Supporting information

Nanoporous Film-Mediated Growth of Free-standing and Ultrathin Metal-Organic Framework Membranes for High-Performance Hydrogen Separation

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1. Experimental section:

(1) Materials. SWCNT (OD: < 2 nm, length: 5-30 μm, purity: > 95%) were provided by Nanjing XFNANO Materials Tech Co., Ltd, China. The mixed cellulose ester (MCE) filter membrane was commercially available from Beijing Shenghe, China. Sodium dodecyl benzenesulfonate (SDBS, 99%), dopamine hydrochloride, $Zn(NO_3)_2 \cdot 6H_2O$ (98%), 2-methylimidazole (Hmim, 99%) and tris(hydroxymethyl)aminomethane (Tris, > 99.8%) were purchased from Sigma-Aldrich (Shanghai, China). Other reagents were purchased from Sinopharm Chemical reagent Co., Ltd (Shanghai, China). Deionized (DI) water was produced by using a Milli-Q Plus system (Millipore Co.).

(2) Preparation of PD/SWCNT films. SWCNT dispersion (concentration: 0.024 mg mL^{-1}) were prepared according to our previous report.[1] Dopamine was added into the dispersion to be 0.1 mg mL^{-1}. After stirring for 1 h, 10 mL HCl-Tris (10 mM, pH = 7.5) was added into the mixed dispersion and stirred further for 24 h at 40 ºC. Then the above dispersion was centrifuged at 10,000 rpm for 30 min and the supernatant solution was collected to obtain polydopamine-wrapped SWCNT (PD/SWCNT). The PD/SWCNT film was prepared through vacuum-filtering PD/SWCNT dispersion onto a mixed cellulose ester filter membrane with a pore size of 0.45 μm. The thickness of PD/SWCNT film was controlled by tuning the amount of filtered PD/SWCNT dispersion. The obtained PD/SWCNT film was then incubated in an oven at 40 ºC for 20 min in order to strengthen the film mechanically stronger. The PD/SWCNT film could be free-standing by releasing it from the MCE filter membrane.

(3) Growth of ZIF-8 membranes on PD/SWCNT films. A PD/SWCNT film was vertically mounted in the middle of a home-made two-cell setup to separate the $Zn(NO_3)_2$ solution (12.5 mM in methanol) and Hmim solution (50 mM in methanol) in the opposite cells as shown in Figure S3. The ZIF-8 crystals then spontaneously grown on the PD/SWCNT film. After a certain time, the ZIF-8 membrane grown on the PD/SWCNT film was rinsed three times with methanol and dried at 50 ºC for 24 h.

2. Characterization:

SEM images were conducted on a field-emission scanning electron microscope (Quanta FEG 250). TEM images were measured on a Tecnai G2 F20 S-Twin field-emission transmission electron microscope. Powder X-ray diffraction (XRD) patterns were acquired with a Bruke D8 diffractometer with Cu Kα (λ = 0.15418 nm). Atomic force microscopy (AFM) images were obtained on an ICON Bruker instrument operating in ScanAsyst mode at room temperature.

3. Gas separation test:

The obtained membrane was sealed in a Wicke-Kallenbach cell to measure their separation performance (Fig. S8).[2] To avoid direct contact of silicone O-ring with the measured membrane and thus damage the membrane, two aluminum tapes with 10 mm diameter holes were used to sandwich the membrane and then high vacuum grease was used to seal the aluminum tapes and the membrane. Single gas permeance experiment was performed using the steady-state gas of H_2, CO_2, N_2 and CH_4 at room temperature (25 ºC). The feed flow rate was constant at 50 mL/min, regulated by mass flow controllers (MFCs, D07, Beijing Sevenstar Electronics Co., Ltd.). Argon with flow rate of 30 mL/min was used as a sweep gas to minimize the influence of back diffusion of the sweeping gas to the feed side and simultaneously bring permeate into a gas chromatography (GC9790-TCD, Zhejiang Fuli Analytical Instrument Co., Ltd.) for composition analysis. There was no pressure drop between the sides of the membrane in order to prevent any damage on the membrane.

Membrane permeance, P_i ($mol \cdot m^{-2} \cdot s^{-1} \cdot pa^{-1}$), was defined according to the following equation:

$$P_i = {Ni}/{\Delta P \cdot A}$$

Where N_i ($mol \cdot s^{-1}$) is the permeate flow rate of component gas I, ΔP_i (Pa) is the transmembrane pressure difference of i, and A (m^2) is the membrane area. The ideal selectivity $S_{i/j}$ was calculated from the relation between the permeance of pure i and j gases.

$$S_{i/j} = {Pi}/{Pj}$$

Supplemental figures

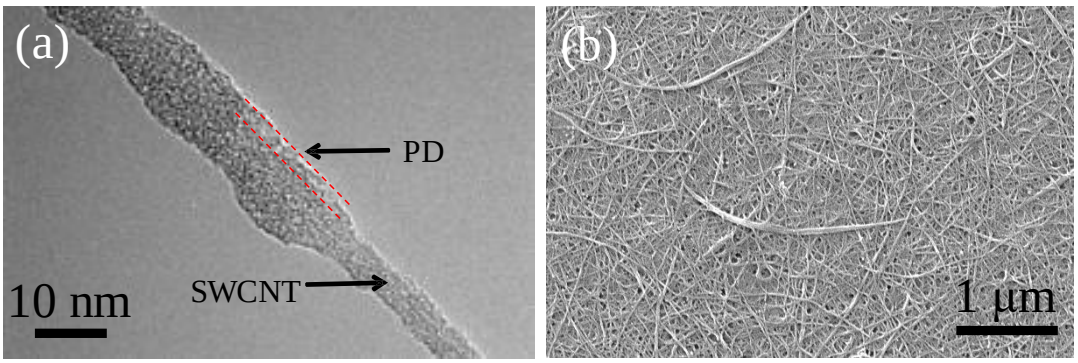

Figure S1. (a) TEM image of an individual polydopamine (PD)-wrapped SWCNT. (b) SEM image of PD/SWCNT film.

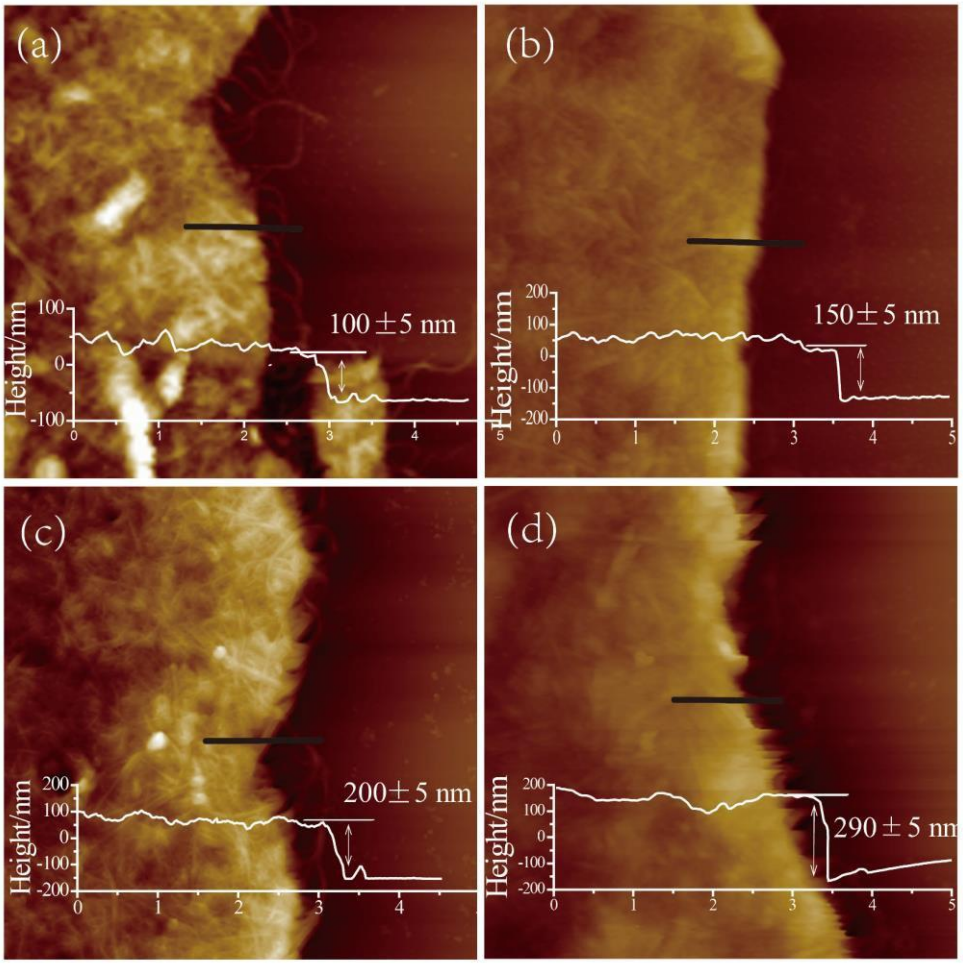

Figure S2. AFM images and their height profiles of PD/SWCNT films with different thickness: (a) ~100 nm, (b) ~150 nm, (c) ~200 nm, and (d) ~290 nm.

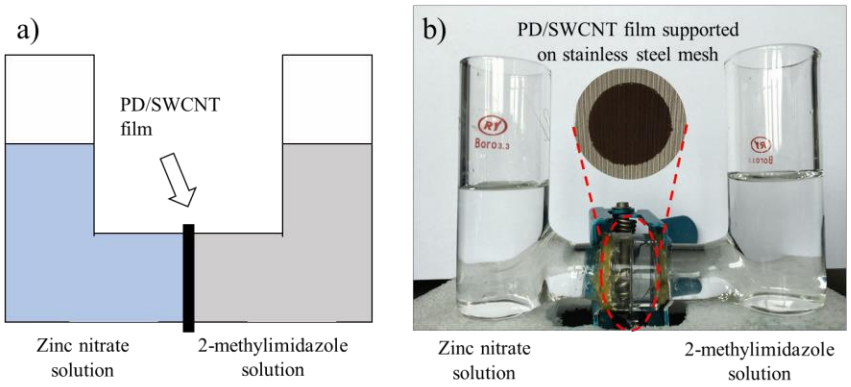

Figure S3. Diagrammatic sketch (a) and photography (b) of a homemade two-cell diffusion setup.

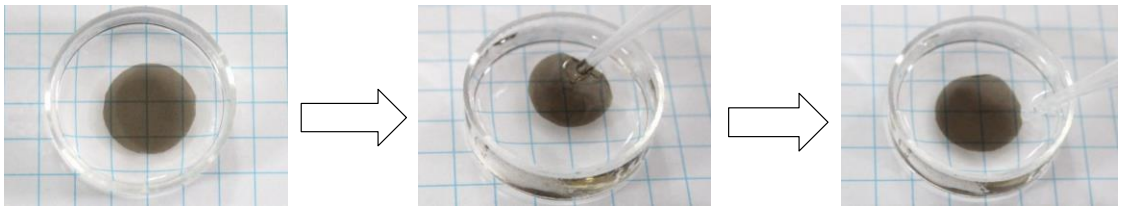

Figure S4. Digital photos of a ZIF-8 membrane floating on an acetone/water surface which could be lifted up by a pipette without cracking.

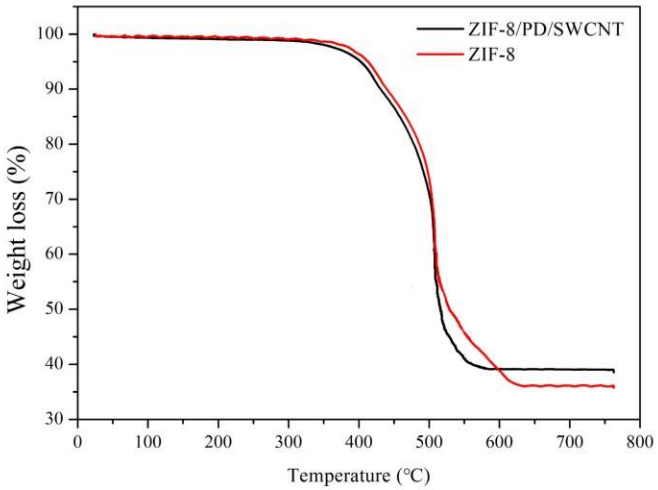

Figure S5. Thermogravimetric analysis (TGA) curves of ZIF-8 crystal and ZIF-8 composite membrane measured in a flow of air.

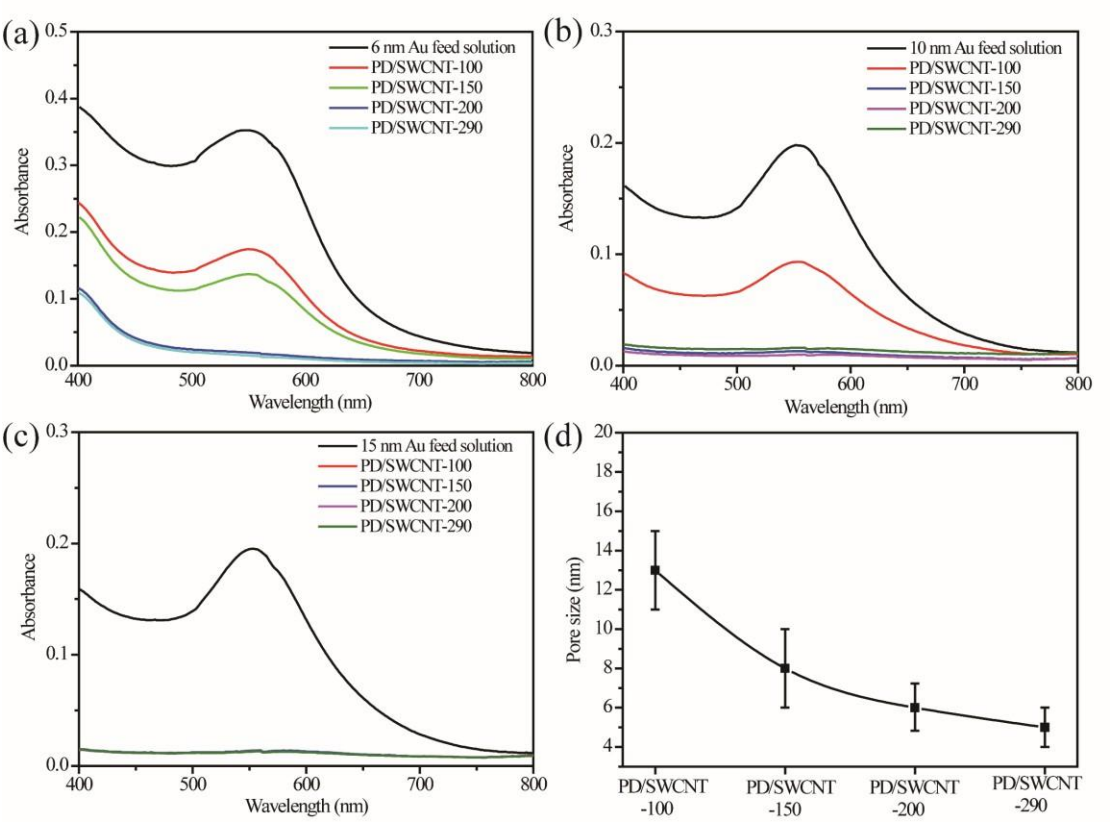

Figure S6. UV−vis absorption spectra of (a) 6 nm, (b) 10 nm, and (c) 15 nm Au nanoparticle solution after permeating through the PD/SWCNT-100, PD/SWCNT-150, PD/SWCNT-200, and PD/SWCNT-290 films. (d) The statistical data of effective pore size vs PD/SWCNT film with different thickness. The rejection rate of Au nanoparticles was calculated from the chnge of absorption intensity at 520 nm of Au nanoparticle solution before and after permeation. It is concluded that the effective pore size of PD/SWCNT-100, PD/SWCNT-150, PD/SWCNT-200, and PD/SWCNT-290 films are in the range of 10-15 nm, 6-10 nm, 5-6 nm, and 4-5 nm, respectively.

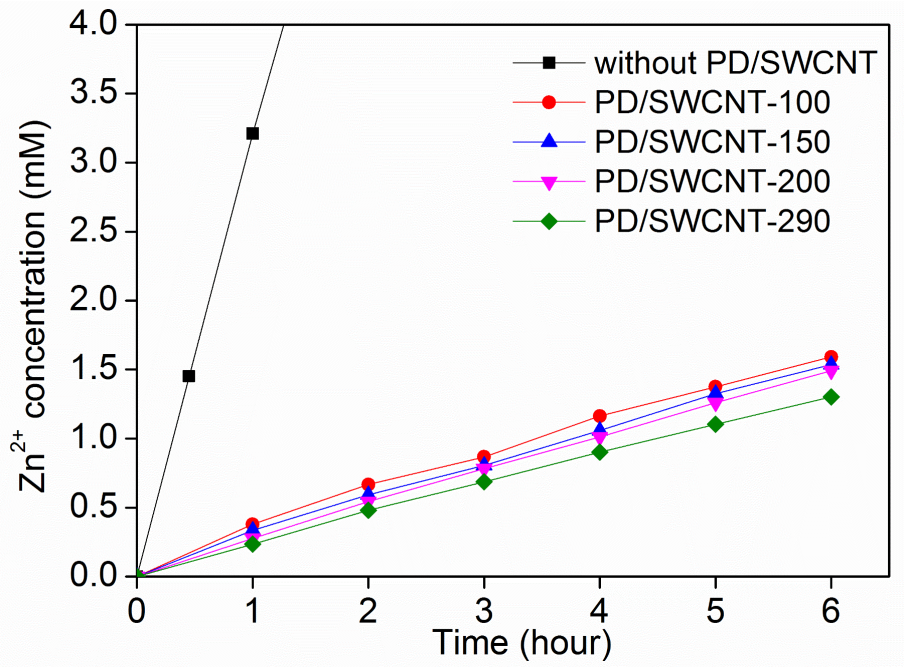

Figure S7. Variation of Zn^{2+} concentration vs diffusion time through PD/SWCNT films with different thicknesses.

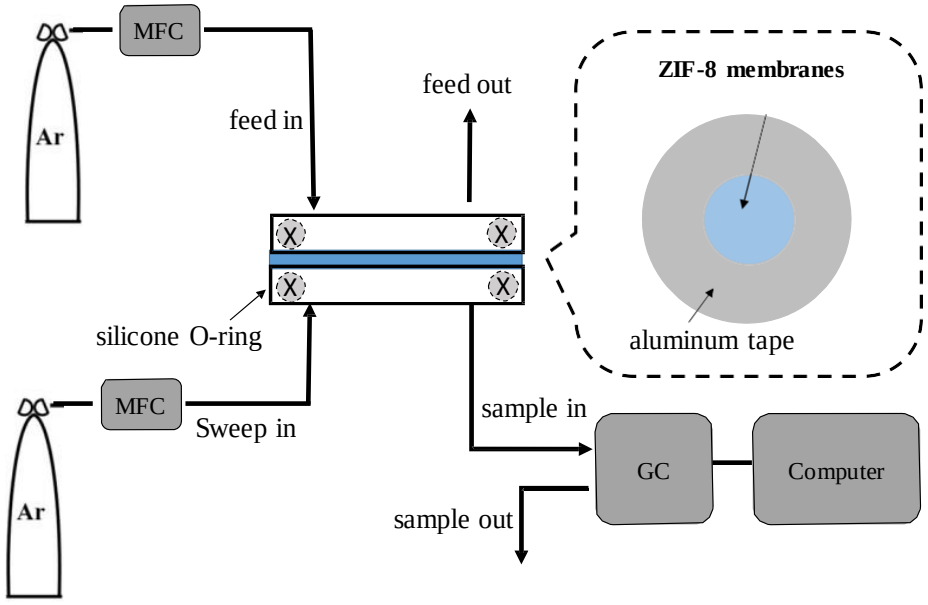

Figure S8. Illustration of the gas separation measurement apparatus used in this work.

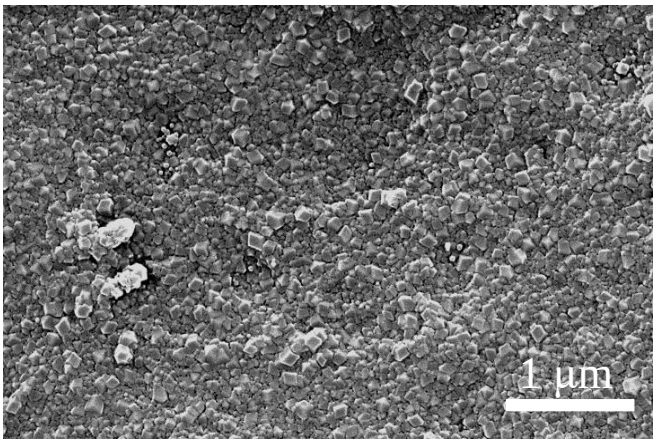

Figure S9. SEM image of ZIF-8 membrane grown on SWCNT-150 without PD wrapping.

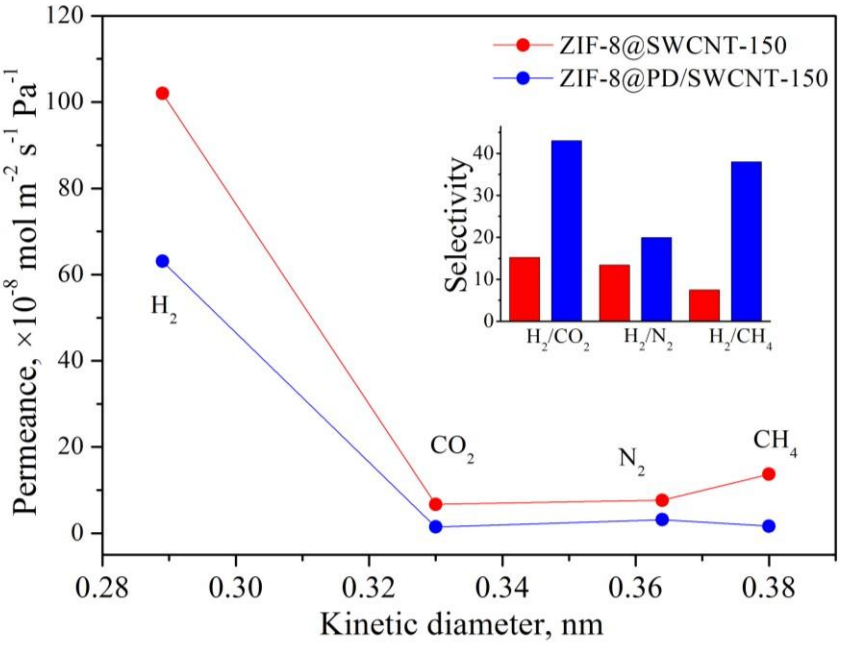

Figure S10. Comparison of gas permeance and ideal gas selectivity between ZIF-8 membranes grown on PD/SWCNT-150 and SWCNT-150 without PD wrapping measured under the same condition.

Supplementary references:

(1) Gao, S. J.; Zhu, Y. Z.; Zhang, F.; Jin, J. *J. Mater. Chem. A* **2015**, *3*, 2895.
(2) Peng, Y.; Li, Y.; Ban, Y.; Jin, H.; Jiao, W.; Liu, X.; Yang, W. *Science* **2014**, *346*, 1356.