Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

High yield and high packing density porous carbons for unprecedented CO_2 capture from the first attempt at activation of *air-carbonized* biomass

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Laboratory preparation of biomass-derived air-carbonised carbons

Motivated by the attractive properties of the ‘air carbonised’ CNL carbon, we explored the possibility of deliberately generating such carbon under controlled lab conditions. The following procedures have proved successful in carbonizing biomass in the presence of air;

Method 1: Between 2 and 10 g of biomass (wood chippings) was dried in a furnace and heated (at a ramp rate of 10 ^{o}C min^{-1}) to ca. 400 ^{o}C under a flow 10% air in nitrogen. The temperature was held at the final temperature for 1 h (under a flow 10% air in nitrogen) and then cooled (under a flow of nitrogen only) to room temperature.

Method 2: Between 2 and 10 g of biomass (wood chippings) was dried in a furnace and heated (at a ramp rate of 10 ^{o}C min^{-1}) to the target temperature (between 350 and 450 ^{o}C). At the target temperature, the gas flow was switched to air only for 10 minutes and then the sample cooled down to room temperature under nitrogen flow.

Table S1. Elemental composition of CNL1 carbon compared to biochar and hydrochar from other biomass precursors.

Sample	Carbonisation conditions	Carbonisation temperature (^oC)	C (wt%)	H (wt%)	N (wt%)	O (wt%	Reference
CNL1 carbon	Air		77.7	3.1	0	19.2	This work
Rice husk char	N_2	400	71.5	/	/	25.5	1
Cherry stone char	Ar	400	77.6	4.6	0.8	16.9	2
Beech pellet char	Ar	800	82.7	2.0	0.4	14.9	3
Tire char	O_2 free	450	72.5	4.7	4.8	15.3	4
Lignite char	N_2	475	65.0	2.4	0.9	18.2	5
Lignin hydrochar	Water	390	66.6	5.1	0	28.3	6
Saw-dust hydrochar	Water	250	69.3	6.8	0	23.9	7

1. L. Muniandy, F. Adam, A. R. Mohamed and E. Ng, *Micropor. Mesopor. Mater.*, 2014, **197**, 316.
2. R. Pietrzak, P. Nowicki, J. Kaźmierczak, I. Kuszyńska, J. Goscianska and J. Przepiórski, *Chem. Eng. Res. Des.,* 2014, **92**, 1187.
3. K. Zeng, D. P. Minh, D. Gauthier, E. Weiss-Hortala, A. Nzihou and G. Flamant, *Bioresource Technol.*, 2015, **182**, 114.
4. V. Makrigianni, A. Giannakas, C. Daikopoulos, Y. Deligiannakis and I. Konstantinou, *Appl. Catal., B,* 2015, **174**, 244.
5. G. Chattopadhyaya, D. G. Macdonald, N. N. Bakshi, J. S. S. Mohammadzadeh and A. K. Dalai, *Fuel Proces. Technol.*, 2006, **87**, 997.
6. W. Sangchoom and R. Mokaya, *ACS Sust. Chem. Eng*., 2015, **3**, 1658.
7. B. Adeniran and R. Mokaya, *Nano Energy*, 2015, **16***,* 173.

Table S2. Carbon yield of activated carbons derived from various precursors.

Activation conditions		Yield[a] from various precursors		
KOH/carbon ratio	Temperature (°C)	CNL1 carbon	Lignin hydrochar[b]	Polypyrrole[c,d]
2	600	80	36	45
2	700	65	27	34
2	800	52	21	22
4	600	68	20	18
4	700	53	19	20
4	800	32	15	15

[a] g of activated carbon/100 g hydrochar.

[b] Data from ref. 57; W. Sangchoom and R. Mokaya, *ACS Sust. Chem. Eng*., 2015, **3**, 1658.

[c] Data from ref 55; M. Sevilla, R. Mokaya and A. B. Fuertes, *Energy Environ. Sci.*, 2011, **4**, 2930.

[d] Data from ref. 56; B. Adeniran and R. Mokaya, *Nano Energy*, 2015, **16**, 173.

Table S3. Textural properties of activated carbons derived from CNL1 carbon at activation temperature of 800 °C and KOH/carbon ratio of 2 or 4 compared to activated carbons from lignin hydrochar (LAC), grass hydrochar (ACGR), carbon nanotube composites (CN) and polypyrrole (Py).

Sample	Surface area[a] ($m^2 g^{-1}$)	Pore volume[b] ($cm^3 g^{-1}$)	Pore size[c] (Å)
CNL1-2800	1326 (1263)	0.60 (0.55)	6/8.5/13
LAC2800	1924 (1839)	0.95 (0.87)	7/9/13
ACGR2800	2735 (2083)	1.47 (0.94)	6.5/9/12
CN2800	2925 (2538)	1.56 (1.18)	6/8/11/21
Py2800	3410 (2530)	1.94 (1.21)	12/25
CNL1-4800	2183 (1886)	1.05 (0.84)	6.5/8.5/16
LAC4800	3235 (1978)	1.77 (0.93)	8/11/27
ACGR4800	2957 (1578)	1.72 (0.75)	8/12/27
CN4800	3802 (33)	2.98 (0.22)	8/12/34
Py4800	3450 (1910)	2.57 (1.22)	13/34

The values in the parenthesis refer to: [a]micropore surface area and [b]micropore volume. [c]pore size distribution maxima obtained from NLDFT analysis.

LAC data from ref. 57; W. Sangchoom and R. Mokaya, *ACS Sust. Chem. Eng.*, 2015, **3**, 1658.
ACGR data from ref. 74; H. M. Coromina, D. A. Walsh and R. Mokaya, *J. Mater. Chem. A*, 2016, **4**, 280.
CN data from ref. 61; B. Adeniran and R. Mokaya, *J. Mater. Chem. A*, 2015, **3**, 5148.
Py data from ref. 55; M. Sevilla, R. Mokaya and A. B. Fuertes, *Energy Environ. Sci.*, 2011, **4**, 2930.

Table S4. Textural properties of activated carbons from various precursors.

Activation conditions[a]	Precursor									
	CNL1 carbon		Lignin hydrochar[g]		Grass Hydrochar[h]		CNT composites[i]		Polypyrrole[j]	
	SA[b] *μSA*[d] **(%μ)**[f]	PV[c] *μPV*[e] **(%μ)**	SA *μSA* **(%μ)**	PV *μPV* **(%μ)**	SA *μSA* **(%μ)**	PV *μPV* **(%μ)**	SA *μSA* **(%μ)**	PV *μPV* **(%μ)**	SA *μSA* **(%μ)**	PV *PV* **(%μ)**
2/600	1190 *1107* **(93)**	0.55 *0.49* **(89)**	1157 *1123* **(97)**	0.59 *0.54* **(92)**	1048 *975* **(93)**	0.51 *0.43* **(84)**	1479 *1400* **(95)**	0.83 *0.67* **(81)**	1700	0.88 *0.74* **(84)**
2/700	1399 *1343* **(96)**	0.63 *0.59* **(93)**	1551 *1502* **(97)**	0.77 *0.72* **(94)**	1512 *1426* **(94)**	0.74 *0.62* **(84)**	2102 *1987* **(95)**	1.18 *0.95* **(81)**	2940 *2660* **(90)**	1.37 *1.14* **(83)**
2/800	1326 *1263* **(95)**	0.60 *0.55* **(92)**	1924 *1839* **(96)**	0.95 *0.87* **(92)**	2735 *2083* **(76)**	1.47 *0.94* **(64)**	2925 *2538* **(87)**	1.56 *1.18* **(76)**	3410 *2530* **(74)**	1.94 *1.21* **(62)**
4/600	1121 *1021* **(91)**	0.53 *0.45* **(85)**	1820 *1627* **(89)**	0.97 *0.75* **(82)**	2396 *2182* **(91)**	1.15 *0.96* **(83)**	2051 *1752* **(85)**	1.09 *0.82* **(75)**	2050 *1670* **(81)**	1.03 *0.74* **(72)**
4/700	1280 *1191* **(93)**	0.65 *0.56* **(86)**	2038 *1832* **(90)**	1.00 *0.84* **(84)**	3144 *2753* **(88)**	1.56 *1.23* **(79)**	3202 *1106* **(35)**	2.14 *0.50* **(23)**	3480 *2190* **(63)**	2.39 *1.18* **(49)**
4/800	2183 *1886* **(86)**	1.05 *0.84* **(80)**	3235 *1978* **(61)**	1.77 *0.93* **(53)**	2957 *1578* **(53)**	1.72 *0.75* **(44)**	3802 *33* **(1)**	2.98 *0.22* **(7)**	3450 *1910* **(55)**	2.57 *1.22* **(47)**

[a] Activation conditions given as x/T, where x is KOH/carbon ratio and T is temperature (^{o}C).

[b] SA is total surface area.

[c] PV is total pore volume.

[d] μSA is micropore surface area.

[e] μPV is micropore volume.

[f] (μ%) is micropore surface area or pore volume as a percentage of total surface or pore volume, respectively.

[g] Data from ref. 57; W. Sangchoom and R. Mokaya, *ACS Sust. Chem. Eng*., 2015, **3**, 1658.

[h] Data from ref. 74; H. M. Coromina, D. A. Walsh and R. Mokaya, *J. Mater. Chem. A*, 2016, **4**, 280.

[i] Data from ref. 61; B. Adeniran and R. Mokaya, *J. Mater. Chem. A*, 2015, **3**, 5148.

[j] Data from ref. 55; M. Sevilla, R. Mokaya and A. B. Fuertes, *Energy Environ. Sci.*, 2011, **4**, 2930.

Table S5. Yield, textural properties and CO_2 uptake of activated CNL1 carbon (CNL1-xT) from air carbonized wood compared to a similarly activated carbon (CNLW-xT) from wood carbonized under nitrogen. (x is KOH/carbon ratio, and T is activation temperature).

Sample	Yield[a] (wt%)	Surface area[b] (m^2 g^{-1})	Pore volume[c] (cm^3 g^{-1})	Pore size[d] (Å)	CO_2 uptake[e] (mmol g^{-1})		
					0.15 bar	1 bar	20 bar
CNL1-2700	**65**	**1399 (1343)**	**0.63 (0.59)**	**6/8.5/12**	**1.3**	**4.8**	**13.4**
CNLW-2700	44	1592 (1289)	0.75 (0.51)	7/9/14	1.2	4.3	12.5
CNL1-2800	**52**	**1326 (1263)**	**0.60 (0.55)**	**6/8.5/13**	**1.0**	**4.3**	**14.1**
CNLW-2800	33	2144 (1361)	1.27 (0.64)	7/12/25	0.8	3.5	20.1
CNL1-4700	**53**	**1280 (1191)**	**0.65 (0.56)**	**6.5/8.5/15**	**1.0**	**3.3**	**10.5**
CNLW-4700	34	2250 (2108)	0.98 (0.89)	12/15	0.9	2.6	19.5
CNL1-4800	**32**	**2183 (1886)**	**1.05 (0.84)**	**6.5/8.5/16**	**0.8**	**3.3**	**14.5**
CNLW-4800	21	2791 (881)	1.75 (0.50)	8/12/29	0.5	2.8	21.6

[a]The yield is based on starting weight of CNL1 carbon. The values in the parenthesis refer to: [b]micropore surface area and [c]micropore volume. [d]Pore size distribution maxima obtained from NLDFT analysis. [e]CO_2 uptake at 25 °C and various pressures (i.e., 0.15 bar, 1 bar and 20 bar).

Table S6. Textural properties of CNL1 carbon compared to biomass (wood chippings) derived lab generated air carbonised carbon.

Sample	Surface area[a] (m^2 g^{-1})	Pore volume[b] (cm^3 g^{-1})	Pore size[c] (Å)
CNL1 carbon	100 (79)	0.60 (0.035)	7/12
Lab air carbonised carbon	122 (85)	0.07 (0.037)	7/12

The values in the parenthesis refer to: [a]micropore surface area and [b]micropore volume. [c]pore size distribution maxima obtained from NLDFT analysis.

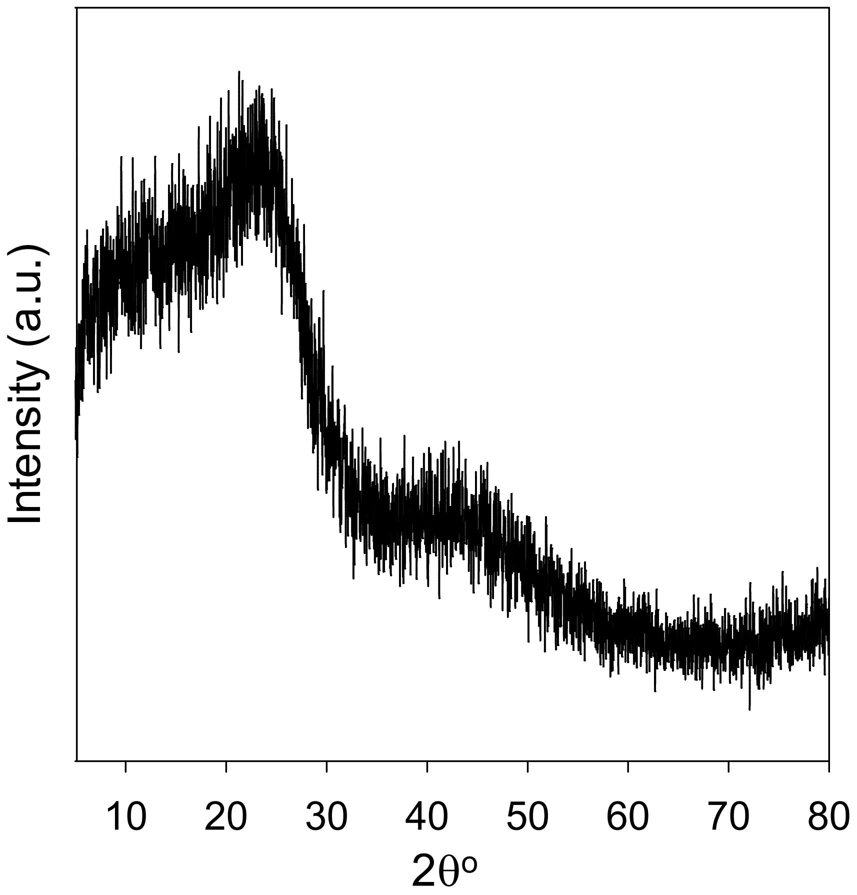
Table S7. Gravimetric and volumetric working capacity for pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) of CO_2 on activated CNL1 carbon (CNL1-xT) from air carbonized wood compared to similarly activated carbon (CNLW-xT) from wood carbonized under nitrogen. (x is KOH/carbon ratio, and T is activation temperature). The CO_2 uptake is at 25 °C for a pure CO_2 gas stream and a 20% partial CO_2 pressure flue gas. The values in parentheses are volumetric uptake or working capacity (in g l^{-1}).

Sample	Packing density (g cm^{-3})	Pure CO_2 uptake[a] (mmol g^{-1})		Flue gas CO_2 uptake[b] (mmol g^{-1})	
		PSA	VSA	PSA	VSA
CNL1-2700	**0.98**	**5.7 (246)**	**5.4 (233)**	**3.7 (160)**	**2.0 (86)**
CNLW-2700	0.71	5.5 (172)	5.0 (156)	3.5 (109)	2.0 (63)
CNL1-2800	**1.01**	**6.3 (280)**	**5.2 (231)**	**3.5 (156)**	**1.8 (80)**
CNLW-2800	0.65	6.5 (186)	4.4 (126)	3.2 (92)	1.3 (38)
CNL1-4700	**0.89**	**4.1 (161)**	**3.5 (137)**	**2.4 (94)**	**1.4 (55)**
CNLW-4700	0.47	5.0 (103)	3.2 (66)	2.1 (43)	1.3 (27)
CNL1-4800	**0.70**	**6.1 (189)**	**4.0 (123)**	**2.7 (83)**	**1.3 (40)**
CNLW-4800	0.41	7.1 (128)	3.7 (67)	2.8 (51)	1.1 (20)

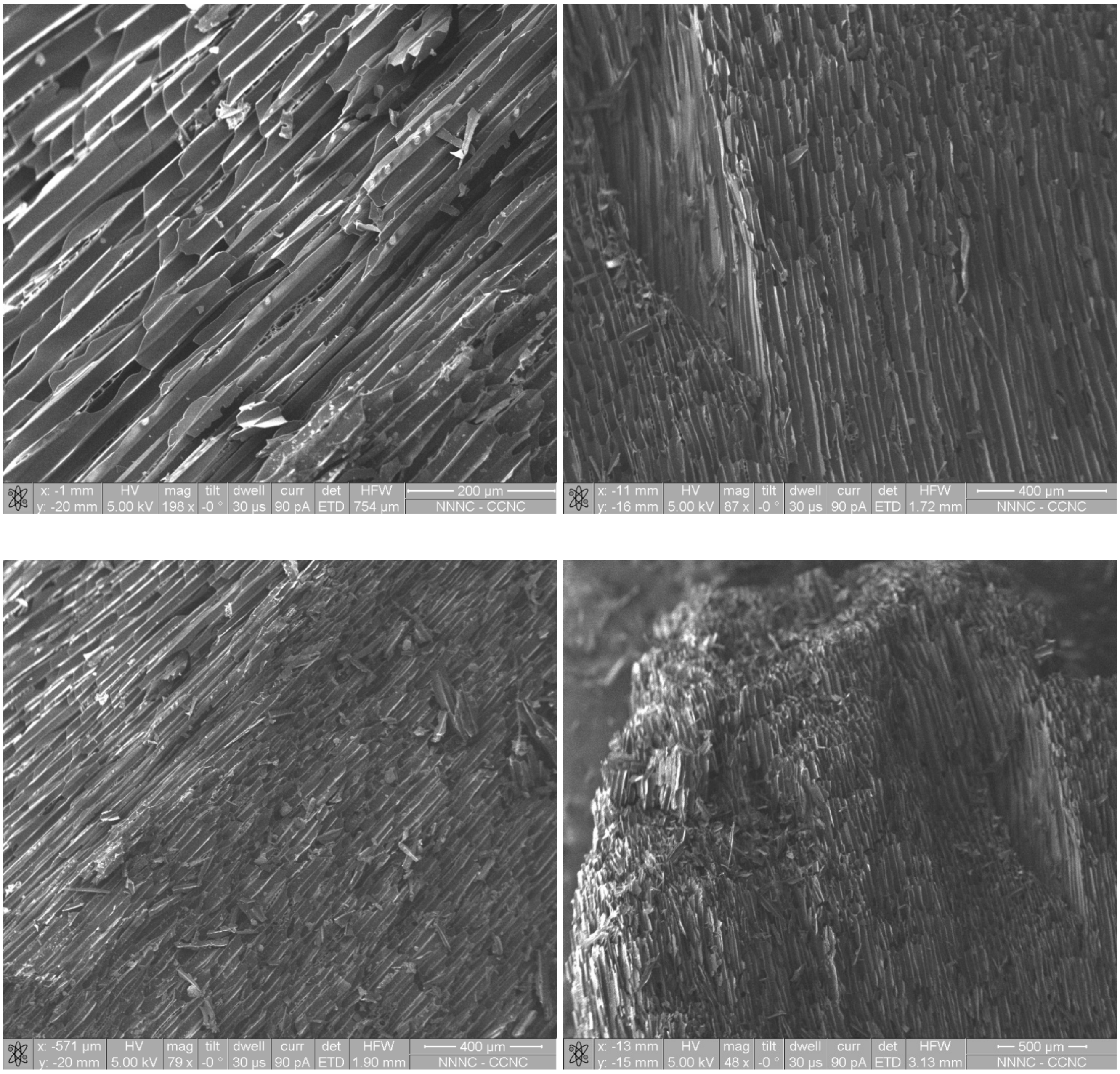
[a] 1 bar to 6 bar for PSA; 0.05 bar to 1.5 bar for VSA. [b] 0.2 bar to 1.2 bar for PSA; 0.01 bar to 0.3 bar for VSA.

Supporting Figure S1. Charred wooden beam from Carbon Neutral Laboratory (CNL1).

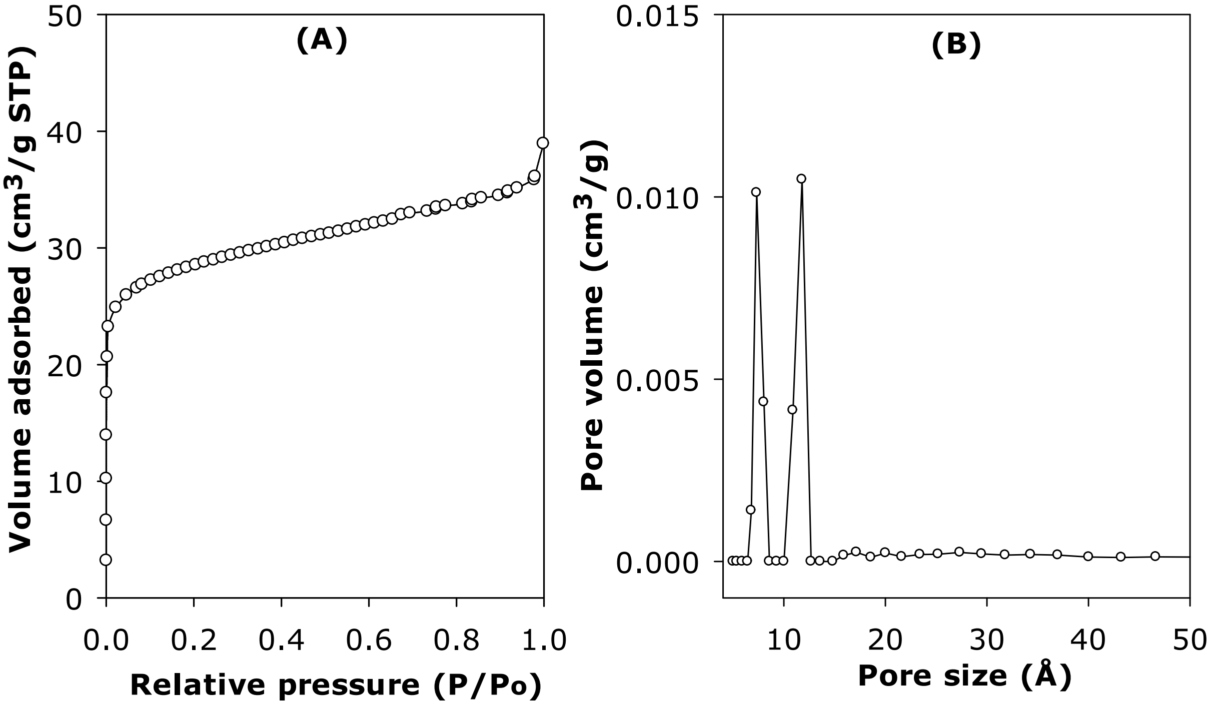
Supporting Figure S2. Cross section of charred wooden beam from Carbon Neutral Laboratory (CNL1).



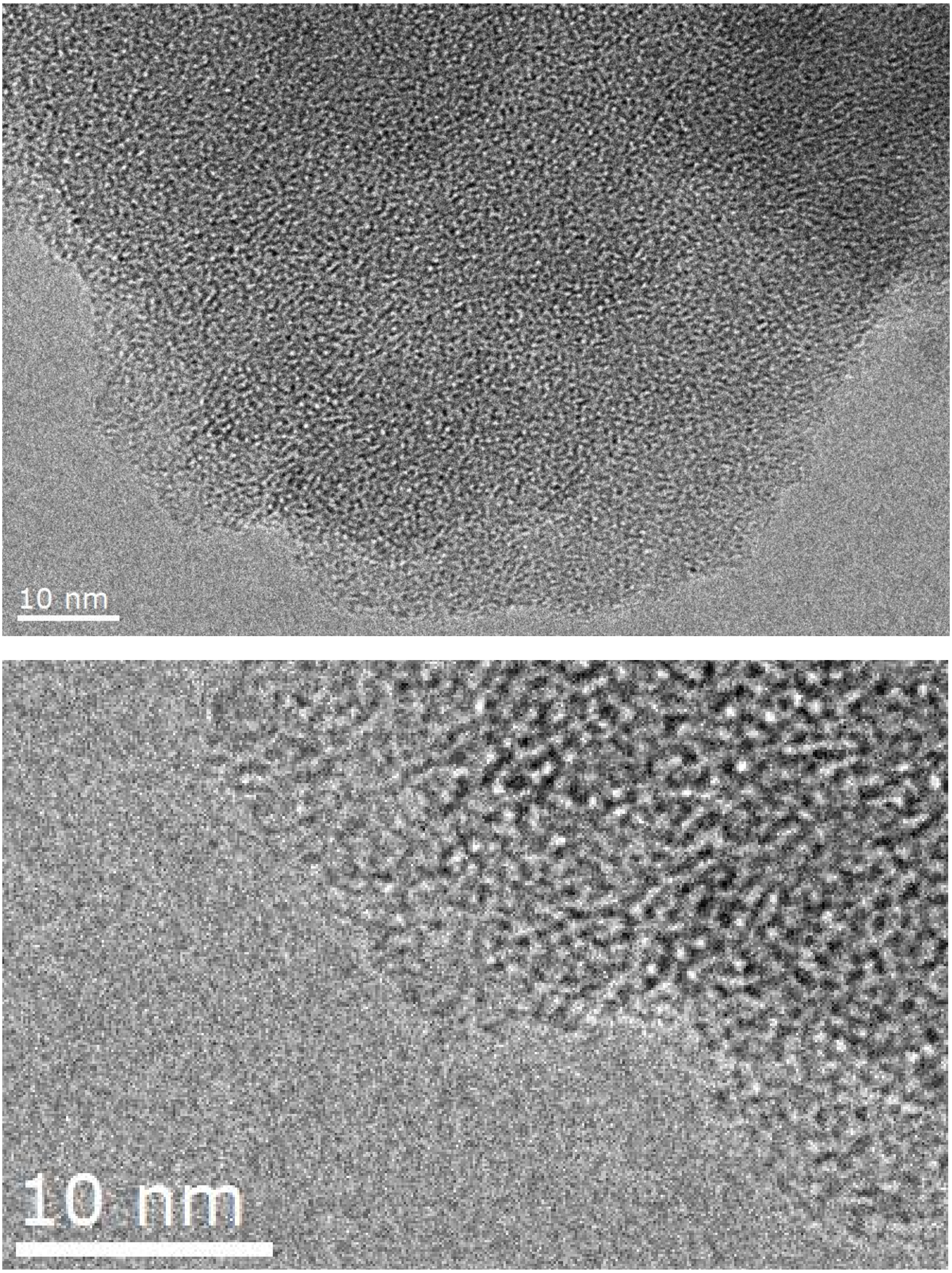
Supporting Figure S3. Powder XRD pattern of CNL1 carbon.



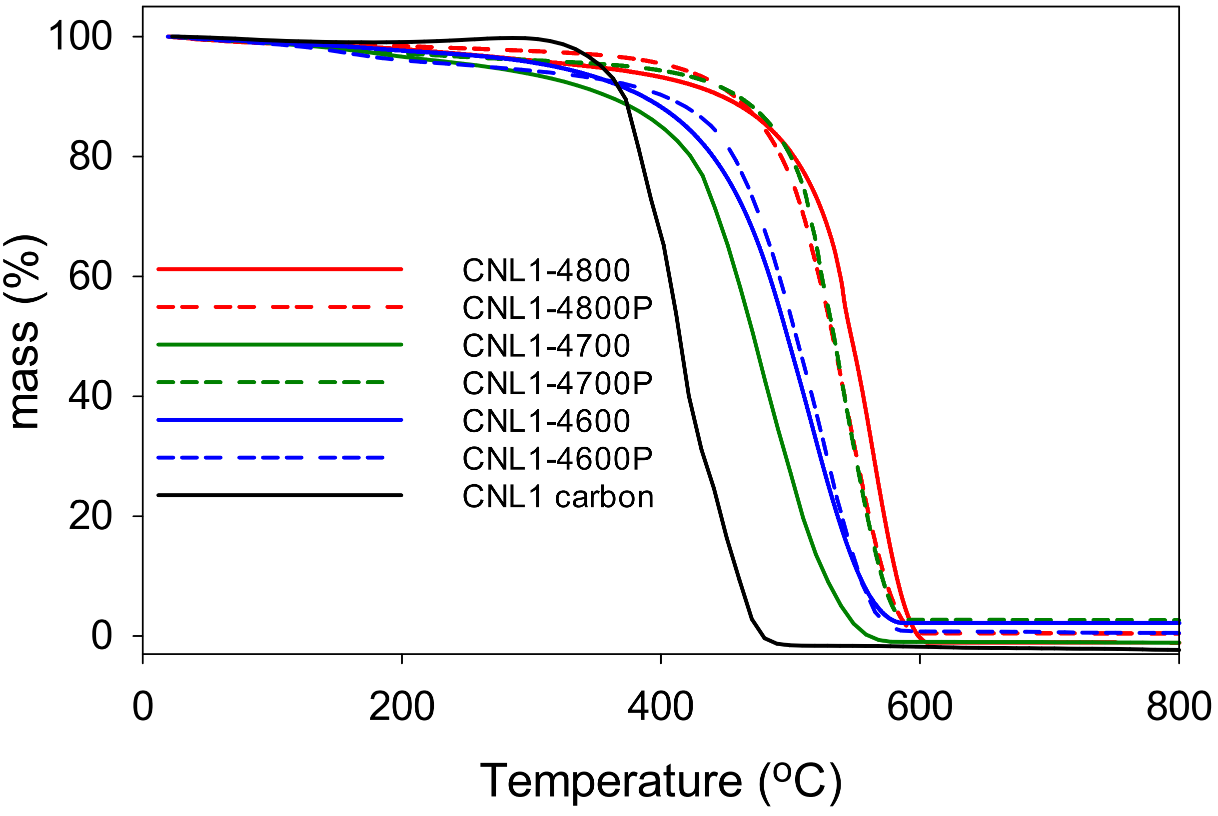
Supporting Figure S4. SEM images of CNL1 carbon.



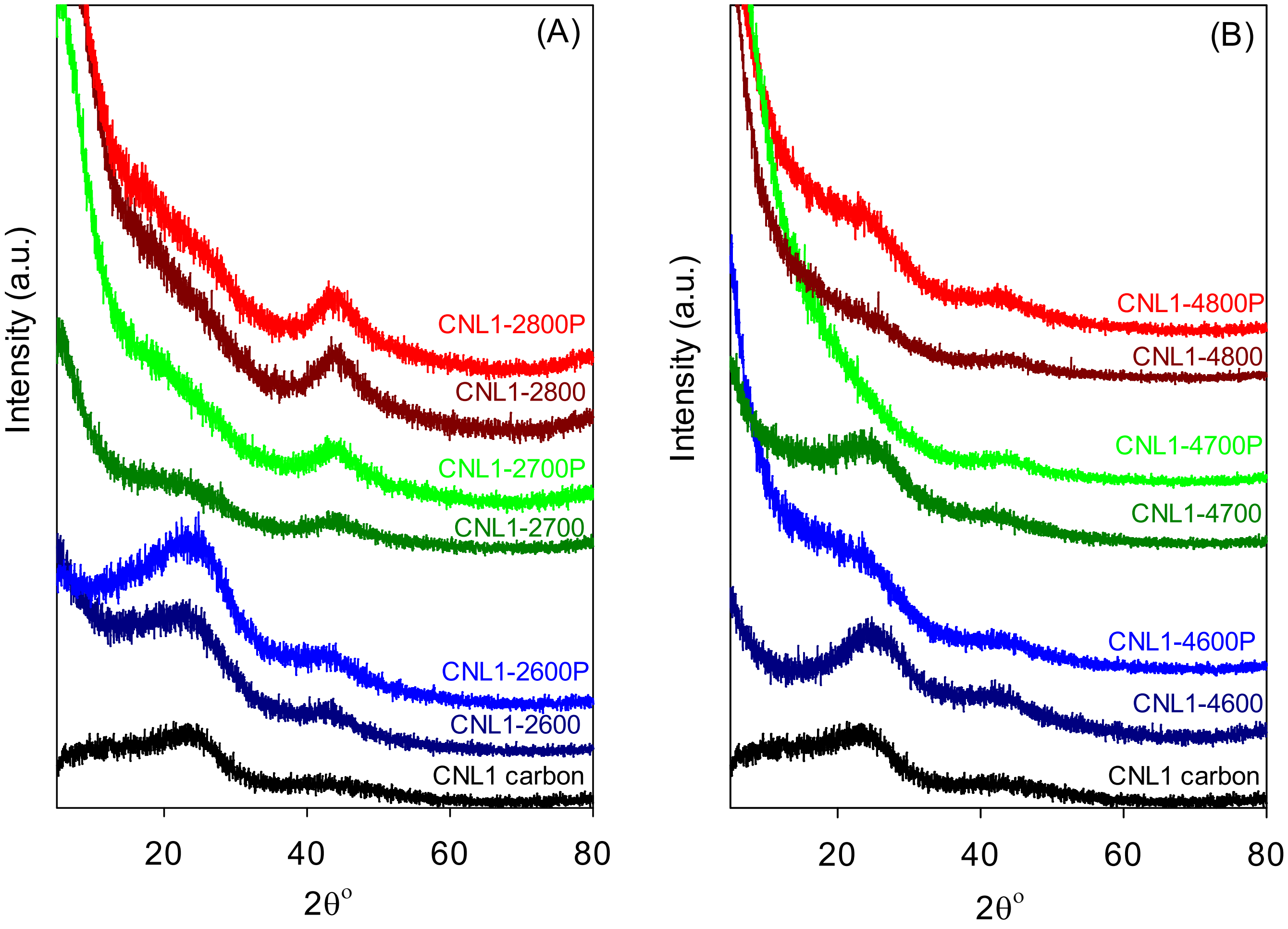
Supporting Figure S5. Nitrogen sorption isotherm (A) and pore size distribution curve (B) of CNL1 carbon.



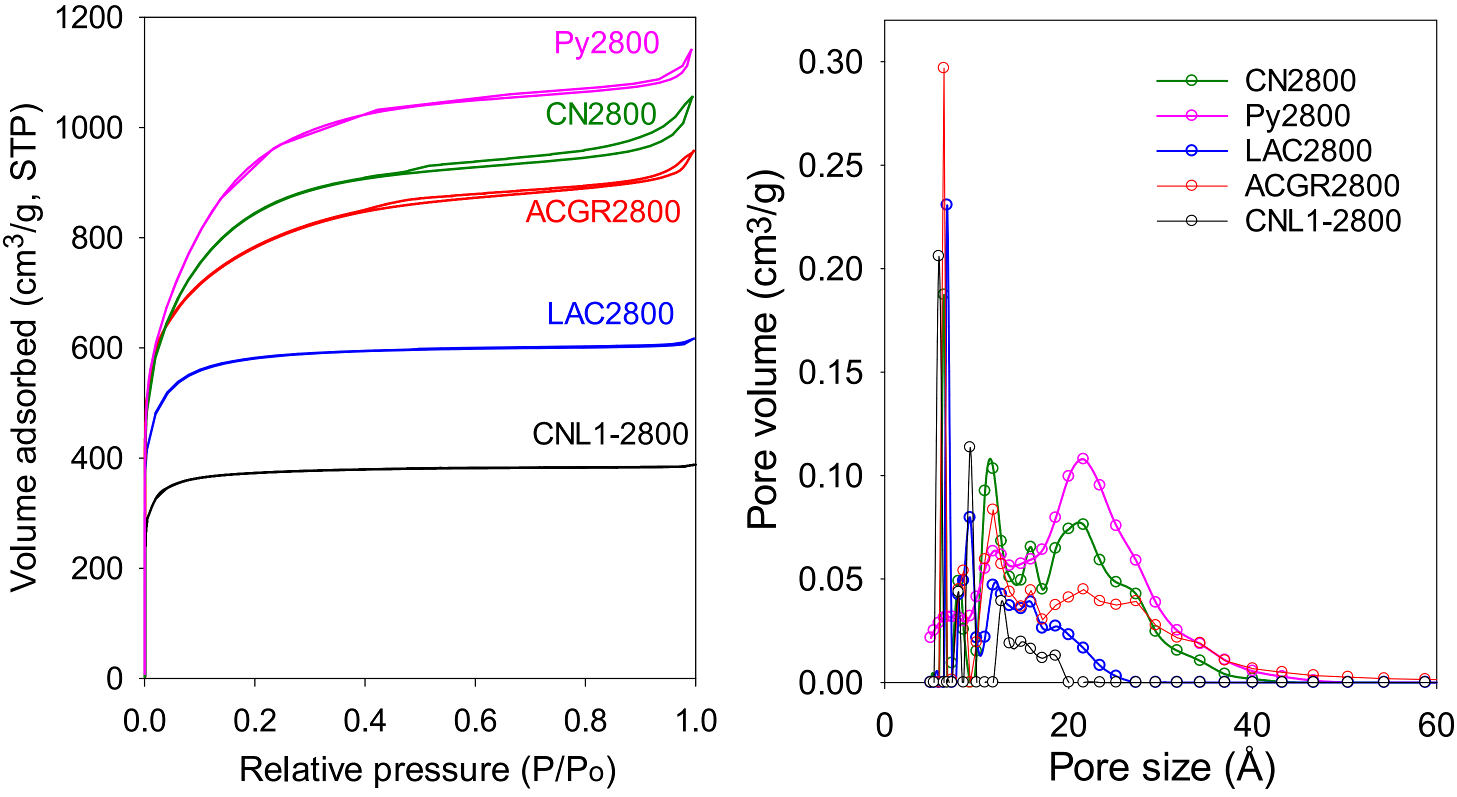
Supporting Figure S6. TEM images of CNL1 carbon.



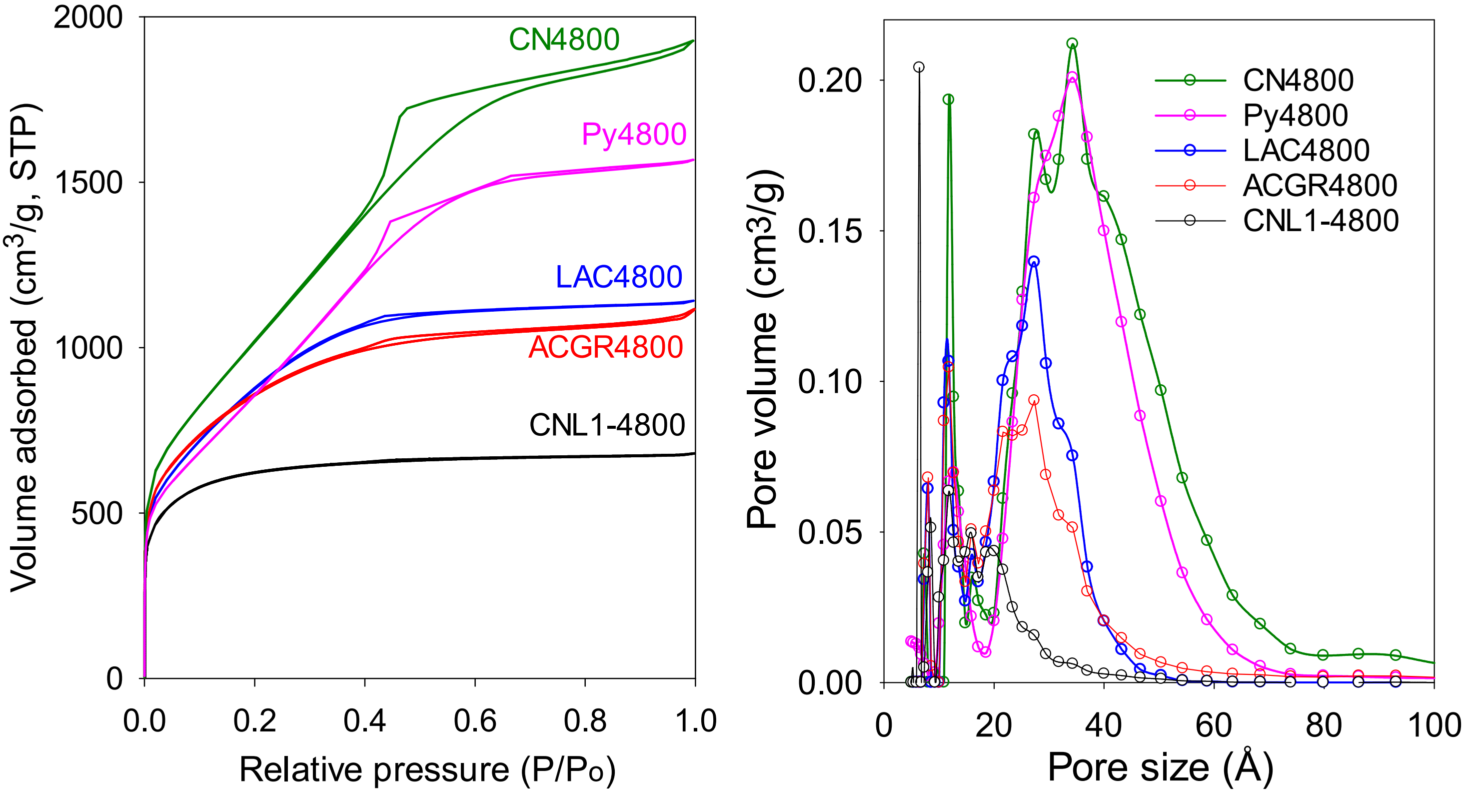
Supporting Figure S7. Thermogravimetric analysis (TGA) curve of CNL1 carbon and activated CNL1-4T carbons thermally treated in air.



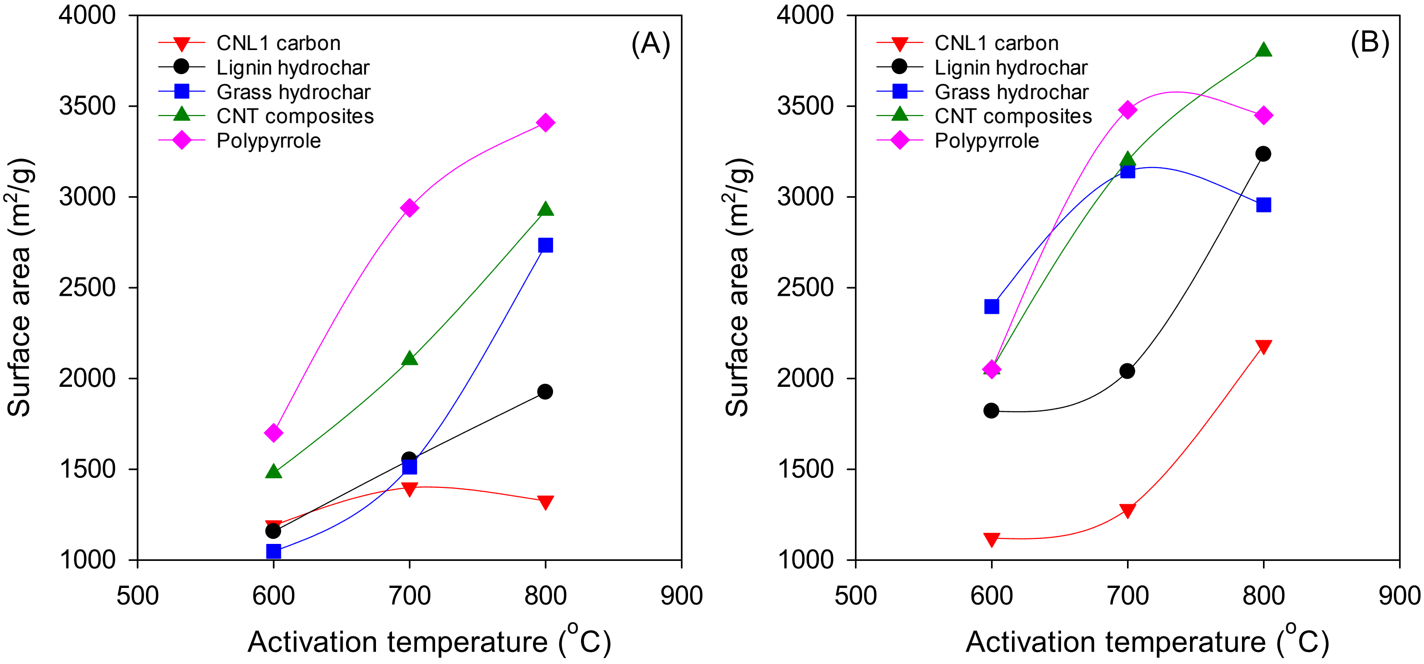
Supporting Figure S8. Powder XRD pattern of CNL1 carbon, and activated CNL1-2T (A) and CNL1-4T (B) carbons.



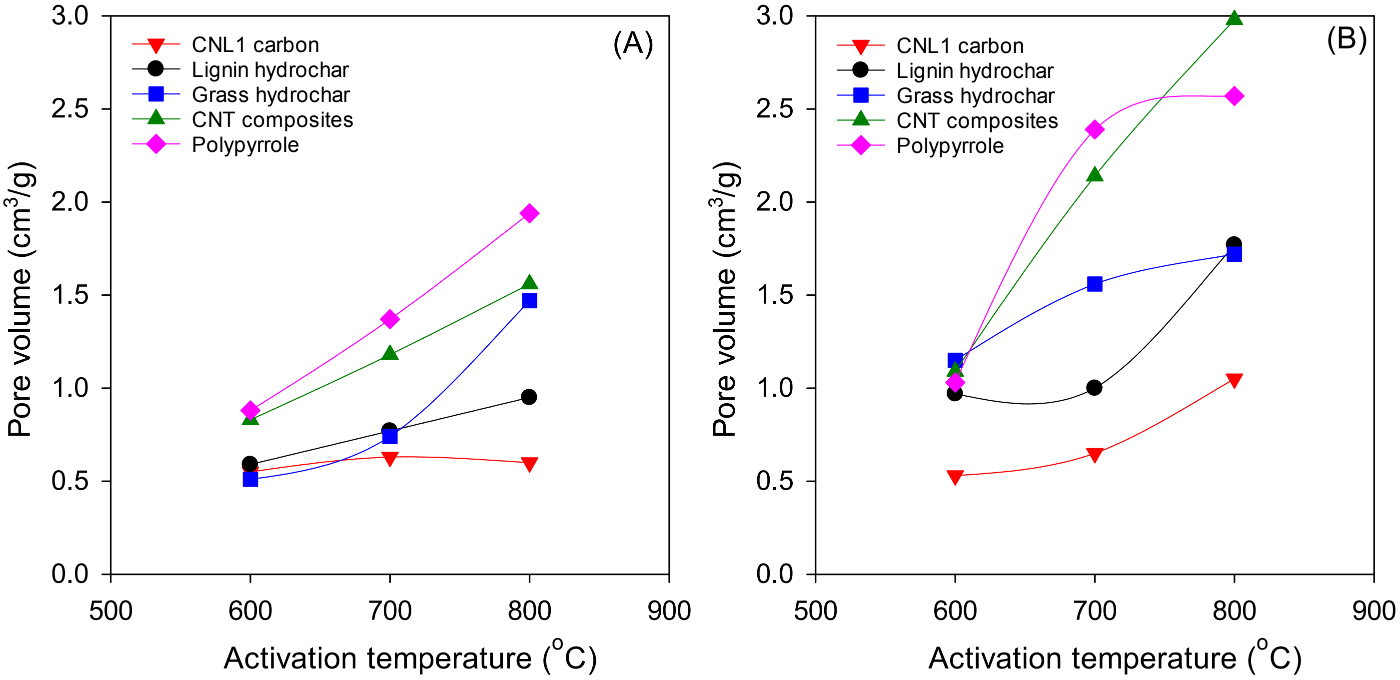
Supporting Figure S9. Nitrogen sorption isotherms and pore size distribution curves of activated CNL1-2800 carbon compared to analogous activated carbons derived from lignin (LAC2800), grass (ACGR2800), carbon nanotube superstructures (CN2800) or polypyrrole (Py2800) under similar activation conditions (i.e., 800 °C and KOH/carbon ratio of 2).



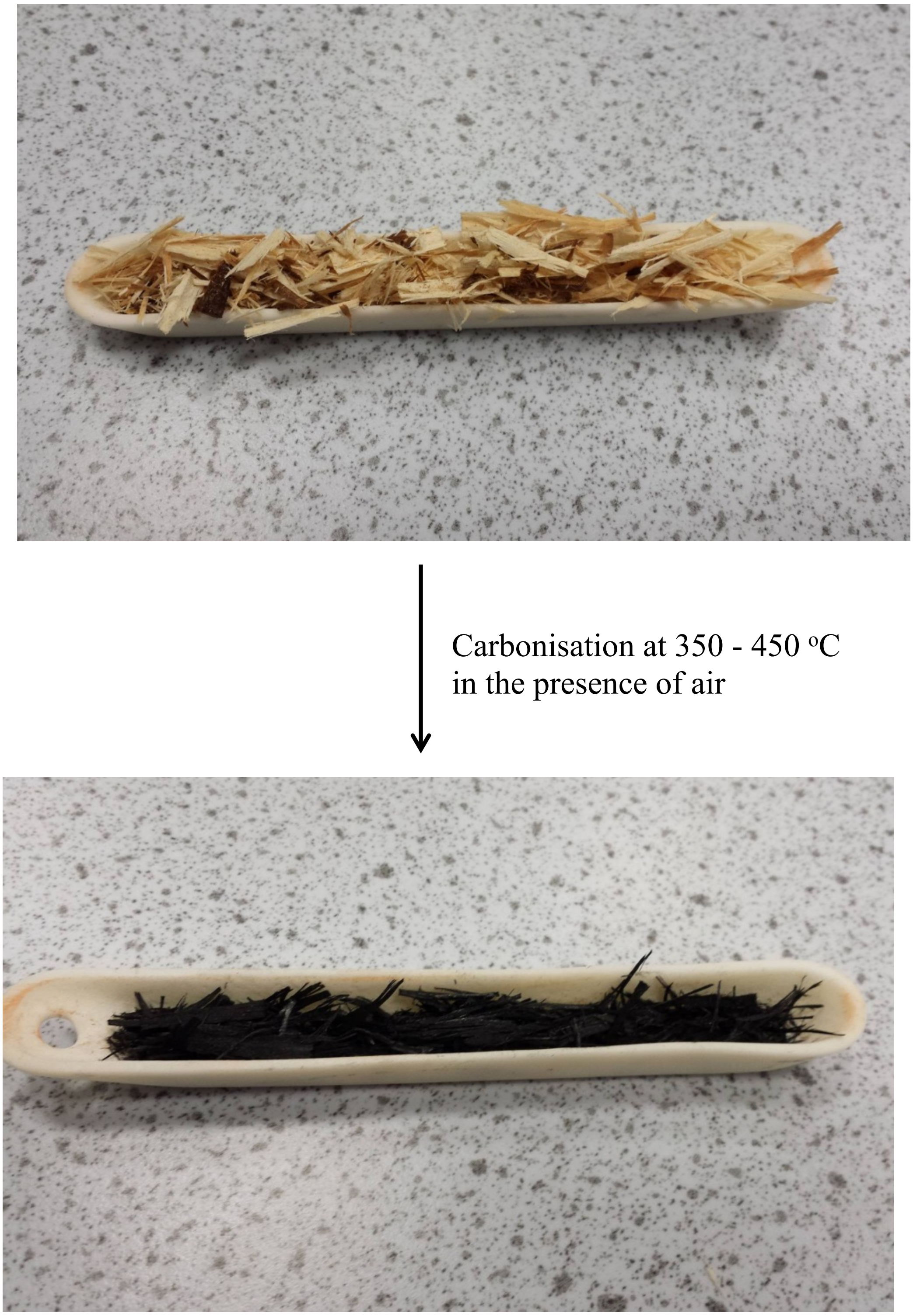
Supporting Figure S10. Nitrogen sorption isotherms and pore size distribution curves of activated CNL1-2800 carbon compared to analogous activated carbons derived from lignin (LAC4800), grass (ACGR4800), carbon nanotube superstructures (CN4800) or polypyrrole (Py4800) under similar activation conditions (i.e., 800 °C and KOH/carbon ratio of 4).



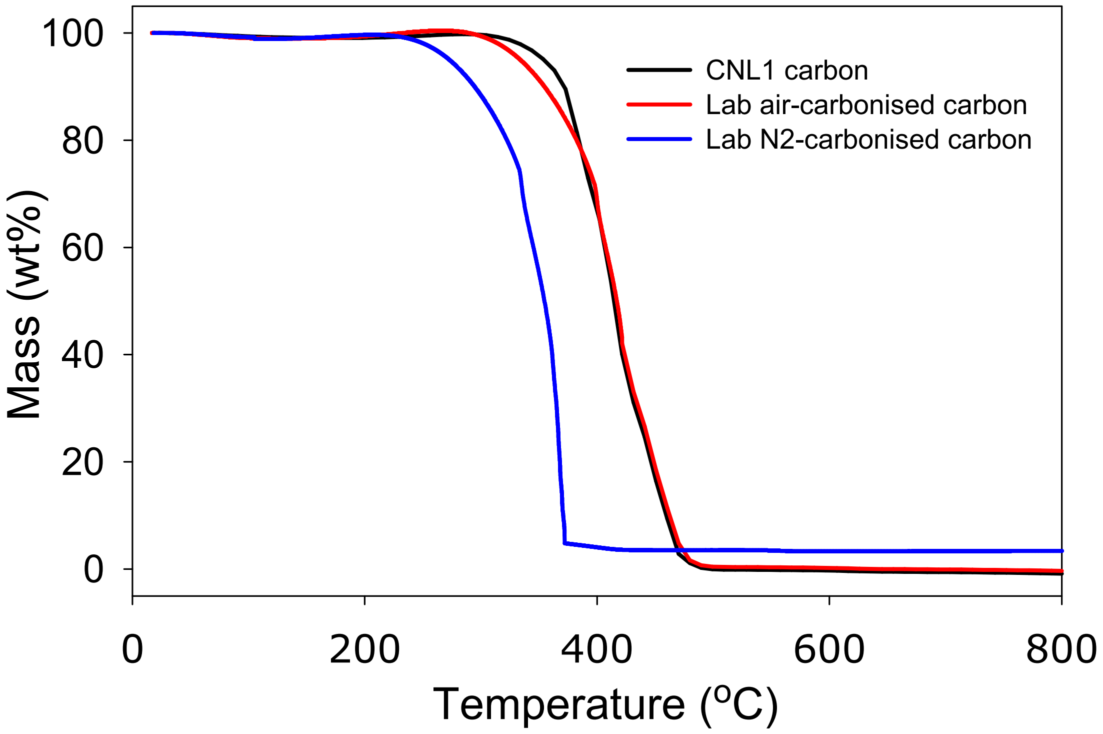
Supporting Figure S11. A plot of total surface area as a function of activation temperature for activated carbons derived from CNL1 carbon and other precursors at KOH/carbon ratio of; (A) 2 and (B) 4.



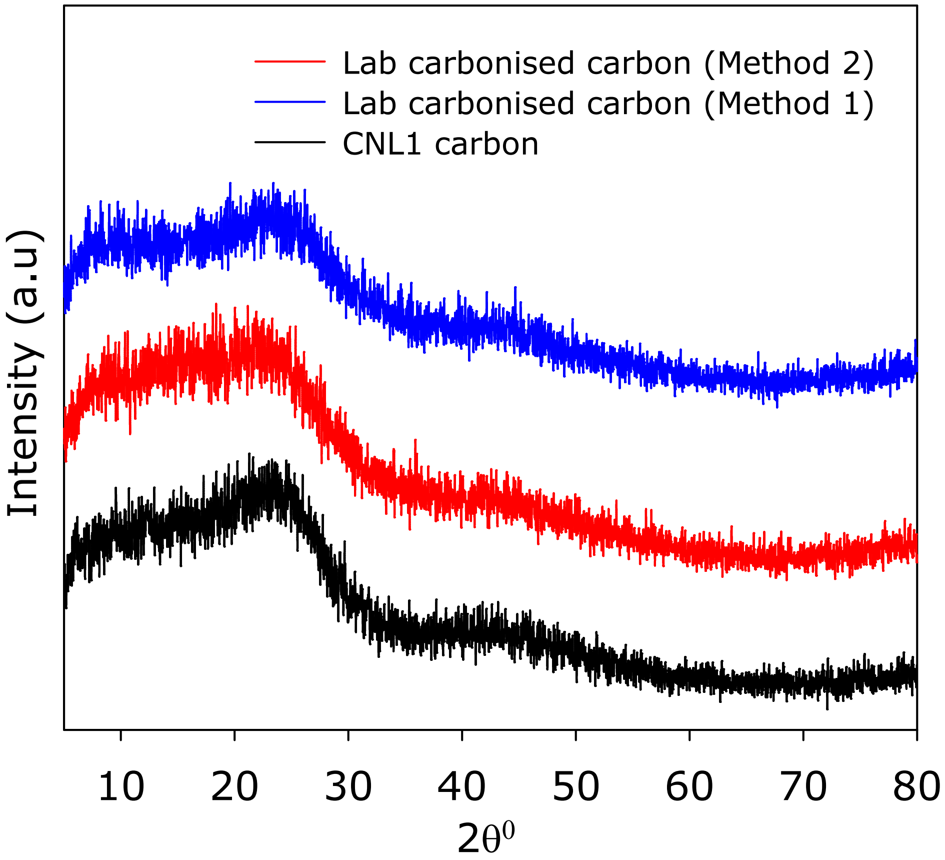
Supporting Figure S12. A plot of total pore volume as a function of activation temperature for activated carbons derived from CNL1 carbon and other precursors at KOH/carbon ratio of; (A) 2 and (B) 4.



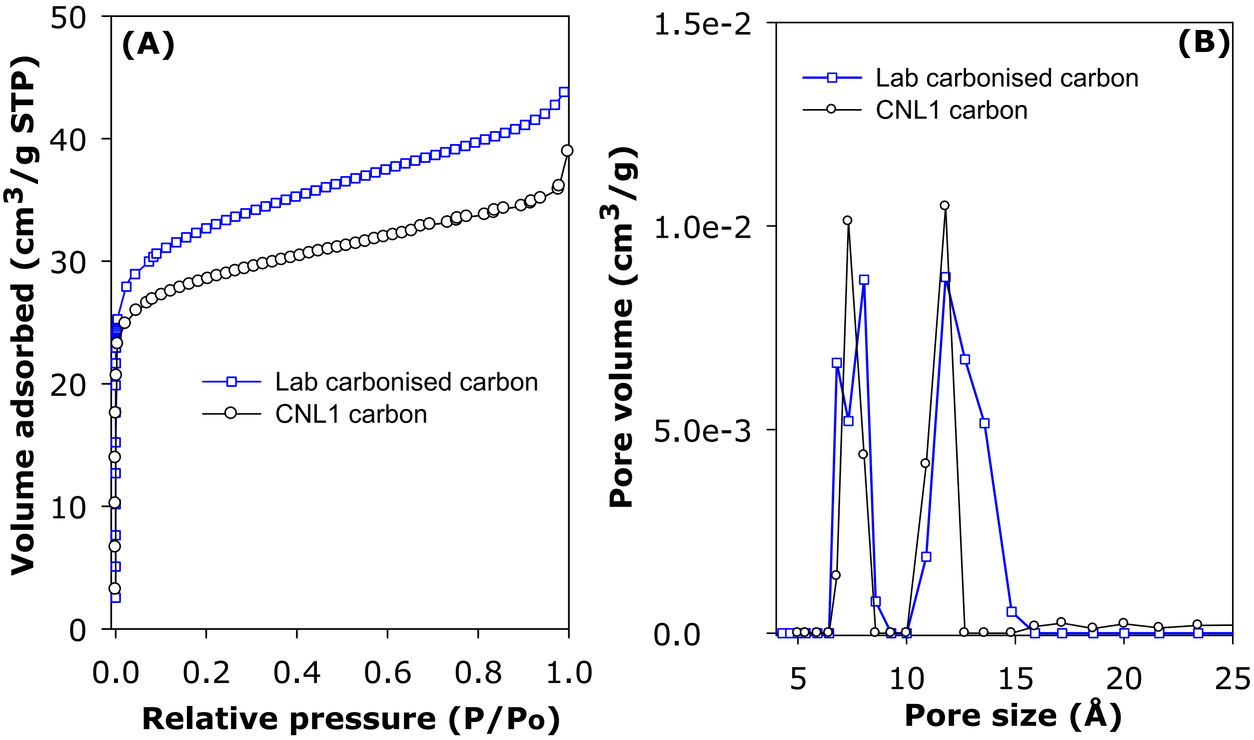
Supporting Figure S13. Photographic images of biomass (wood chippings) before (top) and after (bottom) carbonisation in the presence of air.



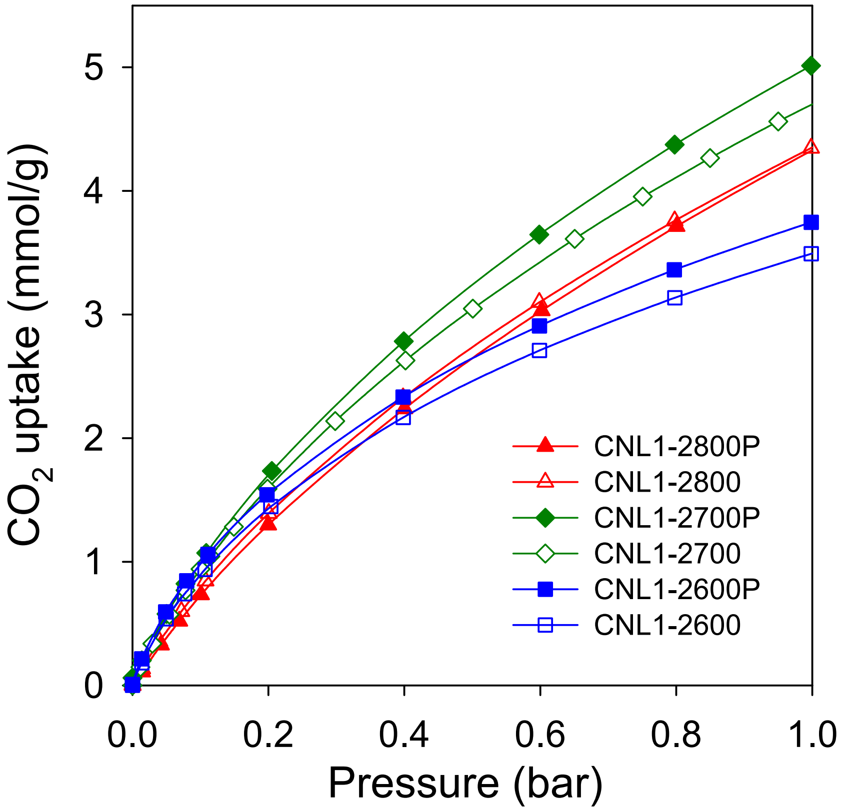
Supporting Figure S14. Thermogravimetric analysis (TGA) curve of CNL1 carbon, and lab-based carbon from pyrolysis (carbonisation) of wood chippings under air (lab air-carbonised carbon) or N_2 (lab N2-carbonised carbon).



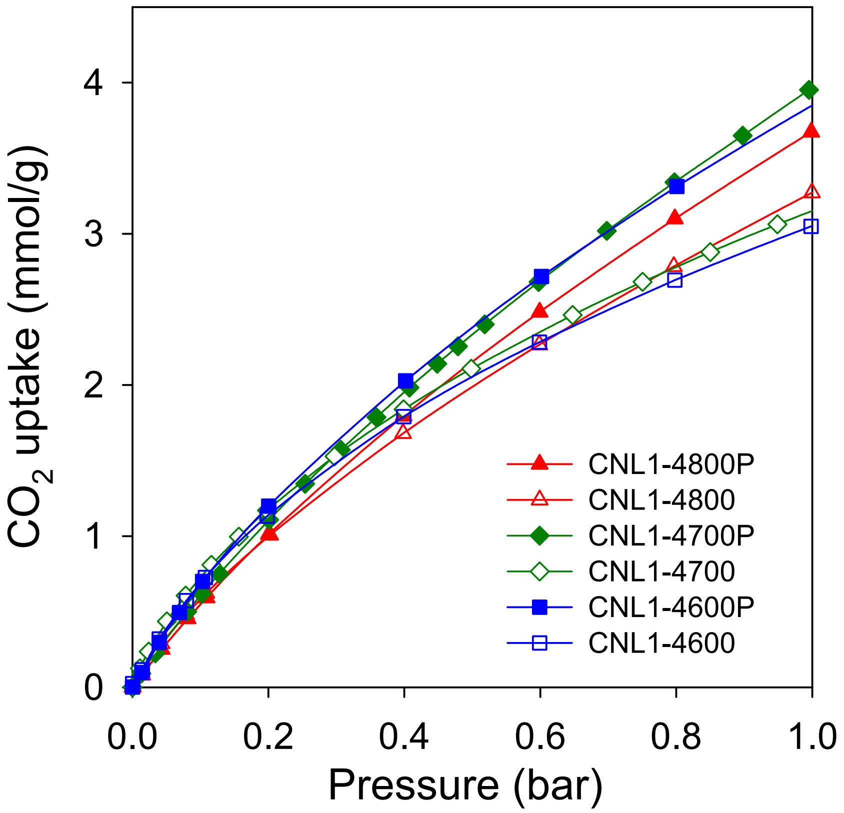
Supporting Figure S15. Powder XRD patterns of CNL1 carbon, and lab-based carbon from pyrolysis (carbonisation) of wood chippings under air containing atmosphere. See above for description of method 1 and 2.



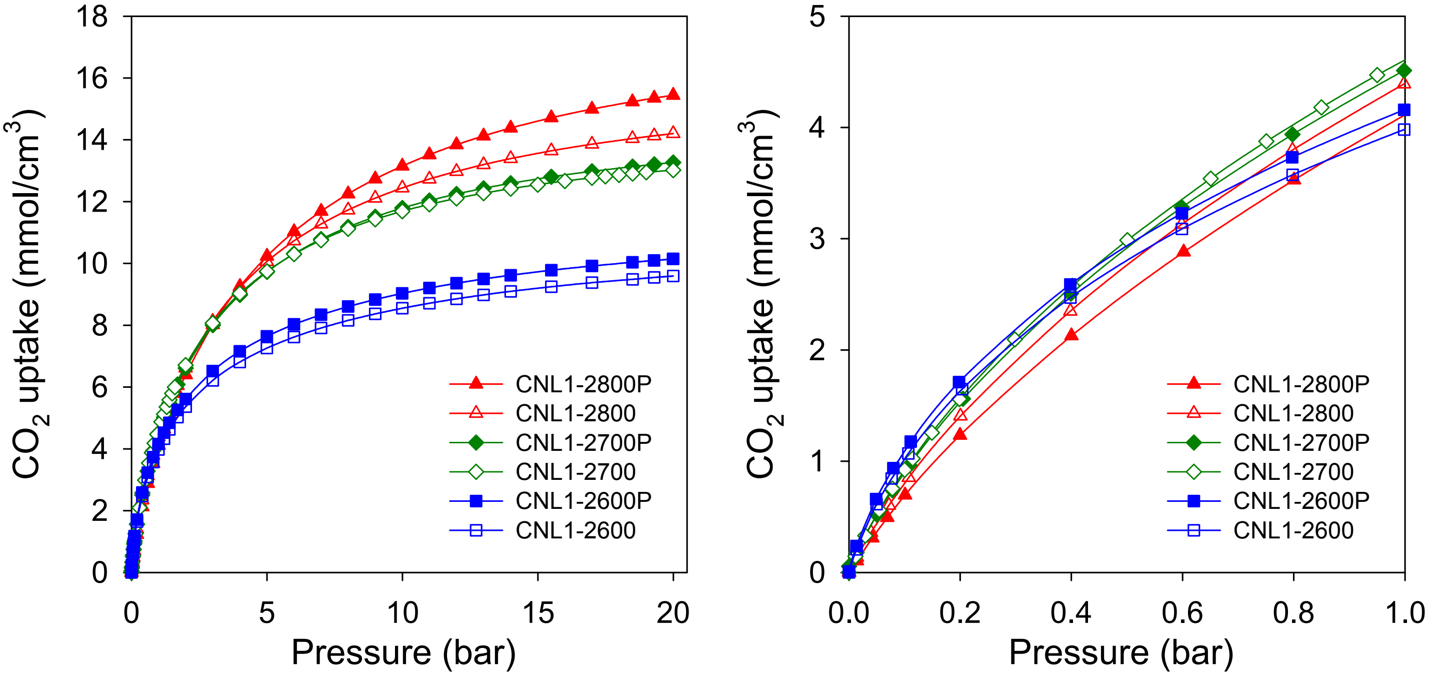
Supporting Figure S16. Nitrogen sorption isotherms (A) and pore size distribution curves (B) of CNL1 carbon and lab-based carbon from pyrolysis (carbonisation) of wood chippings under air containing atmosphere.



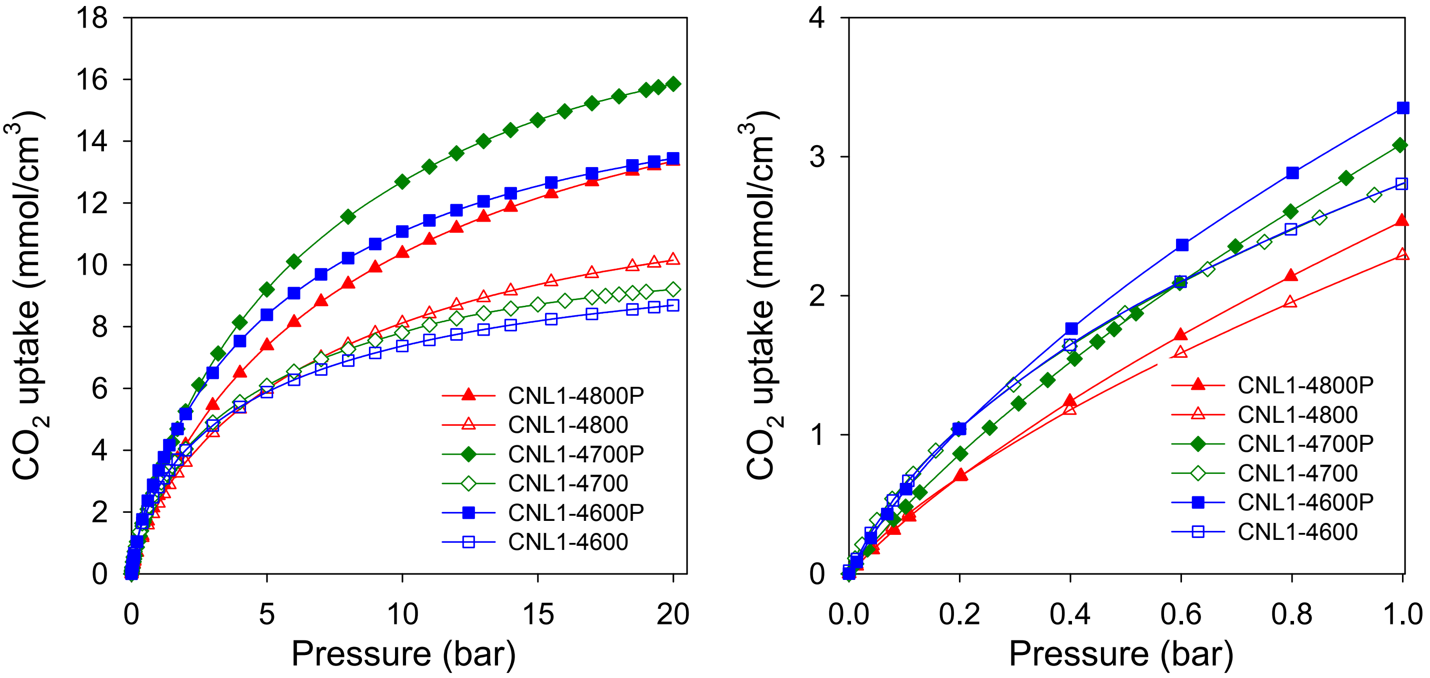
Supporting Figure S17. CO$_2$ uptake isotherms at 25 ^{o}C and 0 - 1 bar for activated CNL1-2T carbons.



Supporting Figure S18. CO$_2$ uptake isotherms at 25 ^{o}C and 0 - 1 bar for activated CNL1-4T carbons.



Supporting Figure S19. Volumetric CO$_2$ uptake isotherms at 25 °C and 0 – 20 bar (left panel) and 0 – 1 bar (right panel) for activated CNL1-2T carbons.



Supporting Figure S20. Volumetric CO_2 uptake isotherms at 25 °C and 0 – 20 bar (left panel) and 0 – 1 bar (right panel) for activated CNL1-4T carbons.