Oriented Zeolitic Imidazolate Framework (ZIF) Nanocrystal Films for Molecular Separation Membranes

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ABSTRACT: The direct synthesis of oriented, defect-free nanocrystal metal–organic framework (MOF) films is a challenging step toward their applications in advanced technologies, such as optics, sensing, and membrane-based separations. Here, we propose a one-step, in-situ growth approach to synthesize oriented zeolitic imidazolate framework-L (ZIF-L) membranes by using an isoporous film as the support. The high metal-binding efficiency, as well as the ordered pore structure, given by the polymeric isoporous support, promote the preferred nucleation and rapid growth of vertically aligned ZIF-L nanocrystals to construct dense membranes. Vertically aligned nanochannels between the inter-lattice of ZIF-L are therefore formed through the polycrystalline membrane. The membrane exhibited a high H₂ permeance, 1635 GPU (1 GPU = 1 × 10⁻⁶ cm³ (STP)/cm² s cmHg), and H₂/C₃H₈ selectivity of 516, when targeting hydrogen separation from hydrocarbon in a steam reforming process. The membrane can be further used in organic solvents nanofiltrations, with a methanol permeance of 38.7 L m⁻² h⁻¹ bar⁻¹, and >90% rejection of organic dye molecules. Furthermore, by taking advantage of the anisotropic pore structure, the ZIF-L membrane could be further hydrolyzed to produce ultrathin ZIF-L nanosheets with a thickness ~5 nm, which provides a facile platform to synthesize two-dimensional MOFs nanosheets.

KEYWORDS: oriented nanocrystal membrane, isoporous support, gas separation, liquid separation, 2D MOF nanosheets
1. Introduction

Nanocrystal materials such as zeolites, metal–organic frameworks (MOFs) and covalent-organic frameworks (COFs) are being widely considered for gas storage, sensing, drug delivery, catalysis and separations.\(^1\) Particularly, MOFs, made from a diverse combination of organic linkers and metal nodes, are recognized for the remarkably high surface area, controllable pore architecture and chemical functionalities.\(^2\) However, MOFs in the form of powders cannot always completely fulfill their potential for realistic applications, and the further processing of MOFs nanocrystals into polycrystalline thin films could be highly useful for that.\(^3\) Currently, various methods have been reported to synthesize polycrystalline MOF films, including \textit{in-situ} growth,\(^4\) seeded secondary growth,\(^5\) interfacial synthesis,\(^6-7\) etc. These methods could possibly produce thin layer MOF films without defects. Besides the continuous growth, for MOFs nanocrystals with anisotropic pore architectures, the preferred orientation may maximize the exposure of desired pore apertures and eliminate the generation of undesired grain boundary defects.\(^8\) However, the development of facile preparation methods to achieve oriented and continuous nanocrystal films remain challenging, especially when they are targeted as defect-sensitive molecular separation membranes, which is regarded as a green process that consumes 90% less energy, compared with traditional distillation.\(^9\)

Currently, the substrate-seeded heteroepitaxy approach on functionalized surfaces is primarily used to synthesize MOF nanocrystal membranes with in-plane or out-of-plane orientations. In these methods, the supports are firstly covered with seed crystals by dip-coating or casting, followed by a few rounds of secondary growth. For instance, Zhong \textit{et al}.\(^10\) synthesized continuous \textit{c}-oriented zeolitic imidazolate framework-L (ZIF-L) membranes from \textit{c}-oriented ZIF-L seed layers. The seed layer was obtained by vacuum filtration of pre-synthesized crystals onto porous
alumina supports in the presence of polyethyleneimine (PEI). Recently, Sun et al.\textsuperscript{11} prepared highly $c$-oriented NH$_2$-MIL-125 membranes by combining the oriented seeding and controlled in-plane epitaxial growth. A dynamic air-liquid interface-assisted self-assembly method guaranteed the uniform, $c$-oriented, coating-monolayer of the crystals on alumina supports. Besides using the oriented crystals as the seeds layers, the randomly oriented seeds layers can also induce oriented MOF membranes. The mechanism is interpreted as the Van der Drift-type growth, which is determined by the competition of growth rates at different crystallographic axes.\textsuperscript{12} Following this principle, ZIF-7 membranes were synthesized by depositing a layer of PEI with randomly oriented ZIF-7 nanoparticles and then promoting a secondary growth.\textsuperscript{5} The produced polycrystalline ZIF-7 membranes were composed of intergrowth ZIF-7 nanorods oriented with the $c$-out-of-plane. Similar approaches have also been demonstrated for ZIF-L,\textsuperscript{10} $M_3$(HCOO)$_6$,\textsuperscript{13} ZIF-69\textsuperscript{14} membranes.

It is noteworthy that all the reported approaches employed the pre-seeding process. The orientation of the resulting membranes is crucially dependent on the uniformity and distribution of the seeds covering the support and the optimization of this process demands delicate manipulation methods.\textsuperscript{11, 15} In addition, extra organic molecules, like PEI, are frequently introduced as a buffer layer to promote the MOF growth, as well as to build a robust attachment between the substrate and the MOF layers.\textsuperscript{5, 10} Furthermore, the tedious multiple secondary growths adds complexity to the synthesis procedure.

In contrast to the secondary growth method, the one-step \textit{in-situ} growth to produce oriented MOF nanocrystal membranes seems to be a more straightforward approach.\textsuperscript{16} However, since the nucleation and crystallization of MOFs occur simultaneously in the bulk solution and on the substrate surface, a precise orientation and defect control is not easy, which depends on the surface chemistry as well as the architecture of the substrate. Presently, by adopting the \textit{in-situ} approach,
limited success has achieved in oriented MOF membranes\textsuperscript{17-18}. Moreover, for these membranes, the separation is based on the crystal defects rather than the intrinsic pore of MOF. Achieving oriented MOFs membranes free from grain boundary defects, aimed for molecular sieving, is more challenging.

Herein, we demonstrated that by using a polymeric isoporous support, oriented polycrystalline MOF membranes can be fabricated by using a direct and facile way. Our \textit{in-situ}, template-free approach, carried out under mild conditions, enables the efficient growth of dense MOF nanocrystal membranes. We adopted zeolitic imidazolate framework (ZIF)-L, a two-dimensional (2D) ZIF with leaf-like morphology, as the showcase material, because of the unique pore structures along different axes\textsuperscript{10, 19}. ZIF-L is composed of 2D lattice layers along the \textit{c} direction. Compared to the well-known sodalite topology of 3D structure of ZIF-8, in ZIF-L not all imidazole linkers are Zn-coordinated and are more available for H-bond forming with other linkers. They stack along the \textit{c} axis mainly \textit{via} the hydrogen bonding between 2-methylimidazole (2-MI) groups\textsuperscript{19}. These H-bonds are easier to disrupt than the stronger imidazole-Zn\textsuperscript{2+} links and exfoliated planes are more conveniently formed.

Compared with other attempts to grow ZIF-L membranes\textsuperscript{10, 20-21}, the yield defect-free ZIF-L membranes with vertically aligned interlayer channels showed high molecular sieving performance in the purification of hydrogen from light hydrocarbons, which have great significance in chemical, environmental and energy-related industries\textsuperscript{22}. The membrane was also tested in the organic solvent nanofiltration process, a common separation involved in pharmaceutical industries\textsuperscript{23}. More interestingly, by using the oriented ZIF-L nanocrystal membrane as a precursor, we performed simple water hydrolysis to obtain ultrathin 2D ZIF-L nanosheets with a thickness of \textasciitilde 5 nm, which provide a new platform to synthesize 2D MOFs.
2. Materials and Methods

2.1 Preparation of PS-b-P4VP supports

The PS-b-P4VP support was prepared by the self-assembly and nonsolvent-induced phase separation (SNIPS) method following our previously reported procedure with minor modifications (Figure S1).\(^{24}\) Firstly, a dope solutions containing 16 wt% PS-b-P4VP, 24 wt% DMF, 44 wt% dioxane and 16 wt% acetone was prepared and cast on a glass plate with a doctor blade having a gap of 200 μm. After an evaporation for 20 seconds, the cast solution was immersed in a nonsolvent bath (water) until the film detached from the glass plate. The fabricated porous films were stored in water for further use.

To make the membrane more stable in organic solvents, while retaining the isoporous structure, we modified the membrane by selective oxidation of PS-b-P4VP.\(^ {25}\) The as-fabricated PS-b-P4VP membrane was placed in a beaker containing CH\(_3\)COOH and H\(_2\)O\(_2\) (1:1 in volume) at 50℃ for 24 h. Under this condition, the P4VP groups were converted into P4VPN-oxide, as shown in Figure S8.

2.2 Preparation of oriented ZIF-L membranes

The oriented ZIF-L membrane was prepared by a facile \textit{in-situ} growth method. Zn(NO\(_3\))\(_2\)·6H\(_2\)O and 2-MI were firstly dissolved in water to obtain the aqueous solutions. Then the isoporous support was fixed on a glass plate to be vertically placed in a beaker containing Zn(NO\(_3\))\(_2\)·6H\(_2\)O solutions for 20 min. Subsequently, an equal volume of 2-MI solution was added and the solution was kept stirring at room temperature (~20 °C) for 2 h. The obtained membrane was rinsed with water for 3 times and kept in a vacuum oven at 60 °C overnight. The mole ratio of 2-MI to Zn\(^{2+}\) is fixed at 8:1, with Zn\(^{2+}\) concentration varies from 0.05, 0.1 and 0.2 M.

2.3 Hydrolysis of oriented ZIF-L membranes:
40 mg ZIF-L flakes and a piece of ZIF-L-M1 membrane (1 cm×1 cm) were separately placed in a vial containing 40 mL water. Then the vials were continuously rolling for 5 days. Afterward, the ZIF-L flakes were repeatedly centrifuged at 9000 rpm for 10 min, washed with methanol and dried. The ZIF-L-M1 membrane was washed with water for 3 times to remove the residues and dried before checking.

3. Results and Discussion

3.1 Formation of ZIF-L nanocrystal membrane

We employed polystyrene-\textit{b}-poly-4-vinylpyridine (PS-\textit{b}-P4VP) block copolymer (chemical structure shown in Figure 1a) to prepare the isoporous support, via the self-assembly and nonsolvent-induced phase separation (SNIPS) method,\textsuperscript{26} following a previous report with minor modifications.\textsuperscript{24} Briefly, the block copolymer self-assembled into micelles after dissolving in a ternary solvent mixture. Afterward, the solution was cast on a glass plate. The solvent was evaporated for 20 s, leading to an ordered isoporous surface layer, which was then kinetically entrapped by immersion in a precipitation water bath.\textsuperscript{27} The detailed information can be found in the Experimental Section and displayed in Figure S1 (Supporting Information). The above process yielded a polymer film with an isoporous skin layer (pore size ~40 nm, layer thickness ~500 nm) and a disordered sublayer (Figure 1b and c). According to the self-assembly mechanism of PS-\textit{b}-P4VP micelles during the film formation, the periphery of isoporous channels is enriched with P4VP blocks,\textsuperscript{28} from which the nitrogen atom bears lone electron pair. The P4VP blocks have been proved to be a strong ligand to coordinate with various metals ions, including Zn\textsuperscript{2+}, Cu\textsuperscript{2+}, and Au\textsuperscript{3+}. To check the coordination efficiency of Zn\textsuperscript{2+} on the membrane surface, we performed the XPS measurement by using PS-\textit{b}-P4VP isoporous films that were pre-dipped in Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, then washed with water. The N and Zn atomic percentages are 6.33 and 4.57%, respectively.
(Figure S2, Supporting Information), which means that a significant portion of N (~72%) of the P4VP groups was coordinated with Zn$^{2+}$. The coordinated Zn$^{2+}$ provides sufficient nucleation sites for the ZIF growth.

To prepare the oriented ZIF-L membrane, we first vertically immersed the PS-\textit{b}-P4VP support in Zn(NO$_3$)$_2$·6H$_2$O solution to implement the coordination, then an equal volume of 2-methylimidazole (2-MI) was added. The solution was then stirred to facilitate the crystal growth on the support. The detailed preparation procedure is described in the Experimental Section and illustrated in Figure 1e. To check the morphology of the membrane building blocks, we synthesized ZIF-L crystals at the same conditions without supports (details are shown in Supporting Information). After the complete reaction of two precursors within 2 h, the obtained ZIF-L crystals exhibit a leaf-like morphology (scanning electron microscopy (SEM) images shown in Figure 1d and Figure S3, Supporting Information).
Figure 1. Preparation of oriented ZIF-L membrane. (a) Chemical structure of PS-b-P4VP, SEM images of (b) the surface and (c) cross-section of the isoporous support film, (d) SEM image of ZIF-L crystals by using Zn$^{2+}$ precursor concentration of 0.1 M. (e) Schematic illustration of the membrane preparation.

We first investigated the effect of Zn$^{2+}$ concentration on the ZIF growth, in all cases the mole ratio of 2-MI to Zn$^{2+}$ is fixed at 8:1 to guarantee the formation of ZIF-L crystals.\textsuperscript{19} The SEM images of membranes, synthesized using Zn$^{2+}$ precursor concentrations of 0.05, 0.1 and 0.2 M, are shown in Figure 2a-f. The results demonstrate that the ZIF-L crystals grew in the $b$-out-of-plane orientation for all three concentrations. The concentration of precursors exerts a significant effect on the crystal structure of ZIF-L membranes. In a dilute Zn$^{2+}$ concentration (0.05 M, Figure 2a and b), the ZIF-L crystals were more separately grown, compared with membranes prepared under higher Zn$^{2+}$ concentrations. The resulting membrane displays microvoids and less ordered
structure, seen from the cross-section, and cannot be regarded as dense. In contrast, increasing the 
Zn$^{2+}$ concentration to 0.1 and 0.2 M could lead to a denser structure with better orientation (Figure 2c-f and Figure S4 (Supporting Information)). In addition, the thickness of the ZIF-L crystals increased from 180 nm to 330 nm and 490 nm due to higher nucleation rates with increasing Zn$^{2+}$ concentration. The atomic force microscope (AFM) images in Figure 2i show a rough surface structure with root mean squared roughness (Rq) value of 491 nm.

The SEM cross-section images at the interlayer (Figure S4g, Supporting Information) indicate an intimate contact between the ZIF-L layer and the isoporous support, which is ascribed to the strong coordination between P4VP and Zn$^{2+}$. The isoporous structure is well-maintained with traces of ZIF infiltration, which can be further proved by the EDS mapping of Zn across the entire membrane (Figure S5, Supporting Information). It should be also noted that, due to the benefits from the isoporous polymer, our ZIF-L membrane has a thickness of only ~2.1 µm, which is 60% less compared with other reported ones$^{10,20}$ and should contribute to a higher permeance.
Figure 2. Morphology and structure of the oriented ZIF-L membranes. (a, c, e) Surface and (b, d, f) cross-section SEM images of ZIF-L membranes prepared with a Zn\textsuperscript{2+} concentrations of (a, b) 0.05, (c, d) 0.1, and (e, f) 0.2 M, respectively. The mole ratio of 2-MI to Zn\textsuperscript{2+} was fixed at 8:1 for all three synthesis conditions. (g) Schematic illustration of the orientation mechanism. (h) The XRD patterns of the ZIF-L powder and ZIF-L membranes. (i) AFM micrograph of the ZIF-L membrane synthesized with a Zn\textsuperscript{2+} concentration of 0.1M.

The oriented growth of ZIF-L crystals can be explained by the Van der Drift growth model, which has been applied to interpret the preferred growth of zeolite and MOF membranes.\textsuperscript{10, 12, 31} For the case of ZIF-L with anisotropic morphology, in the initial stage, the crystals grow in all possible crystallographic directions. However, since the growth rate along \textit{b} direction is much faster than that along others, the structure will develop faster in this direction. When crystals are initiated close to each other on the membrane surface, as they develop, they will reach a point when they tend to touch each other. Growing would then be possible only perpendicularly to the
surface, which direction affords more free space for rapid growth. As illustrated in Figure 2g, the higher precursor concentration could accelerate the growth rate, form thicker crystals and increase the possibility of contact between adjacent ZIF-L crystals easier, hence leading to denser polycrystalline membranes. Moreover, thicker ZIF-L crystals are formed under higher precursor concentration, making the crystal contacting more easily. However, the intrinsic Van der Drift growth mechanism works only efficiently on a well-designed support, on which the parameters include the surface chemistry and pore structure. Compared with other pre-seeding methods, the support we used are enriched with Zn$^{2+}$-binding P4VP groups on the surface. The abundant Zn$^{2+}$ will significantly promote the heterogeneous nucleation of ZIF-L crystals, leading to a preferred growth on the support, rather than in the bulk of the solutions.

On the other hand, the uniform pores give a more ordered orientation. To check the effect of pore uniformity on the morphology of resulting ZIF-L layer, we grew ZIF-L on the back surface of an isoporous film. The back surface has a random porous structure, but the same chemistry property as the top surface. The obtained system had a discontinuous top layer with distributed and random oriented ZIF-L crystals (Figure S6, Supporting Information). The distinct results indicate that a substrate with a uniform pore structure guides the ordered growth of the final ZIF-L layer. The orientation of ZIF-L crystals could be further proved by the X-ray Diffraction (XRD) patterns. The XRD peaks of synthesized ZIF-L powder match well with the simulated ones, indicating the successful synthesis of ZIF-L crystals. The diffractogram of the isoporous support only has three broad peaks (Figure S7, Supporting Information), whereas the ZIF-L membranes (Figure 2h) diffractogram has sharp peaks at the same 2θ positions as those of the ZIF-L powder, but with lower intensity. The crystallographic preferred orientation (CPO) indexing method was used to analyze the degree of orientation. The higher CPO index, indicated by the height ratio of
certain peaks ((020) to (112) for ZIF-L), means a higher degree of orientation. For the ZIF-L powder with random orientation, the CPO_{(020)/112} is 0.47. In contrast, the ZIF-L membranes prepared by Zn^{2+} concentration of 0.05, 0.1 and 0.2 M, have CPO_{(020)/112} values of 7.7, 15.3 and 14.7, respectively, indicating the formation of highly orientated ZIF-L crystals under high precursor concentrations. The CPO index are also higher than that *in-situ* grew on other inorganic supports like Al_{2}O_{3}\textsuperscript{17} and stainless steel meshes\textsuperscript{20}.

### 3.2 Separation performance of ZIF-L nanocrystal membrane

We first tested the gas permeation properties of the ZIF-L membrane to make sure there is no grain boundary defects. As mentioned earlier, the ZIF-L crystal is constituted by a 2D layered structure. The 2D layers are stacked along the $c$ axis mainly *via* hydrogen bonds between the 2-MI groups. The interlayer channels of the neighboring lattices have flexibility due to the weak hydrogen bonding and are therefore more permeable than the more fixed hexagon pores in ZIF-8\textsuperscript{19, 32}. Especially, when the ZIF-L crystals are oriented in the $b$-out-of-plane direction, the 2D flakes naturally construct vertically aligned channels (the structure is illustrated in Figure 3a). By using the PS-$b$-P4VP isoporuous support, and precursor concentration and ratios of $c_{\text{Zn}^{2+}}$=0.1 M, $c_{2\text{-MI}}/c_{\text{Zn}^{2+}}$=8/1, we fabricated ZIF-L-M1 membranes.

The membranes were tested with gas molecules having different kinetic diameters at a feed pressure difference of 1 bar. The gas permeance is a result from the sorption and diffusion through the ZIF-L membrane. CO$_2$, C$_3$H$_6$ and C$_3$H$_8$ are easily condensable gases. They may have preferable interactions with the 2-MI groups in the channels to result in a high sorption capacity\textsuperscript{19}. On the other hand, the gas permeance decreases with increased kinetic diameters, which indicates the gas diffusion is a major contribution to the permeance, similar to the case in some MOF membranes\textsuperscript{20}.\textsuperscript{33} A high H$_2$ permeance of 1635 GPU (1 GPU = $1 \times 10^{-6}$ cm$^3$ (STP)/cm$^2$ s cmHg), and H$_2$/C$_3$H$_8$
selectivity of 515.7 was obtained (Figure 3b). Due to the lower ZIF-L thickness by our in-situ approach, the \( \text{H}_2 \) permeance is \( \sim 1.5 \) times higher than the membranes prepared by other secondary growth methods.\textsuperscript{10,20} And the ZIF-L-M1 membrane showed similar \( \text{H}_2/\text{CO}_2 \) selectivity (6.3) with other \( b \)-oriented ZIF-L membrane (5.5).\textsuperscript{10} These facts all verify the dense structure of ZIF-L membrane. Therefore, by using the isoporous membrane as the support we can achieve the oriented ZIF-L channels by a one-step approach with only 10-20\% of the time used by other methods.

Since the ZIF-L has more flexible channels, we suppose the oriented membranes may be also advantageous in the separation of liquids contaminated by other small molecules. We then performed nanofiltration tests in both aqueous and organic solvent medium by using dye molecules with different sizes. The pristine PS-\( b \)-P4VP support had a water permeance of 852 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). After growing a \( \sim 2.1 \) \( \mu \)m ZIF-L layer, the obtained ZIF-L-M1 membrane, with vertically aligned channels, had a water permeance of 51.6 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). We also evaluated the ZIF-L membrane in organic solvent nanofiltration (OSN), by testing the dye rejection in methanol, which is a commonly applied organic solvent for pharmaceuticals. However, the pristine PS-\( b \)-P4VP membrane used as support swells in methanol. To restrain the excessive swelling of the membrane in methanol, we conducted a mild oxidation (details shown in Experimental Section).\textsuperscript{25} The results in Figure S8 prove the successful oxidation of P4VP groups, with a retained isoporous structure. The obtained polyanionic polymers could attract an abundant amount of \( \text{Zn}^{2+} \) ions via electrostatic interaction, to promote the nucleation and growth of the ZIF-L membranes. The obtained ZIF-L-M2 membrane, prepared in condition analogous to those used for ZIF-L-M1, had similar dense morphology (Figure S8e and S8f). The ZIF-L-M2 membrane exhibited a high methanol permeance of 38.7 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\).
The dye rejection performance with the corresponding tested solute sizes is shown in Figure 3c. We conducted the rejection tests by using a high concentration of dyes (50 ppm), with a 30 mL of feed dye solution and taking the permeate and retentate samples for measurement after 20 mL of the solutions passing through, to eliminate the effect of dye sorption on the rejection performance. The photographs of feed and permeate samples are shown in Figure S9 (Supporting Information), and the UV-Vis of the tested solutions are shown in Figure S10 (Supporting Information). Both ZIF-L membranes exhibited >90% rejection to Acid Fuchsin, a dye with 1.1×1.1 nm size and molecular weight of 585 g/mol. For Methyl Orange (M.W. 327 g/mol, size 1.2×0.7 nm), the rejection was slightly lower but still larger than 80%. It should be mentioned, though the membrane showed high permeance and rejection in nanofiltration process, the rejection performance is lower than anticipated, which should be ~100%, since the membrane has high gas selectivity. The loss in rejection might be explained by the swelling effect of solvent molecules such as water and methanol. During the permeation process, solvent molecules get into the interlayer channels, weaken the hydrogen bonding between the 2-Hmim groups and widen the channel opening. The channel reforming phenomenon in the presence of guest molecules has also been reported for ZIF-L membranes.32 The rejection increases as dye sizes increase, confirming the size sieving ability of the polycrystalline membranes. Moreover, the vertically aligned channels in both ZIF-L and isoporous support layer contribute to a high permeation pathway for the solvent molecules, leading to a higher permeance than other MOF membranes.34-36
Figure 3. Gas permeation and nanofiltration performance of the ZIF-L membranes. (a) The molecular transport mechanism in the membrane. (b) Gas permeance and ideal H$_2$/gas selectivity of ZIF-L-M1 membrane. (c) Dye rejection performance in water and methanol. (d) Long-term stability of the membranes.

The stability of the MOF membranes is highly relevant in liquid separations and has been focus of research in different groups.\textsuperscript{37-39} We tested the long-term stability of the membranes in water and methanol solvents, as shown in Figure 3d. For the first 40 hours, the ZIF-L membranes exhibited stable permeance and rejection in both water and methanol. However, as the test continues, the water permeance rises and the Rose Bengal rejection drops, which implies that the ZIF-L membrane underwent hydrolysis, possibly creating defects. In contrast, the ZIF-L
membrane was stable for 70-hour testing in methanol. The higher stability of membrane in methanol compared with water indicates that water more easily hydrolyzes the ZIF-L membrane by breaking the interlayer hydrogen bond.

### 3.3 Formation of nanosheets

To confirm a potential structure change, we kept the ZIF-L flakes and the ZIF-L membrane in water for 5 days. Surprisingly, their hydrolyzed products had distinct morphologies. Similar to the reports of Low et al., the non-supported ZIF-L flakes were transformed into microsized regular aggregates formed by the assembly of ~800 nm-sized nanoparticles (Figure 4a and b), which were found to be ZIF-8. The mechanism was explained by the solvent-diffusion induced displacement of the 2D crystal lattices, followed by the rotation of 2-MI molecules and formation of Zn–2-MI–Zn bonds. In contrast, the hydrolysis of ZIF-L membranes produced a flower-like morphology composed by ultrathin nanosheets (Figure 4c-e and Figure S11, Supporting Information). The morphology evolution with the time of hydrolysis is shown in Figure S12. The diffractogram of the hydrolyzed membrane has peaks similar to those of the pristine ZIF-L membrane or ZIF-L powder (Figure S13, Supporting Information). Considering the less ordered structure in the hydrolyzed membrane, the ultrathin nanosheets have the same crystallographic structure as the ZIF-L flakes. The thickness of the nanosheets is ~ 5 nm, which is one of the lowest reported for the ZIF-8 family.

With the rising interests in 2D materials, facile methods to prepared 2D nanosheets are highly demanded in various applications. Currently, there are bottom-up (direct synthesis from the precursors) and top-down (exfoliation from the bulk materials) major strategies reported for synthesizing 2D MOFs. As a comparison, we did not succeed to synthesize ZIF-L via the bottom-up strategy by using low precursor concentration (c_{Zn^{2+}}=0.005 M), although a low precursor...
concentration has been reported to favor thinner ZIF-L flakes. However, the obtained particles were micrometer-sized rhombic dodecahedrons, a typical structure of ZIF-8 (Figure S14, Supporting Information). In contrast, our top-down hydrolysis strategy on the supported isoporous membrane is a simple but efficient method.

The formation of ultrathin ZIF-L nanosheets can be possibly explained by a hydrolysis mechanism induced by differential water diffusion/intrusion along the $b$ and $c$ axes (Figure 4f). During the hydrolysis, water diffuses from the surroundings along both $b$ and $c$ axes. The intrusion experiences lower resistance between layers kept together by imidazole-imidazole H-bonds than in points where Zn-imidazole is strongly coordinated. Paths are therefore faster opened along the $b$ axis, preferentially exposing the adjacent bonds to hydrolysis. In the case of flakes grown on a membrane support, the effect is even more pronounced. It takes much longer for the water molecules to transport along the $c$ axis towards the middle part of the membrane. The water intrusion is favored in the inter-lattice spacings along the $b$ axis, displacing the neighboring lattices to produce thinner nanosheets. For the non-supported ZIF-L flakes, prepared in the solution bulk, with a low thickness of $\sim$ 280 nm, the water has practically equal access to the bonds along the $b$ and $c$ axes to promote hydrolysis. Thin nanosheets are not preferentially formed in this case. Therefore, our controlled hydrolysis method under mild conditions provides a new platform for the synthesis of ultrathin 2D MOFs to be used in various applications.
Figure 4. Hydrolysis of ZIF-L flakes and the membranes. (a, b) SEM images of the hydrolyzed ZIF-L flakes. (c–e) SEM surface images of the hydrolyzed ZIF-L membranes. (f) The proposed hydrolysis mechanism.

4. Conclusions

In summary, we synthesized an oriented ZIF-L nanocrystal membrane on a polymeric isoporous support, by a one-step, in-situ growth method in aqueous conditions. The high density of Zn$^{2+}$-binding P4VP groups on the support surface, as well as the ordered pore structure provided by the isoporous structure promote the nucleation and rapid growth of dense ZIF-L membranes within 2 hours. The oriented lattices in ZIF-L membrane constructed vertically aligned channels for a fast molecular transport. The membrane exhibited a high H$_2$ permeance 1635 GPU (1 GPU = $1 \times 10^{-6}$ cm$^3$(STP)/cm$^2$ s cmHg), and H$_2$/C$_3$H$_8$ selectivity of 515.7. When used the membrane in organic solvents nanofiltrations, the methanol permeance reached to 38.7 L m$^{-2}$ h$^{-1}$ bar$^{-1}$, with >90% rejection to dyes with size larger than 1.1 nm. Moreover, the further hydrolysis of the oriented ZIF-L membrane led to the formation of ~5 nm ZIF-L nanosheets. This constitutes a facile
platform to synthesize ultrathin 2D MOFs, which could be used in broad applications, including membranes, adsorption, and catalysis.

ASSOCIATED CONTENT

Supporting Information.

Supporting Information Available: Supporting experimental on chemicals, characterization methods, membrane testing parameters, membrane preparation procedure, XPS of isoporous membranes, SEM images, EDS, and XRD spectra of ZIF-L membranes, the UV-vis spectra of dyes and SEM images of hydrolysis products. This material is available free of charge via the Internet at http://pubs.acs.org

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**Oriented ZIF-L nanocrystal membrane** is synthesized by a one-step, *in-situ* growth approach on a polymeric isoporous film. The membrane has high permeance and molecular rejection in gas and liquid separations. Further hydrolysis of the ZIF-L membrane provides a facile platform to produce ultrathin ZIF nanosheets with 5 nm thickness.