Two-dimensional Ti$_2$CT$_x$ MXene membranes with integrated and ordered nanochannels for efficient solvent dehydration†

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Two-dimensional (2D) material membranes have shown great potential for molecular separation. However, it remains challenging to controllably tune 2D material membrane structures with ordered nanochannels without non-selective defects. Herein, for the first time, 2D Ti$_2$CT$_x$ MXene membranes were designed and fabricated for efficient solvent dehydration via a new strategy. Specifically, positively charged hyperbranched polyethylenimine was intercalated between negatively charged MXene nanosheets to assemble regular stacking structures via electrostatic interactions, followed by interfacial polymerization with trimesoyl chloride to seal possible non-selective defects. This strategy realized integrated Ti$_2$CT$_x$ membranes as thin as ~100 nm with highly ordered 2D nanochannels, thereby exhibiting outstanding separation performance: the water content was enriched to >99 wt% in permeate from 10 wt% water/isopropanol mixtures. Compared with commonly studied Ti$_3$C$_2$T$_x$ MXene membranes prepared by the same approach, the Ti$_2$CT$_x$ membranes showed higher selectivity with similarly high flux. The membrane fabrication approach developed herein offers a powerful platform for the rational design of 2D material thin films for precise molecular separation and other applications.

Introduction

The discovery of graphene initiated a wave of research in a variety of two-dimensional (2D) materials such as silicene, germanene, phosphorene, and chalcogenides.1–3 Due to their atomic thickness, 2D material-assembled membranes can enable minimum transport resistance to realize maximum permeate flux, opening a new era in membrane separation.4–6 Recently, a new family of 2D transition metal carbides and carbonitrides labeled MXenes, with the general formula M$^{n+1-}$X$_n$T$_x$ (n = 1, 2, 3), was discovered, where M refers to an early transition metal, X stands for carbon and/or nitrogen, and T represents the surface-terminating functional groups (–OH, –O, or –F).7–9 MXenes are often synthesized by etching the “A” element from the precursor MAX powders (where A is a group IIIA or IVA element) via fluorine-containing solutions.10,11 After treatment by sonication or hand-shaking,12–15 MXene nanosheets can be obtained with atomic thicknesses, micrometer lateral sizes and various functional groups. In addition to the abovementioned characteristics, the excellent mechanical properties, hydrophilic surfaces and metallic conductivity make MXene nanosheets a promising building block of membranes for molecular separation.11,16–19

Compared to other 2D materials such as graphene oxide (GO), due to their large variety of transition metals and surface functionalities, the versatile chemistry of MXenes allows tuning of their properties for applications such as in energy storage, water purification, and electromagnetic interference shielding.20 Moreover, although GO nanosheets have hydrophilic surfaces and abundant functional groups, GO membranes can disintegrate in water due to electrostatic repulsion between GO nanosheets that arises because the carboxyl groups become negatively charged upon hydration.20 Due to the robust channel structure preservation between MXene nanosheets, MXene membranes can maintain structural integrity after immersion in water for more than one month.20–22 In addition, MXene possesses high metallic conductivity, which may contribute to the research on the molecule transport behavior of MXene membranes under an electric field.

To date, about 70 kinds of MXene materials have been reported, among which Ti$_3$C$_2$T$_x$ is the most studied MXene.23

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‡ Electronic supplementary information (ESI) available: Schematic illustration, the structure of HPEI molecule, digital photos of solution and free-standing membrane, XRD patterns of powders, SEM and AFM images of different membranes, XPS spectra of Ti$_2$CT$_x$–HPEI/TMC membrane, pervaporation performance of MXene-based membrane, effect of temperature and feed concentration on performance. See DOI: 10.1039/c9ta01507h
Recently, some studies on high-performance MXene-based membranes for separating ions, dyes and gas molecules have been reported. Gogotsi et al. firstly reported Ti3C2Tx MXene membranes fabricated by pressure-filtration for rejection of cations with sizes larger than 2.5 nm in water. Different strategies were proposed to tune the Ti3C2Tx membrane structures to further improve the separation efficiency. Qiao et al. fabricated laminar membranes using double-layered Ti3C2Tx MXenes as rigid building blocks. Straight 2 nm channels were formed by direct self-stacking, showing enhanced solvent or water permeance for rejection of dyes with molecular sizes of ~1 nm. However, to our best knowledge, there is no report to date on MXene membranes for small liquid separation, such as solvent dehydration, which is a typically energy-intensive process for traditional separation technologies. This may be due to the disordered channels of MXene membranes induced by swelling of water, which exhibit insufficient separation efficiency.

Generally, molecular transport within 2D-material laminar membranes occurs through in-plane slit-like pores and then through plane-to-plane inter-galleries. However, it is difficult to precisely tune these laminar structures, especially in realizing defect-free and ordered 2D nanochannels. Many studies are devoted to regulating the interlayer space via inserting nanoparticles to improve permeability or selectivity. However, little attention has been paid to controlling the in-plane slit-like pores. 2D-material membranes are generally fabricated via filtration, spray-coating, spin-coating, drop-casting and dip-coating. Unfortunately, this sometimes generates non-selective defects along with out-of-order packing structures, resulting in failure of selective permeation. Our previous work demonstrated that molecular interactions, including hydrogen bonding and electrostatic attraction with polymer chains, can lead to highly ordered stacking of graphene oxide nanosheets to achieve excellent gas molecular sieving properties. In addition, covering polymeric layers on the membrane surface has been proposed to seal defects and thus improve the selectivity; meanwhile, the membrane permeability may be severely decreased due to increased mass transfer resistance.

In this work, we propose a new strategy of fabricating MXene membranes for solvent dehydration which introduces macromolecules between MXene nanosheets followed by interfacial polymerization on the assembled laminar membrane surface (Fig. 1 and S1†). Positively charged hyperbranched polyethylenimine (HPEI) electrostatically interacted with negatively charged MXene nanosheets to realize ordered stacking structures; meanwhile, trimesoyl chloride (TMC) was used to interfacially polymerize with HPEI to seal possible non-selective defects. Moreover, for the first time, Ti2CTx nanosheets were employed as a new building block of 2D-material membranes for molecular separation because of their higher hydrophilicity than Ti3C2Tx, which is favourable for their application in the dehydration of solvent. The microstructures and chemical properties of the resulting membranes were investigated in detail. The membrane transport properties were studied by separation of water/alcohol mixtures via a pervaporation process by varying the membrane fabricating conditions, molecular size of the alcohols and operating conditions such as feed concentration, temperature and long-term continuous operation.

### Experimental

#### Materials

Ti3AlC powder was obtained from 11 Technology Co., Ltd, China. Ti3AlC powder was synthesized according to a method described in previous work. LiF (99.9%) was purchased from Aladdin Industrial Corporation, Shanghai, China. HCl (36% to 38%) was provided by Lingfeng Chemical Reagent, China. Methanol (>99.7%), isopropanol (>99.7%) and ethanol (>99.7%) were purchased from Yasheng Chemical Co. Ltd. Hexane was supplied by Shanghai No. 4 Reagent & H.V. Chemical Limited Company. Hyperbranched polyethylenimine (HPEI, average Mw = 25 000, Fig. S2†) and trimesoyl chloride (TMC) were bought from Sigma-Aldrich. The commercial polyacrylonitrile (PAN) ultrafiltration membrane was obtained from Shandong Megavision Membrane Technology & Engineering Co., Ltd., China. Deionized water was used in all experiments.

#### Synthesis of MXene nanosheets

HCl and LiF were used as etching agents to obtain MXene powders. Taking Ti3CTx MXene as an example, in a typical synthesis process, 0.666 g LiF powder was immersed in 10 mL of 6 mol L−1 HCl solution under stirring; then, 1 g Ti3AlC powder was carefully added. After reacting at 35 °C for one day, the resulting solution was washed with water and ethanol by centrifugation several times. The Ti3CTx powders can be obtained after vacuum drying at room temperature for 12 h. Finally, Ti3CTx nanosheets can be obtained by dissolving a certain amount of Ti3CTx powder in deionized water with the aid of ultrasonication. Ti3C2Tx nanosheets were produced by a similar procedure.

#### Synthesis of MXene-based membranes

A certain amount of MXene nanosheets was added to 100 mL water; after stirring for 20 minutes, the neat MXene membrane was prepared via a facile vacuum filtration method. For the polymer HPEI-induced MXene (defined as MXene–HPEI)
membrane, 0.015 g of HPEI was added to a water solution containing the nanosheets; then, the mixture was filtrated through a PAN substrate. The MXene membrane assisted by interfacial polymerization (named MXene–HPEI/TMC) was fabricated by pouring 100 mL of n-hexane containing 0.001 g of TMC on the MXene–HPEI surface when no residual solution remained. Finally, the resulting membranes were stored under vacuum for further testing.

Taking Ti$_3$C$_2$T$_x$ MXene as an example, free-standing MXene membranes were prepared using anodic aluminium oxide (AAO, average pore size of 100 nm) by a similar method; they could be exfoliated from the substrates after drying for 24 h.

Characterization

X-ray diffraction (XRD) (Rigaku, Miniflex 600, Japan) was applied to characterize the crystal phases of the powders. XRD patterns were collected at a scanning rate of 0.2 s per step. The water contact angles of the membranes were measured by a contact angle measurement system (DSA100, Kruss). The morphologies of the samples were analyzed by field emission scanning electron microscopy (FESEM, JSM-7600F, Japan) with energy dispersive spectrometry (EDS) elemental mapping. A transmission electron microscope (TEM, JEM-2100F, Japan Electron Optics Laboratory Co., LTD, Japan) and polarizing microscope (BM-57XCD, Shanghai BM Optical Instruments Manufacture Company LTD) were used to investigate the morphologies of the membranes. Atomic force microscopy (AFM, XE-100, Park SYSTEMS, Korea) was applied to study the morphologies of the membranes. Exfoliated Ti$_3$C$_2$T$_x$ was fabricated from the precursor 3D Ti$_3$AlC$_2$ powder. Because the Ti–Al bond is metallic, it is difficult to obtain a single Ti$_3$C$_2$T$_x$ layer by simple mechanical shearing. Due to the fact that the Ti–Al bond shows high chemical activity, selective etching of Al element by aqueous fluoride-containing acidic solutions is possible. HCl/LiF mixtures were selected as corrosive agents to selectively etch Al element from the Ti$_3$AlC$_2$ powder. As shown in Fig. 2a and b, after etching Al element, the resulting Ti$_3$C$_2$T$_x$ powders showed accordion-like loosely stacked morphologies, affording ultrathin nanosheets due to the weakened interlayer interactions. The crystallinities of the powders were further studied by XRD (Fig. S3a†). The diffraction peaks corresponding to the Ti$_3$C$_2$T$_x$ powders were located at a 2θ angle of ~7°, which is in accordance with the literature, indicating a successful transformation from Ti$_3$AlC$_2$ powder to Ti$_3$C$_2$T$_x$ powder. Ultrathin Ti$_3$C$_2$T$_x$ nanosheets could be easily obtained via sonication. Fig. 2c shows a TEM image of the ultrathin nanosheets, which are nearly transparent. The AFM image (Fig. 1d) shows that the height of these nanosheets was 1 to 2 nm, which can be considered as single or double layer. Additionally, the lateral size was 1 to 2 μm, which was demonstrated previously to be suitable to form ordered 2D stacking membrane structures and abundant in-plane nanogaps for efficient molecular separation.

Vacuum-filtration was applied to fabricate MXene membranes. As shown in Fig. S4,† the free-standing Ti$_3$C$_2$T$_x$ MXene membrane could be folded into different shapes using a glass rod and tweezers, showing good flexibility. The free-standing Ti$_3$C$_2$T$_x$ MXene membrane was similar to the Ti$_3$C$_2$T$_x$ MXene membrane. The typical laminar structure of MXene

Results and discussion

Ti$_3$C$_2$T$_x$, a member of the MXene family, can be fabricated via an acid-etching method. Meanwhile, it possesses high hydrophilicity, which is expected to offer preferential water sorption properties during pervaporation dehydration of solvent. Therefore, we chose 2D Ti$_3$C$_2$T$_x$ nanosheets as the building blocks of MXene membranes. Exfoliated Ti$_3$C$_2$T$_x$ was fabricated from the precursor 3D Ti$_3$AlC$_2$ powder. Because the Ti–Al bond is metallic, it is difficult to obtain a single Ti$_3$C$_2$T$_x$ layer by simple mechanical shearing. Due to the fact that the Ti–Al bond shows high chemical activity, selective etching of Al element by aqueous fluoride-containing acidic solutions is possible. HCl/LiF mixtures were selected as corrosive agents to selectively etch Al element from the Ti$_3$AlC$_2$ powder. As shown in Fig. 2a and b, after etching Al element, the resulting Ti$_3$C$_2$T$_x$ powders showed accordion-like loosely stacked morphologies, affording ultrathin nanosheets due to the weakened interlayer interactions. The crystallinities of the powders were further studied by XRD (Fig. S3a†). The diffraction peaks corresponding to the Ti$_3$C$_2$T$_x$ powders were located at a 2θ angle of ~7°, which is in accordance with the literature, indicating a successful transformation from Ti$_3$AlC$_2$ powder to Ti$_3$C$_2$T$_x$ powder. Ultrathin Ti$_3$C$_2$T$_x$ nanosheets could be easily obtained via sonication. Fig. 2c shows a TEM image of the ultrathin nanosheets, which are nearly transparent. The AFM image (Fig. 1d) shows that the height of these nanosheets was 1 to 2 nm, which can be considered as single or double layer. Additionally, the lateral size was 1 to 2 μm, which was demonstrated previously to be suitable to form ordered 2D stacking membrane structures and abundant in-plane nanogaps for efficient molecular separation.

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Measurement of membrane separation performance

The separation performance of the MXene-based membranes for solvent dehydration by pervaporation was measured by a home-made apparatus. The operation can be found in our previous work. The concentrations of feed and permeate were measured via gas chromatography (GC). The flux (J) and separation factors (B) can be calculated using the following equations:

$$J = \frac{M}{A \times t}$$

$$B = \frac{Y_i/(1 - Y_i)}{X_i/(1 - X_i)}$$

where M (g) refers to the weight of the permeate sample and t (h) is the collected time. A (m$^2$) represents the effective membrane area. $X_i$ and $Y_i$ represent the contents of component i on the feed and permeate sides, respectively.
layers could be seen in the freestanding MXene membrane (Fig. 3e). To fabricate MXene membranes with much smaller thicknesses for efficient separation, we used PAN membrane with pores of tens of nanometers (Fig. S5†) as a substrate to improve the permeation flux due to its lower mass transfer resistance. We found that the neat MXene membrane exhibited a relatively high mass transfer resistance. This prompted us to develop a method to seal the pore defects of the PAN substrate. The out-of-order packing behavior is likely generated by the following two factors. On one side, the stronger electrostatic repulsion between negatively charged MXene sheets impedes compact and ordered stacking during the assembly process.† On the other side, abundant groups combined with both sides of the MXene sheets disturbed the original conjugation, leading to folds and distortions on the sheets. Disorder stacking of MXene nanosheets via pressure-assisted filtration may result in non-selective membranes. The zeta potential of MXene dispersion was about −33.6 mV (Fig. 3a), indicating that the nanosheets were negatively charged. Thus, it is possible to assemble the MXene nanosheets into regular stacked structures under electrostatic interaction by introducing positively charged polymer molecules. To confirm this hypothesis, positively charged HPEI molecules, as evidenced by their zeta potential of about −30.1 mV (Fig. 3a), were introduced into the MXene interlayer channels. Interestingly, it was observed that the MXene–HPEI mixture remained stable without flocculation after stirring for 20 minutes (Fig. S6†). Presumably, the MXene nanosheets could be (electrostatically and chemically) adsorbed onto the HPEI chains to form a relatively stable suspension consisting of MXene–HPEI blocks. A similar result was found in HPEI-modified GO solution. The MXene–HPEI membrane became more uniform, as shown in Fig. 3c. The zeta potential of the MXene and HPEI mixture solution was about −23.03 mV; this absolute value is lower than that of the pure MXene dispersion or HPEI solution, indicating that the HPEI molecules did work with the MXene nanosheets. In order to seal possible non-selective in-plane slit-like pores formed in the MXene membrane, we further carried out interfacial polymerization, which is a common and scalable method to form ultrathin layers.† Trimesoyl chloride (TMC) was chosen to interfacially polymerize with HPEI, leading to a uniform MXene membrane surface (Fig. 3d). The cross-section SEM image in Fig. 3f shows that the thick Ti2CT–HPEI/TMC layer with a thickness of ~100 nm was firmly adhered on the PAN substrate without structural defects.

The chemical properties of the membranes were studied by FTIR and XPS characterization. As shown in Fig. 4a, compared with pure Ti2CT, MXene, the MXene–HPEI membrane shows two new peaks at around 1455 and 3368 cm−1, which are respectively attributed to the stretching of C–N and N–H originating from HPEI. This verifies the insertion of HPEI and agrees with the EDS data shown in Fig. 5h. For the Ti2CT–HPEI/TMC membrane, the peak located at 1550 cm−1 is assigned to N–H deformation vibration along with C=O stretching from −NHCO− at 1550 cm−1, demonstrating the formation of a polyamide. In addition, the peaks of asymmetric and symmetric vibrations of −CH2− appeared at 2942 and 2805 cm−1, respectively. The peaks at ~3368 and 1618 cm−1 are respectively attributed to −OH and C=O, which belong to MXene. Mean-while, XPS was used to further investigate the chemical nature of the membrane. As shown in Fig. 4b, the N 1s spectrum of the Ti2CT–HPEI membrane can be resolved to two peaks with binding energies located at 398.4 and 399.4 eV, designated as −CH2−NH2 and −CO−NH+, respectively. This indicates that the amine of HPEI reacts with the oxygen-containing groups of MXene, forming C–N covalent bonds. Fig. 4c shows the N 1s spectrum of Ti2CT–HPEI/TMC; a new peak at 400.5 eV attributed to −N−C=O was detected, confirming the generation of polyamide during the interfacial polymerization process. The C 1s XPS spectrum of the MXene membrane (Fig. 4d) showed five peaks corresponding to −C−Ti (281.7 eV), −C−C−H (284.7 eV), −C−O (286.0 eV), −C=O (286.9 eV), and −O−C=O:C−F (287.8 eV). A new peak at 285.0 eV belonging to −C−N/C−O was detected for the MXene–HPEI membrane (Fig. 4e). In addition, −C−O (288.8 eV) and −C−C (284.8 eV) were found. From the C 1s spectrum of the MXene–HPEI/TMC membrane (Fig. 4f), we found that the intensity of −C−N (286.0 eV) decreased compared with that of the MXene–HPEI membrane, mainly due to the reaction between the amine groups of HPEI and the acyl chloride groups of TMC. This reaction was also confirmed by the appearance of −N−C=O (287.9 eV).†

To further investigate the roles of the HPEI molecules and interfacial polymerization in membrane formation, SEM and AFM characterizations were applied to study the membrane morphologies. The neat MXene membrane shows a smooth surface with abundant wrinkles (Fig. 5a). The MXene laminate intercalated by HPEI exhibits a much smoother surface without visible defects (Fig. 5b and c). However, the average roughness (Ra) of the MXene–HPEI membrane (~7.218 nm) is less than that of the pristine MXene laminate (~11.012 nm) (Fig. 5d and e); this confirms that the insertion of HPEI molecules induced more ordered assembly of the nanosheets, resulting in a smoother membrane surface. The EDS results show that the
neat MXene membrane mainly contains Ti, C and O (Fig. 5g).

An N element signal appeared on the surface of the MXene–HPEI membrane (Fig. 5h), indicating the intercalation of HPEI molecules. From the SEM surface (Fig. 5a and b) and cross-section (Fig. S7a and b†) morphologies of the MXene laminates, it is difficult to distinguish their structure differences. The SEM image in Fig. 5c shows that the MXene–HPEI/TMC membrane still displays a wrinkled surface similar to that of the MXene–HPEI membrane. There is no obvious difference in the cross-sections of the membranes (Fig. S7a–c†). However, the average roughness ($R_a$) increases (Fig. 5f); a probable reason is that there are few residual monomers.

We used polarized light characterization to further elucidate the structure evolution induced by the introduction of polymer molecules. As shown in Fig. 6a and b, the MXene–HPEI membrane surface shows a more regular orientation of MXene layers than the neat MXene membrane surface, implying the formation of numerous ordered 2D channels. High-resolution TEM (HRTEM) was further carried out to study the fine nanostructures. Without HPEI-induction, the neat MXene laminate shows a corrugated morphology, indicating a relatively random stacking manner (Fig. 6c). This disordered packing can generate irregular transfer channels and non-selective defects. After intercalating with HPEI molecules, the MXene nanosheets formed well-aligned ordered 2D stacking structures with nanometer spaces (Fig. 6d).

Although ordered stacking structures of the MXene laminates were realized, a few non-selective in-plane slit-like pores may still be present in the membrane, which would lower the separation performance. In order to further improve the membrane quality, we attempted to seal these defects by a facile
interfacial polymerization method using TMC to react with the firstly introduced HPEI molecules in the membrane. The XPS characterization (Fig. S8†) shows that for the MXene–HPEI/TMC membrane, a small Ti 2p signal peak can be detected, which is due to the MXene layers. This indicates that the thickness of the dense layer originating from interfacial polymerization is less than 10 nm (the maximum probing depth of XPS).† XPS depth profiles were utilized to further analyze the membrane structure after the interfacial polymerization. Meanwhile, the vertical distribution of C element through the MXene membrane was investigated by XPS, with detections at different nominal etching depths starting from the membrane surface. As shown in Fig. 7a and b, the C atomic percentage decreased from 60.34% on the surface to 32.99% at a depth of 20 nm and then remained almost unchanged with increasing depth. The C 1s peak intensity on the membrane surface was the strongest compared with other depths. In addition, Cl element was detected on the MXene–HPEI/TMC membrane surface, as shown in the EDS characterization in Fig. 5i. These results reveal that the interfacial polymerization mainly occurred on the membrane surface to effectively seal the non-selective defects. The defect-free membrane surface as well as the ordered stacking structure can be expected to realize efficient molecular separation.

Different water/alcohol mixtures were chosen to probe the transport properties of the Ti2CTx MXene membrane. Solvent dehydration is an energy-intensive separation process which has received great attention due to the widespread use of organic solvents in various industries, including chemical, pharmaceutical, and semiconductor. Methanol, ethanol and isopropanol, with molecular kinetic diameters of 3.6, 4.3 and 4.7 Å, respectively, were used as model solvents to study the membrane dehydration performance. As shown in Fig. 8a, the Ti2CTx–HPEI/TMC membrane has a high water flux of 2237 ± 292.6 g (m²·h⁻¹) with an ultra-low water content of 12.59 wt% in the permeate for methanol dehydration. Meanwhile, for ethanol dehydration, the water content in the permeate is improved and the water flux decreases to 1434 ± 119.9 g (m²·h⁻¹); this may be due to the increased molecular size of the solvent. However, the water content of the permeate is still below 90 wt%, which is not an efficient separation of water and ethanol. It is interesting that when the kinetic diameter of the solvent is increased to 4.7 Å, the water content in the permeate is nearly 100 wt%, showing outstanding dehydration performance for water/isopropanol mixtures.

XRD characterization shows the characteristic peak of the Ti2CTx–HPEI/TMC membrane located at a 2θ of 6.14° (Fig. 9c). According to the Bragg equation, when the thickness of a single MXene nanosheet is ~1 nm, the empty inter-layer space of 4.4 Å is smaller than the molecular kinetic diameter of isopropanol (4.7 Å). Together with effective sealing of the in-plane defects via interfacial polymerization with TMC, the resulting Ti2CTx–HPEI/TMC membrane with highly ordered sub-nanometer size channels realizes efficient molecular separation of water/isopropanol.

To further study the roles of HPEI and TMC, the isopropanol dehydration performance of the membranes un-assisted and assisted by interfacial polymerization was explored. A continuous, dense separation layer was not formed on the substrate, as evidenced by SEM and AFM (Fig. S9a and b†). Thus, the HPEI–TMC membrane has a water flux as high as 7560 ± 405.8 g (m²·h⁻¹) with a very low water content of 19.2 wt% in the permeate (Fig. 8b), showing very limited selectivity for isopropanol dehydration. Moreover, the pure MXene membrane showed non-selectivity; this is presumably due to the out-of-order stacking of the MXene nanosheets, as indicated by the HRTEM and polarizing microscope images (Fig. 6a and c). After inserting HPEI molecules, the MXene laminates become more regular, leading to an increase of the water content in the permeate. However, in-plane non-selective defects may still exist in the membrane. An ultrathin dense layer with a thickness of less than 10 nm (confirmed by XPS, Fig. S8†) formed by interfacial polymerization was used to seal these in-plane defects. As a result, the permeation water content increased to almost 100 wt%, showing that the in-plane defects were inhibited successfully.

To further understand the separation mechanism of the MXene-based membrane in solvent dehydration, we also employed a widely studied MXene, Ti3C2Tx, as an alternative building block to fabricate an MXene membrane by following the same approach as for the Ti2CTx membrane. Ti3C2Tx membranes have shown good performance for molecular separation. To Ti3C2Tx powder was successfully produced,
as confirmed by XRD characterization (Fig. S3b†). Compared with the Ti2CTx–HPEI/TMC membrane (Fig. 5c), fewer wrinkles formed on the surface of the Ti3C2Tx–HPEI/TMC membrane (Fig. S10a†). Its transport path for molecules may be shorter, which probably resulted in higher flux with a similar membrane thickness (Fig. S7c and S10b†).

According to the solution-diffusion model, both sorption and diffusion contribute to the pervaporation performance for solvent dehydration. A quartz crystal microbalance (QCM) technique was employed to probe the water and isopropanol sorption properties of the MXene powders. As shown in Fig. 9a, with increasing test time, the mass loading of water on Ti2CTx increased much faster than on Ti3C2Tx. For both Ti2CTx and Ti3C2Tx, the water and isopropanol sorption reached an almost stable state after 300 min. The final water adsorption capacity of Ti2CTx is ~1.6 times that of Ti3C2Tx, while their isopropanol capacities are similar. This indicates that the Ti2CTx-based membrane can exhibit higher water/isopropanol sorption selectivity than the Ti3C2Tx-based membrane. This was further characterized by water contact angle measurements on the MXene membranes. As shown in Fig. 9b, the water contact angles of both membranes decreased with MXene amount up to ~72.21 mg m⁻²; after that, the angles increased with increasing MXene loading to ~361 mg m⁻². The membrane with a loading of 72.21 mg m⁻² displayed the lowest water contact angle and, thus, the highest hydrophilicity. Moreover, the water contact angle on the Ti2CTx–HPEI/TMC membrane is smaller than that on the Ti3C2Tx–HPEI/TMC membrane, indicating higher hydrophilicity of the Ti2CTx-based membrane. Meanwhile, as confirmed by AFM characterization, the surface of the Ti2CTx–HPEI/TMC membrane is coarser than that of the Ti3C2Tx–HPEI/TMC membrane (Fig. S11 and S12†), leading to a higher surface area for sorption. Therefore, the Ti2CTx-based membranes show higher capability of adsorbing water molecules, which can contribute to higher water content in the permeate.

As expected, the Ti3C2Tx-based membranes exhibit a similar trend of dehydration performance to the Ti2CTx-based membranes (Fig. S13† vs. Fig. 8b), again demonstrating the critical roles of the introduced HPEI and interfacial polymerization. The optimized Ti3C2Tx–HPEI/TMC membrane shows
a similar flux of 1092 ± 139 g (m²·h⁻¹) and a lower water content of 95 wt% than the Ti₂CTₓ–HPEI/TMC membrane (flux: 1069 ± 47, water content: 99 wt%) for isopropanol dehydration. This may be due to the lower hydrophilicity of Ti₃C₂Tx than that of Ti₂CTₓ. In addition, the XRD patterns (Fig. 9c) indicate that the Ti₃C₂Tx-based membrane exhibits a reflection peak at 2θ of 5.70° with a d-spacing of 1.55 nm according to the Bragg equation (Fig. 9c). Considering the thickness of the single Ti₃C₂Tx MXene nanosheets of ~1 nm, the empty inter-layer distance can be calculated as 0.55 nm, which is larger than that of the Ti₂CTₓ-based membrane (0.44 nm). Thus, the size discrimination ability of the Ti₃C₂Tx-based membrane is weaker than that of the Ti₂CTₓ-based membrane from the aspect of diffusion.

Isopropanol is an important chemical which has wide applications in many fields, including pharmacy, plastics and cosmetics.⁶⁹,⁷⁰ The separation performance of the MXene-based membranes was studied and optimized by varying the MXene loading as well as operating conditions such as temperature and feed concentration. The effects of MXene deposition on the water/isopropanol separation performance were studied, as shown in Fig. S14. For both the Ti₂CTₓ– and Ti₃C₂Tx-based membranes, the flux decreased as the MXene loading increased due to the increasing transport resistance. Meanwhile, the water content in the permeate showed an upward trend and then decreased (Fig. S14b). The highest separation performance on the Ti₂CTₓ–HPEI/TMC membrane was achieved with an MXene loading of 72.21 mg m⁻². Due to the absence of a continuous MXene layer, the non-selective pores of the PAN substrate led to lower water content under the absence of a continuous MXene layer, the non-selective defects generated on the membrane surfaces.

The operation temperature was varied from 30 to 70 °C, as shown in Fig. S15. With increasing feed temperature, the driving force can be enhanced to accelerate molecular transport, leading to an increase of flux, whereas the water content decreases slightly. Even when the temperature was as high as 70 °C, the water content was still greater than 96 wt%, showing good resistance of the MXene membrane to high temperature. Additionally, the activation energy E_a can lead to a better understanding of the relationship between flux and temperature.⁷¹ The results show that isopropanol has a positive E_a (8.67 kJ mol⁻¹), while water possesses a E_a value of −19.82 kJ mol⁻¹ (Fig. S15b). This suggests that the permeation of isopropanol is enhanced more than that of water with increasing temperature, resulting in a high flux and low water content. Furthermore, we studied the effects of the water concentration in the feed on the membrane performance for isopropanol dehydration (Fig. S16). The partial pressure was enhanced by increasing the water concentration in the feed, resulting in an improvement of the driving force on water over that on isopropanol. Hence, the total flux increased nearly linearly as the water content in the feed increased.

Furthermore, to study the membrane stability, we investigated the effects of operating time on the Ti₂CTₓ–HPEI/TMC membrane with an MXene loading of 72.21 mg m⁻² for isopropanol dehydration at 50 °C. It can be seen from Fig. 10a that both the flux and water content in the permeate are stable during 120 h of continuous operation, demonstrating stable separation performance of the MXene membrane operated by a cross-flow feed. Additionally, to understand the structure stability, the Ti₂CTₓ–HPEI/TMC membrane was immersed in 10 wt% water/isopropanol mixtures for 120 h and was then dried under vacuum for XRD characterization. No obvious peak shift was found for the long-term-used Ti₂CTₓ–HPEI/TMC membrane, demonstrating good chemical and structural integrity (Fig. S17). This good stability can be attributed to the uniform 2D stacking structure of the nanosheets after intercalating HPEI and elimination of in-plane defects with the interfacial polymerization. We also compared the isopropanol dehydration performance of the membrane with those of other membranes, including polymer, metal–organic framework (MOF) and graphene oxide (GO) membranes. The Ti₂CTₓ-based membrane developed here displayed good performance, with a higher flux and separation factor (Fig. 10b); thus, it is a promising candidate for solvent dehydration.
Conclusions

In this work, for the first time, we designed and fabricated a novel 2D Ti$_2$CT$_x$ MXene membrane for solvent dehydration. This was realized by the proposed strategy of firstly introducing polymer molecules (HPEI) into MXene interlayers, followed by interfacial polymerization between TMC and HPEI. Characterization results revealed that highly ordered 2D stacking nanostructures of Ti$_2$CT$_x$/C$_2$4–100 nm thick, defect-free Ti$_2$CT$_x$-based membranes showed excellent water/isopropanol dehydration performance, with water content in the permeate side of more than 99 wt% (feed side water content: 10 wt%) and a total flux of 1069 ± 47 g (m$^{-2}$·h$^{-1}$). Compared with Ti$_3$C$_2$T$_x$-based membranes, the Ti$_2$CT$_x$-based membranes exhibited better separation performance with a higher permeate water content and a similarly high flux, resulting from both sorption and size-sieving effects. The as-developed ultrathin and integrated MXene membranes show great potential for angstrom-scale separation and other applications.

Conflicts of interest

There are no conflicts to declare.

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