et al. prepared Ti$_3$C$_2$T$_x$/Al composites via seamless sintering and hot extrusion processes using Ti$_3$C$_2$T$_x$ MXene as a solid lubricant and Al [57]. With increasing the Ti$_3$C$_2$Tx content, the Vickers hardness and tensile strength of the composite material continuously increased, and the friction performance under dry sliding conditions was two times lower than that of pure Al.

4.3. Chemical stability

Shein et al. established structural models for MXene and MAX phases using the first-principle band structure theory [58]. In this model, the lattice energy of MXene was negative, with larger negative values indicating highly stable crystal structures. Studies on the thermal stability of MXenes document their instability in air (oxygen) atmosphere, high-temperature environments, and aqueous solutions [59,60].

| Compound          | Bandgap/eV |
|-------------------|------------|
| Ti$_3$C$_2$(OH)$_2$ | 0.05       |
| Ti$_3$C$_2$F$_2$  | 0.10       |
| Ti$_2$CO$_2$      | 1.03       |
| Sc$_2$CO$_2$      | 0.45       |
| Sc$_2$CF$_2$      | 1.80       |
| Sc$_2$CO$_2$      | 0.24       |
| Zr$_2$CO$_2$      | 0.88       |
| Hf$_2$CO$_2$      | 1.00       |

*Indirect bandgap.

4.4. Electronic properties

Generally, MXenes obtained via wet chemical etching are not phase-pure, and the exposed M atoms on the surface form bonds with F$^-$, O$_2^-$, and OH$^-$ in aqueous solution. Density functional theory calculations revealed that pure MXene phases are metallic in nature, whereas MXenes containing certain terminal groups exhibit semiconducting properties [61]. Nevertheless, some studies showed that many MXene materials with mixed functional groups exhibit metallic properties [27,62]. Thus, Ran et al. showed that Ti$_2$C$_2$, V$_2$C, Nb$_2$C, and Ti$_3$C$_2$ are conductive under standard conditions [15,63,64]. Semiconductor materials must possess an appropriate bandgap energy. Table 2 lists the bandgap energy of different MXenes, which are 0.24, 0.88, and 1.0 eV for Ti$_2$CO$_2$, Zr$_2$CO$_2$, and Hf$_2$CO$_2$, respectively, and 0.13–1.18 eV for transition metal disulfide/Sc$_2$C$_2$F$_2$ composites. When used in gas sensing applications, most traditional semiconductors require a working temperature of at least 100 °C. In contrast, some studies have revealed that MXenes can be used as room-temperature NH$_3$ gas sensors [65].

After the A atomic layer in the MAX phase was etched away, the original MA metal bond was destroyed, and other atoms were firmly imprisoned in the layer through covalent bonds. The layers were relatively independent, and the atoms could only move within each layer. Thus, an extremely fast movement of atoms in a relatively confined space occurred, substantially increasing electron mobility. For example, the anisotropy of the electron mobility of Sc$_2$CF$_2$ was obvious at room temperature. Moreover, the electron mobility of the zigzag-type Sc$_2$C$_2$F$_2$ (5.03 × 10$^3$ cm$^2$ V$^{-1}$ s$^{-1}$) is nearly four times higher than that of the armchair-type counterpart (1.07 × 10$^3$ cm$^2$ V$^{-1}$ s$^{-1}$). In contrast, the electron mobility of Sc$_2$CO$_2$ tended to be isotropic. Overall, the excellent electron migration properties of MXene materials considerably improve electrical signal conversion in gas sensors.

4.5. Adsorption performance

The pristine MXenes and MXenes containing terminal functional groups exhibited excellent adsorption performance. Theoretical calculations revealed that the sensing mechanism of a gas molecule on MXene-based sensors is affected by defects and surface functional groups [66]. In the presence of functional groups, gas absorption is induced by dispersion forces, such as electrostatic force, which results in relatively small resistance changes because the intermolecular forces are weak, thus enhancing the adsorption performance [21]. Khaleelaldusti et al. [67] successfully designed MXene materials with specific intrinsic defects, and they found that certain defects can improve the adsorption performance of the resulting MXenes. For example, Mo$_2$Ti$_3$C$_2$T$_x$ with intrinsic defects exhibited particularly good adsorption and conversion performance for CO$_2$. Strong adsorption performance was also reported for other MXenes and MXene-based composites [68,69].

To date, the most common applications of MXenes are catalysis and energy storage because of their large specific surface area, good conductivity, hydrophilicity, and excellent thermal/chemical stability.
Furthermore, their unique accordion-like layered structure, abundant active surface groups, excellent tunable structure, and compositional diversity render them promising materials for gas sensing applications.

5. Types of gas sensors

Gas-sensitive materials are the core of gas sensors. The composition and concentration of the sensed gas are determined according to the changes in the physical and chemical properties of the gas-sensitive materials, such as the electrical resistance. Based on the working principle, sensors can be divided into several types, including semiconductor, catalytic combustion, electrochemical, optical, and thermal conductivity gas sensors.

5.1. Semiconductor gas sensors

The working principle of semiconductor gas sensors is based on the changes in conductivity of the gas-sensitive material upon contacting the sensed gas [70,71]. Because of their simple production, low cost, low operating technology requirements, miniaturization, mass production, and low environmental requirements, these sensors have attracted widespread research attention in the sensor community. However, their poor selectivity limits their practical application. According to the change in the physical characteristics of the semiconductor and the sensed gas, semiconductor gas sensors can be divided into resistive and non-resistive types.

5.1.1. Resistive semiconductor gas sensors

In resistive semiconductor gas sensors, the concentration of the sensed gas changes when it contacts the gas-sensitive material, and the resistance of the sensor surface changes. Zinc oxide (ZnO), a common third-generation n-type semiconductor sensor material with excellent optical, electrical, and piezoelectric properties [72-74], is used to prepare materials for sensing applications. Depending on the external conditions, ZnO can exhibit diverse structures, namely, cubic rock salt, cubic zinc blende, and hexagonal wurtzite. ZnO nanomaterials having different morphologies, i.e., nanoparticles, nanoflowers, nanosheets, nanorods, and nanotubes, have been prepared. It is widely accepted that nanomaterials exhibiting larger specific surface area provide larger contact area for the gas molecules, affording increased gas sensitivity.

5.1.2. Non-resistive semiconductor gas sensors

Non-resistive semiconductor sensors can be divided into diode-type, capacitive-type, and metal oxide semiconductor field-effect transistor-type sensors. Instead of detecting the gas concentration through changes in the resistance, this type of semiconductor sensor detects the gas concentration through changes in some of its own characteristics, e.g., in the microstructure of a capacitive gas sensor. Capacitive gas sensors, which have a simple structure, miniaturized size, high reliability, and low cost [75], comprise a fork-finger capacitor fabricated on a silicon chip via the microelectromechanical system technology and a polymer film as the adsorbing medium [76,77]. Upon contacting the gas, the dielectric constant of the medium changes, causing a change in the capacitance. According to the capacitance change, the concentration of the surrounding gas can be determined. This type of sensor offers good selectivity, simple fabrication, and wide application.

5.2. Catalytic combustion-type gas sensors

Catalytic combustion-type gas sensors are composed of measuring and compensation elements, called black and white elements, respectively. The measuring element is comprises a carrier and a catalyst. The circuit works on the basis of the Wheatstone bridge principle. When the bridge is balanced, the voltage difference between the two bridge arms is zero. The sensitive element in the circuit and the sensed gas burn on the surface without flame, thereby increasing the resistance of the measuring element. This disrupts the balance of the bridge in the circuit, generating a voltage difference that is directly proportional to the concentration of the gas. Although high accuracy, fast response, and good reproducibility are achieved with such gas sensors, the catalyst has a limited lifespan and cannot be used continuously for a long time.

A thick-film catalytic combustion hydrogen sensor [78] was developed to overcome the shortcomings of spherical sensors. In this sensor, an alumina ceramic sheet is used as a base, and a hydrogen sensor and a compensation element form a Wheatstone circuit bridge. The sensor works as follows: When the air diffuses to the measuring bridge arm, the hydrogen reacts with the gas sensor to produce flameless combustion and release heat, thus increasing the resistance of the gas sensor. Subsequently, the bridge loses balance and generates a voltage. Differences in the hydrogen concentrations can be measured by measuring the voltage difference.

5.3. Electrochemical gas sensors

Electrochemical gas sensors have good selectivity, rapid response, as well as high accuracy and are often used to detect toxic gases. Moreover, such sensors can tolerate harsh environments composed of high temperature, high pressure, and high concentration, as well as enable automatic measurement and control. However, more components are used in their manufacturing process, which becomes more complicated. Electrochemical gas sensors comprise a diffusion filter membrane, an acid or alkali electrolyte tank, a working electrode, a counter electrode, and a reference electrode. As the air passes through the diffusive filter membrane, the gas is filtered out and enters the electrolyte, where it contacts the working electrode to be oxidized, while oxygen is reduced at the counter electrode. The potential of the reference electrode changes, which allows the determination of the concentration of the sensed gas [79-81].

5.4. Optical gas sensors

These gas sensors are not based on an increase in the resistance of the sensitive element, thereby avoiding the generation of heat and the possibility of an electric spark, which offers more safety even when working under high-concentration conditions. Thus, these sensors can be used to monitor inflammable and explosive materials with excellent selectivity and accuracy and high sensitivity [82]. The working principle of optical gas sensors is based on the change in the optical properties of the sensitive material such as reflectance, catalytic properties [83], thermal conductivity [84], and optical properties [85]. The light transmittance of gas-sensitive films changes when contacting the sensed gas. By measuring the change in light transmittance, the gas concentration can be measured. The spectral responses to different concentrations of ethanol vapor of SnO$_2$ and SnO$_2$:CuO films, in which CuO as a gas-sensitive optical material is doped on SnO$_2$ [86]. The maximum spectral response is obtained at 675 nm, suggesting that this is the optimal wavelength to achieve the best gas sensitivity [87]. SnO$_2$ films could be used to sense other gases. The transmittance of the same SnO$_2$ gas-sensing film to different reducing gases increases with the increase in the reducing gas concentration. The sensitivity change should be different depending on the reducing gases, which could be expected to enable the sensing of complex gas systems.

5.5. Thermal conductivity gas sensors

The working principle of thermal conductivity gas sensors is based on the thermal conductivity of the sensed gas. When the gas passes via the detection unit, part of the heat of the thermistor heated by the current inside the instrument is released, causing a change in the resistance. The heat conduction depends on the gas type and concentration and can be used to determine the gas concentration [88]. Such sensors have several advantages, including a large range of detection,
Table 3
Gas sensitivity data of MXene-based composite materials for different gases.

| Core material          | Object gas | Operation temperature (°C) | Response time | Gas response (Rg/Ra)         | Ref. |
|------------------------|------------|----------------------------|---------------|------------------------------|-----|
| Ti$_3$C$_2$Tx           | Acetone    | RT                         | NA            | 0.125/200 ppm                | [21]|
| W$_{18}$O$_{49}$/Ti$_3$C$_2$Tx | Acetone | 300                        | 4.6 s/20 ppm  | 11.6/20 ppm                  | [97]|
| CuO/Ti$_3$C$_2$T$_x$MXene | Toluene  | 250                        | 270 s/50 ppm  | 11.4/50 ppm                  | [110]|
| MXene/TiO$_2$           | NH$_3$     | RT                         | 36 s/50 ppm   | 40/50 ppm                    | [20]|
| MXene/TiO$_2$           | NH$_3$     | RT                         | 60 s/10 ppm   | 3.1/10 ppm                   | [112]|
| Li$_2$V$_2$CT$_x$       | NH$_3$     | RT                         | 41 s/50 ppm   | 3.41/500 ppm                 | [10]|
| HF-V$_2$CT$_x$          | methane    | RT                         | 169 s/500 ppm | 1.49/500 ppm                 | [10]|
| Cl$_2$Ti$_2$C$_2$T$_x$  | NH$_3$     | RT                         | 98 s/500 ppm  | 13.2/500 ppm                 | [10]|
| Co$_3$O$_4$PEI/Ti$_3$C$_2$T$_x$ | NO$_x$ | RT                         | 27.9 s/30 ppb | N/A                         | [101]|
| MXene/Co$_3$O$_4$       | HCHO       | RT                         | 83 s/10 ppm   | 9.2/10 ppm                   | [113]|
| SnO-SnO$_2$/Ti$_3$C$_2$T$_x$ | Acetone | RT                         | 18 s/100 ppm  | 12.1/100 ppm                 | [50]|
| Ni(OH)$_2$/Ti$_3$C$_2$T$_x$ | NH$_3$  | RT                         | 78 s/50 ppm   | 6.2/10 ppm                   | [114]|

Fig. 4. (a) Adsorption energies of different gases at the Ti$_2$CO$_2$ MXene surface [108]. (b) Schematic illustration of the Ti$_2$CO$_2$ MXene-based sensor for NH$_3$ detection. (c) Illustration of the two-probe model considering the monolayer V$_2$CO$_2$ as a representative along with the length of the electrodes and the central scattering region (in a unit of Å). (d) Calculated I – V curves along the zigzag (ZZ) and armchair (AR) directions with and without NH$_3$ adsorption. (e) I – V curves along the ZZ direction. (f) Corresponding transmission spectra under 0 V bias for V$_2$CO$_2$-based systems, respectively. The Fermi energy was shifted to zero [10].
moderate stability, simple structure, low cost, and less consumption; however, it suffers from low accuracy and large errors [89].

Among the gas sensors described in this section, semiconductor gas-sensitive sensors have obvious advantages in terms of production cost, responsiveness, and sensitivity.

6. MXene-based gas sensors

Owing to their high metal conductivity, excellent ion-transmission characteristics, biocompatibility, large specific surface area, and easy surface functionalization potential, MXenes are promising materials in the sensor field [90] (Table 3). However, reports on the application of MXenes as gas sensors are limited. In general, MXene materials are used as gas sensors mostly by combining them with a certain gas-sensitive material to form a composite gas-sensitive material with high performance. These systems benefit from the existence of empty spaces in the middle layer of the MXenes for the adherence of gas molecules [91]. Moreover, MXenes offer high stability, considerably improving the stability of the gas sensors for use in harsh industrial environments, and high selectivity owing to the presence of surface functional groups. Sc$_2$C, the MXene with the highest theoretical specific surface area per unit weight, can operate via three adsorption methods, i.e., chemical adsorption, Kubas adsorption, and physical adsorption, which considerably improves the sensitivity of the gas sensor [92]. Fig. 4a shows the adsorption energies of different gases at the MXene surface.

6.1. Hydrogen peroxide gas sensors

Hydrogen peroxide (H$_2$O$_2$) is an important inorganic chemical product with wide applications in medicine, environmental protection, food, textile, and electronics. However, excessive H$_2$O$_2$ poses a serious risk to the human body and the environment, rendering its detection crucial.

In 2017, Lorencova et al. [93] demonstrated that exposing Ti$_3$C$_2$Tx to an anodic potential induces TiO$_2$ formation. The modified Ti$_3$C$_2$Tx could be used for electrochemical reactions in a cathodic potential window, i.e., for super-sensitive detection of H$_2$O$_2$ down to a concentration of 0.7 nM with a response time of ~10 s. Furthermore, Fen et al. reported that TiO$_2$/Ti$_3$C$_2$ nanocomposites exhibited good biocompatibility [94] and could be used as a biosensor for H$_2$O$_2$ with good performance with a wide linear range (0.1–380 μM) and a very low detection limit (14 nM).

In 2019, Neampet et al. prepared a Pt/PANI/MXene nanocomposite to modify a screen-printed carbon electrode to fabricate H$_2$O$_2$ sensors. The modified Pt/PANI/MXene electrode demonstrated a magnified current response toward H$_2$O$_2$ compared with the unmodified electrode and provided a low detection limit of 1.0 μM [95].

6.2. NH$_3$ gas sensors

Ammonia (NH$_3$) is a poisonous and harmful gas as well as an explosive. With the development of the chemical industry, wastewater
and waste gas containing NH3 are discharged into the environment, with concomitant risk to the human body and aquatic organisms. Therefore, developing gas sensors for accurately detecting NH3 is essential. Single-layer Ti3C2O exhibits high sensitivity and selectivity for NH3, the chemical adsorption of which on Ti3C2O causes a charge transfer of 0.174 eV [63], thus indicating and tremendous changes in the electron transmission function and I–V characteristics. Moreover, NH3 adsorption is reversible, suggesting the importance of single-layer Ti3C2O material as an NH3 sensor.

In 2016, Xiao et al. studied the interaction between NH3 and O-terminal MXenes with different charges (M2CO2, M = Sc, Ti, Zr, and Hf), finding that NH3 molecules were considerably adsorbed on M2CO2 with evident electron transfer [96]. Moreover, NH3 release could be easily achieved by controlling the electron injection, suggesting the potential of these MXenes as materials for reusable NH3 sensors. In 2018, Sinha et al. prepared a wearable sensor using an MXene material to effectively detect NH3, ethanol, and acetone [65], which could be applied to the analysis of human breathing for an effective health diagnosis. For example, acetone gas is present in the breath of diabetic patients, and NH3 is present in the breath of people with lung diseases. Sun et al. prepared W18O49/Ti3C2Tx composite materials that demonstrated fast response speed and good selectivity and stability toward low concentrations of acetone (11.6–20 ppm) [97]. The same group used a solvothermal process to remove the fluorine-containing groups in the MXene material, further optimizing its surface chemical properties, which provided new insights for the development of acetone hybrid materials. Fig. 4b presents a schematic of the sensing mechanism of NH3 sensors.

To theoretically study the gas-sensitive properties of V2CTx MXene, the transport properties of monolayer V2CT, the transport properties of monolayer V2CT, MXene, were investigated using DFT calculations and a two-probe device model to visualize the change in conductivity [10], as shown in Fig. 4c. Fig. 4d shows the I–V curves of the monolayer V2CO2X (considering that “O” dominates the functional groups) before and after NH3 adsorption, and the current value through the sensor was approximately three times higher along the zigzag direction than along the armchair direction. This process resulted in reduced conductivity, which can be attributed to the reduced conductance channels for electron transport around the Fermi level, as shown in Fig. 4f. Compare with the before NH3 adsorption, the V3CF2 (considering that “F” dominates the functional groups) after NH3 adsorption exhibited lower conductivity and a larger positive response. Moreover, the V2CCl (considering that “Cl” dominates the functional groups) after NH3 adsorption exhibited a larger current through the sensor, as shown in Fig. 4e. Hence, the —Cl functional group can change the response of V2CTx-based gas sensors from a positive response to a negative response.

6.3. NOx gas sensors

With the continuous improvement in human living conditions and environmental protection awareness, people have gradually begun to pay attention to the living environment and air quality. In this context, the development of accurate and highly sensitive sensors for NOx and other major air pollutants is a pressing concern. NOx can easily combine with hemoglobin in human blood, causing irritation to the lungs and resulting in many serious diseases [98]. Therefore, the real-time monitoring of gas composition and concentration in the living and working environments is particularly important.

Yang et al. [99] used the ultrasonic spray pyrolysis technology to prepare a 3D-shrinkage MXene nanosphere/ZnO composite sensitive electrode effectively solving the problems, including the easy stacking of 2D MXene Ti3C2Tx nanofilms and loss of their high specific surface area, and become the limitation to further improved the electrode performance (Fig. 5a). MXene flakes with ZnO nanoparticles on the surface were self-assembled to form 3D crumpled MXene sphere/ZnO composite. The TEM images clearly show that ZnO nanoparticles were evenly distributed on the surface of the 3D crumpled MXene sphere (Fig. 5b–f). Simultaneously, the sensor made of the composite materials demonstrated good selectivity and sensitivity to NO2 gas (Fig. 6a–c). Koh et al. examined the influence of the gas-induced swelling of Ti3C2Tx MXene films on the gas sensitivity [100]. The results demonstrate that the gas-sensing channel treated with 0.3 mM NaOH had the best selectivity to ethanol vapor and the largest swelling capacity. Their work demonstrated that controlling the interlayer transport of MXenes is important.
to enhancing the selectivity to gas molecules. Moreover, Sun et al. produced $\text{Co}_3\text{O}_4@\text{PEI}/\text{Ti}_3\text{C}_2\text{T}_x$ nanocomposites wherein PEI was used as an electron transfer channel to improve the interactions between MXene and $\text{Co}_3\text{O}_4$ [101]. This composite material was reported to exhibit the highest sensitivity response to $\text{NO}_x$ gas. Furthermore, when 2.4 mg of $\text{Ti}_3\text{C}_2\text{T}_x$ sheet (CoPM-24) was added, the response time to $\text{NO}_x$ gas was $27.9 \pm 2$ s at room temperature with 26 % humidity.

### 6.4. Volatile organic compound (VOC) gas sensors

The US Federal Environmental Protection Agency defines VOCs as carbon-containing compounds involved in atmospheric photochemical reactions, except carbon monoxide, carbon dioxide, metal carbide, carbonic acid, metal carbonate, and ammonium carbonate [102]. VOCs primarily include nonmethane total hydrocarbons such as alkanes, alkenes, alkynes, and aromatic hydrocarbons; oxygen-containing organics including aldehydes, ketones, alcohols, and ethers; chlorine-containing organics; sulfur-containing organics; and nitrogen-containing organics [103].

Kim et al. used $\text{Ti}_3\text{C}_2\text{T}_x$ to prepare a solid-state gas sensor with high sensitivity to VOCs at room temperature with a low 50–100 ppb detection limit, low electrical noise, and strong signal, outperforming traditional semiconductor materials [19]. To develop a gas-sensitive material for the fast detection of toluene, Hermawan et al. focused on CuO, which has a wide response range to VOCs, albeit a small response value, slow response/recovery speed, and low durability [104]. To solve these limitations, they prepared a CuO/$\text{Ti}_3\text{C}_2\text{T}_x$/MXene composite material. The addition of MXene not only improved the response time of CuO but also increased the selectivity, responsivity (270 s), and recovery time (10 s) (Fig. 7a-d and Fig. 8a-f). This work thus demonstrates the potential of metal oxide/2D hybrid materials in the detection of VOC gases.

### 7. Conclusions and outlook

The combination of MXene materials and other gas-sensitive materials is a promising approach toward the development of high-performance gas sensors. However, MXene-based composites gas sensors are still scarce and limited to the detection of $\text{NH}_3$ and certain VOC gases. Future research efforts should be devoted to expanding the application scope of MXene-based gas sensors to other gases and improving their performance. Of particular relevance would be a high-performance MXene-based sensor for $\text{CH}_4$ gas, the detection of which in coal mines is essential to prevent explosions [105]. Currently, the most common semiconductor methane gas sensors are made using metal oxides such as $\text{SnO}_2$; however, they have several disadvantages, including a high working temperature, serious environmental impact, and unsatisfactory long-term stability. Doping of $\text{SnO}_2$ films with an MXene material is worth pursuing to overcome these limitations and improve the sensor performance.

MXene is a novel 2D layered crystal the unique morphology and high surface area of which provide it with good application prospects in the fields of energy storage, catalysis, and gas sensitivity. However, the preparation of MXene materials using the HF etching process is not safe.
Although using HCl/LiF mixtures rather than HF can reduce the experimental risk, the resulting MXenes do not exhibit satisfactory performance. Despite being in its initial stage, great advances have been made in the preparation of MXene materials with better semiconductor performance for high-efficiency gas sensors. Although in-depth research is still required in this regard, the prospect of this novel 2D crystal material is very bright in the field of gas sensors.

CRediT authorship contribution statement

Qixun Xia: Conceptualization, Writing – original draft. Yulong Fan: Software, Investigation. Shiwen Li: Formal analysis, Validation. Aiguo Zhou: Funding acquisition, Supervision, Writing – review & editing. Nanasaheb Shinde: Data curation, Writing – review & editing. Rajaram S. Mane: Visualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Fig. 8. (a) Transient response/recovery curves and (b) response values of CuO/Ti3C2Tx with different Ti3C2Tx amounts; black, red, pink, green, and blue colors represent 0, 10, 20, 30, and 40 wt% of Ti3C2Tx, respectively; (c) linear fitting of R−1 vs. C−1 based on the Langmuir isotherm model; (d) response/recovery times; (e) selectivity of CuO/Ti3C2Tx-30 wt% to 50 ppm of tested gas; and (f) relationship of response value with the specific surface area [110].
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