

Electronic Supplementary Information

Enhanced Selective Adsorption of CO₂ on Nitrogen-Doped Porous Carbon Monolith Derived from IRMOF-3

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EXPERIMENTAL DETAILS

Material synthesis

IRMOF-3 was synthesized according to the literature (Science 2002, **295**, 469-472):

Zinc nitrate tetrahydrate (1.568 g) and 2-aminobenzene-1,4-dicarboxylic acid (0.332 g) were dissolved in DMF (30 mL) in a vial. The mixture was heated to 100°C and kept for 24 h to yield large cubic crystals of IRMOF-3. After cooled down to room temperature, the cubic crystals were repeatedly washed with DMF and anhydrous chloroform, and then soaked in anhydrous chloroform for 12 h. Final product was filtered and dried at 120°C under high vacuum (0.1 Pa) for 48 h.

The carbonization of IRMOF-3 was performed as following:

1.0 g of IRMOF-3 was placed in a quartz crucible, heated in a tubular furnace under flowing N₂ (100 mL/min) to a target temperature (500~800°C) at a ramping rate of 1°C /min, and then kept for 4 h. The resultant N-doped carbon monoliths (NCMs) were denoted as IRMOF-3/*T*, where *T* is the carbonization temperature.

The treatment of synthesized NCMs with HCl was performed as following:

0.3 g of NCMs was added to 40 mL of 5wt.% aqueous HCl, and stirred at 50°C for 24 h. The solid was filtered and washed with deionized water repeatedly until neutral. The final product was dried at 120°C under high vacuum (0.1 Pa) for 12 h. HCl-treated NCMs were denoted as IRMOF-3/*T*-HCl.

Characterization

N₂ adsorption-desorption isotherms at -196°C were measured on a Micromeritics ASAP 2020 system to determine the textural properties. Prior to the measurement, IRMOF-3 was dried at 120°C under high vacuum (0.1 Pa) for 48 h, while NCMs were dried at 200°C under high vacuum (0.1 Pa) for 5 h. Total surface area was calculated from BET equation in the relative pressure range of 0.05~0.25. Total pore volume was calculated from the amount of N₂ uptake at the relative pressure of 0.975. Micropore surface area and micropore volume were calculated from *t*-plot equation in the thickness range of 0.45~0.60 nm. Pore size distribution was derived from N₂ adsorption isotherms using BJH model.

X-ray diffraction (XRD) was collected on a XD-3 diffractometer with Cu K_α radiation ($\lambda = 0.15418$ nm, 40 kV/30 mA) at the scanning step of 2°/min. X-ray photoelectron spectroscopy (XPS) was determined on an ESCALAB250xi spectrometer, and all the binding energies were calibrated by using C1s peak at 284.8 eV as the reference. Scanning electron microscopy (SEM) was taken on FEI QUANTA 450, with an accelerating voltage of 15.0 kV. Transmission electron microscopy (TEM) was taken on JEOL JEM-2100 at 200 kV. ICP data was determined on an Agilent 5100 ICP-OES instrument.

CO₂ and N₂ adsorption

CO₂ and N₂ adsorption isotherms at 0, 25 and 50°C were also measured on a Micromeritics ASAP 2020 system. Prior to the measurement, IRMOF-3 was dried at 120°C under high vacuum (0.1 Pa) for 48 h, while NCMs were dried at 200°C under high vacuum (0.1 Pa) for 5 h.

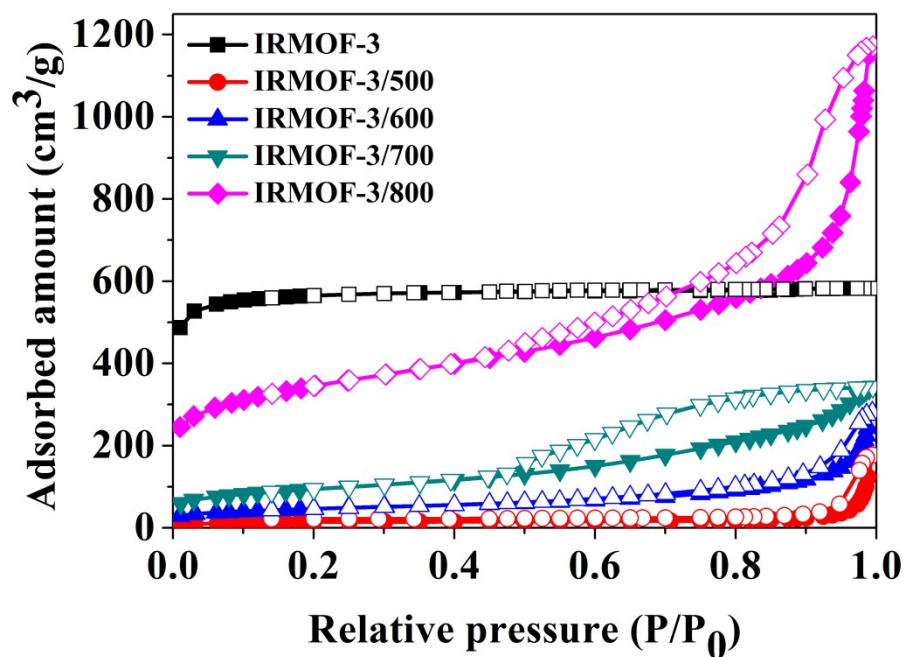


Figure S1. N₂ adsorption-desorption isotherms of IRMOF-3 and NCMs at -196°C.

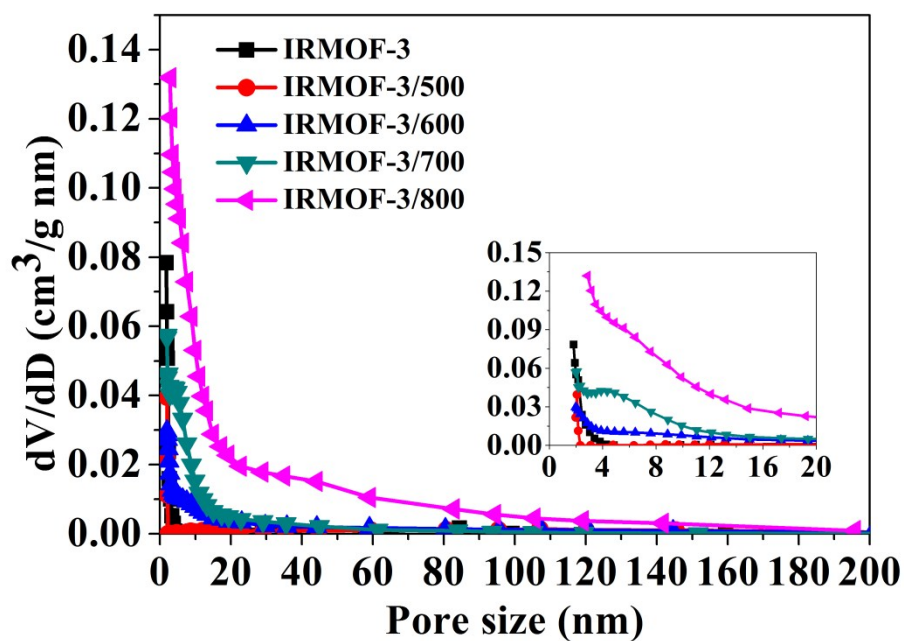


Figure S2. BJH pore size distributions of IRMOF-3 and NCMs calculated from adsorption branch.

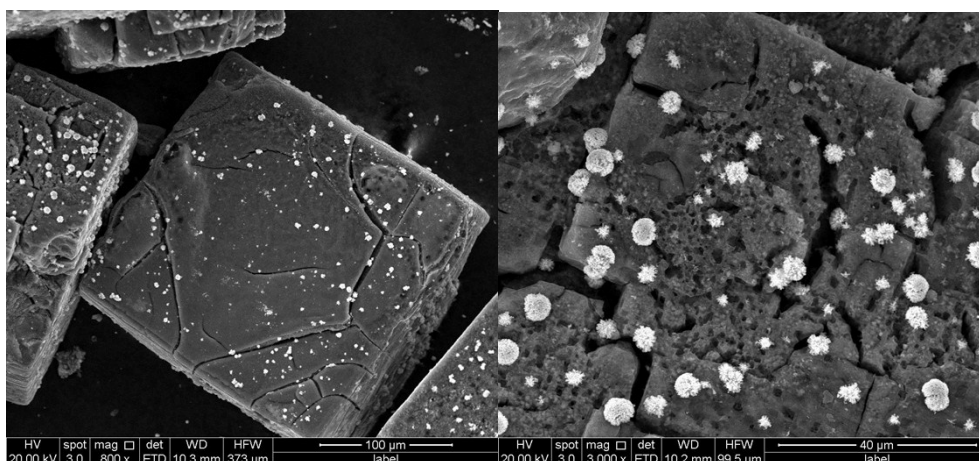


Figure S3. SEM images of IRMOF-3/500.

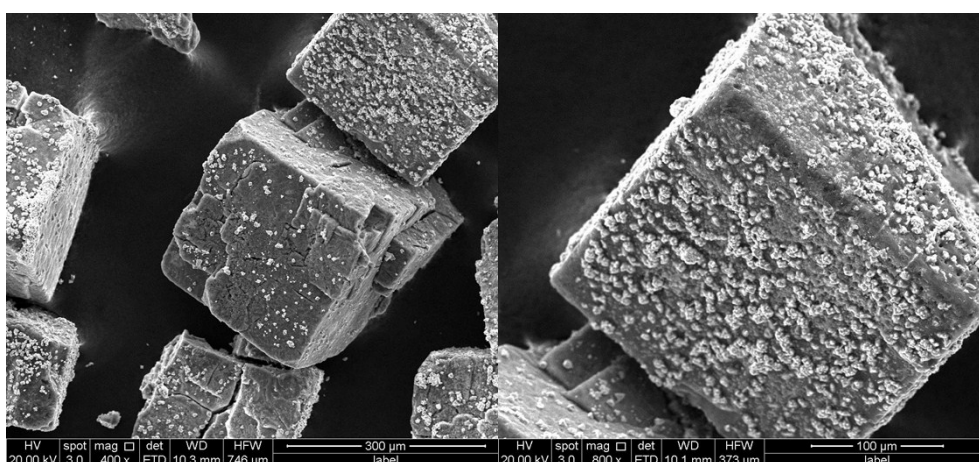


Figure S4. SEM images of IRMOF-3/600.

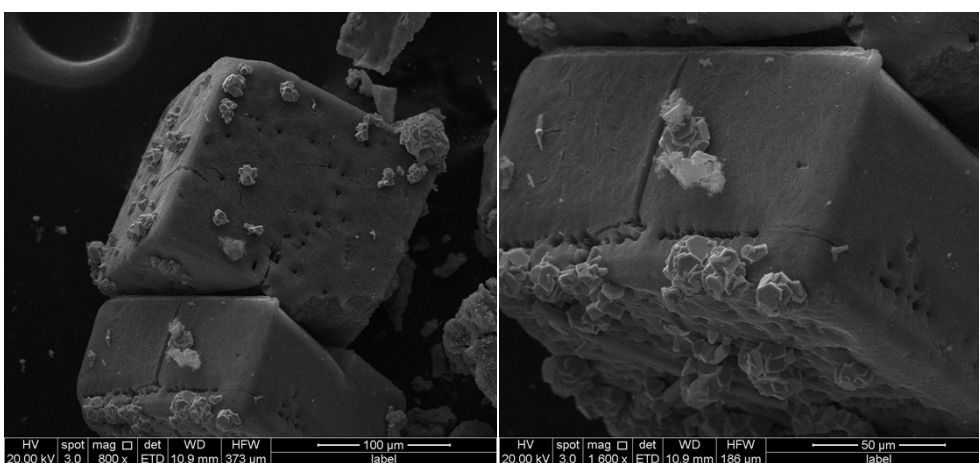


Figure S5. SEM images of IRMOF-3/700.

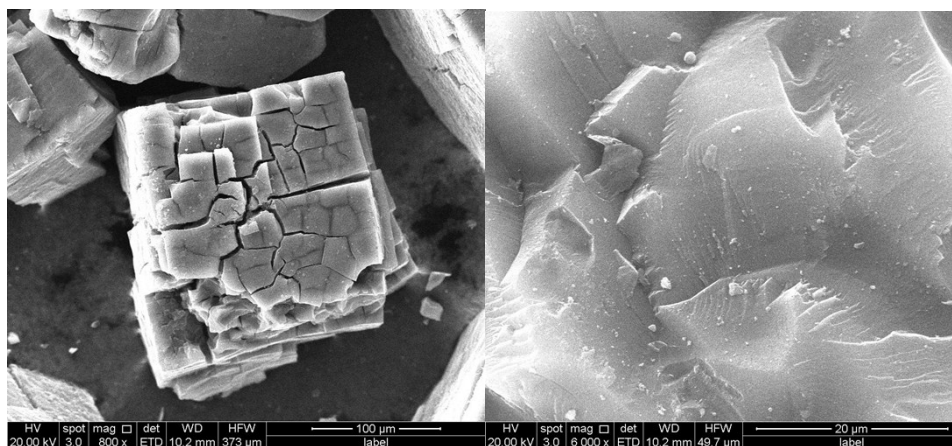


Figure S6. SEM images of IRMOF-3/800.

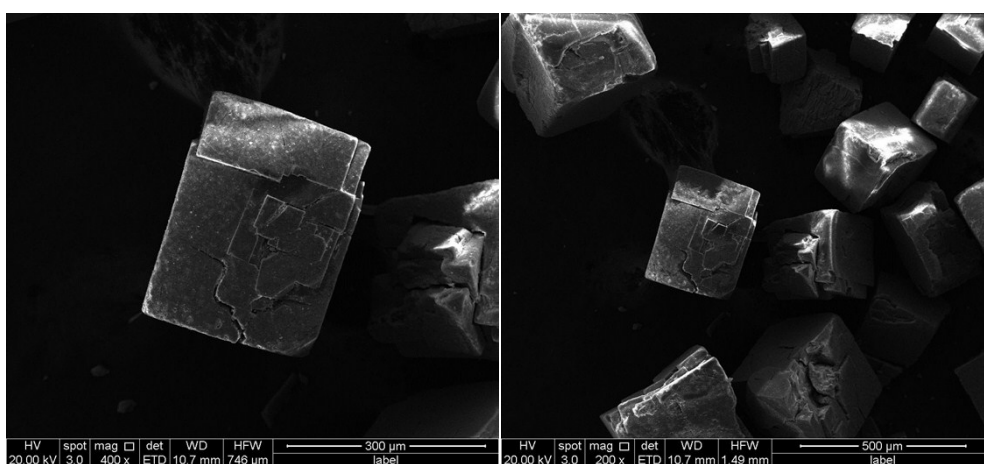


Figure S7. SEM images of IRMOF-3.

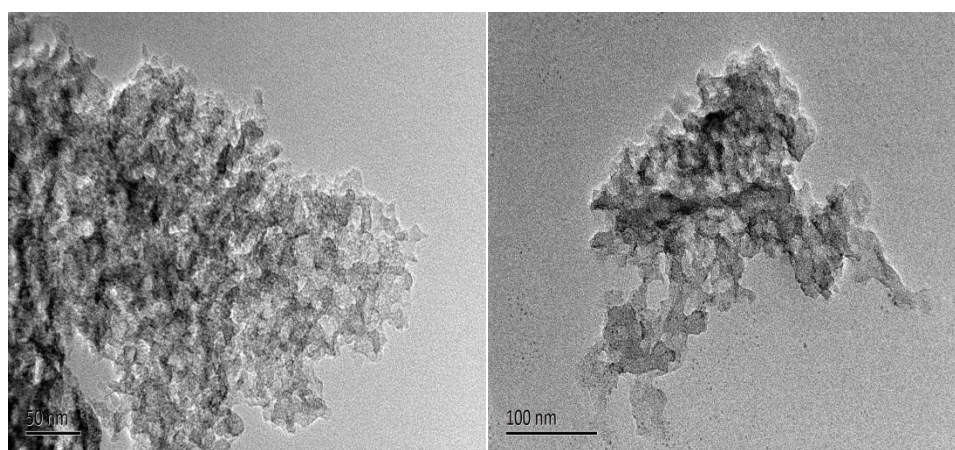


Figure S8. TEM images of IRMOF-3/800.

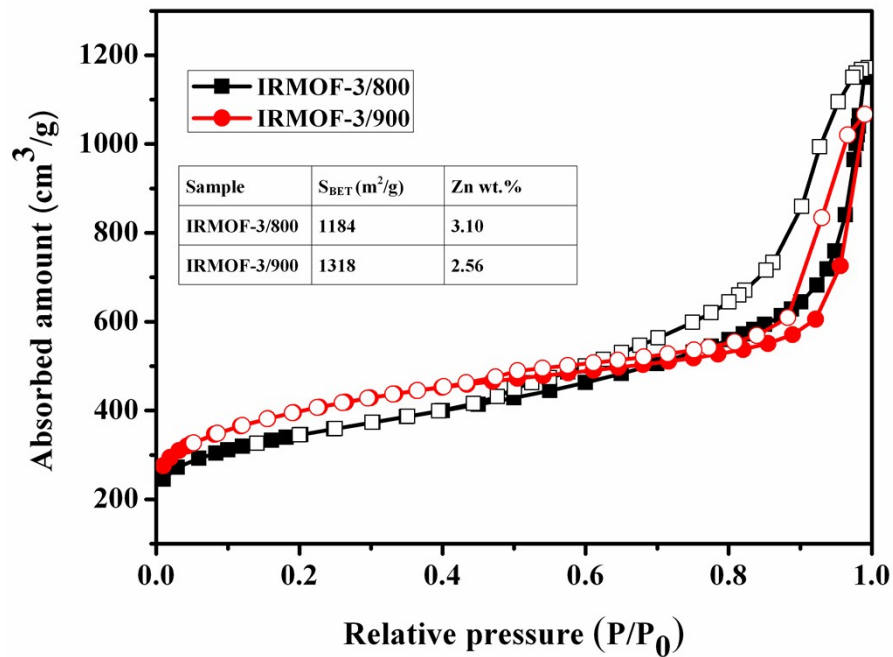


Figure S9. N_2 adsorption-desorption isotherms at -196°C and zinc ICP results of IRMOF-3/800 and IRMOF-3/900.

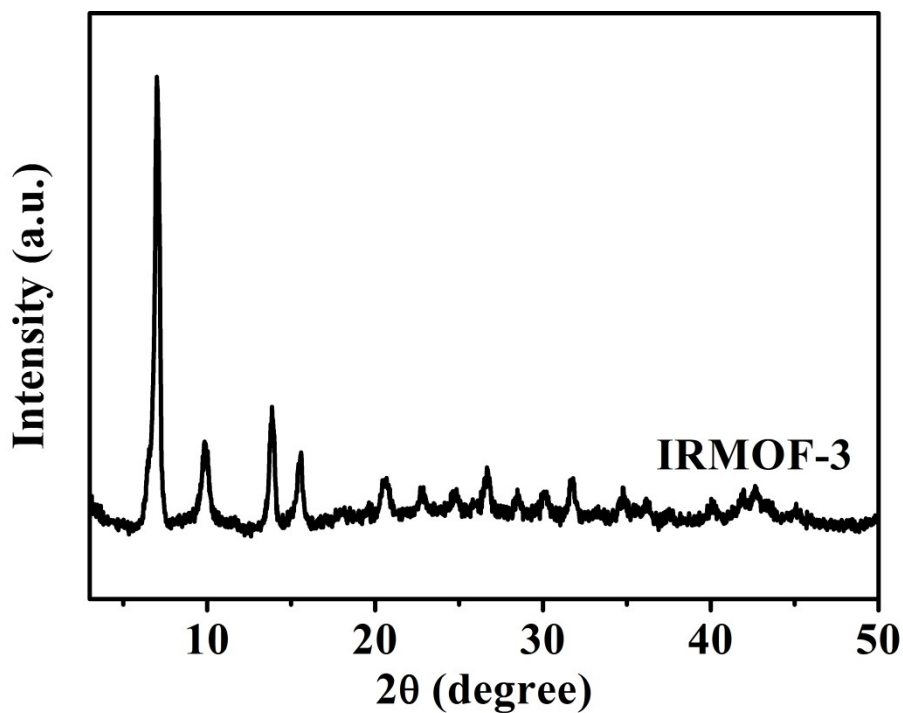


Figure S10. XRD pattern of IRMOF-3.

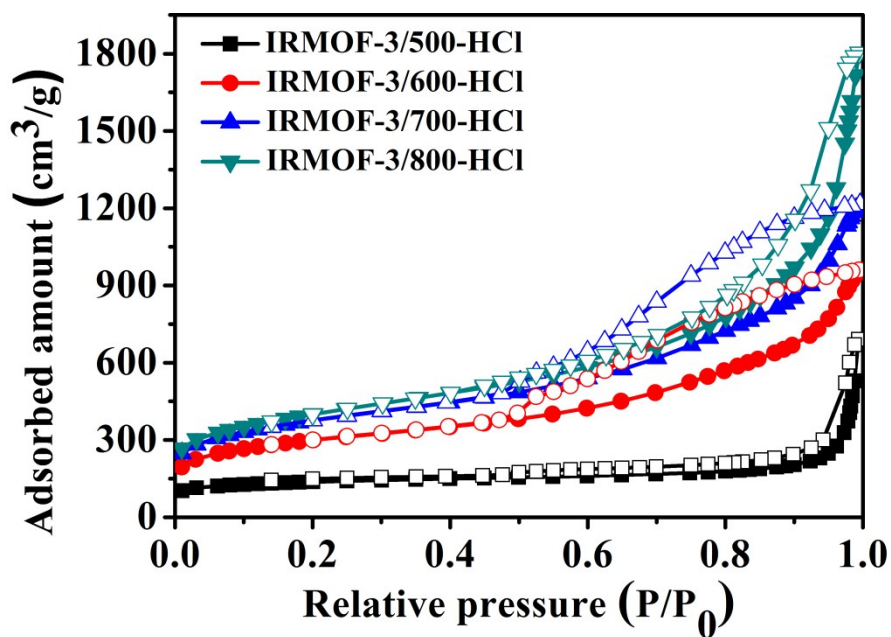


Figure S11. N₂ adsorption-desorption isotherms of HCl-treated NCMs at -196°C.

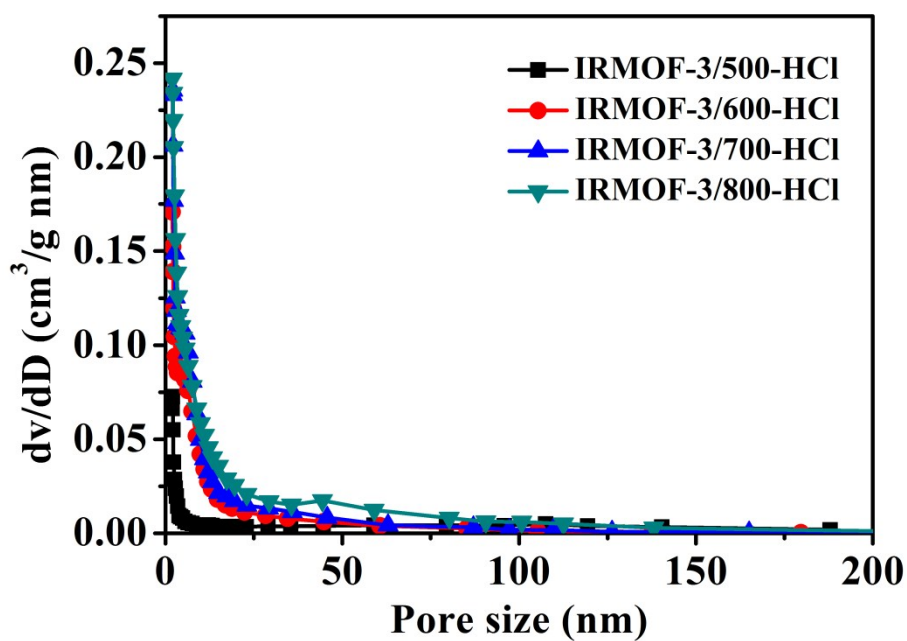


Figure S12. BJH pore size distributions of HCl-treated NCMs calculated from adsorption isotherms.

Table S1. Textual properties of HCl-treated NCMs

Samples	S_{BET} (m^2/g) ^[a]	S_{m} (m^2/g) ^[b]	V_{t} (cm^3/g) ^[c]	V_{m} (cm^3/g) ^[d]
IRMOF-3/500-HCl	459	239	0.51	0.12
IRMOF-3/600-HCl	1033	304	1.35	0.14
IRMOF-3/700-HCl	1306	326	1.75	0.15
IRMOF-3/800-HCl	1393	324	2.24	0.15

[a] Surface area calculated from BET equation in the relative pressure range of 0.05~0.25; [b] micropore surface area calculated from t -plot equation in the thickness range of 0.45~0.60 nm; [c] single point total pore volume calculated at the relative pressure of 0.975; [d] micropore volume calculated from t -plot equation in the thickness range of 0.45~0.60 nm.

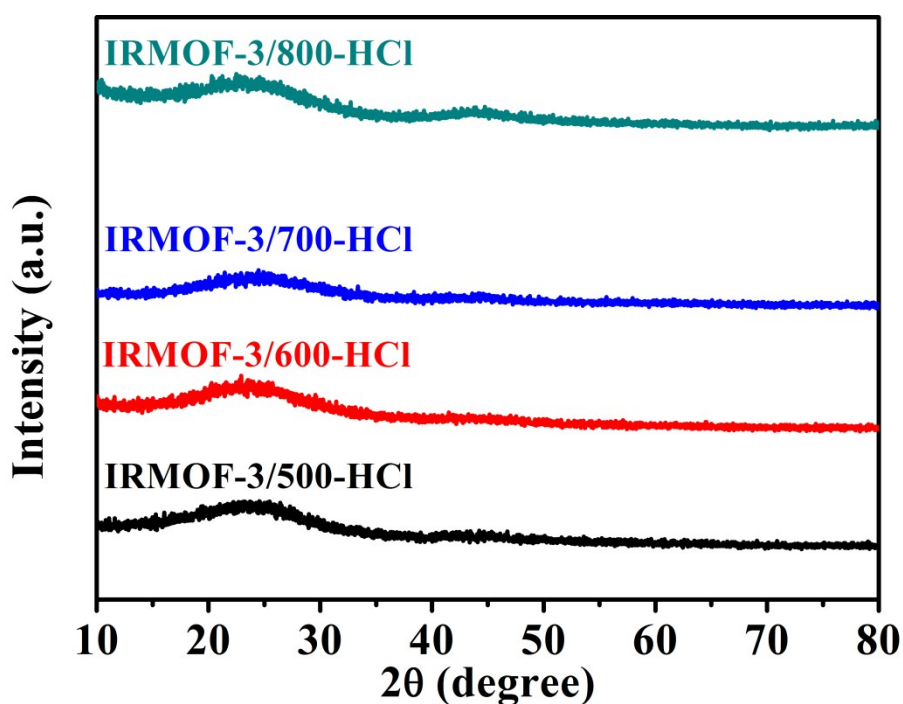


Figure S13. XRD patterns of HCl-treated NCMs.

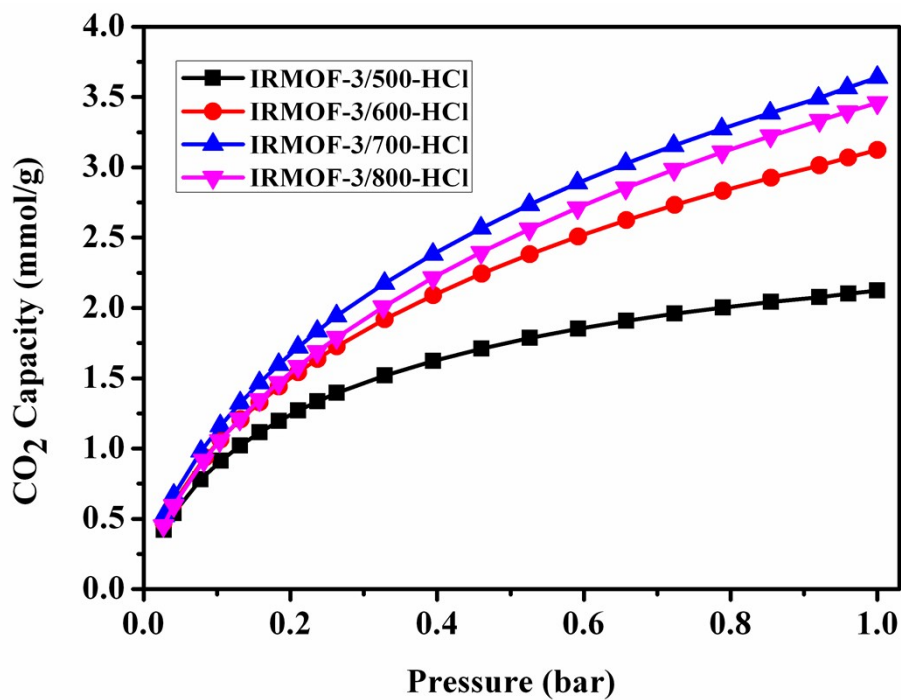


Figure S14. CO₂ adsorption isotherms of HCl-treated NCMs at 0°C.

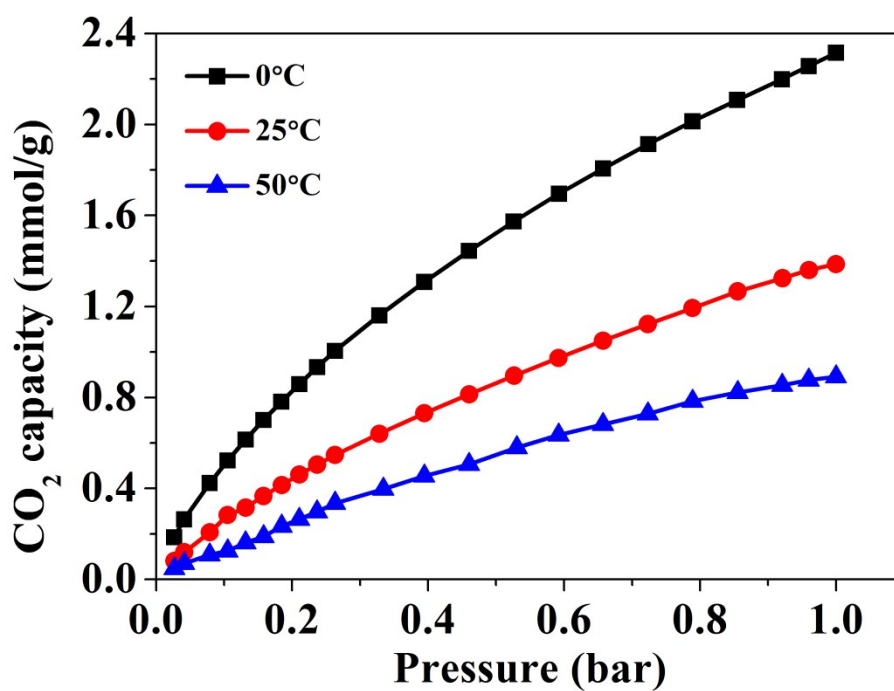


Figure S15. CO₂ adsorption isotherms of IRMOF-3 at 0, 25 and 50°C.

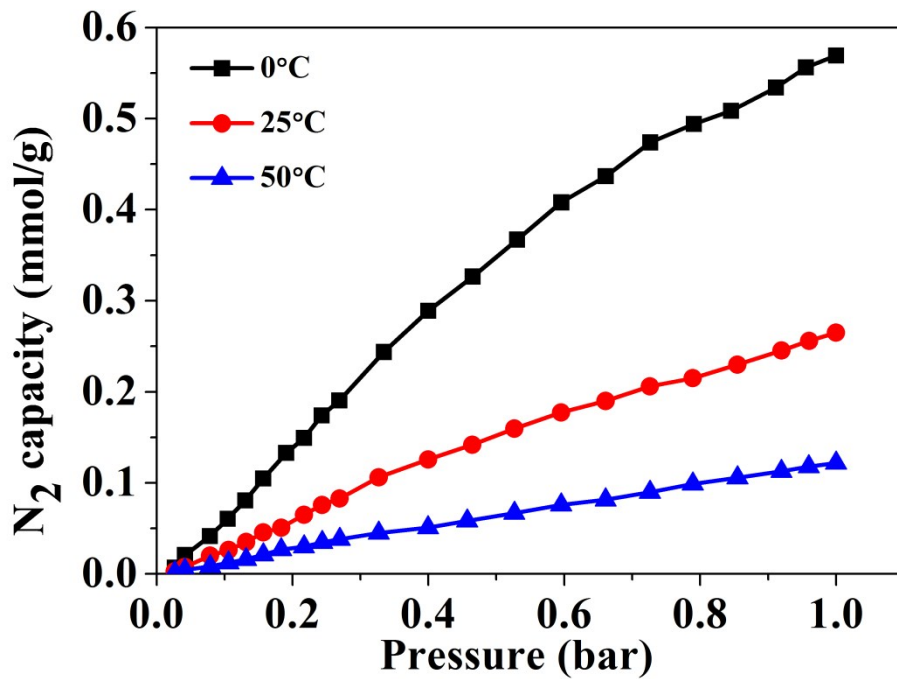


Figure S16. N₂ adsorption isotherms of IRMOF-3 at 0, 25 and 50°C.

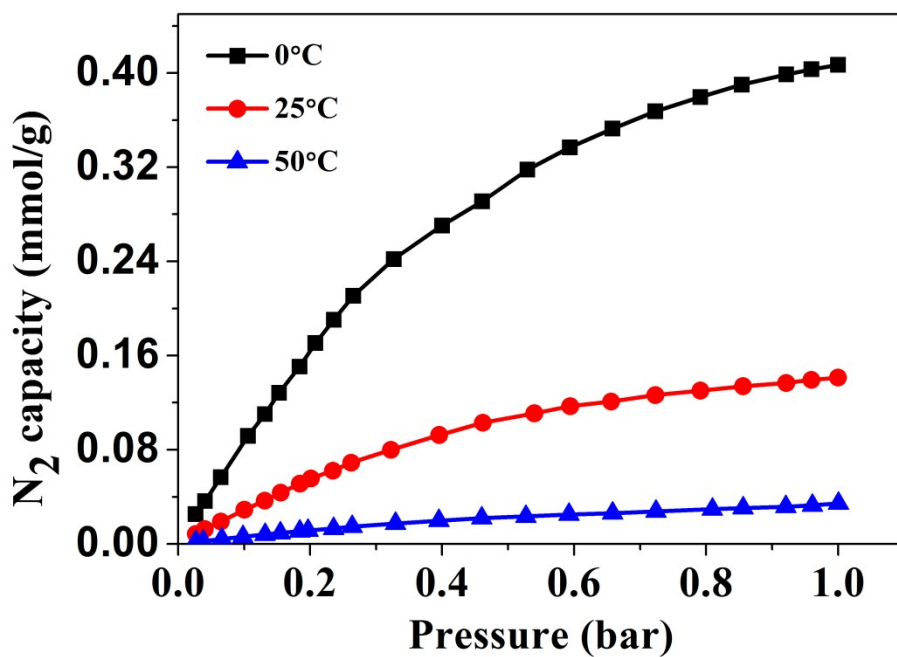


Figure S17. N₂ adsorption isotherms of IRMOF-3/800 at 0, 25 and 50°C

Table S2. IAST selectivities of CO₂/N₂ on some MOFs (entry 1-17) and N-doped carbons (entry 18-33)

Entry	Sample	CO ₂ /N ₂ Selectivity	CO ₂ concentration (%)	Temperature (°C)	Pressure (bar)	Ref.
1	Bio-MOF-11	36	15	25	1	[S1]
2	HKUST-1	21	50	25	2.5	[S2]
3	IRMOF-1	3	50	25	2.5	[S2]
4	IRMOF-11	11	50	25	2.5	[S2]
5	IRMOF-12	3	50	25	2.5	[S2]
6	IRMOF-13	11	50	25	2.5	[S2]
7	IRMOF-14	3	50	25	2.5	[S2]
8	ZIF-68	18.7	50	25	1	[S3]
9	ZIF-69	19.9	50	25	1	[S3]
10	ZIF-70	17.3	50	25	1	[S3]
11	ZIF-78	50.1	50	25	1	[S3]
12	ZIF-79	23.2	50	25	1	[S3]
13	ZIF-81	23.8	50	25	1	[S3]
14	ZIF-82	35.3	50	25	1	[S3]
15	ZIF-95	18	50	25	1	[S3]
16	ZIF-100	5.9	50	25	1	[S3]
17	IRMOF-3	8.6	15	25	1	This work
18	MCN/C	40	10	25	1	[S4]
19	HCM DAH-1	30	10	25	1	[S5]
20	H-NMC-2.5	37	15	25	1	[S6]
21	RFL-500	29	10	25	1	[S7]
22	nZDC-700	76	15	25	1	[S8]
23	NPC-2	31	15	25	1	[S9]
24	NC-650-1	29	15	25	1	[S10]
25	CN-950	12	10	25	1	[S11]
26	a-NDC6	30	10	25	1	[S12]
27	SNS2-20	68.96	15	25	1	[S13]
28	SNS2-20	79.35	15	50	1	[S13]
29	CPC 550	21	10	25	1	[S14]
30	SU-MAC-500	39	10	25	1	[S15]
31	IRMOF-3/800	22.7	15	0	1	This work
32	IRMOF-3/800	38.8	15	25	1	This work
33	IRMOF-3/800	87.0	15	50	1	This work

References

- [S1] Y. F. Chen and J. W. Jiang, *ChemSusChem*, 2010, **3**, 982.
- [S2] B. Liu and B. Smit, *Langmuir*, 2009, **25**, 5918.
- [S3] A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O' Keefe and O. M. Yaghi, *Acc. Chem. Res.*, 2010, **43**, 58.
- [S4] Q. F. Deng, L. Liu, X. Z. Lin, G. Du, Y. Liu and Z. Y. Yuan, *Chem. Eng. J.*, 2012, **203**, 63.
- [S5] G. P. Hao, W. C. Li, D. Qian, G. H. Wang, W. P. Zhang, T. Zhang, A. Q. Wang, F. Schüth, H. J. Bongard and A. H. Lu, *J. Am. Chem. Soc.*, 2011, **133**, 11378.

- [S6] J. Wei, D. Zhou, Z. Sun, Y. Deng, Y. Xia and D. Zhao, *Adv. Funct. Mater.*, 2013, **23**, 2322.
- [S7] G. P. Hao, W. C. Li, D. Qian and A. H. Lu, *Adv. Mater.*, 2010, **22**, 853.
- [S8] S. Gadipelli and Z. X. Guo, *ChemSusChem*, 2015, **8**, 2123.
- [S9] L. Wan, J. L. Wang, C. Feng, Y. H. Sun and K. X. Li, *Nanoscale*, 2015, **7**, 6534.
- [S10] M. L. Yang, L. P. Guo, G. S. Hu, X. Hu, L. Q. Xu, J. Chen, W. Dai and M. H. Fan, *Environ. Sci. Technol.*, 2015, **49**, 7063.
- [S11] X. Y. Ma, M. H. Cao and C. W. Hu, *J. Mater. Chem. A*, 2013, **1**, 913.
- [S12] V. Chandra, S. U. Yu, S. H. Kim, Y. S. Yoon, D. Y. Kim, A. H. Kwon, M. Meyyappan and K. S. Kim, *Chem. Commun.*, 2012, **48**, 735.
- [S13] Y. K. Kim, G. M. Kim and J. W. Lee, *J. Mater. Chem. A*, 2015, **3**, 10919.
- [S14] B. Ashourirad, A. K. Sekizkardes, S. Altarawneh and H. M. El-Kaderi, *Chem. Mater.*, 2015, **27**, 1349.
- [S15] W. F. J. To, J. He, J. Mei, R. Haghpanah, Z. Chen, T. Kurosawa, S. Chen, W. G. Bae, L. Pan, B. H. J. Tok, J. Wilcox and Z. Bao, *J. Am. Chem. Soc.* 2016, **138**, 1001.