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Supporting Information

Electro-deposition Introduced Metal Precursors for in situ Growth of Metal-organic Framework Membranes on Porous Metal Substrates with Excellent Generality

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Experimental details:

Chemicals are used without further purification: zinc nitrate hexahydrate (>99%, aladdin), ammonium nitrate (Guangzhou Chemical Reagent Co Ltd), cobalt nitrate hexahydrate (Tianjin Kemiou Chemical Reagent Co Ltd), cupric nitrate trihydrate (>99%, aladdin), zinc chloride (>99%, aladdin), 2-methylimidazole (>99%, aladdin), sodium formate (>99%, aladdin), cobalt dichloride (99.7%, aladdin), Trimesic acid (98%, aladdin), methanol (Guangzhou Donghong Chemical Reagent Co Ltd), ethanol (Sinopharm Chemical Reagent Co Ltd), stainless steel nets (2500 mesh, yingkaimo Co Ltd).

Electro-deposition of ZnO nanorods on stainless steel nets (SSN): The SSN were cut into disk with a diameter of 18 mm to be used as the substrates. Before the electro-deposition, the supports were cleaned by hydrochloric acid, ethanol and water. Then the supports were immerged in the solution consisting of 0.01 M $Zn(NO_3)_2$ and 0.05 M NH_4NO_3. After preheated at 70 ^oC, a current was conducted for 90 minutes with a density of 1.0 $mA \cdot cm^{-2}$ to generate ZnO nanorods.

Electro-deposition of $Co(OH)_2$ nanosheets on SSN: The SSN were cut into disk with a diameter of 18 mm to be used as the substrates. Before the electro-deposition, the supports were cleaned by hydrochloric acid, ethanol and water. Then the supports were immerged in the solution consisting of 0.02 M $Co(NO_3)_2$ and 0.05 M NH_4NO_3. A current was conducted for 40 minutes at room temperature with a density of 1.2 $mA \cdot cm^{-2}$ to generate Cu(OH)2 nanosheets.

Electro-deposition of Cu_2O nanocubes on SSN: The SSN were cut into disk with a diameter of 18 mm to be used as the substrates. Before the electro-deposition, the supports were cleaned by hydrochloric acid, ethanol and water. Then the supports modified by ZnO were immerged in the solution consisting of 0.04M $Cu(NO_3)_2$ and 0.05M NH_4NO_3. A current was conducted for 90 minutes at room temperature with a

density of 1.2 $mA \cdot cm^{-2}$ to generate Cu2O nanocubes.

In situ growth of ZIF-8 membranes on the ZnO nanorods modified supports: A solid mixture of 0.76 g zinc chloride, 0.92 g 2-methylimidazole and 0.38 g sodium formate was dissolved in 70 mL methanol. The ZnO nanorods modified stainless steel net was vertically placed into a 50 ml Teflon-lined stainless vessel followed by transferring 35 mL of the solution into the vessel. After sealed, the autoclave was put into an oven for 10 hours which was preheated to 100 ^{o}C. Finally, the membrane was taken out and washed with methanol several times and dried at room temperature in air. Before the permeation test, the membranes were heated in vacuum oven at 65 ^{o}C for 24 hours.

In situ growth of ZIF-67 membranes on the $Co(OH)_2$ nanosheets modified supports: A solid mixture of 0.73 g cobalt chloride, 1.38 g 2-methylimidazole and 0.56 g sodium formate was dissolved in 70mL methanol. The $Co(OH)_2$ nanosheets modified stainless steel net was vertically placed into a 50 ml Teflon-lined stainless vessel followed by transferring 35 mL of the solution into the vessel. After sealed, the autoclave was put into an oven for 1000 minutes which was preheated to 100 ^{o}C. Finally, the membrane was taken out and washed with methanol several times and dried at room temperature in air.

In situ growth of HKUST-1 membranes on the Cu_2O nanocubes modified supports: 1.74 g Cupric nitrate trihydrate were dissolved in 40 mL DDI water and 1.01 g Trimesic acid were dissolved in 40 mL ethanol. After stirred for 10 minutes separately, the two solution were mixed together. The Cu_2O modified stainless steel net was vertically placed into a 50 ml Teflon-lined stainless vessel followed by transferring 35 mL of the solution into the vessel. After sealed, the autoclave was put into an oven for 12 hours which was preheated to 110 ^{o}C. Finally, the membrane was taken out and washed with ethanol several times and dried at room temperature in air.

Characterization: The XRD patterns were recorded at room temperature under ambient conditions with Bruker D8 ADVANCE X-ray diffractometer with Cu Ka radiation at 40 kV and 40 mA. The morphology and cross section of the membranes were observed by scanning electron microscopy NOVA Nano SEM430.

***Gas permeation test*:** For the single gas permeation measurement, the prepared MOF membrane was fixed in a module sealed with O-rings. A volumetric flow rate of 50 $ml \cdot min^{-1}$ gas was applied to the feed side of the membrane, and the permeate gas was removed from the permeate side by sweep gas. Pressures at both feed side and permeate side were kept at 1 bar. In most of the cases, N_2 was used as sweep gas, except in the N_2 single gas measurement, where CH_4 was employed as the sweep gas. For the mixed gas permeation measurement, the prepared MOF membrane was fixed in a module sealed with O-rings. A 1:1 mixture of gas was applied to the feed side of the membrane, and the permeate gas was removed from the permeate side by sweep gas. The feed flow rate was kept constant with a total volumetric flow rate of 100 $mL \cdot min^{-1}$ (each gas of 50 $mL \cdot min^{-1}$). Pressures at both feed side and permeate side were kept at 1 bar. In most of the cases, N_2 was used as sweep gas, except in the mixture of H_2 and N_2 measurement, where CH_4 was employed as the sweep gas. A calibrated gas chromatograph (Agilent 7890A) is used to measure the concentration of each gas on the permeate side. The separation factor $\alpha_{i,j}$ of gas pairs is defined as the quotient of the molar ratios of the components (i, j) in the permeate side, divided by the quotient of the molar ratio of the components (i, j) in the feed side:

$$\alpha_{i/j} = \frac{X_{i,perm} / X_{j,perm}}{X_{i,feed} / X_{j,feed}}$$

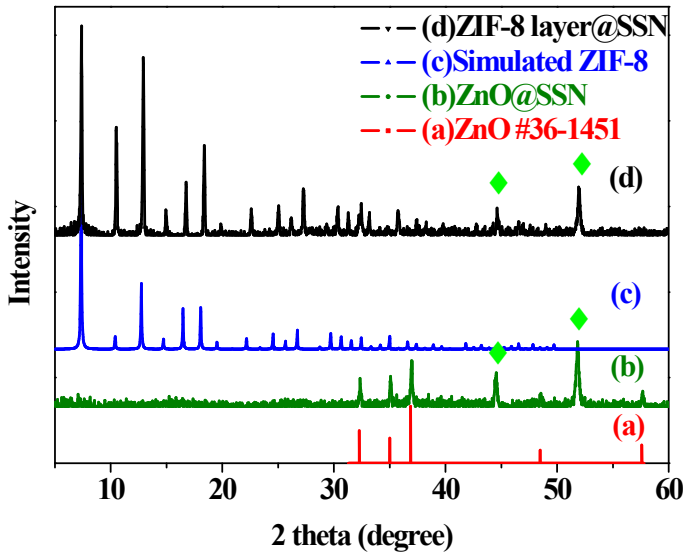

Figure S1. XRD patterns of standard ZnO (a), ZnO nanorods prepared by electro-deposition on porous SSN (b), simulated ZIF-8 (c), and prepared ZIF-8 membrane on porous SSN (d). The peaks marked by ◆ represent the reflection of SSN.

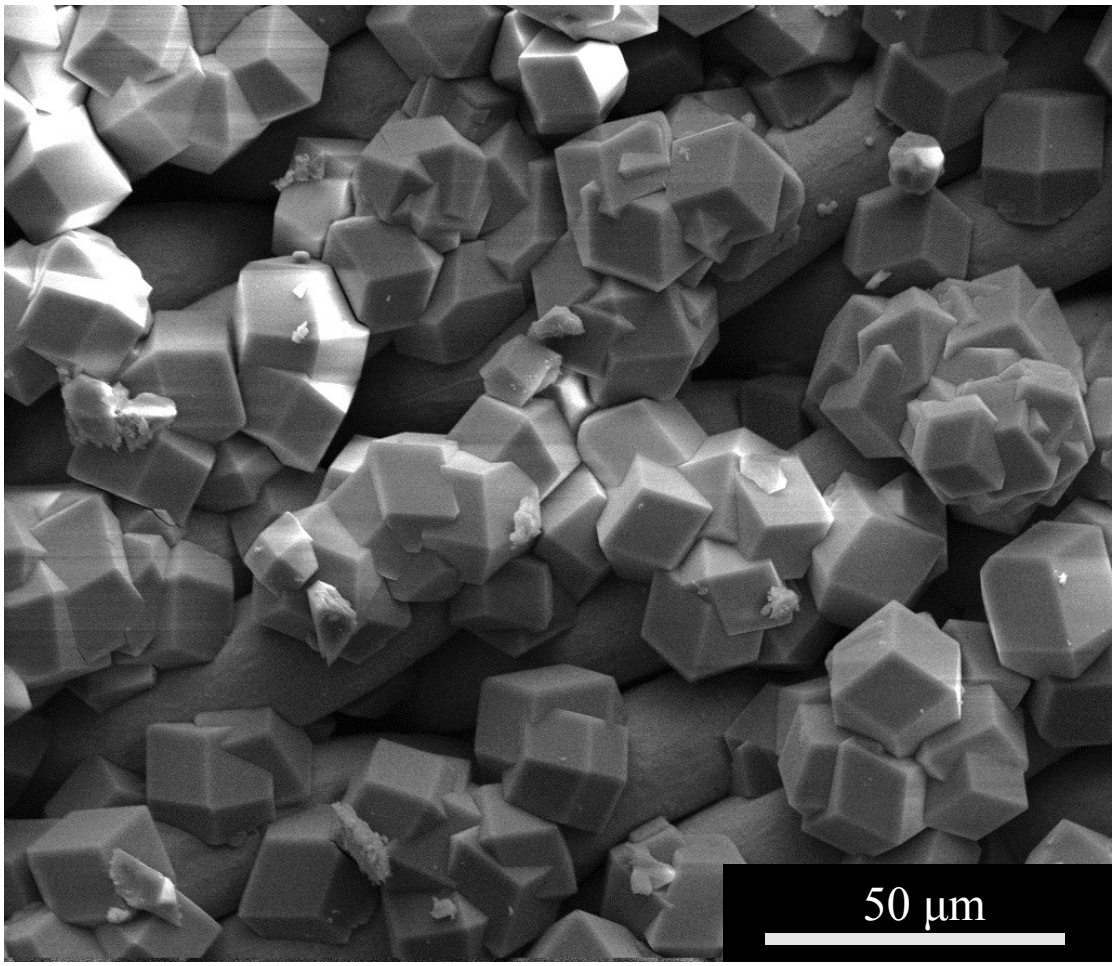

Figure S2. SEM image of in situ growth of ZIF-8 on the bare SSN without electro-deposition. The ZIF-8 crystals are loosely locates on the SSNs, which indicates it necessary to modify the SSN with ZnO nanorods.

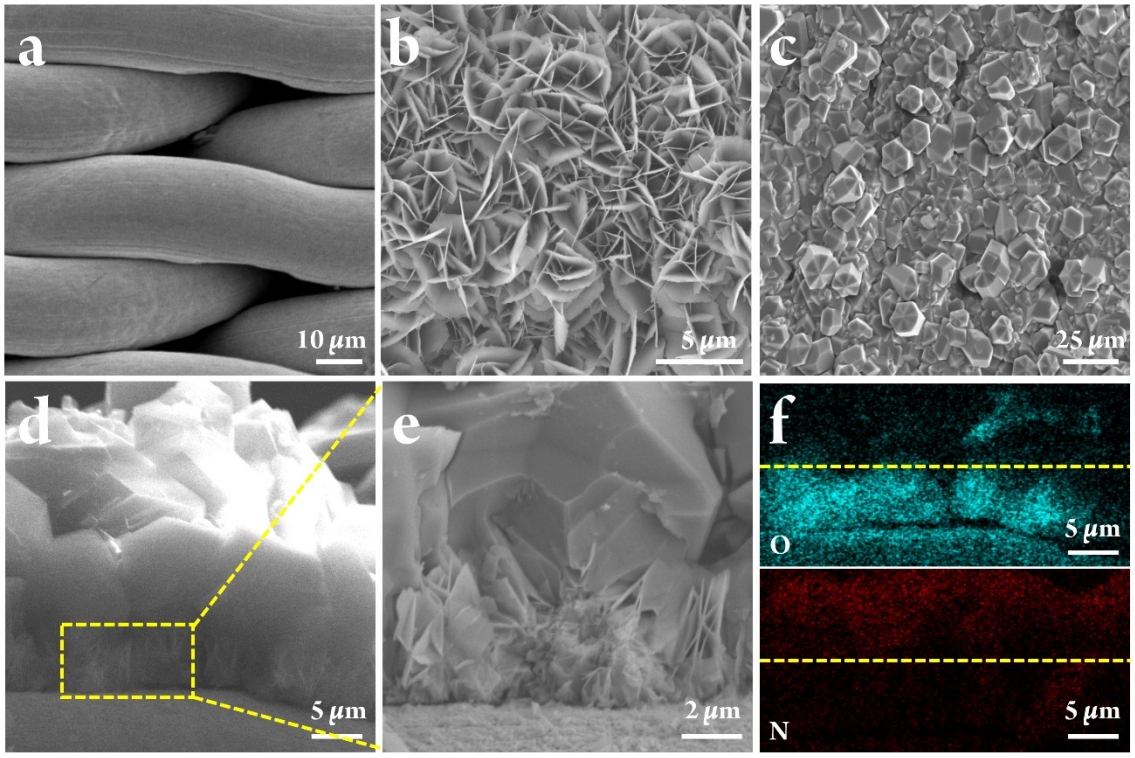

Figure S3. Microstructure images of bare SSN (a), $Co(OH)_2$ nanosheets electro-deposited SSN (b), top view of as-prepared ZIF-67 membrane supported on SSN (c), cross-section view of as-prepared ZIF-67 membrane (d), high magnification image of the intermediate buffer layer (e), and cross-section EDXS images of buffer layer (f).

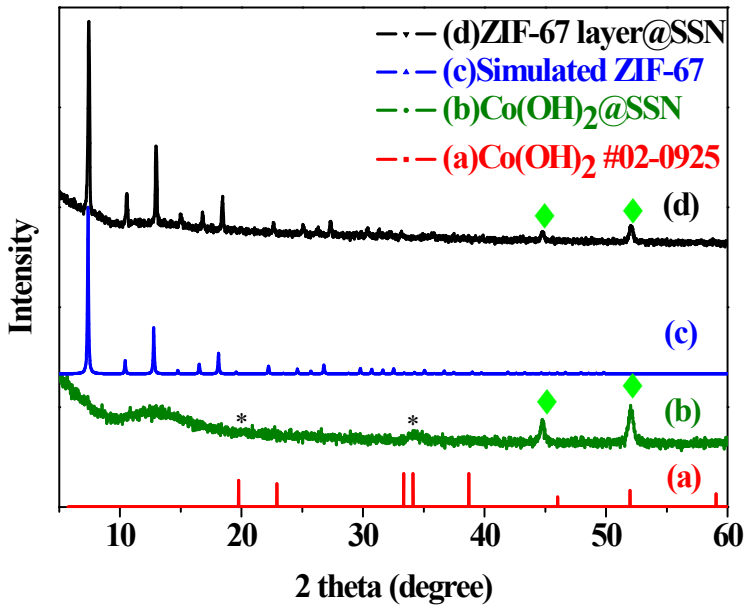

Figure S4. XRD patterns of standard $Co(OH)_2$ (a), $Co(OH)_2$ prepared by electro-deposition (marked by *) on SSN (b), simulated ZIF-67 (c), and as-prepared ZIF-67 membrane on SSN. The peaks marked by ◆ represent the reflection of SSN.

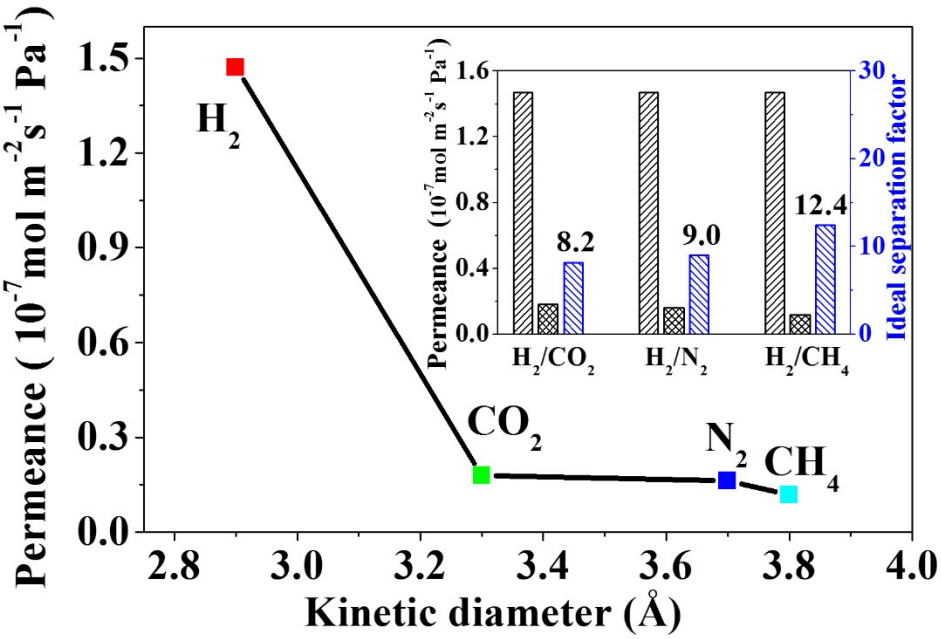

Figure S5. Single gas permeances and ideal separation factors of different gases through the ZIF-67 membrane prepared on $Co(OH)_2$ modified SSN at room temperature as a function of their kinetic diameters. The inset gives the ideal separation factors of different gas pairs.

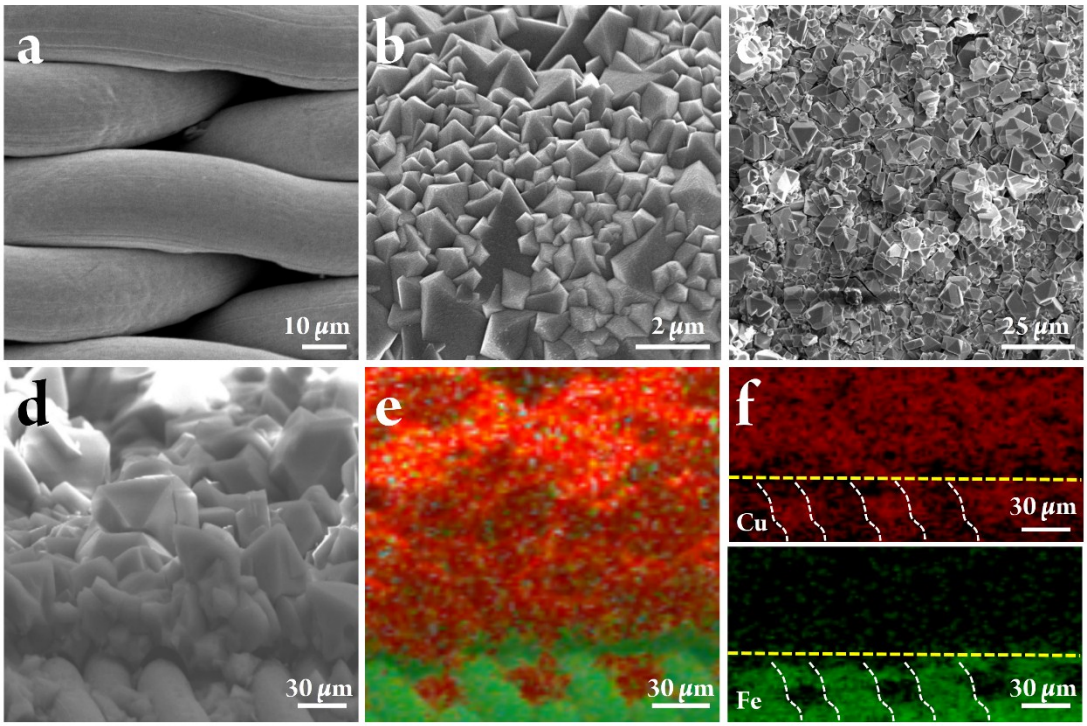

Figure S6. Microstructure images of bare SSN (a), Cu_2O nanocubes electro-deposited SSN (b), top view of as-prepared HKUST-1 membrane supported on SSN (c), cross-section view of as-prepared HKUST-1 membrane (d), and cross-section EDXS images of HKUST-1 membrane (e, f).

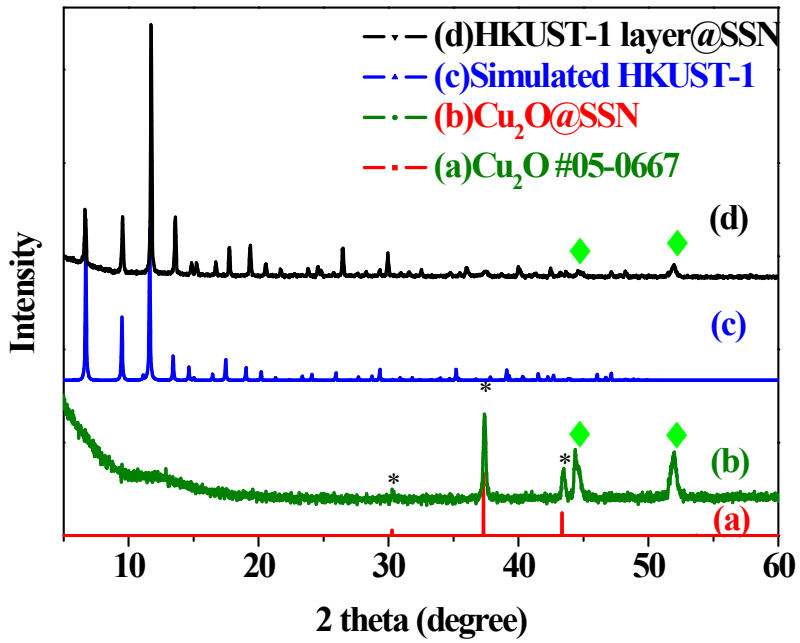

Figure S7. (1) XRD patterns of standard Cu_2O (a), Cu_2O prepared by electro-deposition (marked by *) on SSN (b), simulated HKUST-1 (c), and as-prepared HKUST-1 membrane on SSN. The peaks marked by ◆ represent the reflection of SSN.

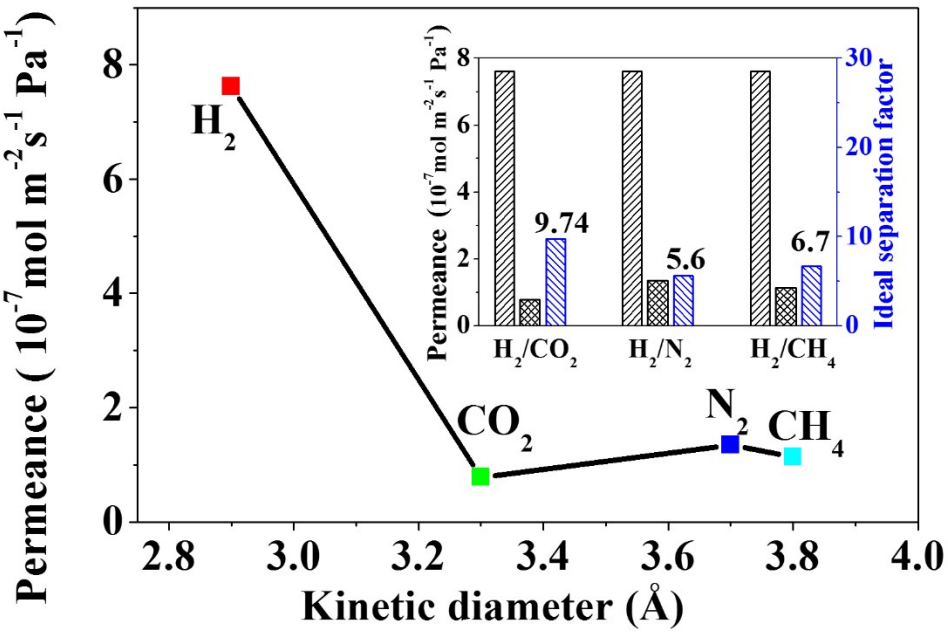

Figure S8. Single gas permeances and ideal separation factors of different gases through the HKUST-1 membrane prepared on Cu_2O modified SSN at room temperature as a function of their kinetic diameters. The inset gives the ideal separation factors of different gas pairs.

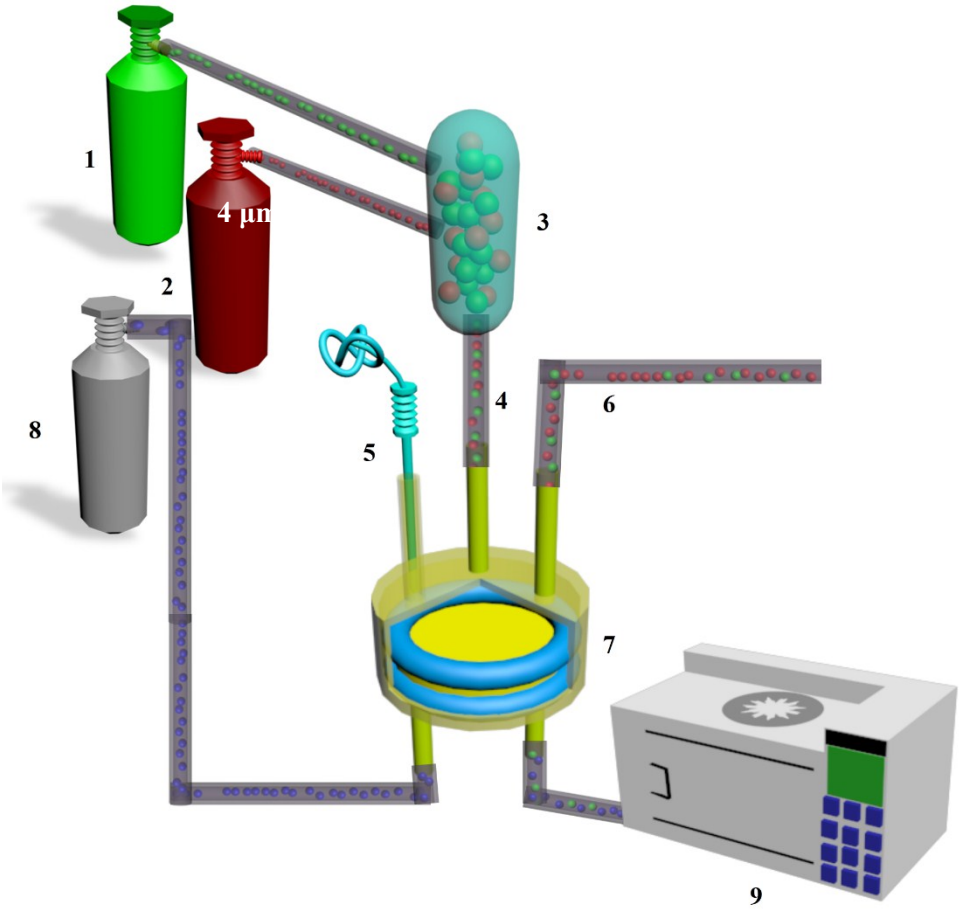

Figure S9. Measurement equipment for mixed gas permeation.

1. Feed gas (i) 2. Feed gas (j) 3. Gas mixing tank 4. Mixed feed gases

5. Thermocouple 6. Retentate gas 7. Permeate cell 8. Sweep gas

9. Gas chromatography

Table S1. Summary of literature reports of MOF membranes.

Support	Membrane	Gas separation performances				Reference
		H_2 permeances (mol•m^{-2}•s^{-1}•Pa^{-1})	Selectivity			
			H_2/CO_2	H_2/N_2	H_2/CH_4	
α-Al_2O_3	ZIF-7	7.4×10^{-8}	6.5	7.7	5.9	S1
α-Al_2O_3	ZIF-7	4.5×10^{-8}	13.6	18	14	S2
α-Al_2O_3	ZIF-8	1.58×10^{-7}	4.6	8.2	9.8	S3
α-Al_2O_3	ZIF-8	1.7×10^{-7}	3.5	11.6	13.0	S4
α-Al_2O_3	ZIF-8	2.1×10^{-7}	8.9	16.2	31.5	S5
α-Al_2O_3	ZIF-8	1.9×10^{-8}	5[a]	11[a]	12[a]	S6
α-Al_2O_3	ZIF-8	7.29×10^{-7}	5.4[a]	9.2[a]	10.8[a]	S7
γ-Al_2O_3	ZIF-8	1.4×10^{-7}	4.2	10.0	12.5	S8
ZnO-Al_2O_3	ZIF-8	1.8×10^{-7}	-	10.4	11.7	S9
AAO	ZIF-8	5.46×10^{-8}	1.6[a]	11.1[a]	11.2[a]	S10
AAO	ZIF-8	1.34×10^{-7}	6.38[a]	4.19[a]	-	S11
TiO_2	ZIF-8	5.1×10^{-8}	4.5[a]	5.8[a]	11.3	S12
BPPO	ZIF-8	7.5×10^{-7}	5.1[a]	8.3[a]	9.1[a]	S13
PVDF	ZIF-8	201×10^{-7}	7.0[4a]	7.8[a]	8.6[a]	S14
TiO_2	ZIF-22	1.6×10^{-7}	7.2	6.4	5.2	S15
α-Al_2O_3	ZIF-90	2.5×10^{-7}	7.2[a]	12.6[a]	15.3	S16
α-Al_2O_3	ZIF-95	1.95×10^{-6}	25.7	10.2	11	S17
Al_2O_3	MIL-53	5×10^{-7}	5.4	4.0	-	S18
PVDF	HKUST-1	2.01×10^{-6}	8.1	6.5	5.4	S19
Cu net	HKUST-1	1×10^{-6}	6.8	7.0	6	S20
Stainless steel nets	ZIF-8	1.1×10^{-7}	8.1	9.6	13.6	This work
Stainless steel nets	ZIF-67	1.47×10^{-7}	8.2[a]	9.0[a]	12.4[a]	This work
Stainless	HKUST-1	7.62×10^{-7}	9.7[a]	5.6[a]	6.7[a]	This

steel nets	work

[a] ideal separation factor

Reference:

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