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# Research status of gas sensing performance of Ti<sub>3</sub>C<sub>2</sub>Tx-based gas sensors: A mini review

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Developing efficient gas sensing materials capable of sensitive, fast, stable, and selective detection is a requisite in the field of indoor gas environment monitoring. In recent years, metal carbides/nitrides (MXenes) have attracted attention in the field of gas sensing because of their high specific surface area, good electrical conductivity, and high hydrophilicity.  $Ti_3C_2Tx$ , the first synthesised MXene material, has also become the most popular MXene material owing to its low formation energy. In this paper, the latest progress in the application of  $Ti_3C_2Tx$ -based nanomaterials in the field of gas sensors are discussed, and possible solutions are proposed, focusing on the use of composite materials to improve their sensing performance for the detection of gaseous volatile organic compounds. This study highlights the application prospects of  $Ti_3C_2Tx$  nanomaterials in gas sensors.

#### KEYWORDS

 ${\rm Ti}_3C_2Tx,$  volatile organic compounds (VOCs) gases, composite materials, surface functionalization, sensing performance

# Introduction

In recent years, with the acceleration of urbanization, the content of volatile organic compounds (VOCs) such as toluene ( $C_7H_8$ ), formaldehyde (HCHO), ethanol ( $C_2H_5OH$ ), and acetone ( $C_3H_6O$ ) in the air has risen rapidly. Subsidence to form ground-level ozone endangers human health (Malakar et al., 2017; Maung et al., 2022; Mozaffar et al., 2020; Yue et al., 2021); the effects and exposure limits are presented in Table 1. Therefore, all sectors of society have focused on the use of gas sensors to monitor toxic and harmful gases in indoor and outdoor environments, where gas monitoring is widely adopted in industrial manufacturing and disease diagnosis (Chaudhary et al., 2022; Chen et al., 2020a; Wang et al., 2022a). Researchers have combined metal oxides (Hu et al., 2021; Peng et al., 2022), transition metal dichalcogenides (TMDs) (Sun et al., 2022; Xin et al., 2019), carbon-based materials (Liu et al., 2021), and some emerging two-dimensional (2D) materials for application in gas sensors to develop a series of sensitive and detection-selective gas sensors. However, although gas sensor materials such as metal oxides and conductive polymers possess good electrochemical performance and gas sensitivity, their

TABLE I Effects of various vOCs on numa
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Harmful gases	Major sources	Harm to human	Lowest exposure range for human
C <sub>7</sub> H <sub>8</sub>	cigarette, paint	Headache, vomiting, confusion	300 ppm
НСНО	volcanic gases, pesticides, paints, furniture	Blurred vision, vertigo	0.1 mg/m <sup>3</sup>
C <sub>2</sub> H <sub>5</sub> OH	industries	Paralysis of the nervous system, damage to the brain	3,300 ppm
$C_3H_6O$	petroleum refining, vehicle emissions	Difficulty breathing, corroded eyes	750 ppm for 15 min and 500 ppm for 8 h
CH <sub>3</sub> OH	Industrial workshop, Food processing plant	Affect the nervous system and blood system of human body	50 mg/m <sup>3</sup>
$C_{4}H_{10}$	Petroleum gas, natural gas and cracked gas	dizziness, headache, lethargy,coma	300 mg/m <sup>3</sup>
$C_6H_{15}N$	Dyestuff, preservative, solvent	Cause pulmonary edema and even death	0.14 mg/m <sup>3</sup>

working environment (200°C) is demanding, which exposes the defects of high power consumption and difficult application.

As a new material that was discovered only in 2011 (Naguib et al., 2011), MXene has a great potential in the sensor field owing to its unique morphology and good electrochemical properties (Zhang et al., 2018). Similar to graphene, MXene is a novel 2D-layered material composed of transition metal carbides/nitrides (Chaudhary et al., 2022). The transition metal carbide  $Ti_3C_2Tx$ , the first MXene material synthesised by etching from the MAX phase, has also become the most popular MXene material because of its relatively low formation energy (Naguib et al., 2011).

 $Ti_3C_2Tx$  has a higher specific surface area, and the contact surface with the air is larger under the same mass condition, which helps to improve the performance of the sensor (Li et al., 2021). Some experiments have demonstrated the feasibility of  $Ti_3C_2Tx$  in gas sensing (Koh et al., 2019; Lee et al., 2017). In this case,  $Ti_3C_2Tx$  is expected to prepare efficient and reliable gas sensors at room temperature. However, scholars have also found that traditional  $Ti_3C_2Tx$  materials possess a large number of -F, -OH or -O terminal groups, which make them degrade rapidly in a humid environment. This also exposes the problems of slow response, slow recovery, easy oxidation and poor stability of  $Ti_3C_2Tx$  sensors under wet conditions (Chae et al., 2019), which is also a huge challenge for  $Ti_3C_2Tx$  gas sensors at this stage.

Many review articles on  $Ti_3C_2Tx$  materials have been published, where the main focus has been the fields of biomedicine and photocatalysis. The application of  $Ti_3C_2Tx$  in gas sensors has not received much attention; in particular, the literature on the detection of VOCs gas remains very limited. In this review, the efficacy of different methods for improving the performance of sensors based on  $Ti_3C_2Tx$  materials is analysed, and the mechanisms are discussed. This study provides guidance for developing more efficient  $Ti_3C_2Tx$ -based sensors.

# Pristine Ti<sub>3</sub>C<sub>2</sub>Tx

In 2017, Lee et al. (2017) first cast  $Ti_3C_2Tx$  on a flexible polyimide platform by solid-solution casting and applied

Ti<sub>3</sub>C<sub>2</sub>Tx in the field of gas sensors, as shown in Figure 1A. The concentrations of ethanol, methanol, ammonia, and acetone were measured at room temperature. The efficacy for ammonia sensing was significantly higher than for the other VOCs. This is because the surface of  $Ti_3C_2Tx$  has abundant functional groups (Figure 1B) that react violently with ammonia gas to increase the resistance change by up to 20%, thus improving the sensing performance. Many factors affect the gas sensing performance of pristine Ti<sub>3</sub>C<sub>2</sub>Tx sensors, such as the film thickness (Kim et al., 2019), MAX phase precursor (Shuck et al., 2019), and oxidation degree (Huang Mochalin, 2020). However, despite optimization of these factors, it is difficult to efficiently and stably detect various VOC gases by relying on pure Ti<sub>3</sub>C<sub>2</sub>Tx. Therefore, compounding Ti<sub>3</sub>C<sub>2</sub>Tx with other materials and functionalizing Ti3C2Tx to improve the gas-sensing performance and selectivity of Ti3C2Tx sensors for VOC gases has also attracted increasing attention.

# Ti<sub>3</sub>C<sub>2</sub>Tx composites

To improve the sensing performance of  $Ti_3C_2Tx$  for VOCs gases, the combination of  $Ti_3C_2Tx$  with other materials has attracted much attention.  $Ti_3C_2Tx$  has been combined with various types of materials, such as metal oxides, graphene, and polymers, as shown in Table 2.

## Ti<sub>3</sub>C<sub>2</sub>Tx/metal oxide gas sensors

Metal oxides are sensitive and selective and can be used to prepare composite materials with high gas-sensing properties. The improved performance plausibly originates from the PN junction or PP junction formed by the combination of two different materials,  $Ti_3C_2Tx$  and a metal oxide. Many studies have been conducted on composites of  $Ti_3C_2Tx$  with metal oxides (Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, ZnSnO<sub>3</sub>, Cu<sub>2</sub>O, In<sub>2</sub>O<sub>3</sub>, and W<sub>18</sub>O<sub>49</sub>) for detecting VOCs.



TABLE 2 G	as sensing	performances	of	Ti3C2Tx-based	gas	sensors.
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Ti <sub>3</sub> C <sub>2</sub> Tx composites	VOCs gas	Conc. (ppm)	Operating Temo(°C)	Response (%)	Response/Recovery time (s/s)	References
ZnSnO <sub>3</sub> /Ti <sub>3</sub> C <sub>2</sub> Tx	НСНО	100	RT	194.7	6.2/5.1	Sima et al. (2022)
Ti <sub>3</sub> C <sub>2</sub> Tx/Co <sub>3</sub> O <sub>4</sub>	HCHO	10	RT	9.2	83/5	Zhang et al. (2021)
rGO/N-Ti <sub>3</sub> C <sub>2</sub> Tx/TiO <sub>2</sub>	HCHO	20	RT	132	N/A	Wang et al. (2020)
Ti <sub>3</sub> C <sub>2</sub> Tx/SnO-SnO <sub>2</sub>	C <sub>3</sub> H <sub>6</sub> O	100	RT	12.1	18/9	Wang et al. (2021)
Ti <sub>3</sub> C <sub>2</sub> Tx/W <sub>18</sub> O <sub>49</sub>	C <sub>3</sub> H <sub>6</sub> O	0.17	300	1.4	5.6/6	Sun et al. (2020)
Ti <sub>3</sub> C <sub>2</sub> Tx/rGO/CuO	C <sub>3</sub> H <sub>6</sub> O	100	RT	52.09	6.5/7.5	Liu et al. (2021a)
$\alpha\text{-}/\gamma\text{-}Fe_2O_3/ex\text{-}Ti_3C_2Tx$	C <sub>3</sub> H <sub>6</sub> O	100	255	215.2	13/8	Huang et al. (2022)
Ti <sub>3</sub> C <sub>2</sub> Tx/WSe <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> OH	40	RT	24	9.7/6.6	Chen et al. (2020a)
Ti <sub>3</sub> C <sub>2</sub> Tx/SnO <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> OH	10	230	5	14/26	Wang et al. (2022b)
Ti <sub>3</sub> C <sub>2</sub> Tx/Co <sub>3</sub> O <sub>4</sub>	$C_2H_5OH$	50	RT	190	50/45	Bu et al. (2022)
Ti <sub>3</sub> C <sub>2</sub> T <i>x</i> /polyaniline	C <sub>2</sub> H <sub>5</sub> OH	200	RT	41.1	0.4/0.5	Zhao et al. (2019)
Ti <sub>3</sub> C <sub>2</sub> Tx/SnO <sub>2</sub>	C6H15N	50	140	33.9	N/A	Liang et al. (2022)
Ti <sub>3</sub> C <sub>2</sub> Tx/Cu <sub>2</sub> O	C6H15N	10	RT	181.6	1,062/74	Zhou et al. (2022)
Ti <sub>3</sub> C <sub>2</sub> Tx/In <sub>2</sub> O <sub>3</sub>	CH <sub>3</sub> OH	5	RT	29.6	6.5/3.5	Liu et al. (2021b)
$S-Ti_3C_2Tx$	$C_7H_8$	10	RT	59.1	N/A	Shuvo et al. (2020)
$Ti_3C_2Tx/Fe_2 (MoO_4)_3$	$C_4H_{10}$	100	RT	43.1	18/24	Zou et al. (2020)

Huang et al. uniformly deposited porous bi-phasic  $\alpha$ -/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles on the surface and interlayer of Ti<sub>3</sub>C<sub>2</sub>Tx by solvothermal and high-temperature calcination and synthesised a stable  $\alpha$ -/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/ex-Ti<sub>3</sub>C<sub>2</sub>Tx-X gas sensor material for acetone detection. The composite gas sensor had a good response to acetone (the response value was 215.2 for 100 ppm acetone at 255°C, and the response and recovery time were 13 and 8 s, respectively). The improved performance originates from the large number of empty cationic sites on the  $\alpha$ -/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> surface, which can serve as strong adsorption sites for acetone. The  $\alpha$ -/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/ex-Ti<sub>3</sub>C<sub>2</sub>Tx-X composites possess

more surface defects, functional groups, porosity, and heterojunction interfaces than conventional  $Ti_3C_2Tx$ , which facilitates the interaction of acetone molecules with the active sites (Huang et al., 2022).

Composites of semiconductor metal oxides and  $Ti_3C_2Tx$ materials have also attracted much attention. (2022) successfully synthesised p-type semiconductor materials by combining  $Co_3O_4$  and  $Ti_3C_2Tx$ , where  $Co_3O_4$  was intercalated into the interlayer structure of  $Ti_3C_2Tx$  to form numerous hybrid heterojunctions. Intercalation significantly increased the specific surface area and gas adsorption sites of the material, thereby improving the gas-sensing performance. Zhang et al. (2021) also found that the ability of Ti<sub>3</sub>C<sub>2</sub>Tx/Co<sub>3</sub>O<sub>4</sub> composite to respond and recover also improved with the increase of bending angle, which is of great significance for the study of flexible wearable sensors that can monitor human health in real time. Using facile electrostatic self-assembly and hydrothermal synthesis, Sima al. (2022) successfully prepared ZnSnO<sub>3</sub>/Ti<sub>3</sub>C<sub>2</sub>Tx et composites, which exhibited good gas-sensing properties for the detection of formaldehyde, because the ohmic contact between ZnSnO3 and Ti3C2Tx formed a small Teky barrier, and the work function between  ${\rm Ti}_3 C_2 Tx$  and -OH (3.9 eV) was lower than that of ZnSnO3 (5.17 eV). According to the principle of Fermi level balance, a large number of electrons is transferred between the ZnSnO3 nanotubes and Ti3C2Tx to reach a relatively balanced state. More electrons will be adsorbed by oxygen on the surface of the ZnSnO3 nanoparticles, resulting in thickening of the electron depletion layer; thus, the resistance change will also increase, and the sensitivity of the sensor will also increase as the resistance change becomes more pronounced. Furthermore, the faster response and recovery are due to the synergistic effect between the two materials, which accelerates the separation rate of hole-electron pairs.

### Ti<sub>3</sub>C<sub>2</sub>Tx/rGO gas sensors

Graphene and Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> are both emerging two-dimensional materials with similar structures. Combining these two materials can enhance their properties through synergy. Liu et al. (2021a) fabricated a Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>/rGO/CuO three-dimensional aerogel sensor material by using a one-step hydrothermal method. The material showed good acetone-sensing performance (the response value to 100 ppm acetone at room temperature was 52.09, and the response and recovery times were 6.5 and 7.5 s, respectively) and stability. The good response is mainly because the 3D porous network structure of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>/rGO/CuO prevents stacking of the composites, which exposes a larger surface area and provides more adsorption sites for O2 and acetone gas. As a second factor, acetone-sensing is related to the p-p junction formed at the interface owing to the different work functions of the three materials. In addition, the large number of functional groups on the surface of  $Ti_3C_2T_x$  form strong hydrogen bonds with acetone gas, the interaction force between the composite material and acetone molecules is enhanced, and the hole concentration is increased, leading to improved gas-sensing performance.

## Ti<sub>3</sub>C<sub>2</sub>Tx/polymer gas sensors

Conductive polymers are low-cost with excellent electrical conductivity and are considered potential gas sensing materials. Polyaniline (PANI) is extensively used in polymer gas sensors, where the material itself and its mixtures show excellent NH3 gas sensing performance. At present, Zhao et al. are the only ones that have prepared  $Ti_3C_2Tx/polymer$  composites by lowtemperature *in situ* polymerisation. They found that the composites have good gas sensitivity to gaseous ethanol as a VOC (response rate to 200 ppm ethanol gas at room temperature is 41.1, with response and recovery times of 0.4 and 0.5 s, respectively). The incorporation of PANI effectively inhibited the interlayer aggregation of  $Ti_3C_2Tx$ , thereby exposing a larger surface area and more functional groups (–O, –OH, and–F groups), all of which increased the resistance of the composite when exposed to ethanol. Thus, the gas-sensing performance can be improved by improving the gas adsorption ability (Zhao et al., 2019).

## Functionalized Ti<sub>3</sub>C<sub>2</sub>Tx

In addition to compounding with other materials, methods of functionalizing  $Ti_3C_2Tx$  materials using single-atom functionalization and surface treatments are attracting increasing attention.

As shown in Figure 2A, Zong et al. modified the surface of  $Ti_3C_2Tx$  with single-atom Pt (Pt SA); the resulting sensor could detect triethylamine (TEA) at levels as low as 14 ppb. The highly catalytically active and uniformly distributed Pt SA had a chemical sensitisation effect, and the excellent adsorption of Pt SA on TEA was the main reason for the improved gassensing performance of the sensor. Furthermore, as shown in Figure 2B, the Pt- $Ti_3C_2Tx$  sensor exhibited good stability in the detection of various VOC gases at room temperature. Based on density functional theory, it was proven that metal single-atom catalyst doping can improve charge transfer in VOC gases during the adsorption process in a pioneering study on the application of metal single-atom catalysts in the field of MXene nanosheet sensors (Zong et al., 2022).

Ti<sub>3</sub>C<sub>2</sub>Tx sensors are unstable in humid environments. To solve this problem, Chen et al. (2020b) embedded fluoroalkyl silane (FOTS) on the surface of Ti<sub>3</sub>C<sub>2</sub>Tx to reduce its surface energy and achieve hydrophobic effects. Ti<sub>3</sub>C<sub>2</sub>Tx-F exhibited good hydration stability, good tolerance in acid/base solutions, and Ti<sub>3</sub>C<sub>2</sub>Tx-F detects 120 ppm ethanol gas at room temperature, showing good repeatability and fast response/ recovery speed (39 s/139 s). As shown in Figure 2C, the interlayer distance of the functionalized Ti3C2Tx is larger, which can adsorb more VOCs molecules. And it is also found that the Ti-O bond length increases from 2.26 Å to 2.57 Å due to the attractive force between the oxygen and the hydrogen atoms of the ethanol, causing the adjacent oxygen atoms of the ethanol molecule to pull outward from the layer. This indicates that the gas sensing performance of Ti<sub>3</sub>C<sub>2</sub>Tx-F material will be enhanced with the adsorption of ethanol molecules. In addition, the  $\mathrm{Ti}_3\mathrm{C}_2\mathrm{Tx}\text{-}\mathrm{F}$  sensor can still monitor ethanol gas well in an environment with a relative humidity of 80%. This also puts



for 20 consecutive days (adapted from Zong et al., 2022). (C) Interlayer distance between Ti3C2Tx materials before and after incorporation into FOTS. (adapted from Chen et al., 2020a) (D–E) Interlayer spacing of Ti3C2Tx materials before and after incorporation of S elements was observed under TEM (adapted from Shuvo et al., 2020).

forward a new idea to solve the shortcomings of  $Ti_3C_2Tx$  sensor, which is easy to oxidize and has poor stability in humid environment.

Shuvo et al. uniformly doped S atoms into the surface and interlayers of  $Ti_3C_2T_x$ , where the responses to toluene at 1 and 50 ppm were 214% and 312%, respectively, which were 2–3 times the response of conventional  $Ti_3C_2T_x$ . The TEM images in Figures 2D,E show that, after the incorporation of S atoms, the interlayer distance of the sensor material expanded significantly, thereby improving the gas sensing performance of the sensor. Furthermore, the S- $Ti_3C_2T_x$  sensor remained stable after 30 days of continuous exposure and exhibited good repeatability over 10 consecutive cycles (Shuvo et al., 2020).

# Modification mechanism

In summary, the composite and functional methods are used to improve the gas-sensing performance of  $Ti_3C_2Tx$  sensor materials to VOCs gas. It is not difficult to find that although the methods are different, the modification mechanism is roughly the same. After summarizing, the author found that the modification mechanism is mainly as follows: ① Inhibiting the aggregation of  $Ti_3C_2Tx$  materials resulting in obtaining more surface area and more abundant functional groups; ② Improving the interaction force between the sensor material and gas molecules, and so accelerating the air The separation rate of the hole-electron pair; ③ increasing the thickness of the electron depletion layer, causing the larger channel for electron flow and thereby improving the sensitivity of the resistance change; ④ compounding with the n-type material to form a non-uniform p-n junction, making the two materials with different work functions connect together (since the Fermi level needs to be kept at the same level, electron transfer will occur between them, thereby a built-in electric field and a Schottky barrier will be formed). ⑤ Introducing other atoms to improve the charge transfer during the adsorption process. All of these reasons can effectively improve the sensing performance of the sensor, which also provides ideas for the discovery of new sensor materials in the future.

# Conclusion

The research status of gas sensors based on  $Ti_3C_2Tx$  in recent years was reviewed, demonstrating that the modification of  $Ti_3C_2Tx$  by compounding with other materials, surface modification, and single-atom doping can effectively improve the gas-sensing performance of  $Ti_3C_2Tx$ -based gas sensors. Combining other materials into the surface and interlayer structure of  $Ti_3C_2Tx$  can increase the interlayer spacing of the structure to expose a larger specific surface area, provide more active sites for target gas molecules, enhance the adsorption capacity of the sensor, and improve the sensitivity. Using density functional theory, it has been proven that metal single-atom catalyst doping can improve charge transfer in VOC gases during the adsorption process, which provides insight for developing high-performance  $Ti_3C_2Tx$ -based gas sensors. We hope that our work will provide guidance for the development of new  $Ti_3C_2Tx$ -based gas-sensor materials in the future.

## Author contributions

BP conceived and designed the experiment. BP analyzed the data. BP and XH wrote the manuscript with input from all authors. All authors read and approved the manuscript.

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# Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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