Selective Toluene Detection with Mo₂CT_x MXene at Room Temperature

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ABSTRACT: MXenes are a promising class of two-dimensional materials with several potential applications, including energy storage, catalysis, electromagnetic interference shielding, transparent electronics, and sensors. Here, we report a novel Mo_2CT_x MXene sensor for the successful detection of volatile organic compounds (VOCs). The proposed sensor is a chemi-resistive device fabricated on a Si/SiO₂ substrate using photolithography. The impact of various MXene process conditions on the performance of the sensor is evaluated. The VOCs toluene, benzene, ethanol, methanol, and acetone are studied at room temperature with varying concentrations. Under optimized conditions, the sensor demonstrates a detection limit of 220 ppb and a sensitivity of 0.0366 Ohm/ppm at a toluene concentration of 140 ppm. It exhibits an excellent selectivity toward toluene against the other VOCs. Ab initio simulations demonstrate selectivity toward toluene in line with the experimental results.

KEYWORDS: MXene, molybdenum carbide, sensor, volatile organic compound, chemi-resistor

1. INTRODUCTION

Air pollution is one of the most pressing problems facing humanity worldwide. A dangerous gas that Nowadays, the detection of toxic gases has become essential in environmental monitoring, industrial safety management, and medical applications. Various gas-sensing techniques exist based on different sensing platforms; these include capacitive devices,¹⁻² resistive devices,³⁻⁴ quartz crystal microbalance sensors,⁵⁻⁶ solid-state field-effect transistors,⁷⁻⁸ and organic field-effect transistors.⁹⁻¹⁰ In particular, among all toxic gases, volatile organic compounds (VOCs) are posing an increasing threat to the environment and human health due to their toxicity and volatility. Researchers have been adopting various transducers and classification models to detect VOCs.¹¹⁻¹² Toluene is regarded as one of the most hazardous VOC pollutants in the air and a major threat to human health,¹³ with even low levels of inhalation causing dizziness, confusion, and color-vision issues.¹⁴ In addition, due to the carcinogenic nature of nitrated toluene, long-term exposure could lead to respiratory cancer.¹⁵ Toluene biomarkers have been found in exhaled breath from smokers at many orders of magnitude higher concentration than in that from non-smokers.¹⁶⁻¹⁸ Since breath analysis has become one of the most important non-invasive methods in disease diagnosis, monitoring and measuring the concentration of toluene in breath could be an effective method of identifying smokers and non-smokers and monitoring the extent of exposure to toluene. Moreover, reports have been made on the acute effects of toluene on the central nervous system, where it acts like a depressant drug.¹⁹ Therefore, the detection of toluene has important implications for improved healthcare. Among various existing gas sensors, those based on metal oxides, such as ZnO²⁰ and SnO₂,²¹ are the most promising candidates for the detection of toluene.²²⁻²³ The poor selectivity issue in metal-oxides based gas sensors can be solved by applying machine learning algorithms.²⁴⁻²⁶ However, metal oxide sensors are required to work at high temperatures, mostly in the range from 300 to 500 °C, which limits their role in real-world applications.

Two-dimensional (2D) materials have been receiving significant attention for their potential in various applications.²⁷ The discovery of graphene and its extraordinary properties has driven researchers to explore different types of 2D materials, such as MoS₂, BN, and MXenes.²⁸⁻²⁹ MXenes were discovered in 2011³⁰ and are derived from MAX phases, which comprise layered ternary carbides or nitrides with formula M_{n+1}AX_n, where M stands for an early transition metal atom, A is a group 13 or 14 element, and X represents carbon and/or nitrogen. Generally, MXenes are prepared by selectively etching A atoms from MAX phases. Upon delamination, ultrathin single/few-layer MXene flakes can be readily obtained. They can be expressed as M_{n+1}X_nT_x, where T stands for the surface functional group, such as –O, –F, and –OH.

Immediately after the discovery of MXenes, Ti-based MXenes, such as Ti₂CT_x and Ti₃C₂T_x, have been widely studied both experimentally and theoretically due to their excellent electric conductivity and hydrophilicity.³¹ Among the MXenes, Mo₂CT_x was synthesized very recently through etching and exfoliation from the bulk Mo₂Ga₂C phase.³²⁻³³ Subsequently, it stands out as a very promising material for applications in energy storage, catalysis, thermoelectric devices, superconductivity, and gas sensing.³⁴⁻³⁸ It is reported that with catalytically active basal planes Mo₂CT_x can serve as an electrocatalyst for hydrogen evolution in clean energy technologies.³⁸ The finding of active basal planes eliminates the need for a deliberate and complex design to maximize the density of exposed edge sites. Lei et al. conducted first-principles calculations on Mo₂CT_x and revealed that it is an appealing superconductor with a well-tunable critical temperature.³⁷ Kim et al. explored the thermoelectric properties of Mo₂CT_x through experimental measurements up to 800 K.³⁶ They found that it exhibits high electric conductivity and an n-type Seebeck coefficient with high thermoelectric power, making it a promising material for thermoelectric devices. Furthermore, by taking advantage of the rich surface functional groups and large effective surface area, MXenes have been used to construct sensors for VOC detection. As the surface functional groups are mostly dominated by –O and –OH, the sensor can react

with many VOCs via hydrogen bonding. Lee et al. proposed a flexible gas sensor based on $\text{Ti}_3\text{C}_2\text{T}_x$ for VOC detection at room temperature and showed p-type sensing behavior.³¹ Kim et al. demonstrated a $\text{Ti}_3\text{C}_2\text{T}_x$ gas sensor with high metallic conductivity and abundant surface functional groups.³⁹ The sensor exhibited a very low limit of detection (LOD) and low noise, thus outperforming other sensors based on 2D materials.

While only few experimental demonstrations have been conducted, various simulations using density functional theory have modeled the gas detection by different MXenes.⁴⁰⁻⁴³ The sensing performance of MXenes still lags behind that of other sensing materials, such as metal oxides. Recently, much work has been focused on enhancing the sensing performance of $\text{Ti}_3\text{C}_2\text{T}_x$ by forming nanocomposites with other materials, such as reduced graphene oxide,⁴⁴⁻⁴⁵ metal oxides,⁴⁶⁻⁴⁸ palladium nanoclusters⁴⁹, and transition metal dichalcogenides;⁵⁰ by doping with sulfur;⁵¹ or by intercalating metal ions.⁵² With these, enhanced sensitivity and selectivity towards VOCs was demonstrated compared to the pristine MXenes. However, composite formation, doping, and ionic intercalation involve high-cost and complex processes, which generally require long optimization of experimental conditions.⁵³ Pristine MXenes can be easily synthesized in a low-cost process, and hence are more cost-effective for real-world applications.

Various works have shown that Mo_2CT_x exhibits superior electronic conductivity than other types of MXenes, which is good for building a low-noise sensing device.^{37, 54} The electro-catalytic study on Mo_2CT_x has revealed that Mo_2CT_x is more chemically active than the Ti-based MXene.³⁸ The high chemical activity can facilitate gas adsorption and potentially improve sensing performance. Its excellent stability and mechanical flexibility have also been demonstrated, providing the potential for building a stable and flexible sensing device.⁵⁵ Moreover, in previous works on MXene-based gas sensors, the change of elemental compositions can lead to different surface interactions and alter the selective preference of the gas sensor towards different types of VOCs. The study on Mo_2CT_x will open up a new

way for specializing MXenes with different compositions as gas sensing materials for selectively sensing various types of VOCs. However, to date, no group has reported a VOC-sensing study on Mo_2CT_x . Thus, we explore the potential of Mo_2CT_x and experimentally realize a Mo_2CT_x gas sensor device with interdigitated electrodes (IDEs) for VOC detection. Gas adsorption results in a resistance change of the device, which is measured as the sensor response. The experimental results reveal that Mo_2CT_x responds to toluene with higher sensitivity than to benzene, ethanol, methanol, and acetone.

To explain the experimental findings and reveal the underlying sensing mechanism, we apply ab initio simulations based on density functional theory to study the interaction between Mo_2CT_x and VOC molecules. Mo_2CT_x is modeled individually for the surface functional groups $-\text{O}$, $-\text{OH}$, and $-\text{F}$, and the reactions with the VOCs tested in the experiments are evaluated. First, the adsorption energy between Mo_2CT_x and the VOCs is calculated. Then, the current-voltage characteristics are simulated to confirm the observed device sensitivity and selectivity and to provide guidance to improvement of the device performance.

2. RESULTS AND DISCUSSION

2.1 Material Characterization

After the successful synthesis of Mo_2CT_x , the corresponding suspension was dropped on a sensor device. The synthesis process and the schematic illustration of the device are shown in **Figure 1**.

A Bruker diffractometer (D8 Advance) with Cu K_α radiation was used to collect X-ray diffraction (XRD) data with a scanning rate of $0.02^\circ/\text{step}$ and 0.5 s/step for 2θ angles of 3° to 70° . A scanning electron microscope (SEM, Zeiss, Berlin, Germany) equipped with an energy-dispersive X-ray spectroscopy (EDS) attachment was used to inspect the surface morphology. Raman spectra were collected on a Hariba Aramis spectrometer with a He-Ne laser at 633 nm. The SEM image of the $\text{Mo}_2\text{Ga}_2\text{C}$ phase shown in **Figure 2** (a) exhibits a typical layered structure. A multilayer structure can be

observed after hydrofluoric acid (HF) etching (**Figure 2 (b)**). After the delamination process, a flexible Mo_2CT_x film can be readily obtained by vacuum filtration (**Figure 2 (c)**). The SEM image confirms that flakes are assembled into a uniform film, displaying a flat surface of Mo_2CT_x . Moreover, digital images in **Figure 2 (d)** show the low concentration Mo_2CT_x suspension and free-standing film. A brown-pink color is observed for the suspension while the film is metallic green, which is in good agreement with previously reported results.³²

Figure 1 (a) Schematic illustration of the synthesis of Mo_2CT_x . The Mo, C, and Ga atoms are represented by purple, brown, and green colors, respectively. **(b)** Schematic drawing of the Mo_2CT_x -based gas sensing device. The Mo_2CT_x solution (dark yellow) was cast on the IDEs.

XRD patterns of the $\text{Mo}_2\text{Ga}_2\text{C}$ phase, HF-etched $\text{Mo}_2\text{Ga}_2\text{C}$, and delaminated Mo_2CT_x are shown in **Figure 3 (a)**. The HF-etched Mo_2CT_x was delaminated with tetramethylammonium hydroxide (TMAOH). After the delamination, the $d\text{-Mo}_2\text{CT}_x$ was intercalated with TBA^+ cations. So the strong (002) peak that appears at a lower angle (< 10 degree) in the $d\text{-Mo}_2\text{CT}_x$ XRD pattern indicates the expanded interlayer spacing, which is related to the intercalation of the TBA^+ cations. It should be noted that during the centrifugation step, the unetched precursor (MAX phase) and unexfoliated thick MXene particles were successfully removed from the $d\text{-Mo}_2\text{CT}_x$, which resulted in the absence of other peaks (except for the (002) peak) of the precursor in the $d\text{-Mo}_2\text{CT}_x$ XRD pattern. This phenomenon indicates an increased c lattice parameter of the produced Mo_2CT_x because of TMAOH intercalation and removal of the MAX

phase from the suspension. A similar phenomenon has also been observed in previous works.^{32-33, 56}

Figure 3 (b) shows the Raman spectra of the as-prepared $\text{Mo}_2\text{Ga}_2\text{C}$ and Mo_2CT_x , which are in good agreement with previous reports.^{36, 57} Specifically, in the case of $\text{Mo}_2\text{Ga}_2\text{C}$ two peaks located at 171 and 230 cm^{-1} represent the E_{2g} and A_{1g} modes, respectively. These two peaks are shifted to 143 and 250 cm^{-1} because of the removal of Ga layers and the terminations that are formed. The peak at 302 cm^{-1} in the $\text{Mo}_2\text{Ga}_2\text{C}$ spectrum is diminished in the case of Mo_2CT_x , which is related to the A_{1g} mode (displacement of the Mo atoms perpendicular to the basal plane and the nearby Ga atoms in the opposite direction).⁵⁸ The peaks at 492 and 687 cm^{-1} are additional E_{2g} and A_{1g} modes, respectively, caused by the presence of surface functional groups. All four peaks agree well with the reported spectrum of Mo_2CT_x .^{57, 59} Overall, these characterization results indicate that a uniformly delaminated Mo_2CT_x with different functional groups is successfully synthesized.

Figure 2 SEM images of (a) Mo₂Ga₂C, (b) HF-etched Mo₂Ga₂C, and (c) Mo₂CT_x free-standing film. Digital image of (d) Mo₂CT_x suspension in water (left) and Mo₂CT_x free-standing film obtained via vacuum filtration (right).

Figure 3 (a) XRD patterns of Mo₂Ga₂C (black), HF-etched Mo₂Ga₂C (pink), and delaminated Mo₂CT_x(blue). (b) Raman spectra of Mo₂Ga₂C (black) and delaminated Mo₂CT_x (blue).

2.2 Optimization of Mo₂CT_x concentration

To study the impact of the Mo₂CT_x concentration in the suspension on the sensing response, we prepared five Mo₂CT_x suspensions by diluting the synthesized Mo₂CT_x suspension to different concentrations, namely, 0.011, 0.033, 0.066, 0.36, and 0.66 mg/mL. For each experiment, 5 μl of Mo₂CT_x suspension was dropped on the device and the measurements were made under the same conditions. The sensing response was measured after 2 min exposure as the change of resistance over the baseline resistance, which is defined as $(R_g - R_b)/R_b \times 100\%$, where R_g is the resistance of the Mo₂CT_x film during exposure to the VOCs, and R_b is the baseline resistance. **Figure 4** shows the measured sensing responses to the VOCs for different Mo₂CT_x concentrations. Since there is a large difference among the Mo₂CT_x concentrations, the x-axis is plotted in a log scale in order to easily compare them. The VOCs

were flowed into the chamber at five different flow rates from 4 sccm, 8 sccm, 12 sccm, 16 sccm, and 20 sccm in a N₂ environment. After the measurements, the flow rates of the VOCs were converted to gas concentrations in parts per million (ppm).^{2, 60} The responses initially increase with the concentration in the low concentration range but drop when the concentration is high. An optimum concentration can be obtained from the results. The reason for the initial increase of the responses is that after the low-concentration Mo₂CT_x suspension was dropped and dried on the IDE, there was no sufficient amount of Mo₂CT_x flakes to form enough conducting paths on the surface, which resulted in a small effective sensing area and poor VOC adsorption. When the concentration increased, more and more conducting paths were formed on the surface and the effective sensing area was enlarged so that more VOC molecules can be attracted on the surface, and the adsorption affected the conductivity change more strongly. On the other hand, at high concentrations, many layers of Mo₂CT_x flakes were formed on the IDE so that there were many other conduction paths underneath the Mo₂CT_x surface that can not interact with the VOCs. When the concentration increased, the deposited Mo₂CT_x film became thicker, and more conducting paths were formed underneath the surface, leading to less conductivity change caused by the VOC adsorption, since VOCs can only interact with Mo₂CT_x on the surface. The same phenomenon has also been reported in a graphene-based gas sensor.⁶¹ It can be observed that in the cases of benzene, ethanol, and methanol (**Figure 4** (b), (c), and (d)) [and acetone (**Figure S1** (a))] the optimal concentration is 0.066 mg/mL at each concentration, while for toluene (**Figure 4** (a)) it is 0.066 mg/mL except at the concentration of 35 ppm. We therefore chose 0.066 mg/mL as the optimal concentration for further experiments.

Figure 4 Measured sensing response to VOCs for different Mo_2CT_x concentrations (0.011, 0.033, 0.066, 0.36 and 0.66 mg/mL): (a) toluene, (b) benzene, (c) ethanol, and (d) methanol. The VOCs were flowed into the chamber at rates from 4 sccm to 20 sccm in a N_2 environment. The flow rates were converted to the corresponding gas concentrations.

2.3 Optimization of sonication time

During the synthesis of the Mo_2CT_x suspension, sonication can effectively delaminate the MXene layers and produce a high fraction of single-layer small-sized flakes that can contribute to a large effective sensing area.³² Thus, to investigate the effect of the sonication on the sensing response, we placed the synthesized Mo_2CT_x suspension into an ultrasonic bath. The sonication times were chosen as 0.5 h, 1.5

h, 3 h, 5 h, and 8 h. The measured responses to different VOCs are shown in **Figure 5** and **Figure S1** (b). The sensing response was measured after 2 min exposure. With the sonication time extending, the response increased significantly at the beginning and then slowed until it reached saturation at the end of the eighth hour. At a high flow rate, the improvement is roughly 2-3 times more than in the case without sonication. The observed improvement can be attributed to the enlarged effective sensing area due to the large portion of single-layer small-sized flakes produced by sonication. As a result, 8 h was selected as the optimal sonication time for further comparison and analysis.

Figure 5 Measured sensing response to VOCs for different sonication times: (a) toluene, (b) benzene, (c) ethanol, and (d) methanol.

2.4 Transient analysis

Figure 6 Transient response of Mo₂CT_x to different VOCs for 2 min exposure: (a) toluene and (b) benzene.

With the optimized parameters, the transient response of the Mo₂CT_x film to different VOCs was measured for various gas concentrations, as displayed in **Figure 6** for toluene and benzene and **Figure S1** (c) for ethanol. The transient response measurements were started after the resistance of the gas-sensing device became stable during N₂ purging. Then, the gas-sensing device was exposed to the VOCs sent from a glass bubbler at different flow rates for 2 min (orange regions). The transient response rises very fast immediately after the injection of the VOCs, which indicates strong gas adsorption. After exposure, the device was revived by N₂ purging that can effectively remove the VOCs adsorbed on the MXene surface. The revival process takes 8-10 min to restore the device resistance to the baseline, depending on the gas flow rate. The fact that the device resistance can be restored to the baseline in a short time implies physical adsorption of the VOCs on Mo₂CT_x. Moreover, MoC₂T_x shows p-type sensing behavior in which the resistance of the MoC₂T_x-based gas sensor increases after the adsorption of VOCs, as shown in the transient resistance change plots (**Figure S2**). It is also reflected by the positive response values upon exposure to VOCs. The p-type behavior could be due to the metallic conductivity of MoC₂T_x. The adsorption of the VOCs can largely reduce the number of charge carriers and hence increase the

channel resistance.³⁹ The p-type behavior of MXene sensing VOCs has also been demonstrated in other MXene-based gas sensors.^{31, 39, 51}

Figure 7 (a) Response under exposure to toluene, benzene, ethanol, methanol, and acetone at 140 ppm. (b) Response as a function of the gas concentration for toluene. The concentration of Mo_2CT_x is 0.066 mg/mL and the sonication time is 8 h.

To quantitatively compare the sensing performance to different VOCs, the response to each gas at 140 ppm is plotted in **Figure 7** (a). The response to toluene, benzene, ethanol, methanol, and acetone is 2.81%, 0.97%, 0.73%, 0.58%, and 0.14%, respectively, showing that Mo_2CT_x is highly selective to toluene. Interestingly, Mo_2CT_x reacts stronger with aromatic VOCs than $-\text{OH}$ and $-\text{O}$ -terminated VOCs that have been reported to be selectively adsorbed on $\text{Ti}_3\text{C}_2\text{T}_x$ through hydrogen bonding.³⁹ The sensing mechanism for selective toluene detection is due to the interaction between the benzene ring in toluene molecules and MoC_2T_x since the benzene ring has high activity. The benzene ring interacts more strongly with MoC_2T_x and reduces the number of charge carriers more substantially thanks to its higher activity compared to other non-aromatic VOCs. The methyl group further improves the activity of the benzene ring in toluene molecules, which explains that toluene shows a higher response than benzene.⁶² The strongest interaction between toluene and MoC_2T_x is also demonstrated in the ab initio simulation

showing the highest absorption energy between them. Furthermore, to investigate the sensitivity and LOD, the response to different gas concentrations is plotted in **Figure 7 (b)** for toluene. It can be observed that the response increases linearly with the gas concentration. The theoretic LOD is defined as the gas concentration corresponding to a signal-to-noise ratio of 3. It can be derived using the root-mean-square deviation (RMSD) method, where the noise is calculated as the root-mean-square error between the measured responses and the fitted responses.^{9, 63} Thus, the LOD is calculated as 220 ppb, corresponding to a signal-to-noise ratio of 3. The sensitivity of the sensing device to toluene at 140 ppm is calculated as 0.0366 Ohm/ppm.

Table 1 Comparison of MXene-based gas sensors. RT stands for room temperature. NA indicates that the relevant data is not available in the reference.

Reference	Material	Condition	VOC leading to the highest sensing response	Limit of detection	Cross sensitivity ratio at 100 ppm	Range of linear response
[31]	Ti ₃ C ₂ T _x	RT	Ammonia	NA	1.47	NA
[39]	Ti ₃ C ₂ T _x	RT	Ethanol	50 ppb	1.75	Nonlinear
[64]	V ₂ CT _x	RT	Ethanol	NA	3.61	NA
[48]	CuO/Ti ₃ C ₂ T _x	250 °C	Toluene	320 ppb	NA	10-40 ppm
[51]	Sulfur-doped Ti ₃ C ₂ T _x	RT	Toluene	NA	NA	0.5-10 ppm
Our work	Mo ₂ CT _x	RT	Toluene	220 ppb	2.65	35-175 ppm

Table 1 compares the performances of different MXene-based gas sensors. The Ti₃C₂T_x-based gas sensor reported by Kim et al.³⁹ shows the lowest LOD. The V₂CT_x-based gas sensor reported by Lee

et al.⁶⁴ (highest response for ethanol) shows the highest cross sensitivity ratio (ratio between the highest and the second highest response). Our Mo₂CT_x-based gas sensor shows the highest response to an aromatic VOC, toluene, and it exceeds the cross sensitivity ratio of the Ti₃C₂T_x-based gas sensor. In the case of toluene detection, compared with the CuO/Ti₃C₂T_x composite and sulfur-doped Ti₃C₂T_x, our gas sensor has the advantages of room temperature operation, low LOD, and wide range of linear response. Also, with further optimizations, MXene devices could be monolithically integrated into other electronic platforms such as metal-oxide semiconductors⁶⁵ to realize gas-sensing arrays.

2.5 Ab initio simulation

We present the first ab initio simulations of VOC sensing by Mo₂CT_x to support and explain the experimental data. The results also provide insights that can be used to engineer the sensing device such that its performance is optimized. The simulations are based on spin-polarized density functional theory, as implemented in the Vienna Ab Initio Simulation Package (projector-augmented wave method; plane waves basis with 500 eV energy cutoff).⁶⁶⁻⁶⁷ The generalized gradient approximation of Perdew–Burke–Ernzerhof is used for the exchange-correlation potential,⁶⁸ accounting for the long-range van der Waals interaction by the DFT-D3 method with Becke–Johnson damping.⁶⁹⁻⁷⁰ $4 \times 4 \times 1$ supercells of Mo₂CT_x with 18 Å vacuum along the *c*-axis (to avoid unphysical interlayer interaction) are used. The Brillouin zone is sampled on a $3 \times 3 \times 1$ Monkhorst–Pack k-mesh.⁷¹ All models are optimized (conjugate gradient method) until the total energy and forces on each atom remain below 10^{-6} eV and 10^{-3} eV/Å, respectively. Current-voltage characteristics are calculated for Mo₂CO₂ using the nonequilibrium Green’s function formalism of the SMEAGOL package.⁷²⁻⁷³ We use the generalized gradient approximation of Perdew–Burke–Ernzerhof and a double-zeta basis with a cutoff energy of 700 Ry. The Brillouin zone is sampled on $1 \times 9 \times 50$ and $1 \times 9 \times 1$ Monkhorst–Pack k-meshes in the electrode and transport calculations, respectively. Considering the structural anisotropy of MXenes, transport calculations are performed for the armchair and zigzag directions. The transport models consist of a scattering region (armchair: 11.5 Å

$\times 10.0 \text{ \AA}$; zigzag: $10.0 \text{ \AA} \times 11.5 \text{ \AA}$) sandwiched between two semi-infinite electrodes (armchair: $11.5 \text{ \AA} \times 10.0 \text{ \AA}$; zigzag: $10.0 \text{ \AA} \times 11.5 \text{ \AA}$).

Figure 8 (a) Top and side views of Mo_2CO_2 , (b) electronic band structure of Mo_2CO_2 , and (c) top and side views of the lowest-energy configurations of acetone, methanol, ethanol, benzene, and toluene adsorbed on Mo_2CO_2 . The Mo, C, O, and H atoms are represented by purple, brown, red, and magenta colors, respectively.

During the experimental exfoliation process using HF acid, the surfaces of MXenes are functionalized with $-\text{F}$, $-\text{O}$ and $-\text{OH}$ groups.³² We therefore consider Mo_2C with these groups placed at different surface sites: H_{Mo} (hollow site on top of a Mo atom), H_{C} (hollow site on top of a C atom), and T_{Mo} (on top of a Mo atom). We find that the $-\text{F}$ and $-\text{OH}$ groups favor the H_{Mo} site and that the $-\text{O}$ group favors the H_{C} site. **Figure 8** (a) shows top and side views of the atomic structure of Mo_2CT_x with $-\text{O}$ functionalization (Mo_2CO_2). Mo_2CT_x with $-\text{F}$ and $-\text{OH}$ functionalization is shown in **Figure S3**. The electronic band structure reveals that Mo_2CO_2 is metallic (**Figure 8** (b)). Mo_2CF_2 is semiconducting and $\text{Mo}_2\text{C}(\text{OH})_2$ is metallic (**Figure S3**). VOC molecules are attached to the H_{Mo} , T_{Mo} , and T_x (on top of the

X group) sites in different orientations. The lowest-energy configurations that are obtained are illustrated in **Figure 8** (c) for Mo₂CO₂ and in **Figure S4** for Mo₂CF₂ and Mo₂C(OH)₂. All molecules align parallel to the surface at the sites indicated in **Table 2** and **Table S1**. The binding strength of a molecule on Mo₂CT_x is evaluated in terms of the adsorption energy $E_{ad} = E_{MXene+molecule} - (E_{MXene} + E_{molecule})$, where $E_{MXene+molecule}$, E_{MXene} , and $E_{molecule}$ are the total energies of the combined system, Mo₂CT_x, and VOC molecule, respectively. The results are listed in **Table 2** and **Table S1**. When the calculated adsorption energies are compared with the experimental sensing response at 140 ppm (**Figure 7** (a)), the best agreement is obtained for Mo₂CO₂, which suggests that the –O group dominates at the surface of the experimental samples.

Table 2 Adsorption energies and lowest-energy adsorption sites of VOC molecules on Mo₂CO₂.

VOC	Adsorption energy (eV)	Adsorption site
Acetone	–0.69	T _O
Methanol	–0.47	H _{Mo}
Ethanol	–0.55	T _{Mo}
Benzene	–0.75	T _O
Toluene	–1.00	Intermediate

Figure 9 (a, b) shows the current-voltage characteristics along the armchair and zigzag directions of Mo₂CO₂ before and after the adsorption of a VOC molecule. When a voltage of less than 0.3 V is applied, the sensing response is the highest for toluene for both transport directions (**Figure 9** (c, d)). At an applied voltage of 0.2 V the sensing response follows the order toluene > benzene > ethanol > methanol > acetone, which is consistent with the experimental results in **Figure 7** (a). Note that in the experiment a voltage of 0.5 V is applied. However, due to the contact resistance of the IDEs, the effective voltage is smaller than the actual applied voltage. Thus, the response trend of **Figure 9** (c, d) agrees with the experimental result.

Figure 9 Current-voltage characteristics along the (a) armchair and (b) zigzag directions for different VOCs on Mo₂CO₂ (pristine = no VOC is adsorbed). Sensing responses along the (c) armchair and (d) zigzag directions for different VOCs on Mo₂CO₂.

3. CONCLUSIONS

In summary, we demonstrated a chemi-resistive sensor for toluene detection based on the 2D MXene Mo₂CT_x. We optimized the desired concentration of the MXene (0.066 mg/mL) and the sonication time (8 h) to attain higher sensitivity. When compared to other VOCs, toluene was selectively identified with the micro-fabricated sensor that embeds Mo₂CT_x flakes. Ab initio simulations of Mo₂CT_x were used to determine the interaction strengths with various VOCs. The current-voltage characteristics that were obtained matched quantitatively well with the experimental data. The developed sensor device

showed a sensitivity of 0.0366 Ohm/ppm at 140 ppm and a LOD of 220 ppb, with a linear response for a toluene concentration in the range from 35 ppm to 175 ppm. Transient analysis of the device for 2 min at different VOC concentrations confirmed revival of the sensor. We anticipate that Mo₂CT_x-based sensors are promising for applications in environmental monitoring.

4. EXPERIMENTAL METHODS

4.1 Materials

HF and TMAOH solutions were purchased from Sigma Aldrich. Deionized water was used to prepare the solutions. Mo₂C powder and Ga were purchased from Alfa Aesar, Ward Hill, MA, both of 99.5 wt% purity.

4.2 Synthesis of delaminated Mo₂CT_x

The synthesis process of delaminated Mo₂CT_x is illustrated in **Figure 1** (a). The Mo₂Ga₂C precursor was prepared following previous reports.^{32, 74} First, HF etching was applied to remove the Ga layers and obtain Mo₂CT_x. Specifically, 2 g Mo₂Ga₂C powder was immersed slowly in a bottle containing ~25 wt% HF solution (Fisher Scientific) with a ratio of 1 g to 40 ml. Afterwards, the bottle was placed in an oil bath over a stirred hot plate held at 55 °C for 8 days. The resulting suspension was washed with deionized water thoroughly until a pH of ~6 was reached. The resultant Mo₂CT_x powder was dried in a vacuum oven overnight. After that, 1 M TMAOH solution was used to delaminate the multilayer Mo₂CT_x. 0.5 g Mo₂CT_x powder was mixed with 10 ml TMAOH solution and stirred for 18 h at room temperature. The resultant suspension was washed with deionized water for 3 times and centrifuged for 30 min (5000 rpm) to remove the residual TMAOH. The delaminated Mo₂CT_x suspension was then collected after centrifugation (4500 rpm for 5 min) for further experiments. A free-standing Mo₂CT_x film was obtained by vacuum filtering the suspension through a nanoporous polypropylene membrane.

4.3 Device fabrication

Our Mo₂CT_x-based gas-sensing device was fabricated on a Si/SiO₂ wafer. IDEs were patterned on the wafer by depositing titanium/gold through the lift-off process. Initially, a 2 μm thick oxide layer was grown through a wet-oxidation process, and subsequently 280 nm thick IDEs with a spacing of 10 μm were deposited. For the deposition of the MXene film, 5 μl of the synthesized Mo₂CT_x suspension was dropped on the IDEs and dried overnight in a desiccator.

4.4 Electrical measurements

The fabricated gas-sensing devices were inserted into a gas chamber, which was then purged by N₂ gas. After the device resistance remained stable, we began to obtain our baseline, the purging was stopped, and the VOC was sent into the chamber at different flow rates. We tested the devices for toluene, benzene, ethanol, methanol, and acetone at room temperature. We also used five different flow rates for the VOC gases. At each flow rate, the sensor was exposed to the VOC for a duration of 2 min. Then, the chamber was purged with N₂ gas until the device resistance recovered to its baseline. The resistance of the device was measured using a precision multimeter (Agilent 6 1/2 digital multimeter 34401A). The data acquisition and controlling of the gas flow were performed through the LabVIEW interface. The sensing response to VOCs was calculated as the measured resistance change over the baseline resistance,

$$Response = \frac{R_g - R_b}{R_b} \times 100(\%) = \frac{I_b - I_g}{I_g} \times 100(\%)$$

where R_g is the resistance of the Mo₂CT_x film during exposure to the VOC, R_b is the baseline resistance, I_g is the current flowing through the Mo₂CT_x film during exposure to the VOC, and I_b is the baseline current.

Supporting Information Available:

The supporting information presents experimental results for acetone and ethanol as well as computational results for Mo₂CF₂ and Mo₂C(OH)₂.

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Notes

The authors declare no competing financial interest

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