Electronic Supplementary Information

An Efficient Low-Temperature Route to Nitrogen-Doping and Activation of Mesoporous Carbon for CO_2 Capture

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Experimental Details

Material synthesis: Mesoporous carbons (MCs) were synthesized by carbonization of nanostructured polymeric composites, which were obtained by self-assembly of block copolymer (Pluronic F127) and phenolic resin (phloroglucinol-formaldehyde) under acidic conditions via an established soft-templating route.[1] Synthesized MCs were denoted as MCT_1, where T_1 is the carbonization temperature (400–850 °C). The N-doping and activation of MCs by $NaNH_2$ was performed by as following: 1 g of MC and 2 g of $NaNH_2$ were placed in a nickel crucible and then heated in a tubular furnace under flowing N_2 (100 mL/min) to a target temperature (230–380 °C) at 5 °C/min and then keep the temperature for 1–10 h. The resultant powder was washed with deionized water to neutral, followed by being dried at 120 °C for 12 h. The obtained N-doped MCs were named as NMCT_1-T_2-t, where T_2 is the N-doping temperature and t is the N-doping period of time (1–10 h). The N-doping of MCs by NH_3 was by thermal treatment of MC600 (0.25 g) in a NH_3 flow (50 mL/min) at a target temperature (T_3 = 600 and 800˚C) for 1 h with a heating rate of 10 °C /min, and the obtained N-doped carbon was denoted as NMCT_1-NH_3-T_3-t.

Characterization: N_2 adsorption isotherms at –196 °C and CO_2 adsorption isotherms at 0 °C were measured on a Micromeritics Gemini 2390a surface area analyzer to determine the textural properties of carbons. Prior to the measurement, each sample was dried at 200 °C under flowing N_2 for 2 h. Total surface area was calculated from N_2 adsorption isotherms using BET equation in the relative pressure range of 0.02–0.15. Total pore volume was determined from the amount of N_2 adsorbed at the relative pressure of 0.97. Micropore surface area and micropore volume were calculated from N_2 adsorption isotherms using Carbon Black STSA t-plot equation within the thickness range of 0.45–0.60 nm. Pore size distribution was derived from N_2 adsorption isotherms using BJH model. Moreover, small micropore size distribution was calculated from CO_2 adsorption isotherms using NLDFT theory by assuming slit-like geometry of micropores. X-ray photoelectron spectroscopy (XPS) data were collected using a PHI 3056 spectrometer with an Al anode source operated at 15 kV and an applied power of 350 W. Due to the close overlap with peaks there was no charge correction applied but the lowest energy C1s data was around 284.8 eV. High resolution data was collected at pass energy of 23.5 eV with 0.05 eV step sizes and a minimum of 60 scans to improve the signal to noise ratio. Electron microscopy was performed on a Zeiss Auriga Crossbeam scanning electron microscope at an acceleration voltage of 5 kV. Energy dispersive X-ray (EDX) analysis was conducted on a Zeiss Libra200 transmission electron microscope for element mapping of nitrogen, oxygen, and carbon on the synthesized N-doped MCs.

CO_2 and N_2 adsorption: CO_2 and N_2 adsorption isotherms were measured at 0, 25, and 40 °C on a Micromeritics Gemini 2390a surface area analyzer. Prior to the measurement, each sample was dried at 200 °C under flowing N_2 for 2 h.

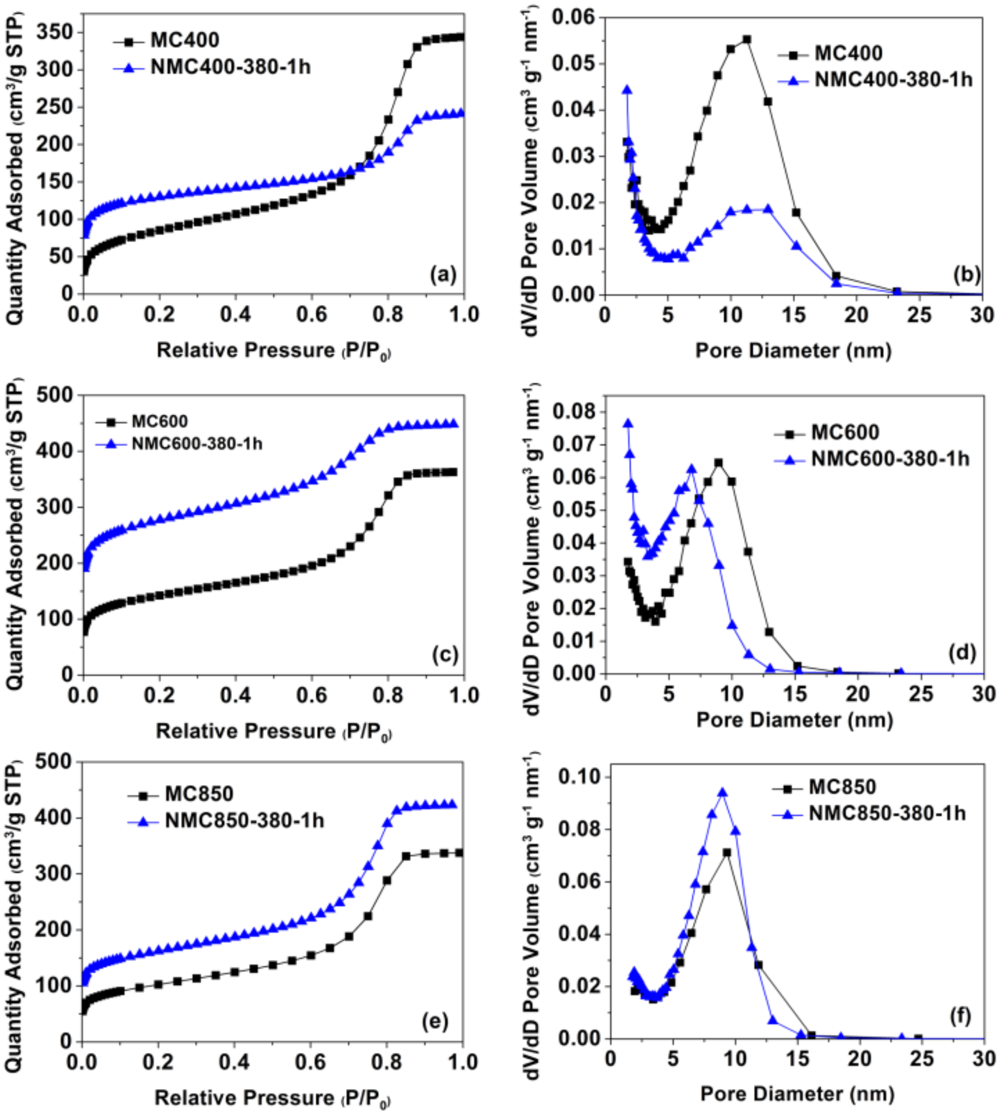

Figure S1. N_2-sorption isotherms at -196˚C (a, c, e) and BJH pore size distributions (b, d, f) of pristine and N-doped MCs.

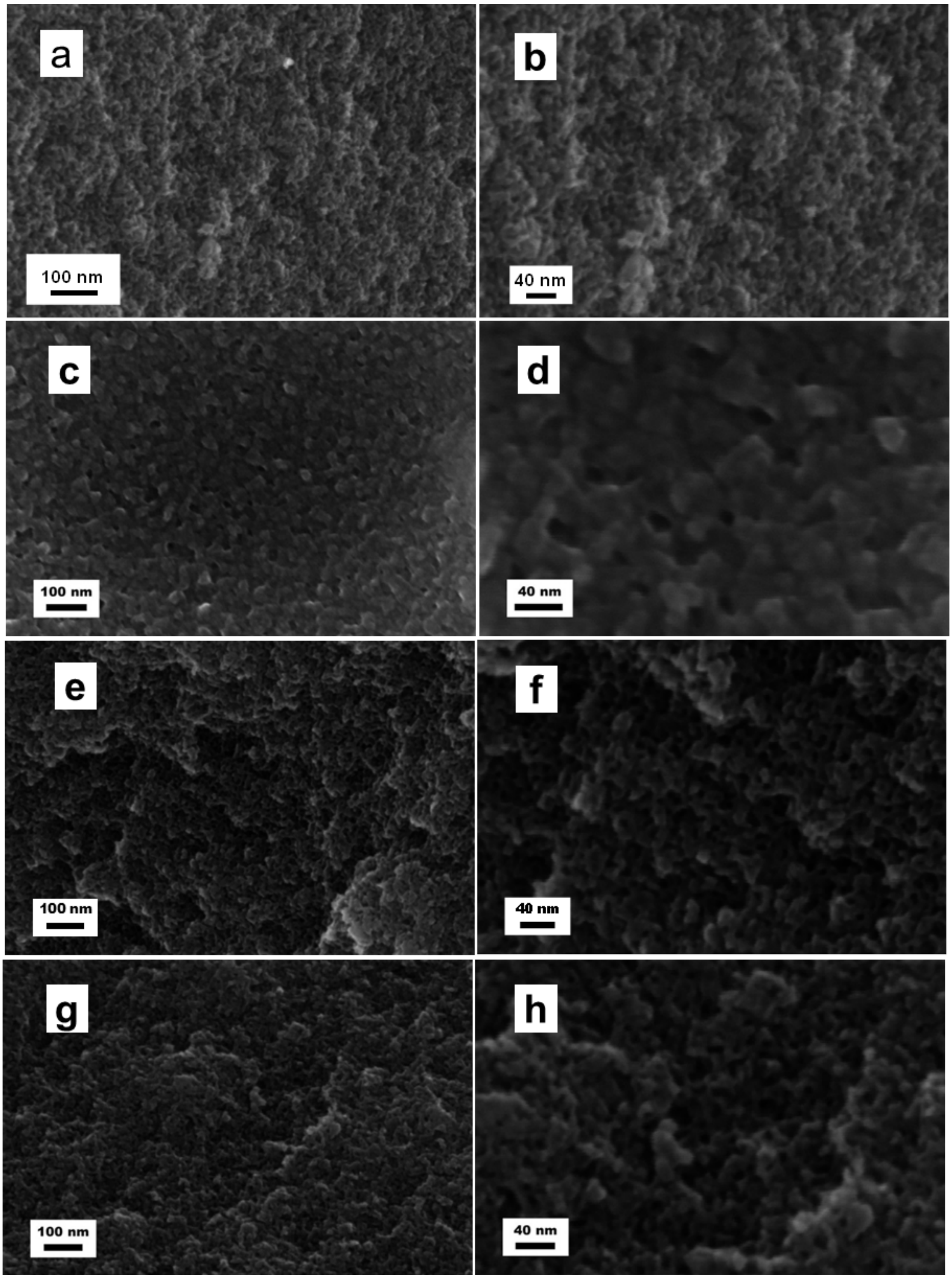

Figure S2. SEM images of MC400 (a, b), NMC400-380-1h (c, d), MC600 (e, f) and NMC600-380-1h (g, d).

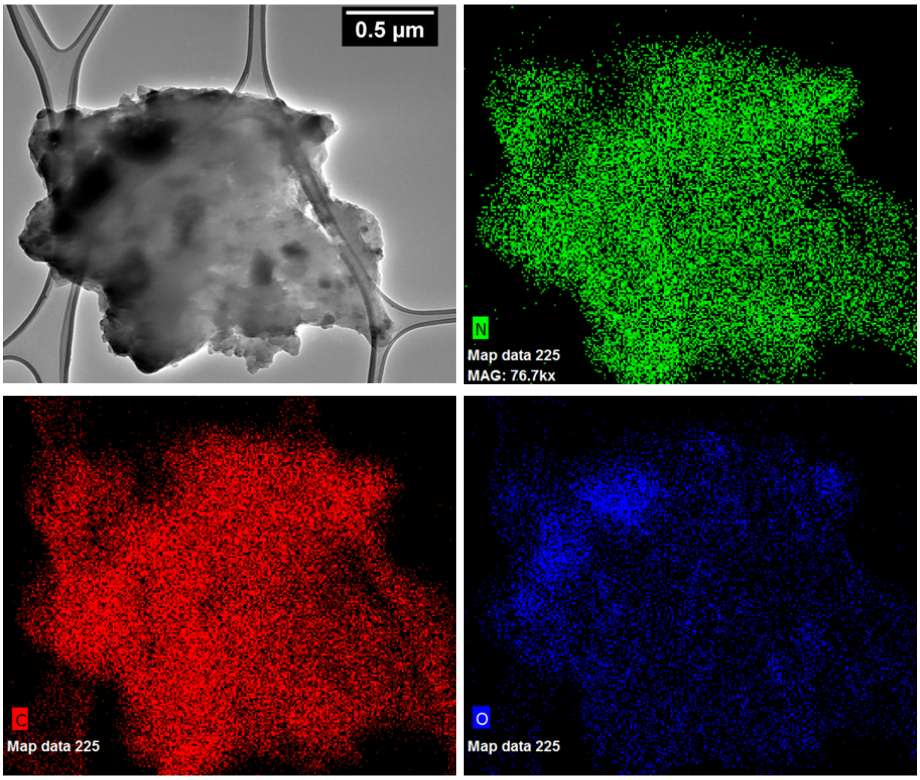

Figure S3. Elemental mapping of nitrogen, oxygen, and carbon on NMC600-380-1h by EDX.

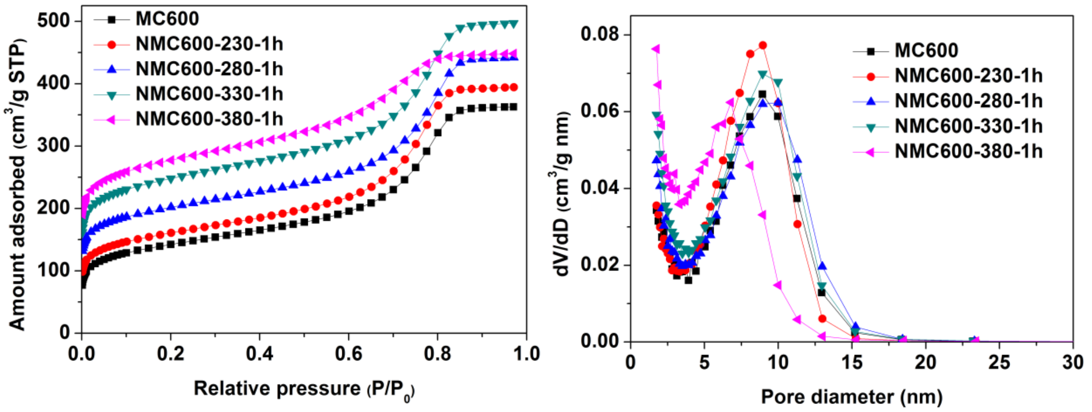

Figure S4. N_2-adsorption isotherms at –196 ºC (left) and BJH pore size distributions (right) of N-doped MC600 as a function of N-doping temperature: 230 (NMC600-230-1h), 280 (NMC600-280-1h), 330 (NMC600-330-1h), and 380 (NMC600-380-1h) ºC.

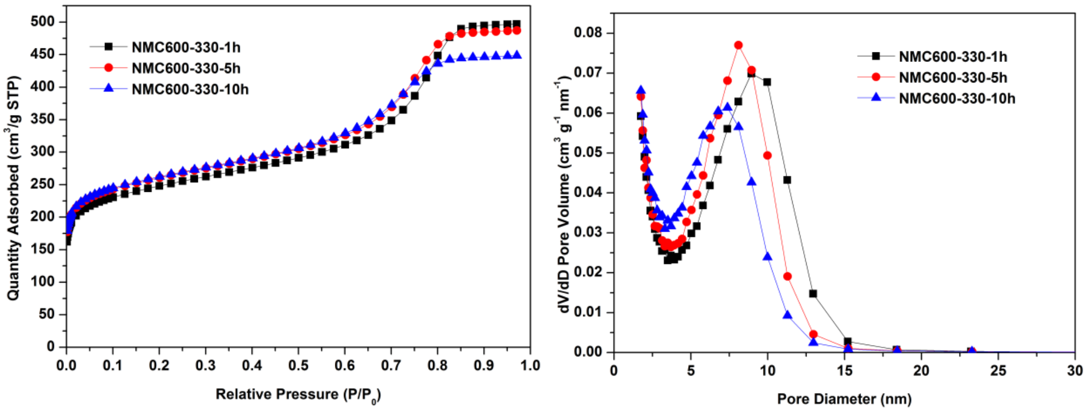

Figure S5. N_2-adsorption isotherms at –196 ºC (left) and BJH pore size distributions (right) of N-doped MC600 as a function of N-doping period of time: 1 (NMC600-330-1h), 5 (NMC600-330-5h), and 10 (NMC600-330-10h) h.

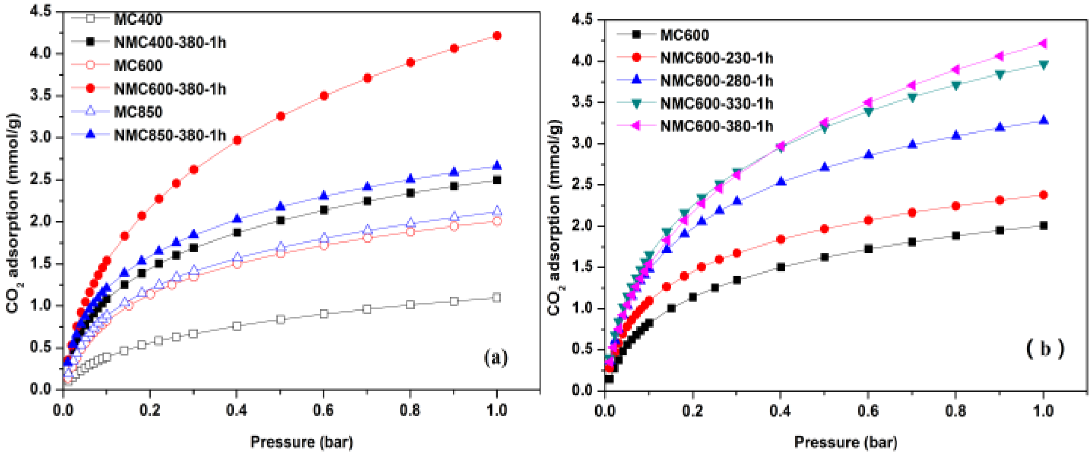

Figure S6. CO_2 adsorption isotherms at 0°C for parent and N-doped MCs as a function of carbonization temperature (a) and N-doping temperature (b).

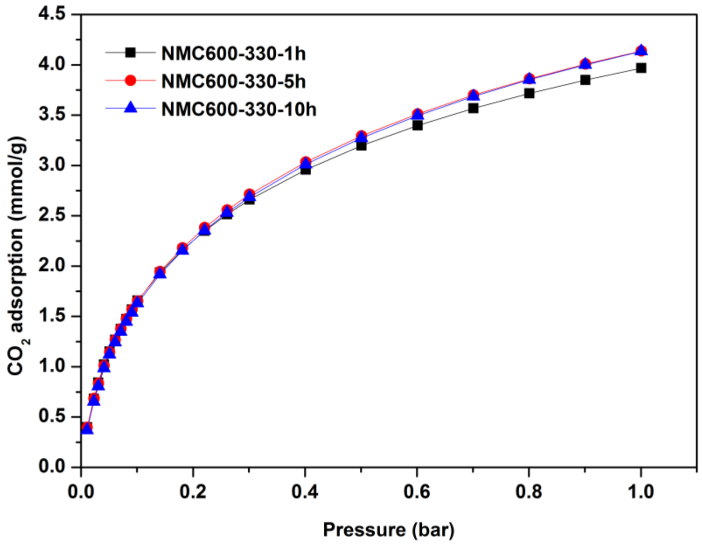

Figure S7. CO_2 adsorption isotherms at 0 ºC of N-doped MC600 as a function of N-doping period of time: 1 (NMC600-330-1h), 5 (NMC600-330-5h), and 10 (NMC600-330-10h) h.

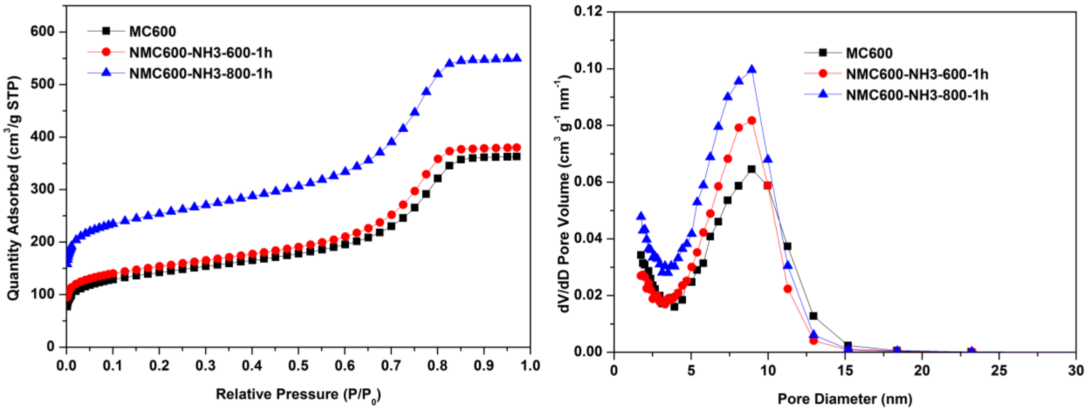

Figure S8. N_2-adsorption isotherms at –196 ˚C (left) and BJH pore size distributions (right) of N-doped MC600 synthesized at 600 ($NMC600-NH_3-600-1h$) and 800 ($NMC600-NH_3-800-1h$) ˚C using gaseous NH_3 as the doping agent.

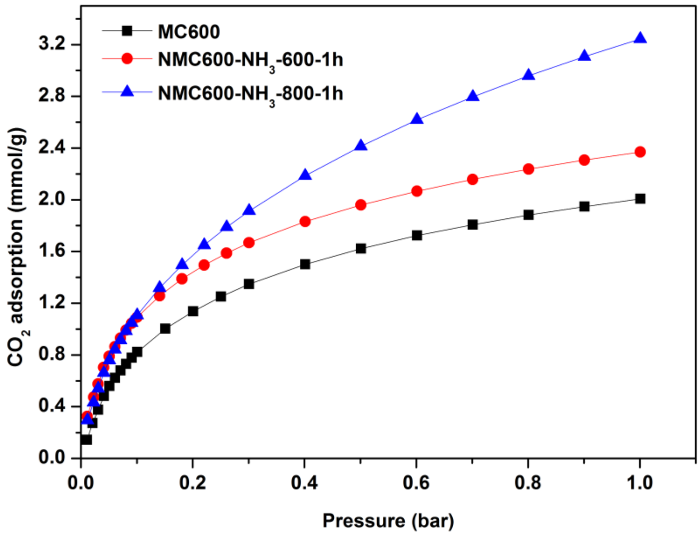

Figure S9. CO_2 adsorption isotherms at 0˚C of N-doped MC600 synthesized at 600 ($NMC600-NH_3-600-1h$) and 800 ($NMC600-NH_3-800-1h$) ˚C using gaseous NH_3 as the doping agent.

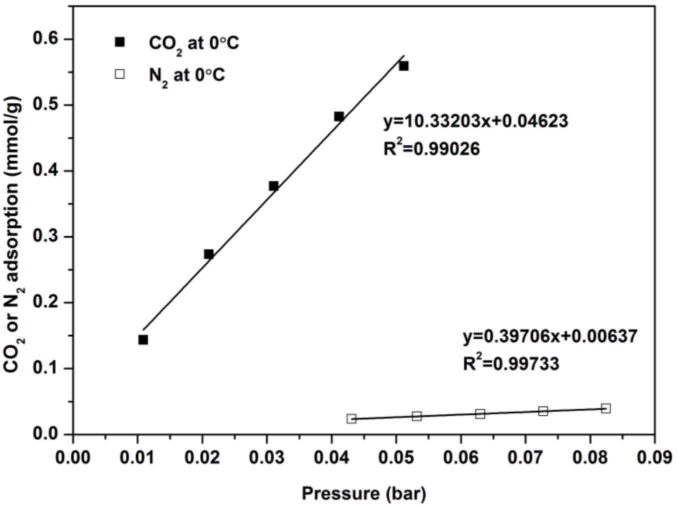

Figure S10. Calculation of ideal CO_2/N_2 selectivity at 0˚C for MC600.

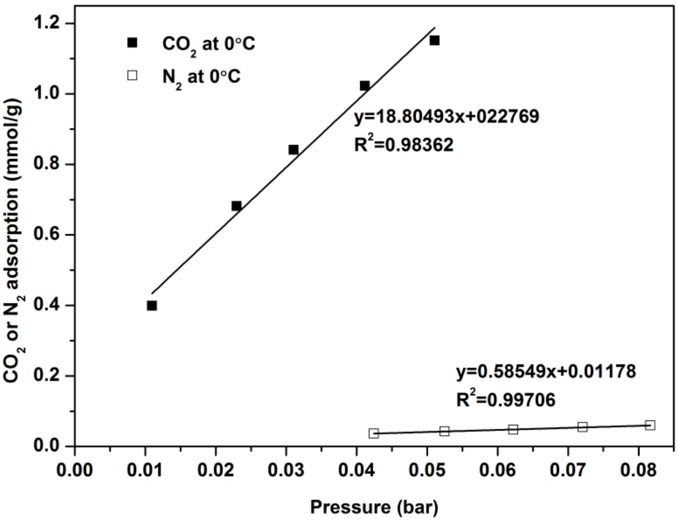

Figure S11. Calculation of ideal CO_2/N_2 selectivity at 0 ˚C for NMC600-330-1h.

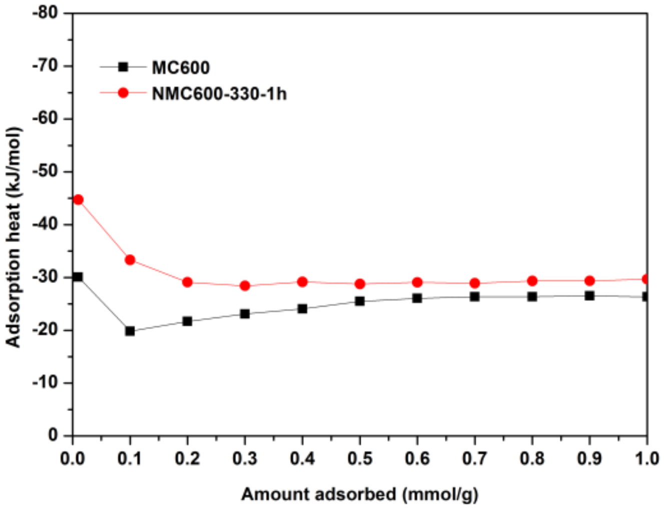

Figure S12. Calculated isosteric heats of CO_2 adsorption on MC600 and NMC600-330-1h.

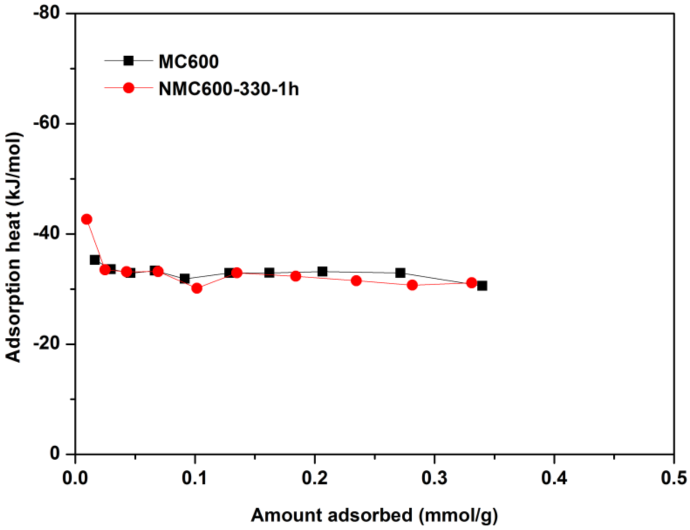

Figure S13. Measured isosteric heats of CO_2 adsorption on MC600 and NMC600-330-1h.

Effect of $NaNH_2$/MC mass ratio

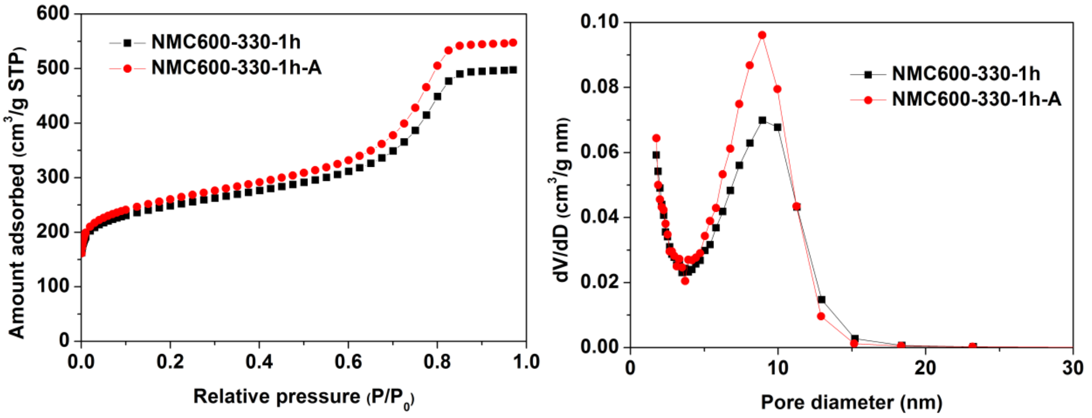

Figure S14. N_2-adsorption isotherms at –196 ºC (left) and BJH pore size distributions (right) of N-doped MC600 as a function of $NaNH_2$/MC mass ratio: 2 (NMC600-330-1h) and 3 (NMC600-330-1h-A).

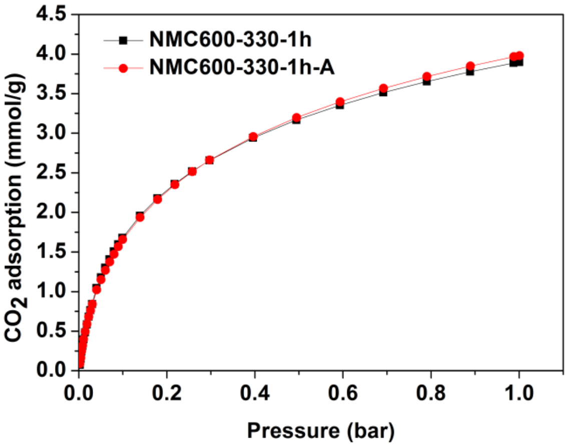

Figure S15. CO_2 adsorption isotherms at 0 ºC of N-doped MC600 as a function of $NaNH_2$/MC mass ratio: 2 (NMC600-330-1h) and 3 (NMC600-330-1h-A).

When the mass ratio of $NaNH_2$/MC was increased to 3, the resultant N-doped carbon NMC600-330-1h-A has similar BET surface area and micropore volume to NMC600-330-1h (904 vs. 907 m^2/g and 0.25 vs. 0.25 cm^3/g), and the total pore volume of NMC600-330-1h-A is slightly larger than that of NMC600-330-1h (0.85 vs. 0.77 cm^3/g). In addition, the CO_2 adsorption capacity at 0°C and 1 bar of NMC600-330-1h-A is also similar to that of NMC600-330-1h (3.98 vs. 3.90 mmol/g). Therefore, increasing the mass ratio of $NaNH_2$/MC can slightly enlarge the total pore volume of resultant N-doped carbon, but has no obvious contribution to improving the BET surface area, micropore volume and CO_2 adsorption capacity.

Recycle of CO_2 adsorption

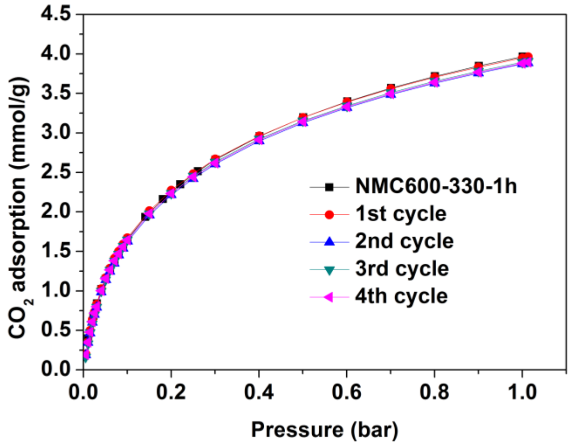

Figure S16. Recycle of CO_2 adsorption of NMC600-330-1h (adsorption: 0 ºC, desorption: drawing a vacuum at room temperature).

NMC600-330-1h was tested for the recycle of CO_2 adsorption. Adsorption was performed at 0°C and 0~1 bar, and desorption was performed at room temperature by drawing a vacuum. After five cycles, NMC600-330-1h maintains its adsorption capacity of CO_2 very well.

Small micropore size distributions

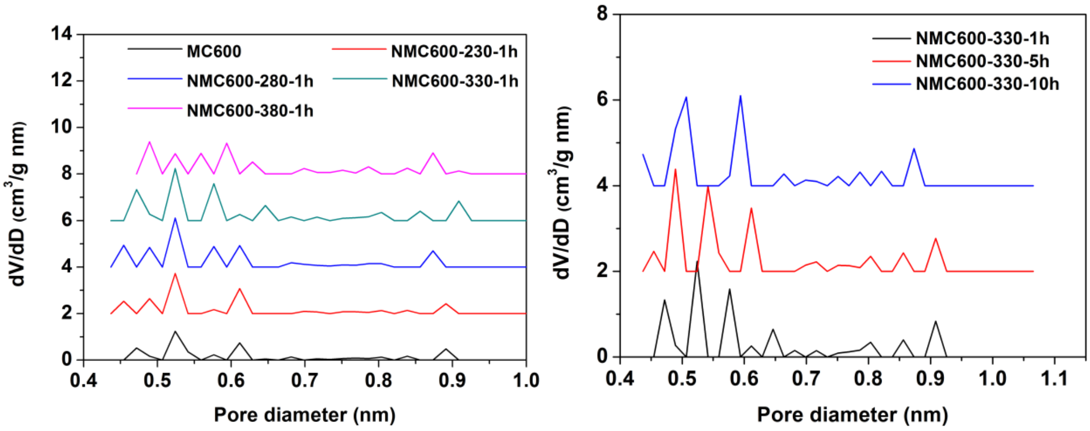

Figure S17. Small micropore size distribution of NMC600 samples calculated from CO_2 adsorption isotherms using NLDFT theory by assuming slit-like geometry of micropores: effect of N-doping temperature (left) and N-doping period of time (right).

All the NMC600 samples have similar small micropore size distributions, indicating the slight effect of N-doping temperature and N-doping period of time on the small micropore size of synthesized N-doped carbons.

Table S1. Yield and textual properties of N-doped MC600 synthesized at 600 (NMC600-NH3-600-1h) and 800 (NMC600-NH3-800-1h) ˚C using gaseous NH_3 as the doping agent.

Carbons	Yield[a] (%)	S_{BET}[b] (m^2/g)	S_{m}[c] (m^2/g)	V_{t}[d] (cm^3/g)	V_{m}[e] (cm^3/g)	N[f] (at.%)	O[g] (at.%)
MC600	-	479	231	0.56	0.11	0	16.4
NMC600-NH_3-600-1h	92.2	515	356	0.59	0.13	5.5	15.9
NMC600-NH_3-800-1h	66.0	842	472	0.85	0.23	5.3	5.9

[a] Yields based on the mass of pristine MC. [b] Surface area calculated from BET equation in the relative pressure range of 0.02~0.15. [c] Micropore surface area calculated using Carbon Black STSA *t*-plot equation within the thickness range of 0.45~0.60 nm. [d] Single point pore volume calculated from adsorption isotherms at the relative pressure of 0.97. [e] Micropore volume calculated using Carbon Black STSA *t*-plot equation within the thickness range of 0.45~0.60 nm. [f] Nitrogen content measured by XPS. [g] Oxygen content measured by XPS.

Reference

1. X. Q. Wang, J. S. Lee, C. Tsouris, D. W. DePaoli and S. Dai, *J Mater Chem*, 2010, 20, 4602-4608.