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ARTICLE TYPE

Zinc hydroxide nanostrands: unique precursor for ZIF-8 thin membranes toward highly size-sieving gas separation

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Well-intergrown ZIF-8 membranes are prepared directly from zinc hydroxide nanostrands without any modification of the substrate in ethanol/water at room temperature in a short time, and exhibit nice molecular sieving performance for gas separation after secondary growth. This strategy exhibits excellent reproducibility and versatility, and is suitable for large-scale production.

Metal-organic frameworks (MOFs) composed of metal ions or clusters and organic ligands are a new class of nanoporous crystalline organic-inorganic hybrid materials with well-defined pore structure.[1] Due to their particular topological structure, high porosity, and large surface area,[2] MOFs offer great potential in applications including gas adsorption,[3] separation,[4] catalysis,[5] sensing,[6] luminescence[7] and biomedicine.[8] Especially, zeolite imidazolate frameworks (ZIFs), a subclass of MOFs, containing metal nodes bridged through the nitrogen atom of imidazolate ligands with zeolite topology, combine the ideal features of MOFs and exceptional stability and microporosity of zeolite,[9,10] which make their membranes be broadly explored as ideal candidates for gas separation membrane,[11] gas sensor,[12] *etc*.[13]

Currently, the synthesis of MOF membranes is still in its infancy, which faces many challenges.[14,15] Because the heterogeneous nucleation of MOF crystal on substrates is not favored, it is difficult to fabricate compact MOF membranes through in-situ synthesis method, so that the modification of the substrate[16,17,18] and seed coating[19] used to promote the heterogeneous nucleation and crystal growth on the substrate are indispensable. However, these additional procedures complicate the synthesis process, which not only increase the cost of fabrication, but also limit its reproducibility and large-scale production. Furthermore, the preparation processes are mostly carried out under the condition of high temperature or high energy by using organic solvent such as DMF[20] or DEF,[21] which is expensive and may cause pollution to the environment.[22] Therefore, it is very necessary to develop a simple, effective, energy-efficient, and environmentally friendly strategy for the synthesis of MOF membranes.

The precursor of metal ions in the solution is mostly used to synthesize MOF membranes through heterogeneous nucleation on the substrate.[14] While, metal oxide/hydroxide can be used as precursor to fabricate MOF or MOF membranes through simple acid and alkali neutralization reaction that is waste-free.[23] ZnO,[18,20,24-27] CuO[28] and Al_2O_3[29] have been used as the modification of the support or reactive seeding to promote the heterogeneous nucleation and membrane adhesion to assist the synthesis of some MOF membranes. Nanoscopic $Cu(OH)_2$ thin film has been used as the unique metal source to fabricate HKUST-1 gas separation membranes with Knudsen selectivity at room temperature,[30] and bulk $Zn(OH)_2$ has been reported to produce ZIFs in pure or aqueous methanol.[23,31,32] Although the broadly studied IRMOFs and most of ZIFs are composed of Zn ions, to the best of our knowledge, dense and well-intergrown zinc related MOF membranes have not been reported by using nanoscopic solid zinc oxide/hydroxide as Zn source.

ZIF-8, one of the most studied prototypical ZIFs compounds, has sodalite (SOD) zeolite-type structure, large cavities of 11.6 Å accessible through small pore apertures of 3.4 Å in diameter, hydrophobic property and robust synthesis protocol.[31,33,34] Herein, dense and well-intergrown ZIF-8 membranes are directly synthesized by using zinc hydroxide nanostrands as the unique metal source to control the nucleation site without any modification of the support in ethanol/water at room temperature. After secondary growth, the obtained ZIF-8 membranes have shown nice molecular sieve performance for gas separation.

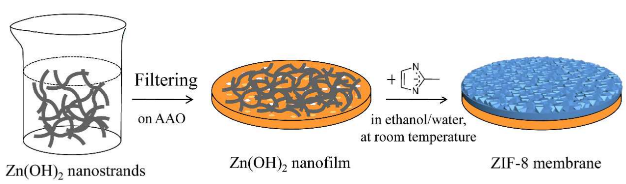

Figure 1. Schematic illustration of the synthesis process of the ZIF-8 membrane from zinc hydroxide nanostrands.

The synthesis process of the ZIF-8 membrane from zinc hydroxide nanostrands is depicted in Figure 1. Generally, the zinc hydroxide nanostrands are synthesized according to previous reports[35,36] and the nanoscopic precursor thin film is obtained by vacuum suction filtering 10 mL of the solution containing zinc hydroxide nanostrands on AAO. Then it is immersed into 10 mL ethanol/water solution (vol 1:4) containing 25 mM Hmim (Hmim=2-methylimidazole) without any modification at room temperature for 24 h to obtained the ZIF-8 membrane. Small amount of sodium formate is added to help to obtain better morphology.[16] The reaction process follows the formula: $Zn(OH)_2+2Hmim=Zn(mim)_2+2H_2O$.

Figure 2 shows the morphologies of the pristine zinc hydroxide thin film and the obtained ZIF-8 membrane from zinc hydroxide nanostrands. The precursor thin film is composed of fiber structures with the diameter of about 3 nm (Figure 2a), and its thickness is about 900 nm (Figure 2b). The thickness can be simply adjusted by varying the volume of the filtering solution (Figure S1). Obviously, ZIF-8 crystals start to appear as soon as the precursor is immersed into the solution after only 30 min (Figure S2b), and uniform and continuous polycrystalline layer consisted of rhombic ZIF-8 crystals with random orientation is obtained after 24 h (Figure 2c). The ZIF-8 crystals appear to overlap each other very well. The membrane is dense, and there is no visible gap at the grain boundary. Also, no interrupt exists in the cross-section image (Figure 2d). Therefore, the obtained ZIF-8 membrane from zinc hydroxide is well-intergrown. From the cross-section, it can be seen that the thickness of the obtained ZIF-8 membrane from zinc hydroxide nanostrands is about 800 nm (Figure 2d).

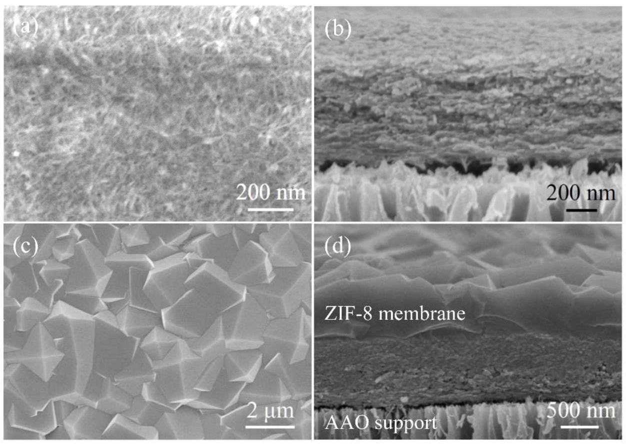

Figure 2. SEM images of the top view and cross-section: (a), (b) the zinc hydroxide thin film; (c), (d) the obtained ZIF-8 membrane from zinc hydroxide nanostrands, respectively.

The XRD partterns of the as-prepared ZIF-8 membrane from zinc hydroxide nanostrands (Figure 3c), are in good agreement with that reported in literatures unequivocally,[33] which confirms the formation of pure crystalline ZIF-8 phase. The peak with the highest intensity corresponds to the {011} plane of the ZIF-8 rhombic dodecahedron. Compared with simulated XRD patterns of the crystal powder,[19] no obvious preferred orientation is observed, which is consistent with the SEM results.

Different from conventional methods to synthesize MOF membranes, no exotic metal source is used in the proposed strategy. Therefore, it is sure that the Zn ions in ZIF-8 come from original zinc hydroxide nanostrands. At the early stage of 10 min, the fiber structure of the nanostrands is faintly visible, but many nanoparticles appear around them (Figure S2a). It means that the ultra-thin and highly positive surface of zinc hydroxide nanostrands mesoporous thin film[35,37] reacts with Hmim rapidly to form the ZIF-8 crystal nucleus by sacrificing themselves to provide Zn source. With prolonging the reaction time, $Zn(OH)_2$ nanostrands continues to be consumed and react with Hmim, which leads to the growth of ZIF-8 crystals (Figure S2b, c, and e). The precursor layer becomes thinner and thinner, while, the ZIF-8 layer becomes thicker and thicker (Figure S2d and f). The process doesn't stop until the ZIF-8 crystals develop into a compact membrane, when the reactant moleculars are hard to pass through the ZIF-8 membrane to further react due to the diffusion limitation. No free-standing ZIF-8 particels are found in the solution, which indicates that the whole formation process of ZIF-8 crystals is strictly limited on the surface of the precursor film. Therefore, on the one hand, the $Zn(OH)_2$ precursor film can provide metal ions through sacrificing themselves and initiate the growth of ZIF-8 without any surface modification. On the other hand, the precursor film exhibits an obvious structural directing effect that is in agreement with the transformation process of other solid precursors to MOFs.[30, 38-40]

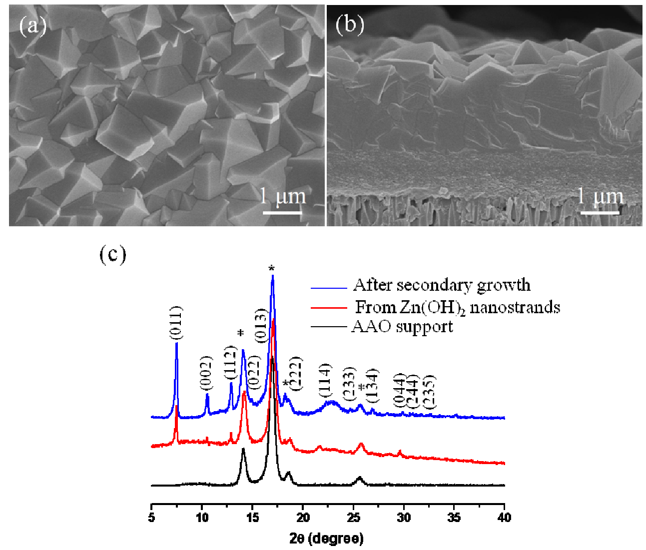

Figure 3. (a), (b) SEM images of the top view and cross-section of the obtained ZIF-8 membrane after secondary growth, and (c) XRD patterns of the ZIF-8 membranes from zinc hydroxide nanostrands and after secondary growth, respectively. Reflections from the AAO support are marked by the asterisks.

In order to illustrate the influence of the reaction conditions to fully understand the formation process, systematic experiments were carried out. It is found that the solvent component that has an effect on pH and solubility is crucial for the formation process of well-defined ZIF-8 membrane from zinc hydroxide nanostrands. As the ratio of ethanol in the solvent increases, the crystals become more and more loosely packed, and smaller and smaller (Figure S4a-d). This phenomenon may be attributed to the less basicity of ethanol than water[27,41] (The pH value changes of Hmim solution in different solvent components are shown in Figure S3) and less solubility of $Zn(OH)_2$ in ethanol.[27,38] The slow dissolution rate of $Zn(OH)_2$ limits the growth process. The acidity increases and more Hmim appears in its neutral form, so, after a period of reaction, enough neutral Hmim will be available in the solution for terminating the growth of ZIF-8 as stabilizing units, leading to the formation of small crystals.[16,42-44] Similarly, too much water dosen't benefit the reaction process (Figure S4e), which may be attributed to that as a kind of amphoteric compound like ZnO,[27,38] $Zn(OH)_2$ is prone to dissolve in acidic or basic solutions, hence, the coordination process tends to take place in solution rather than on the surface of zinc hydroxide nanostrands. In the synthesis strategy, the molar ratio of Hmim to Zn (not more than 12.5:1) is much lower than that of about 70:1 in other facile synthesis strategy using Zn ions as the precursor,[41] which can reduce the amount of the ligand used to a large extent.

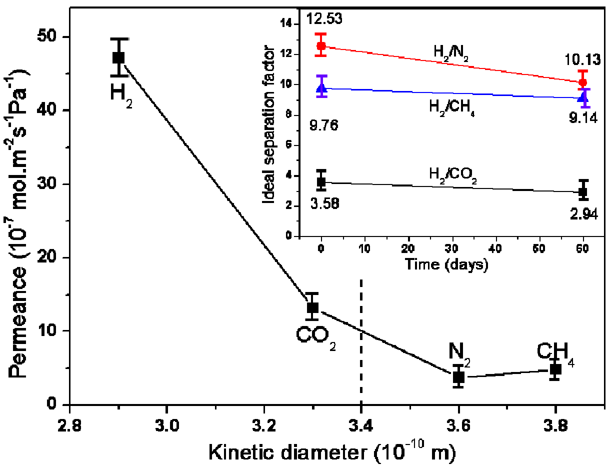

Figure 4. Single gas permeances through the ZIF-8 membrane after secondary growth as a function of the kinetic diameters of different gases. The dash line is the simulated ZIF-8 pore size, and the inset is the change of the ideal separation factors after the aforementioned membrane has been exposed to the ambient condition for two months. The permanence and selectivity is the averaged value for each point from five measurements data.

Due to the obtained ZIF-8 membranes from zinc hydroxide nanostrands are too thin to suffer from the high pressure when they are used for gas separation, secondary growth of the ZIF-8 membranes according to Pan *et al.*'s approach[41] is conducted. More compact and thicker membranes of which the thickness is about 2.5 μm are obtained (The details of the morphology and crystal structure are supplied in Figure 3), and their gas separation performances are also investigated. The permeances of a series of single gases through the membrane after secondary growth are independent of the trans-membrane pressure drop, which shows no existence of micropores or cracks in the membrane (Figure S5). Obviously, the permeances of different gases through the membrane after secondary growth depend on the kinetic diameters of the permeanting molecular: H_2 (2.9 Å), CO_2 (3.3 Å), N_2 (3.6 Å) and CH_4 (3.8 Å), which exhibits excellent molecular sieving property (Figure 4). Among them, the permeance of H_2 is about 47.14×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1}, which is about 40 times bigger than what has been reported by Bux *et al.*,[34] and about 10 times larger than 4×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} of Pan *et al.* that the thickness of the membrane is similar.[41] Due to the flexibility of the framework of ZIF-8,[34] N_2 and CH_4 whose dimension is bigger than the aperture of ZIF-8 (3.4 Å) can also pass through the membrane. The ideal separation factors of H_2/CO_2, H_2/N_2, H_2/CH_4 are 3.58, 12.53 and 9.76, respectively. It indicates that the obtained ZIF-8 membrane after secondary growth with a relatively high selectivity achieves higher H_2 permeability than most of the ZIF-8 membranes with the similar selectivity that have been reported,[15] which may be attributed to that the very thin and well-intergrown ZIF-8 membrane obtained from zinc hydroxide nanostrands produce the same thin ZIF-8 membrane, but with better quality after secondary growth. The reproducibility and durability of the gas separation performance were also examined. After exposed to the ambient condition for two months, the ZIF-8 membrane after secondary growth maintains the large permeance (26.05×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} of H_2) and the high ideal separation factors (Figure 4 inset).

In order to demonstrate the potential of general applicability of our method to synthesize MOF membranes from zinc hydroxide nanostrands, we extend it to the popular MOF-5 membrane. From the characterizations, it can be seen that, similar to the ZIF-8 membrane from zinc hydroxide nanostrands, the MOF-5 membrane is phase-pure, continuous and dense (Figure S6), which proves the feasibility that our method can be used to fabricate other MOF membranes. Moreover, this novel strategy used to simply synthesize well-intergrown ZIF-8 membrane from nanoscopic zinc hydroxide precursor at room temperature posses good reproducibility, and versatility that it is easy to flexibly transfer to different unmodified supports, such as flexible polymer or tubular porous substrates, which offers unique opportunities for large-scale practical applications.

In conclusion, well-intergrown ZIF-8 membranes with the thickness of about 800 nm have been directly synthesized using zinc hydroxide nanostrands as zinc source without any modification of the substrate in ethanol/water at room temperature. Zinc hydroxide nanostrands can react with Hmim rapidly, and proper solvent component is crucial for the formation of well-intergrown ZIF-8 membranes. To achieve better gas separation performance, the obtained 800 nm thick ZIF-8 membrane is used as the seed layer for the formation of more dense and thicker ZIF-8 membrnaes with the thickness of 2.5 μm by secondary growth. The final ZIF-8 membranes after secondary growth demonstrate higher selectivity and faster H_2 permeability than those of the ZIF-8 membranes that have been reported. This simple, effective, economical and ecological strategy for the synthesis of zinc related MOF membranes by using zinc hydroxide nanostrands as metal source presents excellent reproducibility and general applicability, and is prone to transfer to other unmodified porous substrate that is suitable for large-scale production.

Notes and references

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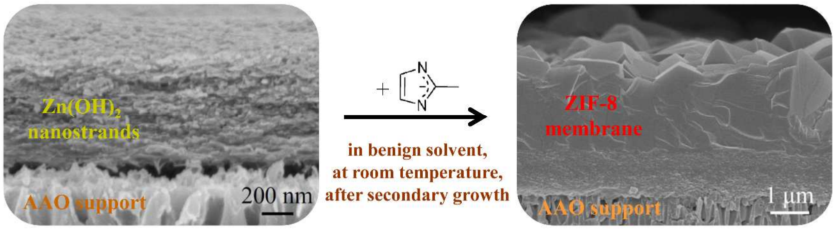

Well-intergrown ZIF-8 membranes are perepared by using zinc hydroxide nanostrands as the the unique zinc source in benign solvent at room temperature, and exhibit very fast H_2 permeability and high selectivity for gas separation after secondary growth.