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# A transport channel-regulated MXene membrane *via* organic phosphonic acids for efficient water permeation†

 Ming Yi,<sup>abc</sup> Frédéric Héraly,<sup>c</sup> Jian Chang,<sup>c</sup> Atefeh Khorsand Kheirabad,<sup>c</sup> Jiayin Yuan,<sup>ib</sup> Yan Wang<sup>\*ab</sup> and Miao Zhang<sup>ib</sup>\*<sup>c</sup>

A series of organic phosphonic acids (OPAs) were applied as multi-functional spacers to enlarge the inner space of carbide MXene ( $\text{Ti}_3\text{C}_2\text{T}_x$ ) laminates. A synergistic improvement in permeance, rejection and stability is achieved *via* introducing OPA to create pillared laminates. This strategy provides a universal way to regulate transport channels of MXene-based membranes.

Two-dimensional transition metal carbides, nitrides, and carbon-nitrides, known as MXenes, have experienced an avalanche of research advances in diverse applications, including energy storage, electrocatalysis, and water treatment, to name a few.<sup>1–5</sup> Among them, titanium-based MXenes ( $\text{Ti}_3\text{C}_2\text{T}_x$ ) are of particular interest for water purification in the postgraphene era, due to their favorable features of rich surface chemistry, excellent mechanical properties, and environment-friendly characteristics.<sup>6–11</sup> Pristine  $\text{Ti}_3\text{C}_2\text{T}_x$  membranes with selective sieving of various metal ions and dye cations have been reported by Ren *et al.* as the first attempt of an MXene-based separation membrane.<sup>12</sup> Thereafter, extensive strategies have been developed to engineer MXene-based nanolaminate membranes with desirable microstructures. For instance, template and spacer strategies have been developed to improve water permeability.<sup>13–16</sup> Despite encouraging results in water permeation, the disordered interlayer space resulting from *laissez-faire* assembly of MXene flakes impedes the efficient separation of different molecules, due to the unstable mass transport. Moreover, for a water-related scenario, oxidative degradation of MXene nanosheets, which imperils their stability and practical significance, is

another issue that needs to be considered.<sup>17–19</sup> Therefore, a strategy to enable both fast molecular sieving and water stability remains a challenging task.

Given the 2D nature of MXene nanosheets, the critical point to engineering high-performance membranes is meticulous control of the nanogalleries formed by the stacking of adjacent nanosheets on the nanoscale. Judicious choice of crosslinkers can not only bridge the MXene nanosheets to endow them with better stability and regulate the parameters of the nanogalleries for more precise sieving, but also arrest the oxidative issue of MXene under aqueous conditions. Herein, we reported a facial strategy by introducing a series of organic phosphonic acids (OPAs) bearing different numbers of phosphonic acid groups as spacer sequences to enlarge the inner space of an MXene laminate membrane (Fig. 1). These active phosphonic acid groups tend to combine with MXene flakes to form a covalent Ti–O–P bond *via* interfacial nucleophilic addition and sequential condensation reaction.<sup>20</sup> The pillared membrane with well-defined nanochannels delivers a five-fold increase in water

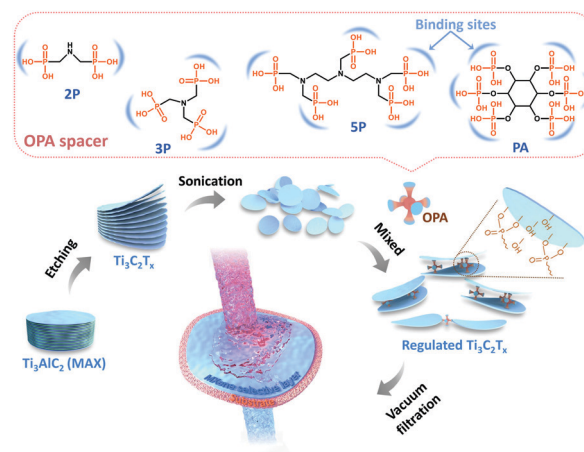


Fig. 1 Schematic of the fabrication of organic phosphonic acid (OPA) modified MXene membranes.

<sup>a</sup> Key Laboratory of Material Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology), Ministry of Education, Wuhan, 430074, P. R. China. E-mail: wangyan@hust.edu.cn

<sup>b</sup> Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science & Technology, Wuhan, 430074, P. R. China

<sup>c</sup> Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, 10691, Sweden. E-mail: miao.zhang@mmk.su.se

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permeance in comparison with the pure one. Equally importantly, the retained high rejection and the remarkable tolerance to harsh aqueous environments make this methodology a step forward for future practical applications.

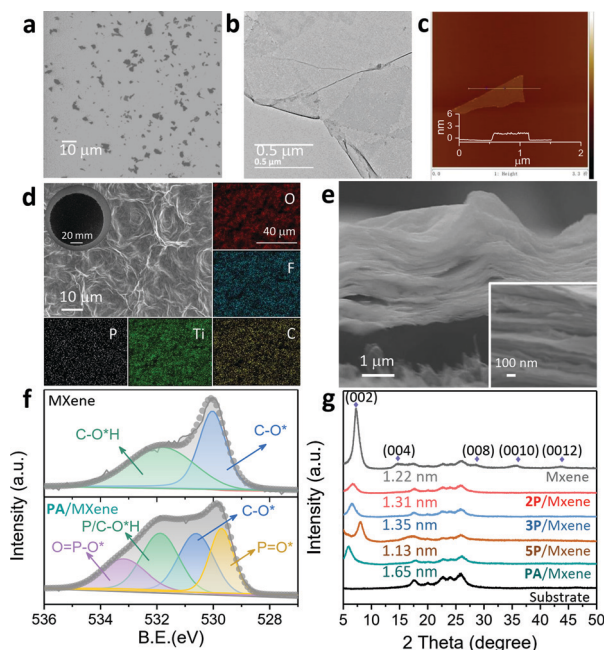
The  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets were synthesized following the well-established procedure.<sup>21</sup> To initiate the reaction and intercalation of OPA to  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets, certain amounts of iminodi(methylphosphonic acid), nitrilotri(methylphosphonic acid) and diethylenetriaminepentakis (methylphosphonic acid) (termed  $n\text{P}$ , where  $n$  denotes the number of phosphonic acid groups), and phytic acid (PA) were added into suspensions of  $\text{Ti}_3\text{C}_2\text{T}_x$ . MXene membranes were prepared by vacuum filtration. The as-prepared  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets were first characterized by scanning electron microscopy (SEM, Fig. 2a), transmission electron microscopy (TEM, Fig. 2b), and atomic force microscopy (AFM, Fig. 2c). Corresponding images consistently indicate that the nanosheets are smooth yet rigid with a height of  $\sim 2$  nm and lateral size of 0.5–5  $\mu\text{m}$ . Given the theoretical thickness of  $\sim 1.0$  nm for a monolayer,<sup>22</sup> the extra thickness can be attributed to water molecules absorbed on the  $\text{Ti}_3\text{C}_2\text{T}_x$  surface terminal groups.<sup>23</sup> The corresponding elemental distribution of the  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets can be found in the mapping results of energy dispersive X-ray spectroscopy (EDS) (Fig. S1, ESI<sup>†</sup>). Successful etching, exfoliation, and restacking are further confirmed by X-ray diffraction (XRD) patterns (Fig. S2, ESI<sup>†</sup>), as the peak at  $39^\circ$  for (104) planes disappeared and the diffraction peak for (002) planes shifted to lower angles

after etching.<sup>24</sup> The high-resolution transmission electron microscope (HRTEM) image identifies the high crystallinity and structural integrity of monolayer  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets (Fig. S3, ESI<sup>†</sup>). Furthermore, clear lattice fringes of the Ti atom layer shown in the selected area electron diffraction (SAED) patterns indicate the well-preserved hexagonal symmetry structure (Fig. S3, ESI<sup>†</sup>).<sup>25</sup> The zeta potential of the  $\text{Ti}_3\text{C}_2\text{T}_x$  suspension is measured as  $\sim -38.9$  mV at pH 7, implying a good dispersion stability of  $\text{Ti}_3\text{C}_2\text{T}_x$  in water.

The dynamic light scattering (DLS) results of the corresponding mixed suspensions show that the average particle size of OPA modified  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets is enlarged compared to that of the pristine one (Fig. S4, ESI<sup>†</sup>), indicating the cross-linking of MXene laminates. Accordingly, the zeta potential value of OPA-added samples is more negative than that of the pristine  $\text{Ti}_3\text{C}_2\text{T}_x$  suspension, indicative of successful modification of  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets (Fig. S5, ESI<sup>†</sup>). In addition, the corresponding  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets were sedimented after 12 h with the modification of PA (Fig. S6, ESI<sup>†</sup>), further demonstrating the successful crosslinking of  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets by PA. It is worth noting that the particle size of  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets studied here follows the order of  $5\text{P}/\text{MXene} > 2\text{P}/\text{MXene} > 3\text{P}/\text{MXene} > \text{PA}/\text{MXene} > \text{MXene}$ , manifesting the differing interaction between  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets and different OPAs. This enables the possibility to produce tailor-made  $\text{Ti}_3\text{C}_2\text{T}_x$  composite microstructures by varying the OPA.

Corrugations can be observed on the surface of both pristine and OPA modified MXene membranes (Fig. 2d and Fig. S7, ESI<sup>†</sup>). The inset macroscopic membrane images show uniform deposition of MXene onto the support without visible defects. The OPA-modified MXene membranes display looser stacking with larger thicknesses (2.814, 2.957, 3.430 and 3.525  $\mu\text{m}$  for 2P, 3P, 5P and PA/MXene membrane, respectively) than that of the pristine one (2.051  $\mu\text{m}$ ) (Fig. 2e and Fig. S8, ESI<sup>†</sup>), which provides preliminary evidence for successful intercalation and opening of nanochannels.

Fourier transform infrared (FTIR) was applied to characterize the Ti–O–P bonding between OPA molecules and MXene nanosheets (Fig. S9, ESI<sup>†</sup>). The spectrum of PA/MXene exhibited P–O and P=O bands at  $1010\text{ cm}^{-1}$ ,  $1210\text{ cm}^{-1}$  and  $1365\text{ cm}^{-1}$ ,<sup>20</sup> respectively, suggesting the successful chemical grafting of OPA molecules onto MXene nanosheets. To probe the phosphorus (P) content, X-ray photoelectron spectroscopy (XPS) analysis and EDS mapping are conducted. Unsurprisingly, all OPA modified MXene membranes possess obviously higher P amounts compared with the pure one (Fig. S7, S10 and Tables S1, S2, ESI<sup>†</sup>). For OPA-modified MXene membranes, the peaks at 529.7 and 533.2 eV are assigned to P=O\* and O=P–O\* species, respectively, indicative of the presence of phosphoric acid groups (Fig. 2f and Fig. S10, ESI<sup>†</sup>).<sup>26</sup> These results further manifest the intercalation of OPA molecules. The cross-sectional EDS mapping indicates the homogeneous modification of OPA molecules on MXene nanosheets (Fig. S11, ESI<sup>†</sup>). The direct result of the successful intercalation of OPA into nanosheets is the regulation of the interlayer distance for MXene-based membranes. This was further studied by XRD. The pure MXene membrane displays the (002)



**Fig. 2** (a) SEM images, (b) TEM images, and (c) AFM images of  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets. (d) Surface and the corresponding element mapping, and (e) cross-sectional SEM images of the PA/MXene membrane. Inset shows the digital photo of the corresponding membrane on a nylon-66 substrate. (f) Peak deconvolution of narrow-scan spectra of O 1s for pure and PA/MXene membranes. (g) XRD patterns of pure and OPA modified MXene membranes.





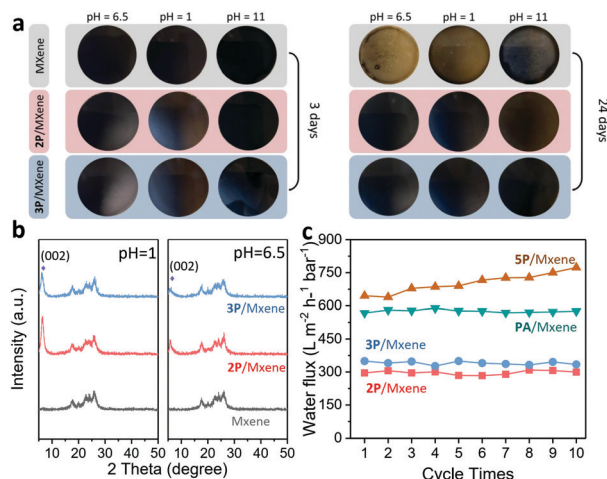


Fig. 4 (a) The stability of pure and OPA modified MXene membranes in natural, acid and alkaline solutions. (b) XRD patterns of the pure, 2P/MXene and 3P/MXene membrane after the solution immersion. (c) The variations of permeance with cycle times for pure and OPA modified MXene membranes.

(pH = 1) and alkaline (pH = 11) environments, demonstrating that OPA modified MXene membranes are fairly robust to tolerate harsh environments. XRD spectra were further collected to examine the regularity and integrity of the membranes' interlayer channels. Obviously, the peaks of the (002) plane for the pure MXene membrane disappear completely (Fig. 4b), suggesting the radical destruction and oxidation of MXene laminates. In contrast, OPA modified MXene membranes could still retain barely changed *d*-spacings (Fig. 4b) without oxidation. Such promising stability may be attributed to the capping effect of OPA molecules that blocks the water and oxygen attacking the metal sites of the nanosheets.

Besides the static test, the dynamic stability of the OPA modified membrane was also evaluated under long-term filtration of pure water. Excluding the 5P/MXene membrane, the OPA-modified MXene membranes show no significant decrease in permeance in a 10-cycle test (each cycle for 30 min filtration) (Fig. 4c), and the XRD results (Fig. S16, ESI<sup>†</sup>) of the corresponding MXene also give a well-maintained *d*-spacing, showing their promising stability for practical applications.

In conclusion, we successfully regulated the nanochannels of MXene laminates *via* the intercalation of OPA molecules between adjacent nanosheets. Such membranes show five-fold increases in water permeance compared with the pure one. More importantly, owing to the strong interactions between OPA molecules and MXene nanosheets, these laminates possess relatively regular and stable stacking to diminish inevitable defects during the membrane fabrication. This contributes to the precise molecular sieving, and also the tolerance of membranes to harsh chemical environments. This study paves a way for the development of highly channel-regulated MXene membranes with superior selectivity and stability.

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## Conflicts of interest

There are no conflicts to declare.

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