Electronic Supplementary Information

From ionic-liquid@metal-organic framework composites to heteroatom-decorated large-surface area carbons: superior CO₂ and H₂ uptakes

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1. Materials and Instrumentation

All chemicals were purchased commercially and used without further purification: Trimethyl-1,3,5-trimesate (TCI), aluminum nitrate (Sigma-Aldrich), 1-Ethyl-3methylimidazolium dicyanamide (EMIM DCN) (Sigma-Aldrich), 1-ethyl-3methylimidazolium tetracyanoborate (EMIM TCB) (Merck), nitric acid (TCI) and hydrofluoric acid (46%, Kishida Chemical Co. Ltd).

Powder X-ray diffraction (PXRD) measurements were performed on a Mac Science MXP3 V diffractometer with Ni filtered Cu-K α radiation ($\lambda = 0.15406$ nm) (40 kV, 20 mA). X-ray photoelectron spectroscopic (XPS) analyses were carried out on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using an Mg K α source (10 kV, 10 mA). The sorption isotherms of nitrogen and other gases were measured by using automatic volumetric adsorption equipments BELSORP max and BELSORP mini II, respectively, and the surface areas were calculated using N₂ sorption data in the relative pressure range of 0.05-0.20. The gas sorption measurements for all these carbon materials were performed after preactivation at 120 °C overnight. The pore-size distributions were calculated by non-localized density functional theory (NLDFT) using N₂ adsorption isotherms at 77 K. Elemental (CHN) analyses were performed on CE EA1110 instrument. Transmission electron microscopy (TEM) images and scanning transmission electron microscopy (STEM) images were recorded on Titan3 G2 60-300 (FEI) with an operating voltage of 300 kV. Electron energy loss spectroscopy (EELS) mapping analyses were performed on Quantum ERS (Gatan) inbuilt in Titan3 G2 60-300 (FEI).

2. Preparation of MIL-100(Al)

Aluminum-based MOF MIL-100(Al) was synthesized following reported procedure in the literature.¹ A mixture of Al(NO₃)₃·9H₂O (230 mg), (CH₃O)₃C₆H₃ (denoted as btcMe₃) (104 mg), HNO₃ (1M) (0.77 mL) and deionized water (2.8 mL) were placed in a 10 mL Teflonliner autoclave and heated at 210 °C for 3.5 h. After slow cooling to room temperature within 12 h, the resulting yellow powder were filtered off, washed with distilled water several times, and then further purified by solvothermal and hydrothermal treatments with DMF at 150 °C (6 h) and water at 110 °C (24 h), respectively. The resulting white solid was immediately filtered, washed with hot water several times, and finally dried overnight at 200 °C under vacuum for further use.

3. Preparation of C-Samples (C600, C800 and C1000)

The as-synthesised MIL-100(Al) (250 mg) was directly transferred into a ceramic boat and placed in a furnace under Ar flow. The samples were preheated at 200 °C for 12 h, and subsequently carbonized at 1000, 800 and 600 °C for 7 h. After cooling, the resulting black solids were ground into powders, and then washed with HF solutions (20 %) by stirring for 2 days. The black solids were separated by centrifugation and washed with distilled water for several times. After drying under vacuum at 120 °C for overnight, the resulting samples were labeled as CT, where T is the carbonization temperature.

4. Preparation of NC800

Prior to precursor loading, the as-synthesized MIL-100(Al) (250 mg) was again activated at 200 °C for 12 h to get completely desolvated sample. In an air-tight vessel, the resultant sample was soaked into 0.25 g of ionic liquid, 1-Ethyl-3-methylimidazolium dicyanamide (EMIM DCN), and mixed homogeneously by stirring. The composite was directly transferred into a ceramic boat and placed in a furnace under Ar flow. The sample was preheated at 200 °C for 12 h, and subsequently carbonized at 800 °C for 7 h. After cooling, the resulting black solid was ground into a powder, and then washed with HF solution (20 %) by stirring for 2 days. The black solid was separated by centrifugation and washed with distilled water for several times. After drying under vacuum at 120 °C for overnight, the resulting samples were labeled as NC800.

5. Preparation of BNC800-1 and BNC800-2

Prior to precursor loading, the as-synthesized MIL-100(Al) (250 mg) were again activated at 200 °C for 12 h to get completely desolvated samples. In an air-tight vessel, the resultant samples were soaked into 1-ethyl-3-methylimidazolium tetracyanoborate (EMIM TCB) (0.25 g for BNC-1 and 0.125 g for BNC-2), and mixed homogeneously by stirring. The

samples were preheated at 200 °C for 12 h, and subsequently carbonized at 1000, 800 and 600 °C for 7 h. After cooling, the resulting black solids were ground into powders, and then washed with HF solutions (20 %) by stirring for 2 days. The black solids were separated by centrifugations and washed with distlled water for several times. After drying under vacuum at 120 °C for overnight, the resulting samples were used for further works.

6. Preparation of carbons directly from ILs

The ionic liquid, 1-ethyl-3-methylimidazolium dicyanamide (EMIM DCN) (or 1-ethyl-3methylimidazolium tetracyanoborate (EMIM TCB)), was directly transferred into a ceramic boat and placed in furnace under Ar flow. The sample was subsequently carbonized at 800 °C for 7 h. After cooling, the resulting black solid was ground into powder and used for further measurements.

7. Selectivity measurements

The selectivity (S) for adsorption of CO_2 over N_2 was calculated from the single-component isotherm data. For CO_2 capture, this value typically reports the ratio of the adsorbed amount of CO_2 at 0.15 atm to the adsorbed amount of N_2 at 0.75 atm; the value is normalized for the pressures chosen, according to equation:

$$S(CO_2: N_2) = (q_{CO2}/q_{N2})/(P_{CO2}/P_{N2})$$

where q is the amount adsorbed and P is the relative pressure.

Reference:

Volkringer, C.; Popov, D.; Loiseau, T.; Férey, G.; Burghammer, M.; Riekel, C.; Haouas, M.; Taulelle, F. *Chem. Mater.* 2009, *21*, 5695.

Samples	Surface area (m ² /g)	Pore volume (cm ³ g ⁻¹)	CO ₂ uptake (mmol g ⁻¹) at 298 K	CO ₂ uptake (mmol g ⁻¹) at 273 K	H ₂ uptake (wt%) at 77 K
C800	2731	1.76	2.6	4.1	1.8
NC800	2397	1.37	3.8	5.7	1.7
BNC800-1	1068	0.52	3.1	4.0	1.4
BNC800-2	1522	0.78	3.2	4.4	1.7
C600	1125	0.75	-	-	-
C1000	1864	1.56	-	-	-

Table S1. BET surface area, pore volume, CO_2 and H_2 uptakes of as-synthesized N- and BN-decorated carbons.



Figure S1. Powder XRD patterns of as-synthesized MIL-100(Al).



Figure S2. N₂ sorption isotherms of MIL-100(Al) (filled and open symbols represent adsorption and desorption branches, respectively).



Figure S3. Powder XRD patterns of (a) C800, (b) CN800 and (c) BCN800-1.



Figure S4. TEM image of C800. S7



Figure S5. TEM image of NC800.



Figure S6. TEM image of BNC800-1.



Figure S7. XPS spectra of (a) C800, (b) CN800 and (c) BCN800-1.



Figure S8. XPS spectrum of BCN800-1 at B 1s level.



Figure S9. XPS spectra of C800 (a) before and (b) after HF washing.



Figure S10. N₂ sorption isotherms of (a) C600 and (b) C1000 (filled and open symbols represent adsorption and desorption branches, respectively).



Figure S11. N₂ sorption isotherms of carbons obained from direct carbonization of ionic liquids (a) 1-ethyl-3-methylimidazolium dicyanamide (EMIM DCN) and (b) 1-ethyl-3-methylimidazolium tetracyanoborate (EMIM TCB) (filled and open symbols represent adsorption and desorption branches, respectively).

Table S2. Comparison of the textural properties of as-synthesized BNC samples with reported materials

BN-decorated carbon Samples	Preparation method (carbonization temperature)	Specific surface area (m²/g)	Pore sizes (nm)	Dominating pores	Reference
$B_{0.15}C_{0.10}N_{0.17}O_{0.27}H_{0.31}$	Silica template (800 °C)	610	1-10	Meso	2
$B_{0.36}C_{0.12}N_{0.32}O_{0.11}H_{0.09}$	Silica template (1400 °C)	1560	1-12	Meso	2
$\mathrm{BC}_4\mathrm{N}$	Direct carbonization of MOF	988	1-2	Micro	3
MBCN(1450)	Silica template (1450 °C)	740	1-5	Meso	4
BCN	Silica template (1150 °C)	380	~5	Meso	5
BNC800-1	IL@MOF (800 °C)	1068	1-3	Micro	This work
BNC800-2	IL@MOF (800 °C)	1522	1-3	Micro	This work

References:

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3. K. Jayaramulu, N. Kumar, A. Hazra, T. K. Maji, C. N. R. Rao, *Chem. Eur. J.*, 2013, **19**, 6966 6966.

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