# Tubular MXene/SS Membranes for Highly Efficient H2/CO2 Separation

Mide Luo<sup>1</sup>, Zong Lu<sup>1</sup>, Yali Zhao<sup>1</sup>, Yufei Wang<sup>1</sup>, Yanying Wei<sup>1</sup>, and Haihui Wang<sup>2</sup>

<sup>1</sup>South China University of Technology <sup>2</sup>Tsinghua University

December 28, 2022

#### Abstract

Accurately constructing membranes based on two-dimensional (2D) materials on commercial porous substrates remains a significant challenge for H2 purification. In this work, a series of tubular 2D MXene membranes are prepared on commercial porous stainless steel substrates via fast electrophoretic deposition. Compared with other methods, such as filtration or drop coating, etc. such preparation route shows the advantages of simple operation, high efficiency for membrane assembly (within 5 min) with attractive reproducibility, and ease for scale-up. The tubular MXene membranes present excellent gas separation performance with hydrogen permeance of 1290 GPU and H2/CO2 selectivity of 55. Furthermore, the membrane displays extremely stable performance during the long-term test for more than 1250 h, and about 93% of the membranes from one batch have exceeded the DOE target for CO2 capture. Most importantly, this work provides a valuable referential significance for other types of 2D materials-based membranes for future application development.

# Tubular MXene/SS Membranes for Highly Efficient H<sub>2</sub>/CO<sub>2</sub> Separation

Mide Luo<sup>a</sup>, Zong Lu<sup>a</sup>, Yali Zhao<sup>a</sup>, Yufei Wang<sup>a</sup>, Yanying Wei<sup>a,\*</sup>, Haihui Wang<sup>b,\*</sup>

<sup>a</sup> School of Chemistry & Chemical Engineering, Guangdong Provincial Key Lab of Green Chemical Product Technology, State Key Laboratory of Pulp and Paper Engineering, South China University of Technology

No. 381 Wushan Road, Guangzhou 510640, China

<sup>b</sup> Beijing Key Laboratory for Membrane Materials and Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

\*E-mail address: ceyywei@scut.edu.cn; hhwang@scut.edu.cn

#### Abstract

Accurately constructing membranes based on two-dimensional (2D) materials on commercial porous substrates remains a significant challenge for  $H_2$  purification. In this work, a series of tubular 2D MXene membranes are prepared on commercial porous stainless steel substrates via fast electrophoretic deposition. Compared with other methods, such as filtration or drop coating, etc. such preparation route shows the advantages of simple operation, high efficiency for membrane assembly (within 5 min) with attractive reproducibility, and ease for scale-up. The tubular MXene membranes present excellent gas separation performance with hydrogen permeance of 1290 GPU and  $H_2/CO_2$  selectivity of 55. Furthermore, the membrane displays extremely stable performance during the long-term test for more than 1250 h, and about 93% of the membranes from one batch have exceeded the DOE target for  $CO_2$  capture. Most importantly, this work provides a valuable referential significance for other types of 2D materials-based membranes for future application development.

#### **KEYWORDS**

Inorganic membrane, membrane separation, gas separation, MXene

# **1 INTRODUCTION**

As is known, hydrogen is one of the green and environmentally friendly clean fuels in the world, which has the potential to replace traditional fossil fuels for carbon peaking and carbon neutrality goals. In industry, a large number of hydrogen-containing mixed gas, mainly H<sub>2</sub> and CO<sub>2</sub>, are produced through the steam reforming process of natural gas, thus subsequent purification is required to obtain high-purity hydrogen.<sup>1</sup> Pressure swing adsorption (PSA) and low-temperature distillation are usually applied in industrial gas separation and purification, but both are energy-intensive processes. According to relevant research reports, energy consumption during the separation stage is extremely high, accounting for up to 85% of total energy costs.<sup>2</sup> To reduce energy consumption and cost, researchers and engineers have turned their attention to membrane separation technology, which typically requires less investment and operating costs than mainstream alternative technologies such as PSA and cryogenic distillation, which is also more economical and energy-efficient.<sup>3-7</sup>However, the most challenging issue in membrane separation is efficiently preparing membranes with high selectivity/permeability and stability.

Although the polymeric membranes are easy to prepare at low cost, their separation performance is usually limited by the Robson Bound, where the gas permeability and selectivity have a trade-off phenomenon, thus the corresponding  $H_2/CO_2$  separation performance is far away from the requirement for industrialization.<sup>8-13</sup> Many other membranes composed of metal organic membranes (MOFs), covalent organic frameworks (COFs), zeolite molecular sieves (Zeolites), or other types of materials are also restricted from complex and timeconsuming preparation process, difficulty in forming a continuous defect-free membrane layer, high cost, etc.<sup>14-30</sup> In this decade, a kind of lamellar membrane based on 2D materials has attracted increasing attention, which shows the potential to break through the performance upper bound of traditional membranes.<sup>31</sup> Various 2D nanosheet membranes constructed by graphene,<sup>32</sup> graphene oxide,<sup>4,33-37</sup> molybdenum sulfide,<sup>38,39</sup> MXenes,<sup>40-43</sup> 2D zeolites,<sup>44,45</sup> 2D MOF,<sup>46,47</sup> and 2D COF,<sup>48</sup> etc. have been studied for gas separation, pervaporation and ion sieving, etc. In our previous work, the lamellar membranes based on MXene, a type of 2D transition metal carbides or carbonitrides prepared on the porous disk-shaped anodic aluminum oxide (AAO) substrate, showed good  $H_2/CO_2$  separation performance.<sup>42</sup> In addition, Jin et al.<sup>43</sup> prepared an ultra-thin (20 nm thick) MXene membrane on an AAO substrate, showing the performance of hydrogen permeability of 1584 GPU with  $H_2/CO_2$  selectivity of 27. Moreover, the research group proposed an external force-driven assembly approach (EFDA) to prepare a series of GO membranes on flaky α-Al<sub>2</sub>O<sub>3</sub> substrates, which exhibited good molecular sieving performance with  $H_2/CO_2$  selectivity of 30 and hydrogen permeability of 1000 GPU.<sup>35</sup> On brittle AAO substrates, a g-C<sub>3</sub>N<sub>4</sub>-GO membrane was developed with outstanding hydrogen permeation capability (hydrogen permeance: 645 GPU,  $H_2/CO_2$  selectivity: 39).<sup>36</sup> Furthermore, Lai et al.<sup>38</sup> prepared GO-MoS<sub>2</sub> hybrid membranes via a vacuum filtering approach on flaky AAO substrates, which exhibited hydrogen permeance of 857 GPU with  $H_2/CO_2$  selectivity of 44.  $H_2/CO_2$  selectivity of 30 and hydrogen permeance of 70 GPU were observed in self-crosslinked MXene membranes produced by filtering on yttria-stabilized zirconia hollow fiber.<sup>41</sup>

Although many 2D material-based membranes have been reported in the field of gas separation, the diskshaped AAO,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, or some other fragile substrates were often chosen as the substrates for 2D nanosheet assembly in most research, which are not suitable for practical application due to the limited membrane area, difficulty of sealing, high-cost, and brittleness of the substrates. On the contrary, tubular membranes are more commonly used in industrial applications, which present the advantages of a relatively small footprint with large effective membrane area per unit volume, higher packing density, ease to seal for gastight, convenient to replace or repair any one from the entire membrane modules if necessary, etc. There are a few works that utilized tubular ceramic substrates for membrane construction, which are still too fragile in practical application for gas separation.<sup>40,41</sup> Till now, seldom study has been reported to prepare 2D nanosheet membranes using cheap commercial porous substrates, whose pore size is usually large up to 20  $\mu$ m with big curvature, because membrane defects are more likely to occur during the preparation process, resulting to a poor gas separation performance.<sup>41</sup> Actually, one commercial stainless steel tube with macro-size pores ( $^2 \mu m$ ) is a promising substrate. Since the porous stainless steel tube exhibits good corrosion resistance, high-temperature resistance, enough mechanical strength, and good welding performance compared with other materials, which is convenient to integrate with the equipment of different unit operations for H<sub>2</sub> production and purification. Besides the substrate, the membrane preparation method also determines whether it could be utilized for scale-up production in industrialization, where a fast and efficient membrane assembly route with acceptable repeatability is urgently required.

In this work, a series of tubular MXene membranes are successfully constructed on commercially available macroporous stainless steel via electrophoresis, which is considered to be a simple preparation process with high efficiency and good membrane uniformity. The entire membrane preparation, including substrate modification, can be finished in  $2^{-10}$  minutes. The membranes had exceptional gas separation performance with H<sub>2</sub>/CO<sub>2</sub>selectivity of 55 and hydrogen permeability of 1290 GPU. The separation temperature, water vapor and relative humidity, preparation process repeatability and long-term stability of the tubular MXene membranes have been investigated in detail, which is helpful and valuable for future industrial applications. Furthermore, this study would help promote the amplification of tubular MXene membranes and provide some experience for other 2D materials to be closer to actual industrialization.

## **2 EXPERIMENTAL SECTION**

#### 2.1 Materials and chemicals

Ti<sub>3</sub>AlC<sub>2</sub> powder (200 mesh) was purchased from Laizhou Kaien Ceramic Materials Co., Ltd. HCl (36<sup>-38</sup>%) was purchased from Guangzhou Chemical Reagent Co., Ltd. LiF (99.9%) was provided by Aladdin Reagent Co., Ltd. Anhydrous ethanol (99.9%) was purchased from Guangzhou Donghong Reagent Co., Ltd. Multiwalled carbon nanotubes (CNTs) were purchased from Jiangsu Xianfeng Nanomaterials Technology Co., Ltd. On-site deionized water was obtained from ELGA Lab Water Purification Systems. A stainless steel cleaning agent was provided by Shenzhen Xinchangyuan Chemical Co., Ltd. Nanjing Gaoqian Functional Materials Technology Co., Ltd. provided the tubular porous stainless steel substrates ( $\Phi 8 \text{ mm} \times \delta 2 \text{ mm} \times 1500 \text{ mm}$ ) with an average pore size of 2 µm, which can be cut to the desired length.

#### 2.2 Preparation of MXene nanosheets

In this study, monolayer or multilayer  $Ti_3C_2T_X(ML-Ti_3C_2T_X, MXene)$  was obtained by mild selective etching of the Al layer in  $Ti_3AlC_2$  (MAX) by HCl and LiF using commercial  $Ti_3AlC_2$  powder with 200 mesh as a precursor. The MXene nanosheet solution was prepared in accordance with our previous work for subsequent membrane assembly.<sup>42</sup> The schematic diagram of the fabrication process of  $Ti_3C_2T_X$  MXene nanosheets is shown in Figure 1A.

#### 2.3 Pretreatment of the substrate

The purchased microporous stainless steel substrate was polished to smooth the surface and then ultrasonically cleaned three times with a commercial cleaning agent, absolute ethanol, and deionized water for 0.5 h, respectively. The impurities on the stainless steel surface were washed off and the substrate was dried for subsequent use. An appropriate amount of multi-walled CNTs was weighed and poured into 1 L deionized water with ultrasonic treatment for 60 min to prepare a solution of CNTs with uniform density for use. The tubular porous stainless steel (SS) was then cut with appropriate length and immersed in the as-prepared CNTs solution, followed by vacuum filtration to modify the outer wall of the stainless steel to decrease the pore size with good electrical conductivity for subsequent electrophoretic deposition. We would wipe the CNTs on the tube surface to better fill the substrate's pores and large holes. The surface flatness was further improved, which is beneficial to reduce membrane defects in the subsequent nanosheet assembly process.

#### 2.4 Fabrication of Tubular MXene/SS membrane



An appropriate MXene nanosheet solution was diluted to 0.25 mg/ml for use. The tubular porous stainless steel modified with multi-walled CNTs was put into a homemade electrophoretic deposition (EPD) device containing the MXene solution to construct a membrane via electrophoresis. The schematic diagram of the fabrication process of the tubular MXene/SS membrane is shown in Figure 1B. The electrophoresis voltage was 5 V with electrophoresis time in the range of  $0^{-5}$  min. The electrophoresis time could be controlled to adjust the desired membrane thickness.

FIGURE 1 Schematics of the fabrication processes of A)  $Ti_3C_2T_X$  MXene nanosheets and B) tubular MXene/SS membrane supported on the stainless steel.

## 2.5 Characterizations

X-ray diffraction (XRD) patterns were obtained using a Bruker-D8 ADVANCE under Cu K $\alpha$  radiation (40 kV, 40 mA). Scanning electron microscopy (SEM) with a Hitachi SU8100 equipped with an Oxford Energy Dispersive X-ray Spectrometer was used to investigate the morphology of the materials (Oxford EDS, INCA software). Atomic force microscopy (AFM) pictures were captured on Bruker MultiMode 8. Fourier transform infrared spectroscopy (Nicolet 5700 spectrometer) was employed to determine the chemical structures of the membranes in the 400<sup>-4000</sup> cm<sup>-1</sup> range. X-ray photoelectron spectroscopy (XPS) measurements were carried out utilizing a conventional Al K $\alpha$  source on an Escalab 250Xi spectrometer outfitted with two ultra-high vacua (UHV) chambers. The Zeta potential and lateral size of the nanosheets were tested with a Zetasizer ULTRA nanoparticle size and Zeta potential analyzer produced by Malvern Instruments, UK. The pore size distribution of the porous stainless steel substrate was measured with a PSDA-30 microfiltration membrane pore size analyzer produced by Nanjing Gaoqian Functional Materials Technology Co., Ltd., China.

### 2.6 Gas separation performance test

All tests to assess the gas separation performance of membranes were accomplished in a home-made mem-

brane module in the classic Wicke-Kallenbach test method. As shown in Figure 2, the tubular membrane was sealed with high-temperature resistant O-rings to ensure good gastight. The gas separation performance evaluation were divided into two types: single gas permeation test and mixed gas separation test. The feed gas was introduced into the shell side of the tubular membrane module. The feed gas flow (H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>) for the single gas permeation test was 50 ml/min, while the feed gas flow (H<sub>2</sub>, CO<sub>2</sub>) for the mixed gas separation test was 100 ml/min with the volume ratio of 1:1 and the sweep gas was argon (50 ml/min). During the test, the pressure on both sides was kept at 1 atm, and the temperature was adjusted as needed. Most experiments were carried on at room temperature unless specified. The flow rate of all gases was measured with a mass flow controller and calibrated with a soap bubble flowmeter. The gas on the permeate side was swept into the gas chromatograph (GC Agilent-7890B) with a TCD detector for analysis. The experimental data was obtained by taking the average value of at least three data points after the gas separation performance was stable to ensure accuracy. The gas permeance expressed the gas separation performance of the single or mixture gas  $P_i(mol \cdot m^{-2} \cdot s^{-1} \cdot pa^{-1})$ , the ideal selectivity of the single gas  $S_{i/j}$  and the gas mixture separation factor  $\alpha_{i/j}$ , respectively, as defined by the following formula,

$$P_i = \frac{N_i}{(\Delta P_i \cdot S)} \tag{1}$$

where  $N_i$  was the permeation rate mol  $\cdot s^{-1}$  of the gas component *i*,  $\Delta P_i$  was the transmembrane pressure difference of the gas component *i*, and *S* was the effective utilization area of the membrane. Considering gas permeance was usually reported in a more widely used unit of GPUs, thus it can be converted from the standard unit through the following equation.<sup>54</sup>

$$1 \ GPU = 3.35 \times 10^{-10} \text{mol} \cdot m^{-2} \cdot s^{-1} \cdot pa^{-1} \tag{2}$$

The ideal selectivity of a single gas  $S_{i/i}$  referred to the ratio of the gas permeance of different gas components,

$$S_{i/j} = \frac{P_i}{P_j} \tag{3}$$

The separation factor  $\alpha_{i/j}$  of the mixture can be calculated by the following formula,

$$\alpha_{i/j} = \frac{x_{i[\text{perm}]}/x_{j[\text{perm}]}}{y_{i[\text{feed}]}/y_{j[\text{feed}]}} \tag{4}$$

where  $x_{i[perm]}$  and  $x_{j[perm]}$  refer to the molar fraction of gas component *i* and gas component *j* on the permeation side, while  $y_{i[feed]}$  and  $y_{j[feed]}$  refer to the molar fraction of gas component *i* and gas component *j* in the feed gas, respectively.



FIGURE 2 Schematic diagram of the experimental set-up for the gas separation performance evaluation of the membranes.

## **3 RESULTS AND DISCUSSION**

## 3.1 Characterizations of MXene nanosheets

The gas separation performance of the membrane depends on the quality of the building blocks of MXene nanosheets. In this work, the most classical acid etching synthesis method was used to synthesize MXene nanosheets. The microstructure of the MAX bulk phase as raw material, acid-etched  $Ti_3C_2T_X(MXene)$ powder and dispersive MXene nanosheet could be observed in Figure 3 A-C. The MXene powder exhibited an obvious furrow structure after acid etching, while the AAO substrate could be seen clearly through the electronic transparent MXene nanosheet upon it, indicating that the nanosheet is very thin. The AFM result of Figure 3D showed the thickness of the MXene nanosheet was about 1.5 nm, which was close to the theoretical thickness of a monolayer MXene nanosheet (1.0 nm).<sup>55</sup> Since there might be adsorbed impurities such as water on the nanosheet, the nanosheet with the such thickness could be considered a monolayer.<sup>56</sup> In this work, TEM and SAED analysis of selected electron diffraction were also carried out on the MXene nanosheets. Figure 3E showed that the nanosheets were extremely transparent under the irradiation of an electron beam, which also indicated that the nanosheets were extremely thin. As can be seen in Figure 3F. the synthesized nanosheets had a hexagonal structure on the basal plane with high crystallinity, indicating that the nanosheets were of good quality. The XRD patterns of the Ti<sub>3</sub>AlC<sub>2</sub> MAX powder and synthesized MXene nanosheets are shown in Figure 3G. In contrast to the  $Ti_3AlC_2$  MAX, the diffraction peak in the (104) plane located at  $39^{\circ}$  did not exist in that of  $Ti_3C_2T_X$  MXene, indicating that the Al layer was successfully removed by etching.<sup>49,57</sup> More importantly, the main diffraction peak located at crystal plane 002 shifted from 9.44° of  $Ti_3AlC_2$  to 6.58° of etched  $Ti_3C_2T_X$  after acid etching treatment, and the shape of the peak was extremely sharp, showing excellent crystallinity. To understand the lateral size of the synthesized nanosheet and the stability of the nanosheet solution, the synthesized MXene nanosheet solution was characterized by a Malvern nanoparticle analyzer. As shown in Figure 3H, the lateral size of the nanosheet is roughly distributed from 1 to 6  $\mu$ m, and the predominant size was about 3  $\mu$ m, indicating a relatively large lateral size. In addition, Figure 3I showed that the Zeta potential of the MXene nanosheet solution was -47 mV. It is generally believed that if the absolute value of Zeta potential is greater than 30 mV, the nanosheet solution system is relatively stable.<sup>58</sup> Therefore, the MXene nanosheet solution prepared in this work was exceptionally stable and could be well used for subsequent electrophoretic membrane preparation.



FIGURE 3 SEM images of A) MAX powder, B) Synthetic MXene powder, and C) MXene nanosheets placed on AAO substrate. D) AFM image of the MXene nanosheets. E) TEM image of the MXene nanosheet. F) Selective area electron diffraction pattern (SAED) pattern of the MXene nanosheet. G) XRD patterns of MAX and MXene. H) Lateral size distribution of the MXene nanosheets. I) Zeta potential and Tyndall effect of the MXene nanosheet solution.

# 3.2 Characterizations of tubular MXene/SS membranes

The microstructures of the tubular stainless steel substrates and the MXene membranes prepared by electrophoresis were then characterized by SEM. Figure 4A shows the bare commercial stainless steel substrate  $(SS_{bare})$  without pretreatment, where the surface was rough with amounts of large holes (diameter greater than 10 µm). It was difficult to prepare continuous MXene membranes on such substrate without any pretreatment. In order to reduce the surface roughness, the substrate was polished and the corresponding microstructure is shown in Figure 4B. Additionally, the polished stainless steel substrate was modified with CNTs (SS<sub>CNTs</sub>) by vacuum suction to cover the large surface pores. As shown in Figure 4C, the filamentous CNTs were filled in the big pores of the surface of the porous substrate without blocking the ventilation channels of the substrate itself nor reducing the gas permeability (see following data in section 3.3). From the characterization of the pore size distribution, as shown in Figure 4D, the average aperture of both the substrates before and after modification was around 2 µm. After modification with CNTs, most pore sizes did not change significantly. That is to say, only the surface pores of the substrate were filled by CNTs, while most pores of the bulk substrate were not blocked, indicating that the modification with filamentous CNTs showed a successful pretreatment for the substrate aiming for consequent membrane assembly. Figure 4E-F compared the surface structure of the MXene membrane assembled on the substrate before and after modification. It could be clearly seen that a large number of defects existed on the MXene membrane/SS<sub>bare</sub>due to the rough substrate with large pores (Figure 4E). On the contrary, the  $MXene/SS_{CNTs}$  membrane had a comparatively flat surface, and there were no obvious large holes or pinhole defects (Figure 4F). Moreover, the surface view and cross-section of the MXene/SS membranes grown with various electrophoresis time were shown in Figure 5, all the MX ene membranes were relatively flat without obvious defects, and the membrane thickness was positively correlated with the electrophoresis time, where the thickness increased from ~100nm to  $\tilde{330}$  nm when the assembly time increased from 1.5 min to 4 min. The fast preparation process of MXene membrane by electrophoretic deposition had the advantages of high efficiency, as well as favorable conditions for membrane scale-up production.



FIGURE 4 SEM images of A) the bare substrate without modofication, B) substrate after polishing, C) substrate after polishing and CNTs filtration, D) substrate pore size distribution before and after surface modification, E) MXene membrane assembled on bare subatrate, F) MXene membrane assembled on substrate after modification.



FIGURE 5 Cross-sectional and Top-view (inset) SEM images of the tubular MXene/SS membranes grown with different electrophoresis time.

XRD characterization of the tubular MXene/SS membranes with different electrophoresis time was performed, as shown in Figure 6. The corresponding d -spacing could be calculated using the Bragg equation  $2d \sin \theta = n\lambda$  and finally the empty interlayer spacing  $l = d - l_0$  was calculated, where  $l_0$  was the thickness of the theoretical monolayer MXene nanosheet. Since it was inconvenient for sample preparation due to the hard tubular stainless steel substrate, an electric conductive adhesive (ECA) was used to stick the membrane on the holder to perform XRD characterization. Because the ECA contained metal aluminum flakes, there were diffraction peaks of metal aluminum at 44.59, 64.97, and 78.12° in the XRD patterns, respectively. The angle of (002) diffraction peak of a series of tubular MXene/SS membranes prepared by electrophoretic deposition was around 6.42° with *d* -spacing of 1.375 nm, where the empty interlayer spacing was 0.375 nm. To verify whether the electrophoretic deposition process had an effect on the interlayer spacing of the tubular MXene/SS membrane, another MXene membrane prepared by vacuum filtration (labeled as MXene/ECA<sub>VF</sub>) was also performed. It could be obtained from the XRD patterns that the MXene/ECA<sub>VF</sub> membrane exhibited a diffraction peak of 002 crystal plane at an angle of 6.50° with the *d* -spacing of 1.358 nm (empty interlayer spacing of 0.358 nm), which was consistent with our previous work and other literature.<sup>59,60</sup>



FIGURE 6 XRD patterns of the tubular MXene/SS membranes with different electrophoresis time.

In this work, the  $MXene/SS_{2.5}$  membrane was chosen for EDS characterization in order to confirm the element distribution. The SEM image of a cross-section of the MXene/SS<sub>2.5</sub> membrane was shown in Figure 7A. Figure 7B-E represented the EDS images of C, Ti, O, and F, respectively, indicating the uniform distribution of each element. There was no obvious cross-sectional distribution in Figure 7B because the electric conductive adhesive sticking to the MXene membrane also contained C element. Subsequently, XPS and FTIR analysis of the tubular MXene/SS membranes were performed to investigate the chemical bonds in the membranes. As shown in Figure 8A, the MXene membrane was primarily consisted of four elements (C, Ti, O, and F), while there were no peaks belonging to Al element, indicating that it had been etched off thoroughly in the MXene membrane, which was also consistent with the XRD characterization results. A more detailed high-resolution XPS spectra analysis of the four elements is shown in Figure 8B-E. Five different chemical groups appeared in the spectrum of Ti element, namely Ti-C (454.8 eV), Ti<sup>2+</sup> (455.7 eV),  $Ti^{3+}(456.5 \text{ eV})$ , Ti-O (458.1 eV), and Ti-F (459.6 eV). It should be noted that the chemical bond of Ti-O accounted for about 5.5% of the total Ti element. That's because the MXene nanosheets were prepared by chemical etching, it was inevitable that a small amount of Ti atoms would be oxidized.<sup>61,62</sup> The high-resolution XPS spectra of O1s could be resolved into four components as 529.4, 530.0, 531.3, and 532.5 eV, and their corresponding chemical bonds were O-Ti, O-Ti/OH, O-C/OH, H<sub>2</sub>Oad, respectively. The C1s spectrum also consisted of four sub-peaks, representing chemical bonds of C-Ti (281.7 eV), C-C (284.7 eV), C-O(285.8 eV), and C-O=C/C-F (288.5 eV), which were consistent with the literatures.<sup>63-65</sup> The fitted curves in the F1s spectrum correspond to two chemical bonds of F-Ti (684.7 eV) and F-C (686.4 eV), respectively. In this work, the functional groups that combined with oxygen on the surface of the prepared membranes were further characterized to use FTIR. As shown in Figure 8F, there were two stretching vibration peaks in the FTIR spectra of the tubular MXene/SS membrane, which belonged to -OH at 3457 cm<sup>-1</sup> and C=O at 1641 cm<sup>-1</sup>. -OH denoted the -OH functional group on the membrane surface or the adsorbed water between the interlayers, while C=O represented the terminal functional groups at the edge of the MXene nanosheets.49



FIGURE 7 Cross-sectional SEM image and the corresponding element distribution mappings of the tubular  $MXene/SS_{2.5}membrane$ . Scale bar: 1  $\mu m$ .



FIGURE 8 The XPS analysis of the tubular MXene/SS<sub>2.5</sub>membrane surface. A) Survey XPS spectrum of the MXene/SS<sub>2.5</sub> membrane. High-resolution XPS spectra of B) Ti 2p, C) O 1s, D) C 1s, E) F 1s of the MXene/SS<sub>2.5</sub>membrane. F) FTIR result of the tubular MXene/SS<sub>2.5</sub>membrane.

### 3.3 Gas separation performance

In order to identify the most suitable gas separation system, the single gas permeation experiment was first performed on the tubular MXene/SS membrane. As shown in Figure 9A, different gases were tested and the ideal selectivity of each gas was calculated. According to the experimental data, the permeance of H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub> were 1450 GPU, 22 GPU, 61 GPU, 45 GPU, and 8 GPU, respectively, while the corresponding ideal selectivity of  $S(H_2/CO_2)$ ,  $S(H_2/N_2)$ ,  $S(H_2/CH_4)$  and  $S(H_2/C_2H_4)$  were 65, 24, 33, and 186, which were all larger than the Knudsen selectivity. Obviously, the MXene/SS membrane showed a cut-off between H<sub>2</sub> and CO<sub>2</sub> molecules. Moreover, the effect of different electrophoretic deposition time on the gas separation performance of the tubular MXene/SS membranes was also investigated. As shown in Figure 9B, for better comparison, the H<sub>2</sub> gas permeance of the bare stainless steel substrate and the substrate after modification were tested to be 5323 GPU and 4908 GPU with similar H<sub>2</sub>/CO<sub>2</sub> selectivity of ~5, respectively. The comparable results indicated the use of filamentous CNTs as surface fillers could

only modify the substrate surface without reducing the gas permeance of the original substrate, which was a promising candidate as a substrate modification. With the prolongation of electrophoresis time, the MXene membrane grew thicker, resulting in fewer defects, so the hydrogen permeance of the tubular MXene/SS membrane became lower, while the gas selectivity increased initially and then stayed almost unchanged. When the electrophoresis time was 2.5 min, the  $H_2/CO_2$  selectivity of the membrane reached the maximum of 55 with comparable hydrogen permeance of 1290 GPU, thus the tubular MXene/SS<sub>2.5</sub> membrane was the optimal one in this study.



FIGURE 9 A) Series of gas permeability through the tubular MXene/SS<sub>2.5</sub> membrane. B) Effect of electrophoresis time on the  $H_2/CO_2$  separation performance of the membranes. Tests condition: the feeding mixed gas (50 ml: 50 ml of  $H_2/CO_2$ ) at 1 atm and 25°C.

In addition, the effect of the operation parameters on the gas permeance, such as temperature and feed gas humidity, had also been investigated. The temperature-dependent  $H_2/CO_2$  separation performance of the tubular MXene/SS<sub>2.5</sub> membrane was depicted in Figure 10A, where three temperature cycles included heating and cooling processes. When the temperature was raised from 25 °C to 125°C, the hydrogen permeance gradually was raised from 1283 GPU to 1880 GPU, while the  $H_2/CO_2$  selectivity decreased from 55 to 19. During the cooling stage, the hydrogen permeance fell from 1880 GPU to 1634 GPU, and the selectivity was raised from 19 to 50. Furthermore, the performance of the  $MXene/SS_{2.5}$  membrane could still recover well after three heating and cooling cycles, with  $H_2/CO_2$  selectivity of 51 and hydrogen permeance of 1568 GPU , demonstrating the tubular  $MXene/SS_{2.5}$  membrane had good thermal resistance. The apparent activation energy of the system was illustrated in Figure 10B via Arrhenius equation. The apparent activation energies E<sub>act (H2)</sub> and E<sub>act (CO2)</sub> of the two gases were 1.61 kJ/mol and 11.04 kJ/mol, respectively. It could be found that the apparent activation energies were all positive, which indicated that gas diffusion rather than adsorption was primarily responsible for controlling the gas separation process, which was consistent with the literatures.<sup>66</sup> Moreover, the synthesis gas produced by the methane steam reforming process always contains water vapor (usually < 3 vol%), so a water vapor-containing test on the separation system was required. Different saturated salt solutions were used to produce water vapor with different relative humidity to explore gas permeability.<sup>4</sup> As shown in Figure 10C, as the relative humidity increased from 0% to 92%, the hydrogen permeance decreased from 1244 to 1168 GPU, while the  $CO_2$  permeance slightly increased from 21 to 22 GPU, thus the corresponding  $H_2/CO_2$  selectivity decreased from 57 to 51. Obviously, as the relative humidity of the feed gas increased, the condensable water molecules in the feed gas condensed in the pores or interlayer spacing of the membrane, obstructing the transmission of non-condensable small molecular gas of  $H_2$ . Because  $CO_2$  is more soluble in condensed water than  $H_2$ , it diffused through the membrane more quickly, reducing the selectivity of  $H_2/CO_2$ , which was consistent with the phenomenon of layered graphene at various humidity conditions.<sup>4</sup>



FIGURE 10 A) Effect of temperature on  $H_2/CO_2$  separation performance of the tubular MXene/SS<sub>2.5</sub> membrane. B) Apparent activation energy of  $H_2/CO_2$  separation through the membrane. C) Effect of feed humidity on  $H_2/CO_2$  separation performance.

Furthermore, in order to evaluate whether the tubular MXene/SS membranes prepared by electrophoretic deposition had the potential for scale-up and practical applications, the long-term stability, water-vapor stability, and replicability were explored in detail. As illustrated in Figure 11A, during the long-term separation experiment up to 1100 h, both the  $H_2/CO_2$  selectivity and the hydrogen permeance were relatively stable as a whole with only a small fluctuation. The average hydrogen permeance was 1452 GPU, while the average  $H_2/CO_2$  selectivity was 63. Water vapor with a volume fraction of 3% was introduced into the feed gas continuously for 24 hours each time and then turned back to the dry system, the operation was carried out three times to guarantee the correctness of the test. When water vapor was added, the average hydrogen permeance decreased to 1321 GPU, and the corresponding  $H_2/CO_2$  selectivity decreased to 56. When the water vapor was interrupted, the hydrogen permeance returned to 1468 GPU, and the selectivity returned to 65, demonstrating that the MXene/SS membrane had excellent water vapor resistance and stability.

In order to investigate the issue of membrane reproducibility, we evaluated the separation performance of 15 pieces of tubular MXene/SS membranes from one batch. As shown in Figure 11B, the hydrogen permeance of the produced membranes ranged from 880<sup>-1474</sup> GPU with an average value of 1224, whereas the range of  $H_2/CO_2$  selectivity was 47<sup>-64</sup> with an average value of 56. According to the US Department of Energy (DOE) estimation, it would approach the DOE target for 90% CO<sub>2</sub> capture if the  $H_2/CO_2$  selectivity and hydrogen permeance could reach 40 and 900 GPU for a membrane, respectively. The  $H_2/CO_2$  selectivity of these tubular MXene/SS membranes prepared in one batch completely meets the requirement and except only one membrane gave an hydrogen permeability less than 900 GPU. In other words, 93% of the membranes prepared in this batch exceeded the DOE target, promising further scale-up preparation with good repeatability.

Last but not least, a comparison of the state-of-the-art membranes including 2D and 3D membranes for  $H_2/CO_2$  separation, was shown in Table 1. Compared with the 3D membranes, it was obvious that the 2D membranes had better gas separation performance. However, these excellent 2D membranes were mainly prepared on porous ceramic alumina or AAO substrates, both of which were fragile and inconvenient for further scale-up, and the preparation methods (vacuum filtration, hot drop coating, etc.) were also not suitable for rapid membrane production. Hence, we sought to solve the problem of how to prepare 2D MXene membranes that could be closer for actual industrial production. Using the industrially mature electrophoretic

deposition process has been proven to be more convenient for large-scale scale-up, and the MXene membranes can be prepared on commercial porous tubular stainless steel substrates for  $H_2/CO_2$  separation with good weldability. In contrast to many other membranes in Table 1, the MXene membrane prepared in this work achieved long-term stability of more than 1250 h, with  $H_2/CO_2$  selectivity of 55 and hydrogen permeance of 1290 GPU, which further demonstrated the feasibility of the practical application.



FIGURE 11 Study on stability and repeatability of the  $MXene/SS_{2.5}$  membrane. A) Long-term  $H_2/CO_2$  separation and water vapor-stability test. B) Repeatability of the membrane preparation.

Table 1	Comparison	of the s	tate-of-the-art	membranes	including 2I	) and 3D	membranes	for $H_2/C$	$O_2$ sepa-
ration.									

Number	Membrane material	Membrane substrate	Membrane geome- try	Thickness()	Preparation µMethod	${ m H_2~Per}-{ m meance}{ m (GPU)^a}$	$ m H_2/CO_2$ Selectiv- ity	Long- term stability (h)	Re
1	PIM- EA-TB	-	Disk	181	Film disper- sion method	42	1.1 <sup>b</sup>	-	9
2	PIM- SBI- TB	-	Disk	157	Film disper- sion method	138	$0.8^{\mathrm{b}}$	-	9
3	Pure PBI	Matrimid	Hollow fiber	2	Polymerization reaction	<b>52</b> 1	9	-	10
4	PZM10- I B	Matrimid	Hollow fiber	18	Electrostatic spinning	65	12	-	10
5	PZM33- I B	Matrimid	Hollow fiber	16	Electrostatic spinning	202	8	-	10
6	PBI	Glass	Disk	10	Knife casting method	3	16	120	12
7	BILP- 101x	Porous α- Al <sub>2</sub> O <sub>3</sub>	Disk	0.4	Interfacial polymerization	24 on	40	800	13

Number	Membrane material	Membrane substrate	Membrane geome- try	Thickness(	Preparation p <b>M</b> ethod	${ m H_2}$ Per- nmeance $({ m GPU})^{ m a}$	$ m H_2/CO_2$ Selectiv- ity	Long- term stability (h)	R
8	Silicon Carbide	Porous silicon carbide	Tube	2	Slip- casting and dip- coating techniques	27	50	528	14
9	ZSM- 5/Silicalite	Porous α- Al <sub>2</sub> O <sub>3</sub>	Disk	9.5	Catalytic crack- ing deposi- tion (CCD)	377	25	40	15
10	CAU-1	Porous α- AlaOa	Hollow fiber	4	Solvotherma synthesis	1 322	12	50	17
11	ZIF-8	Porous $\alpha$ -	Hollow fiber	6	Solvotherma synthesis	1472	5	-	19
12	ZIF-8	Porous stain- less steel	Disk	3.4	Solvent- free in situ growth	439	69	700	21
13	Amine- Mg- MOF- 74	Porous α- Al <sub>2</sub> O <sub>3</sub>	Disk	10	Solvotherma synthesis	1224	28	-	23
14	ACOF- 1	Porous α- Al <sub>2</sub> O <sub>3</sub>	Disk	0.6	Solvotherma synthesis	12045	14	110 <sup>c</sup>	24
15	COF- LZU1- ACOF- 1	Porous α- Al <sub>2</sub> O <sub>3</sub>	Disk	1	Solvotherma synthesis	1669	24	110 <sup>c</sup>	24
16	[COF- 300]- [Uio- 66]	$\begin{array}{c} Porous\\ SiO_2 \end{array}$	Disk	100	Solvotherma synthesis	l 1190	17	-	25
17	HKUST- 1(MOF)	Copper net	Disk	60	Solvotherma synthesis	l 2985	7	25	26
18	COF- MOF	Porous $SiO_2$	Disk	97.2	Solvotherma synthesis	l 1132	14	2	27
19	GO	Porous AAO	Disk	4	Vacuum- assister filtration	25	30	-	4
20	GO	Porous α- Al <sub>2</sub> O <sub>3</sub>	Disk	1	Vacuum- spin	1000	30	100	35

Number	Membrane material	Membrane substrate	Membrane geome- try	Thickness(	Preparation pMethod	H <sub>2</sub> Per- nmeance (GPU) <sup>a</sup>	$ m H_2/CO_2$ Selectiv- ity	Long- term stability (h)	R
21	g- C <sub>3</sub> N <sub>4</sub> - GO	Porous AAO	Disk	0.7	Vacuum- assister filtration	645	39	75	36
22	ZIF- 8@GO	Porous α- Al <sub>2</sub> O <sub>3</sub>	Disk	20	Solvotherma synthe- sis and LBL deposition	1379	15	72 <sup>c</sup>	37
23	$MoS_2$ - GO	Porous AAO	Disk	0.15	Vacuum- assister filtration	857	44	72	38
24	2D MoS <sub>2</sub>	Porous AAO	Disk	0.65	Vacuum- assister filtration	2045	8	-	39
25	2D MXene	Porous yttria- stabilized zirco- nia (YSZ)	Hollow fiber	0.22	Vacuum- assister filtration	70	30	120	41
26	2D MXene	Porous AAO	Disk	2	Vacuum- assister filtration	1113	167	700	42
27	2D MXene	Porous AAO	Disk	0.02	Vacuum- assister filtration	1584	27	110	43
28	MXene/ZIF- 8	Copper plate	Disk	1.25	Electrophore deposi- tion (EPD) and fast current- driven synthe- sis (FCDS)	ot <b>1</b> 678	77 <sup>b</sup>	100	59
29	2D ZIFS	Porous α- Al <sub>2</sub> O <sub>3</sub>	Disk	-	Hot- drop coating	2700	291	120	46
30	2D MOFS	Porous AAO	Disk	0.04	Hot- drop coating	880	225	167	47
31	2D COF- LZU1	Porous α- Al <sub>2</sub> O <sub>3</sub>	Disk	2	Solvotherma synthesis	1 3655	32	100	48

Number	Membrane material	Membrane substrate	Membrane geome- try	$\mathbf{Thickness}(\mathbf{x})$	Preparation pMethod	${f H_2}$ Per- nmeance (GPU) <sup>a</sup>	$ m H_2/CO_2$ Selectiv- ity	Long- term stability (h)	R
32	2D TFB- BD	Porous α- Al <sub>2</sub> O <sub>3</sub>	Disk	2	Solvotherma synthesis	1 3802	26	-	48
33	2D MXene	Porous stain- less steel	Tube	0.3-0.5	Suction filtra- tion and Elec- trophoretic deposi- tion (EPD)	1290	55	1250	th wo

a In this column, all gas permeance was converted with unit of GPU.1  $GPU = 3.35 \times 10^{-10} \text{mol} \cdot m^{-2} \cdot s^{-1} \cdot pa^{-1}$ 

b The value was recorded for the ideal selectivity of the single gas.

c The value was recorded for  $H_2/CH_4$  separation.

# 4 CONCLUSIONS

In conclusion, we successfully fabricated tubular MXene/SS membranes on commercial porous stainless steel substrates rapidly via electrophoretic deposition. Filamentous CNTs were used as fillers for macroporous substrates for the first time, which could effectively fill the big holes only on the substrate surface and modify the surface flatness without reducing the permeability of the substrate itself. After optimizing the electrophoresis process, the tubular MXene/SS<sub>2.5</sub> membrane achieved excellent  $H_2/CO_2$  separation performance. The corresponding  $H_2/CO_2$  selectivity and hydrogen permeance were 55 and 1290 GPU, respectively, and the membrane showed outstanding long-term stability for up to 1250 h with good water vapor stability. Moreover, the repeatability of membrane preparation had also been adequately validated, where 93% of the membranes prepared in one batch exceeded the DOE target, showing great potential for industrial scale-up and practical application. Most importantly, this work proposed a method for the efficient preparation of 2D MXene nanosheet membranes on commercial tubular stainless steel substrates, which provided a valuable reference for the preparation of other types of 2D materials-based membranes. Furthermore, the work has also made specific contributions to the large-scale fabrication of 2D MXene membranes and the promotion of actual industrial applications.

## ACKNOWLEDGMENT

We gratefully acknowledge the support from the National Key Research and Development Program (2021YFB3802500) and the Natural Science Foundation of China (22022805 and 22078107). This work was supported by State Key Laboratory of Pulp and Paper Engineering (Project Number of 2022PY04) and Fundamental Research Funds for the Central Universities (2022ZYGXZR010).

# AUTHOR CONTRIBUTIONS

Mide Luo: Formal analysis (lead), Investigation (supporting), Data curation (lead), Methodology (lead), Writing – original draft (lead). Zong Lu: Investigation (supporting), Writing – original draft (supporting). Yali Zhao: Investigation (supporting), Methodology (supporting). Yufei Wang:Investigation (supporting), Formal analysis (supporting). Writing – original draft (supporting). Yanying Wei: Writing – review & editing (lead). Haihui Wang: Writing – review & editing (lead).

## CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

# DATA AVAILABILITY STATEMENT

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

## REFERENCES

1. Rostrup-Nielsen JR, Rostrup-Nielsen T. Large-scale hydrogen production. Cattech. 2002;6(4):150-159.

2. Van Miltenburg A, Zhu W, Kapteijn F, Moulijn JA. Adsorptive separation of light olefin/paraffin mixtures. Chem Eng Res Des. 2006;84:350-354.

3. Lin JYS. Molecular sieves for gas separation. Science. 2016;353(6295):121-122.

4. Kim HW, Yoon HW, Yoon SM, et al. Selective gas transport through few-layered graphene and graphene oxide membranes. Science. 2013;342(6154): 91-95.

5. Li YS, Liang FY, Bux H, Feldhoff A, Yang WS, Caro J. Molecular sieve membrane: supported metalorganic framework with high hydrogen selectivity. Angew Chem Int Ed. 2010;122(3):558-561.

6. Shen J, Liu G, Huang K, Jin W, Lee KR, Xu N. Membranes with fast and selective gas-transport channels of laminar graphene oxide for efficient  $CO_2$  capture. Angew Chem Int Ed. 2015;127(2):588-592.

7. Wang XR, Chi CL, Tao JF, et al. Improving the hydrogen selectivity of graphene oxide membranes by reducing nonselective pores with intergrown ZIF-8 crystals. Chem Commun. 2016;52:8087-8090.

8. Yáñez M, Ortiz A, Gorri D, et al. Comparative performance of commercial polymeric membranes in the recovery of industrial hydrogen waste gas streams. Int J Hydrogen Energy. 2021;46(33):17507-17521.

9. Carta M, Malpass-Evans R, Croad M, et al. An efficient polymer molecular sieve for membrane gas separations. Science. 2013;339(6117):303-307.

10. Massoumilari Ş, Doğancı M, Velioğlu S. Unveiling the potential of MXenes for  $H_2$  purification and  $CO_2$ capture as an emerging family of nanomaterials. AIChE J. 2022;68:e17837.

11. Yang T, Shi GM, Chung TS. Symmetric and asymmetric zeolitic imidazolate frameworks (ZIFs)/polybenzimidazole (PBI) nanocomposite membranes for hydrogen purification at high temperatures. Adv Energy Mater. 2012;2(11):1358-1367.

12. Zhu L, Swihart MT, Lin H. Unprecedented size-sieving ability in polybenzimidazole doped with polyprotic acids for membrane  $H_2/CO_2$  separation. Energy Environ Sci. 2018;11(1):94-100.

13. Shan MX, Liu XL, Wang XR, et al. Facile manufacture of porous organic framework membranes for precombustion CO<sub>2</sub>capture. Sci Adv. 2018;4(9):1698.

14. Elyassi B, Sahimi M, Tsotsis TT. Silicon carbide membranes for gas separation applications. J Membr Sci. 2007;288:290-297.

15. Wang H, Lin YS. Synthesis and modification of ZSM-5/silicalite bilayer membrane with improved hydrogen separation performance. J Membr Sci. 2012;396:128-137.

16. Helberg RML, Torstensen JØ, Dai Z, et al. Nanocomposite membranes with high-charge and size-screened phosphorylated nanocellulose fibrils for  $CO_2$  separation. Green Energy Environ. 2021;6(4):585-596

17. Zhou S, Zou X, Sun F, et al. Development of hydrogen-selective CAU-1 MOF membranes for hydrogen purification by 'dual-metal-source' approach. Int J Hydrogen Energy. 2013;38(13):5338-5347.

18. Su P, Tang H, Jia M, et al. Vapor linker exchange of partially amorphous metal-organic framework membranes for ultra-selective gas separation. AIChE J. 2022;68(5):e17576.

19. Zhang XF, Liu YG, Li SH, et al. New membrane architecture with high performance: ZIF-8 membrane supported on vertically aligned ZnO nanorods for gas permeation and separation. Chem Mater. 2014;26(5):1975-1981.

20. Gu Z, Yang Z, Sun Y, et al. Large-area vacuum-treated ZIF-8 mixed-matrix membrane for highly efficient methane/nitrogen separation. AIChE J. 2022;68(9):e17749.

21. Hou J, Hong XL, Zhou S, et al. Solvent-free route for metal-organic framework membranes growth aiming for efficient gas separation. AIChE J. 2019;65(2):712-722.

22. Huang AS, Bux H, Steinbach F, et al. Molecular-sieve membrane with hydrogen permselectivity: ZIF-22 in LTA topology prepared with 3-aminopropyltriethoxysilane as covalent linker. Angew Chem Int Ed. 2010;122(29):5078-5081.

23. Wang NY, Mundstock A, Liu Y, et al. Amine-modified Mg-MOF-74/CPO-27-Mg membrane with enhanced  $H_2/CO_2$  separation. Chem Eng Sci. 2015;124:27-36.

24. Fan HW, Mundstock A, Feldhoff A, et al. Covalent organic framework-covalent organic framework bilayer membranes for highly selective gas separation. J Am Chem Soc. 2018;140(32):10094-10098.

25. Das S, Ben T. A [COF-300]-[UiO-66] composite membrane with remarkably high permeability and  $H_2/CO_2$  separation selectivity. Dalton Trans. 2018;47(21):7206-7212.

26. Guo HL, Zhu GS, Hewitt IJ, et al. "Twin copper source" growth of metal-organic framework membrane:  $Cu_3(BTC)_2$  with high permeability and selectivity for recycling H<sub>2</sub>. J Am Chem Soc. 2009;131(5):1646-1647.

27. Fu JR, Das S, Xing GL, et al. Fabrication of COF-MOF composite membranes and their highly selective separation of  $H_2/CO_2$ . J Am Chem Soc. 2016;138(24):7673-7680.

28. Zhang C, Kumar R, Koros WJ. Ultra-thin skin carbon hollow fiber membranes for sustainable molecular separations. AIChE J. 2019;65(8):e16611.

29. Venna SR, Lartey M, Li T, et al. Fabrication of MMMs with improved gas separation properties using externally-functionalized MOF particles. J Mater Chem A. 2015;3(9):5014-5022.

30. Zhao Z, Ma X, Kasik A, Li Z, Lin YS. Gas separation properties of metal organic framework (MOF-5) membranes. Ind Eng Chem Res. 2013;52(3):1102-1108.

31. Dai L, Huang K, Xia Y, et al. Two-dimensional material separation membranes for renewable energy purification, storage, and conversion. Green Energy Environ. 2021;6(2):193-211.

32. Cohen-Tanugi D, Grossman JC. Water desalination across nanoporous graphene. Nano Letters. 2012;12(7):3602–3608.

33. Wang WT, Eftekhari E, Zhu GS, et al. Graphene oxide membranes with tunable permeability due to embedded carbon dots. Chem Commun. 2014;50(86):13089-13092.

34. Kang J, Zhang HY, Duan XG, et al. Magnetic Ni-Co alloy encapsulated N-doped carbon nanotubes for catalytic membrane degradation of emerging contaminants. Chem Eng J. 2019;362:251-261.

35. Shen J, Liu GP, Huang K, et al. Subnanometer two dimensional graphene oxide channels for ultrafast gas sieving. ACS Nano. 2016;10(3):3398–3409.

36 Zhou YS, Zhang Y, Xue J, et al. Graphene oxide-modified  $g-C_3N_4$  nanosheet membranes for efficient hydrogen purification. Chem Eng J. 2021;420:129574.

37. Huang AS, Liu Q, Wang NY, et al. Bicontinuous zeolitic imidazolate framework ZIF-8@GO membrane with enhanced hydrogen selectivity. J Am Chem Soc. 2014;136(42):14686-14689.

38 Ostwal M, Shinde DB, Wang X, et al. Graphene oxide-molybdenum disulfide hybrid membranes for hydrogen separation. J Membr Sci. 2018;550:145-154.

39. Achari A, Sahana S, Eswaramoorthy M. High performance MoS<sub>2</sub> membranes: effects of thermally driven phase transition on CO<sub>2</sub> separation efficiency. Energy Environ Sci. 2016;9(4):1224-1228.

40. Fan YY, Li JY, Wang SD, et al. Nickel (II) ion-intercalated MXene membranes for enhanced H<sub>2</sub>/CO<sub>2</sub>separation. Front Chem Sci Eng. 2021;15(4):882-891.

41. Qu K, Dai LH, Xia YS, et al. Self-crosslinked MXene hollow fiber membranes for  $H_2/CO_2$  separation. J Membr Sci. 2021;638:119669.

42. Ding L, Wei YY, Li LB, et al. MXene molecular sieving membranes for highly efficient gas separation. Nat Commun. 2018;9(1):155.

43. Shen J, Liu GZ, Ji YF, et al. 2D MXene nanofilms with tunable gas transport channels. Adv Funct Mater. 2018;28(31):1801511.

44. Tsapatsis M. 2-Dimensional zeolites. AIChE J. 2014;60(7):23742381.

45. Agrawal KV, Topuz B, Pham TC, et al. Oriented MFI membranes by gel-less secondary growth of sub-100 nm MFI-Nanosheet seed layers. Adv Mater. 2015;27(21):3243-3249.

46. Peng Y, Li YS, Ban YJ, Jin H, Jiao WM, Liu XL, Yang WS. Metal-organic framework nanosheets as building blocks for molecular sieving membranes. Science. 2014;346(6215):1356-1359.

47. Wang XR, Chi CL, Zhang K, et al. Reversed thermo-switchable molecular sieving membranes composed of two-dimensional metal-organic nanosheets for gas separation. Nat Commun. 2017;8(1):14460.

48. Fan HW, Peng MH, Strauss I, et al. High-flux vertically aligned 2D covalent organic framework membrane with enhanced hydrogen separation. J Am Chem Soc. 2020;142(15):6872-6877.

49. Naguib M, Kurtoglu M, Presser V, et al. Two-dimensional nanocrystals produced by exfoliation of Ti<sub>3</sub>AlC<sub>2</sub>. Adv. Mater. 2011;23(37):4248-4253.

50. Shahzad F, Alhabeb M, Hatter CB, et al. Electromagnetic interference shielding with 2D transition metal carbides (MXenes). Science. 2016;353(6304):1137-1140.

51. Lukatskaya MR, Kota S, Lin Z, et al. Ultra-high-rate pseudocapacitive energy storage in two-dimensional transition metal carbides. Nat Energy. 2017;2(8):1-6.

52. Li RY, Zhang LB, Shi L, et al. MXene  $Ti_3C_2$ : an effective 2D light-to-heat conversion material. ACS Nano. 2017;11(4):3752-3759.

53 Xu BZ, Zhu MS, Zhang WC, et al. Ultrathin MXene-micropattern-based field-effect transistor for probing neural activity. Adv. Mater. 2016;28(17):3333-3339.

54. Zhou FL, Dong QB, Chen JT, et al. Printed graphene oxide-based membranes for gas separation and carbon capture. Chem Eng J. 2022;430:132942.

55. Anasori B, Lukatskaya MR, Gogotsi Y. 2D metal carbides and nitrides (MXenes) for energy storage. Nat Rev Mater. 2017;2(2):16098.

56. Lukatskaya MR, Mashtalir O, Ren CE, et al. Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide. Science. 2013;341(6153):1502-1505.

57. Zhao L, Dong BL, Li SZ, et al. Interdiffusion reaction-assisted hybridization of two-dimensional metal-organic frameworks and  $Ti_3C_2T_X$  nanosheets for electrocatalytic oxygen evolution. ACS nano, 2017;11(6):5800-5807.

58. Duman O, Tunc S. Electrokinetic and rheological properties of Na-bentonite in some electrolyte solutions. Micropor Mesopor Mater. 2009;117:331-338.

59. Hong XL, Lu, Z. Zhao YL, et al. Fast fabrication of freestanding MXene-ZIF-8 dual-layered membranes for H<sub>2</sub>/CO<sub>2</sub> separation. J Membr Sci. 2022;642:119982.

60. Deng J, Lu Z, Ding L, et al. Fast electrophoretic preparation of large-area two-dimensional titanium carbide membranes for ion sieving. Chem Eng J. 2021;408:127806.

61. Zhang CJ, Pinilla S, McEvoy N, et al. Oxidation stability of colloidal two-dimensional titanium carbides (MXenes). Chem Mater. 2017;29(11):4848-4856.

62. Lipatov A, Alhabeb M, Lukatskaya MR, et al. Effect of synthesis on quality, electronic properties and environmental stability of individual monolayer  $Ti_3C_2$  MXene flakes. Adv Electron Mater. 2016;2(12):1600255.

63. Halim J, Cook KM, Naguib M, et al. X-ray photoelectron spectroscopy of select multi-layered transition metal carbides (MXenes). Appl Surf Sci. 2016;362:406-417.

64. Wang LB, Zhang H, Wang B, et al. Synthesis and electrochemical performance of  $Ti_3C_2T_X$  with hydrothermal process. Electron Mater Lett. 2016;12(5):702-710.

65. Han MK, Yin XW, Wu H, et al.  $Ti_3C_2MX$  enes with modified surface for high-performance electromagnetic absorption and shielding in the X-band. ACS Appl Mater Interfaces. 2016;8(32):21011-21019.

66. Wu R, Li YH, Huang AS. Synthesis of high-performance Co-based ZIF-67 membrane for  $H_2$  separation by using cobalt ions chelated PIM-1 as interface layer. J Membr Sci. 2021;620:118841.