Preparation of $Ti_3C_2T_X$ MXene/PVA Composite Films for Gas and Humidity Sensing Applications

Fan Wu [a], Yuke Chu [b], and Guangjian Xing*[c1]
*College of New Materials and Chemical Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, China;

ABSTRACT.

The development of sensing materials with high conductivity and large surface area is the focus of future research as these characteristics are crucial for achieving high sensitivity in resistive sensors. In this study, a $Ti_3C_2T_x$ MXene dispersion was prepared using an LiF/HCl etching process. PVA microfibers films prepared with an electrospinning method were then impregnated into the above $Ti_3C_2T_x$ dispersion for the preparation of $Ti_3C_2T_x$/PVA composite films using a dipping-drying method. The gas sensing and humidity sensing properties of these composites films were investigated in detail. The composite films exhibited high sensitivity to NH_3 in gas sensing, with a sensitivity of 0.075 over a wide range (10-200 ppm), along with a fast response time (26 s), fast recovery time (17 s), and good cyclic stability. In terms of humidity sensing, the $Ti_3C_2T_x$/PVA composite films demonstrated high sensitivity within a wide range (0.83, 11-33% RH; 13.93, 33-84% RH; 54.78, 84-97% RH), with the moisture hysteresis being approximately 4.45% RH. Moreover, it displayed a rapid response time (5 s) and recovery time (4.5 s), as well as good cycle stability. Overall, the MXene/PVA composite film has wide applications and demonstrates great potential in both gas and humidity sensing.

Keywords: $Ti_3C_2T_x$; MXene; PVA; Composite films; Gas sensing; Humidity sensing.

1. INTRODUCTION

Sensors play a critical role in future technological developments, especially in the fields of the Internet of Things (IoT) and artificial intelligence (AI) [1, 2]. Sensors are devices that convert detection information into detectable electrical signals and are widely used in various sectors, including industry, pharmaceuticals, agriculture, and environmental monitoring. Sensing materials are the core components of sensors, and their microstructure and surface properties are the key factors that determine the performance of sensors. It is necessary to use sensing materials with high conductivity and large specific surface areas in order to enhance sensitivity and provide sufficient adsorption sites for analytes [3]. Over the past few decades, researchers have developed functional materials with different structures and conduction mechanisms to improve sensitivity and response speed, such as semiconductor metal oxides, polymers, and two-dimensional (2D) materials. Among various 2D materials, such as graphene, nitrogenated carbon, black phosphorus, and transition metal carbides, MXenes have attracted great attention due to their unique properties. MXenes, also known as transition metal carbides/nitrides, are a new type of 2D nanomaterials with a chemical formula of $M_{n+1}X_nT_x$, where M represents the transition metal element (such as Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, etc.), X represents carbon or nitrogen element, Tx represents surface functional groups such as -OH, -O, and -F), and n is 1~4 [4]. MXenes exhibit similar morphology to graphene and demonstrate large surface area, metal-like conductivity, mechanical flexibility, excellent hydrophilicity, and adjustable surface functional groups. These features make MXenes highly suitable for various applications, including energy storage [5], electromagnetic interference shielding [6], catalysis [7], sensing [8] and other fields. $Ti_3C_2T_x$, among all the synthesized MXenes, has gained significant research attention since its first report in 2011 [9], thanks to its relatively easy synthesis and high stability. With its good performance, $Ti_3C_2T_x$ has the potential to become a promising sensitive material for gas and humidity detection.

In this study, the $Ti_3C_2T_x$ MXene dispersion was prepared using a LiF/HCl etching method. PVA film was prepared using an electrospun process and then $Ti_3C_2T_x$/PVA composite film was obtained using a dip-drying method. The as-prepared $Ti_3C_2T_x$/PVA composite film exhibits both gas sensing and humidity sensing properties. For gas sensing application, it demonstrates selectivity towards NH_3 with a high sensitivity of 0.075 in the concentration range of 10-200

[1] [1a] fanwoo@foxmail.com, [b] chuyuke@bipt.edu.cn, [c]*xingguangjian@bipt.edu.cn

The International Conference Optoelectronic Information and Optical Engineering (OIOE2024), edited by Yang Yue, Lu Leng, Proc. of SPIE Vol. 13513, 135130S · © 2025 SPIE · 0277-786X · © The Authors. Published under a Creative Commons Attribution CC-BY 3.0 License · doi: 10.1117/12.3045406

ppm. Additionally, it shows a short response time of 26 s, recovery time of 17 s, and good cycle stability. In terms of humidity sensing, it exhibits high sensitivity in a wide range, with sensitivity values of 0.83 (11-33% RH), 13.93 (33-84% RH), and 54.78 (84-97% RH). The humidity hysteresis detected is approximately 4.45% RH, with a short response time of 5 s, recovery time of 4.5 s, and good cycle stability. Considering these performance characteristics, the $Ti_3C_2T_x$/PVA composite film holds great potential as a gas sensing and humidity sensing material.

2. EXPERIMENTAL

2.1 Materials and chemicals

$Ti_3C_2T_x$ precursor (≥99.9%, 400 mesh) was purchased from Foshan Xinxi Technology Co., Ltd. Lithium fluoride (LiF, 99.0%) was purchased from Shanghai Yien Chemical Technology Co., Ltd. Hydrochloric acid (HCl, 36.0~38.0%) and polyvinyl alcohol (PVA, 1750±50) were provided by China National Pharmaceutical Group Chemical Reagent Co., Ltd.

2.2 Preparation of $Ti_3C_2T_x$ MXene

The $Ti_3C_2T_x$ MXene was prepared using the LiF/HCl etching method. Briefly, 1.6 g of LiF was slowly added to 20 mL of 9 M HCl and stirred for 15 minutes at 45℃. 1 g of Ti_3AlC_2 MAX phase precursor was gradually added to the above mixture solution and further stirred for 48 hours at 45℃. After the reaction, the obtained slurry was centrifuged at 3500 rpm for 3 minutes with several times until a black dispersion appears. The dispersion was proceeded to ultrasonic at 1000W for 1 hour, then the supernatant after centrifugation was collected and $Ti_3C_2T_x$ suspension was obtained.

2.3 Preparation of MXene/PVA composite films

The PVA film was prepared using the electrospinning method. Firstly, a PVA aqueous solution (5.0 wt%) was prepared and injected into the syringe. The flat electrospinning device was set to a high voltage of 10 kV with a collecting distance of 12 cm and a constant flow rate of 2.5 ml h−1 for 2 hours. After that, the obtained PVA film was placed in a saturated boric acid solution for 10 minutes, and then dried at 45℃ for 15 minutes. 10 mL of $Ti_3C_2T_x$ MXene suspension was poured into a culture dish. Then, the prepared PVA film was immersed for 10 minutes. After taking out, the PVA film was dried in a 45℃ oven. Repeat the immersion and drying steps for 3 times and the MXene/PVA composite film was obtained.

2.4 Characterizations

The morphology of the MXene/PVA composite film was studied using field emission scanning electron microscopy (FESEM, S-4800, Hitachi) with an acceleration voltage of 5 kV and high-resolution transmission electron microscopy (HETEM, Tecnai G2 F30, FEI) with an acceleration voltage of 200 kV. The crystal structure was characterized using Kα X-ray diffraction (XRD, D8 Focus, Bruker) technique.

2.5 Sensing performance tests

A series of experiments were conducted to assess the sensing performance of the MXene/PVA composite film. The film was connected to electrode wires coated with conductive silver paste and then dried. The gas sensing testing system consisted of a gas source, gas path, gas flowmeter, and a sealed chamber of 20 L, an LCR instrument, and a computer. The MXene/PVA composite film was placed inside the sample chamber, with its electrode wire connected to the LCR instrument. By adjusting the gas flowmeters, the concentration of gas entering the chamber could be controlled accurately. The LCR instrument measured the electrical response of the film to different gas concentrations, and the data was displayed in real-time on a computer connected to the LCR instrument. To evaluate the sensitivity of the MXene/PVA composite film to varying humidity levels, a series of saturated solutions containing substances like lithium chloride (LiCl), potassium acetate (CH_3COOK), magnesium chloride ($MgCl_2$), potassium carbonate (K_2CO_3), magnesium nitrate ($Mg(NO_3)_2$), ammonium nitrate (NH_4NO_3), sodium chloride (NaCl), potassium chloride (KCl), potassium nitrate (KNO_3), and potassium sulfate (K_2SO_4) were prepared. Each solution was sealed in a separate container to create a specific humidity environment with relative humidity (RH) of 11%, 23%, 33%, 43%, 54%, 62%, 75%, 84%, 93%, and 97%, The film was connected to the LCR instrument via a wire and placed inside each container with the corresponding saturated solution.

3. RESULT AND DISCUSSION

3.1 Characterizations

Fig. 1(a, b) show the FESEM images of Ti_3AlC_2, displaying large particles with a closely packed layered structure. As shown in Fig. 1(c, d), the FESEM images display etched $Ti_3C_2T_x$ MXene, which retains a layered structure but exhibits an accordion-like morphology. After centrifugation and ultrasound dispersion, Fig. 1(e) shows an optical image of the dispersed $Ti_3C_2T_x$ MXene suspension, displaying a light green color with a noticeable Tyndall effect, indicating small size, thin thickness, good dispersibility, and colloidal properties of $Ti_3C_2T_x$ MXene. Fig. 1(f) presents a TEM image of

the prepared MXene, indicating transparent thin sheets with dimensions of approximately 1000 * 400 nm. The HRTEM image in Fig. 1(g) confirms good crystallization of MXene, with clear lattice fringes and a lattice spacing of 0.268 nm, corresponding to the (200) crystal plane. XRD analysis in Fig. 1(h) shows that the diffraction peaks of Ti_3AlC_2 crystal planes are observed. While for $Ti_3C_2T_x$ MXene, only the (002) peak is present, indicating an increase in interlayer spacing. This is consistent with existing literature and confirms successful extraction of MXene from Ti_3AlC_2 [10].

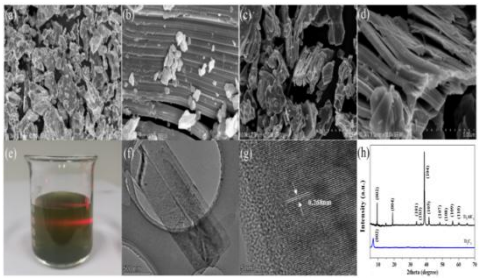

Figure. 1 (a, b) FESEM images of Ti_3AlC_2 with different magnifications, (c, d) FESEM images of $Ti_3C_2T_x$ with different magnifications, (e) Tyndall effect of $Ti_3C_2T_x$, (f) TEM image of MXene nanosheets, (g) HETEM image of MXene nanosheets, (h) XRD patterns of Ti_3AlC_2 and $Ti_3C_2T_x$.

Fig. 2(a) shows a low-magnification FESEM image of the MXene/PVA composite film. The film consists of intertwining linear PVA nanofibers, forming a porous network structure with a high specific surface area. This structure allows for the loading of MXene and provides additional adsorption sites for molecules, making it a suitable material for sensing applications. In Fig. 2(b), a high-magnification FESEM image reveals PVA fibers with diameters ranging from approximately 500 to 1500 nm. The roughened surfaces of the fibers indicate the successful loading of MXene. Fig. 2(c) presents an optical image of the MXene/PVA composite film. The initially white PVA film turns black after impregnation and drying process, indicating the effective attachment of MXene. Fig. 2(d) illustrates the contact angle measurement for the MXene/PVA composite film. The contact angle of the MXene/PVA composite film is determined to be 44.6°, indicating good hydrophilicity. The presence of hydrophilic groups in both the polyvinyl alcohol and the surface of $Ti_3C_2T_x$ MXene contribute to the film's hydrophilicity, making it suitable for humidity-sensitive sensing applications.

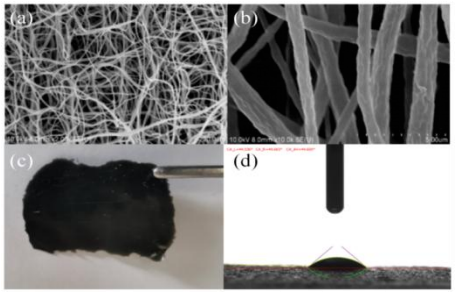

Figure. 2 (a, b) FESEM images with different magnifications, (c) Optical image, and (d) Water contact angle measurement of MXene/PVA composite film.

3.2 Gas and humidity sensing properties

The sensitivity of the MXene/PVA composite film to different gases was studied using an experiment with a concentration of 100 ppm. As shown in Fig.3(a), the resistance change rate of the MXene/PVA composite film to gases such as CO_2, methanol, and ethanol is less than 1%, slightly higher than 2% for gases like H_2S, acetone, and ethyl acetate. However, the resistance change rate of the film to ammonia (NH_3) is about 8%, indicating a stronger response compared to other gases. This high selectivity towards NH_3 can be attributed to the hydroxyl groups at the surface of the MXene/PVA composite film. Subsequent experiments were conducted using NH_3 for further testing. The sensitivity of a gas sensor is an important parameter for evaluating device performance, usually defined as:

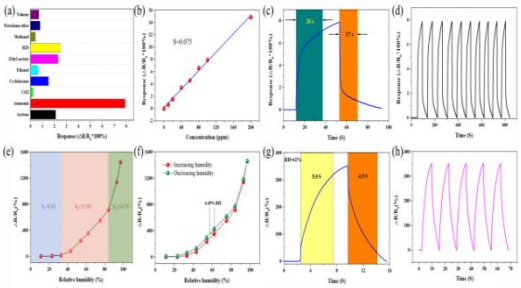

Figure. 3 (a) Resistance change rate to different gases, (b) Sensitivity to NH_3, (c) Response and recovery time to NH_3, (d) Cycling stability to NH_3, (e) Sensitivity to different ranges of humidity, (f) Humidity hysteresis loop, (g) Response and recovery time to humidity, and (h) Humidity cycling stability of MXene/PVA composite film.

$$S = \frac{\frac{\Delta R}{R_0}}{\Delta ppm} \times 100\% \quad (1)$$

where R_0 denotes the resistance value of the sample in air, ΔR is the difference between the resistance value of the sample after introducing the test gas and Δppm is the relative variation of gas concentration. The sensitivity of the MXene/PVA composite film to different NH_3 concentrations is shown in Fig. 3(b). With the increase of NH_3 concentration, the rate of resistance change also increases. There are two aspects to the principle of gas sensitivity. On one hand, gas molecules provide electrons to the MXene/PVA film, causing the PVA matrix to expand and the MXene conductive network to break, resulting in a significant increase in the resistance of the film due to a decrease in the concentration of charge carriers (holes) in the film. On the other hand, when a large number of gas molecules adsorb in the overlapping area of adjacent MXene flakes, the lateral intermolecular forces between the gas molecules cause a change in the microstructure of the upper layer of MXene. At this time, the interlayer spacing significantly increases, making it more difficult for electrons to tunnel between the layers, resulting in an increase in the resistance of the film as the interlayer distance increases, equivalent to an increase in the length of the conductive path, thus increasing the resistance value. When the sample is returned to air, the resistance decreases significantly. According to the fitting calculation, the resistance change rate is linearly related to the ammonia gas concentration, with a linearity of 0.99. The MXene/PVA composite film has a sensitivity of 0.075 within a wide concentration range of 10-200 ppm. The film exhibits high sensitivity to low concentrations of NH_3 (10 ppm) with a resistance change rate of 0.64. In practical applications, gas sensors require not only high selectivity and sensitivity, but also fast response and recovery times. As shown in Fig. 3(c), when the NH_3 concentration is 100 ppm, the response time of the MXene/PVA composite film is 26 s, and the recovery time is 17 s. Fig. 3(d) shows that the MXene/PVA composite film also exhibits excellent reproducibility and cycling stability in the response to NH_3.

The MXene/PVA composite film is not only sensitive to gases, but also shows excellent sensing performance to humidity. Sensitivity is also an important parameter for evaluating the performance of humidity sensors, usually defined as:

$$S = \frac{\frac{\Delta R}{R_0}}{\Delta RH\%} \times 100\% \quad (2)$$

where R0 is the initial humidity resistance value of the sample, ΔR is the difference between the resistance value of the sample after an increase in humidity and $\Delta RH\%$ is the value of relative change in humidity. As shown in Fig. 3(e), the rate of resistance change increases with increasing relative humidity. In the range of 11 to 33%, the sensitivity is low (0.83). However, at humidity levels of 33 to 84% RH, the rate of resistance change increases rapidly, with a sensitivity of 13.93. In addition, at humidity levels of 83 to 97%, the rate of resistance change is even higher, with a sensitivity of 54.78. This suggests that the MXene/PVA composite film has lower sensitivity to low humidity and higher sensitivity to high humidity. The difference in sensitivity is attributed to the water condensation effect on the composite film at higher humidity levels, which leads to a significant mass load effect [11]. It is worth noting that the MXene/PVA composite film has a wide detection range of 11-97% RH. Fig. 3(f) analyzes the moisture absorption and desorption behavior of the MXene/PVA composite film by sequentially immersing in solutions of increasing humidity and then placing back in a low humidity solution. The resistance value at each placement point is recorded, and the rate of resistance change is calculated. A hysteresis curve is generated to compare the moisture absorption and desorption curves of the film. The results show that the MXene/PVA composite film has a small moisture hysteresis, with a maximum hysteresis rate of 4.45%. This indicates that when the ambient humidity decreases, the absorbed water molecules in a high humidity

environment can be relatively quickly and thoroughly separated from the film. In practical humidity sensing applications, fast response and quick recovery are crucial. As shown in Fig. 3(g), at 62% humidity, the response-recovery curve of the MXene/PVA composite film displays a very short response time (5 s) and a short recovery time (4.5 s), indicating its fast response speed and strong recovery ability. This facilitates the rapid and repetitive detection of humidity using the MXene/PVA composite film. Fig. 3(h) evaluates the cycling stability. At 62% humidity, the response and recovery cycles of the MXene/PVA composite film show consistent behavior over 5 cycles, with the sensitivity and response/recovery time remaining almost unchanged. This indicates that the MXene/PVA composite film has good stability and cycling performance.

4. SUMMARY

In this study, $Ti_3C_2T_x$ MXene suspension was prepared using the LiF/HCl etching method. Then, the electrospun PVA membrane is composited with MXene to prepare MXene/PVA film through dip-coating and drying method. The prepared MXene/PVA composite film exhibits excellent gas-sensing and humidity-sensing properties. In the gas-sensing test, the MXene/PVA composite film shows selectivity to NH_3 with high sensitivity. It has a sensitivity of 0.075 in the concentration range of 10-200 ppm with a short response time (26 s), short recovery time (17 s), and good cyclic stability. In terms of humidity sensing, it has high sensitivity (0.83, 11-33% RH; 13.93, 33-84% RH; 54.78, 84-97% RH), with a hysteresis rate of about 4.45% RH, short response time (5 s), short recovery time (4.5 s), and good cyclic stability. Therefore, the MXene/PVA composite film is a gas-sensing and humidity-sensing material with broad application prospects.

5. REFERENCES

[1] Pu X, Guo H, Chen J, et al. Eye Motion Triggered Self-Powered Mechnosensational Communication System using Triboelectric Nanogenerator. Sci Adv. 2017, 3 (7): 1700694.

[2] Ding Z, Zou M, Yao P, et al. A Triboelectric Nanogenerator Based on Sodium Chloride Powder for Self-Powered Humidity Sensor. Nanomaterials. 2021, 11 (10) 2657.

[3] Pan Y, Zuo J, Hou Z, et al. Preparation of Electrochemical Sensor Based on Zinc Oxide Nanoparticles for Simultaneous Determination of AA, DA, and UA. Front Chem. 2020, 8: 592538.

[4] Zhang J, Uzun S, Seyedin S, et al. Additive-Free MXene Liquid Crystals and Fibers. ACS Cent Sci. 2020, 6 (2): 254-265.

[5] Guo Y, Du Z, Cao Z, et al. MXene Derivatives for Energy Storage and Conversions. Small Methods. 2023, 7 (8): 2201559.

[6] Yun T, Kim H, Iqbal A, et al. Electromagnetic Shielding of Monolayer MXene Assemblies. Adv Mater. 2020, 32 (9): 1906769.

[7] Li Z, Zhuang Z, Lv F, et al. The Marriage of the FeN_4 Moiety and MXene Boosts Oxygen Reduction Catalysis: Fe 3d Electron Delocalization Matters. Adv Mater. 2018, 30 (43): 1803220.

[8] Lei D, Liu N, Su T, et al. Roles of MXene in Pressure Sensing: Preparation, Composite Structure Design, and Mechanism. Adv Mater. 2022, 34 (52): 2110608.

[9] Naguib M, Kurtoglu M, Presser V, et al. Two-dimensional Nanocrystals Produced by Exfoliation of Ti_3AlC_2. Adv Mater. 2011, 23 (37): 4248-53.

[10] Mi X, Li H, Tan R, et al. The TDs/aptamer cTnI Biosensors Based on HCR and Au/Ti_3C_2-MXene Amplification for Screening Serious Patient in COVID-19 Pandemic. Biosens Bioelectron. 2021, 192: 113482.

[11] Zhang Q, Wang Y, Li D, et al. Flexible Multifunctional Platform Based on Piezoelectric Acoustics for Human-machine Interaction and Environmental Perception. Microsyst Nanoeng. 2022, 8: 99.