
Micro-oxidized MXene membrane with superior stability for efficient water purification

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ABSTRACT:

MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) can be utilized to modify water-related membranes to provide favorable properties, including pronounced hydrophilicity and chemical stability, and higher flux compared with GO membranes. In order to improve the properties of composite membrane properties, new methods of modifying MXene membranes have been receiving increasing attention. Nowadays, the performance of MXene membranes is mainly limited by methods of modification and stability. In this study, a high-performance composite membrane utilizing MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) was fabricated through a mild and rapid pre-oxidation method. The composite membrane had a high water permeability of $\sim 690 \text{ L m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$, a dye rejection of $\sim 99.9\%$ and an adsorption rate of only 1%. Compared with the unoxidized MXene membranes, the composite membranes showed improved the permeation inhibition efficiencies of 42.39% and 37.51% for NaCl and MgCl_2 , respectively. The rapid oxidation by Fe(III) formed a composite nano-layer of anatase TiO_2 and magnetite Fe_3O_4 supported by carbon sheets which protected the internal $\text{Ti}_3\text{C}_2\text{T}_x$ from further oxidation. The characteristic morphology of a two-dimensional, layer by layer material, was maintained. In addition, the composite membrane demonstrated long-term stability in terms of both structure/appearance and flux in water. Therefore, this work presents new thoughts on the structural tuning and performance optimization of MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) membranes.

KEYWORDS: MXene; TiO_2/C ; stability; high removal rate; membrane technology;

1. Introduction

At present, technologies based on two-dimensional materials are a promising field of research. Due to their unique nano-scale properties, membranes based on two-dimensional materials are expected to solve some important challenges of conventional polymer membranes [1,2]. Early studies of membranes prepared from two-dimensional materials have mostly focused on the use of graphene oxide (GO) and achieved good results [3,4]. Nowadays, methods such as vacuum filtration, layer-by-layer assembly, and solution casting have been successfully used to prepare a variety of functionalized GO membranes [5]. The prepared membranes have the characteristics of high flux, strong anti-fouling ability, and good chemical resistance [6]. However, due to the limited nature of the materials used in these membranes, the scope for adjusting their properties is similarly limited [7]. For example, the instability/disintegration of GO membranes seriously hinders their separation performance and practical application in aqueous solutions [8,9].

Two-dimensional membranes based on MXene materials, because of the diversity of components of MXene, have the potential to vary their properties to achieve a wide range of performance [10,11]. The general expression for MXene is $M_{n+1}X_nT_x$ ($n=1-3$). This is a large class of materials which comprise transition metal carbides, nitrides and carbo-nitrides, where M refers to the early metal transition group, X refers to carbon or nitrogen, and T_x refers to the surface end groups (-OH, -O- and -F) [11]. In recent years, a number of studies have shown that MXenes are advantageous in many application fields such as electromagnetic interference shielding [12], energy storage [13], pressure sensing [14], and water purification [15]. In

principle, MXene can be utilized to modify water-related membranes to provide favorable properties, including a pronounced hydrophilic nature, an excellent electrical conductivity and chemical stability [4,16]. Compared with GO, the flux of MXene membrane has been reported to be greater.[15] In addition, the favorable hydrophilicity of MXene membranes makes them amenable to be used for water treatment [4,17]. Previous studies have investigated the use of MXene membranes for water treatment, and have achieved good results [18–21].

However, the present types of MXene membrane have low stability, and their separation performance drastically decreases under humid conditions, which seriously hinders the long-term storage and application of MXene membranes [22,23]. MXene has strong chemical reducibility, and Shen et al [24]. found that MXene can reduce Fe^{3+} to Fe^{2+} . This characteristic causes MXene to be easily oxidized. Habib et al.[25] found that MXene had the fastest oxidation rate in liquid media, making it prone to chemical degradation by oxidation to TiO_2 . Under different oxidation conditions, 2D $\text{Ti}_3\text{C}_2\text{T}_x$ can be converted to TiO_2 with different crystal structures and particle sizes, supported by carbon sheets [26]. The use of improved synthesis methods and subsequent processing or storage technology can obtain high quality MXene with good surface functional group control, large lateral size and few defects, and which provide improved stability [23,27–29]. In addition, some teams have studied the methods of metal ion oxidation or cross-linking to change the surface morphology of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (Table S1) [30–32], but few studies have considered the effect of Fe(III) oxidation on $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. Even though there are some studies on self-reduction of Fe(III) on the surface of MXene [33,34], these methods are not completely appropriate for the field of

membrane separation, so we propose a simple and easy to perform method to obtain a membrane with improved performance and morphology. We improved the purification and separation effect of $\text{Ti}_3\text{C}_2\text{T}_x$ by oxidation using Fe(III) and the roles of adsorption and interception in the separation process were defined. The surface of $\text{Ti}_3\text{C}_2\text{T}_x$ formed a nano-layer with TiO_2 , carbon and Fe oxides as the main component after the oxidation by Fe(III). This nano-layer can protect the internal $\text{Ti}_3\text{C}_2\text{T}_x$ from further oxidation, so as to maintain the two-dimensional layered structure. In addition, the problem of MXene membrane stability in water treatment was avoided.

MCE membranes are highly porous and hydrophilic [35], effectively supporting MXene nanosheets [36] to ensure membrane permeability [37] and structural integrity, resulting in excellent rejection and stability in water filtration. Moreover, MCE membranes have good mechanical properties [38] and are commercially available materials that are suitable for compatibility with industrial equipment, helping to realize a wide range of applications in water purification technology. Therefore, we selected MCE membrane as the support layer for MO10 membrane for water purification.

In view of the foregoing, we propose a different approach for enhancing the stability of MXene membranes in water by micro-oxidizing the surface of MXene, while maintaining their excellent membrane performance. The research findings summarized in this work describe this new approach, involving the micro-oxidation of MXene with Fe(III) to obtain a new composite membrane, which has demonstrated not only an enhanced rejection capability, but also greater stability.

2. Experimental section

2.1 Materials and chemicals

The mixed cellulose ester (MCE) membrane (pore size 0.22 μm) was purchased from JinTeng (China). Ti_3AlC_2 (MAX) powder (≥ 98 wt%, 200 mesh) was purchased from Laizhou Kaisen ceramic material Co., Ltd (China). Coomassie brilliant blue R, iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99%) and Lithium fluoride (LiF, 99.0%) were obtained from Aladdin (China). Hydrochloric acid (HCl, AR) was obtained from Merck (Germany). Deionized (DI) water was utilized for the preparation of MXene solutions and in the membrane filtration tests.

2.2 Synthesis of MXene ($\text{Ti}_3\text{C}_2\text{T}_x$)

Titanium carbide ($\text{Ti}_3\text{C}_2\text{T}_x$) MXene nanosheets were chemically etched and exfoliated from MAX Ti_3AlC_2 according to a modified minimally intensive layer delamination (MILD) method. 1 g LiF was added to 20 ml of 9 M HCl and then magnetically stirred for 5 min. Next, $\text{Ti}_3\text{C}_2\text{T}_x$ powder (1.0 g) was slowly added, followed by continual stirring for 30 h at 45 $^\circ\text{C}$ in an oil bath. After that, the final reaction mixture was then washed by centrifugation with DI water (centrifuge at 5000 rpm for 5 min per cycle) until the pH of the supernatant reached about 7 - 8. Subsequently, the $\text{Ti}_3\text{C}_2\text{T}_x$ mixture was ultrasonicated in an ice bath for 1 h with vigorous shaking for about 10 min. Finally, the suspension was centrifuged for 20 min (at 4000 rpm) to remove the unpeeled sheets, and the upper layer of liquid was taken as MXene solution. The resulting liquid can be used for subsequent experiments without further modification. The concentration of the prepared MXene solution was determined to be 4.6 mg/mL by UV-

labeling method.

2.3 Fabrication of MXene membranes oxidized by FeCl₃

We used a commercial mixed cellulose ester (MCE) membrane (0.22 μm) as a supporting layer for MXene membrane oxidized by FeCl₃. Initially, an aqueous suspension containing 10 mg of MXene was prepared by mixing with ultrasonic vibration for 5 min to achieve even dispersion. MXene membrane supported by MCE were fabricated using a flow cell (Millipore Amicon, 50 mL, USA). Oxidized MXene membranes were prepared by filtering a freshly prepared FeCl₃ solution of a constant volume (50 mL), but of different concentrations. The concentrations of FeCl₃ solution were: ≥ 100 mM, 10 mM, 5 mM, 1 mM, 0.5 mM. In this paper, the oxidized MXene membranes are referred to as MOX, where X represents the concentration of the FeCl₃ used for oxidation. The reaction time between the MOX (MO1-MO10 and overdosed) samples and FeCl₃ solution was 1800 s. For the MO10 sample, the reaction reached electronic balance at ~ 1500 s.

2.4 Characterization

Scanning electron microscopy (SEM, QUANTA FEG 250, FEI, USA) was utilized to capture surface and cross-sectional images of the microstructure of the MXene membranes and MO1~10. Transmission electron microscopy (TEM; Talos F200X G2) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific, America) were employed to determine the elementary composition. 20 nm was chosen as the depth of surface etching which

can avoid surface carbon pollution to the greatest extent and help us understand the internal structure of MO10 sample. Fourier transform infrared spectroscopy (FT-IR, BRUKER, ALPHA-P, USA) was utilized to examine the oxygen-containing function groups in the MXene membranes post-oxidation with FeCl₃. The hydrophilic nature of oxidized and un-oxidized membranes was indicated by water contact angle measurements (WCA, OCA15ED, Dataphysics, Germany) of membrane surfaces using the sessile drop method. UV–visible absorption spectroscopy (UV-2600, Shimadzu, Japan) was employed to determine the concentrations of organic dye molecules in the permeate solutions of the membrane. Surface charge properties of the membrane were analyzed using a solid-surface zeta potential analyzer (SurPASSTM 3, Anton Paar, Germany), and an average zeta potential value was calculated based on 3 measurements.

2.5 Membrane properties and performance testing

The effectiveness of the FeCl₃-oxidized MXene membranes was assessed by measuring water permeability and solute rejection during filtration experiments with DI water and organic contaminant solutions. The membrane samples were tested for the rejection of 100 mM of organic dyes (Table S5) including Coomassie Brilliant Blue (CBB), Methyl Blue (MB), Rhodamine B (RhB), Crystalline Violet (CV) and Methylene Blue (MNB). In this case, Coomassie brilliant blue dye was used as a representative organic contaminant. Filtration experiments were carried out with a stable applied pressure of 1 bar using a commercial filtration system (Millipore, Amicon 8400, USA) operated with nitrogen gas. In order to mitigate the adverse effects of concentration polarization, a rotor in the filtration device was used for stirring during the dead-end filtration process (Figure S1). The water flux J (L m⁻² h⁻¹) was calculated by the following equation:

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

where V represents the volume of the permeate water after collection of t and A represents the effective surface area of the membrane. The membrane's stability was assessed by determining the pure water flux over a period of seven consecutive days, and conducting physical observation of the membrane.

The solute rejection R_s (%) can be calculated as follows:

$$R_s = (1 - C_p/C_f) \times 100\%$$

where C_p and C_f are the permeate and feed solute concentrations, respectively.

R_a is the true rejection rate of the membrane, accounting for the adsorption of solute. The actual rejection R_a (%) can be expressed as follows:

$$M_a = V_f \cdot C_f - V_p \cdot C_p - V_c \cdot C_c$$

$$M_i = V_p \cdot C_f - V_p \cdot C_p - M_a$$

$$M_p = V_p \cdot C_f - M_i - M_a = V_p \cdot C_p$$

$$R_a = M_i/(V_p \cdot C_f) \times 100\%$$

The symbols M_a , M_i , M_p represent the mass (mg) of solute adsorbed, intercepted and in the permeate; V_f , V_p , V_c represent the volume (L) of total feed solution, permeate solution and concentrated solution; and C_f , C_p , C_c represent the solute concentration (mg/L) of the feed, permeate and concentrated solutions, respectively. In 'dead-end' filtration mode, the volume ratio of permeate to concentrate was 3:2 by default.

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171 3. Results and discussion

3.1 Characterization of the TiO₂/C@Fe₃O₄ Membrane

Titanium carbide (Ti₃C₂T_x) MXene nanosheets were chemically etched and exfoliated from Ti₃AlC₂ (MAX) powder based on a modified minimally intensive layer delamination (MILD) method [39]. As shown in Figure 1a, a solution of MXene showed a typical Tyndall effect. The X-ray diffraction (XRD) patterns (Figure 1b) of the MAX (Ti₃AlC₂) and MXene (Ti₃C₂T_x) demonstrated characteristic diffraction peaks corresponding to (002), and the (008) planes of MXene were detected for titanium carbide (Ti₃C₂T_x), respectively [34]. The transmission electron microscopy (TEM) image of Ti₃C₂T_x in Figure 1c showed monolayer, single-crystalline Ti₃C₂T_x flakes. The high resolution transmission electron microscopy (HRTEM) image of Ti₃C₂T_x in Figure 1d showed multiple Ti₃C₂T_x flakes stacked and the flakes of Ti₃C₂T_x were composed of hexagonal arrangements of atoms, as indicated by the selected-area electron diffraction (SAED, inset of Figure 1d) [40]. This indicated that the MXene suspension was successfully prepared. Figure 1e illustrated the fabrication process of MOX membranes. Firstly, MXene was deposited on the surface of a commercial mixed cellulose ester (MCE) base membrane/substrate (pore size of 0.22 μm) by pressure filtration. Subsequently, the MXene membranes were continuously (moderately) oxidized by freshly prepared FeCl₃ solution, at a constant volume but at different concentrations. The oxidized MXene membranes were denoted as MO1 to MO10, where “M” represents the MXene/MCE substrate, “O” represents the moderate oxidation of MXene, and the number represents the concentration of FeCl₃ solution (mM L⁻¹) used for oxidation. In the mild oxidation process of MXene by Fe(III) (Figure 1g), Fe(III) was reduced to Fe(II), and the surface of MXene membrane was oxidized

to produce the TiO₂@C composite nano-layer. The pure (un-oxidized) MXene membrane was black in appearance, as was the MO1 membrane, while the MO10 appeared russet in colour.

Figure 1.

Surface images obtained by SEM analysis in shown in Figure 1h-j revealed the morphology of the MXene, MO1 and MO10 membranes. The pure MXene membrane displayed some wrinkling on its surface (Figure 1h). These morphological features were inherent properties of the stack of 2D ultra-thin lamellar nanomaterials[41]. In comparison, the different degrees of broken state caused by Fe³⁺ oxidation can be observed by the corresponding top views in Figure 1i-j. More severe damage on the surface of the MO membrane was evident following oxidation by an over-dose (≥ 100 mM) of Fe(III) (Supporting Information, Figure S2; from the inset image of Figure S2f, the larger flocs visible were iron oxides).

The cross-sectional images of MO10 membranes were obtained by SEM analysis, and the stacked layers of nanosheets were clearly visible (Figure 2a and Figure S3), which indicated the existence of 2D nanochannels for water flow/transport. Figure S3 demonstrated the thickness of pure MXene and MO10 membranes of 697 nm and 541 nm, respectively. The decrease in membrane thickness was attributed to the partial deconstruction of Ti₃C₂ nanosheets on the membrane surface after Fe(III) micro-oxidation, forming carbon flakes and anatase TiO₂, while losing some C and Ti during the oxidation process. In addition, the undulations on the surface of the membrane are typical folds of two-dimensional materials and

these can be observed in the cross-sectional images. Figure S4 also showed the cross-sectional SEM of MOX (1, 2.5, 5, 10 mM) membrane oxidized with different Fe(III) concentrations, indicating that the 2D layered structure and typical folds were maintained during the oxidation process. The surface chemical state of all the kinds of membranes was further analyzed by XPS spectroscopy (Figure 2b and Supporting Information, Figure S5-S10). For the MO10 results shown in Figure 2b, the narrow scan of the Fe (2p) XPS spectrum included Fe 2p_{3/2} and Fe 2p_{1/2} satellite peaks. The peaks at 710.8 and 724.2 eV were assigned to the Fe–O bond of the Fe²⁺ ion and the other two peaks at 713.6 and 726.8 eV were assigned to the Fe–O bond of the Fe³⁺ ion [42]. This suggested that Fe(III) was reduced to Fe (II) species by Ti₃C₂T_x, and eventually Fe₃O₄ was formed which coincided with the XRD results in Figure 5a. However, the high-resolution XPS spectrum of the surface of MO10 Ti 2p_{3/2} and 2p_{1/2} can be fitted by two peaks at 458.8 and 464.5 eV, respectively (Figure 2b). The 5.7 eV splitting energy between Ti 2p_{3/2} and Ti 2p_{1/2} peaks was consistent with the typical value for the Ti atom in TiO₂ [43]. From the XPS spectrum, it can be seen that the form of Ti was changed. The absence of distinctive peaks corresponding to the C-Ti bond on the surface of MO10 indicated the oxidation of Ti₃C₂T_x and the creation of TiO₂. This indicated that TiO₂ and Fe oxides were the primary elements in the nano layer present on the surface of the oxidized membrane.

Figure 2.

Examination of the full XPS spectra of pure MXene membrane (Figure S5) showed that in addition to the identified C 1s, O 1s, Ti 2p₃, and Cl 2p, the peaks at binding energy values

of 33, 59, 531, 684, 826, 971 and 1067 eV were assigned to Ti_2O_3 3p [44], Ti_2O_3 3s [44], Ti 2s [45], F 1s [46], F KLL [47], C KLL [47] and Ti LMM [48], respectively. The etching process of MAX introduced an abundance of oxygen-terminated functional groups on the nanosheet surface, resulting in a pronounced O 1s peak signal. Additionally, the presence of F 1s and Cl 2p peaks could be attributed to the inclusion of HCl and LiF in the etching solution of MAX[36]. Comparing the full spectra of pure MXene and MO10, as shown in Figure S5a-b, it can be observed that a small amount of Fe existed in the surface of MO10, and the proportion of O increased significantly, while the proportion of Ti decreased. Further details in the SI (Table S2) gave a more complete description of the elemental composition of MXene and MO10. The atomic contents of Ti, O, C, Fe, and F elements on the surface of the MXene membrane and MO10 membrane, had been included in Table S2. Compared to MXene, the results showed that the Ti and F concentrations of MO10 decreased, while the contents of O and C were significantly increased. Clearly, the element concentrations from the XPS studies further proved the degradation of superficial MXene and creation of TiO_2 and carbon layer in the oxidation processes of Fe(III). The high-resolution XPS spectrum for O 1s of the MO10 surface (Figure S8) can be fitted by four peaks at 529.9, 531.2, 532.0 and 533.8 eV, corresponding to TiO_2 and Fe_3O_4 , C=O, C-O and $\text{H}_2\text{O}_{\text{ads}}$ bonds, respectively. This indicated that oxygen not only existed in metal oxides, but also participated in the formation of many surface functional groups. This FT-IR spectra (Figure S9) was also confirmed by this, with the broad band at 3400~3200 cm^{-1} corresponding to the stretching vibration of the hydroxy (-OH) group. The peaks at 1850~1660 cm^{-1} , 1300~1000 cm^{-1} , 900~1150 cm^{-1} , corresponded to the -C=O stretching

vibration in the carboxyl group, C-O stretching vibration and C-O-C stretching vibration. Oxidizing MXene with varying iron concentrations led to differing degrees of enhancement in oxygen-containing functional groups on the membrane surface. Compared with the pure (un-oxidized) MXene membrane, the stretching vibration of -OH and -COOH increased significantly for MO10.

A representative TEM image of MO10 (Figure 2c) showed the flake structure, which proved that the oxidized MO10 still retained the two-dimensional layered structure at the microscopic level. HRTEM images (Figure 2d-e) of MO10 and selective area electron diffraction (SAED) patterns (inset of Figure 2e) indicated that some areas were of high crystallinity. A lattice fringe of nearly 3.5 Å, corresponding to the (101) plane of anatase TiO₂ (Figure 2e) confirmed the existence of TiO₂ [49]. SAED patterns also confirmed the amorphous characteristics, showing two quite diffuse halos (inset of Figure S10a). This indicated that some areas were of low crystallinity which represented the existence of amorphous carbon. Transmission electron microscope (TEM) image of MO10 (Figure S10b) showed that the nanocrystals were embedded in thin sheets. The findings confirmed that the surface composition of the MO10 membrane was predominantly composed of anatase TiO₂ and carbon sheets, while anatase may be the nano-block and supported by mostly amorphous carbon sheets (Figure S10b and S28). To further investigate the elemental distribution of MO10, EDX elemental mapping was performed. The elemental mapping results shown in Figure 2f displayed the presence and even distribution of C, Ti, O and Fe elements across the MO10 nanosheets, while the signal of Fe was slightly weaker than that of Ti and O, indicating that the

Fe content was low. Moreover, the elemental map of Fe (Figure 2f) showed that the Fe was distributed homogeneously on the surface of MO10, which confirmed the uniformity of iron oxides arranged in the MO10. The cross sections of MXene and MO10 membranes can be seen in Figure 2g-h, where the two-dimensional characteristics of stacked layers were clearly visible. As shown in Figure 2g, the layer spacing of MXene membrane was 1.620 nm, while that of MO10 membrane in Figure 2h was 1.833 nm. Although the layer spacing changed, the lamellar structure of the oxidized membrane was still preserved. As TiO_2 and iron oxide particles were present in the lamella of MO10 membrane, the spacing of some layers was widened. The circled part of the Figure 2h proved the existence of this phenomenon. The size of iron oxide was slightly larger than the two-dimensional layer spacing, so when particles existed inside the membrane, they will open the channel and make it wider. The composite nanolayer on the surface of the membrane helped to preserve the two-dimensional layered structure inside $\text{T}_3\text{C}_2\text{T}_x$ despite the slow oxidation of O_2 .

3.2 Properties of the MXene Membranes Oxidized by Different Concentrations of Fe(III)

The filtration performance of the membranes, oxidized by various concentrations of Fe(III), was assessed based on water flux and rejection rate of the organic dye (Coomassie brilliant blue, CBB) in water (Figure 3a-b). The water flux of the pure $\text{T}_3\text{C}_2\text{T}_x$ membrane was $85.0 \text{ L m}^{-2} \text{ h}^{-1}$. As the increase of Fe(III) concentration, the oxidation degree of $\text{T}_3\text{C}_2\text{T}_x$ increased, and the flux of the oxidized membrane decreased at low Fe(III) oxidation, but

increased at higher Fe(III) oxidation (but was always less than the un-oxidized membrane). Coomassie brilliant blue dye was selected as the representative pollutant (solute) to evaluate the rejection performance of MOX. In doing so, an important distinction was made between actual and apparent interception of the dye, as components of the rejection. Pure MXene membrane had a strong adsorption capacity because of its special structure, but the interception capacity will be greatly reduced after it reached adsorption saturation. Therefore, an optimal performance was where the adsorption ratio was as low as possible, and the actual interception as great as possible. As shown in Figure 3b, the apparent interception of pure MXene membrane was ~85.8%, while the actual interception was only ~77.5%. With oxidation, and increasing Fe(III) concentration, the apparent rejection rates of MO1, MO2.5, MO5 and MO10 all increased to 99~100%, while the actual rejection rates were 94.0%, 97.7%, 98.0% and 99.0%, respectively. Compared with the pure MXene membrane, the adsorption ratio in the apparent rejection of MOX membranes decreased significantly. The actual interception of MO10 membrane was 26.5% higher than that of the MXene membrane.

This can be elucidated as follows: We believe that these two mechanisms, the original 2D channel sieving and the gap sieving between particles, can coexist [50]. The dense nano-layer of the surface of MO10 formed by Fe(III) oxidation mainly relied on gap sieving between particles to separate and purify macromolecular substances. This was an important reason why the adsorption capacity of MO10 was reduced but the actual rejection is greatly improved. As shown in Figure S12, the initial contact angle of MO10 was smaller than that of the pure MXene membrane, indicating that MO10 had a greater hydrophilicity, which may be caused by more

hydroxyl and oxygen-containing functional groups. In fact, anatase TiO_2 had a strong hydrophilic nature, and its surface contained rich hydroxyl groups [51]. A stable and dense hydration layer can be formed on the surface of TiO_2 , showing a highly ordered water molecular network structure [52]. In addition, the 2D channel sieving mechanism of internal $\text{T}_3\text{C}_2\text{T}_x$ also played an important role. This was due to the low particle content in the membrane, and most of the two-dimensional structure was retained inside the MO10 membrane, which enabled the membrane to remain stable in this situation. As the number of carboxyl and hydroxyl groups increased, the nano layers/sheets became more tightly connected through hydrogen bonding. Furthermore, the zeta potential of the MO10 membrane exceeded that of the MXene membrane (Figure S22). Due to the presence of Fe^{2+} and Fe^{3+} , the oxygen-containing functional groups with negative charge were able to retain the connections between the nano layers/sheets by electrostatic forces. Meanwhile, hydrophilicity significantly impacted membrane adsorption effectiveness [53]. Upon oxidation of the MXene membrane, its hydrophilicity experienced significant enhancement, attributed to the introduction of oxygen-containing functional groups and TiO_2 . The increased hydrophilicity contributed to the formation of a compact hydration layer, diminishing the interaction between hydrophobic contaminants and the membrane surface, and thus greatly reduced the adsorption effect of the membrane [52].

To further investigate the effect of Fe(III) micro-oxidation on the rejection performance of the composite membranes, experiments on the rejection rate of other dyes by the MO10 membrane were conducted (SI, Figure S23). The results revealed that the rejection rates of

MO10 membrane for some common dyes were significantly improved compared with those of pure MXene membrane. The apparent rejection rates of MB, RhB, CV and MNB dyes by MO10 membrane increased to more than 80%, while the actual rejection rates were around 97.1%, 81.3%, 74.2% and 73.2%, respectively, which were much higher than those of pure MXene membrane. The decrease in the actual rejection rates of the other dyes compared to CBB was mainly attributed to the decrease in dye size and carried charge. The molecular weights of MB, RhB, CV, and MNB dyes gradually decreased, leading to a reduction in the separation performance of the MO10 membrane based on the original 2D channel sieving as the main separation mechanism for these dyes. However, Fe(III) micro-oxidation generated TiO₂ particles within the interlayer spaces, allowing the MO10 membrane to be sieved through gap sieving. Therefore, the decline in rejection performance with size was much lower than that of the pure MXene membrane. Meanwhile, owing to the higher zeta potential of the MO10 membrane (SI, Figure S22), the adsorption rates of positively charged CV and MNB dyes were also much lower than those of the pure MXene membrane. Therefore, Fe(III) micro-oxidation contributes to the dye rejection performance of MXene membranes.

The apparent rejection rate of the over-dose (≥ 100 mM) Fe(III) oxidized sample was as high as $\sim 100\%$, but the actual rejection (interception) rate was only $\sim 47\%$. This was because the excessive Fe(III) formed iron oxide flocs with stronger adsorption capacity. However, the MXene membrane was oxidized by a small amount of Fe(III) (10 mM) and did not form large flocs, so the adsorption capacity was very small. The adsorption effect of MO10 membrane only accounted for 1%. The long-term variation of substrate rejection of MXene and MO10

membranes for CBB was shown in Figure S24. The rejection rate of the MO10 membrane decreased very little after long time operation. After cleaning the surface, the rejection effect can be restored to the initial rejection rate. However, due to the serious adsorption effect of the MXene membrane, the rejection rate decreased from ~86% to ~52% after running for 180 min. A performance comparison of the $\text{TiO}_2/\text{C}@\text{Fe}_3\text{O}_4$ membrane with previous reported membrane materials has been provided in Table S4 (SI) [54–60]. It was evident that the $\text{TiO}_2/\text{C}@\text{Fe}_3\text{O}_4$ membrane in this work had a good performance in terms of water flux and dye rejection.

Figure 3.

To compare the ion retention performance of mildly oxidized and unoxidized MXene membranes, the permeation rates of sodium chloride and magnesium chloride were assessed using a custom-designed U-shaped instrument (SI, Figure S13). The left chamber of the apparatus was filled with a 0.2 mol/L salt solution, while the right chamber contained an equal volume deionized water. Both solutions were subjected to magnetic stirring within their respective chambers to ensure the elimination of any concentration gradient across the instrument. The conductivity of the permeate side was measured to estimate ion concentration and to determine ion transport. Figure 3c showed the linear growth of concentrations of both salts during the continuous measurement within one hour. The permeability of the three membranes to MgCl_2 exhibited a greater decrease compared to that of NaCl . This discrepancy can be primarily attributed to the variance in the hydration ion radii. Compared with the non-oxidized MXene membrane, the permeability of MO1 and MO10 membranes was significantly

379 reduced, which can effectively inhibit the infiltration of salt ions. The permeability of the MO1
380 membrane was slightly lower than that of MO10, which corresponded to the low flux of the
381 MO1 membrane. As depicted in Figure 3d, comparison to the unoxidized MXene membranes,
382 the osmotic inhibition efficiency of NaCl and MgCl₂ increased by 42.39% and 37.51% for the
383 MO10 membranes (completely oxidized by Fe(III)), while the osmotic inhibition efficiency of
384 MO1 membranes (partially oxidized by Fe(III)), increased by 32.60% and 35.56% respectively.
385 These results confirmed that the MOX membranes oxidized by Fe(III) had a certain
386 desalination capacity and that the desalination capacity mainly depended on the size of the
387 layer spacing, and was poorly related to the physical adsorption capacity of the lamellar. As
388 depicted in Figure 3e, the flux of all membranes exhibited a linear increase when the
389 transmembrane pressure escalated from 1 bar to 3 bar. This observation indicated that the
390 microstructures of membranes remained undamaged despite the compression resulting from
391 the pressure increase. It also suggested that the prepared membranes demonstrated excellent
392 resistance to compression [61]. The SEM images before and after the pressure experiment
393 (Figure S12) showed typical folds on the surface of the MO10 membrane without cracks,
394 indicating the structural stability of the MO10 membrane. However, in the pressure-flux
395 diagram, the slopes of each linear relationship were different. The slope of the MXene
396 membrane was the largest, while the slope of the MO1 membrane was the smallest. The slope
397 of the compression curve represented the relative difference of permeability after compaction,
398 indicating that the permeability of the MO10 membrane was greater than that of the MO1
399 membrane, but slightly less than that of the MXene membrane.

400 By reference to the schematic processes shown in Figure 3f-h, the reasons for the change
401 in flux can be explained as follows: firstly, the water channels of MXene membranes were
402 mainly composed of two-dimensional sheets separated in stacks by nanochannels. Furthermore,
403 with the addition of a small amount of Fe(III), part of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets were oxidized
404 producing more oxygen-containing functional groups and hydrogen bonds, thereby
405 strengthening the connection between the sheets. The Ti/C nano-layer formed by oxidation on
406 the surface of the MXene membrane prevented the smooth flow of water to some extent. Due
407 to the increase of functional groups and Fe ions, the transport resistance of water in the MO10
408 nanochannels was greater, leading to the decrease of flux. At the same time, a small amount of
409 Fe(III) played a cross-linking role in the form of ionic bonds, which also led to the reduction
410 of membrane flux (Figure 3g). After exposure of MXene to higher concentrations of Fe(III),
411 the $\text{Ti}_3\text{C}_2\text{T}_x$ sheets on the surface of membrane were extensively, or completely, oxidized,
412 thereby forming anatase TiO_2 nanoparticles supported by carbon sheets. Under these conditions,
413 the defects on the membrane surface increased, and part of the Fe was deposited in the form of
414 oxides. Iron oxides with larger particle diameters will increase the distance between the sheets,
415 and the flow rate will be greater, resulting in a slight increase in flux (Figure 3a & 3h). The
416 trend of FeCl_3 flux change over time during oxidation was recorded (SI, Figure S15) and was
417 found to be directly related to the degree of oxidation. Therefore, at the maximum concentration
418 of Fe(III) of 10 mM, the flux decreased fastest and gradually became stable after approximately
419 1500 s, with the final flux consistent with the water flux of MO10 membranes. The trend of
420 flux change of MO10 membranes meant that the rate of oxidation was the greatest and that the

MXene was completely oxidized at the end of the observed period. When the Fe(III) concentration was 5 mM, the trend of flux change was similar to that of 10 mM but the rate of decrease was slightly lower. However, for Fe(III) concentrations of 1 and 2.5 mM, the rate of membrane flux decrease was lower, and the flux did not become stable by the end of the observed period.

3.3 Tests of the TiO₂/C@Fe₃O₄ Membrane Stability

As can be seen in Figure 4a, the rate of natural oxidation was relatively fast. After soaking in water for ten days, the MXene membrane was still undergoing slow oxidation by oxygen, forming a gray solid layer, but the oxidized membrane did not have any filtration capability. However, the high-resolution XPS spectra of naturally oxidized samples were approximately similar to those of the MO10 membrane, except for the absence of Fe in naturally oxidized samples. TiO₂ was also generated after natural oxidation, but its two-dimensional structure and membrane appearance were greatly changed. As shown in the SI (Figure S17), the MXene membranes after natural oxidation did not have the characteristic fold structures of two-dimensional materials and appeared to have cracked into small nano fragments. This was the main reason why the membrane did not have a filtration performance (SI, Table S3). In contrast, the MXene membrane underwent intense oxidation when exposed to the strong oxidant H₂O₂, and was almost completely oxidized and degraded within five minutes (SI, Figure S16). Moreover, the membrane oxidized by H₂O₂ had no separation performance (SI, Table S3). In contrast, the MO10 membrane formed by Fe(III) oxidation maintained a relatively complete

membrane appearance and a good apparent stability after soaking in water for ten days (Figure 4b). By comparing the results given in Figure 4c, the flux of pure MXene membrane soaked in water increased by ~125% compared with the initial flux after 7 days, while during 10 days, the flux of MO10 varied by less than 5%. The small variation was mainly due to the change of air pressure, which may be affected by the temperature and environment. The concentration of Fe used for oxidation of the MO10 membrane, the residual concentration of Fe in water filtered by the MO10 membrane and the concentration of Fe in deionized water, were detected by ICP-MS (SI, Figure S19). As depicted in Figure S19, the residual Fe concentration in the filtrate was approximately 9.3 $\mu\text{g/L}$, which was similar to the concentration of Fe in the deionized water, at the level of parts-per-billion (ppb). Therefore, it was clear that the leaching of Fe by the MO10 membrane was negligible, indicating good stability of the membrane and the avoidance of any secondary pollution downstream in practice (e.g. to the aquatic ecosystem). The results of CCB dye rejection experiments (SI, Figure S20) showed that the actual rejection rate of the MO10 membrane remained above 90% after soaking for 10 days, which was much higher than 38.2% of the pure MXene membrane (after soaking for 7 days). This was consistent with the results of the flux tests, demonstrating that the Fe(III) micro-oxidized MO10 membrane had strong stability and anti-oxidant properties.

Figure 4.

XRD analysis of the membranes was performed to investigate the chemical composition and their changes in water (Figure 5a). After soaking the membrane in water for 5 days, the

characteristic diffraction peaks corresponding to (002) planes of MXene had disappeared, while the characteristic peak corresponding to (101) of anatase TiO_2 (PDF#75-1537) appeared. On the other hand, some characteristic diffraction peaks corresponding to (111) and (101) planes of magnetite Fe_3O_4 (PDF#79-0416) and anatase TiO_2 (PDF#75-1537) were detected for the MO10 membrane. Significantly, the characteristic diffraction peaks did not shift by soaking in water. These results demonstrated a significant change in the chemical composition of the MXene membrane, whereas the MO10 membrane remained stable.

The Raman spectra of MXene and MO10 membranes were given in the SI (Figure S18 and S28). The Raman spectrum of the MO10 samples (Figure S18) contained peaks 145, 199, 397, 517, and 638 cm^{-1} , corresponding to the E_g^1 , E_g^2 , B_{1g}^1 , $B_{1g}^2 + A_{1g}$, and E_g^3 vibrational modes of anatase TiO_2 [43,62], respectively. It was expected that anatase TiO_2 would be produced during the oxidation process of $\text{Ti}_3\text{C}_2\text{T}_x$ precursors. As shown in Figure S28, two peaks corresponding to the D mode at $\sim 1350\text{ cm}^{-1}$ and G mode at $\sim 1581\text{ cm}^{-1}$ of MO10 represented disordered and graphitic structures, respectively [63]. The MO10 sample formed a highly disordered graphitic structure on the surface after the oxidation of Fe(III) which was different from the MXene. When the MO10 membrane was soaked in water for five days, the characteristic peak of carbon remained constant, indicating that the carbon skeleton hadn't changed.

Figure 5.

3.4 Mechanistic Insights into the Oxidation of MXene to TiO₂/C@Fe₃O₄

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was recognized as a potent tool for high-resolution nanoscale three-dimensional (3D) characterization and structural reconstruction. It excelled in detecting ionized elements and molecule fragments at the ppb level due to its exceptional sensitivity (Figure 6a-d). Therefore, TOF-SIMS analysis method was adopted to conduct further structural analysis of the composite membranes. The 3D images of chemical composition distribution were recovered by 3D reconstruction technology of in-depth analysis. It can be seen that Fe element was more distributed in the surface layer of the composite membrane, and Ti element presented a state of encapsulation. Therefore, it was speculated that the nano layer which contained the Fe element on the membrane surface served a protective function for the inner Ti structure. With the deepening of the etching depth, it can be seen that the Fe content became less, while the Ti content remains relatively stable. This was also consistent with the previous in-depth analysis data of XPS: it indicated that the Fe content deep into the membrane was reduced, and the nano protective layer on the surface can protect the internal MXene from oxidative degradation, so the oxidation degree inside the membrane was weakened.

As shown in Figure 6e, the high-resolution XPS spectrum of MXene Ti 2p_{3/2} (2p_{1/2}) can be fitted by ten peaks at 455.0 (461.2), 455.8 (461.3), 457.2 (462.9), 459.3 (464.2), 460.2 (466.2) eV, corresponding to the Ti, Ti²⁺, Ti³⁺, TiO₂-xF_x and C-Ti-F_x bonds, respectively [64]. Here, a depth of 20 nm was chosen to etch the surface of MO10. The XPS spectra in Figure 6g showed that the Ti 2p peaks of Ti, Ti²⁺, Ti³⁺, TiO₂ inside MO10 which was not completely oxidized.

Although the TiO_2 content increased significantly compared with $\text{Ti}_3\text{C}_2\text{T}_x$, inside MO10 still retained the unique structure of $\text{Ti}_3\text{C}_2\text{T}_x$. By comparing Figures 6f and 6h, it can be seen that the number of Ti-C and C-C bonds decreased, while the number of C-O and C=O bonds increased. This meant that MO10 does undergo oxidation, but still retained a certain Ti/C structure, which was the key to maintaining the two-dimensional layered structure. As shown in Figure 2, the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ formed a nano-layer with TiO_2 , carbon and Fe oxides as the main component after the oxidation of Fe(III). This nano-layer can protect the internal $\text{Ti}_3\text{C}_2\text{T}_x$ from further oxidation, so as to maintain the two-dimensional layered structure. According to the obtained results (SI, Table S2), we found that there was still a certain amount of C inside the MO10 after Fe (III) oxidation. Element C was not lost entirely or oxidized to form CO_2 . The low content of Fe inside the MO10 membrane meant that the oxidation degree inside the membrane was very low.

Figure 6.

A schematic illustration representing the transformation of MXene flakes into anatase structures, as observed during the different oxidized conditions, was given in Figure 7. We hypothesized that in the natural oxidation process, the oxidation rate was slow. The carbon structure cannot recombine and retain the complete lamellar structure in this process (SI, Figure S17), so it was difficult to maintain the two-dimensional structure after oxidation [23,25]. The Ti and C layers were completely oxidized and degraded by natural oxidation (Figure 7b).

In contrast, for the concentrations of 10 mM Fe(III) (applied concentration of FeCl_3), the

Ti layers at the top was preferentially oxidized to form the protective nano-layer and some small size iron oxide was deposited in the nano-layer (Figure 7c). When the Ti element in the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets formed anatase TiO_2 nanosheets [26,65], the remaining C element spontaneously began to form a C layer, thus forming the C/ TiO_2 nano-layer [66]. Comparing the zeta potential of the MXene and MO10 membranes (Fig. S22), the electronegativity of the surface of the MO10 membrane was obviously weaker than that of the MXene membrane, which meant that the positively charged Fe(II) and Fe(III) in the nano-layer could be bound to the negatively charged C layer and Ti layer by electrostatic forces. The peaks of Ti 2p_{1/2} and 2p_{3/2} of the surface of MO10 showed larger negative shifts of 0.44 and 0.45 eV, relative to those in the MXene membrane by natural oxidation, indicating strong electron interaction between the Fe and Ti of the nano-layer (Figure S25) [67].

However, with the higher concentration of FeCl_3 (over-dose) oxidation, the amounts of oxides increased with the concentration of FeCl_3 , and the floccules with larger diameters were formed which was not conducive to improving the performance.

Figure 7.

The oxidation process of Fe(III) was rapid and mild, and Ti/C nanolayer at the top of MO10 can be recombined with Fe oxides during the oxidation process, so that the complete lamellar structure inside can be retained. A prior investigation examined how oxidants influence the behavior of MXenes [68]. Through manipulation of oxidation levels (oxidant content and reaction time), it became possible to preserve the original layered structure

543 selectively [69]. In summary, we believe that when Fe(III) was used as oxidant, the original
544 layered structure of MXene membrane can be selectively retained by regulating the degree of
545 oxidation.
546

4. Conclusions

In this study the benefits of applying different concentrations of FeCl_3 solution to oxidize MXene membranes were evaluated and an optimal dose of 10 mM (MO10 membrane) was found to provide a high level of membrane stability in solution and solute rejection. At the optimal dose of Fe(III) the mildly oxidized MXene flakes formed a thin layer of thin TiO_2 nanoparticles supported by carbon sheets, in which there were uniformly distributed Fe oxides. This nano-layer can protect the internal $\text{Ti}_3\text{C}_2\text{T}_x$ from further oxidation, so as to maintain the two-dimensional layered structure. The solute separation performance, based on dye rejection, was much greater than a pure (un-oxidized) MXene membrane, corresponding to ~99.9%, of which adsorption contributed only 1%. Relative to the unoxidized MXene membrane, the osmotic inhibition efficiency of NaCl and MgCl_2 experienced respective increments of 42.39% and 37.51% upon utilization of the MO10 membrane. In addition, the MO10 membrane also performed well in stability tests, maintaining a visually intact membrane structure and stable water flux. After soaking the membrane in water for 5 days, the chemical composition and the carbon skeleton of MXene membrane changed dramatically whereas the MO10 membrane has remained stable. Compared with other oxidation methods, Fe(III) oxidation is a more mild and effective approach, which greatly improved the membrane performance (stability and solute/substrate rejection). Thus, this work presents a novel consideration of MXene membrane structure regulation and performance optimization. This novel approach not only provides a valuable reference for the design of other two-dimensional membranes, such as GO and C_3N_4 , but also enables opportunities in the future for the development and application of two-

568 dimensional materials in adsorption, catalysis and energy storage.

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591 **Notes**

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599

600 **Appendix A. Supplementary data**

601 The Supporting (supplementary) Information contains 28 Figures and 5 Tables as follows:
602 Filtration device with a rotor indicated by red circle; b) Filtration device during rotor operation.
603 **(Figure S1);**
604 SEM images (top view) of membranes oxidized by different concentration of Fe(III) **(Figure**
605 **S2);**
606 Cross-sectional SEM images of MXene and MO10 membranes **(Figure S3);**
607 Cross-sectional SEM images of MO1, MO2.5, MO.5 and MO10 membranes **(Figure S4);**
608 The XPS full spectra for MXene membranes, MO10 membranes and MXene membranes after
609 natural oxidation **(Figure S5);**
610 The XPS spectra for: Ti 2p, O 1s and F 1s of MXene membrane **(Figure S6);**
611 The XPS spectra for: Ti 2p, O 1s and C 1s of MXene membrane after natural oxidation **(Figure**
612 **S7);**
613 The XPS spectra for O 1s of MO10 membrane **(Figure S8);**
614 FT-IR spectra of MXene membrane and MXene oxidized by different concentrations of Fe³⁺

615 (Figure S9);

616 HRTEM images of MO10 (Figure S10);

617 Element analysis and energy-dispersive X-ray spectroscopy (EDX) for MO10 membrane

618 (Figure S11);

619 Variation of contact angle with time of pure MXene and MO10 membranes (Figure S12);

620 The customized U-shaped instrument (for ion retention tests) (Figure S13);

621 The SEM images of MO10 membrane surface before and after the pressure experiment (Figure

622 S12);

623 Temporal variation of flux of MXene membrane oxidized with different concentrations of

624 Fe(III) (Figure S15);

625 Photographic images relating to membrane stability: MXene membranes oxidized by H₂O₂

626 (Figure S16);

627 SEM image (top view) of MXene membrane after natural oxidation for 5 days (Figure S17);

628 Raman spectra of MXene and MO10 membranes (Figure S18);

629 The concentration comparison of Fe³⁺ used for oxidation of the MO10 membrane, in water

630 filtered by MO10 membrane, and in deionized water (Figure S19);

631 The CCB rejection of membrane samples varied with soaking time in water (Figure S20);

632 The UV-visible absorption spectra of the feed, permeate and concentrate solutions of

633 Coomassie brilliant blue dye for MXene and oxidized MXene membranes (Figure S21);

634 The zeta potential of MXene and MO10 membranes (Figure S22);

635 Variation of substrate rejection of different dyes by MO10 and pure MXene membranes

636 (Figure S23);

637 Long-term variation of substrate rejection of MXene and MO10 membranes for CBB (180 min)

638 (Figure S24);

639 The XPS spectra for Ti 2p of MO10 membrane and MXene membrane by natural oxidation

640 (Figure S25);

641 Photographs of MO10 membrane (Figure S26);

642 TGA analysis of the MXene and MO10 in Ar (Figure S27);

643 Raman spectra of MO10 membranes before and after soaking in water for 5 days (Figure S28);

644 Comparison of Fe(III) micro-oxidation with previously reported MXene-based membranes of

645 different preparation methods (Table S1).

646 The XPS elemental composition of MXene membrane and MO10 membrane (Table S2);

647 Comparison of rejection and flux for MXene membrane, MO10 membrane, MXene membrane

648 oxidized by H₂O₂, and MXene membrane oxidized by natural oxidation (Table S3);

649 Performance comparison of TiO₂/C@Fe₃O₄ membrane with previous reported membrane

650 materials (Table S4);

651 The properties of organic molecules used in this study (Table S5);

652

References

- [1] L. Shao, Z.X. Wang, Y.L. Zhang, Z.X. Jiang, Y.Y. Liu, A facile strategy to enhance PVDF ultrafiltration membrane performance via self-polymerized polydopamine followed by hydrolysis of ammonium fluotitanate, *Journal of Membrane Science* 461 (2014) 10–21. <https://doi.org/10.1016/j.memsci.2014.03.006>.
- [2] M. Chen, M. Trubyanov, P. Zhang, Q. Wang, Z. Li, K.S. Novoselov, D.V. Andreeva, Comprehensive characterization of gas diffusion through graphene oxide membranes, *Journal of Membrane Science* 676 (2023) 121583. <https://doi.org/10.1016/j.memsci.2023.121583>.
- [3] Q. Ji, X. An, H. Liu, L. Guo, J. Qu, Electric Double-Layer Effects Induce Separation of Aqueous Metal Ions, *ACS Nano* 9 (2015) 10922–10930. <https://doi.org/10.1021/acsnano.5b04027>.
- [4] B. Akuzum, K. Maleski, B. Anasori, P. Lelyukh, N.J. Alvarez, E.C. Kumbur, Y. Gogotsi, Rheological Characteristics of 2D Titanium Carbide (MXene) Dispersions: A Guide for Processing MXenes, *ACS Nano* 12 (2018) 2685–2694. <https://doi.org/10.1021/acsnano.7b08889>.
- [5] H. Gao, Y. Wang, M.A. Afolabi, D. Xiao, Y. Chen, Incorporation of Cellulose Nanocrystals into Graphene Oxide Membranes for Efficient Antibiotic Removal at High Nutrient Recovery, *ACS Appl. Mater. Interfaces* 13 (2021) 14102–14111. <https://doi.org/10.1021/acsaami.0c20652>.
- [6] G. Liu, W. Jin, N. Xu, Two-Dimensional-Material Membranes: A New Family of High-Performance Separation Membranes, *Angewandte Chemie International Edition* 55 (2016) 13384–13397. <https://doi.org/10.1002/anie.201600438>.
- [7] C.E. Ren, K.B. Hatzell, M. Alhabeb, Z. Ling, K.A. Mahmoud, Y. Gogotsi, Charge- and Size-Selective Ion Sieving Through Ti₃C₂T_x MXene Membranes, *J. Phys. Chem. Lett.* 6 (2015) 4026–4031. <https://doi.org/10.1021/acs.jpclett.5b01895>.
- [8] X.-B. Lv, R. Xie, J.-Y. Ji, Z. Liu, X.-Y. Wen, L.-Y. Liu, J.-Q. Hu, X.-J. Ju, W. Wang, L.-Y. Chu, A Novel Strategy to Fabricate Cation-Cross-linked Graphene Oxide Membrane with High Aqueous Stability and High Separation Performance, *ACS Appl. Mater. Interfaces* 12 (2020) 56269–56280. <https://doi.org/10.1021/acsaami.0c15178>.
- [9] T. Liu, L. Tian, N. Graham, B. Yang, W. Yu, K. Sun, Regulating the Interlayer Spacing of Graphene Oxide Membranes and Enhancing their Stability by Use of PACl, *Environ. Sci. Technol.* 53 (2019) 11949–11959. <https://doi.org/10.1021/acs.est.9b04418>.
- [10] Y.A.J. Al-Hamadani, B.-M. Jun, M. Yoon, N. Taheri-Qazvini, S.A. Snyder, M. Jang, J. Heo, Y. Yoon, Applications of MXene-based membranes in water purification: A review, *Chemosphere* 254 (2020) 126821.

<https://doi.org/10.1016/j.chemosphere.2020.126821>.

[11] M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M.W. Barsoum, Two-Dimensional Nanocrystals Produced by Exfoliation of Ti_3AlC_2 , *Advanced Materials* 23 (2011) 4248–4253. <https://doi.org/10.1002/adma.201102306>.

[12] D.N. Nguyen, G.S. Gund, M.G. Jung, S.H. Roh, J. Park, J.K. Kim, H.S. Park, Core–Shell Structured MXene@Carbon Nanodots as Bifunctional Catalysts for Solar-Assisted Water Splitting, *ACS Nano* 14 (2020) 17615–17625. <https://doi.org/10.1021/acsnano.0c08436>.

[13] C. (John) Zhang, S.J. Kim, M. Ghidui, M.-Q. Zhao, M.W. Barsoum, V. Nicolosi, Y. Gogotsi, Layered Orthorhombic $\text{Nb}_2\text{O}_5@\text{Nb}_4\text{C}_3\text{Tx}$ and $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{Tx}$ Hierarchical Composites for High Performance Li-ion Batteries, *Advanced Functional Materials* 26 (2016) 4143–4151. <https://doi.org/10.1002/adfm.201600682>.

[14] W. Chen, L.-X. Liu, H.-B. Zhang, Z.-Z. Yu, Kirigami-Inspired Highly Stretchable, Conductive, and Hierarchical $\text{Ti}_3\text{C}_2\text{Tx}$ MXene Films for Efficient Electromagnetic Interference Shielding and Pressure Sensing, *ACS Nano* 15 (2021) 7668–7681. <https://doi.org/10.1021/acsnano.1c01277>.

[15] T. Liu, X. Liu, N. Graham, W. Yu, K. Sun, Two-dimensional MXene incorporated graphene oxide composite membrane with enhanced water purification performance, *Journal of Membrane Science* 593 (2020) 117431. <https://doi.org/10.1016/j.memsci.2019.117431>.

[16] S. Munir, A. Rasheed, T. Rasheed, I. Ayman, S. Ajmal, A. Rehman, I. Shakir, P.O. Agboola, M.F. Warsi, Exploring the Influence of Critical Parameters for the Effective Synthesis of High-Quality 2D MXene, *ACS Omega* 5 (2020) 26845–26854. <https://doi.org/10.1021/acsomega.0c03970>.

[17] K. Rasool, R.P. Pandey, P.A. Rasheed, S. Buczek, Y. Gogotsi, K.A. Mahmoud, Water treatment and environmental remediation applications of two-dimensional metal carbides (MXenes), *Materials Today* 30 (2019) 80–102. <https://doi.org/10.1016/j.mattod.2019.05.017>.

[18] Y. Li, J. Ma, T.D. Waite, M.R. Hoffmann, Z. Wang, Development of a Mechanically Flexible 2D-MXene Membrane Cathode for Selective Electrochemical Reduction of Nitrate to N_2 : Mechanisms and Implications, *Environ. Sci. Technol.* 55 (2021) 10695–10703. <https://doi.org/10.1021/acs.est.1c00264>.

[19] Peng-Fei Sun, Zhe Yang, Xiaoxiao Song, Jeong Hoon Lee, Chuyang Y. Tang, Hee-Deung Park, Interlayered Forward Osmosis Membranes with $\text{Ti}_3\text{C}_2\text{T}_x$ MXene and Carbon Nanotubes for Enhanced Municipal Wastewater Concentration, *Environmental Science & Technology* 55 (2021) 13219–13230. <https://doi.org/10.1021/acs.est.1c01968>.

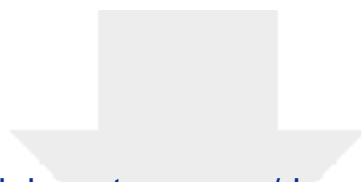
- [20] C.E. Ren, M. Alhabeb, B.W. Byles, M.-Q. Zhao, B. Anasori, E. Pomerantseva, K.A. Mahmoud, Y. Gogotsi, Voltage-Gated Ions Sieving through 2D MXene Ti₃C₂Tx Membranes, *ACS Appl. Nano Mater.* 1 (2018) 3644–3652. <https://doi.org/10.1021/acsanm.8b00762>.
- [21] H. Gao, W. Chen, C. Xu, S. Liu, X. Tong, Y. Chen, Two-Dimensional Ti₃C₂Tx MXene/GO Hybrid Membranes for Highly Efficient Osmotic Power Generation, *Environ. Sci. Technol.* 54 (2020) 2931–2940. <https://doi.org/10.1021/acs.est.9b05100>.
- [22] W.Y. Chen, S.-N. Lai, C.-C. Yen, X. Jiang, D. Peroulis, L.A. Stanciu, Surface Functionalization of Ti₃C₂Tx MXene with Highly Reliable Superhydrophobic Protection for Volatile Organic Compounds Sensing, *ACS Nano* 14 (2020) 11490–11501. <https://doi.org/10.1021/acsnano.0c03896>.
- [23] C.J. Zhang, S. Pinilla, N. McEvoy, C.P. Cullen, B. Anasori, E. Long, S.-H. Park, A. Seral-Ascaso, A. Shmeliov, D. Krishnan, C. Morant, X. Liu, G.S. Duesberg, Y. Gogotsi, V. Nicolosi, Oxidation Stability of Colloidal Two-Dimensional Titanium Carbides (MXenes), *Chem. Mater.* 29 (2017) 4848–4856. <https://doi.org/10.1021/acs.chemmater.7b00745>.
- [24] H. Song, D. Zu, C. Li, R. Zhou, Y. Wang, W. Zhang, S. Pan, Y. Cai, Z. Li, Y. Shen, J. Ma, Ultrafast activation of peroxydisulfate by reduction of trace Fe³⁺ with Ti₃C₂ MXene under neutral and alkaline conditions: Reducibility and confinement effect, *Chemical Engineering Journal* 423 (2021) 130012. <https://doi.org/10.1016/j.cej.2021.130012>.
- [25] T. Habib, X. Zhao, S.A. Shah, Y. Chen, W. Sun, H. An, J.L. Lutkenhaus, M. Radovic, M.J. Green, Oxidation stability of Ti₃C₂Tx MXene nanosheets in solvents and composite films, *Npj 2D Mater Appl* 3 (2019) 1–6. <https://doi.org/10.1038/s41699-019-0089-3>.
- [26] H. Ghassemi, W. Harlow, O. Mashtalir, M. Beidaghi, M. R. Lukatskaya, Y. Gogotsi, M. L. Taheri, In situ environmental transmission electron microscopy study of oxidation of two-dimensional Ti₃C₂ and formation of carbon-supported TiO₂, *Journal of Materials Chemistry A* 2 (2014) 14339–14343. <https://doi.org/10.1039/C4TA02583K>.
- [27] O. Mashtalir, M.R. Lukatskaya, A.I. Kolesnikov, E. Raymundo-Piñero, M. Naguib, M.W. Barsoum, Y. Gogotsi, The effect of hydrazine intercalation on the structure and capacitance of 2D titanium carbide (MXene), *Nanoscale* 8 (2016) 9128–9133. <https://doi.org/10.1039/C6NR01462C>.
- [28] V. Natu, J.L. Hart, M. Sokol, H. Chiang, M.L. Taheri, M.W. Barsoum, Edge Capping of 2D-MXene Sheets with Polyanionic Salts To Mitigate Oxidation in Aqueous Colloidal Suspensions, *Angewandte Chemie* 131 (2019) 12785–12790. <https://doi.org/10.1002/ange.201906138>.

- [29] X. Wu, Z. Wang, M. Yu, L. Xiu, J. Qiu, Stabilizing the MXenes by Carbon Nanoplatting for Developing Hierarchical Nanohybrids with Efficient Lithium Storage and Hydrogen Evolution Capability, *Advanced Materials* 29 (2017) 1607017. <https://doi.org/10.1002/adma.201607017>.
- [30] R. P. Pandey, K. Rasool, V. E. Madhavan, B. Aïssa, Y. Gogotsi, K. A. Mahmoud, Ultrahigh-flux and fouling-resistant membranes based on layered silver/MXene (Ti₃C₂Tx) nanosheets, *Journal of Materials Chemistry A* 6 (2018) 3522–3533. <https://doi.org/10.1039/C7TA10888E>.
- [31] Z. Lu, Y. Wei, J. Deng, L. Ding, Z.-K. Li, H. Wang, Self-Crosslinked MXene (Ti₃C₂Tx) Membranes with Good Antiswelling Property for Monovalent Metal Ion Exclusion, *ACS Nano* 13 (2019) 10535–10544. <https://doi.org/10.1021/acsnano.9b04612>.
- [32] K. Rasool, K.A. Mahmoud, D.J. Johnson, M. Helal, G.R. Berdiyrov, Y. Gogotsi, Efficient Antibacterial Membrane based on Two-Dimensional Ti₃C₂Tx (MXene) Nanosheets, *Sci Rep* 7 (2017) 1598. <https://doi.org/10.1038/s41598-017-01714-3>.
- [33] M. Ding, W. Chen, H. Xu, Z. Shen, T. Lin, K. Hu, C. hui Lu, Z. Xie, Novel α -Fe₂O₃/MXene nanocomposite as heterogeneous activator of peroxymonosulfate for the degradation of salicylic acid, *Journal of Hazardous Materials* 382 (2020) 121064. <https://doi.org/10.1016/j.jhazmat.2019.121064>.
- [34] A. Ali, K. Hantanasirisakul, A. Abdala, P. Urbankowski, M.-Q. Zhao, B. Anasori, Y. Gogotsi, B. Aïssa, K.A. Mahmoud, Effect of Synthesis on Performance of MXene/Iron Oxide Anode Material for Lithium-Ion Batteries, *Langmuir* 34 (2018) 11325–11334. <https://doi.org/10.1021/acs.langmuir.8b01953>.
- [35] K. Kwon, C.-W. Park, D. Kim, High-flowrate, compact electroosmotic pumps with porous polymer track-etch membranes, *Sensors and Actuators A: Physical* 175 (2012) 108–115. <https://doi.org/10.1016/j.sna.2011.12.050>.
- [36] M. Mu, N. Graham, W. Yu, K. Sun, X. Xu, T. Liu, Optimal cross-linking of MXene-based membranes for high rejection and low adsorption with long-term stability for water treatment, *Journal of Membrane Science* 701 (2024) 122738. <https://doi.org/10.1016/j.memsci.2024.122738>.
- [37] S. Zhang, S. Liao, F. Qi, R. Liu, T. Xiao, J. Hu, K. Li, R. Wang, Y. Min, Direct deposition of two-dimensional MXene nanosheets on commercially available filter for fast and efficient dye removal, *Journal of Hazardous Materials* 384 (2020) 121367. <https://doi.org/10.1016/j.jhazmat.2019.121367>.
- [38] S. Wan, X. Li, Y. Wang, Y. Chen, X. Xie, R. Yang, A.P. Tomsia, L. Jiang, Q. Cheng, Strong sequentially bridged MXene sheets, *Proceedings of the National Academy of Sciences of the United States of America* 117 (2020) 27154. <https://doi.org/10.1073/pnas.2009432117>.

-
- [39] S. Wan, X. Li, Y. Chen, N. Liu, Y. Du, S. Dou, L. Jiang, Q. Cheng, High-strength scalable MXene films through bridging-induced densification, *Science* 374 (2021) 96–99. <https://doi.org/10.1126/science.abg2026>.
- [40] H. Tang, W. Li, L. Pan, K. Tu, F. Du, T. Qiu, J. Yang, C.P. Cullen, N. McEvoy, C. (John) Zhang, A Robust, Freestanding MXene-Sulfur Conductive Paper for Long-Lifetime Li–S Batteries, *Advanced Functional Materials* 29 (2019) 1901907. <https://doi.org/10.1002/adfm.201901907>.
- [41] Y. Lu, M. Zhang, J. Chang, A. Sikdar, N. Wang, Q.-F. An, J. Yuan, Heterostructure membranes of high permeability and stability assembled from MXene and modified layered double hydroxide nanosheets, *Journal of Membrane Science* 688 (2023) 122100. <https://doi.org/10.1016/j.memsci.2023.122100>.
- [42] X. Zhang, Y. Niu, X. Meng, Y. Li, J. Zhao, Structural evolution and characteristics of the phase transformations between α -Fe₂O₃, Fe₃O₄ and γ -Fe₂O₃ nanoparticles under reducing and oxidizing atmospheres, *CrystEngComm* 15 (2013) 8166–8172. <https://doi.org/10.1039/C3CE41269E>.
- [43] X. Zhang, W. Yuan, Y. Yang, Y. Chen, Z. Tang, C. Wang, Y. Yuan, Y. Ye, Y. Wu, Y. Tang, Immobilizing Polysulfide by In Situ Topochemical Oxidation Derivative TiC@Carbon-Included TiO₂ Core–Shell Sulfur Hosts for Advanced Lithium–Sulfur Batteries, *Small* 16 (2020) 2005998. <https://doi.org/10.1002/sml.202005998>.
- [44] F. Werfel, O. Brümmer, Corundum Structure Oxides Studied by XPS, *Phys. Scr.* 28 (1983) 92. <https://doi.org/10.1088/0031-8949/28/1/013>.
- [45] A. Lebugle, U. Axelsson, R. Nyholm, N. Mårtensson, Experimental L and M Core Level Binding Energies for the Metals 22Ti to 30Zn, *Phys. Scr.* 23 (1981) 825. <https://doi.org/10.1088/0031-8949/23/5A/013>.
- [46] K. Hamrin, G. Johansson, U. Gelius, C. Nordling, K. Siegbahn, Valence Bands and Core Levels of the Isoelectronic Series LiF, BeO, BN, and Graphite Studied by ESCA, *Phys. Scr.* 1 (1970) 277. <https://doi.org/10.1088/0031-8949/1/5-6/018>.
- [47] Y. Cao, Q. Deng, Z. Liu, D. Shen, T. Wang, Q. Huang, S. Du, N. Jiang, C.-T. Lin, J. Yu, Enhanced thermal properties of poly(vinylidene fluoride) composites with ultrathin nanosheets of MXene, *RSC Adv.* 7 (2017) 20494–20501. <https://doi.org/10.1039/C7RA00184C>.
- [48] J.F. Moulder, J. Chastain, eds., *Handbook of X-ray photoelectron spectroscopy: a reference book of standard spectra for identification and interpretation of XPS data*, Update, Perkin-Elmer Corporation, Eden Prairie, Minn, 1992.
- [49] W. Hu, Z. Wen, X. Yu, P. Qian, W. Lian, X. Li, Y. Shang, X. Wu, T. Chen, Y. Lu, M. Wang, S. Yang, In Situ Surface Fluorination of TiO₂ Nanocrystals Reinforces Interface Binding of Perovskite Layer for Highly Efficient Solar Cells with Dramatically

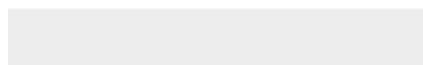
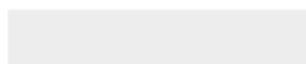
-
- Enhanced Ultraviolet-Light Stability, *Advanced Science* 8 (2021) 2004662. <https://doi.org/10.1002/advs.202004662>.
- [50] P. Li, M. Yang, Y. Liu, H. Qin, J. Liu, Z. Xu, Y. Liu, F. Meng, J. Lin, F. Wang, C. Gao, Continuous crystalline graphene papers with gigapascal strength by intercalation modulated plasticization, *Nat Commun* 11 (2020) 2645. <https://doi.org/10.1038/s41467-020-16494-0>.
- [51] U. Diebold, The surface science of titanium dioxide, *Surface Science Reports* 48 (2003) 53–229. [https://doi.org/10.1016/S0167-5729\(02\)00100-0](https://doi.org/10.1016/S0167-5729(02)00100-0).
- [52] N. Li, Z. Xu, S. Zheng, H. Dai, L. Wang, Y. Tian, Z. Dong, L. Jiang, Superamphiphilic TiO₂ Composite Surface for Protein Antifouling, *Advanced Materials* 33 (2021) 2003559. <https://doi.org/10.1002/adma.202003559>.
- [53] Z. Hao, S. Zhao, Q. Li, Y. Wang, J. Zhang, Z. Wang, J. Wang, Reverse osmosis membranes with sulfonate and phosphate groups having excellent anti-scaling and anti-fouling properties, *Desalination* 509 (2021) 115076. <https://doi.org/10.1016/j.desal.2021.115076>.
- [54] J.-L. Han, M.R. Haider, M.-J. Liu, H. Wang, W.-L. Jiang, Y.-C. Ding, Y.-N. Hou, H.-Y. Cheng, X. Xia, A.-J. Wang, Borate Inorganic Cross-Linked Durable Graphene Oxide Membrane Preparation and Membrane Fouling Control, *Environ. Sci. Technol.* 53 (2019) 1501–1508. <https://doi.org/10.1021/acs.est.8b04194>.
- [55] R. Chang, S. Ma, X. Guo, J. Xu, C. Zhong, R. Huang, J. Ma, Hierarchically Assembled Graphene Oxide Composite Membrane with Self-Healing and High-Efficiency Water Purification Performance, *ACS Appl. Mater. Interfaces* 11 (2019) 46251–46260. <https://doi.org/10.1021/acsami.9b18018>.
- [56] L. Zhu, X. Guo, Y. Chen, Z. Chen, Y. Lan, Y. Hong, W. Lan, Graphene Oxide Composite Membranes for Water Purification, *ACS Appl. Nano Mater.* 5 (2022) 3643–3653. <https://doi.org/10.1021/acsanm.1c04322>.
- [57] S. El Meragawi, A. Akbari, S. Hernandez, A. Tanksale, M. Majumder, Efficient Permeance Recovery of Organically Fouled Graphene Oxide Membranes, *ACS Appl. Bio Mater.* 3 (2020) 584–592. <https://doi.org/10.1021/acsabm.9b00975>.
- [58] Y. Mo, X. Zhao, Y. Shen, Cation-dependent structural instability of graphene oxide membranes and its effect on membrane separation performance, *Desalination* 399 (2016) 40–46. <https://doi.org/10.1016/j.desal.2016.08.012>.
- [59] Y. Xing, G. Akonkwa, Z. Liu, H. Ye, K. Han, Crumpled Two-Dimensional Ti₃C₂Tx MXene Lamellar Membranes for Solvent Permeation and Separation, *ACS Appl. Nano Mater.* 3 (2020) 1526–1534. <https://doi.org/10.1021/acsanm.9b02322>.
- [60] Y. Li, R. Dai, H. Zhou, X. Li, Z. Wang, Aramid Nanofiber Membranes Reinforced by MXene Nanosheets for Recovery of Dyes from Textile Wastewater, *ACS*

-
- Appl. Nano Mater. 4 (2021) 6328–6336. <https://doi.org/10.1021/acsanm.1c01217>.
- [61] Y. Wang, L. Li, Y. Wei, J. Xue, H. Chen, L. Ding, J. Caro, H. Wang, Water Transport with Ultralow Friction through Partially Exfoliated g-C₃N₄ Nanosheet Membranes with Self-Supporting Spacers, *Angewandte Chemie International Edition* 56 (2017) 8974–8980. <https://doi.org/10.1002/anie.201701288>.
- [62] R. Li, X. Ma, J. Li, J. Cao, H. Gao, T. Li, X. Zhang, L. Wang, Q. Zhang, G. Wang, C. Hou, Y. Li, T. Palacios, Y. Lin, H. Wang, X. Ling, Flexible and high-performance electrochromic devices enabled by self-assembled 2D TiO₂/MXene heterostructures, *Nat Commun* 12 (2021) 1587. <https://doi.org/10.1038/s41467-021-21852-7>.
- [63] N. Li, Y. Jiang, C. Zhou, Y. Xiao, B. Meng, Z. Wang, D. Huang, C. Xing, Z. Peng, High-Performance Humidity Sensor Based on Urchin-Like Composite of Ti₃C₂ MXene-Derived TiO₂ Nanowires, *ACS Appl. Mater. Interfaces* 11 (2019) 38116–38125. <https://doi.org/10.1021/acsami.9b12168>.
- [64] J. Halim, K.M. Cook, M. Naguib, P. Eklund, Y. Gogotsi, J. Rosen, M.W. Barsoum, X-ray photoelectron spectroscopy of select multi-layered transition metal carbides (MXenes), *Applied Surface Science* 362 (2016) 406–417. <https://doi.org/10.1016/j.apsusc.2015.11.089>.
- [65] M. Naguib, O. Mashtalir, M. R. Lukatskaya, B. Dyatkin, C. Zhang, V. Presser, Y. Gogotsi, M. W. Barsoum, One-step synthesis of nanocrystalline transition metal oxides on thin sheets of disordered graphitic carbon by oxidation of MXenes, *Chemical Communications* 50 (2014) 7420–7423. <https://doi.org/10.1039/C4CC01646G>.
- [66] X. Li, X. Yin, M. Han, C. Song, X. Sun, H. Xu, L. Cheng, L. Zhang, A controllable heterogeneous structure and electromagnetic wave absorption properties of Ti₂CT_x MXene, *Journal of Materials Chemistry C* 5 (2017) 7621–7628. <https://doi.org/10.1039/C7TC01991B>.
- [67] R.-K. Ye, S.-S. Sun, L.-Q. He, S.-R. Yang, X.-Q. Liu, M.-D. Li, P.-P. Fang, J.-Q. Hu, Surface engineering of hematite nanorods by 2D Ti₃C₂-MXene: Suppressing the electron-hole recombination for enhanced photoelectrochemical performance, *Applied Catalysis B: Environmental* 291 (2021) 120107. <https://doi.org/10.1016/j.apcatb.2021.120107>.
- [68] B. Ahmed, D. H. Anjum, M. N. Hedhili, Y. Gogotsi, H. N. Alshareef, H₂O₂ assisted room temperature oxidation of Ti₂C MXene for Li-ion battery anodes, *Nanoscale* 8 (2016) 7580–7587. <https://doi.org/10.1039/C6NR00002A>.
- [69] X. Li, Z. Huang, C. Zhi, Environmental Stability of MXenes as Energy Storage Materials, *Frontiers in Materials* 6 (2019). <https://doi.org/10.3389/fmats.2019.00312>.



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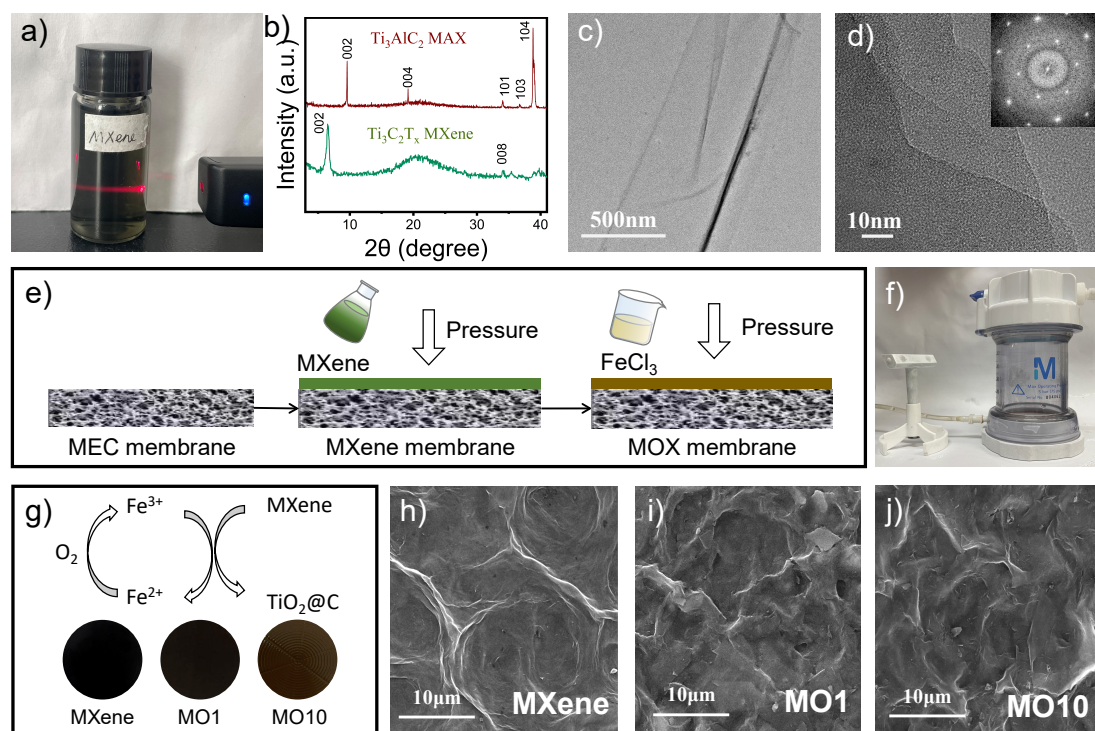


Figure 1. (a) Photograph of Tyndall effect of MXene; (b) XRD spectra of Ti_3AlC_2 (MAX) and $\text{Ti}_3\text{C}_2\text{T}_x$ (MXene); (c) TEM of the delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ flakes; (d) HRTEM of multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ flakes, and inset is the SAED of the $\text{Ti}_3\text{C}_2\text{T}_x$; (e) Schematic images of the fabrication of MXene substrates via pressure filtration of MXene on the surface of commercial mixed cellulose ester (MCE) membranes and the fabrication of MOX composite membranes on MXene substrates; (f) Photograph of flow cell in which the MXene substrates were manufactured; (g) Schematic of the oxidation process and photographs of the membrane surface of MXene, MO1 and MO10. SEM images (top view) of (h) MXene, (i) MO1 and (j) MO10

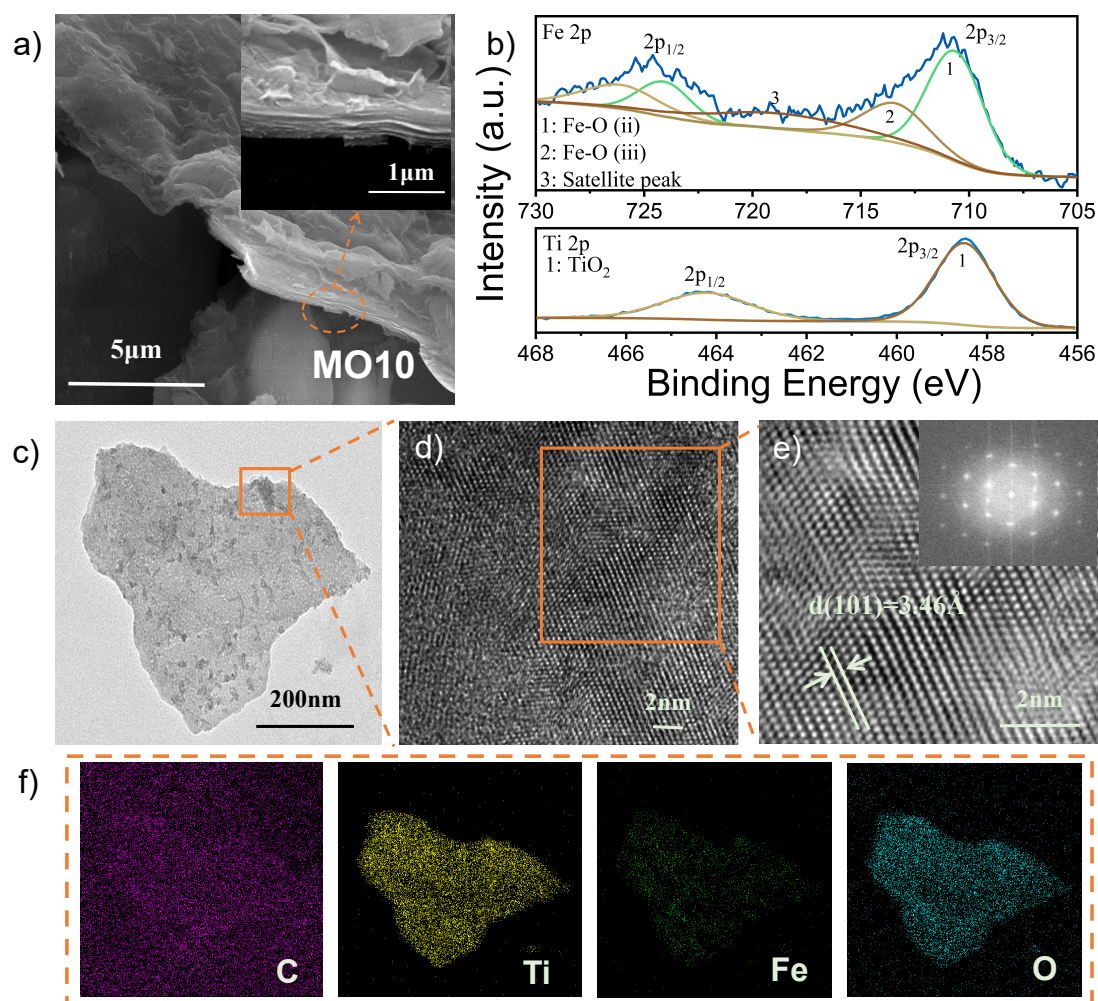


Figure 2. Characterization of oxidized membranes: (a) Cross-sectional SEM images of MO10; (b) The XPS spectra for: Ti 2p and Fe 2p of MO10; (c) TEM and (d, e) HRTEM images of MO10 and inset is the SAED; (f) TEM images corresponding to the elemental mapping of MO10; Cross-sectional TEM images of (g)MXene and (h) MO10.

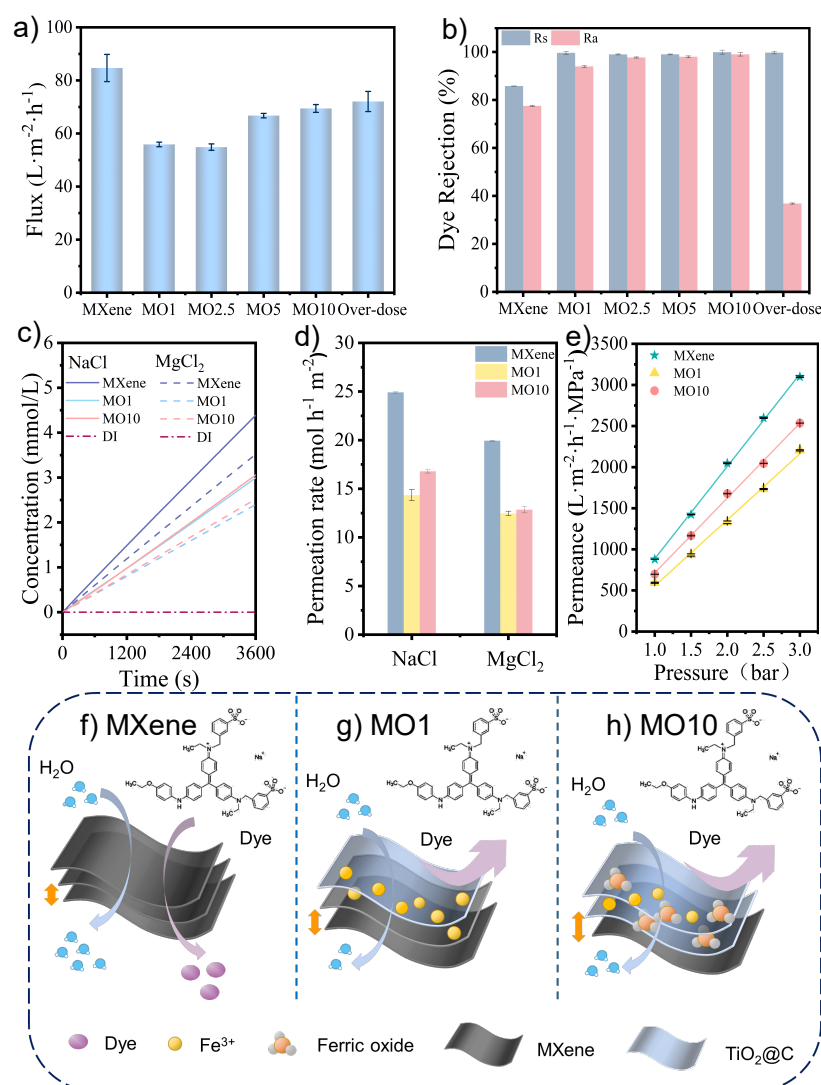


Figure 3. (a) Water flux of membrane oxidized with different concentrations of Fe(III) ; (b) Variation of substrate rejection of membrane oxidized with different concentrations of Fe^{3+} for Coomassie brilliant blue. ‘Over-dose’ in figures (a) and (b) means that the concentration of FeCl_3 solution $\geq 100 \text{ mM L}^{-1}$; Comparison of the permeability within one hour (c), and permeation rates (d), of ions in NaCl or MgCl_2 solutions for three kinds of membranes; (e) The variation of water flux of the three kinds of membranes with pressure. Schematic diagrams of substrate rejection by (f) pure MXene, (g) MO1 and (h) MO10 membranes. Flux was recorded by measuring the mass of flow continuously with an electronic balance (AX523ZH, Ohaus, USA) for a certain time

10 (0.5 h) under an applied pressure of 0.1 MPa. Each data of dye rejection and salt
11 permeability was obtained by a new membrane sample. All the collected data were
12 averages of three parallel tests, and standard deviation was calculated

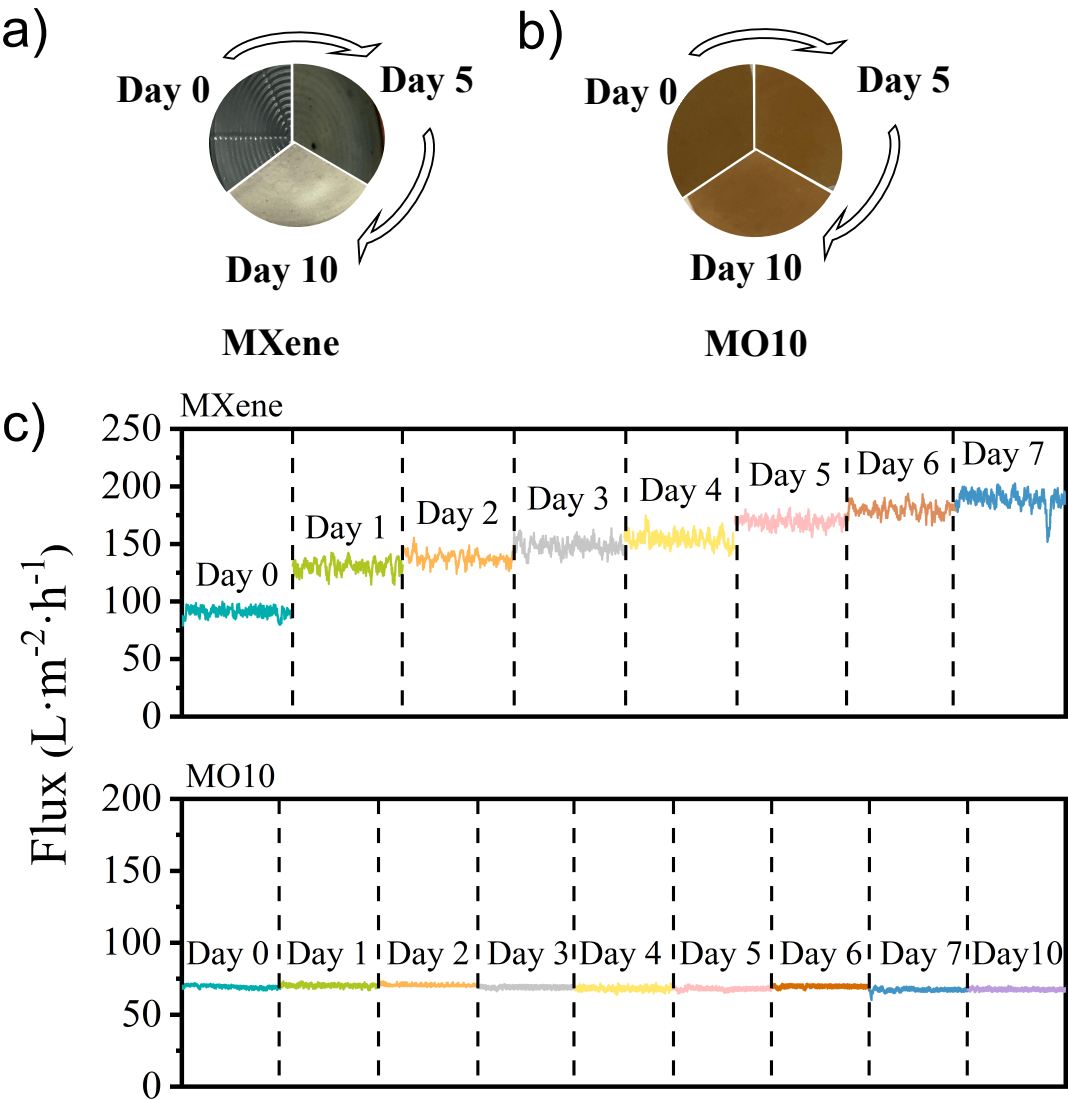
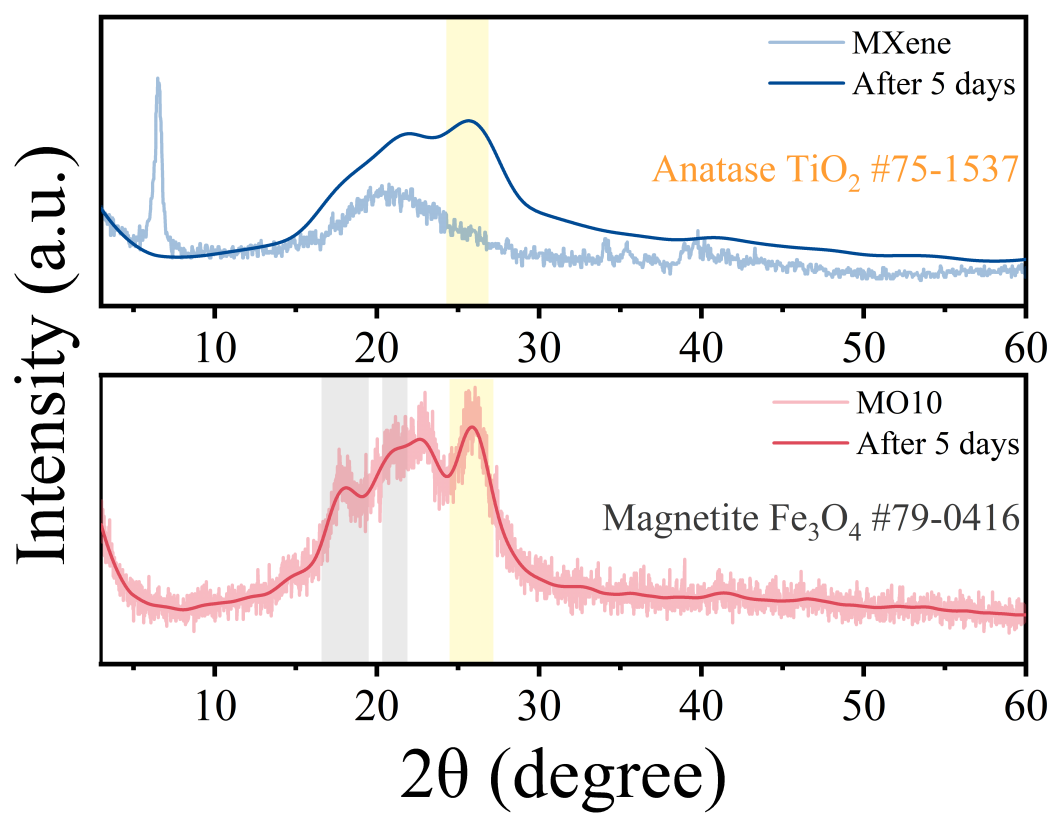


Figure 4. (a-b) Photographic images relating to membrane stability: (a) MXene membranes after natural oxidation and (b) MO10 membranes; (c) Continuous testing of flux of MXene membrane and MO10. Flux was recorded by measuring the mass of flow continuously with an electronic balance (AX523ZH, Ohaus, USA) for a certain time (0.5 h) under an applied pressure of 0.1 MPa.



1 **Figure 5.** XRD spectra of the MXene and MO10 membranes before and after soaking
2 in water for 5 days. XRD data of the MXene and MO10 membranes after soaking in
3 water for 5 days were normalized for comparison with pre-soaking.

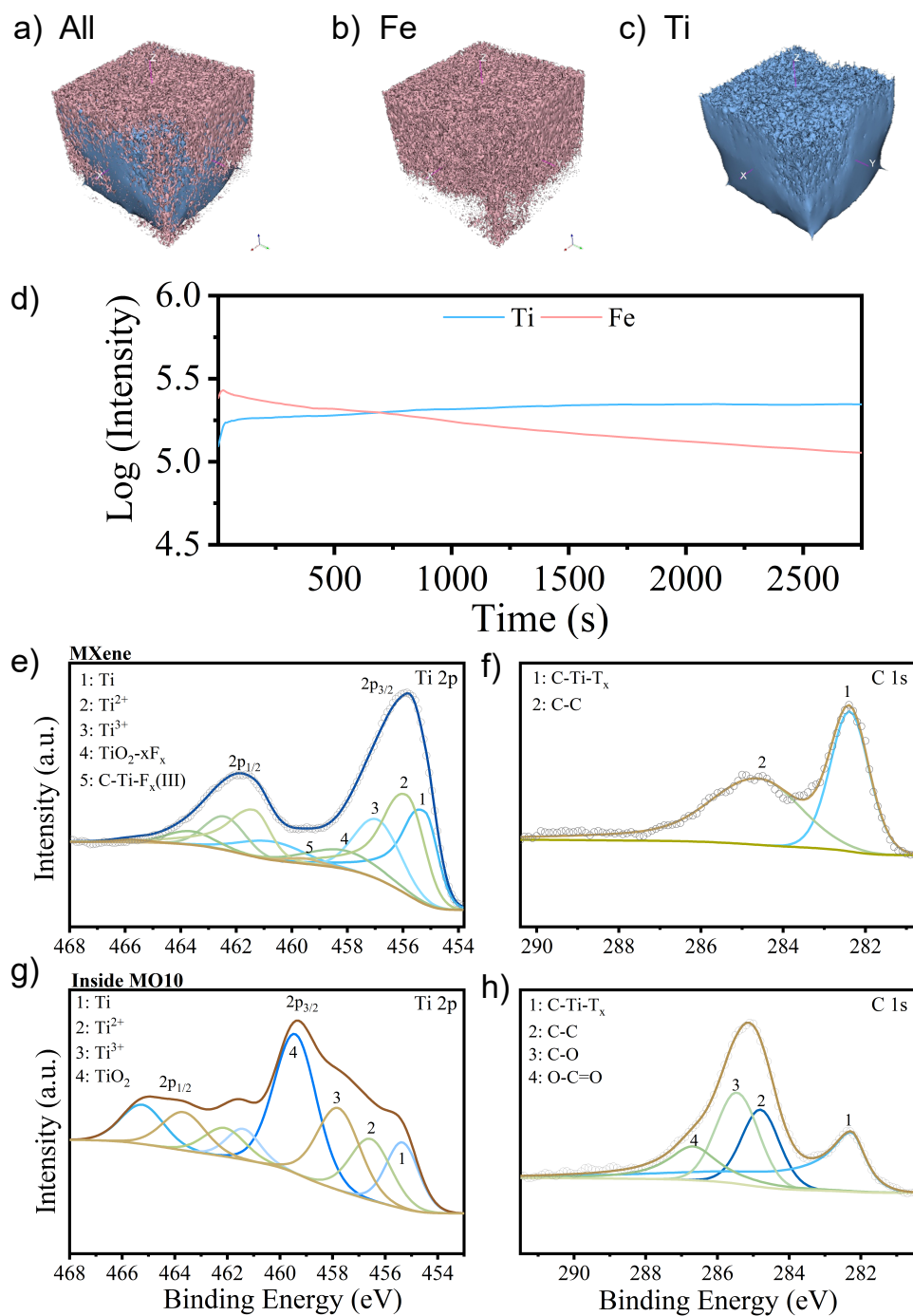


Figure 6. (a-c) 3D variation of the TOF-SIMS intensity related to the corresponding charged fragments; (d) Depth profile curves of TOF-SIMS in negative mode. The XPS spectra for: (e) Ti 2p, (f) C 1s of MXene membrane and (g) Ti 2p, (h) C 1s of inside MO10 membrane. During the XPS detection, a depth of 20 nm was chosen to etch the surface of MO10.

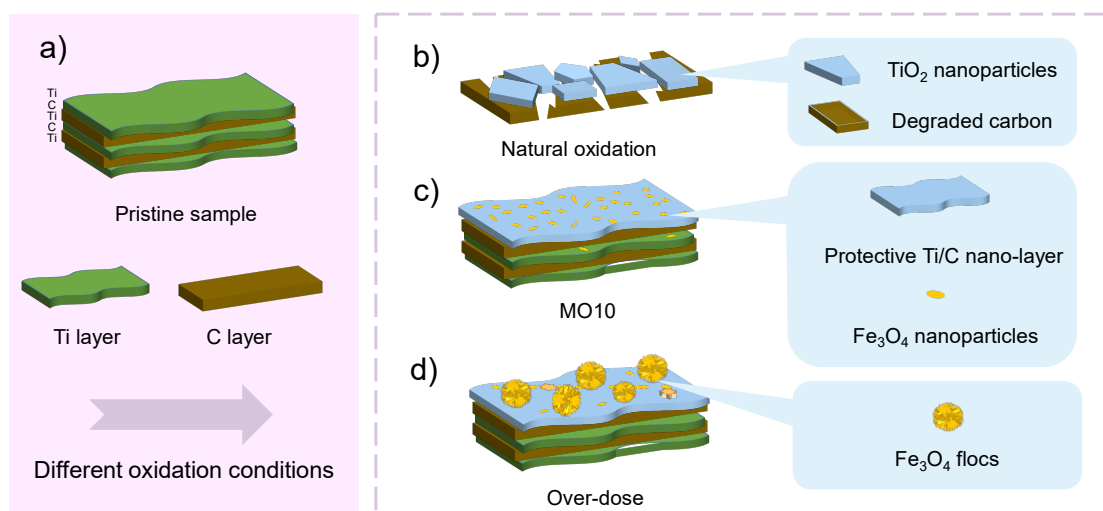


Figure 7. Schematic of the oxidation mechanisms: (a) shows the pristine layered structure of MXene; (b) represents the product by natural oxidation, where both the Ti and C layers were completely oxidized and degraded; (c) represents MO10 by the concentration of 10 mM FeCl₃ oxidation, where the Ti layers at the top was preferentially oxidized to form the protective nano-layer and some small size iron oxide was deposited; (d) represents the higher concentration of FeCl₃ (over-dose) oxidation, where the amount of oxide increased with the concentration of FeCl₃, and particles with larger diameters were formed. Over-dose in Figure (h) means that the concentration of FeCl₃ solution $\geq 100 \text{ mM L}^{-1}$.