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Guangyu Chen

Kunming University of Science and Technology

Junhao Zhang

Kunming University of Science and Technology

Ming Hou

houmingkmust@163.com

Kunming University of Science and Technology

Li Yang

Kunming University of Science and Technology

Shenghui Guo

Kunming University of Science and Technology

Dongyang Shi

Kunming University of Science and Technology

Yi Xia

Kunming University of Science and Technology

Qiuni Zhao

Kunming University of Science and Technology

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**Microwave-Plasma-Engineered Ti₃C₂T_x-TiO₂-SnO₂ Heterostructures for
Room-Temperature Hydrogen Sensing**

**Guangyu Chen^{1#}, Junhao Zhang^{1#}, Ming Hou^{1, 2,3,4*}, Li Yang^{1, 2,3,4},
Shenghui Guo^{1, 2,3,4}, Dongyang Shi¹, Yi Xia¹, Qiuni Zhao^{1**}**

1.College of Metallurgy and Energy Engineering, Kunming University of
Science and Technology, Kunming 650093, Yunnan, China

2.State Key Laboratory of Complex Nonferrous Metal Resources Clean
Utilization, Kunming University of Science and Technology, Kunming 650093, China

3.National and Local Joint Engineering Laboratory for Microwave Energy
Engineering Application and Equipment Technology, Kunming 650093, Yunnan,
China.

4.International Joint Research Center for Advanced Manufacturing Technology
of Super Hard Materials, Kunming 650093, Yunnan, China.

Corresponding author: Ming Hou (houmingkmust@163.com)
Qiuni Zhao (qiunizhao90s@163.com)

Abstract

Hydrogen, as a high-density and zero-carbon energy carrier, is crucial for global clean energy transition, yet its ultralow ignition energy and wide explosive concentration range (4–75%) impose critical demands on gas sensing technologies. Conventional metal oxide semiconductor sensors suffer from high operating

temperatures and limited low-concentration detectability, while pure MXene materials are restricted by ambient oxidation and layer agglomeration. To address these issues, we synthesize a ternary $\text{Ti}_3\text{C}_2\text{T}_\text{x}$ - TiO_2 - SnO_2 composite via LiF - HCl hydrothermal etching of $\text{Ti}_3\text{C}_2\text{T}_\text{x}$ MAX followed by microwave plasma chemical vapor deposition oxygen–argon plasma modification with varied MXene/ SnO_2 ratios and O_2/Ar volume ratios. The phase composition, microstructure, and surface chemical states are characterized by X-ray diffraction, scanning electron microscopy, and X-ray photoelectron spectroscopy, respectively. Results demonstrate that the optimal MTS-1-15%-40min sample, processed under low-oxygen plasma ($\text{O}_2/\text{Ar} = 15:85$), well preserves the layered $\text{Ti}_3\text{C}_2\text{T}_\text{x}$ conductive framework while inducing controlled surface oxidation to TiO_2 and constructing high-density TiO_2 - SnO_2 n–n heterojunctions with abundant oxygen vacancies and Ti^{3+} defects. This optimized heterostructure achieves a room-temperature response of 32.36% toward 1000 ppm H_2 , an ultralow detection limit of 1 ppm, excellent selectivity against interfering gases, good humidity tolerance up to 50% RH, and outstanding long-term stability over 17 days with 94.5–97.5% retention. The enhanced performance arises from the synergistic interplay of oxygen vacancy-enhanced gas adsorption, the high-conductivity MXene electron transport channel, and heterojunction-modulated carrier dynamics. This work offers a viable plasma-assisted strategy for room-temperature, low-power hydrogen detection.

Keywords

MXene $\text{Ti}_3\text{C}_2\text{T}_\text{x}$; H_2 ; Microwave plasma chemical vapor deposition; Gas sensing at room temperature; $\text{Ti}_3\text{C}_2\text{T}_\text{x}$ - TiO_2 - SnO_2 composites

1 Introduction

The large-scale industrialization and urbanization process have led to the continuous consumption of fossil energy, triggering a series of environmental issues such as the greenhouse effect, atmospheric acid rain, and water and soil pollution, which seriously threaten ecological security and human health [1]. To alleviate the environmental pressure brought by traditional energy sources, clean and low-carbon new energy technologies have become the core direction of global energy transformation. Hydrogen, with its high energy density and zero carbon emission advantages, is a highly promising clean energy carrier [2, 3], widely used in industrial scenarios such as aerospace, fuel cell vehicles, and hydrogen metallurgy[4-6] . However, the extremely low ignition energy of hydrogen gas and the wide explosion concentration range of 4% - 75% make it have an extremely high leakage, explosion risk [7], and its small molecular size and fast diffusion speed greatly increase the safety hazards in hydrogen storage, transportation and application. Therefore, the development of highly sensitive, fast-response, and low-power hydrogen gas sensors is the key technical support for ensuring the safe and stable operation of the entire hydrogen energy chain [8].

The existing hydrogen gas sensing technologies include MOS type, electrochemical type, optical type, catalytic combustion type, etc. Each technology has its own advantages and disadvantages in terms of detection accuracy, power consumption, and environmental adaptability. Metal oxide semiconductor (MOS) sensors, with their mature process, high sensitivity, and low cost, are the mainstream devices in the field of hydrogen gas detection at present. N-type semiconductors have high carrier mobility and excellent gas sensing performance, and are the core functional materials in the sensing field, including TiO_2 , SnO_2 , WO_3 , In_2O_3 , etc. [9-12]. Among them, SnO_2 is a typical wide bandgap N-type semiconductor ($E_g = 3.6$ eV), and its intrinsic oxygen vacancy structure gives it excellent multi-component gas detection capabilities [13-15], while also having the advantages of being non-toxic, having a fast response at low concentrations, and good stability. It is one of the most widely used hydrogen-sensitive materials [16, 17]. Nevertheless, pristine SnO_2 still

exhibits several intrinsic limitations. The adsorption, dissociation, and surface reaction of hydrogen and oxygen species generally require sufficient thermal energy; consequently, SnO₂-based sensors usually operate at elevated temperatures. This requirement increases power consumption and may cause nanoparticle coarsening and long-term signal drift. In addition, the limited number of accessible active sites, aggregation of SnO₂ nanoparticles, weak modulation of the resistance at low hydrogen concentrations, and nonspecific reactions with other reducing gases can result in insufficient sensitivity, slow response/recovery, and poor selectivity [18]. Therefore, regulating the surface reactions and carrier-transport behavior of SnO₂ is essential for achieving high-performance hydrogen sensing at reduced operating temperatures.

Constructing semiconductor heterojunctions provides an effective strategy for overcoming these limitations. TiO₂ is an n-type semiconductor with excellent chemical stability, favorable oxygen adsorption ability, and abundant surface-active sites. Coupling TiO₂ with SnO₂ can form a TiO₂/SnO₂ n-n heterojunction because of the differences in their work functions and energy-band structures. Furthermore, the heterogeneous interfaces and defect sites can provide additional adsorption and reaction sites, facilitate oxygen activation, and improve the dispersion of the oxide nanoparticles.

Ti₃C₂T_x, as a typical MXene material, combines ultra-high conductivity, tunable interlayer spacing, and a variety of surface functional groups, allowing it to efficiently respond to hydrogen gas at room temperature.[18-20]. Its unique dorbital charge transport characteristics and controllable surface chemical structure can achieve precise functionalization modification that is difficult to achieve with graphene [21], showing great application potential in energy storage, biological sensing, etc. [22, 23]. Its excellent specific surface area and charge transport characteristics enable MXene to achieve high sensitivity and high selectivity detection of trace gases [24], suitable for industrial safety and environmental monitoring. Ti₃C₂T_x as a typical MXene material, combines ultra-high conductivity, adjustable layer spacing, and rich surface functional groups, enabling efficient hydrogen gas sensing response at room

temperature, making it an ideal material platform for constructing low-power hydrogen gas sensors [25], and its good dispersibility and flexibility are suitable for the preparation of flexible devices. At the same time, it can produce titanium dioxide through in-situ oxidation reactions, making it an ideal material platform for building low-power hydrogen sensors.

Conventional $\text{TiO}_2/\text{SnO}_2$ composites are generally prepared by sol-gel processing, hydrothermal synthesis, electrospinning, or template-assisted methods, which usually involve prolonged wet-chemical reactions and subsequent high-temperature calcination or annealing. For example, sol-gel-derived $\text{TiO}_2/\text{SnO}_2$ composite films require multiple solution preparation, coating, and drying steps, followed by annealing at $500\text{ }^\circ\text{C}$ for 1 h [26]. Similarly, an inverse-opal $\text{TiO}_2/\text{SnO}_2$ composite was obtained through a multistep template-assisted process and subsequent heat treatment at $500\text{ }^\circ\text{C}$ for 3 h [27]. Microwave plasma modification is an efficient and green technology for optimizing the microstructure and surface properties of MXene. The high-energy particles of plasma can replace the functional groups on the surface of MXene, remove residual fluorine groups, introduce abundant oxygen-active sites, and effectively improve the material's surface wettability and interface charge transmission ability. At the same time, plasma bombardment can construct surface defects, expand interlayer spacing, inhibit layer aggregation, and improve specific surface area and gas diffusion efficiency. This technology can achieve precise functional modification without damaging the structure of the MXene substrate, providing a reliable technical path for improving the comprehensive performance of MXene-based gas-sensitive and catalytic materials .

2 Experimental component

All the washing and solution preparation water used in this experiment were laboratory-made ultrapure water. The reagents and equipment parameters used in the experiment are shown in Tables 1 .

Table 1

Comparison of the gas sensing properties of materials in this paper and existing literature.

Lab materials	Molecular formula	Purity	Manufacturer
Hydrochloric acid	HCl	12mol/l	Xilong Science
MAX	Ti ₃ AlC ₂	/	11 Technology
Lithium fluoride	LiF	99.9%	MacLean
alcohol	CH ₃ CH ₂ OH	99.7%	Tianjin Zhiyuan Chemical Reagents Co., Ltd.

2.1 Preparation of MXene (Ti₃C₂T_x):

Take 20 mL of concentrated hydrochloric acid with a graduated cylinder and add 60 mL of ultrapure water to prepare a 12 mol/L hydrochloric acid solution. Accurately weigh 2 g of Ti₃AlC₂ MAX powder and 1.3 g of lithium fluoride (LiF), and put them together into a polytetrafluoroethylene reactor. Add the prepared hydrochloric acid solution and place it in a magnetic stirring rotor for 5 minutes to complete the initial mixing. Place the sealed reactor in an electrically heated and ventilated drying oven, set at 120 °C for 5 days to complete the hydrothermal etching reaction. After the reaction is finished, let the reactor body cool to room temperature, transfer the mixed product to a 50 mL centrifuge tube, set the centrifuge speed at 4000 r/min, and perform a single centrifugation for 4 minutes. The washing process is as follows: wash with deionized water twice, wash with anhydrous ethanol twice, and then repeatedly wash with deionized water 4-5 times until the pH of the suspension approaches neutrality, removing residual lithium salts, aluminum ions, etc. After washing, seal the centrifuge tube and place it in a vacuum drying oven for vacuum drying for 24 hours to obtain black Ti₃C₂T_x MXene powder.

2.2 Preparation of Ti₃C₂T_x - TiO₂ - SnO₂ Ternary Composite Materials

Set three groups of MXene and SnO₂ mass ratios, respectively label them as MTS 1, MTS 2, and MTS 3: MTS 1 is 0.06 g MXene + 0.14 g SnO₂; MTS 2 is 0.10 g MXene + 0.10 g SnO₂; MTS 3 is 0.14 g MXene + 0.06 g SnO₂. Add anhydrous ethanol to each group of samples, shake well to obtain a uniformly dispersed suspension. Use a pipette to drop the suspension onto a clean silicon wafer substrate,

and vacuum dry to obtain the precursor body. Place the dried silicon wafer in the MPCVD reaction chamber, close the door, evacuate to high vacuum, remove the air impurities in the chamber. Introduce Ar and O₂ mixed gas into the chamber, maintain a total pressure of 1 kPa, substrate temperature 400 °C, and process time 40 minutes. Set the oxygen-argon volume ratio gradients as 15:85, 30:70, and 45:55 to complete the in-situ plasma modification under different atmospheres. The sample naming rule is MTS X oxygen content processing time, for example, MTS 1 15% 40min, representing MTS 1 ratio, oxygen-argon volume ratio 15:85, plasma processing 40 minutes. Under the action of high-energy plasma particles, part of the Ti₃C₂T_x surface is oxidized in situ to generate TiO₂, and finally obtain the Ti₃C₂T_x - TiO₂ - SnO₂ ternary composite sample. The preparation process of the ternary composite Ti₃C₂T_x-TiO₂-SnO₂ and the gas sensing test procedure are shown in Fig. 1.

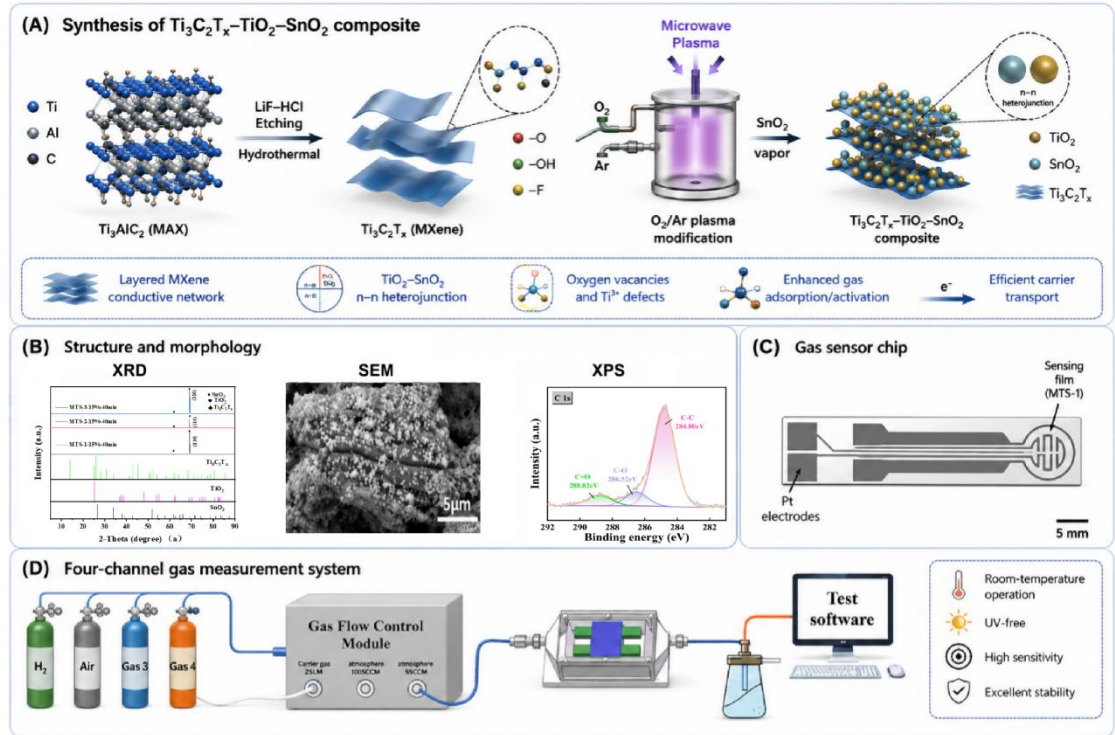


Fig.1. The preparation process of the ternary composite material Ti₃C₂T_x-TiO₂-SnO₂

2.3 Material Characterization Methods

X-ray diffraction (XRD) is used to analyze the crystal phase structure. The scanning angle is set from 10° to 90°. The standard PDF cards are compared to

identify the $\text{Ti}_3\text{C}_2\text{T}_x$, TiO_2 , and SnO_2 phases, and to analyze the changes in oxidation degree. Scanning electron microscope (SEM) is used to observe the microstructure of the samples. Before testing, the samples are adhered to the conductive adhesive sample stage. The accelerating voltage is set at 5 to 20 kV. The layer structure integrity, oxide particle size, dispersion state, and agglomeration situation are observed, and the influence of different plasma atmospheres on the microstructure is analyzed. X-ray photoelectron spectroscopy (XPS) is used to analyze the chemical state of surface elements, to analyze the bonding state of Ti, Sn, O, and C, to identify Ti^{3+} and oxygen vacancy defects, and to study the charge transfer phenomenon at the heterojunction interface.

2.4 Gas Sensing Performance Testing

The sensor chip uses a laboratory-made alumina ceramic substrate. First, platinum electrode paste is screen-printed. It is dried at 80°C for 60 minutes. The muffle furnace is programmed to increase the temperature at $2^\circ\text{C}/\text{min}$, with a 2-hour holding at 350°C and 10 minutes at 800°C . The chip with integrated heating electrodes and measurement electrodes is obtained. The composite material paste to be tested is printed in the sensitive area of the chip to complete the preparation of the sensing chip. The gas sensing test system consists of four parts: gas mixing unit, temperature control unit, humidity control unit, and data acquisition unit. The gas mixing unit precisely mixes dry air and hydrogen using a mass flow controller (MFC), with the hydrogen concentration range controlled at 1 to 1000 ppm. The temperature control unit controls the working temperature of the chip at 25 to 200°C , with a temperature control accuracy of $\pm 1^\circ\text{C}$. The humidity unit introduces water vapor to regulate the environmental relative humidity at 0 to 50% RH. The Agilent 34970A data acquisition instrument records the changes in sensor resistance in real time.

Gas sensing response calculation formula:

$$S = \frac{|R_a - R_g|}{R_a} \times 100\%$$

In the formula: R_a represents the baseline resistance of the sensor in dry air; R_g represents the resistance value after the target gas to be tested is introduced and

reaches a steady state. Test process: The chip is placed in an air environment and waits for the resistance to stabilize completely. Then, the target gas is introduced, and the resistance stabilizes again. After that, the air is cut off and the response and recovery cycle is completed. Subsequently, temperature variation tests, humidity gradient tests, selectivity tests, concentration gradient detection lower limit tests, and long-term stability cycle tests are carried out successively.

3 Results and Discussion

Fig. 2 shows the XRD patterns of MTS-1, MTS-2, and MTS-3 composites modified with different oxygen-argon plasma ratios (15:85, 30:70, 45:55). The vertical lines at the bottom correspond to the standard diffraction positions of $\text{Ti}_3\text{C}_2\text{T}_\text{x}$, anatase TiO_2 , and rutile SnO_2 . None of the samples show the characteristic peaks of Ti_3AlC_2 MAX phase, indicating that the Al layer has been completely etched and a $\text{Ti}_3\text{C}_2\text{T}_\text{x}$ matrix has been successfully prepared. Under low oxygen conditions ($\text{O}_2/\text{Ar} = 15:85$, Fig.2(a)), all three groups of samples simultaneously show the diffraction peaks of $\text{Ti}_3\text{C}_2\text{T}_\text{x}$, TiO_2 , and SnO_2 phases. As the MXene loading ratio increased from MTS-1 to MTS-3, the diffraction intensity of SnO_2 gradually decreased, while the MXene diffraction signal increased, consistent with the ratio of raw materials. This atmosphere is a mild oxidation environment, with only the surface of MXene layers undergoing in situ oxidation to form TiO_2 , and the two-dimensional layered crystal framework is well preserved. When the oxygen-argon ratio increased to 30:70 (Fig. 2(b)), the concentration of active oxygen particles increased, the Ti-C bonds partially broke, and the diffraction peak of TiO_2 strengthened, while the diffraction intensity of $\text{Ti}_3\text{C}_2\text{T}_\text{x}$ overall decreased. The highest MXene proportion in MTS-3 had the most significant oxidation loss; MTS-1 with a high SnO_2 content was shielded by oxide particles and the attenuation of the MXene diffraction peak was less. The diffraction peak of SnO_2 remained unchanged throughout the process, proving that plasma treatment does not alter the crystal structure of SnO_2 . When the oxygen proportion was further increased to 45:55 (Fig. 2(c)), the characteristic peaks of $\text{Ti}_3\text{C}_2\text{T}_\text{x}$ significantly weakened or even disappeared, and TiO_2 became the dominant phase, indicating that the high-oxygen atmosphere caused severe oxidation degradation of

the MXene matrix and the two-dimensional framework was destroyed. In summary, the 15:85 low-oxygen atmosphere can achieve controlled surface oxidation of MXene, while preserving the intrinsic conductive framework of MXene during the construction of a ternary heterojunction. This is a superior modification condition, and the evolution rule of this phase can provide a crystal structure-level explanation for the subsequent gas-sensing performance.

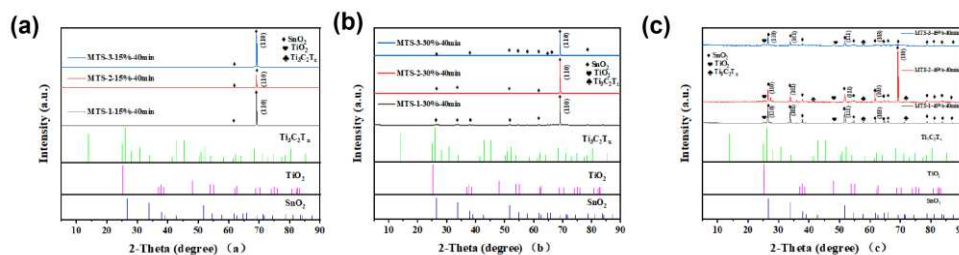


Fig.2. The XRD patterns of MTS with an oxygen-argon ratio of 15:85, (b) MTS with an oxygen-argon ratio of 30:70, and (c) MTS with an oxygen-argon ratio of 45:5

Figs. 3 (a-i) show the SEM images of the MTS series samples after different MXene/SnO₂ ratios and different O₂/Ar plasma atmospheres treatment. The three rows correspond to the oxygen-argon ratios of 15:85, 30:70, and 45:55; the three columns are MTS-1, MTS-2, and MTS-3. The scale bar is 5 μ m. Under the low oxygen plasma conditions (15:85, a-c), the samples completely retain the typical accordion-like layered structure of Ti₃C₂T_x, with clear two-dimensional layer profiles. The nano SnO₂ particles are uniformly anchored and dispersed on the surface and interlayer gaps of the MXene layers, forming a closely contacting heterogeneous interface. The SnO₂ particles density is the highest in MTS-1; as the MXene proportion increases to MTS-3, the surface particle coverage gradually decreases, consistent with the feeding ratio. Under this condition, the MXene layer sheets show no obvious etching damage, only mild oxidation occurs on the surface, which is consistent with the aforementioned XRD results. When the oxygen-argon ratio increases to 30:70 (d-f), the high-energy oxygen plasma has an etching effect on the layer sheets. The edges of the MXene layer sheets become rough, and small etching pits can be seen locally; the in-situ generated TiO₂ nanoparticles and SnO₂ are jointly

loaded on the layer sheet surface. Due to the high MXene proportion in MTS-3, the layer sheets are more severely damaged by etching compared to MTS-1, but the layered framework is generally still maintained. In the high oxygen environment of 45:55 (g-i), the original layered structure of the MXene is severely damaged. The edges of the layer sheets become blurred, some layer sheets undergo powdering and fragmentation, and a large number of oxidation particles aggregate. Especially for MTS-3 sample, the two-dimensional layered morphology is significantly degraded, and the corresponding $\text{Ti}_3\text{C}_2\text{T}_x$ diffraction peak in XRD almost disappears. In contrast, MTS-1 is shielded by the SnO_2 particles, and the layer sheet structure is relatively better preserved. SEM directly confirms: 15:85 low oxygen plasma can achieve controllable surface modification, while retaining the two-dimensional conductive framework of MXene and constructing a rich heterogeneous interface; an excessively high oxygen ratio will cause irreversible damage to the MXene structure, which is not conducive to the gas sensing performance.

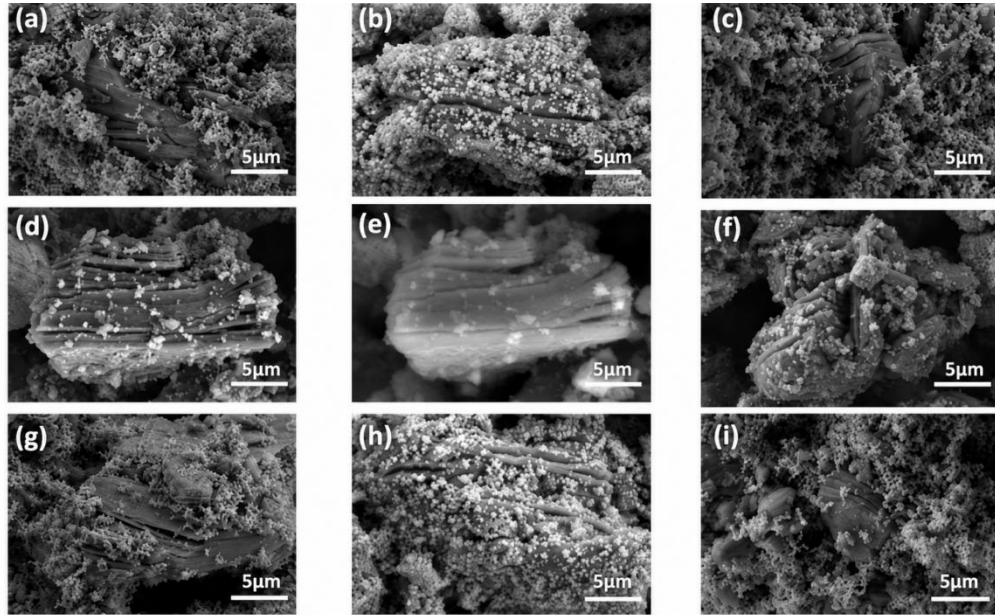


Fig.3. SEM images of various samples (a) MTS-1-15% - 40min, (b) MTS-2-15% - 40min, (c) MTS-3-15% - 40min, (d) MTS-1-30% - 40min, (e) MTS-2-30% - 40min, (f) MTS-3-30% - 40min, (g) MTS-1-45% - 40min, (h) MTS-2-45% - 40min, (i) MTS-3-45% - 40min, SEM images of scanning electron microscope

To reveal the chemical state of surface elements, defects, and interfacial interactions of the optimal sample MTS-1-15%-40min, X-ray photoelectron

spectroscopy (XPS) characterization was conducted (Fig.4). The high-resolution C 1s spectrum can be fitted to obtain three characteristic peaks: C-C (284.80 eV), C-O (286.52 eV), and C=O (288.82 eV), corresponding to the carbon skeleton and surface oxygen-containing functional groups. The characteristic signal of the Ti-C bond significantly weakened, confirming that the microwave oxygen argon plasma disrupted some Ti-C bonds, promoting the in-situ oxidation of the MXene matrix to generate TiO₂. This result is consistent with the XRD characterization. The Ti 2p high-resolution spectrum shows that 458.85 eV (Ti 2p_{3/2}) and 464.50 eV (Ti 2p_{1/2}) belong to TiO₂ with Ti⁴⁺, and the spin-orbit splitting difference is 5.65 eV, which is consistent with the standard spectroscopic features of anatase TiO₂. The main peak of Ti 2p_{3/2} on the low binding energy side has a clear asymmetric shoulder-like tail, which originates from the Ti³⁺ defects induced by plasma bombardment. Ti³⁺ usually coexists with oxygen vacancies and is a key active site for gas sensing reactions. The high-resolution O 1s spectrum is fitted into three groups of characteristic peaks: 530.45 eV belongs to the metal lattice oxygen of TiO₂ and SnO₂; the wide peak at 531.96 eV is the superimposed signal of oxygen vacancy defects, surface hydroxyl groups, and physical adsorbed oxygen, proving that the MPCVD oxygen argon plasma successfully introduced oxygen vacancies on the material surface; 533.65 eV belongs to the C-O bond on the MXene matrix. Oxygen vacancies can capture oxygen molecules in the air, generating more reactive oxygen species, directly promoting the adsorption-oxidation reaction of hydrogen, and playing a key role in improving the gas sensing response. The Sn 3d high-resolution spectrum at 486.77 eV (Sn 3d_{5/2}) and 495.19 eV (Sn 3d_{3/2}) corresponds to Sn⁴⁺ in SnO₂, and the spin-orbit splitting distance is 8.42 eV. Compared with the pure SnO₂ standard spectrum, Sn 3d_{5/2} shifts to a higher binding energy by approximately 0.37 eV, proving that TiO₂ and SnO₂ form a tight n-n heterojunction, with electron redistribution occurring at the interface, and the electron cloud density around the Sn site decreases. The charge transfer at the heterojunction interface can regulate the depletion layer thickness and carrier concentration, and combined with the high conductivity MXene framework, it can achieve excellent hydrogen sensing ability at room temperature.

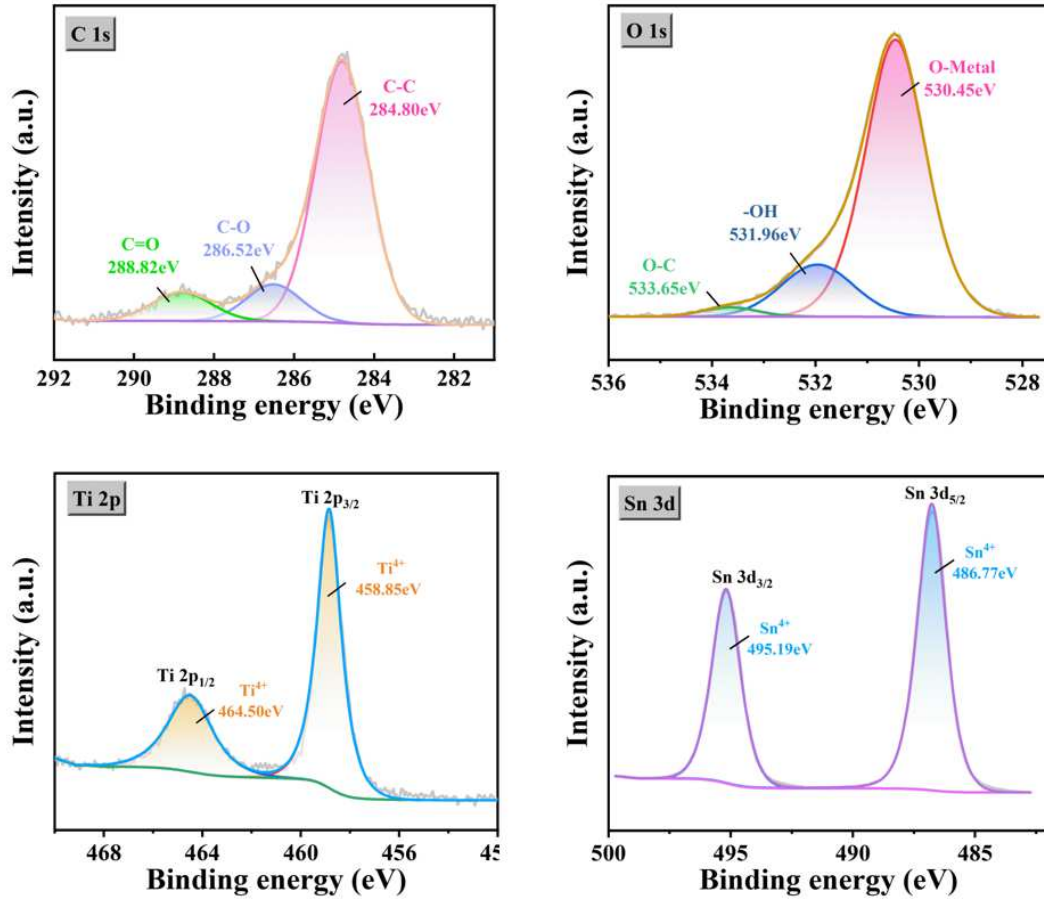


Fig.4. XPS analysis chart of MTS-1-15% material

Fig. 5 shows the dynamic response recovery curves of the target gas for MPCVD plasma modified samples with different MXene/SnO₂ ratios (MTS-1, MTS-2, MTS-3) and different oxygen-argon volume ratios (15:85, 30:70, 45:55) at a gradient working temperature range of 25 °C - 200 °C. Figs. (a-c), (d-f), (g-i), (j-l), (m-o) correspond to the test conditions of 25 °C, 75 °C, 125 °C, 175 °C, and 200 °C respectively. Each column represents the three plasma atmospheres of O₂/Ar = 15:85, 30:70, and 45:55.

From the temperature perspective, all MTS series composites exhibit significant temperature-dependent gas sensing behavior. At room temperature of 25 °C, the samples can generate distinguishable response signals, among them, the MTS-1-15% sample exhibited the highest response value, reaching 32.36%. As the working temperature gradually increases to 200 °C, the response value of the MTS-1-15% sample decreased to 7.18%. Improving that the Ti₃C₂T_x-TiO₂-SnO₂ ternary heterostructure effectively reduces the energy barrier of gas adsorption reactions and achieves low-temperature sensing capability.

When comparing the raw material ratios at the same temperature, MTS-1 (high SnO₂ content) has the highest response in all temperature and atmosphere conditions; MTS-2 has a middle performance; MTS-3 (high MXene content) has the weakest overall response. In the MTS-1 system, SnO₂ provides a large number of surface oxygen adsorption active sites, and the TiO₂ and SnO₂ generated in situ by MPCVD plasma form a tight oxide heterojunction, while the intact Ti₃C₂T_x serves as a

high-conductivity pathway, rapidly transporting the carriers generated during the sensing process, achieving the synergy of active sites - heterojunction - conductive network. Although MTS-3 has a high MXene content, the active phase content of SnO_2 is insufficient, and there are few surface sites available for gas reactions, even though the MXene conductivity is excellent, it cannot achieve a high sensing response.

By comparing the plasma oxygen-argon ratio, it can be observed that the full temperature range sensing performance of the 15:85 low-oxygen modification group is significantly better than the 30:70 and 45:55 high-oxygen groups. The response of the sample treated by 45:55 high-oxygen plasma significantly decreases. This result is consistent with the XRD and SEM characterization: high-concentration active oxygen particles cause excessive oxidation of the $\text{Ti}_3\text{C}_2\text{T}_x$ matrix, the two-dimensional layered skeleton is etched and pulverized, and the intrinsic metal conductivity of MXene is severely damaged. Although increasing the test temperature can activate the surface reaction, the internal conductive pathways of the material have undergone irreversible damage, the carrier migration is blocked, and the heterojunction's sensing gain effect cannot be fully exerted. Even though MTS-1 has a higher SnO_2 content providing shielding protection, the performance still significantly declines after high-oxygen treatment.

It is noteworthy that the optimal sample MTS-1-15%-40 min simultaneously achieves both room-temperature detectability and high-temperature high-response characteristics. Low-oxygen plasma realizes controlled oxidation of the MXene surface, generating only TiO_2 on the sheet surface, which constructs rich $\text{TiO}_2/\text{SnO}_2$, $\text{TiO}_2/\text{MXene}$ heterojunction interfaces, and maximally preserves the layered conductive skeleton of $\text{Ti}_3\text{C}_2\text{T}_x$, making it the optimal modification process for this ternary system. Conversely, plasma modification with excessively high oxygen pressure falls under deteriorating conditions, and it will damage the sensing function of the composite material at the levels of crystal structure and micro-morphology.

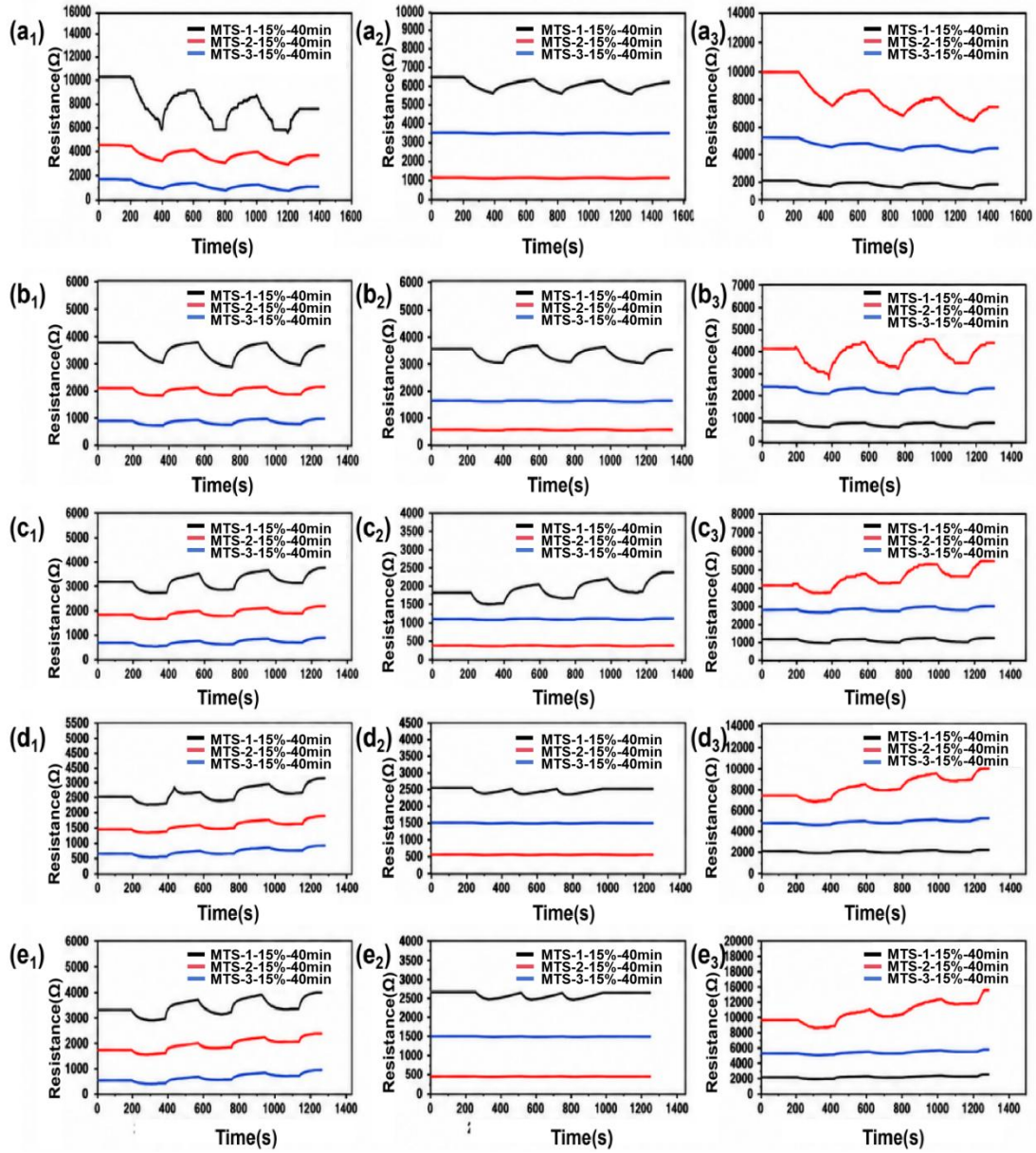


Fig.5. Response curves of MTS series materials at different temperatures, (a₁)(a₂)(a₃) Response curves of MTS series materials treated with different oxygen-argon ratios at 25°C, (b₁)(b₂)(b₃) Response curves of MTS series materials treated with different oxygen-argon ratios at 75°C, (c₁)(c₂)(c₃) Response curves of MTS series materials treated with different oxygen-argon ratios at 125°C, (d₁)(d₂)(d₃) Response curves of MTS series materials treated with different oxygen-argon ratios at 175°C, (e₁)(e₂)(e₃) Response curves of MTS series materials treated with different oxygen-argon ratios at 200°C

Fig. 6 compares the gas sensing responses of MTS-1, MTS-2, and MTS-3 at 0% - 50% relative humidity. Overall, it can be observed that as the environmental relative humidity increases, the sensing responses of the three samples continue to decline. Water vapor has a significant inhibitory effect on this ternary system. Under dry conditions (RH = 0%), MTS-1 has the highest response, MTS-3 follows, and MTS-2

has the lowest. This is consistent with the performance pattern of the temperature gradient test. In the dry environment, the material surface preferentially adsorbs oxygen molecules, generating active oxygen species such as O^{2-} and O^- . The ternary heterojunction fully plays its role in regulating carriers, achieving the optimal sensing output. After the humidity increases, water molecules compete for adsorption sites with the target gas; water molecules dissociate on the material surface to produce hydroxyl groups, consuming surface active oxygen and weakening the redox reaction, reducing the efficiency of charge transfer. At the same time, the inherent surface functional groups of MXene are hydrophilic, allowing water molecules to invade the interlayer and change the contact resistance of the layers, disrupting the bending of the heterojunction energy band, and further deteriorating the sensing signal. Within the entire humidity range, MTS-1 always maintains the highest response and has the best resistance to humidity interference, as SnO_2 provides sufficient backup active sites; MTS-3 with a high MXene content shows more significant attenuation under humidity influence. Even when the RH reaches 50%, MTS-1 still retains the ability to recognize the response, proving that the material has good humidity tolerance.

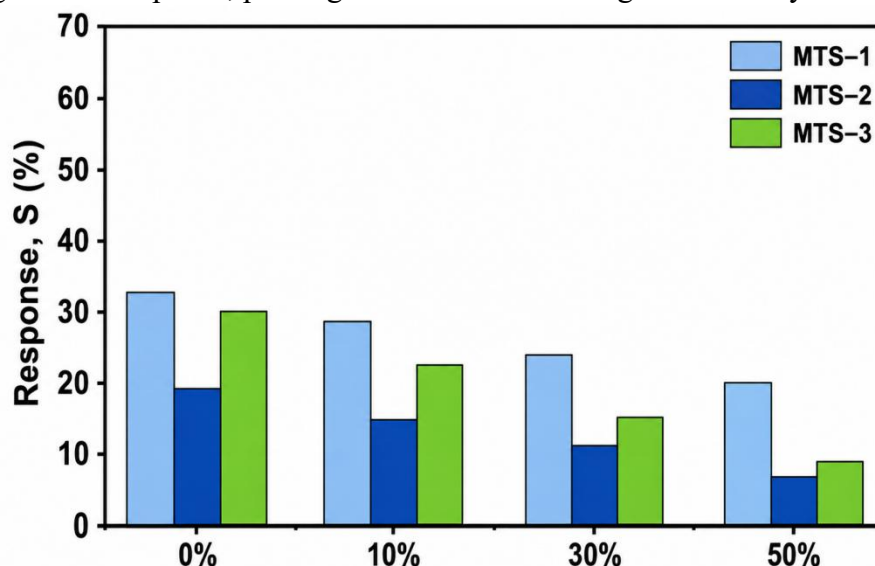


Fig.6. Response values of MTS series materials under different humidity levels

Fig. 7 compares the sensing responses of MTS-1, MTS-2, and MTS-3 composite materials to five typical gases: SO_2 , CO , NH_3 , H_2 , and CH_4 . This is used to systematically evaluate the gas recognition ability of the $Ti_3C_2T_x-TiO_2-SnO_2$ ternary heterojunction. From the Fig, it can be clearly observed that all three samples show significantly higher response amplitudes to H_2 compared to the other four interfering gases. Among them, MTS-1 has a response of approximately 33% to H_2 , MTS-3 follows, and MTS-2 is relatively lower; while the responses to SO_2 , CO , NH_3 , and CH_4 are all effectively suppressed at a relatively low level. This result directly proves that the $Ti_3C_2T_x-TiO_2-SnO_2$ ternary heterojunction constructed by O_2/Ar microwave plasma modification has excellent specificity for H_2 molecules.

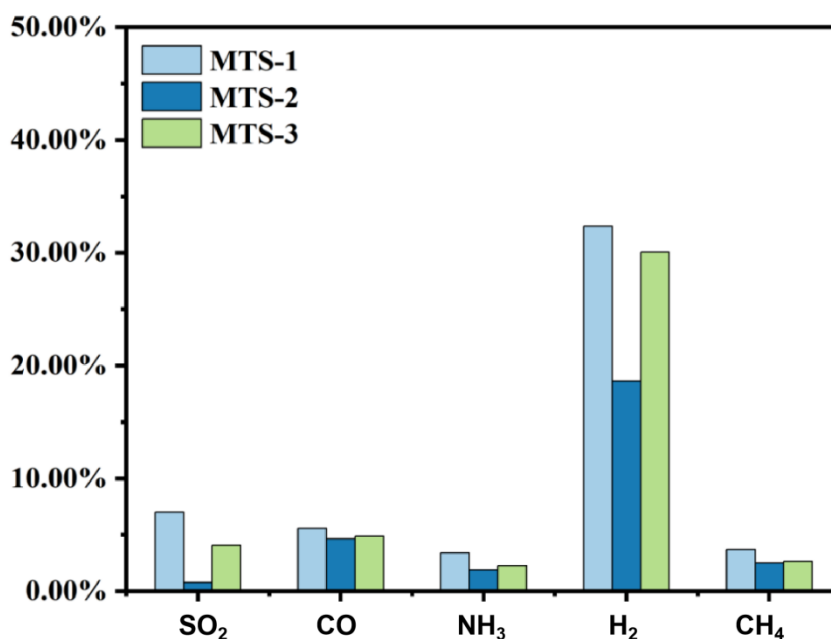


Fig.7. Gas sensitivity and selectivity of MTS series materials to different gases

The detection limit is also one of the key performance indicators for a material's gas-sensing capability. Based on the above results, this study provides an overall evaluation of the hydrogen detection limit for the composite material. The detection limit of the MTS-1-15% material was tested at room temperature, as shown in the Fig. The material exhibited a response value of 2.57% even to a hydrogen concentration of 1 ppm, confirming its excellent H₂ gas sensing ability.

Fig. 8b presents the long-term stability test results of the optimal sample over 17 consecutive days. During the long-term cycling test period, the sensor response of the sample fluctuates slightly within the range of 94.5% - 97.5% of the initial value, without significant continuous decay. The fluctuations mainly result from minor environmental temperature and humidity disturbances and test system errors. Overall, it proves that the Ti₃C₂T_x-TiO₂-SnO₂ composite material modified by plasma has excellent long-term working stability. The TiO₂ protective layer generated in situ by MPCVD inhibits the further spontaneous oxidation of MXene in the air, stabilizing the two-dimensional layered microstructure and maintaining the stability of the heterojunction interface, avoiding the continuous failure of active sites. This result indicates that the modification strategy effectively alleviates the inherent defect of MXene-based materials prone to oxidation degradation, which is crucial for the reliable operation of actual sensor devices.

Based on the results of detection limit and stability, MTS-1 can not only capture ppm-level low-concentration hydrogen signals but also has good temporal dimension reliability. This further corroborates the practical potential of this ternary composite material in hydrogen sensing.

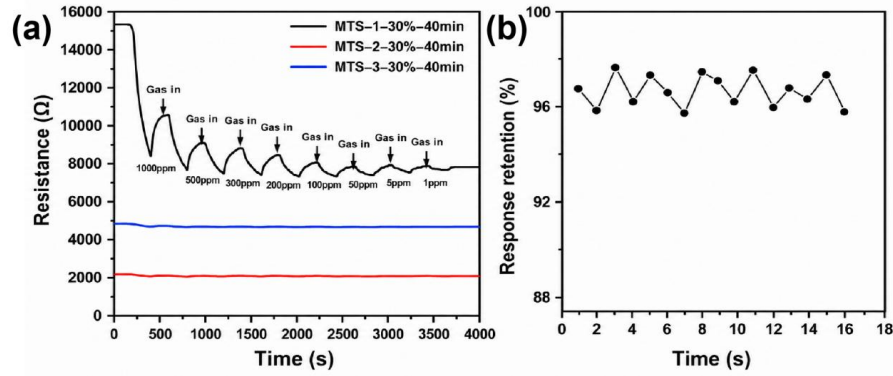


Fig.8. Detection limits and long-term stability of MTS materials

The gas sensing mechanism diagram is shown in Fig. 9. Based on the comprehensive characterization and gas sensing test results, the MTS-1 material exhibits excellent room-temperature hydrogen sensing performance. This is attributed to the synergistic effect of oxygen vacancy defects, the high conductivity framework of MXene, and the n-n heterojunction of $\text{TiO}_2\text{-SnO}_2$. When the sensor is placed in an air environment, oxygen molecules in the gas phase adsorb onto the material surface, capturing free electrons in the semiconductor to generate active oxygen ions such as O^{2-} and O^- . The electron depletion layer on the material surface widens, causing an increase in the baseline resistance of the sensor. When reducing hydrogen gas is introduced, the H_2 molecules undergo oxidation reactions with the surface active oxygen ions, and the captured electrons are released back into the material, causing the depletion layer to contract and thicken, resulting in a decrease in the sensor resistance. This enables the conversion of hydrogen gas signals.

MPCVD O_2/Ar plasma treatment introduces a large number of oxygen vacancies and Ti^{3+} defects, serving as highly active adsorption centers, significantly enhancing the efficiency of oxygen adsorption activation. At room temperature, sufficient active oxygen species can be generated. $\text{Ti}_3\text{C}_2\text{T}_x$ retains a complete two-dimensional layered structure, constructing a continuous and fast electron transmission channel, reducing the barrier for electron transport in gas sensing reactions, and solving the problem of low carrier mobility in metal oxides at room temperature. The TiO_2 and SnO_2 form an n-n heterojunction, where the interface undergoes band bending, forming a combined potential barrier, regulating the carrier concentration and transmission efficiency, and further amplifying the amplitude of resistance changes before and after hydrogen gas introduction. The cooperation of these three elements enables this ternary composite material to break away from the dependence of traditional MOS sensors on high-temperature thermal excitation, achieving high-sensitivity hydrogen detection at room temperature.

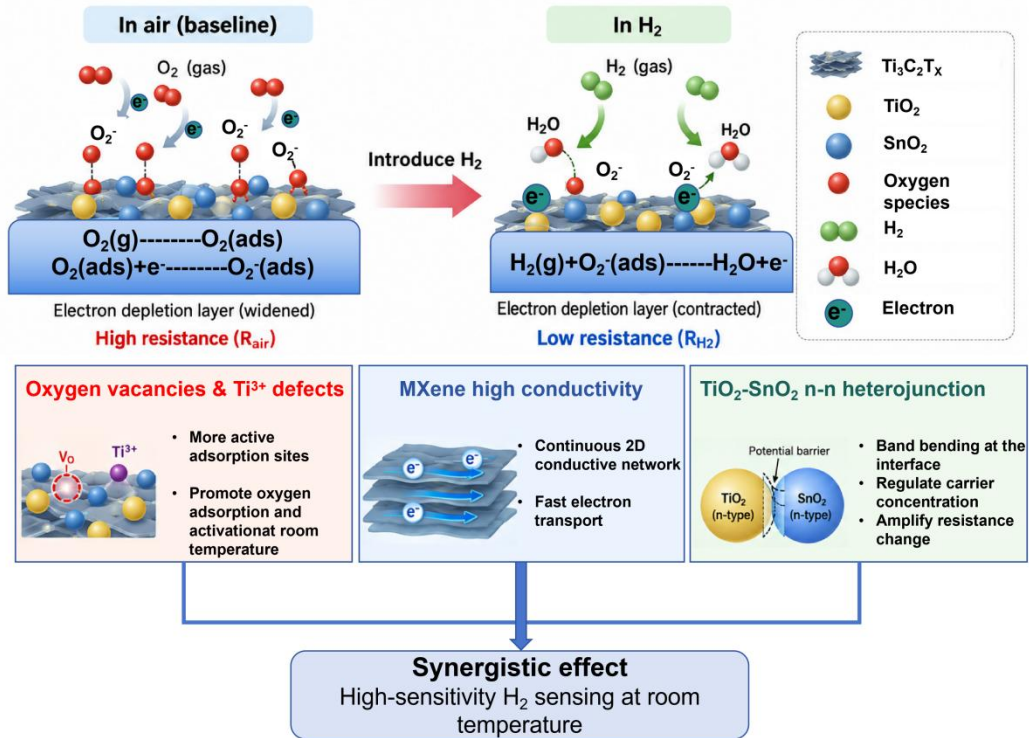


Fig.9. Schematic diagram of the gas sensing mechanism of MTS materials

4 Conclusions

This study utilized LiF-HCl hydrothermal etching to prepare $Ti_3C_2T_x$ MXene, and combined MPCVD oxygen-argon plasma in-situ reconstruction modification to successfully synthesize a ternary hydrogen gas sensor composite material of $Ti_3C_2T_x$ - TiO_2 - SnO_2 . The influence of raw material ratios and O_2 /Ar plasma atmosphere on the microstructure, surface chemical state, and gas sensing performance was systematically investigated, and the following main conclusions were obtained:

(1) The oxygen-argon volume ratio of 15:85 is the optimal plasma process for this system. This condition can well preserve the layered conductive framework of $Ti_3C_2T_x$ and achieve in-situ oxidation of MXene's surface to generate TiO_2 , while constructing a high-density n-n heterojunction with SnO_2 , simultaneously introducing oxygen vacancies and Ti^{3+} active defects. Excessive oxygen content will cause excessive oxidation of MXene, collapse of the layered structure, and deterioration of gas sensing performance.

(2) The MTS-1-15%-40min sample has the best comprehensive gas sensing performance. At room temperature (25 °C), it responds to 1000 ppm H_2 with a response of 32.36%, and has the lowest stable detection limit of 1 ppm hydrogen. It also has good gas selectivity, certain anti-wetness ability, and 16-day long-term cycling stability, effectively overcoming the shortcomings of traditional metal oxide hydrogen gas sensors with high operating temperature and high power consumption.

(3) The improvement of the material's hydrogen gas sensing performance is the result of the synergy of oxygen vacancies, the high conductivity path of MXene, and the n-n heterojunction of TiO_2 - SnO_2 . Oxygen vacancies enhance the gas adsorption activation ability; MXene provides a fast electron transmission channel; the

heterojunction interface regulates the carrier transport behavior. This work provides a new material idea and modification process for room-temperature low-power hydrogen gas sensors.

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