

Review



Research Progress on Ammonia Sensors Based on Ti₃C₂T_x MXene at Room Temperature: A Review

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Abstract: Ammonia (NH₃) potentially harms human health, the ecosystem, industrial and agricultural production, and other fields. Therefore, the detection of NH₃ has broad prospects and important significance. Ti₃C₂T_x is a common MXene material that is great for detecting NH₃ at room temperature because it has a two-dimensional layered structure, a large specific surface area, is easy to functionalize on the surface, is sensitive to gases at room temperature, and is very selective for NH₃. This review provides a detailed description of the preparation process as well as recent advances in the development of gas-sensing materials based on Ti₃C₂T_x MXene for room-temperature NH₃ detection. It also analyzes the advantages and disadvantages of various preparation and synthesis methods for Ti₃C₂T_x MXene's performance. Since the gas-sensitive performance of pure Ti₃C₂T_x MXene regarding NH₃ can be further improved, this review discusses additional composite materials, including metal oxides, conductive polymers, and two-dimensional materials that can be used to improve the sensitivity of pure Ti₃C₂T_x MXene to NH₃. Furthermore, the present state of research on the NH₃ sensitivity mechanism of Ti₃C₂T_x MXene-based sensors is summarized in this study. Finally, this paper analyzes the challenges and future prospects of Ti₃C₂T_x MXene-based gassensitive materials for room-temperature NH₃ detection.

Keywords: Ti₃C₂T_× MXene; gas sensors; ammonia; room-temperature; sensitivity mechanism

1. Introduction

NH₃ is a colorless, alkaline gas with a pungent odor that is now widely used in industry, agriculture, and other fields such as refrigerant and nitrogen fertilizer production. Excessive NH₃ emissions are closely related to the biological environment and the health of humans, such as the formation of acid rain and some human diseases [1,2]. According to the Occupational Safety and Health Administration (OSHA), when the human body is exposed to 35 ppm of NH₃ for more than 15 min, this will endanger human health, and when the concentration of NH₃ reaches 500 ppm, people will suffer from acute toxicity, eye pain, shortness of breath, and other symptoms, as well as the risk of asphyxiation [3,4]. In addition, NH₃ can be a marker gas for human diseases such as kidney, liver, or H. pylori infections [5], and NH₃ can be used for the early prevention of diseases and monitoring of the disease process via changes in the concentration of exhaled NH₃ in the human body [6].

A gas sensor is a sensitive device capable of converting the gas concentration that needs to be measured into an electrical signal. By analyzing the electrical signal, the sensor can obtain information such as the gas concentration present in the environment [7–9]. In recent decades, traditional commercialized NH₃ gas-sensitive materials have focused on metal oxide semiconductors (MOS) such as SnO₂, TiO₂, WO₃, ZnO, and other materials. Scientists have conducted many studies on them because they have high gas-response

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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/license s/by/4.0/). values [10]. However, most of the MOS-based NH₃ sensors operate at temperatures above 100 °C, and the higher operating temperature and their consumption of large amounts of energy limit their applications at room temperature and the flexible wearable applications of NH₃[11]. Therefore, the development of a sensing material that can realize the real-time and efficient detection of NH₃, which exhibits strong sensitivity and a rapid response and can work at room temperature, is urgently needed for production safety and human health [12].

Two-dimensional (2D) transition metal carbons and nitrides (MXenes) are emerging 2D materials with a graphene-like layered structure with the general formula M_{n+1}X_nT_x, where the "M" stands for the early transition metals, such as Ti, V, Ta element, etc.; the "X" is the C or N element; the "n" is 1, 2, or 3; and the "T" is the surface functional group, such as hydroxyl (-OH), oxygen (-O), fluorine (-F), chlorine (-Cl), and so on [13]. MXenes were first discovered by Prof. Yury Gogotsi in 2011 [14]. Their excellent electrical conductivity, large specific surface area, and rich surface functional groups that provide more active sites for gas adsorption and reaction have attracted widespread attention and led to their use in energy storage, photovoltaic devices, supercapacitors, and gas sensors [15–17]. Ti₃C₂T_x is one of the first and most extensively studied MXene materials [18]. It has been shown both theoretically and experimentally that Ti₃C₂T_x MXene has excellent NH₃ sensitivity at room temperature [19]. Density functional theory (DFT) calculations have shown that the -F, -O, and -OH groups on the surface of Ti₃C₂T_x MXene materials have high adsorption energies with NH₃. It was also shown that Ti₃C₂T_x MXene materials are effective at sensitizing gases to NH₃ [20,21].

However, it is the high adsorption energy between Ti₃C₂T_x MXene and NH₃ that also leads to the resistance drift and long recovery time from the NH₃ environment to the air. NH₃ sensors based on pure Ti₃C₂T_x MXene often exhibit poor selectivity, slow response and recovery times, and low response values [22,23]. So, in order to obtain an excellent NH₃-sensitive performance at room temperature, scientists have paid a lot of attention and conducted a lot of research focused on the choice of synthesis method, composite modification, and systematic sensitization mechanism of Ti₃C₂T_x MXene-based ammonia sensors.

In this context, this paper begins with Ti₃C₂T_× MXene synthesis methods, provides a classified overview of the most recent research progress in Ti₃C₂T_× MXene synthesis, which is primarily classified as HF etching, in situ HF etching and alkali solution etching, and summarizes the benefits and drawbacks of the various etching techniques. In addition, several types of composites, including metal–oxide semiconductors, conductive polymers, and 2D material composites, are briefly discussed in order to enhance the NH₃-sensitive behavior of NH₃ sensors based on pure Ti₃C₂T_× MXene. These Ti₃C₂T_× MXene composites are further analyzed to prove that the primary mechanisms of the enhanced NH₃-sensing performance of these sensors are the synergistic effects between the composites, such as the formation of a heterojunction of the composites, adsorption energy and charge transfer, chemical sensitization and electron sensitization, and the increase in specific surface area and adsorption sites due to their unique morphology [24,25].

Finally, this paper reviews the research progress regarding the sensitization mechanism of NH₃ sensors based on Ti₃C₂T_× MXene, then summarizes and discusses the two current sensitization mechanisms that can explain the p-type response of MXene to either electron acceptor or electron donor gases: (1) MXene is metallic in nature, and the number of carriers decreases and the electrical resistance increases after the gas adsorption. When they exhibit semiconductor properties, the charge transfer mechanism follows the Wock-enstein model [26–28]. (2) When the MXenes are exposed to the gas, the interlayer expansion hinders electron transfer and the resistance increases [16]. Finally, the paper summarizes the key challenges and potential paths forward for NH₃ sensors based on Ti₃C₂T_× MXene. We expect that this review will provide novel ideas for the development of high-performance, room-temperature Ti₃C₂T_× MXene NH₃ sensors.

2. Synthesis of Ti₃C₂T_x MXene

The majority of Ti₃C₂T_x MXene materials are produced by selectively etching the precursor MAX phase (a hexagonal layered structure with the common structural formula $M_{n+1}A_nX_n$, where the "n" = 1, 2, or 3; examples of such materials are Ti₂AlC, Ti₃AlC₂, Ti₂SiC, Ti₄AlN₃, etc.; the "A" is a group IIIA or IVA element [29,30]). The A atomic layer is more easily etched away during the reaction with the etchant, leaving a 2D layered structure with alternating M and X layers because the M-A bonds in the MAX phase are stronger than the M-X bonds in terms of bond strength.

The functional groups -OH, -O, and -F in the etching system are easily attached to the surface of this alternating layer structure, eventually forming a 2D layered structure, Ti₃C₂T_x MXene [31,32]. Ti₃AlC₂ is most used in the MAX phase, as shown in Figure 1, which presents a schematic diagram of the etching process of Ti₃AlC₂ by HF, where the Ti₃AlC₂ structure consists of a single Ti₃C₂ layer separated by Al atoms. The Al atom layers between the Ti₃AlC₂ layers are eliminated by the HF treatment, and the subsequent loss of metallic bonds causes the individual Ti₃Al₂C layers to separate, producing Ti₃C₂T_x. The reaction process is shown in Equations (1)–(3):

$$Ti_{3}AlC_{2} + 3HF = AlF_{3} + 3/2H_{2} + Ti_{3}C_{2}$$
(1)

$$Ti_{3}C_{2} + 2H_{2}O = Ti_{3}C_{2}(OH)_{2} + H_{2}$$
⁽²⁾

$$Ti_3C_2 + 2HF = Ti_3C_2F_2 + H_2$$
 (3)

The substitution of the -F functional group represented by Equation (3) is similar to that of -OH; therefore, its reaction mechanism can be considered to regard -OH in Figure 1 as -F.



Figure 1. Ti₃AlC₂ is etched as Ti₃C₂T_x. (a) Structural schematic diagram of Ti₃AlC₂, (b) schematic of the process by which -OH replaces Al atoms after HF treatment, and (c) hydrogen bond breaking and nanolayer separation after sonication treatment [14].

The different etching methods and the choice of etchant can change the types and ratios of the functional groups at the end of the Ti₃C₂T_x MXene material, thus affecting the adsorption behaviors of Ti₃C₂T_x MXene and NH₃ and influencing the NH₃-sensitive performance of the sensors. In the current study, most Ti₃C₂T_x-based NH₃-sensing materials are synthesized using HF etching and in situ HF etching. In addition, there are a small number of research papers that mention the alkaline solution etching method. Therefore,

this chapter will briefly describe these three etching methods and their effects on ammonia gas-sensing.

2.1. HF Etching

HF etching is a useful approach for preparing $Ti_3C_2T_x$ MXene, which can be created by etching the MAX phase. In 2011, Naguib et al. [14] prepared the first 2D Ti_3C_2 phase MXene by etching Ti_3AlC_2 powder with high concentrations of HF. Figure 2a shows an HFtreated SEM image of Ti_3AlC_2 , revealing that the $Ti_3C_2T_x$ basal plane is accordion-like with a fan-like dispersion. The energy band structure of the synthesized MXene (Ti_3C_2) terminated with the –OH and –F end groups was calculated, and the results displayed that the mechanism of the electrical conductivity of the Ti_3AlC_2 material changed from metallic to semiconducting after etching due to a change in its surface chemistry (Figure 2b). Due to the simplicity of the HF etching method, it remains one of the most commonly used etchants for synthesizing $Ti_3C_2T_x$ MXene.





The specific surface area of Ti₃C₂T_× MXene has a great influence on its gas-sensitive properties. The gas-sensitive properties can be improved by increasing the specific surface area of Ti₃C₂T_× Mxene through intercalation and layering. For the further intercalation and delamination of Ti₃C₂T_× obtained by HF etching, Lian et al. [33] reported a method involving 2D Ti₃C₂T_× nanosheets synthesized by intercalation and a delamination reaction in tetramethylammonium hydroxide (TMAOH) solution after dilute HF etching. They added a quantitative amount of Ti₃AlC₂ powder to a 5% concentrated HF solution, which was magnetically stirred at room temperature for 24 h. Then, the suspension was washed with deionized water until the pH of the supernatant was 5–6 and centrifuged. After that, the precipitate was put in a 25% solution of tetramethyl hydroxide (TMAOH) and

magnetically agitated for another 24 h to allow for more intercalation and delamination. Afterward, the precipitate was centrifuged to obtain the two-dimensional, less-layered Ti₃C₂T_x nanosheets. Figure 2c displays the XRD spectra of Ti₃AlC₂ and Ti₃C₂. After HF etching, the (104) diffraction peak of Ti₃AlC₂ at $2\theta \approx 39.1^{\circ}$ almost disappeared, which indicated that the Ti₃C₂ was completely stripped [34,35]. The SEM image of the Ti₃C₂ nanoflakes intercalated with TMAOH is shown in Figure 2d. A high level of delamination is indicated by the two-dimensional structure, semi-transparent, and wrinkled textures of the Ti₃C₂ nanoflakes. In future research, we can increase the specific surface area of Ti₃C₂T_x MXene-sensitive materials through the intercalation and delamination of Ti₃C₂T_x to increase the adsorption sites on the surface of the materials to promote their adsorption and gas reaction with ammonia molecules, ultimately aiming to achieve the purpose of improving the sensitivity of Ti₃C₂T_x MXene.

2.2. In-Situ HF Etching

Although the HF etching process is easy to operate, it has obvious disadvantages, such as a longer etching time and a more dangerous operation [36]. Furthermore, the $Ti_3C_2T_x$ MXene obtained by this process has more shortcomings: HF is dangerous to humans and the environment, and fluorine-containing functional groups are inert, degrading their properties. In 2014, Ghidiu et al. [37] presented a method to synthesize $Ti_3C_2T_x$ MXene by etching the Ti_3AlC_2 phase in situ with LiF and HCl solution. Specifically, LiF was added to a 6 M HCl solution and stirred to dissolve before slowly adding Ti_3AlC_2 powder and maintaining this at 40 °C for 45 h. After that, the mixture was washed until the pH of the supernatant was 6. The obtained deposit formed a clay-like paste, which was rolled between the roller mill's permeable membranes to produce pliable, freestanding thin films within a few minutes. When diluted, it can be applied as an ink to deposit or print MXene on various substrates.

During the reaction process, Li⁺ can spontaneously insert into the interlayer of Ti₃C₂T_x MXene, and due to the hydrophilicity of Ti₃C₂T_x MXene, water molecules can easily enter the interlayer, leading to a much larger lattice parameter for Ti₃C₂T_x MXenes obtained by LiF/HCl etching than for Ti₃C₂T_x MXenes obtained by HF etching. This process produces large-component monolayer Ti₃C₂T_x flakes with a high yield, large lateral size, and excellent quality. More importantly, using LiF and HCl to etch MAX avoids the use of concentrated HF, which is very corrosive and poisonous, while also reducing the nanoscale defects generated by direct etching with HF. Furthermore, the simplicity of this method contrasts with previous films produced through laborious insertion, layering, and filtration techniques [38]. It is noteworthy that MXenes can still be obtained when H₂SO₄ is used instead of HCl. However, fine-tuning the etching reagent might affect the surface chemistry or the intercalation ions, which needs more exploration. Currently, in situ etching by LiF and HCl solutions is widely used in the synthesis of Ti₃C₂T_x MXene materials.

Han et al. [39] compared the ammonia sensitivity of Ti₃C₂T_× MXene materials synthesized by HF etching and LiF/HCl etching. They found that the Ti₃C₂T_× materials prepared by the LiF/HCl etchant had better gas sensitivity than that of HF etchant. They could detect a wide range of NH₃ at room temperature with higher sensitivity and stability. The higher sensing performance of the Ti₃C₂T_× MXene materials obtained by the LiF/HCl etching method was analyzed to be due to the high ratio of -O and -OH functional groups on the surface of Ti₃C₂T_× materials prepared by this method.

2.3. Alkali Solution Etching

Yang et al. [40] improved the humidity and NH₃-sensing properties of organ-like $Ti_3C_2T_x$ MXene synthesized from HF solution via alkalization. Organ-like $Ti_3C_2T_x$ MXene is a class of $Ti_3C_2T_x$ MXene materials that can provide a fast pathway for charge and ion transfer, thereby preventing the reduction in specific surface area due to the restacking of layers. Firstly, $Ti_3C_2T_x$ MXene powder was prepared through HF acid etching using Ti_3AlC_2 and a 45 wt% HF solution. Subsequently, the obtained $Ti_3C_2T_x$ MXene powder was

put into a 5 M NaOH solution and subjected to continuous magnetic stirring at room temperature for 2 h, and the alkalized Ti₃C₂T_x powder was finally obtained. The alkali treatment embeds Na⁺ in the interlayer of Ti₃C₂T_x, which plays a crucial role in regulating water for humidity sensing. During stage 1 of Figure 3, several water molecules are coupled with a single Na⁺ ion, forming a stable [Na(H₂O)_m]⁺ cluster structure. Meanwhile, in stage 2 of Figure 3, the alkaline treatment enhances the N-Ti bonding sites due to the increased -O terminus, resulting in higher NH₃ adsorption. The alkalized Ti₃C₂T_x devices have an improved sensing performance for humidity and NH₃ compared to non-alkalized Ti₃C₂T_x, due to the embedding of Na⁺ and the higher oxygen-to-fluorine atomic number ratio ([O]/[F]), and have the opposite response signal.

Although there is no report on the synthesis of Ti₃C₂T_x MXene ammonia-sensitive materials using only alkali etching, this method allows for the preparation of Ti₃C₂T_x MXene with a large number of oxygen-containing functional groups, is simple to perform, and does not contain inert groups -F. Therefore, it is expected to be applicable to the synthesis of Ti₃C₂T_x MXene-based ammonia-sensitive materials in the future and to obtain sensitive materials with a strong ammonia-adsorption capacity.

Ti₃C₂T_× MXene synthesized by conventional fluoride-containing methods usually uses fluoride ion-containing solutions as an etchant, which is harmful to the environment. In addition, highly reactive fluoride ions can penetrate into the human body and cause fatal damage to body tissues [41,42]. It has been demonstrated that fluoride-based etching procedures generate a large number of -F-terminal functional groups [43,44], which substantially limit charge transfer and diminish chemically active sites, hence compromising the electrochemical characteristics of Ti₃C₂T_× MXene [45–47]. Therefore, modulating the terminal functional groups of Ti₃C₂T_× MXene can affect its electrochemical properties and NH₃ sensitivity [48]. Furthermore, the popular HF and LiF/HCl etching methods are typically time-consuming [49]. Therefore, it is important to develop environmentally friendly and F-free synthesis routes for NH₃ sensor-based Ti₃C₂T_× MXene in the future.



Figure 3. Adsorption process of H₂O and NH₃ molecules on the surface of alkalized Ti₃C₂T_x [40].

3. Ti₃C₂T_x MXene-Based Nanocomposites Material Gas Sensors for NH₃

Ti₃C₂T_× Mxenes are a typical new 2D material with high selectivity for ammonia at room temperature. Dillon, Lipatov et al. [35,50] measured the high electrical conductivity of Ti₃C₂T_× MXene to be 6500 S cm⁻¹ and 4600 ± 1100 S cm⁻¹. Halim et al. [51] have also reported that Ti₃C₂ films exhibit metal conductivity at a temperature of about 100 K. Ti₃C₂T_× MXenes is considered to have good application prospects for ammonia detection at room temperature due to its excellent electrical conductivity, unique structure, and the large number of adsorption sites provided by functional groups such as -O and -OH on the surface [52–54]. Due to the low response values, serious base-resistance drift, and poor stability of pure Ti₃C₂T_× MXenes when utilized as ammonia-sensing materials, it is essential to combine Ti₃C₂T_× MXene with other sensitive materials to enhance their sensing capabilities [25,55,56]. In this chapter, a brief overview will be provided of the most-researched methods of compositing several sensitive materials with Ti₃C₂T_× MXenes to improve their sensing performance. These methods include combining them with MOS materials, conductive polymer materials, and certain 2D materials.

3.1. Metal Oxide Modification

MOS materials such as TiO₂, SnO₂, In₂O₃, WO₃, and Ti₃C₂T_× MXene usually use synergistic effects such as the Fermi energy level effect (Fermi level bending, carrier separation, depletion layer regulation, and increase in interfacial barrier energy) between the composites, the formation of heterojunctions, and the specific morphology, etc., to enhance the gas-sensitive performance of the sensors [57–59]. In particular, for TiO₂/Ti₃C₂T_× MXene nanocomposites, in addition to the introduction of TiO₂ material in the matrix, due to the instability of Ti₃C₂T_× MXene, TiO₂can be synthesized through partial oxidization to Ti₃C₂T_× MXene, leading to in situ derivatization using techniques such as high-temperature sintering.

When a semiconductor material is irradiated by UV light whose optical energy is larger than its band gap, photocarrier pairs are generated at the interface of the sensitive material [60,61], and the additionally generated photogenerated electrons and holes can promote the adsorption and desorption processes and redox reactions of gases, thus improving the response value and shortening the response recovery time of the sensor [62,63]. Therefore, using the UV irradiation of gas sensors to obtain highly NH₃-sensitive Ti₃C₂T_× MXene-based sensors operating at room temperature is a feasible strategy.

To overcome the limitations of Ti₃C₂T_x MXene as a room-temperature ammonia gas sensor, such as limited its sensitivity and selectivity, Zhang et al. [64] proposed growing TiO₂ on Ti₃C₂T_× MXene in situ. They also utilized UV light (the light energy of the used 365 nm UV light source is 3.4 eV, which is larger than the band gap 1.6 eV of (001)TiO₂/Ti₃C₂T_x) to boost the performance of the (001) TiO₂/MXene heterostructure ammonia gas sensor. The Ti₃C₂T_x powder was prepared by removing the Al layer from MAX (Ti₃AlC₂) with a 50% HF solution. NaBF₄ (0.1 mol/L, 8 mL) was introduced as a control agent for the crystal surface in the HCl solution of Ti₃C₂T_x. The mixture was then hydrothermally treated at 160 °C for 8, 12, 16, and 32 h. The hydrothermal reaction promoted the formation of (001) planes during the crystal growth process, converting Ti in Ti₃C₂ into hydrated Ti3+ ions and binding F ions to the (001) planes with the aid of NaBF4 as an inducer. As shown in Figure 4a, the T-T-12 h TiO₂/MXene sensor that undergoes a hydrothermal reaction for 12 h is more sensitive to ammonia, with a lower detection limit than that of the pure Ti₃C₂T_x-based sensor, and also exhibits good durability in terms of its response/recovery time, repeatability, and selectivity. Analyzing the energy band diagram schematic of the T-T-12 h TiO₂/MXene-based sensor demonstrated in Figure 4c, it can be concluded that the enhanced gas-sensitive performance of NH₃ is obtained because Ti₃C₂T_x greatly facilitates the separation of electron-hole pairs by storing holes through the Schottky junctions formed at the interfaces with TiO_2 , which enhances the ammoniasensing performance. In Figure 4d, we can see that adding UV light to the highly active (001) crystalline TiO₂ makes the charge separation of the T-T-12 h TiO₂/MXene sensor when exposed to UV light even better, which leads to a better gas-sensing performance. Figure 4b also shows a two-fold increase in sensitivity compared to when UV is absent. The TiO₂/MXene sensor type T-T-12 h exhibited 34 times more sensitivity to 30 ppm of ammonia compared to pristine Ti₃C₂T_x. Density functional theory reveals that the (001) side of the TiO₂ and Ti₃C₂T_x composite has the greatest attraction in terms of ammonia adsorption [64].

To further improve the sensing performance of pure Ti₃C₂T_× MXene for NH₃, Kan et al. [65] combined surface-functionalized In₂O₃ nanotubes with Ti₃C₂T_x nanosheets. The composite was further loaded onto thermoplastic polyurethane (TPU) foam, a dual-functional sensing platform constructed based on Ti₃C₂T_x/In₂O₃ nanocompositesand modified TPU foam sensors. The produced nanocomposites exhibited an improved ammonia-sensing performance and pressure-sensitive properties, utilizing the strong synergistic effect of the sensing of In₂O₃ nanotubes and high conductivity of Ti₃C₂T_× nanoflakes, as well as the foam substrate's pressure-sensitive and gas-permeable capabilities. Ti₃C₂T_× nanoflakes are negatively charged on the surface due to the terminal functional groups such as -OH and -F. At this time, the modification of In₂O₃ with the cationic surfactant (3-aminopropyl) triethoxysilane (APTES) can make the surface of In₂O₃ positively charged, and the two can be compounded to obtain Ti₃C₂T_x/In₂O₃ composites via simple ultrasonication with electrostatic adsorption, which was shown to have higher NH₃ response values than pure Ti₃C₂T_× nanoflakes. In₂O₃ is an n-type sensing material, which has a bandgap in the range of 3.55–3.75 eV [66] and a work function of about 4.28 eV [67]; Ti₃C₂T_x MXene behaves as a p-type sensing material, which has a bandgap of 0.19 eV [68] and a work function of about 4.5 eV [69]. Two main factors are used to investigate the enhanced sensing ability: First, n-type In₂O₃ has a high Fermi energy level, and electrons will be transferred from the In_2O_3 nanotubes to the $Ti_3C_2T_x$ nanoflakes until the Fermi energy levels of the two reach equilibrium, thus forming a space charge layer at the Ti₃C₂T_x and In₂O₃ interface. At the same time, the energy bands at the interface are bent on both sides, generating a potential barrier that increases the base value resistance of the sensor, thus increasing the gas response. Second, the In₂O₃ nanotubes work as isolators to inhibit the re-stacking of Ti₃C₂T_× nanoflakes, thereby increasing the layer space and effectively facilitating the diffusion and permeation of gases in the sensing layer. In addition, the sensor achieves the flexible and interference-free detection of complex exhaled environments at room temperature, with a memory function for detecting NH³ gases down to 1 ppm, realizing the dualmode detection of NH3 gases.



Figure 4. (a) Dynamic response curves of TT8 h-, TT12 h-, TT16 h- and TT32 h-based sensors; (b) dynamic response curves with UV illumination on T-T-12 h and without UV illumination on TT12 h; (c) schematic illustration of band diagrams of $Ti_3C_2T_x$ and (001) TiO_2 ; (d) schematic illustration of ammonia gas-sensing mechanism under UV irradiation [64]. (e) The transient response curves of the composite sensors with different WO₃ contents to 1 ppm NH₃ at room temperature; (f) the

dependence of the composite sensor response on the WO₃ content; (g) schematic illustration of the gas-sensing mechanism and the energy band structure diagram of Ti₃C₂T_x/WO₃ before and after exposed NH₃ [70].

To address the limited sensitivity of Ti₃C₂T_× MXene gas sensors, Guo et al. [70] reported a Ti₃C₂T_×/WO₃ composite resistive sensor that had excellent NH₃ sensitivity at room temperature. Ti₃C₂T_×/WO₃ composites with WO₃ nanoparticles anchored on Ti₃C₂T_× nanosheets were prepared using an ultrasonic technique. As demonstrated in Figure 4e, f, the detection sensitivity of the Ti₃C₂T_×/WO₃-50% sensor was up to 22.3%, which was 15.4 times higher than that of the pure Ti₃C₂T_× sensor, at 1 ppm NH₃ at room temperature. The improved NH₃-sensing performance is mainly attributed to the increase in the aspect ratio of the composite, the increase in the active sites provided by WO₃, and the more effective charge transfer bestowed by the formed heterojunction (Figure 4g). It was demonstrated that the Ti₃C₂T_×/WO₃-50% sensor remained effective over a wide range of relative humidity (RH) conditions (3.5% ~ 72.9% RH), and low concentrations of NH₃ sensing gradually decreases. Humidity compensation methods, which are often used in practical applications, can help to solve the humidity effect's limitations.

Table 1 outlines the gas-sensitive properties of different MOS/Ti₃C₂T_x MXene composites towards NH₃ at room temperature in recent years. The acronym "LOD" in the table refers to "the limit of detection".

Materials	Concentration (ppm)	Response Value (R₄/R₅, R₅/R₄) or Response Rate [(∆R/R₅) × 100%]	LoD	Response/Recover y Time (s)	Ref./Year
NiO/Ti3C2Tx	50	6.13	10 ppm	60/19	[71]/2023
Ti3C2Tx/In2O3	30	63.8%	2 ppm	42/209	[57]/2022
TiO ₂ /Ti ₃ C ₂ T _x	10	3.1%	0.5 ppm	33/277	[22]/2019
Ti ₃ C ₂ T _x /WO ₃	1	22.3%	1 ppm	119/228	[70]/2021
Ti ₃ C ₂ T _x /CuO	5	46.7%	5 ppm	12/25	[72]/2023
ZnO/Ti ₃ C ₂ T _x	20	39.16%	89.41 ppb	92/104	[58]/2023
In2O3/Ti3C2Tx	5	60.6%	5 ppm	3/2	[73]/2022
Ti3C2Tx/ZnO	50	196%	1 ppm	119/307	[74]/2023
Ti ₃ C ₂ T _x /TiO ₂	30	40.6%	5 ppm	10/5	[64]/2022
Ti ₃ C ₂ T _x /SnO ₂	50	40%	0.5 ppm	36/44	[68]/2021
Ti ₃ C ₂ T _x /SnO	10	67%	1 ppm	61/119	[75]/2022
Ti3C2Tx/TiO2/CuO	100	56.9%	10 ppm	75/80	[54]/2023
α -Fe ₂ O ₃ /Ti ₃ C ₂ T _x	5	18.3%	5 ppm	2.5/2	[76]/2022

Table 1. The gas-sensitive properties of various MOS/Ti₃C₂T_x MXene nanocomposites to NH₃ at room temperature.

3.2. Conductive Polymer Addition

Conducting polymers, such as polyaniline (PANI), polypyrrole (PPy), polydioxothiophene (PEDOT), and their derivatives, possess the advantages of high flexibility, the ability to work at room temperature, and a high response to ammonia. As a result, they are receiving increasing attention for their use in NH₃ sensing at room temperature [77,78]. To address the issues of Ti₃C₂T_× MXene resistance drift, the long recovery time, the low response value, and susceptibility to mechanical deformation, it has been proposed to hybridize Ti₃C₂T_× MXene with conductive polymers. This approach aims to enhance the sensitivity and wearable performance at room temperature of Ti₃C₂T_× MXene through the heterojunctions formed between the two materials and the high flexibility of the conducting polymers [79,80].

Polyaniline (PANI) has been widely used in room-temperature ammonia sensors due to its strong electrical conductivity, superior selectivity to ammonia, and room-temperature workability [81,82]. Yang et al. [82] used electrostatic spinning to combine polyaniline with Ti₃C₂T_x nanosheets to construct polyaniline/Ti₃C₂T_x composite nanofibers with excellent ammonia responsiveness for room-temperature flexible ammonia sensors. The SEM image in Figure 5a demonstrates that the synthesized Ti₃C₂T_x exhibits a distinct layer structure, and the Tyndall phenomenon can be seen in the inset. Figure 5b is an SEM image of PANI/Ti₃C₂T_x, which reveals a 3D network fiber structure with random fiber orientation. Figure 5c shows that the PANI/Ti₃C₂T_x flexible sensor has a greater NH₃-sensing response at 25 °C (2.3 times the response value at 20 ppm compared to pure PANI), with good selectivity, repeatability, and long-term stability. Figure 5f demonstrates that by adjusting the bending angle $(0^{\circ}-150^{\circ})$ and the number of bending times (up to 3200), a high sensing performance at 20 ppm NH₃ and enduring flexible bending stability can be attained. PANI is a conductive p-type semiconductor with a band gap of about 2.47 eV [83]; the resistance of the pure Ti₃C₂T_x sensor, exhibiting a metallic nature, was tested to be about 24 Ω [79], and the Ti₃C₂T_x band gap was reviewed in the literature to be about 0.19 eV [68]. In the UPS results of the composites in Figure 5d,e, the figures of merit for $Ti_3C_2T_*$ and PANI/Ti₃C₂T_× composite nanofibers are 2.99 eV and 3.44 eV, respectively (UV is He I, 21.22 eV). Therefore, the formation of the Schottky junction at the interface between Ti₃C₂T_x and PANI enhances the resistance modulation of the flexible sensor. The gas sensitivity of the PANI/Ti₃C₂T_× flexible sensor was shown to be enhanced because the composite of the PANI and Ti₃C₂T_x nanosheets constitutes a Schottky junction, the degree of PANI protonation is increased, and the two are hybridized to form a special three-dimensional reticulated fibrous structure, which has great potential for the construction of flexible ammonia gas sensors.

In addition, electrostatic spinning has been widely used in conductive polymer sensors as an easy, efficient, low-cost nanofiber preparation technique. Compared with the traditional synthesis method, the electrostatic spinning method can greatly increase nanomaterials' specific surface area volume ratio [84]. By integrating polymers with nanofiber structures into resistive gas sensors, porous materials with a high surface area and large porosity can be prepared to enhance the adsorption of ammonia molecules by the sensors and improve the sensitivity of the sensors, as well as to further optimize the properties of the polymer-sensitive materials, such as their hydrophobicity, conductivity, and flexibility [85,86]. In addition, these sensors also showed fast response and recovery times. Zhang synthesized polyaniline and polymethyl methacrylate (PMMA) nanocomposite fibers using electrostatic spinning [87]. This sensitive material was shown to have a fast response and high sensitivity to NH3, with a sensitivity of 4.5% to 5 ppm NH3 and a response/recovery time of about 5 s/12 s. On this basis, through the composite of different conductive polymer materials and Ti₃C₂T_x MXene, as well as the optimization of the electrostatic spinning process conditions, the development of NH₃-sensitive materials with a high sensing performance is expected. This is essential for further optimizing the ammonia sensor performance of the conducting polymer/Ti₃C₂T_x MXene composites.

Poly (3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) has attracted a lot of attention in the field of gas sensing because of its good electrical conductivity, low bandgap, environmental friendliness, capacity to detect dangerous chemicals at low operating temperatures [88–91], and environmental stability [92,93]. Jin et al. [94] created PEDOT:PSS/Ti₃C₂T_× MXene composites by combining 3,4-ethylenedioxythiophene (PE-DOT) and poly (4-styrenesulfonate) (PSS) on a Ti₃C₂T_× MXene material on a polyimide (PI) substrate through in situ polymerization. Figure 5g,h show the SEM images of Ti₃C₂T_× MXene and PEDOT:PSS/Ti₃C₂T_× MXene composites, respectively, where the Ti₃C₂T_× exhibits a monolayered or few-layered lamellar structure after the introduction of the PE-DOT:PSS, where the surface of Ti₃C₂T_× MXene is covered by micro- and submicrometer PEDOT:PSS plates. Comparing Figure 5i,j reveals that the introduction of PEDOT:PSS increases the gap between the layers of the composite material. The gas sensitivity of NH₃ achieved the highest response value (Figure 5k) when Ti₃C₂T_x MXene contained 15 wt% and the fastest recovery/response with 36.6% response to 100 ppm NH₃ at room temperature, a 116 s response time, and a 40 s recovery time. Furthermore, Figure 5l shows a bending test of the sensor at a maximum angle of 240°, and the gas response of the device does not change with the change in the bending angle, indicating that it has good mechanical stability.



Figure 5. (a) SEM image of Ti₃C₂T_× MXene; (b) SEM image of PANI/Ti₃C₂T_×; (c) PANI/Ti₃C₂T_× composite nanofiber sensor for the detection of NH₃ at room temperature; (d) UPS spectra of pure Ti₃C₂T_× sensor and (e) PANI/Ti₃C₂T_× composite sensors; (f) the PANI/Ti₃C₂T_×-based flexible sensor bent at different angles [82]. FESEM images of (g) Ti₃C₂T_× MXene (inset is Ti₃C₂T_× MXene on an AAO membrane) and (h) PEDOT:PSS/Ti₃C₂T_× MXene composites. The cross-sectional FESEM images of (i) Ti₃C₂T_× MXene films and (j) PEDOT:PSS/Ti₃C₂T_× MXene films, (k) effect of the Ti₃C₂T_× MXene content in PEDOT-PSS on the sensor response toward 100 ppm NH₃ at room temperature (27 °C), and (l) gas response of the PEDOT:PSS/Ti₃C₂T_× MXene composite-based sensor against 100 ppm NH₃ bent at different angles [94].

The mechanism for analyzing the gas-sensitive performance enhancement of the PE-DOT:PSS/Ti₃C₂T_× MXene composite mainly involves the redox reaction between the composite and the analyte, the charge transfer between the composite and the analyte, and synergistic effect of the increase in the specific surface area of the composite materials. Compared with pure PEDOT:PSS and Ti₃C₂T_× MXene-based sensors, the composite sensors have a high gas response, fast response/recovery, a low detection limit, good reproducibility, high selectivity, and excellent mechanical stability. A number of studies have demonstrated that the NH₃ sensors prepared from Ti₃C₂T_× MXene and conductive polymer hybrid materials have a low detection limit, flexibility, and an excellent sensing performance [95].

Table 2 outlines the gas-sensing properties of different conductive polymer $/Ti_3C_2T_x$ MXene composites towards NH₃ at room temperature that were determined in recent years.

Table 2. The gas-sensitive properties of various conductive polymer/Ti₃C₂T_x MXene nanocomposites to NH₃ at room temperature.

Materials	Concentration (ppm)	Response Value (R₄/Rg, Rg/R₄) or Response Rate [(ΔR/Rg) × 100%]	LoD	Response/Recovery Time (s)	Ref./Year
PANI/Ti3C2Tx	10	1.6	25 ppb	—	[79]/2020
PANI:PSS/Ti3C2Tx	1	57%	20 ppb	276/388	[80]/2023

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20	55.9%	5 ppm	—	[82]/2023
10	13%	10 ppm	—	[96]/2022
10	2.3	20 ppb	266/342	[24]/2023
200	4.7%	—	12.7/14.6	[97]/2020
100	31.9%	5 ppm	38/383	[98]/2022
100	36.6%	10 ppm	116/40	[94]/2020
0.5	2.2%	500 ppb	—	[99]/2022
	20 10 10 200 100 100 0.5	$\begin{array}{cccc} 20 & 55.9\% \\ 10 & 13\% \\ 10 & 2.3 \\ 200 & 4.7\% \\ 100 & 31.9\% \\ 100 & 36.6\% \\ 0.5 & 2.2\% \end{array}$	20 55.9% 5 ppm 10 13% 10 ppm 10 2.3 20 ppb 200 4.7% - 100 31.9% 5 ppm 100 36.6% 10 ppm 0.5 2.2% 500 ppb	20 55.9% 5 ppm - 10 13% 10 ppm - 10 2.3 20 ppb 266/342 200 4.7% - 12.7/14.6 100 31.9% 5 ppm 38/383 100 36.6% 10 ppm 116/40 0.5 2.2% 500 ppb -

3.3. Other 2D Material Hybrids

In addition to MXene, graphene, as well as various emerging 2D materials such as transition metal disulfide compounds (TMDs), reduced graphene oxide (rGO), and black phosphorus (BP), have been rapidly developed for NH₃-sensing due to their graphenelike layered structure, large specific surface area, semiconducting properties, and room-temperature operation. It has been demonstrated that the heterojunction constructed by compositing Ti₃C₂T_x MXenes with these 2D materials can obtain complementary electrical and adsorption properties, which enhances their sensing performance [95].

It has been demonstrated that when MXenes are combined with TMDs, such as molybdenum disulfide (MoS₂), tin disulfide (SnS₂), tungsten disulfide (WS₂), and other transition metal disulfide compounds, their charge transfer and adsorption abilities are enhanced, which leads to better sensing effects [100,101]. In addition, the composite of TMDs and MXene has almost no lattice mismatch [102], and is expected to replace the traditional metal oxide composite with MXene to construct high-performance ammonia gas-sensitive materials [103,104]. In order to overcome the difficulty of detecting ultra-low concentrations of ammonia at room temperature in chemical-based gas sensors, He et al. [56] developed an MXene/SnS₂ heterojunction-type chemoresistive sensor SM-5 (the nominal weight ratio of MXene/SnS is 1:5), as shown in Figure 6a,b, which exhibits an excellent gas-sensitive performance for ammonia at sub-ppm at room temperature. The SM-5 sensor can detect NH₃ concentrations of as low as 10 ppb at room temperature. In addition, Figure 6c shows the excellent long-term stability of the sensor, with a decrease in response value of about 3.4% in 20 days. Meanwhile, the SM-5 sensor showed good selectivity to a wide range of possible interfering gases, such as HCHO, C2H5OH, CH3OH, C3H6O, C6H6, and NO2. The sensing mechanism of the MXene/SnS2-based sensor is closely related to the formation of heterostructures. DFT calculations show that the higher sensitivity and selectivity may be due to the more effective charge transfer bestowed by the formed heterostructure, the better catalytical activity, and the stronger NH₃ adsorption of the formed MXene/SnS₂ composite material.

Our group [30] demonstrated a Ti₃C₂T_x MXene@TiO₂/MoS₂ nanocomposite gas sensor, which successfully realized the detection of 500 ppb NH₃ at room temperature. MoS₂ nanosheets were grown in situ on the etched Ti3C2Tx MXene material via the hydrothermal method, and then some of the Ti₃C₂T_x MXene was converted into rectangular TiO₂ particles through hydrothermal reaction. The SEM images of Ti3C2Tx MXene@TiO2/MoS2 at different scales are shown in Figure 6e; it can be observed that rectangular TiO₂ nanoparticles are attached between the layers of the material and on the surface, which increase the spacing of the layers of the composite material and can provide more reaction sites for the target gas. As shown in Figure 6f, this novel gas sensor (MTM-0.2) based on a layered structure exhibits the advantages of a fast response and high stability in detecting NH₃. At 100 ppm ammonia, the composite gas sensor had 1.79 and 2.75 times higher response values than the pristine Ti₃C₂T_× MXene and MoS₂. Furthermore, at room temperature, the Ti₃C₂T_x MXene@TiO₂/MoS₂ nanocomposite gas sensor exhibited high selectivity for triethylamine, trimethylamine, n-butanol, acetone, formaldehyde, and nitrogen dioxide. As shown in Figure 6g, MoS² is an n-type sensing material, which has a bandgap in the range of 1.2–1.9 eV [105] and a work function of about 3.9 eV [106]. Ti₃C₂T_× MXene behaves as a p-type sensing material, which has a bandgap of 0.19 eV [68] and a work function of about 4.5 eV [69]. The heterojunction of the p-type Ti₃C₂T_× MXene and n-type MoS₂ was the primary reason for the sensor's improved gas-sensitive performance for NH₃. Bader charge analysis can further obtain the adsorption between sensitive materials and gases by evaluating the amount of charge transfer between gas molecules and sensitive material models [107]. Bader analysis further confirmed that ammonia molecules increase charge transfer in the heterojunction, which enhances the interaction of Ti₃C₂T_× MXene@TiO₂/MoS₂ nanocomposites with ammonia.



Figure 6. The resistance variation curves of the SM-5 sensor to (**a**) ppm-level NH₃ concentration from 2 to 100 ppm and (**b**) ppb-level NH₃ concentration from 10 ppb to 1 ppm at 18 °C; (**c**) the long-term stability of the SM-5 sensor to 1 ppm NH₃ for 20 days [56]. (**d**,**e**) Ti₃C₂T_× MXene@TiO₂/MoS₂; (**f**) dynamic sensing performance of the sensor-based Ti₃C₂T_× MXene to NH₃ at a room temperature of 27 °C and an RH of 43%; (**g**) energy band diagrams of Ti₃C₂T_× MXene@TiO₂/MoS₂ sensors [30].

Graphene fibers (GFs) have a high mechanical flexibility, electrical conductivity, and wear ability and have enormous potential for application in wearable electronic devices [108,109]. Lee et al. [19] reported a simple, scalable, and effective strategy for wet-spinning MXene/graphene-based hybrid fibers using a wet-spinning process to obtain metal-free binder Ti₃C₂T_x MXene/graphene hybrid fibers. These hybrid fibers have excellent mechanical and electrical properties, making them suitable for flexible, wearable gas sensors. The synergistic effect of the electronic properties and gas adsorption capacity of MXene/graphene resulted in a high NH₃ gas sensitivity at room temperature. Figure 7a compares the response values of MXene, rGO fiber, and MXene/rGO fiber sensors, and shows that the Ti₃C₂T_x MXene/graphene hybrid fiber exhibited a significantly improved NH₃-sensing response ($\Delta R/R_0 = 6.77\%$). The hybrid fiber exhibits excellent mechanical flexibility. Figure 7b depicts a schematic diagram of the device used to detect the stability of the fiber optic sensor by bending it repeatedly and detecting the change in the resistance of the sensor. As shown in Figure 7c, the resistance fluctuation remains small, ±0.2%, even after more than 2000 bends. In addition, the highly flexible MXene/rGO hybrid fiber was woven/knitted into the lab coat using a simple conventional weaving procedure, demonstrating a dependable sensing capability. The synergistic effect of the optimized bandgap and the enhanced atomic oxygen content at the MXene end of the MXene/rGO hybrid fiber significantly improved the NH3-sensing response performance of the MXene/rGO hybrid fiber with low power consumption.



Figure 7. (a) Comparison of the gas response of MXene film, rGO fiber, and MXene/rGO hybrid fiber; (b) schematic illustration of the fiber bending test. The "M" stands for multimeter. (c) Cyclic bending fatigue versus resistance difference of the rGO fiber and MXene/rGO hybrid fiber [19]. (d) FE-SEM images of Ti₃C₂T_x MXene/GO/CuO/ZnO nanocomposite and (e) pristine Ti₃C₂T_x Mxene. (f) Schematic diagram of the energy band structure of the Ti₃C₂T_x MXene/GO/CuO/ZnO heterostructure [25].

Yotsarayuth et al. [25] successfully synthesized Ti₃C₂T_x Mxene/GO/CuO/ZnO nanocomposites by mixing common NH3-sensing materials such as graphene oxide (GO), copper oxide (CuO), and zinc oxide (ZnO) into Ti₃C₂T_x Mxene via a simple and low-cost hydrothermal method. Figure 7d shows the SEM images of the composites, and the Ti₃C₂T_x Mxene/GO/CuO/ZnO nanocomposites exhibit a highly uniform two-dimensional stacked structure. A comparison with the SEM image of pure Ti₃C₂T_x MXene in Figure 7e reveals that the composites have a high surface roughness, which enhances the active sites for the adsorption of NH3 gas molecules. Figure 7f depicts Ti3C2Tx MXene, GO, CuO, and ZnO figures of work functions of 4.35, 4.78, 4.7, and 5.14 eV [19,110–112], respectively, with Ti₃C₂T_× MXene having the lowest figure of work function. As a result, electrons are transferred from Ti₃C₂T_x MXene to the other three materials to achieve Fermi energy level equilibrium, forming multiple p-n heterojunctions at the interfaces of the different materials. Ti₃C₂T_× MXene/GO/CuO/ZnO exhibits a 59.9% response to 100 ppm NH₃ at room temperature, with a response time of 26 s and a recovery time of 25 s. The $Ti_3C_2T_x$ MXene/GO/CuO/ZnO exhibits excellent selectivity, high responsiveness, good repeatability, strong stability, a quick response recovery time, and humidity independence. The Ti₃C₂T_x MXene/GO/CuO/ZnO gas sensor exhibits a remarkable NH₃-sensing performance. This is because of the inherent features and properties of the nanocomposites, including their functional groups, their bonding, the strong intermolecular attraction between NH3 molecules, the nanocomposites, and the formation of a p-n heterojunction.

Table 3 outlines the gas-sensitive properties of different 2D materials/Ti₃C₂T_× MXene composites towards NH₃ at room temperature in recent years.

Table 3. The gas-sensitive properties of various 2D material $/Ti_3C_2T_x$ MXene nanocomposites to NH₃ at room temperature.

Materials	Concentration (ppm)	Response Value (R₄/R₅, R₅/R₄) or Response Rate [(ΔR/R₅) × 100%]	LoD	Response/Recovery Time (s)	Ref./Year
Ti ₃ C ₂ T _x @TiO ₂ /MoS ₂	100	163.3%	500 ppb	117/88	[30]/2022
Ti ₃ C ₂ T _x /SnS ₂	10	42.9%	10 ppb	161/80	[56]/2023

Ti ₃ C ₂ T _x /rGO	50	6.77%	10 ppm	_	[19]/2020
Ti3C2Tx/GO/CuO/ZnO	100	59.9%	4.1 ppm	26/25	[25]/2023
Ti ₃ C ₂ T _x /MoS ₂	100	81.7%	200 ppb	3/—	[110]/2022
Ti ₃ C ₂ T _x /TiO ₂ /graphene	50	36.8%	22.23 ppb	19/29	[113]/2024
SnS/Ti ₃ C ₂ T _x	5	1.031	250 ppb	7/—	[114]/2022

4. Ti₃C₂T_x MXenes-Based Nanocomposite Material Mechanism for NH₃

The unique properties of terminating functional groups on the surface of MXenes make them ideal for ammonia-sensitive materials. Bhardwaj et al. [115] found that the effective adsorption energy of Ti₂CO₂ with NH₃ was –0.37 eV using DFT calculations, and the charge transfer between monolayer Ti₂CO₂, which has a similar structure to that of Ti₃C₂O₂ and NH₃, was 0.174 e. Similarly, Atkare et al. [95] discovered that MXenes, including monolayers of Ti₃C₂O₂, Ti₂C(OH)₂, and others, exhibit a significant affinity to NH₃, resulting in a charge transfer of 0.117 e.

At room temperature, the reaction mechanism of $Ti_3C_2T_x$ MXene to NH₃ molecules can consist of two parts: the reaction between NH₃ molecules and oxygen molecules on the surface of the sensitive material and the reaction between NH₃ molecules and specific functional groups at the end of $Ti_3C_2T_x$ MXene [18,57]. First, the adsorption of O₂ molecules on the surface of the sensitive material traps electrons in the form of oxygen ions, mainly in the form of O². When the sensor is exposed to a reducing gas such as NH₃, the O²⁻ will react with the NH₃ molecules to form NO and H₂O while releasing electrons. The resistance decreases when these electrons return to the conduction band of $Ti_3C_2T_x$ MXene and its composites. The reaction process is shown in Equations (4)–(6):

$$O_2 (gas) \rightarrow O_2 (ads)$$
 (4)

$$O_2(ads) + e^- \to O_2^- \tag{5}$$

$$4NH_3 + O_2^- \to 4NO + 6H_2O + 5e^- \tag{6}$$

The gas-sensing mechanism of $Ti_3C_2T_*/In_2O_3$ composites to NH₃ shown in Figure 8b can be used as a reference. In addition to the electron transfer process between oxygen ions and NH₃ molecules on the surface of $Ti_3C_2T_*$ MXene-sensitive materials, Lee et al. [57] mentioned that the reaction of -O and -OH on the surface of $Ti_3C_2T_*$ with NH₃ resulted in hole–electron complexation and a subsequent increase in resistance, and the conjectured mechanism diagram is shown in Figure 8a. The reaction formulae are shown in Equations (7) and (8) as follows:

$$2NH_3 + 30^- \to N_2 + 3H_20 + 3e^-$$
(7)

$$\mathrm{NH}_3 + \mathrm{OH}^- \to \mathrm{NH}_2 + \mathrm{H}_2\mathrm{O} + \mathrm{e}^- \tag{8}$$



Figure 8. (a) Schematic diagram of the possible gas-sensing mechanisms of the Ti₃C₂T_x MXene for NH₃ [18]. (b) The gas-sensing mechanism diagram of the Ti₃C₂T_x/In₂O₃ composite materials. (c,d) Schematic diagram of the electron transfer at the interface of Ti₃C₂T_x/In₂O₃ composite materials in the air and NH₃ [57].

The mechanism for the enhanced gas sensitivity of Ti₃C₂T_x MXene composite materials to NH₃ is generally achieved by the synergistic effect between the two materials, such as the formation of a heterojunction of the composites, adsorption energy and charge transfer, chemical sensitization and electron sensitization, unique morphology, etc. [11,61]. When heterojunctions are formed, the gap in the work function between Ti₃C₂T_x MXene and its composite material causes electrons to transfer directionally from the lower to the higher work function. This transfer occurs due to the equilibrium of the Fermi energy levels when the materials come into contact with each other. This results in the formation of an electron depletion layer and an electron accumulation layer on the low-work-function material. The electron accumulation layer promotes oxygen adsorption on the surface of the sensing material. In contrast, the electron depletion layer increases the potential energy barrier at the interface, while the height of the intergranular barrier hinders the transport of carriers, resulting in an increase in the initial resistance [116] and a higher gas response. As an illustration, Zhou et al. [57] synthesized Ti₃C₂T_x/In₂O₃ nanocomposites. In₂O₃ is classified as an n-type semiconductor, while Ti₃C₂T_x is regarded as a metallic phase because of its excellent conductivity. When Ti₃C₂T_× comes into contact with In₂O₃, it exhibits a high work function. As a result, electrons migrate from In₂O₃ to Ti₃C₂T_x, forming a Schottky barrier and a depletion layer at the interface of In₂O₃ and Ti₃C₂T_x (as shown in Figure 8c,d). As a result, the charge transfer is blocked, and the base-value resistance of Ti₃C₂T_x/In₂O₃ becomes high in the air, resulting in a significant increase in the gas-sensitive response [22]. In addition, the improved gas-sensitive performance of the sensitive material is also related to its lattice mismatch, and the oxygen vacancies generated at the heterojunction due to the lattice mismatch will also provide additional active sites for the sensitive material [117].

The most significant characteristic of MXenes is their demonstration of similar metallic properties to their precursor MAX, with a fixed electron density near the Fermi energy level. In fact, the gas-sensing mechanism of MXene is notably more complex than the classical charge transfer model [95]. Lee et al. [18] were the first to report the gas-sensing mechanism of Ti₃C₂T_x MXene. They observed increased resistance in Ti₃C₂T_x sensors when exposed to four electron donor gases (ethanol, methanol, acetone, and ammonia). Conversely, the resistance of $Ti_3C_2T_x$ films decreased without the presence of these gases. Therefore, they inferred that $Ti_3C_2T_x$ films exhibit p-type sensing behavior. The analysis suggests that the p-type semiconductor nature of $Ti_3C_2T_x$ MXene may be due to the many molecules introduced during the Al etching process acting as p-type dopants to $Ti_3C_2T_x$, such as water and oxygen.

It is well known that gas sensors for semiconductor materials exhibit either a positive or negative resistance change depending on the gas type [118]. Specifically, an n-type semiconductor-sensitive material exposed to oxidizing gases decreases in resistance due to the loss of electrons and increases due to the gain in electrons when exposed to reducing gases, and the opposite is true for p-type semiconductor-sensitive materials. In contrast, Kim et al. [118] found that Ti₃C₂T_x exhibits a positive resistance change under oxidized or reduced gas conditions, indicating that the carrier transport of Ti₃C₂T_x will be blocked when it adsorbs gases. In other words, the sensing mechanism of Ti₃C₂T_× is different from that of semiconductor materials such as metal oxides. Therefore, the mechanism for the universal p-type response of Ti₃C₂T_x was proposed. Due to the metallic conductivity of Ti₃C₂T_× MXene [119], the gas adsorption reduces the number of carriers and therefore increases the channel resistance. While Koh et al. [120] investigated the effect of the interlayer swelling of Ti₃C₂T_x MXene films upon gas action on the gas-sensitive properties, the change in the interlayer space of Ti₃C₂T_x MXene upon the introduction of gas was studied by in situ XRD measurements, which found that the degree of swelling of Ti₃C₂T_× MXene films was consistent with the gas response. Therefore, another mechanism is proposed: gas-phase molecules are inserted into the MXene interlayer instead of surface adsorption, and the interlayer expansion induced to reduce the conductivity due to the metallic nature of Ti₃C₂T_x MXene is one of the reasons why MXene generally exhibits a p-type response to various gases.

Both mechanisms currently explain MXene's p-type response to the electron acceptor gas and the electron donor gas. To date, the gas-sensing mechanism of $Ti_3C_2T_x$ MXene and its composites has not been explained in a unified manner. The electron transfer model of the adsorbed gas molecules on the surface of $Ti_3C_2T_x$ composites may be more complex than reported and thus needs to be further developed and refined through experimental validation.

5. Conclusion and Outlook

Ti₃C₂T_× MXene, as the earliest discovered MXene material, which has been extensively studied in the field of ammonia gas sensing, has been regarded as an excellent room-temperature NH₃-sensing material due to its graphene-like two-dimensional lamellar structure, which confers a large specific surface area, good room-temperature sensitivity, and a high adsorption capacity between its surface-rich functional groups and NH₃. This review describes the current research progress in modulating the ammonia gas-sensing properties of Ti₃C₂T_× MXene by means of its preparation method and composite modification. Ti₃C₂T_× MXene with differences in its morphology, surface functional groups, electrochemical properties, nano-defects, and stability can be obtained through improvements in the preparation method to achieve the desired performance, which in turn affects the NH₃-sensing behavior of the sensors. Ti₃C₂T_× MXene-based composites incorporating additional composites can demonstrate enhanced response values, lower detection limits, quicker response recovery, and an improved stability compared to pure Ti₃C₂T_× MXene.

Although significant progress has been made in the design and modification of Ti₃C₂T_x MXene materials for ammonia gas sensors in recent years, there are still many challenges and much room for further development in optimizing and improving the sensing performance. Since the gas-sensing mechanism of MXenes is much more complex than the traditional semiconductor classical charge-transfer model, further calculations and investigations regarding the charge transfer and adsorption–desorption are needed in terms of the NH₃-sensing principle of Ti₃C₂T_x MXene. Meanwhile, a large number of

studies have demonstrated that the surface-functional groups of $Ti_3C_2T_x$ MXene have a significant effect on its electrochemical properties and stability. Therefore, synthesizing $Ti_3C_2T_x$ MXene materials with controllable surface-functional groups is significant for its application in room-temperature ammonia gas sensors. Furthermore, $Ti_3C_2T_x$ MXene's composite structure can be further optimized to improve its NH₃-sensing performance. In the next step, we could design $Ti_3C_2T_x$ MXene sensors with excellent long-term stability and a response value that is less impacted by humidity to widen their applications. In the future, we should broaden our research on $Ti_3C_2T_x$ MXene in these fields to develop higher-performance $Ti_3C_2T_x$ MXene-based room-temperature ammonia sensors.

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