

Supplementary Information

Carbon nanotube modified carbon composite monoliths as superior adsorbents for carbon dioxide capture

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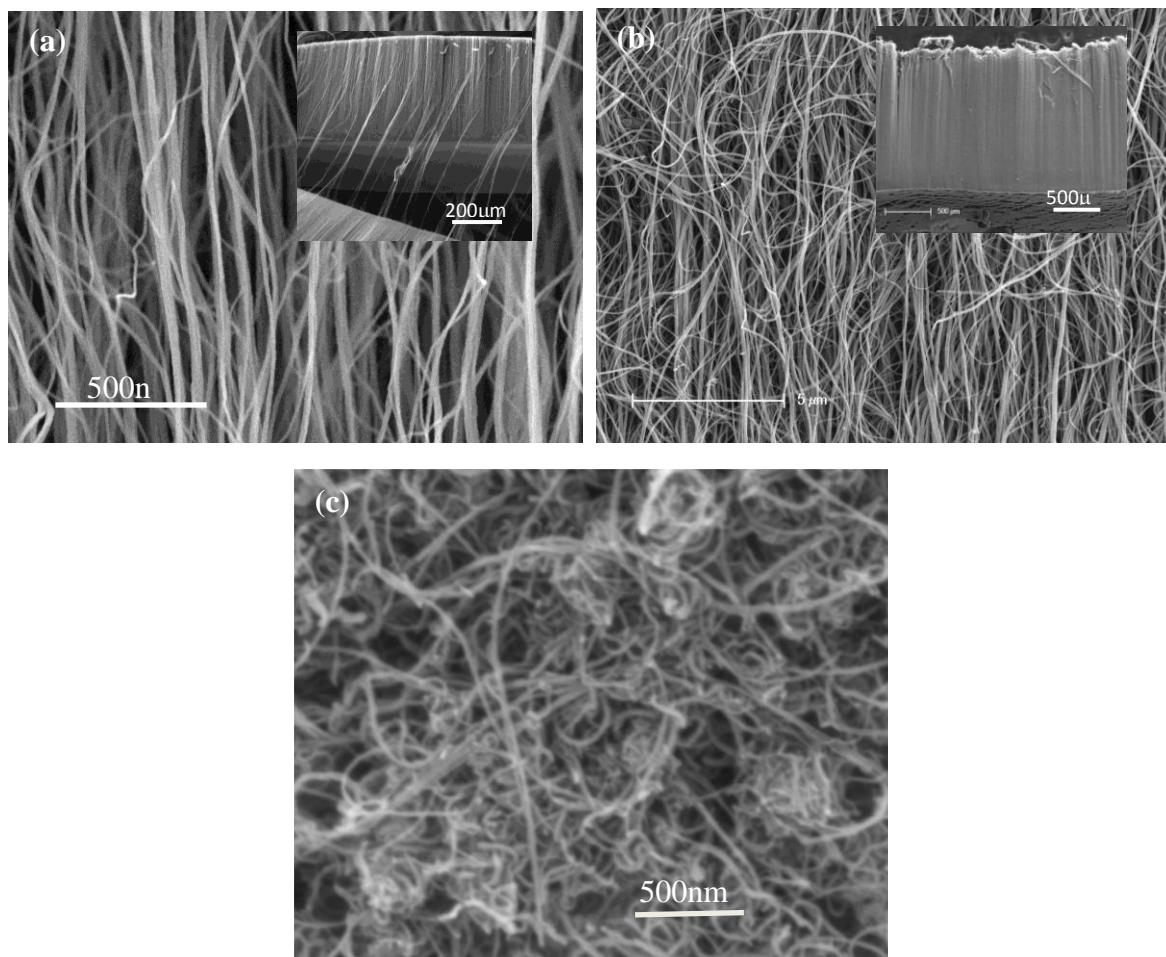
Experimental

Synthesis of CCM adsorbents: CPD CNTs were grown in a quartz tube reactor (44mm id) within a three zone furnace by chemical vapour deposition (CVD) as aligned forests on silicon wafer bearing 50 nm thermal oxide and Fe catalyst pre-deposited (2.5 nm) by e-beam.²⁵ After annealing in helium (1000 sccm, 40 min, 680 °C), hydrogen and acetylene (25/25 sccm, 15 min) was added to produce CNTs of 300 μm length and 10 nm mean diameter. CCI CNTs were grown in a quartz-lined stainless steel reactor (72 mm id) within a five zone furnace by CVD as aligned forests on quartz glass slides and liners. Catalyst was co-injected as a 1 wt% ferrocene solution in *o*-xylene (4 ml h^{-1}) with argon carrier (500 sccm) at 1 atm and a plateau temperature of 750 °C.²⁸ After 5 h, CNTs of 1500 μm length and 80 nm mean diameter were recovered. The commercial multiwall CNT (Com) was obtained from Nanotech Port Co. Ltd, China. To render all CNT samples hydrophilic and dispersed, they were each stirred at room temperature for 3 h in a 70:30 (v/v) mixture of H_2SO_4 (96%) and H_2O_2 (30%), poured onto an excess of ice, filtered, rinsed with NaHCO_3 (1 M) and washed to neutral pH, taking care to prevent the filter cake drying. A small sample was dried to determine water content and the rest made up to a 1% dispersion in 2% MC (Aldrich, viscosity (2% in H_2O) = 4,000 cp) gel by stirring with the appropriate amount of 2% and 4% gels.

CCM adsorbents were prepared by mixing the CNT gel paste with commercial Novolac phenolic resin (Durez 7716) to give a final composition of resin, CNTs, MC and water in the ratio of 100:1:6:300 respectively, followed by molding, drying, curing, carbonization and activation. In a typical synthesis of the CPD CCM, 5 g of resin was mechanically mixed with 5 g of 1% CNT in 2% MC and 10 g of 2% MC. The resultant highly viscous mixture was transferred into a cylindrical polypropylene mold (with 5 channel pins), and then dried and oven cured at 150 °C

for 1.5 h to solidify the structure. After de-molding, the hard resin cylinder was carbonized at 650 °C in a tube furnace for 1 h under N₂ flow (0.8 slm) with a heating rate of 15 °C min⁻¹. The cooled carbonized sample was weighed, returned to the tube furnace and heated to 950 °C at 15 °C min⁻¹ under N₂ (0.8 slm). At the setpoint temperature, the gas flow was switched to CO₂ (0.8 slm) for a given period to activate the sample, then back to N₂ (0.8 slm) as the sample was cooled. The activated sample was weighed to determine the burn-off arising from activation.

Materials characterization: N₂ and CO₂ adsorption measurements were carried out on a Micromeritics ASAP 2020 volumetric analyzer at various temperatures. Ultrahigh-purity-grade gases were used in all adsorption measurements. Before the measurements were taken, the samples were degassed overnight in vacuo at 473 K. The heat of CO₂ adsorption were calculated using CO₂ isotherms at 273, 298 and 323K based on the Clausius-Clapeyron equation. The rate of CO₂ adsorption was measured with a built-in function in Micromeritics ASAP 2020 by recording the change of amount adsorbed vs. time at a fixed dose of 0.04 mmol CO₂ g⁻¹ until achieving the target equilibrium pressure around 25 mmHg. Mercury porosimetry was performed on the carbonized samples using a mercury porosimeter (Micromeritics AutoPore IV 9500). Morphologies of samples (uncoated) were examined using SEM (Nava Nano SEM 430) at an operating voltage of 5kV. TEM was performed on a FEI Tecnai T12 at an operating voltage of 120 KV. TGA on the treated CPD CNT was performed on a Perkin Elmer TGA7 under air flow at a heating rate of 10 °C min⁻¹.



Specifications of as-produced/as-received CNTs

CNT samples	Diameter, D (nm)	Length, L (μm)	Alignment	Purity (%)	Aspect ratio, L/D
CPD	10	300	highly aligned	99.8	30,000
CCI	80	1500	aligned, some branching	97	18,750
Com	10-20	5-15	very tangled	95	400-1,500

Fig. S1 SEM images of in-house grown multiwall CNTs synthesized by the (a) catalyst pre-deposition process (CPD) and (b) catalyst co-injection process (CCI) and (c) the commercial multiwall CNT (Com). Specifications of three types of CNTs are tabulated.

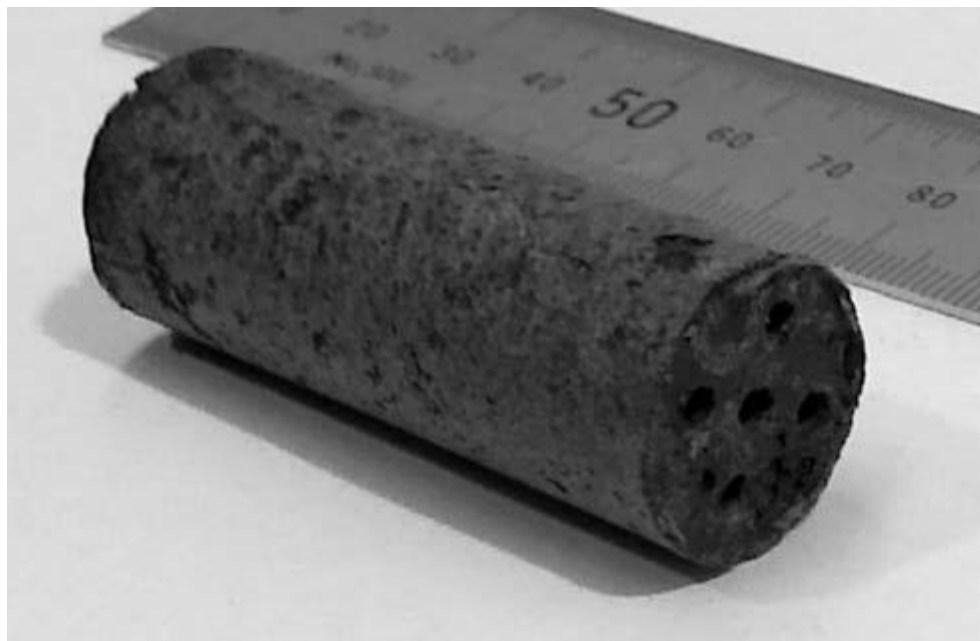


Fig. S2 Photograph of the CPD carbon composite monolith (CCM)

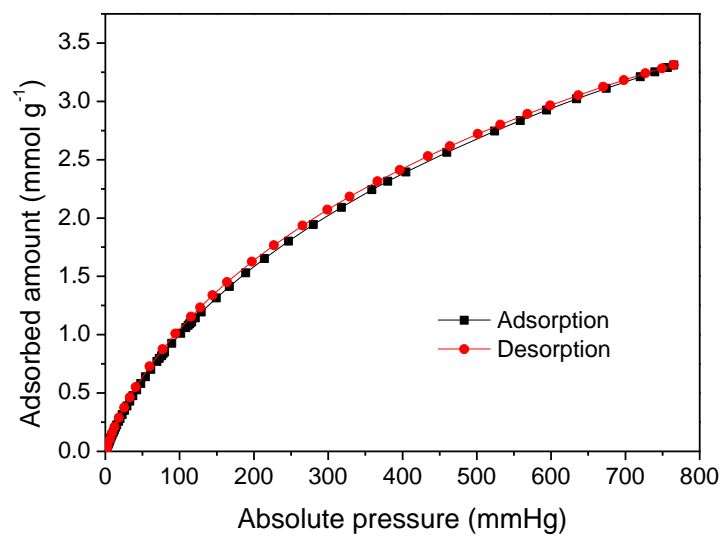


Fig. S3 CO₂ adsorption and desorption isotherms for CPD-15 at 298 K.

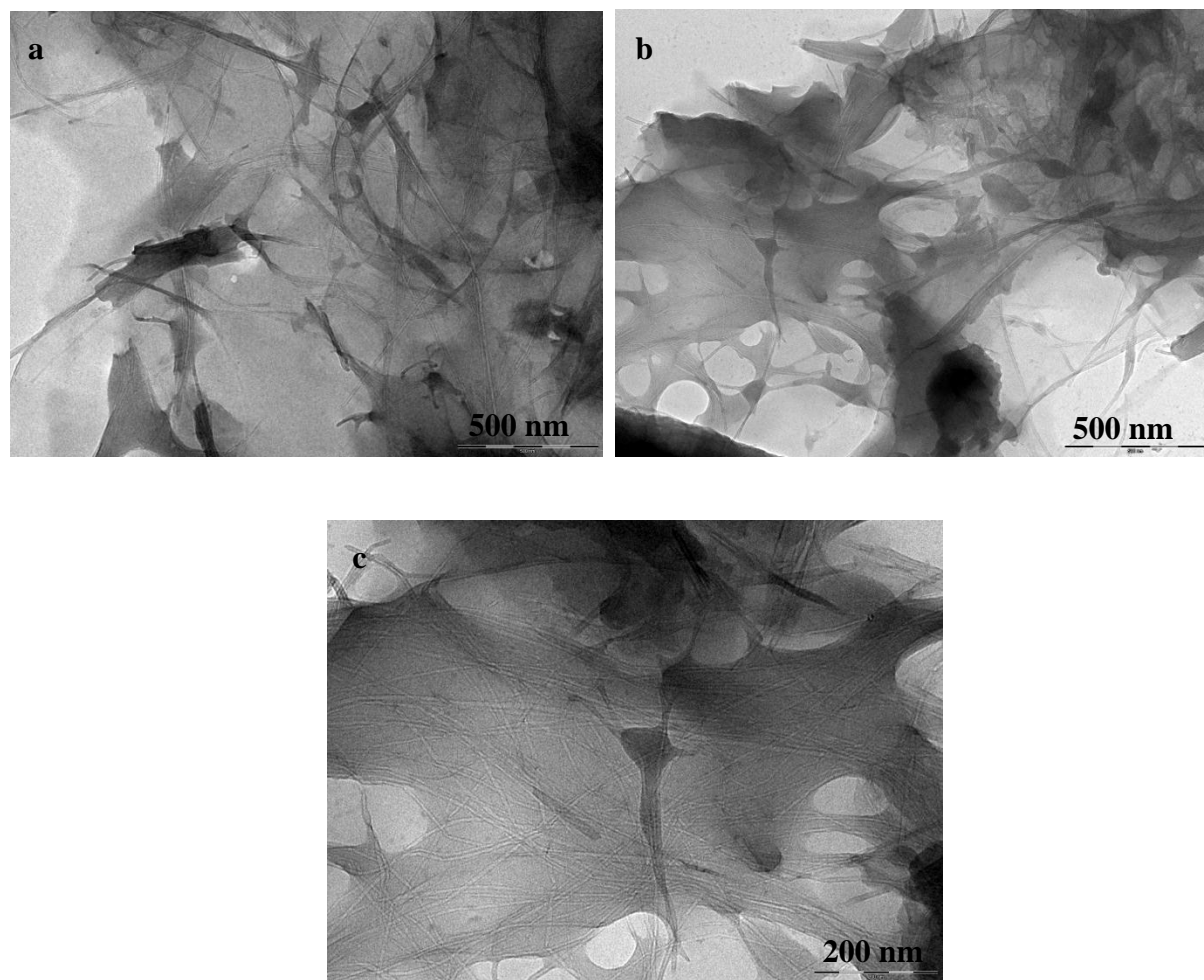


Fig. S4 TEM images of CPD-15.

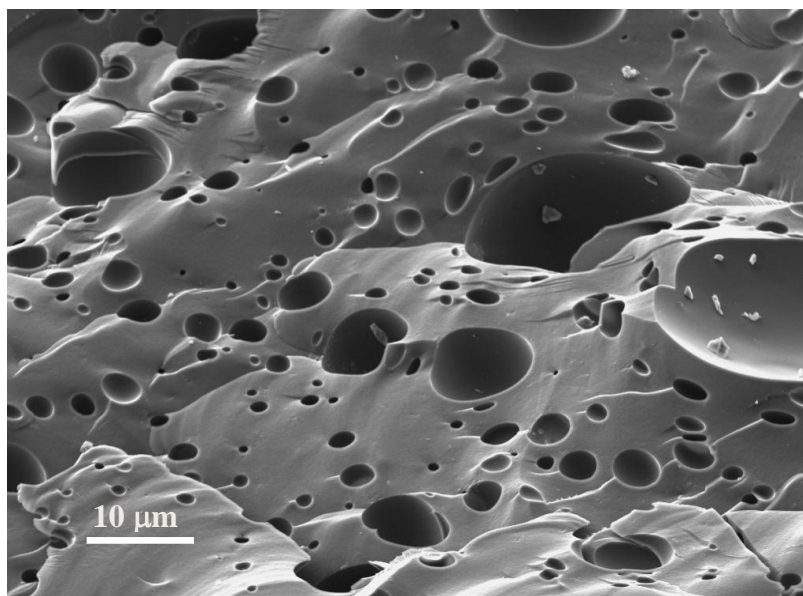


Fig. S5 SEM image of Res-60.

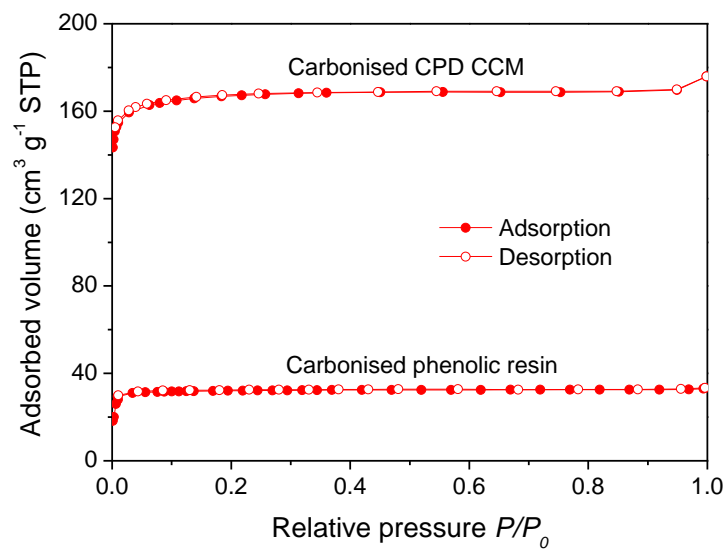


Fig. S6 N₂ sorption isotherms at 77 K of the carbonized CPD carbon composite monolith and the carbonized phenolic resin (prior to activation).

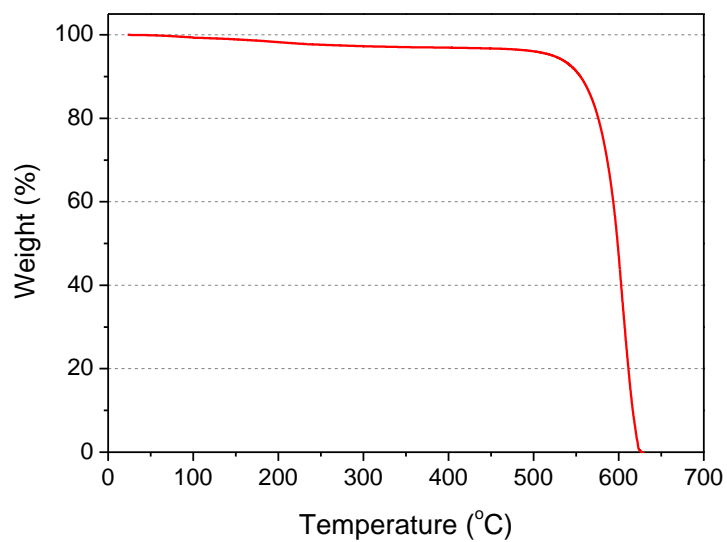


Fig. S7 Thermogravimetric analysis for the acid-treated CPD CNT that was used for preparing the carbon composite monolith (CCM).

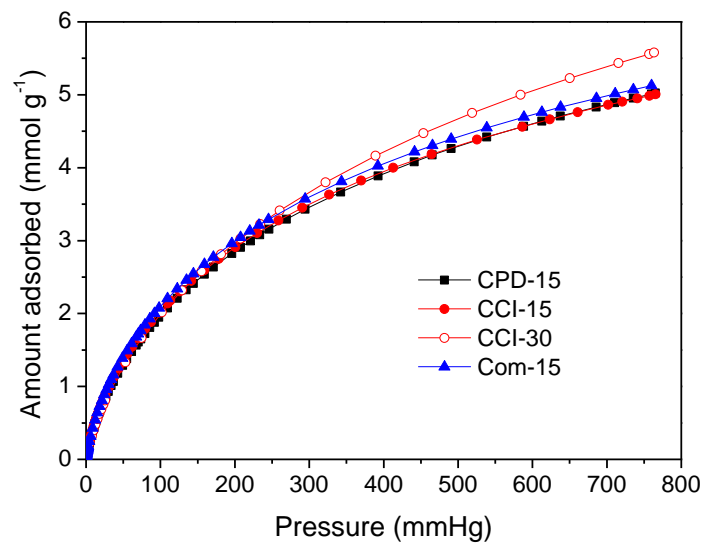


Fig. S8 CO₂ adsorption isotherms at 273 K for CPD-15, CCI-15, CCI-30 and Com-15.

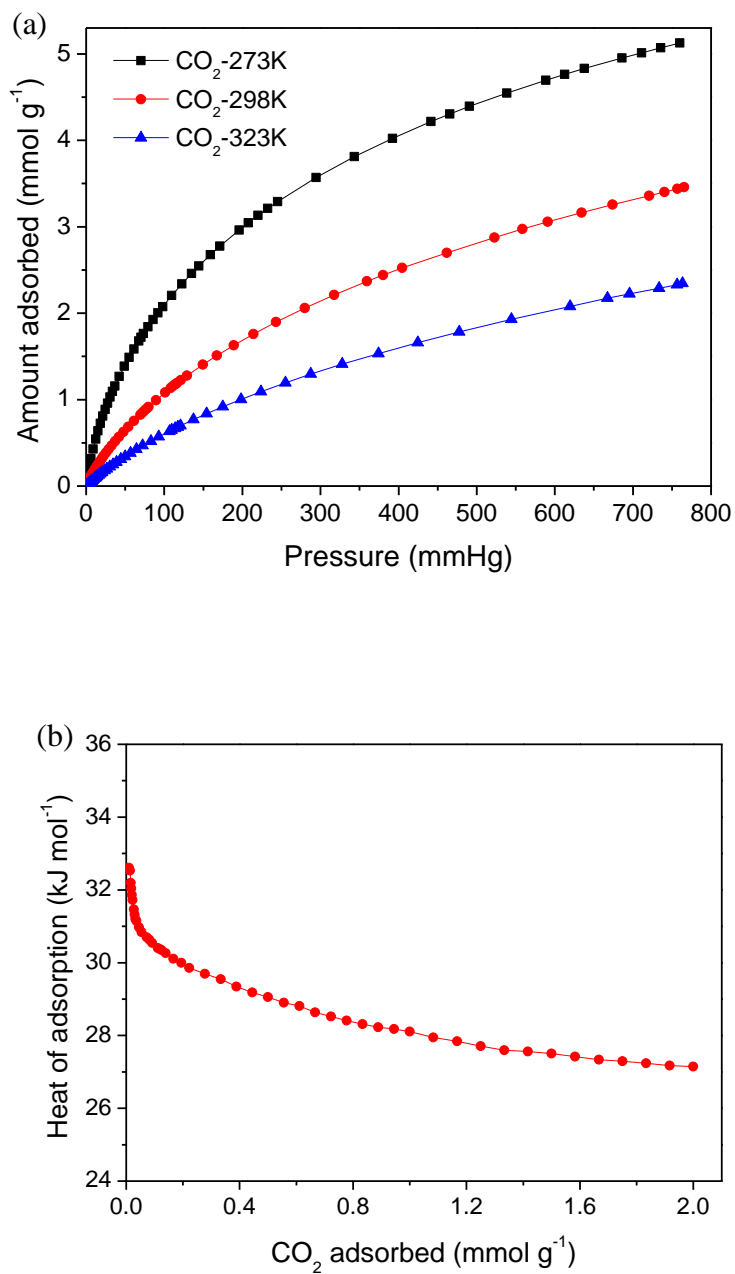


Fig. S9 (a) CO₂ adsorption isotherms for sample Com-15 at 273, 298 and 323 K. (b) Isothermic heat of CO₂ adsorption for Com-15 obtained from CO₂ adsorption isotherms in (a).

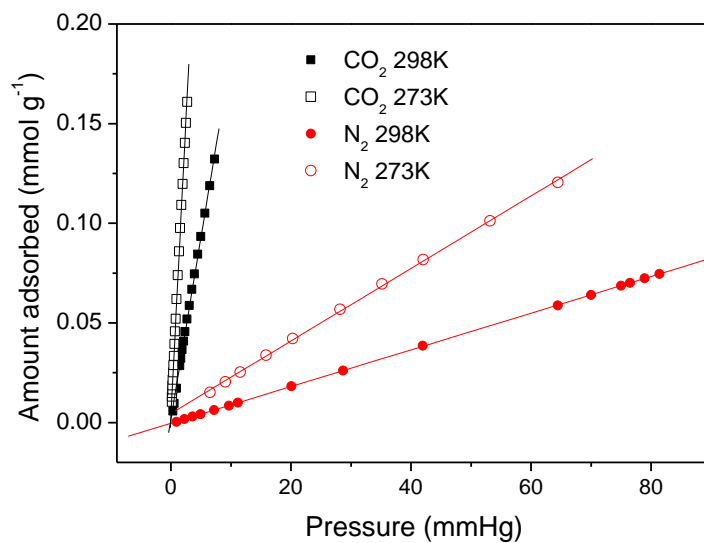


Fig. S10. Fittings of initial adsorption isotherms of CO₂ and N₂ for Com-15 to obtain the Henry's law constants for estimation of CO₂/N₂ selectivity.

Table S1. Comparisons of CO₂ adsorption capacities (C_{100} and C_{15}) for porous carbon adsorbents*

Category	Materials description	CO ₂ uptake at 298K & 1atm, C_{100} (wt%)	CO ₂ uptake at 298K & 114mmHg, C_{15} (wt%)	Reference
Commercial activated carbon	MAXSORB	9.5	2.3	11
	BPL	9.2	3.1	29
	G-32H	11.0		30
	GC-C30	7.0	1.8	This work
Pristine carbons-physical activation	Novolac phenolic resin (home-made)	9.0		31
	Novolac phenolic resin (commercial)	8.2	2.4	This work
	Novolac phenolic resin with organic additives	10.8		31
	Biomass (olive stones/almond shells) based	10.8	3.6	32
	CNT carbon composite monoliths	15.9	5.2	This work
Pristine carbons-chemical activation	Carbon molecular sieves KOH/pitch precursor mass ratio=3	20	4.4	11
	Sawdust-based porous carbon KOH/precursor mass ratio=2	21.2	5.1	14
	Activated mesoporous carbon (CMK-3) KOH/carbon mass ratio=2	14.3	4.2	33
	Activated graphite fibers	5.9	1.7	34
N-doped carbons	Polypyrrole-based KOH/polypyrrole mass ratio=2 (10.1 wt% N)	16.9	4.7	16
	Resorcinol-formaldehyde based monoliths	13.7	5.6	15
	Porous carbon monoliths with amines	14.5	4.1	13
	Zeolite templated carbons by chemical vapor deposition	19.3	4.2	17
	Ammonia treated activated carbon	9.6	3.6	32

*When not directly reported, the uptake values were estimated from adsorption isotherms in the corresponding reference.