

Supporting Information

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

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1. Experimental Section

Materials

Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aminoethanol ($\text{NH}_2\text{-CH}_2\text{CH}_2\text{OH}$), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and dimethylformamide (DMF) were purchased from Acros Chemicals. 2-methylimidazole (Hmim), benzenedicarboxylic acid (BDC) and anhydrous sodium formate (HCOONa) were obtained from Sigma-Aldrich. All of them were used without further purification. The supports were porous anodic alumina oxide (AAO) membranes of Whatman with an average pore size of 200 nm, a total diameter of 25 mm and an effective diameter of 19 mm. Deionized water of 18.2 M Ω used throughout the experiments was produced by a Millipore Direct-Q system.

Preparation of zinc hydroxide nanostrand film

Zinc hydroxide nanostrands were prepared by mixing 50 mL ethanol/water (vol 2:3) solution containing 1.6 mM aminoethanol with an equal volume ethanol/water solution containing 4 mM zinc nitrate under vigorous stirring for 5 min and aging for 30 min. Then, the precursor was prepared by suction filtering 10 mL of the sample solution on an AAO membrane. It was dried in the air for 1 d.

Synthesis of ZIF-8 membranes from zinc hydroxide nanostrands

The obtained zinc hydroxide nanostrand film was immersed face-down into 2 mL ethanol/water (vol 1:4) solution containing 25 mM Hmim in a beaker at room temperature for 24 h. For optimization of the condition, small amount of sodium formate (Hmim:HCOONa=1:1) was added into the solution. After that, the obtained samples were washed with abundant ethanol/water solution firstly, then washed with large amount of methanol, finally, dried at 60 °C for 12 h in an vacuum oven for later characterization. The effect of different solvent components was investigated without sodium formate added, keeping other conditions constant.

Secondary growth of ZIF-8 membranes

The secondary growth solution was prepared by mixing 20 mL solution containing 0.11 g (0.37 mmol) $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 20 mL solution containing 2.27 g (27.65 mmol) Hmim in a baker under vigorous stirring for 1 min. The ZIF-8 membrane obtained from zinc hydroxide nanostrands was placed vertically in the solution. The baker was covered and then transferred to an oven that was preheated to 30 °C for 6 h. After that, the membrane was taken out, rinsed with DI water and methanol for three times, and then immersed in 30 mL fresh methanol for another 12 h. Finally, it was dried in ambient condition for 24 h for the permeation test.

Synthesis of MOF-5 membranes from zinc hydroxide nanostrands

The as-prepared zinc hydroxide nanofilm by filtering 15 mL precursor solution was immersed into 10 mL DMF solution containing 0.9 mM BDC in a autoclave and heated at 100 °C for 48 h in a oven. After that, the autoclave was cooled to room temperature at the rate of 10 °C/h. The obtained samples were washed with abundant DMF for three times and dried at 60 °C for 12 h in a vacuum oven.

Characterization and gas separation performance

The morphologies of the obtained samples were characterized by a field emission scanning electron microscope (SEM, Hitachi S-4800) at an acceleration voltage of 10 kV. The phases of the products were characterized by X-ray diffraction (XRD) equipment (X'Pert PRO XRD analyzer, with Cu K α radiation of 1.5406 Å). The gas permeation was carried out by using a dead-end separation system with a stainless steel filter holder (Millipore XX4502500, 25 mm, max inlet pressure 345 bar) and a mass flow meter (Seven-star D07-19BM). The purity of the gases used was 99.9%.

2. The thickness of the precursor film depending on the filtering volume of the solution containing zinc hydroxide nanostrands

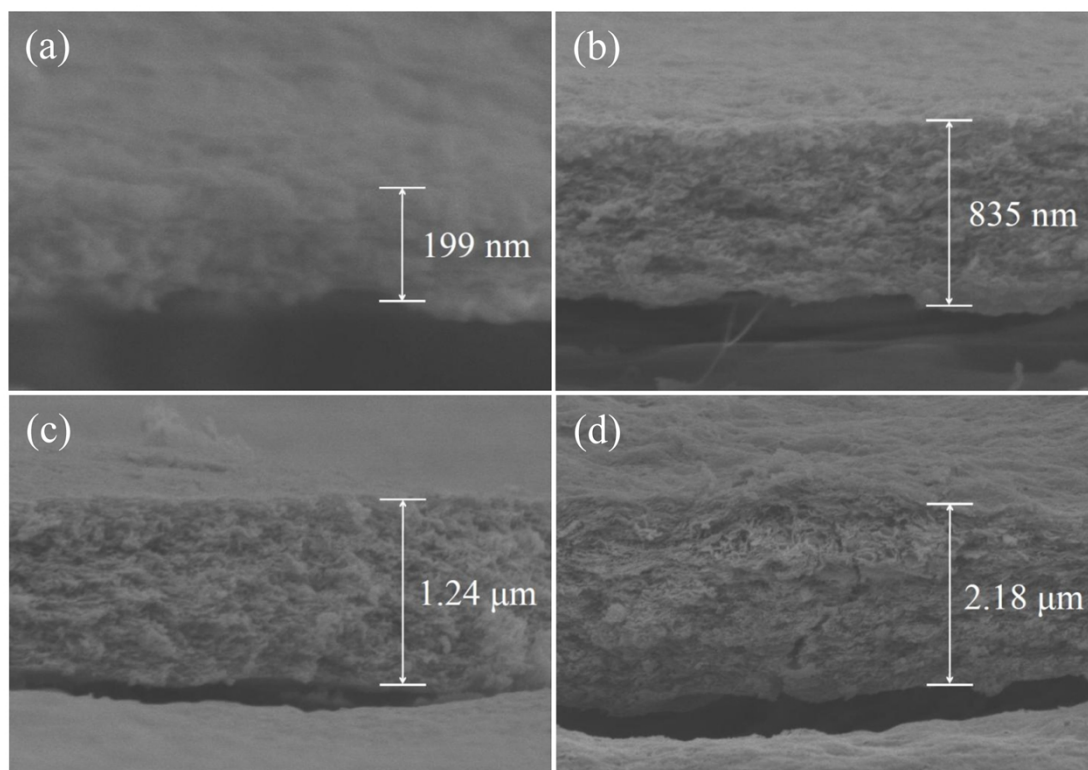


Figure S1. Cross-section SEM images of zinc hydroxide thin films obtained by filtering different volume of the precursor solution: (a) 5 mL, (b) 10 mL, (c) 15 mL, and (d) 20 mL, respectively.

3. SEM images of the ZIF-8 samples synthesized by immersing the zinc hydroxide thin film in Hmim solution for different time

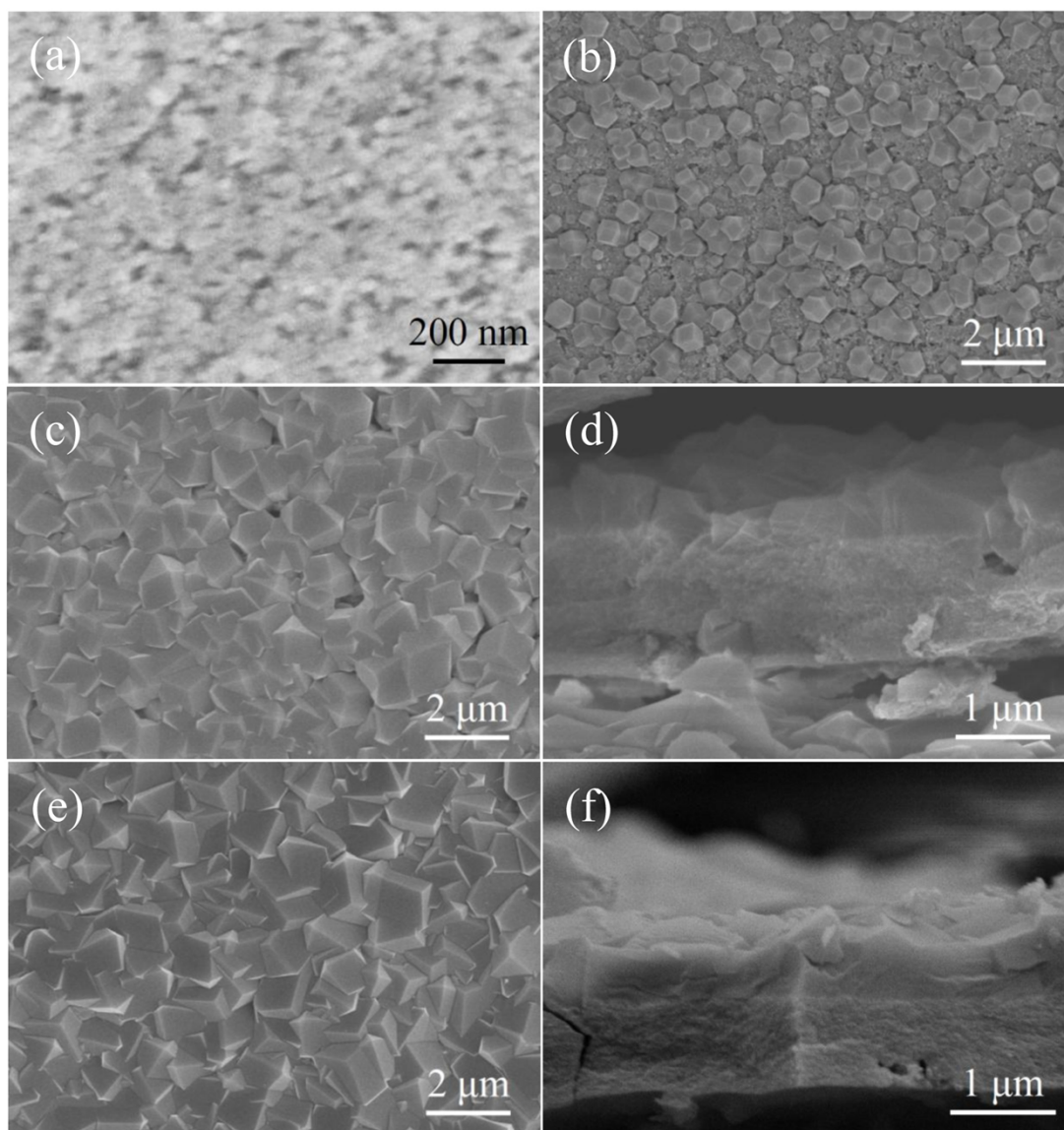


Figure S2. SEM images of the top view and cross-section of the ZIF-8 samples synthesized by immersing the zinc hydroxide thin film in Hmim solution for (a) 10 min; (b) 30 min; (c), (d) 2h; and (e), (f) 6 h; respectively (keeping other conditions constant).

4. pH values of different solvent components

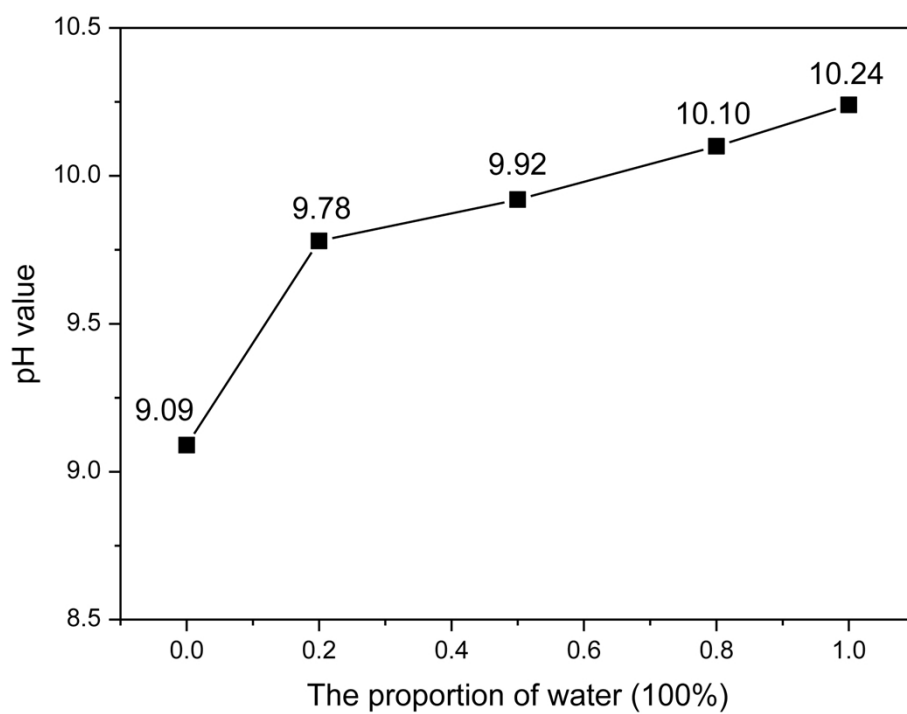


Figure S3. pH values of the Hmim solution with different ratios of ethanol to water without HCOONa: 10:0, 8:2, 5:5, 2:8, and 0:10, respectively.

5. The influence of different solvent components on the morphologies of the ZIF-8 membranes from zinc hydroxide nanostrands

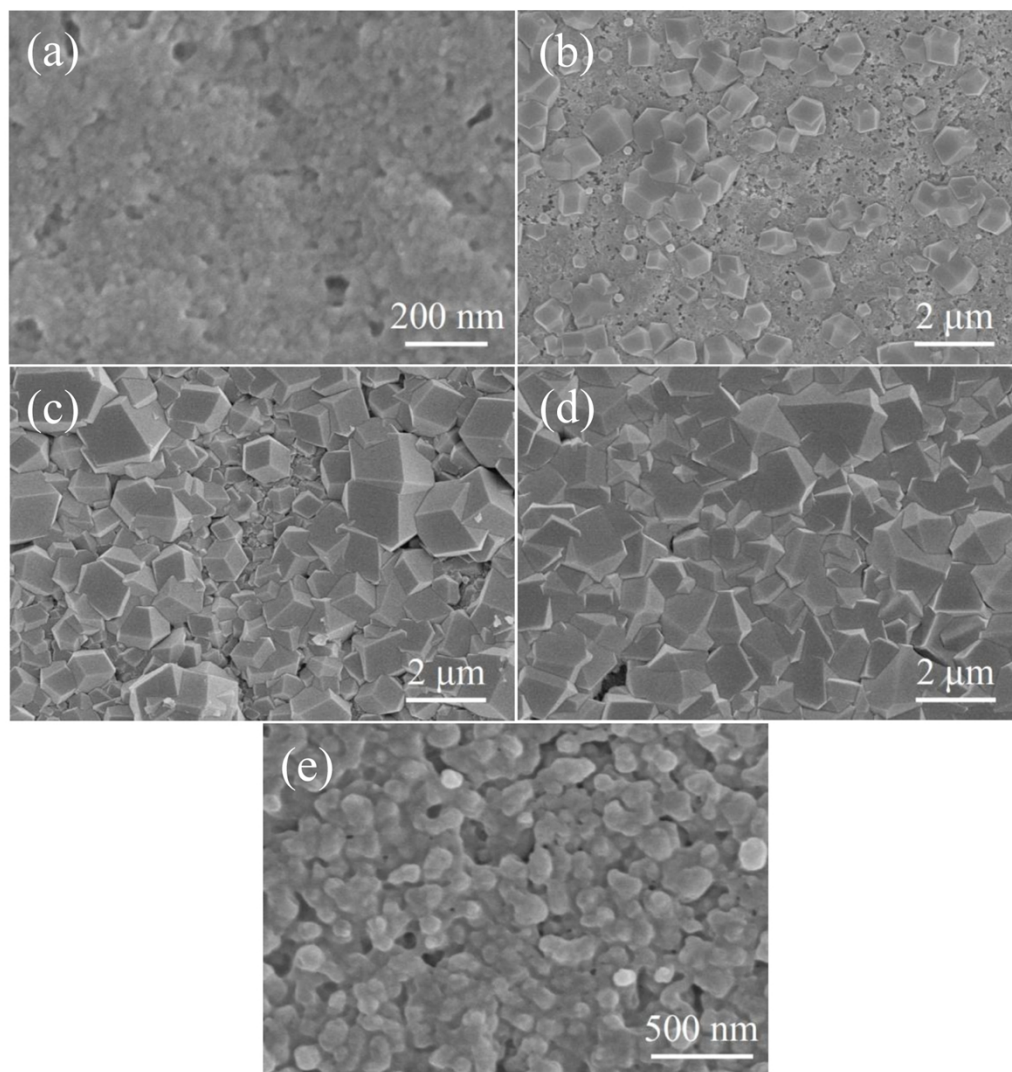


Figure S4. SEM images of the samples synthesized from zinc hydroxide nanostrands in different ratios of ethanol to water without HCOONa for 24 h: (a) pure ethanol, (b) 8:2, (c) 5:5, (d) 2:8, and (e) pure water, respectively.

6. Trans-membrane pressure-dependent permeation measurement through the ZIF-8 membrane after secondary growth

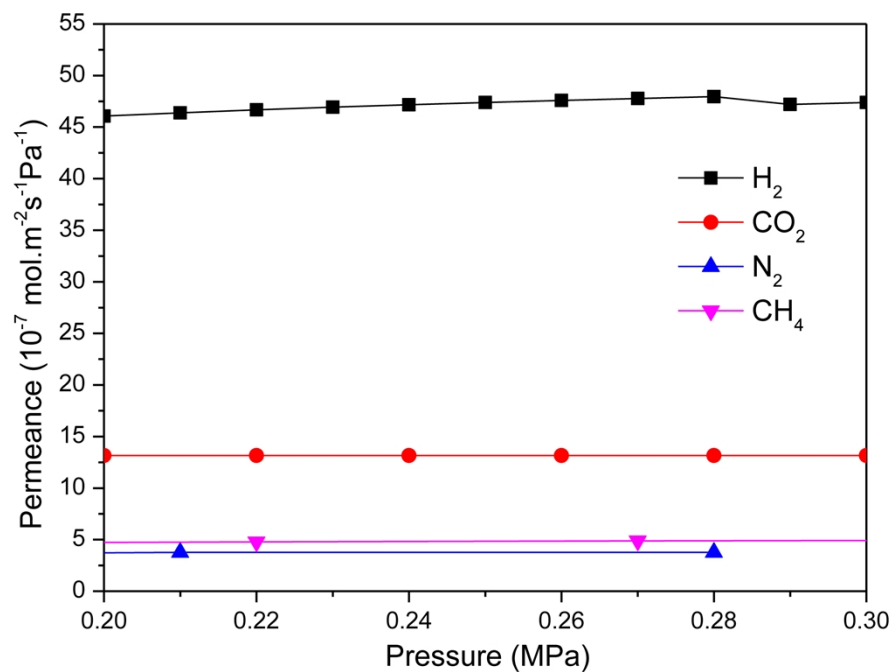


Figure S5. Trans-membrane pressure-dependent permeation measurement of different gases through the ZIF-8 membrane after secondary growth.

7. MOF-5 membrane synthesized from zinc hydroxide strands

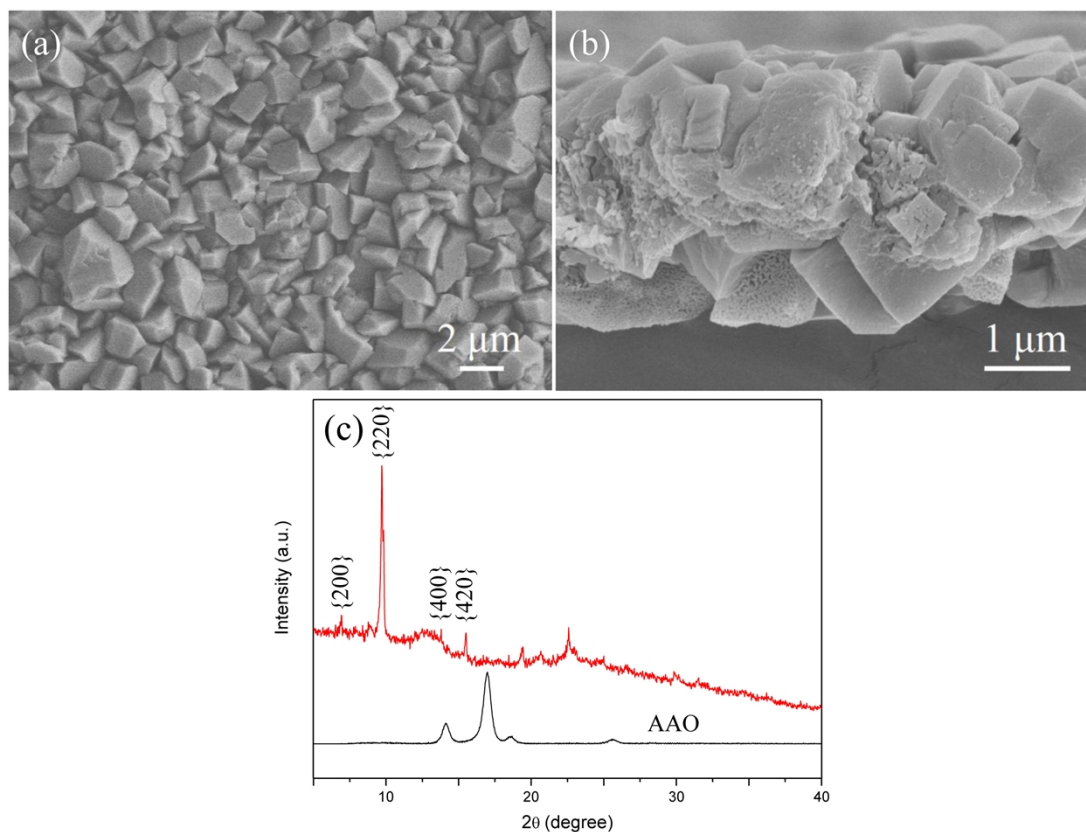


Figure S6. (a), (b) SEM images of the top view and cross-section of the MOF-5 membrane synthesized from zinc hydroxide nanostrands, and (c) the corresponding XRD patterns, respectively.