## Supporting Information

# Copolymer-Templated Nitrogen-Enriched Porous Nanocarbons for $CO_2$ Capture

Mingjiang Zhong,[a,b] Sittichai Natesakhawat,[b,c] John P. Baltrus,[b] David Luebke,[b] Hunaid Nulwala,*[a,b] Krzysztof Matyjaszewski,*[a,b] and Tomasz Kowalewski*[a]

[a]Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania, 15213

[b]National Energy Technology Laboratory, United States Department of Energy, P.O. Box 10940, Pittsburgh, Pennsylvania, 15236

[c]Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260

*To which all correspondences should be addressed: hnulwala@andrew.cmu.edu, tomek@andrew.cmu.edu, km3b@andrew.cmu.edu

## 1. Experimental Materials and Methods

**Materials**: Acrylonitrile (AN), *n*-butyl acrylate (BA), methyl 2-bromopropionate (MBP), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), 2,2′-bipyridine (bpy), CuBr, CuCl, $CuBr_2$, anisole, dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), and methanol were all obtained from Sigma-Aldrich. CuCl and CuBr were purified by stirring in glacial acetic acid followed by washing with ether and dried overnight under vacuum. Monomers were passed through a basic alumina column prior to use. All other chemicals were used as received.

**Preparation of Poly(*n*-butyl acrylate) (PBA) macroinitiator.** 60 mL of BA ($4.20 \times 10^{-1}$ mol), $1.94 \times 10^{-1}$ mL of PMDETA ($9.29 \times 10^{-4}$ mol), $3.99 \times 10^{-1}$ mL of MBP ($3.57 \times 10^{-3}$ mol), 4.0 mg of $CuBr_2$ ($1.8 \times 10^{-5}$ mmol), and 30 mL of anisole were mixed in a 100 mL Schlenk flask equipped with a magnetic stirring bar. The flask was subjected to five freeze-pump-thaw (FPT) cycles. Then, $1.28 \times 10^{-1}$ g of CuBr ($8.93 \times 10^{-4}$ mol) was added to the flask while the contents were at a solid state and deoxygenated by vacuum followed by back-filling with nitrogen three times. The flask was placed in an oil bath set at 70 °C for 5.5 h. The reaction was terminated by the addition of aerated THF and passing through a column of alumina to remove the catalyst followed by evaporation. The solid products were dried in a vacuum oven.

**Preparation of poly(*n*-butyl acrylate)-block-polyacrylonitrile copolymers (PBA-*b*-PAN)**. 9.86 g of the above PBA macroinitiator ($1.02 \times 10^{-3}$ mol; $M_n$ (GPC) = 9700 and $M_w/M_n$ = 1.15), 21.7 mL of AN ($3.34 \times 10^{-1}$ mol), and 21.7 mL of DMSO were mixed in a 50 mL Schlenk flask equipped with a magnetic stirring bar. The flask was subjected to five FPT cycles. Then, $1.21 \times 10^{-1}$ g of CuCl ($1.22 \times 10^{-3}$ mol) and $3.81 \times 10^{-1}$ g of bpy ($2.44 \times 10^{-3}$ mol) were added to the flask, as above, and purged by back-filling with nitrogen. The flask was then placed in an oil bath set at 60 °C for 7 h. At the end of this time, the reaction mixture was dissolved in DMF, and the polymer was precipitated by adding the solution to 50% aqueous methanol. The solid product was dried under vacuum.

**Characterization of polymers**: Conversion of monomers was measured by gas chromatography (GC) using a Shimadzu GC14-A gas chromatograph with a FID detector equipped with a J&W Scientific 30m DB WAX Megabore column. Injector and detector were kept at 250 °C. The molecular weight ($M_n$) of PBA macroinitiator and molecular weight distributions ($M_w/M_n$) were determined by gel permeation chromatography (GPC) (Polymer Standards Services (PSS); columns (guard, $10^5$, $10^3$, and $10^2$ Å), with DMF for polyacrylonitrile (PAN) and PBA-*b*-PAN or THF for PBA eluent at 35 °C, flow rate = 1.00 mL/min, and differential refractive index (RI) detector (Waters, 2410)) calibrated with linear polystyrene standards using WinGPC 6.0 software from PSS. Toluene was used as the internal standard. Polystyrene standards were employed for the GPC calibration. $^1$H nuclear magnetic resonance (NMR) spectra recorded on a Bruker Avance spectrometer (300 MHz) was used to determine the $M_n$ of PBA-*b*-PAN in DMF-d7.

**Preparation of CTNC**. The polymer sample was stabilized at 280 °C for 2 h under air flow (150 mL/min) with a heating rate of 1 °C/min, purged with nitrogen gas for one hour during cooling, and then pyrolyzed at 500 - 800 °C for 0.5 h under nitrogen or 4 h under $CO_2$ gas flow (150 mL/min) with a heating rate of 10 °C/min.

**Characterization of carbon powder**: Small angle X-ray scattering (SAXS) experiments were carried out at the D1 station of Cornell High Energy Synchrotron Source (CHESS). A wide bandpass (1.7%) double-bounce multilayer monochromator supplied an intense beam of 10 keV photons. The SAXS scattering intensities were recorded with an area detector (Medoptics) with a resolution of 50 μm per pixel and a total area of about 50 mm by 50 mm. The scattering data was collected twice at a distance of 1888 mm/562 mm from the sample to the detector. X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5600ci instrument equipped with a monochromatic Al X-ray source ($h$ = 1486.6 eV) operated at 400 W. The pass energy of the analyzer was set at 58.7 eV. Elemental surface concentrations were calculated from peak areas based on the sensitivity factors provided by the manufacturer. The nanostructure of the samples was also investigated by a FEI Tecnai F20 transmission electron microscope.

**Gas sorption measurements.** Sorption isotherms of $CO_2$ and $N_2$ were collected using a Quantachrome Autosorb 1-C. Prior to measurements, samples were degassed at 300 °C under vacuum overnight. Brunauer–Emmett–Teller (BET) surface areas were determined from $N_2$ adsorption isotherms at 77 K. Multipoint BET measurements were performed at relative pressures ($P/P_0$) in the range of 0.05-0.2. $CO_2$ and $N_2$ adsorption isotherms were conducted in the temperature and pressure ranges of 0-50 °C (only 25 °C for $N_2$) and 0-760 Torr, respectively. The micropore surface area ($S_{\mathrm{micro}}$) was obtained from a *t*-plot method using the de Bore equation.[1] The mesopore surface area ($S_{\mathrm{meso}}$) is simply calculated from the value of $S_{\mathrm{BET}}$ - $S_{\mathrm{micro}}$. The mesopore size distribution was obtained from Barett-Joyner-Halenda (BJH) method from the desorption branch.

**Table S1.** Evaluation of $CO_2$ capture by CTNCs synthesized under different pyrolysis conditions.[a]

| Entry | Gas flow | $T_p$ (°C) | Surface area ($m^2$/g) | | | N/C (%)[b] | Capacity (mmol/g)[c] | | $CO_2/N_2$ Selectivity[d] |
|---|---|---|---|---|---|---|---|---|---|
| | | | $S_{BET}$ | $S_{micro}$ | $S_{meso}$ | | 0 °C | 25 °C | |
| CTNC-N500 | $N_2$ | 500 | 455 | 145 | 310 | 18.2 | 2.53 | 1.97 | 10.2 |
| CTNC-N600 | $N_2$ | 600 | 480 | 167 | 313 | 16.0 | 2.78 | 2.13 | 8.5 |
| CTNC-N700 | $N_2$ | 700 | 495 | 176 | 319 | 13.9 | 2.85 | 2.23 | 7.7 |
| CTNC-N800 | $N_2$ | 800 | 535 | 214 | 321 | 11.2 | 2.98 | 2.27 | 7.5 |
| CTNC-C500 | $CO_2$ | 500 | 505 | 154 | 351 | 16.3 | 2.88 | 2.25 | 10.1 |
| CTNC-C600 | $CO_2$ | 600 | 562 | 203 | 359 | 13.6 | 3.21 | 2.50 | 8.1 |
| CTNC-C700 | $CO_2$ | 700 | 657 | 232 | 425 | 11.7 | 3.64 | 2.72 | 7.7 |
| CTNC-C800 | $CO_2$ | 800 | 988 | 556 | 432 | 6.5 | 4.37 | 3.00 | 7.0 |

[a] Conditions: (1) Stabilization: 280 °C under air at the rate of 1 °C/min, held for 1 h; (2) Carbonization: held for 30 min under a $N_2$ flow or 4 h under a $CO_2$ flow. [b] N/C is the atomic ratio of nitrogen to carbon; [c] The capacity is the amount of adsorbed $CO_2$ at 760 Torr; [d] The selectivity is defined as the molar ratio of adsorbed $CO_2$ and $N_2$ at 25 °C and 760 Torr which were obtained from separate adsorption isotherms of pure $CO_2$ and $N_2$.

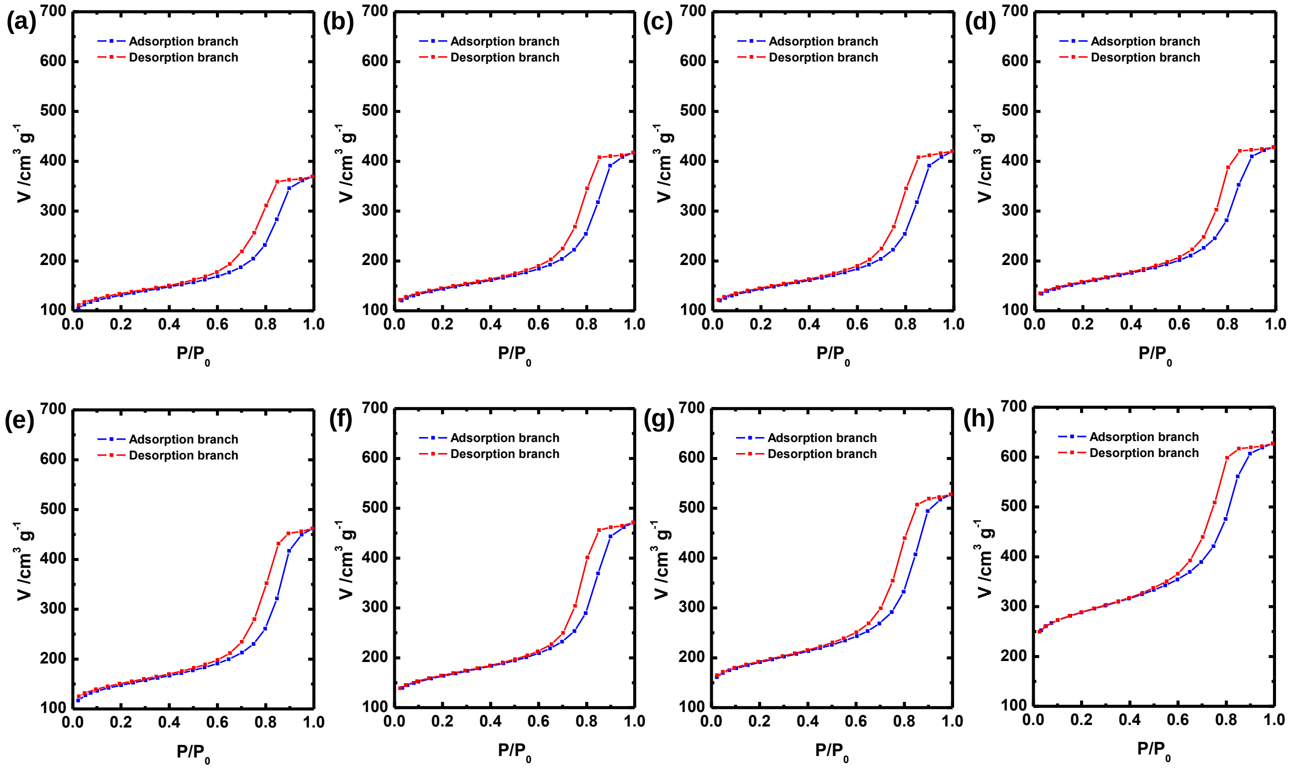


**Fig. S1** $N_2$ adsorption/desorption isotherms at -196 °C. (a) CTNC-N500; (b) CTNC-N600; (c) CTNC-N700; (d) CTNC-N800; (e) CTNC-C500; (f) CTNC-C600; (g) CTNC-C700; (h) CTNC-C800.

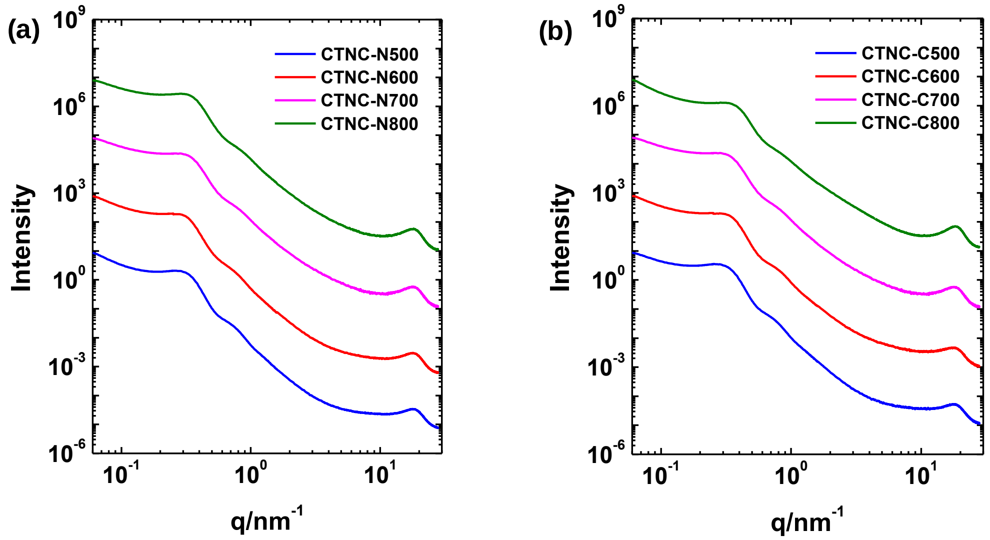


**Fig. S2** SAXS profiles in which the curves have been shifted vertically for a clear comparison. (a) CTNC-N; (b) CTNC-C.

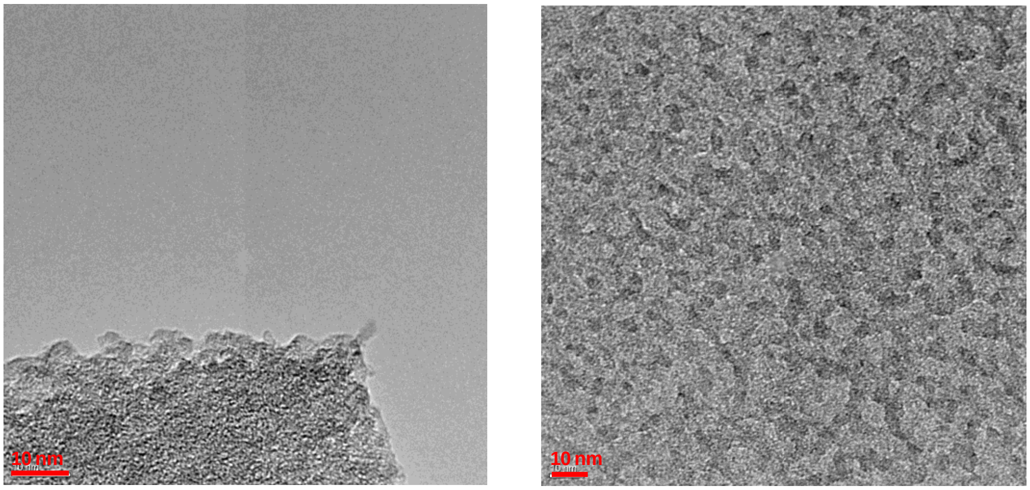


**Fig. S3** TEM images of CTNC-N700.

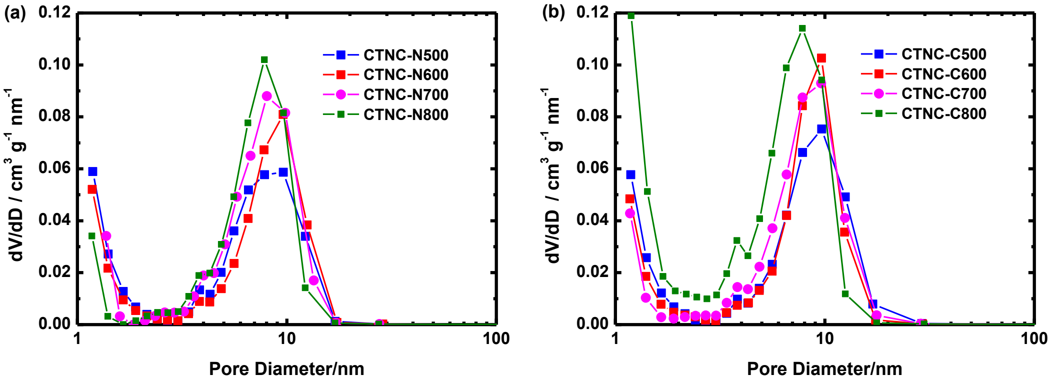


**Fig. S4** Mesopore size distribution calculated by BJH method. (a) CTNC-N; (b) CTNC-C.

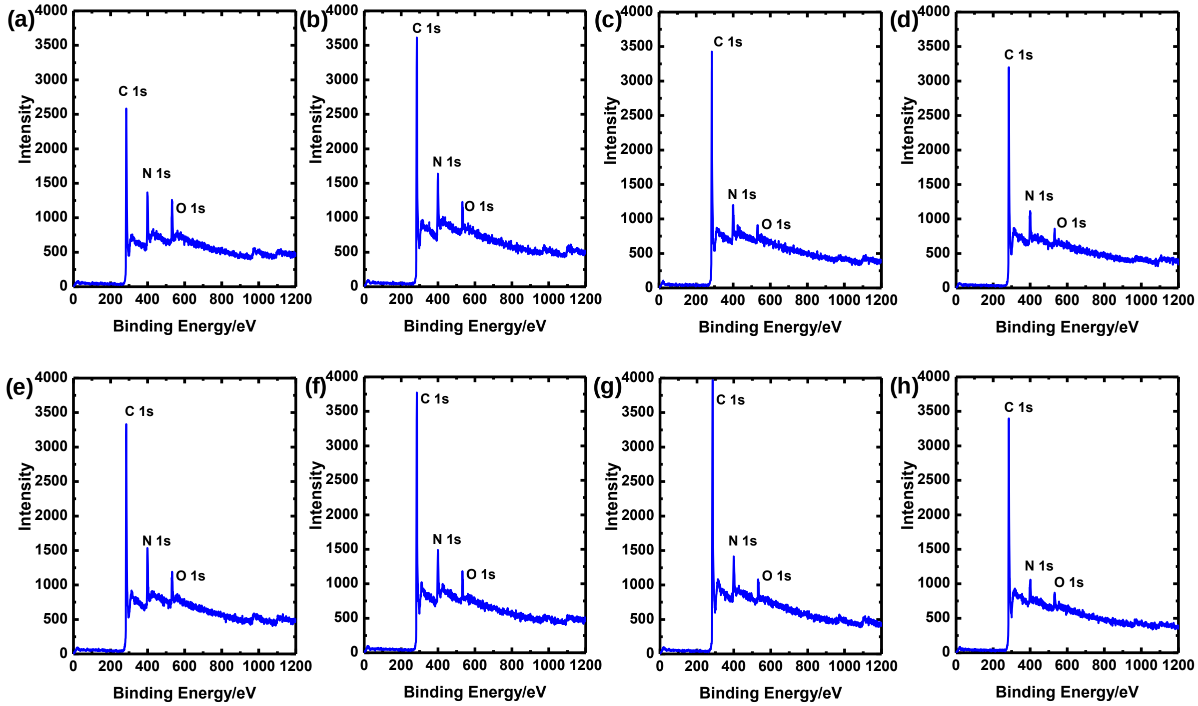


**Fig. S5** XPS survey spectra of CTNCs. (a) CTNC-N500; (b) CTNC-N600; (c) CTNC-N700; (d) CTNC-N800; (e) CTNC-C500; (f) CTNC-C600; (g) CTNC-C700; (h) CTNC-C800.

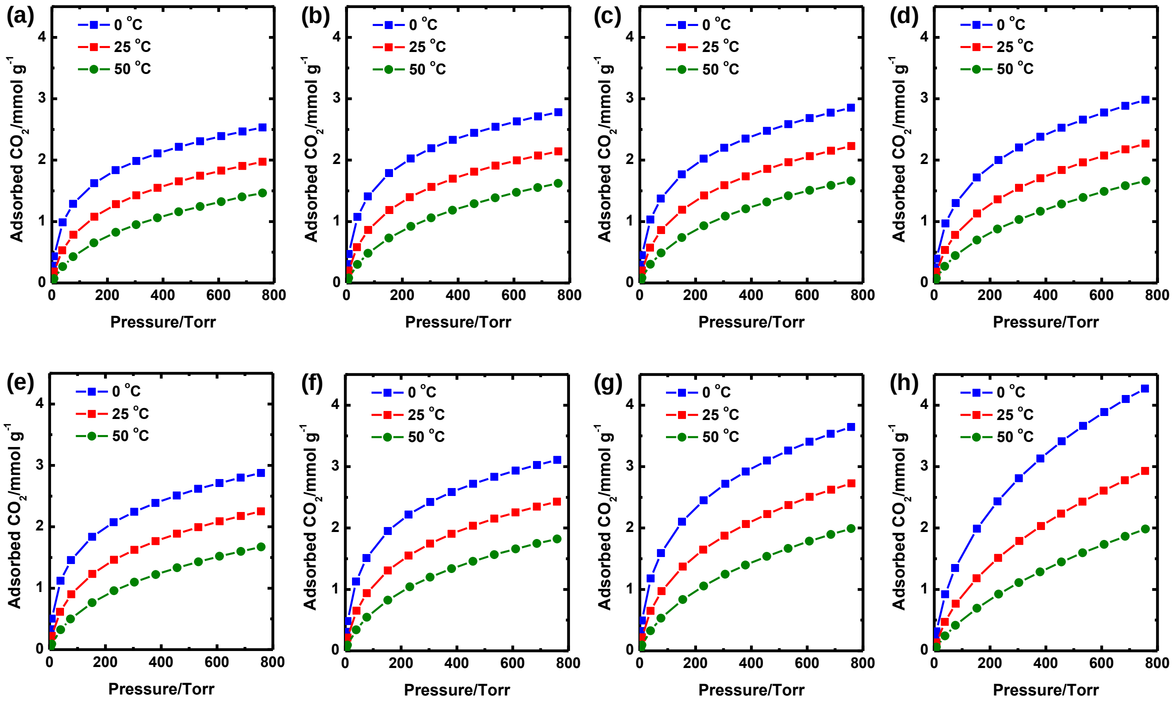


**Fig. S6** $CO_2$ adsorption isotherms at different temperatures. (a) CTNC-N500; (b) CTNC-N600; (c) CTNC-N700; (d) CTNC-N800; (e) CTNC-C500; (f) CTNC-C600; (g) CTNC-C700; (h) CTNC-C800.

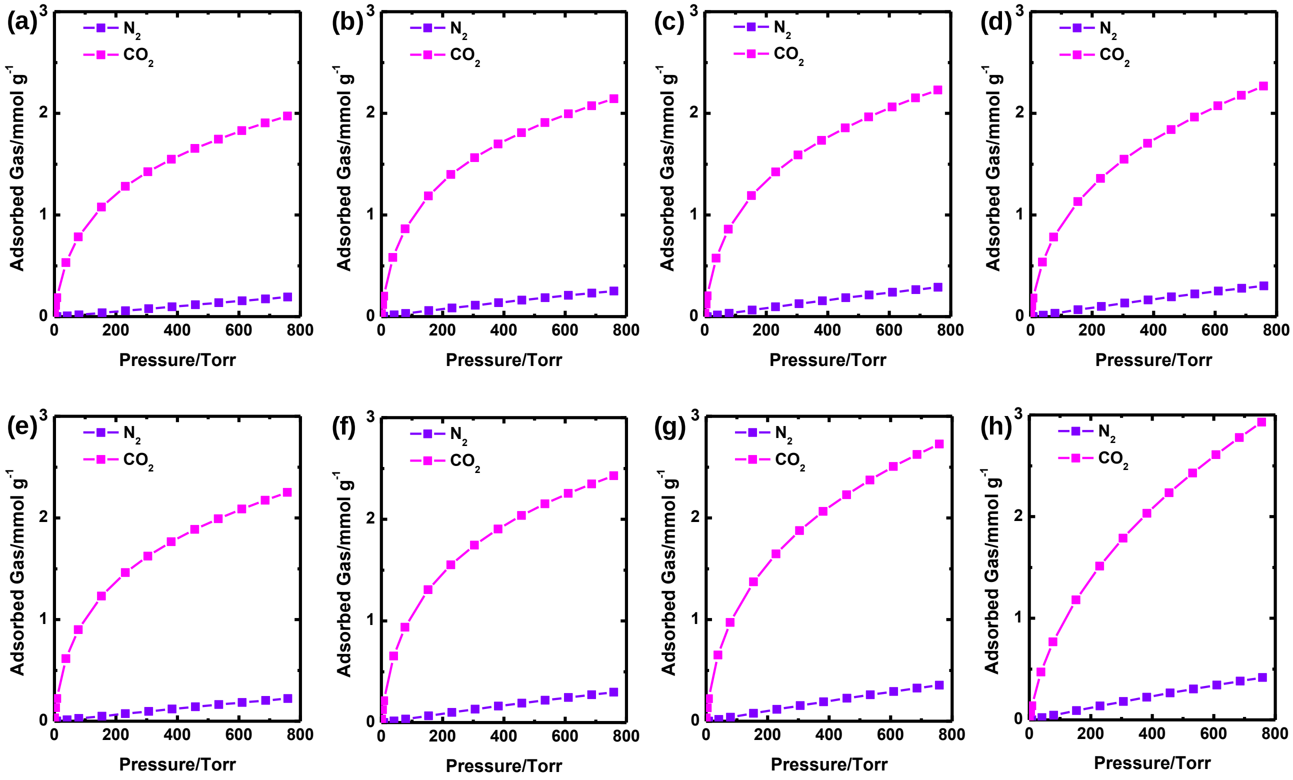
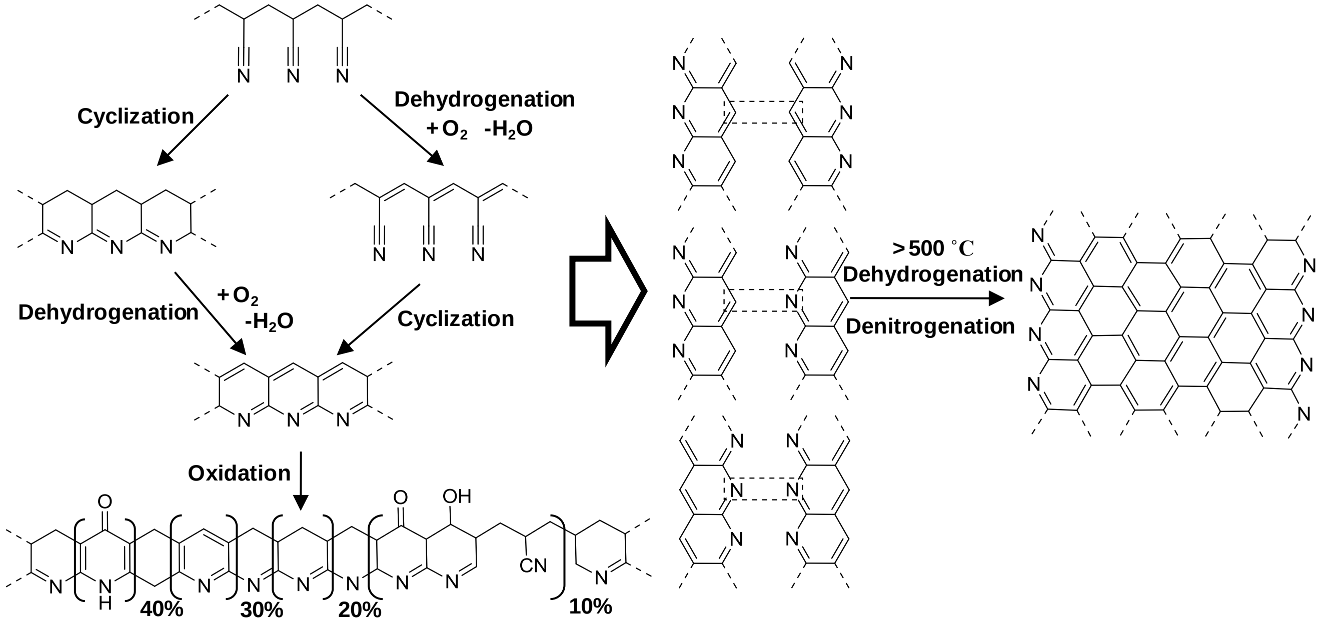


**Fig. S7** Comparison of $CO_2$ and $N_2$ isothermal adsorption of CTNC at 25 $^{o}$C; (a) CTNC-N500; (b) CTNC-N600; (c) CTNC-N700; (d) CTNC-N800; (e) CTNC-C500; (f) CTNC-C600; (g) CTNC-C700; (h) CTNC-C800.

## 2. Mechanism of PAN Carbonization

**Scheme S1 Mechanism of thermal chemistry of PAN carbonization**

Thermal stabilization which involves dehydrogenation and denitrogenation (left) is followed pyrolysis (right), leading to partially graphitic structure.[3]



## References

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