Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Supplementary Figures

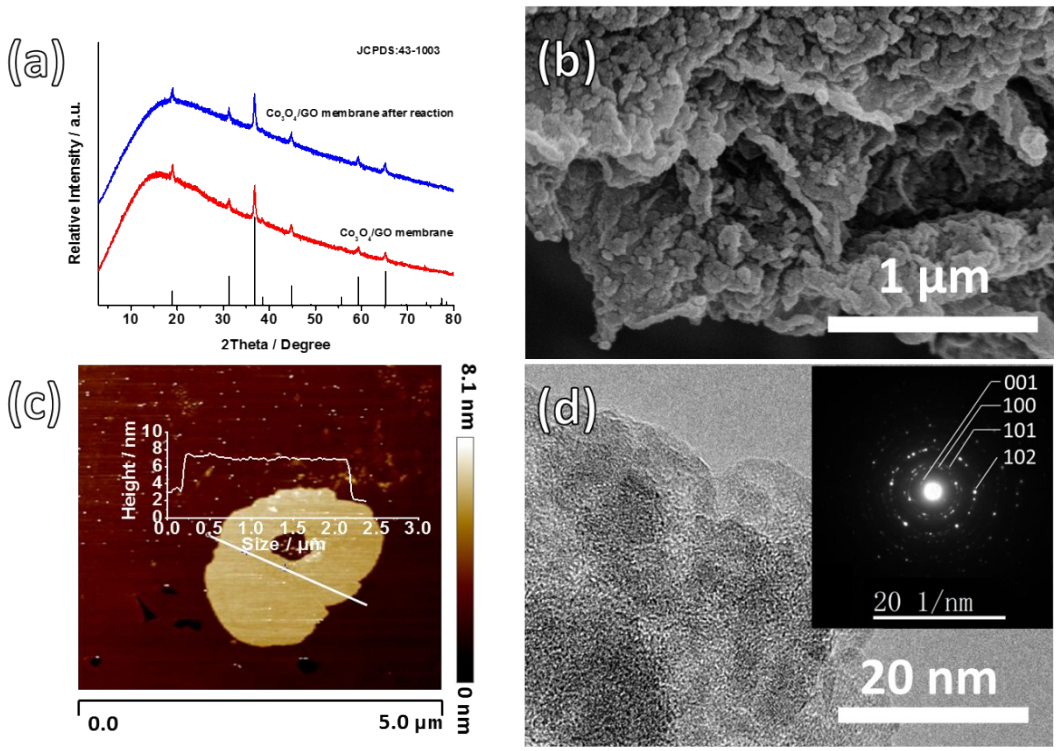

Figure S1. (a) PXRD of the Co_3O_4/GO membranes before and after reaction with 2-MIM, (b) SEM images of the $Co(OH)_2$/GO-I membrane. (c) AFM and (d) TEM images (inset: SAED patterns) of the $Co(OH)_2$ NS.

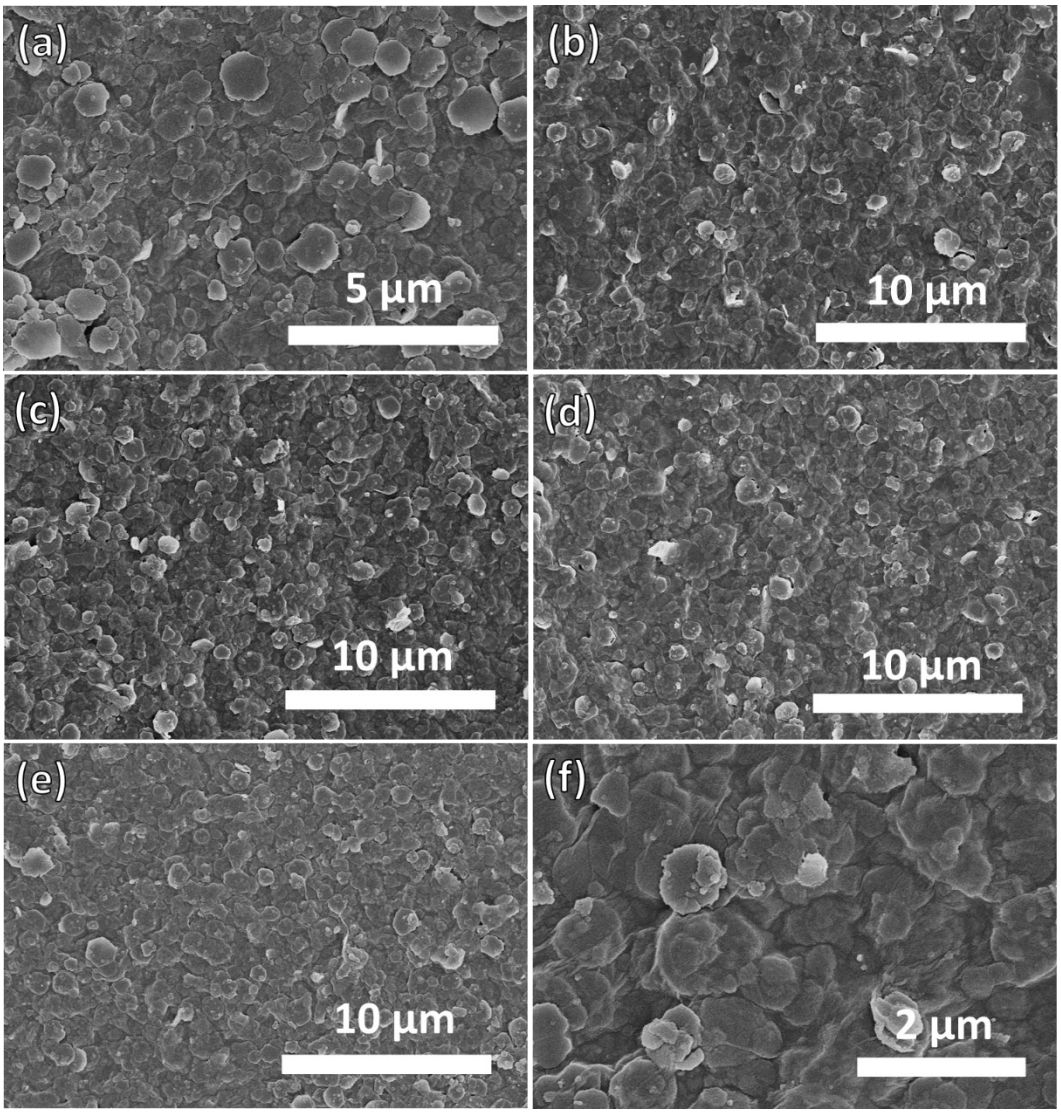

Figure S2. Top-view SEM images for the $Co(OH)_2$/GO-x membranes prepared with varied volume of $Co(OH)_2$/GO mixtures. (a) 20 mL, (b) 25 mL, (c) 30 mL, (d) 35 mL and (e, f) 40 mL.

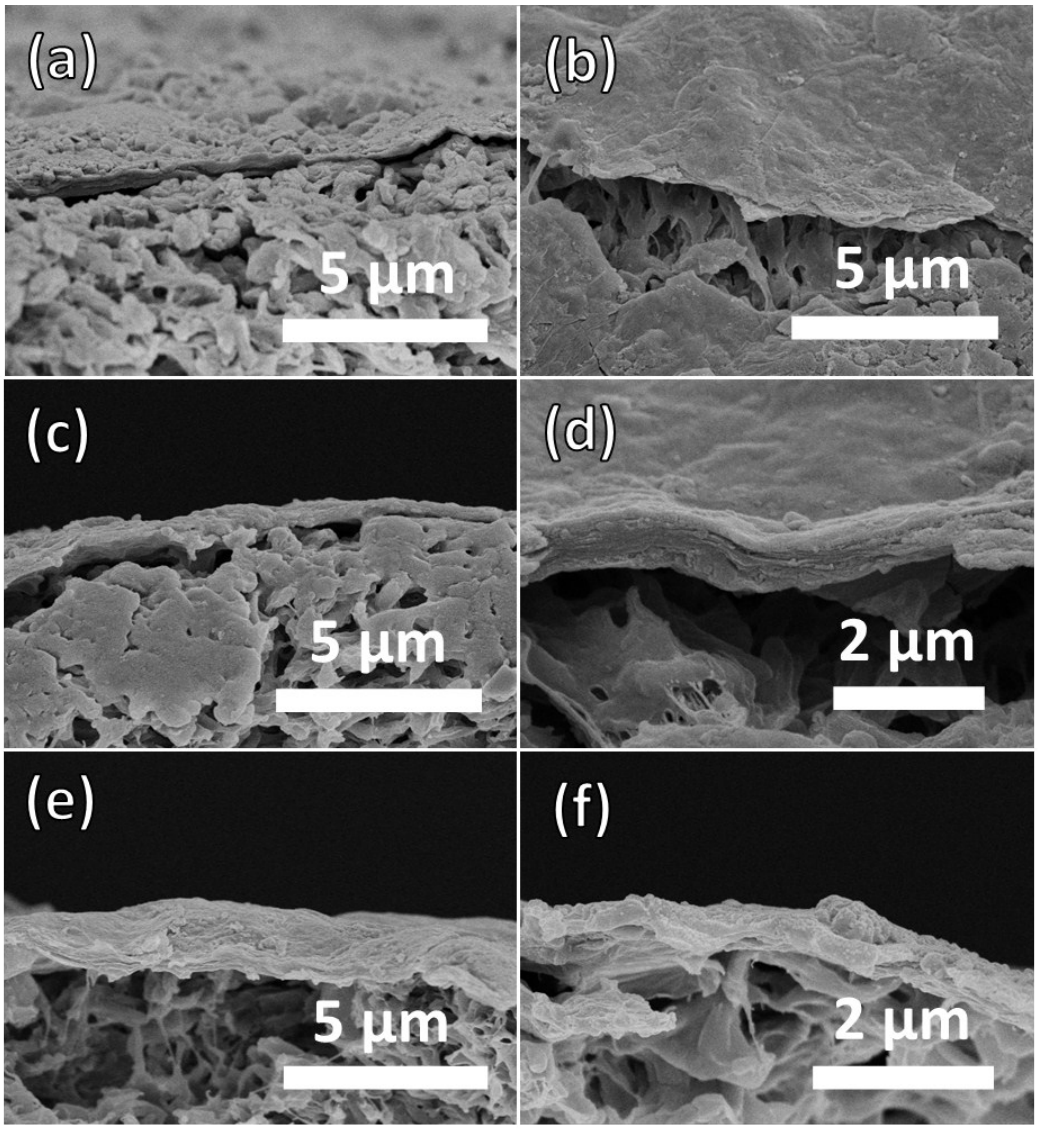

Figure S3. Cross-section SEM images for the $Co(OH)_2$/GO-x membranes prepared with varied volume of $Co(OH)_2$/GO mixtures. (a) 20 mL, (b) 25 mL, (c) 30 mL, (d) 35 mL and (e, f) 40 mL.

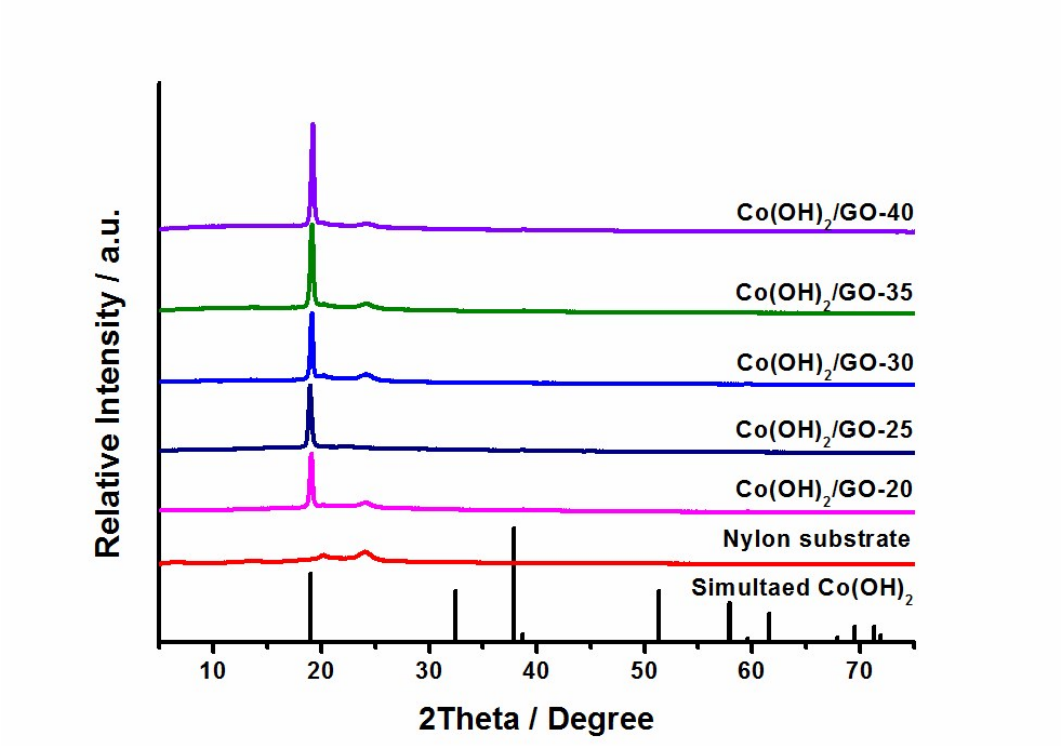

Figure S4. PXRD of the $Co(OH)_2$/GO-x membranes.

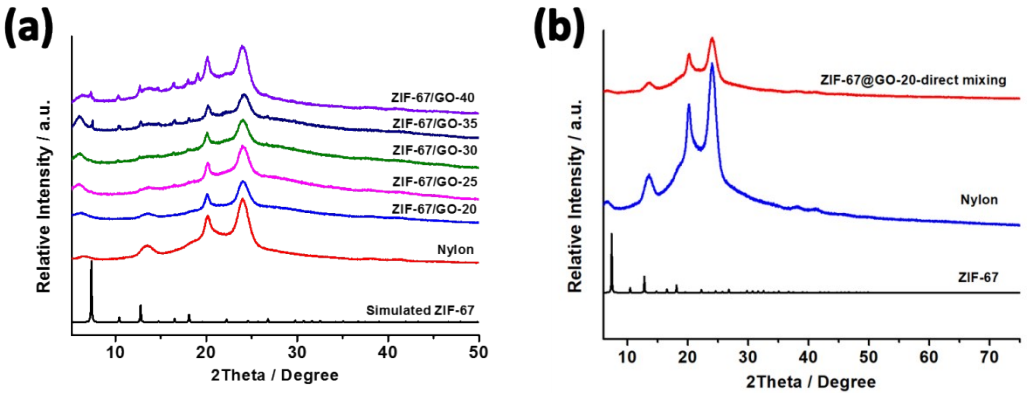

Figure S5. PXRD patterns of (a) ZIF-67/GO-x membranes and (b) the membrane by direct mixing ZIF-67 and GO with the same ratio of ZIF-67/GO-20.

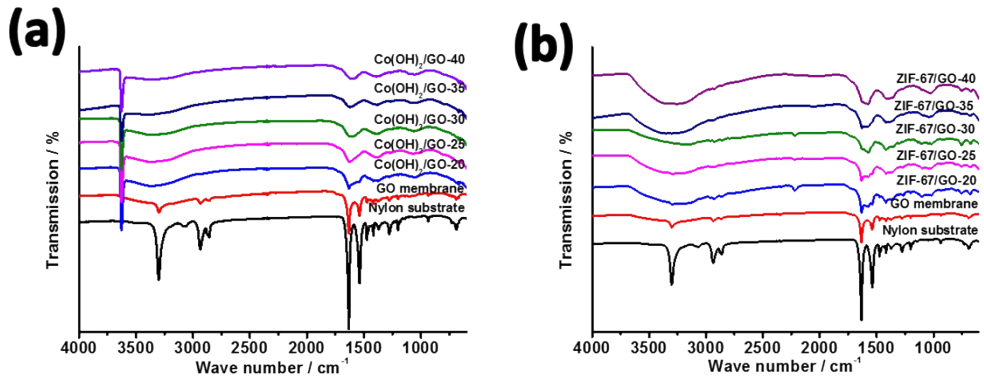

Figure S6. FTIR spectra of the Nylon substrate, GO membrane, $Co(OH)_2$/GO-x and ZIF-67/GO-x membranes.

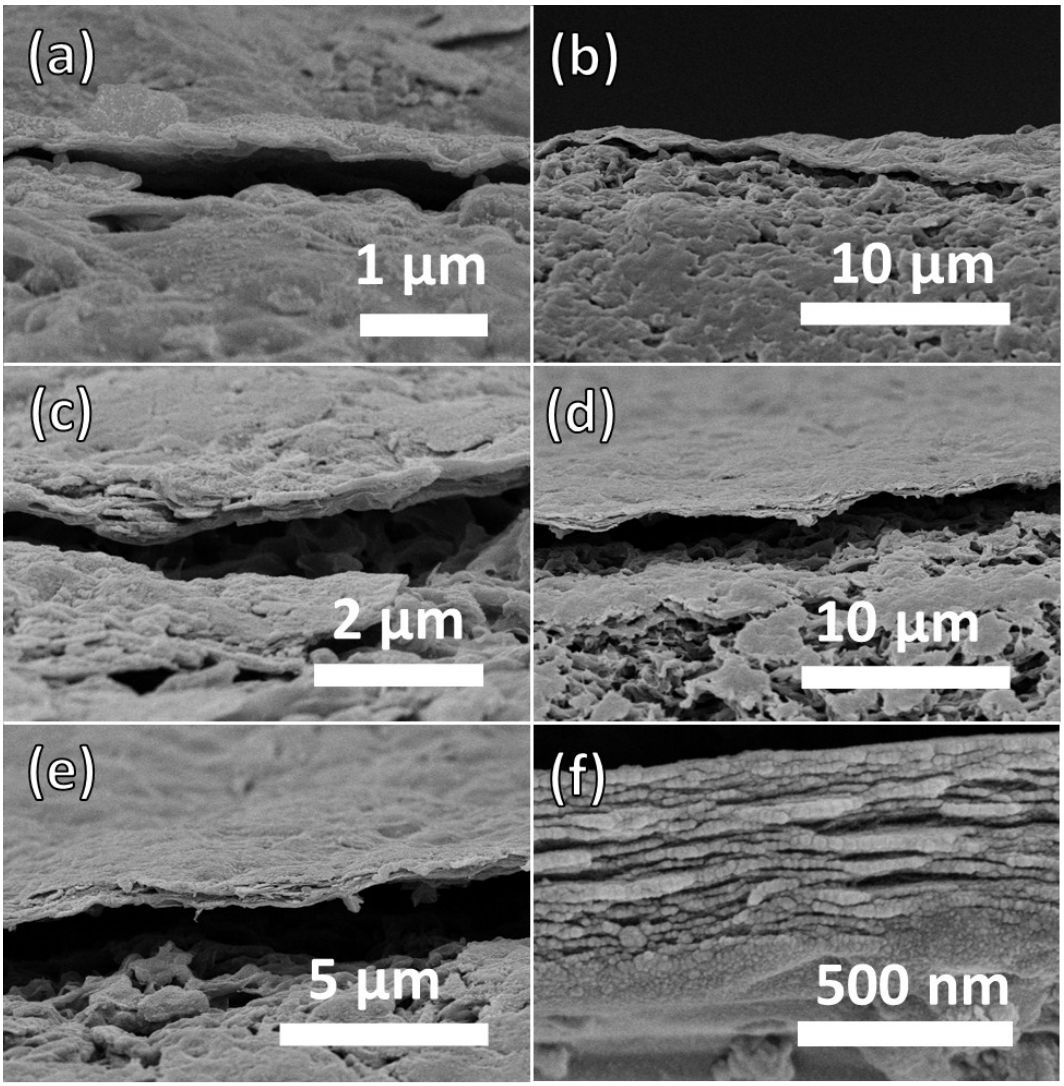

Figure S7. Cross-section SEM images for the ZIF-67/GO-x membranes prepared with varied volume of $Co(OH)_2$/GO mixtures. (a) 20 mL, (b) 25 mL, (c) 30 mL, (d) 35 mL and (e, f) 40 mL.

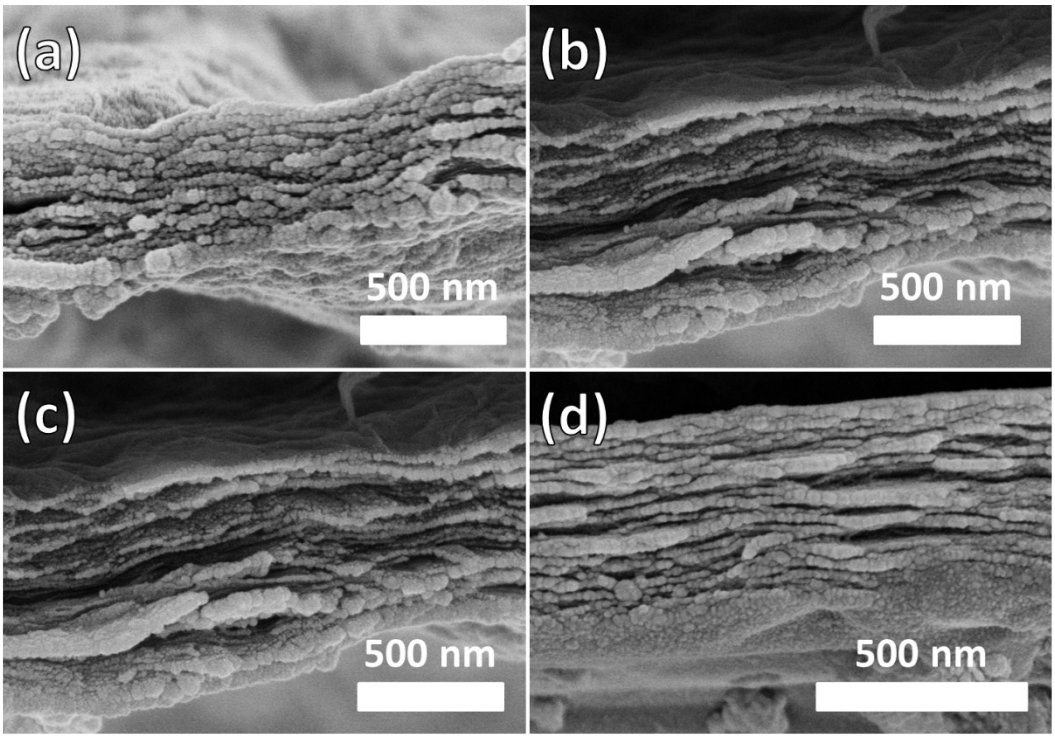

Figure S8. Cross-section SEM images of the ZIF-67/GO-40 membranes.

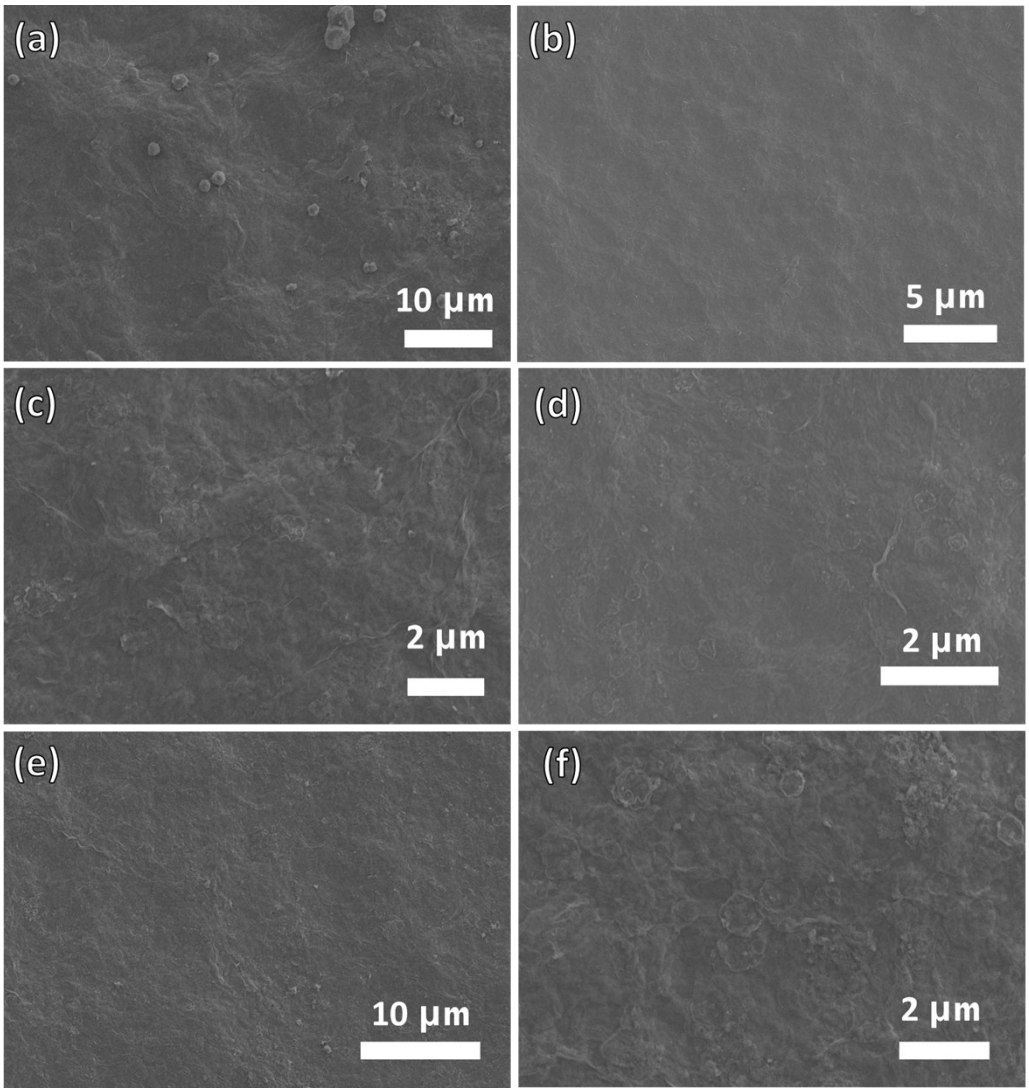

Figure S9. Top-view SEM images for the ZIF-67/GO-x membranes prepared with varied volume of $Co(OH)_2$/GO mixtures. (a) 20 mL, (b) 25 mL, (c) 30 mL, (d) 35 mL and (e, f) 40 mL.

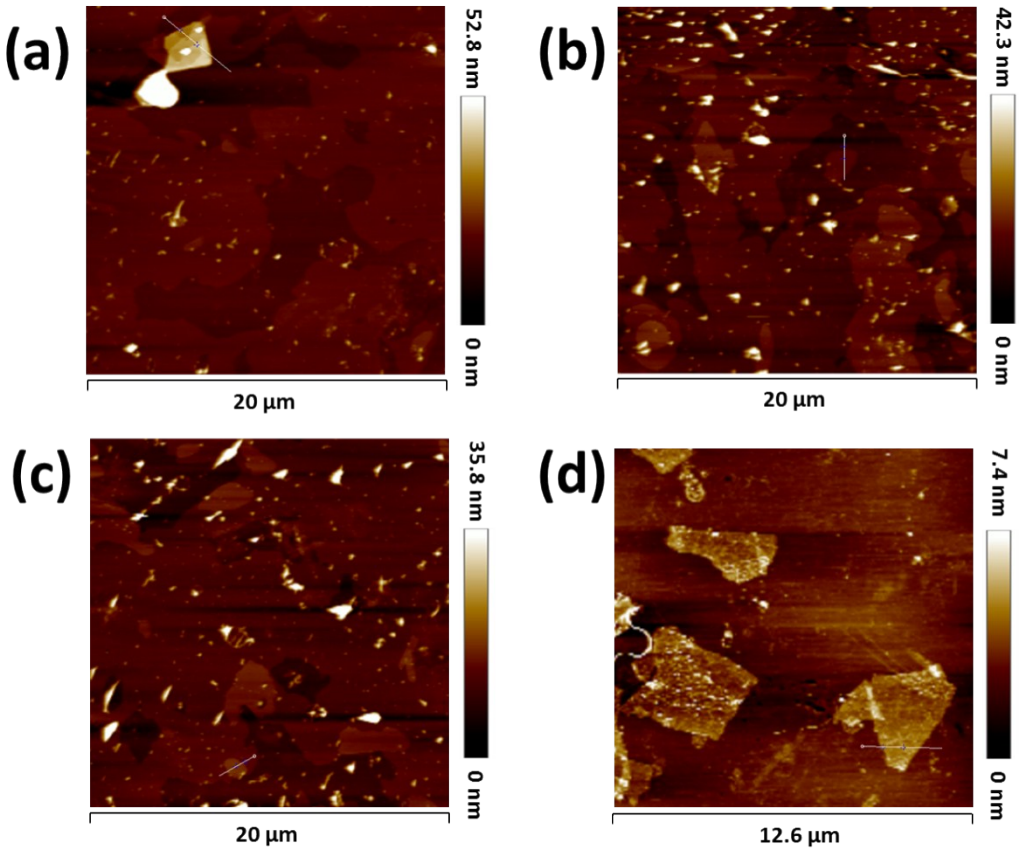

Figure S10. AFM images of the samples scraped from ZIF-67/GO-40 membranes. The sample was dispersed in DI water by sonication and dropped on the Si wafer, then dried in the oven.

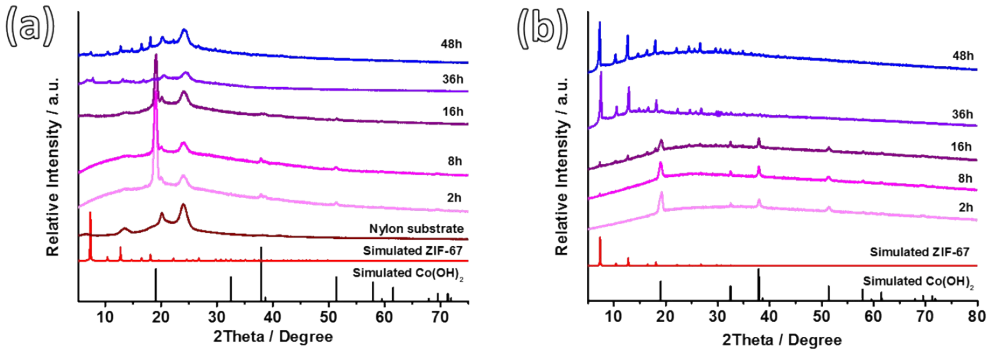

Figure S11. PXRD of the samples in the conversion process (a) with and (b) without GO after different time (2h, 8h, 16h, 36h and 48h).

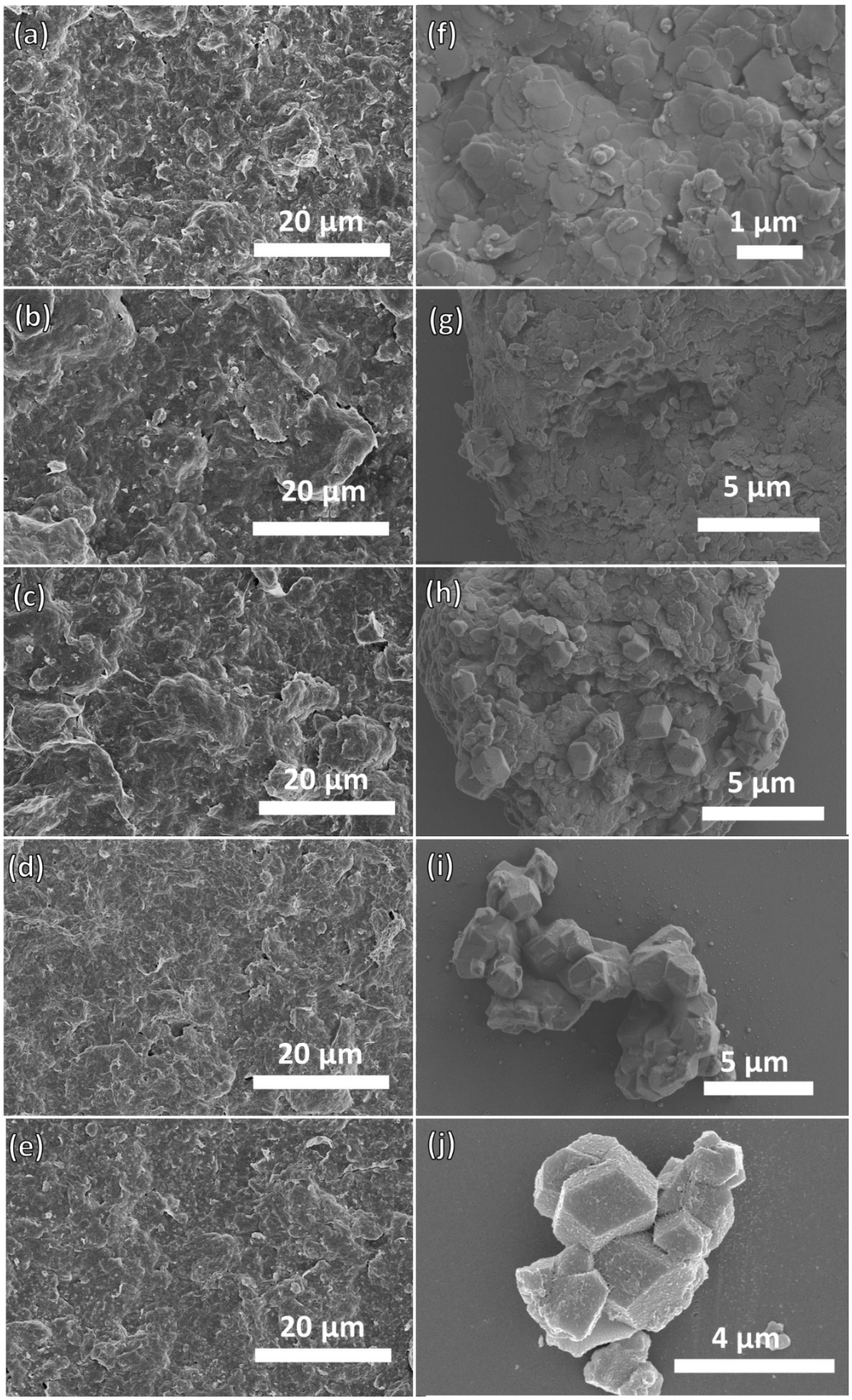

Figure S12. SEM images of the samples in the conversion process (a-e) with and (f-j) without GO after different time (2h, 8h, 16h, 36h and 48h).

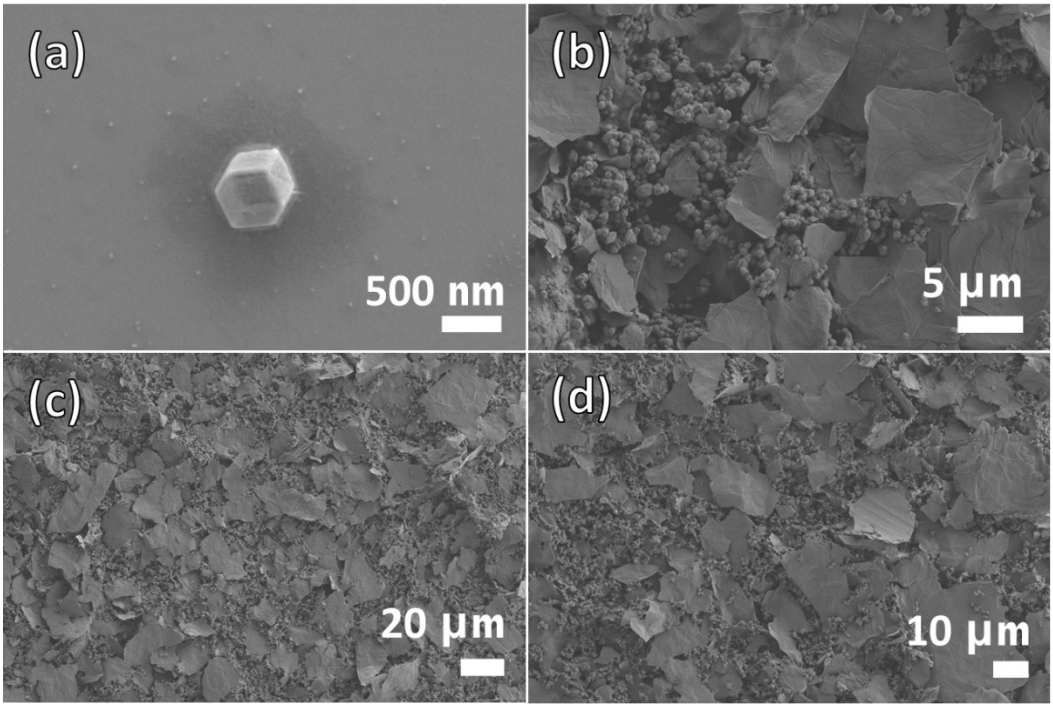

Figure S13. SEM images of (a) ZIF-67 NC and ZIF-67/GO-D membranes prepared with different volume of ZIF-67NC/GO mixtures: (b) 20 mL, (c) 30 mL and (d) 40 mL.

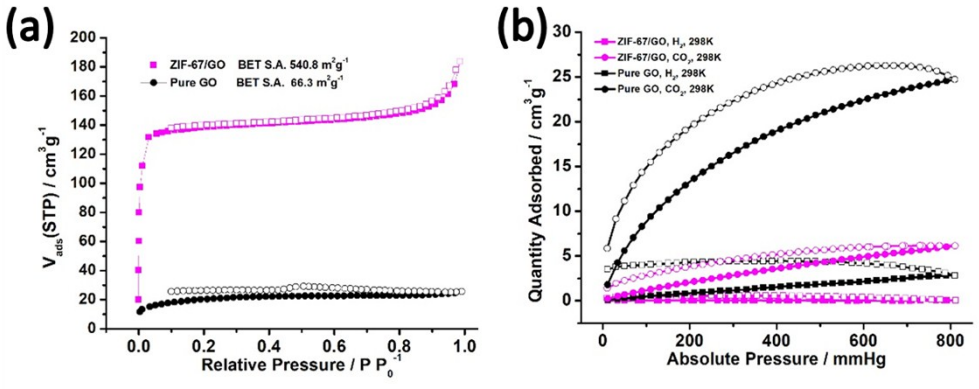

Figure S14. (a) N_2 adsorption and desorption isotherm curves for GO and ZIF-67/GO at 77K. (b) H_2 and CO_2 adsorption amount on ZIF-67/GO at 298K.

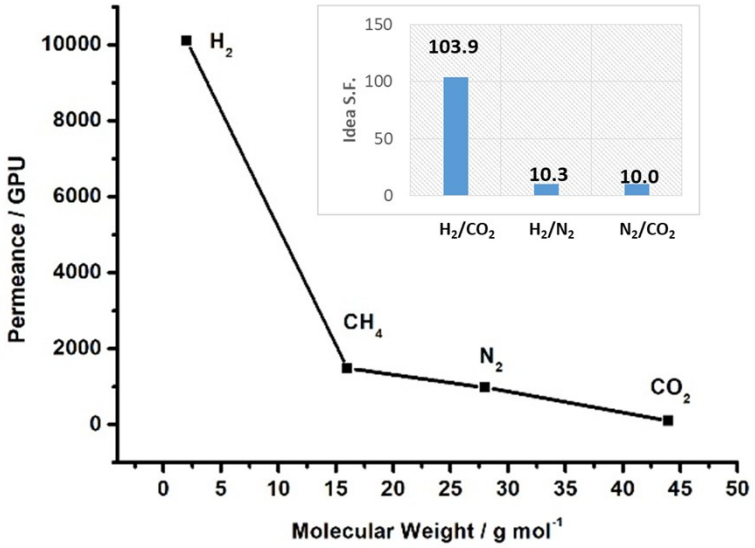

Figure S15. Single gas permeance on the ZIF-67/GO-40 membrane.

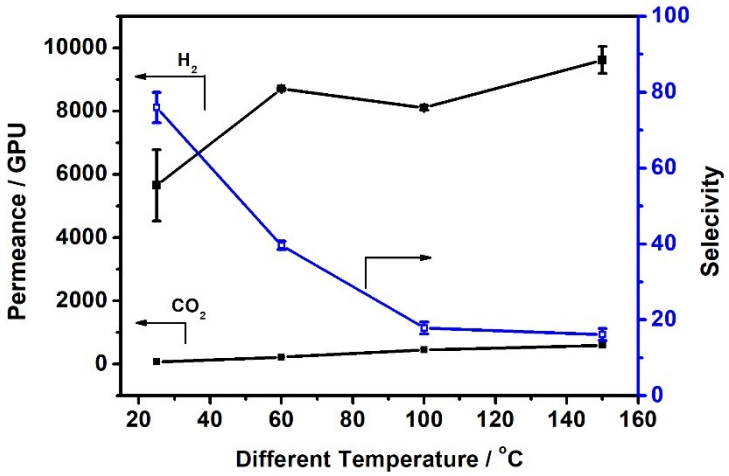

Figure S16. The influence of operation temperatures for H_2/CO_2 mixed gases separation performances on the ZIF-67/GO-40 membranes.

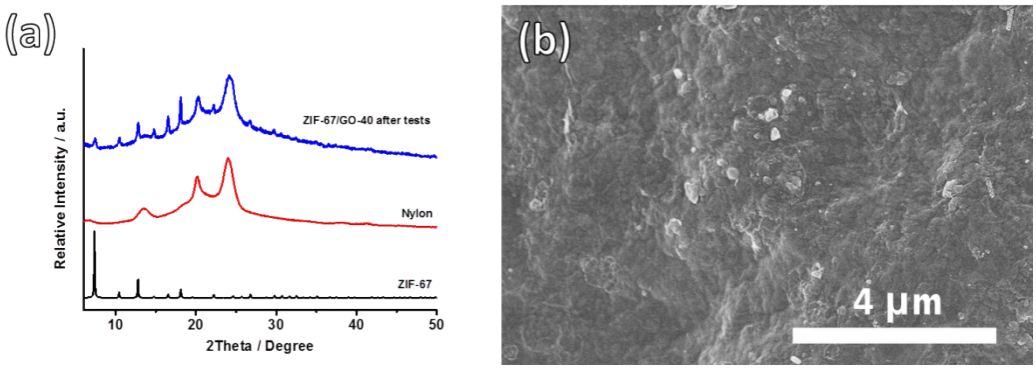

Figure S17. (a) PXRD and (b) SEM images of ZIF-67/GO-40 membranes after long time and high temperature tests.

Supplementary Tables

Table S1. Summary of the preparation conditions for the different membranes based on GO

ID	Doping process	Metal Precursor	Precursor/GO ratio	Conversed membrane
$Co(OH)_2$/GO-20[a]	Physical mixing	$Co(OH)_2$	4:1	ZIF-67/GO-20
$Co(OH)_2$/GO-25[a]	Physical mixing	$Co(OH)_2$	4:1	ZIF-67/GO-25
$Co(OH)_2$/GO-30[a]	Physical mixing	$Co(OH)_2$	4:1	ZIF-67/GO-30
$Co(OH)_2$/GO-35[a]	Physical mixing	$Co(OH)_2$	4:1	ZIF-67/GO-35
$Co(OH)_2$/GO-40[a]	Physical mixing	$Co(OH)_2$	4:1	ZIF-67/GO-40
$Co(OH)_2$/GO-50[a]	Physical mixing	$Co(OH)_2$	4:1	Off the substrate
$Co(OH)_2$/GO-A	Physical mixing	$Co(OH)_2$	2:1	Fail to converse
$Co(OH)_2$/GO-B	Physical mixing	$Co(OH)_2$	5:1	Agglomeration
Co_3O_4/GO	Physical mixing	Co_3O_4	4:1	Fail to converse
$Co(OH)_2$/GO-I	*In situ* growth	$Co(OH)_2$	4:1	Agglomeration
ZIF-67/GO-D	Directly mixing ZIF-67 and GO	-	-	ZIF-67/GO-D

a: different volume (x mL) of $Co(OH)_2$/GO mixtures were used to prepare membranes

Table S2. N 1s and C 1s spectral fitting parameters: binding energies (eV) and corresponding functional groups for ZIF-67 powder and ZIF-67/GO membranes.

Samples	Binding energies and functional groups			
	N 1s		C 1s	
Pure ZIF-67	399.3	Co-coordinated Imidazole N	284.3	-C=C-/-C-C-
			284.8	-C-N
			285.5	-C=N
ZIF-67/GO membrane	399.2	Co-coordinated Imidazole N	284.3	-C=C-/-C-C-
	400.3	H-bonded N	284.8	-C-N
			285.3	-C=N
			286.5	-C-OH
			288.7	-C=O

Table S3. Summary of ZIF-67 loading amounts calculated based on ICP results.

Membrane	Initial weight (mg)	Co ion amount (mg)	ZIF-67 ratio (%)
ZIF-67/GO-20	0.74	0.004783	2.57
ZIF-67/GO-25	0.37	0.007609	8.16
ZIF-67/GO-30	1.00	0.02457	9.75
ZIF-67/GO-35	1.24	0.08109	25.96
ZIF-67/GO-40	3.35	0.3185	37.74

Table S4. Summary of the concentration of Co ions in the solution after conversion

Membrane	ZIF-67 ratio (wt %)	solution volume (mL)	Co ion concentration in the solution after conversion (mgL^{-1})
ZIF-67/GO-20	2.57	64	6.96
ZIF-67/GO-40	37.74	61	13.43

Table S5. H_2/CO_2 mixed gas permeation results from the different membranes of ZIF-67@GO-40

Membrane ID	H_2 permeance (GPU)	CO_2 permeance (GPU)	Selectivity
M1	6773	94	72
M2	5302	67	79
M3	4922	65	75
M4	5837	81	72
M5	6776	90	75

Table S6. Summary of H_2/CO_2 mixed gases separation performances on the membranes from this work and references

Membrane	Temperature (°C)	H_2 Permeance (GPU)	Selectivity (H_2/CO_2)	Ref.
GO	25	1002	240	[1]
GO	25	840	33	[2]
MoS_2	35	2446	4.6	[3]
$Zn_2(Bim)_4$	25	2700	291	[4]
$Zn_2(Bim)_4$	25	2927	109	[4]
MAMS-1	40	881	225	[5]
MAMS-1	20	6131	40	[5]
ZIF-8@rGO	170	5718	26.4	[6]
ZIF-8@GO	250	383	14.9	[7]
ZIF-8/GO	25	91	406	[8]
ZIF-67	25	433	8.2[a]	[9]
ZIF-67/ZIF-9	150	212	8	[10]
GO	25	9093±110[b]	9.3±0.5	this work
ZIF-67/GO-40	25	5922±1000[c]	75±4	this work
ZIF-67/GO-40	150[d]	3625±252[e]	31±3	this work

a ideal separation factors, b CO_2 permeance: 979±22 GPU, c CO_2 permeance: 79±15 GPU, d feed gas containing ~4 mol% water vapor, e CO_2 permeance: 119±19 GPU.

Supplementary References

[1] C. Chi, X. Wang, Y. Peng, Y. Qian, Z. Hu, J. Dong, D. Zhao, *Chem. Mater.* **2016**, 28, 2921.

[2] J. Shen, G. Liu, K. Huang, Z. Chu, W. Jin, N. Xu, *ACS nano* **2016**, 10, 3398.

[3] D. Wang, Z. Wang, L. Wang, L. Hu, J. Jin, *Nanoscale* **2015**, 7, 17649.

[4] Y. L. Yuan Peng, Yujie Ban, Hua Jin, Wenmei Jiao, Xinlei Liu, Weishen Yang, *Science* **2014**, 346, 1356.

[5] X. Wang, C. Chi, K. Zhang, Y. Qian, K. M. Gupta, Z. Kang, J. Jiang, D. Zhao, *Nat Commun* **2017**, 8, 14460.

[6] W. Li, Y. Zhang, P. Su, Z. Xu, G. Zhang, C. Shen, Q. Meng, *J. Mater. Chem. A* **2016**, 4, 18747.

[7] A. Huang, Q. Liu, N. Wang, Y. Zhu, J. Caro, *J. Am. Chem. Soc.* **2014**, 136, 14686.

[8] X. Wang, C. Chi, J. Tao, Y. Peng, S. Ying, Y. Qian, J. Dong, Z. Hu, Y. Gu, D. Zhao, *Chem. Commun.* **2016**, 52, 8087.

[9] S. Zhou, Y. Wei, L. Zhuang, L.-X. Ding, H. Wang, *J. Mater. Chem. A* **2017**, 5, 1948.

[10] F. Cacho-Bailo, I. Matito-Martos, J. Perez-Carbajo, M. Etxeberria-Benavides, O. Karvan, V. Sebastian, S. Calero, C. Tellez, J. Coronas, *Chemical science* **2017**, 8, 325.