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ARTICLE

Enhanced water adsorption properties of Ti₃C₂T_x MXene/bentonite thin films for highly sensitive humidity sensing ¹



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ABSTRACT

Humidity sensors are integral to modern technology and extensively utilize $Ti_3C_2T_x$ MXene for its superior sensitivity and accuracy. This material's effectiveness stems from its abundant hydrophilic functional groups and high electrical conductivity. In this study, we enhanced the responsiveness to relative humidity changes by incorporating bentonite, a 2D clay mineral known for its robust water adsorption capacity and ionic conductivity, attributable to its distinctive structure. Our analysis of MXene/bentonite thin films through sheet resistance measurements indicated a clear inverse relationship in resistance changes above and below a specific MXene-to-bentonite ratio. Impedance analysis further revealed that the dominant conduction mechanisms within these films vary according to the mix ratio. In fabricating conductive-type humidity sensors from MXene/bentonite films, we observed a remarkable increase in humidity sensitivity. Particularly, MXene rich film (33 wt. % MXene) demonstrated a sensitivity of ~58.1 times greater than MXene film, and bentonite rich film (10 wt. % MXene) demonstrated about 5000 times greater than MXene film. This study not only underscores the potential of MXene/bentonite composites in humidity sensing but also highlights the critical role of composition in optimizing sensor performance.

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Humidity sensors are critical in various sectors, including medical, industrial, and agricultural monitoring.^{1,2} Therefore, the development of sensors that can detect changes in relative humidity (RH) with high sensitivity and accuracy is essential. A broad range of functional materials such as metal oxides,^{3,4} carbon materials,^{5–7} and conductive polymers^{8,9} have been explored for their potential in highly sensitive humidity sensing. In recent years, 2D nanomaterials, such as graphene oxide (GO) and black phosphorus, have attracted considerable attention as efficient sensing materials due to their extensive specific surface areas rich in surface functional groups, providing ample water adsorption sites.^{10,11}

MXene represents a class of 2D nanomaterials comprising transition metal carbides or nitrides and has emerged as a promising alternative. First reported in 2011,¹² MXene is characterized

by the formula $M_{n+1}X_nT_x$, where M represents a transition metal such as titanium or vanadium, X is carbon or nitrogen, and T_x includes surface functional groups like –OH, –O, or –F. Known for its strong hydrophilicity due to these surface functional groups, MXene offers enhanced water adsorption and intercalation properties.¹³ The intercalation of water molecules expands the interlayer space in MXene, leading to an increase in inter-flake resistance.^{14,15} This property makes MXene an excellent candidate for sensing relative humidity changes, proving to be a highly sensitive and accurate material for humidity sensors.^{16,17}

In this study, we have explored the use of bentonite as an additive to enhance water molecule adsorption in the development of a highly sensitive humidity sensor based on $Ti_3C_2T_x$ MXene. Bentonite is a layered clay mineral, consisting of an Al octahedral

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sheet sandwiched by two Si tetrahedral sheets. In this structure, Al and Si are partially substituted by Mg and Si, respectively, leading to a net negative charge within the lattice. To balance this charge disparity, cations such as Na⁺ and Ca²⁺ are integrated onto the surface of bentonite. These properties contribute to bentonite's high water absorbency, and it has been applied in various technologies, including brackish water desalination and water–oil separation membranes.^{18,19} Additionally, bentonite demonstrates a significant oxygen adsorption capacity. When combined with MXene, it can prevent the oxidation of MXene, enhancing the material's stability for long-term uses.²⁰ Bentonite also exhibits ionic conductivity, a result of the dissolution of surface-attached cations in water, which then freely move.^{21,22}

This study further examines the effectiveness of MXene/bentonite thin films for humidity sensing. The relationship between the mixing ratio of the sensing materials, their conductivity, and their sensitivity to humidity changes is critical.²³ We have analyzed how the conductivity of MXene/bentonite thin films varies with different mixing ratios, observing that the trend in sheet resistance inversely correlates beyond a specific threshold. Impedance measurements were conducted to understand the reasons behind these conductivity changes. Our findings confirm that incorporating bentonite into MXene not only enhances water molecule adsorption but also significantly improves the sensor's sensitivity to humidity changes.

MXene/bentonite thin films were fabricated using the vacuumassisted filtration method, illustrated schematically in Fig. 1(a). This process involved filtering a mixture of MXene and bentonite dispersions under vacuum. The MXene dispersion was prepared through a multi-step procedure: Initially, tetramethylammonium hydroxide pentahydrate (TMAOH \cdot 5H₂O) was mixed into 2 ml of nitrogenbubbled deionized water. Subsequently, 40 mg of Ti₃C₂T_x MXene powder and 20 ml of super-dehydrated tetrahydrofuran (THF) were added to the mixture and stirred at 700 rpm for five days under a nitrogen atmosphere. After stirring, 20 ml of isopropanol (IPA) was added, and the mixture was centrifuged at 4500 rpm for 10 min. Following the removal of the supernatant, the residue was redispersed in 20 ml of nitrogen-bubbled deionized water and centrifuged at 1500 rpm for 30 min. The final MXene dispersion was obtained after centrifuging the last supernatant at 3500 rpm for 30 min. In parallel, the bentonite dispersion was prepared by adding 40 mg of bentonite powder to 20 ml of deionized water, ultrasonically treating the mixture for three hours, and centrifuging at 3500 rpm for 5 min to obtain the supernatant as the bentonite dispersion. Detailed information on the characteristics of MXene and bentonite flakes is available in the supplementary material, S1.

In this study, MXene and bentonite were combined in specific mass ratios and subsequently processed through filtration. During this process, MXene and bentonite flakes randomly stacked to form a thin film on the filter, depicted in Fig. 1(b). The filter with the MXene/bentonite thin film was then immersed in deionized water for ~1 min. Subsequently, the wet film was carefully positioned on a substrate, with the MXene/bentonite side facing down. Upon drying, the filter was peeled away, leaving the MXene/bentonite thin film adhered to the substrate. Figure 1(c) showcases the transferred MXene/bentonite thin film on a polyethylene naphthalate (PEN) substrate, demonstrating the film's transparency.

To determine the electronic conduction properties of the MXene/bentonite thin film, we measured its sheet resistance across various MXene-to-bentonite ratios using the four-probe method (MCP-T370, Nittoseiko Analytech Co., Ltd.), with results presented in Fig. 2(a). The sheet resistance increases with the MXene content up to 20 wt. %, where it peaks, aligning with percolation behavior, which typically describes the variation of conductivity in a mixture of conductive and insulating materials.^{24,25} Contrary to typical percolation behavior where resistance decreases as conductive filler is added to an insulator, the sheet resistance in our MXene/bentonite films decreases beyond a MXene ratio of ~20 wt. %. Given the molecular weights of Ti₃C₂T_x (assumed surface terminations are -O, –OH, –F at a ratio of 1:1:1) is 202.3, and bentonite $(\mathrm{Al}_2\mathrm{O}_3\cdot 4\mathrm{SiO}_2$ \cdot H₂O) is 360.3, it could be qualitatively reasonable that the trend of resistance change depending on MXene content occurs at a MXene mass ratio lower than 50 wt. %.

This study hypothesizes that the observed variations in conduction mechanisms within the MXene/bentonite thin films are attributable to differences in mixing ratios. Specifically, when the



FIG. 1. Fabrication of MXene/bentonite thin films. (a) Schematic illustration of vacuum-assisted filtration. (b) MXene/bentonite thin films showing various mixing ratios of MXene to bentonite post-filtration: (I) MXene:bentonite = 10:0 (pure MXene), (II) MXene:bentonite = 9:1, (III) MXene:bentonite = 1:1, (IV) MXene:bentonite = 1:9, and (V) MXene:bentonite = 0:10 (pure bentonite). (c) MXene/bentonite thin film (MXene:bentonite = 1:1) transferred onto the PEN substrate.



FIG. 2. (a) Sheet resistance of MXene/bentonite thin films across various mixing ratios. (b) and (c) Schematic representations of conduction mechanisms: (b) ionic conduction in bentonite-rich films and (c) electronic conduction in MXene-rich films.

MXene content is below ~20 wt. %—a condition referred to as "bentonite-rich"—ionic conduction primarily derived from bentonite dominates [Fig. 2(b)]. In this region, an increase in sheet resistance is observed, potentially due to the disruption of the ionic conduction network as the proportion of MXene increases. Conversely, when the MXene content exceeds about 20 wt. %—termed "MXene-rich"—electron conduction from MXene becomes predominant [Fig. 2(c)]. This scenario suggests that an increased MXene content enhances electron conduction, thereby reducing the sheet resistance.

To test this hypothesis, impedance analyses were conducted on both MXene-rich (MXene ratios of 33 and 50 wt. %) and bentoniterich (MXene ratio of 10 wt. %) thin films. Impedance measurements were conducted using an LCR meter (ZM2376, NF CORPORA-TION) by sweeping frequencies. The input signal was set at a voltage level of 1 V, covering a frequency range from 100 mHz to 100 kHz. The MXene/bentonite thin films, formatted as strips on a PEN substrate, had copper wires affixed to both ends with silver paste for connectivity.

An equivalent circuit model, illustrated in Fig. 3(a), was utilized to better understand the relationship between the proportion of MXene to bentonite and their respective conduction mechanisms, as suggested by the trends shown in Figs. 2(b) and 2(c). The model incorporates both ionic and electronic conduction paths connected in parallel. Within this circuit, R_{ct} represents the electron transfer resistance, R_{ion} is the resistance component due to ionic conduction, R_e represents the resistance component due to electronic conduction, and $R_{contact}$ denotes the contact resistance between the MXene/bentonite composite and the electrode. Additionally, a constant-phase element (CPE) accounts for pseudo-capacitance, reflecting the heterogeneity at the interface. Further details on the circuit components and the overall impedance analysis are available in supplementary material, S2.

Initially, Fig. 3(b) presents the Nyquist plot and Bode diagram for a thin film with a 50 wt. % MXene ratio. The Nyquist plot illustrates that the data points predominantly align along the real axis across the entire frequency range. Correspondingly, the Bode plot indicates that both the absolute value and the phase of the impedance remain constant across varying frequencies. These observations suggest that the resistive component of the electron conduction pathway is prevalent in films with a higher MXene content. Figure 3(c) displays the Nyquist plot and Bode diagram for the thin film containing 33 wt. % MXene. In contrast to the 50 wt. % scenario, the phase begins to decrease at lower frequencies. This shift is indicative of the capacitive effects becoming more pronounced in the higher frequency region, likely due to the influence of ionic conduction elements.

Figure 3(d) presents the Nyquist plot and Bode diagram for films rich in bentonite. The Nyquist plot reveals a semicircular trajectory in both low and high frequency regions, suggesting significant influence from ionic conduction pathways. To determine the dominant mechanism among electronic and ion conduction mechanisms, a fitting was performed using the least-squares method based on the equivalent circuit model shown in Fig. 3(a). The fitting result is represented by a green line on the Nyquist plot in Fig. 3(d), illustrating the estimated dynamics within the circuit. Although precise quantification of each parameter is challenging, initial estimations using the approximate formulas from the equivalent circuit model indicate that the resistance due to electronic conduction,²⁶ R_e (= $R_{e,intra} + R_{e,inter}$), is ~5 × 10⁸ Ω , while the resistance due to ionic



FIG. 3. (a) Equivalent circuit model for MXene/bentonite thin films. Nyquist and Bode plots for MXene-rich films at (b) MXene:bentonite = 1:1, (c) MXene:bentonite = 1:2, and (d) bentonite-rich films at MXene:bentonite = 1:9.

conduction, R_{ion} (= $R_{ion,1} + R_{ion,2}$), is ~3 × 10⁷ Ω . These results confirm the predominance of ionic conduction in bentonite-rich thin films.

To assess the potential of MXene/bentonite thin films in humidity sensor applications, the response of MXene-rich and bentonite-rich films to varying humidity levels was examined. The response to humidity is defined as Response (%) = 100 × ($|Z| - |Z|_{min}$)/ $|Z|_{min}$, where |Z| represents the absolute value of impedance under specific humidity conditions. Humidity levels were controlled within a custom-designed chamber (detailed in supplementary material, S3), introducing dry N₂ and humid N₂ gases to achieve relative humidity levels of 10%, 30%, 50%, 70%, and 90%.

Figure 4(a) displays the response measurements for MXenerich thin films across varying mixing ratios. In these films, the impedance increases with rising humidity, demonstrating a positive correlation. This effect is likely due to the increasing resistance between MXene flakes as more water molecules are adsorbed, thereby expanding the interlayer distance. Such a trend aligns with the behavior observed in other MXene-based humidity sensors.²⁷ Notably, augmenting the proportion of bentonite in the mix results in an enhanced response; for instance, at 90% relative humidity (RH), the response of an MXene:bentonite film with a ratio of 1:2 is 345%, which is ~58.1 times greater than that of a film composed solely of MXene (5.94%). This significant increase is attributed to the higher water molecule adsorption afforded by the additional bentonite, which improves overall water absorption. Consequently, films with a higher bentonite content, particularly those with an MXene:bentonite ratio of 1:2, exhibit greater sensitivity to humidity compared to films containing only MXene, making them highly suitable for humidity sensor applications. Furthermore, the response of these films to changes in relative humidity is reversible, as depicted in Fig. 4(b).

Conversely, Fig. 4(c) illustrates the response of a bentoniterich (MXene:bentonite = 1:9) thin film, which exhibits varying impedance values depending on the frequency, reproducing the patterns observed in Fig. 3(c). In the case of bentonite-rich films, there is a notable negative humidity dependence, contrasting with the



FIG. 4. Response of MXene-rich films to various relative humidity levels. (a) Response of MXene and MXene-rich films across different mixing ratios. (b) Dry-wet cycles of MXene-rich films (MXene:bentonite = 1:2). (c) Response of bentonite-rich films (MXene:bentonite = 1:9) at different frequencies and (d) MXene/bentonite thin films (MXene:bentonite = 1:3).

Materials	RH dependence	Sensitivity (%)	RH range (%)	Ref.
MXene	Positive	5.94	10-90	This work
MXene:bentonite = 9:1	Positive	13.0	10-90	This work
MXene:bentonite = 2:1	Positive	56.9	10-90	This work
MXene:bentonite = 1:1	Positive	1.39×10^{2}	10-90	This work
MXene:bentonite = 1:2	Positive	3.45×10^{2}	10-90	This work
MXene:bentonite = 1:9	Negative	3.00×10^4 (at 1 Hz)	30-90	This work
Ti ₃ C ₂ T _x /GO	Positive	1.08×10^2	3-90	28
Curly flake Ti ₃ C ₂ T _x	Negative	1.2×10^7	11-97	29
Alkalized Ti ₃ C ₂ T _x	Negative	3.0×10^{5}	11-95	27
Ti ₃ C ₂ T _x /polyelectrolyte	Positive	50-60	10-70	30
$Ti_3C_2T_x/TiOF_2$	Negative	$1.08 imes 10^6$	11-95	31
Ti ₃ C ₂ T _x /MWCNT	Positive	1.65×10^{2}	10-90	17
$Ti_3C_2T_x/K_2Ti_4O_9$	Positive	49.0	11-95	32
Ag/Fe ₃ O ₄	Negative	6.60×10^{3}	11-95	4
Polyaniline/sodium lauryl sulfate	Positive	99.2	5-95	33
Nanofibrillated cellulose/CNT	Positive	69.9	11-95	6
Black phosphorus	Negative	4.50×10^{2}	20-90	11
Carbon black/reduced GO	Positive	1.61×10^{2}	16-95	5

TABLE I. Comparison with conductive-type humidity sensors.

MXene-rich films. Specifically, an increase in humidity results in a decrease in resistance. This phenomenon occurs because higher humidity levels lead to greater adsorption of water molecules on the bentonite, thereby increasing the number of ions as carriers. This increase arises as more cations attached to the bentonite surface dissolve in the water. Notably, the response of the bentonite-rich thin film surpasses that of any MXene-rich ratio, especially at 1 Hz, where it reaches 30 000%, which is about 5000 times more sensitive than that of a pure MXene thin film. This increased sensitivity is due to the increased water molecule adsorption by bentonite as humidity rises, resulting in significant changes in impedance. However, bentonite-rich thin films exhibit high impedance values (greater than $10^9 \Omega$) at low humidity levels (below 30% RH) because the surface-attached cations do not move freely. Consequently, the lower humidity detection limit for bentonite-rich films may be higher than that for MXene-rich films. To improve the performance in a low humidity range, it is effective to reduce the resistance of the bentonite rich thin film itself.

Figure 4(d) depicts the RH dependence of the MXene:bentonite 1:3 thin film, demonstrating that the trend varies with relative humidity. In the lower frequency region, the response positively correlates with changes in relative humidity. Moreover, at higher frequencies, the relative humidity threshold at which the response shifts to negative becomes lower. These results indicate a blend of electronic and ionic conduction within the film, with electronic conduction more pronounced in conditions of lower relative humidity and frequency and ionic conduction becoming more significant in higher humidity and frequency settings.

Table I presents a comparison of the humidity dependence results in this study with various other conductive-type humidity sensors. As illustrated in Table I, the response of our MXene/bentonite thin films demonstrates high sensitivity with a broad humidity detection range. These performance metrics are comparable to, or surpass, those reported in previous studies involving conductive-type humidity sensors.

In this study, $Ti_3C_2T_x$ MXene/bentonite thin films were developed as highly sensitive materials for humidity sensors. By varying the mixing ratio of MXene and bentonite, it was observed that the sheet resistance of these films peaked at a specific ratio, with distinct trends in resistance observed above and below this point. Impedance analysis suggests that these trends are due to differences in the dominant conduction mechanisms within the films, depending on their composition. Specifically, in films with a higher concentration of bentonite, ionic conduction, primarily derived from the bentonite, predominates. Conversely, in films where MXene is more abundant, electronic conduction is the primary mechanism. Furthermore, the impedance of these thin films relative to humidity shows a positive dependence in MXene-rich films and a negative dependence in bentonite-rich films. The introduction of bentonite significantly enhanced the sensitivity to changes in relative humidity, with MXene-rich films exhibiting a sensitivity increase of ~58.1 times and bentonite-rich films showing an increase of about 5000 times compared to films composed solely of MXene. These findings highlight the potential of the MXene/bentonite thin films to serve as highly sensitive components in humidity sensors.

See the supplementary material for detailed information about material characterization and our measurement system.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Hiroya Morotomi: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Methodology (lead); Resources (lead); Visualization (lead); Writing – original draft (lead). Yuki Matsunaga: Conceptualization (supporting); Formal analysis (supporting); Methodology (equal); Resources (equal); Writing – review & editing (supporting). Lijun Liu: Conceptualization (supporting); Writing – review & editing (supporting). Hisashi Sugime: Conceptualization (supporting); Writing – review & editing (supporting). Jun Hirotani: Conceptualization (lead); Funding acquisition (lead); Methodology (lead); Supervision (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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