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

Supporting Information

A simple flash carbonization route for conversion of biomass to porous carbons with high CO_2 storage capacity

Edward Hirst, Alison Taylor, and Robert Mokaya*

School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, U. K.

*Corresponding author. E-mail: r.mokaya@nottingham.ac.uk (R. Mokaya)

Table S1. Elemental composition of air-carbonised sawdust-derived carbon (ACSD) and activated carbons derived from the ACSD compared to sawdust-derived hydrochar (SD hydrochar) and activated carbons from the SD hydrochar ([a] Atomic ratio).

Sample	C [%]	H [%]	O [%]	(O/C)[a]	(H/C)[a]
ACSD	72.4	3.2	24.2	0.251	0.530
SD Hydrochar	57.4	5.6	37.0	0.483	1.171
ACSD-2600	77.5	1.9	19.7	0.191	0.294
SD2600	72.3	0.7	27.0	0.280	0.116
ACSD-2700	83.4	0.9	15.7	0.141	0.129
SD2700	72.4	0.3	28.3	0.293	0.049
ACSD-2800	88.1	0.4	11.5	0.098	0.055
SD2800	85.2	0.1	14.8	0.130	0.014
ACSD-4800	88.7	0.4	10.9	0.092	0.054
SD4800	89.7	0.1	10.3	0.086	0.013

Table S2. The ratio of peak intensity of the D-peak to G-peak (I_D/I_G) of activated carbons derived from either air-carbonised sawdust (ACSD-xT) or sawdust hydrochar (SDxT).

Sample	I_D/I_G
ACSD-2600	0.86
SD2600	0.79
ACSD-2700	0.91
SD2700	0.81
ACSD-2800	0.93
SD2800	0.84
ACSD-4800	0.94
SD4800	0.86

Table S3. A comparison of textural properties and CO_2 uptake of activated carbons derived from either air-carbonised sawdust (ACSD-xT) or sawdust hydrochar (SDxT).

Sample	Surface area[a] (m^2 g^{-1})	Pore volume[b] (cm^3 g^{-1})	Pore size[c] (Å)	CO_2 uptake[d] (mmol g^{-1})		
				0.15 bar	1 bar	20 bar
ACSD-2600	1511 (1338)	0.65 (0.54)	8.5	1.2	4.3	12.0
SD2600	1202 (1133)	0.65 (0.49)	5/7/9	1.3	4.4	9.7
ACSD-2700	1830 (1657)	0.78 (0.67)	8.5/13	1.1	4.9	14.0
SD2700	1557 (1294)	0.75 (0.53)	6/8/12	1.3	4.6	12.1
ACSD-2800	2150 (1861)	0.91 (0.74)	9/13	1.1	4.7	16.8
SD2800	2377 (1512)	1.40 (0.70)	7/12/25	0.8	3.6	18.1
ACSD-4800	2610 (1892)	1.15 (0.74)	6/8/10/16	0.9	4.0	19.7
SD4800	2783 (694)	1.80 (0.36)	8/12/30	0.6	3.0	21.7

The values in the parenthesis refer to: [a]micropore surface area and [b]micropore volume. [c]Pore size distribution maxima obtained from NLDFT analysis. [e]CO_2 uptake at 25 ^oC and various pressures (i.e., 0.15 bar, 1 bar and 20 bar).

Table S4. A comparison of textural properties and CO_2 uptake of activated carbons derived from either air-carbonised sawdust (ACSD-xT) or CNL1 carbon (CNL1-xT).

Sample	Surface area[a] (m^2 g^{-1})	Pore volume[b] (cm^3 g^{-1})	Pore size[c] (Å)	CO_2 uptake[d] (mmol g^{-1})		
				0.15 bar	1 bar	20 bar
AC sawdust	127 (87)	0.06 (0.039)	5.5/7/12			
CNL1 carbon	100 (79)	0.06 (0.035)	7/12			
ACSD-2600	1511 (1338)	0.65 (0.54)	8.5	1.2	4.3	12.0
CNL1-2600	1190 (1107)	0.55 (0.49)	5.5/7/9	1.2	3.5	8.4
ACSD-2700	1830 (1657)	0.78 (0.67)	8.5/13	1.1	4.9	14.0
CNL1-2700	1399 (1343)	0.63 (0.59)	6/8.5/12	1.3	4.8	13.4
ACSD-2800	2150 (1861)	0.91 (0.74)	9/13	1.1	4.7	16.8
CNL1-2800	1326 (1263)	0.60 (0.55)	6/8.5/13	1.0	4.3	14.1
ACSD-4800	2610 (1892)	1.15 (0.74)	6/8/10/16	0.9	4.0	19.7
CNL1-4800	2487 (2296)	1.16 (1.01)	6.5/8.5/16	0.8	3.7	19.4

The values in the parenthesis refer to: [a]micropore surface area and [b]micropore volume. [c]Pore size distribution maxima obtained from NLDFT analysis. [d]CO_2 uptake at 25 ^oC and various pressures (i.e., 0.15 bar, 1 bar and 20 bar).

Table S5. Textural properties of flash carbonised activated ACSD-xT carbons derived from sawdust at activation temperature of 800 ^{o}C and KOH/carbon ratio of 2 or 4 compared to activated carbons from CNL1 carbon (CNL1), 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)
ACSD-2800	2150 (1861)	0.91 (0.74)	9/13
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
ACDS-4800	2610 (1892)	1.15 (0.74)	6/8/10/16
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.

CNL1 data from ref. 40; E. Haffner-Staton, N. Balahmar and R. Mokaya, *J. Mater. Chem. A* 2016, **4**, 13324.

LAC data from ref. 12; W. Sangchoom and R. Mokaya, *ACS Sust. Chem. Eng*., 2015, **3**, 1658.

ACGR data from ref. 713; H. M. Coromina, D. A. Walsh and R. Mokaya, *J. Mater. Chem. A*, 2016, **4**, 280.

CN data from ref. 50; B. Adeniran and R. Mokaya, *J. Mater. Chem. A*, 2015, **3**, 5148.

Py data from ref. 46; M. Sevilla, R. Mokaya and A. B. Fuertes, *Energy Environ. Sci.*, 2011, **4**, 2930.

Table S6. Evaluation of the reproducibility of the textural properties of ACSD-xT activated carbons derived from air-carbonised sawdust.

Sample	Surface area[a] (m^2 g^{-1})	Pore volume[b] (cm^3 g^{-1})
ACSD-2700	1830 (1657)	0.78 (0.67)
ACSD-2700*	1715 (1658)	0.77 (0.72)
ACSD-2800	2150 (1861)	0.91 (0.74)
ACSD-2800*	2163 (1866)	0.93 (0.74)

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 working capacity for pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) of CO_2 on sawdust-derived activated ACSD-xT carbons, compared to activated carbons from sawdust via hydrothermal carbonisation (SDxT), or CNL1 carbon (CNL1-xT) at 25 ^oC for a pure CO_2 gas stream and a 20% partial CO_2 pressure flue gas.

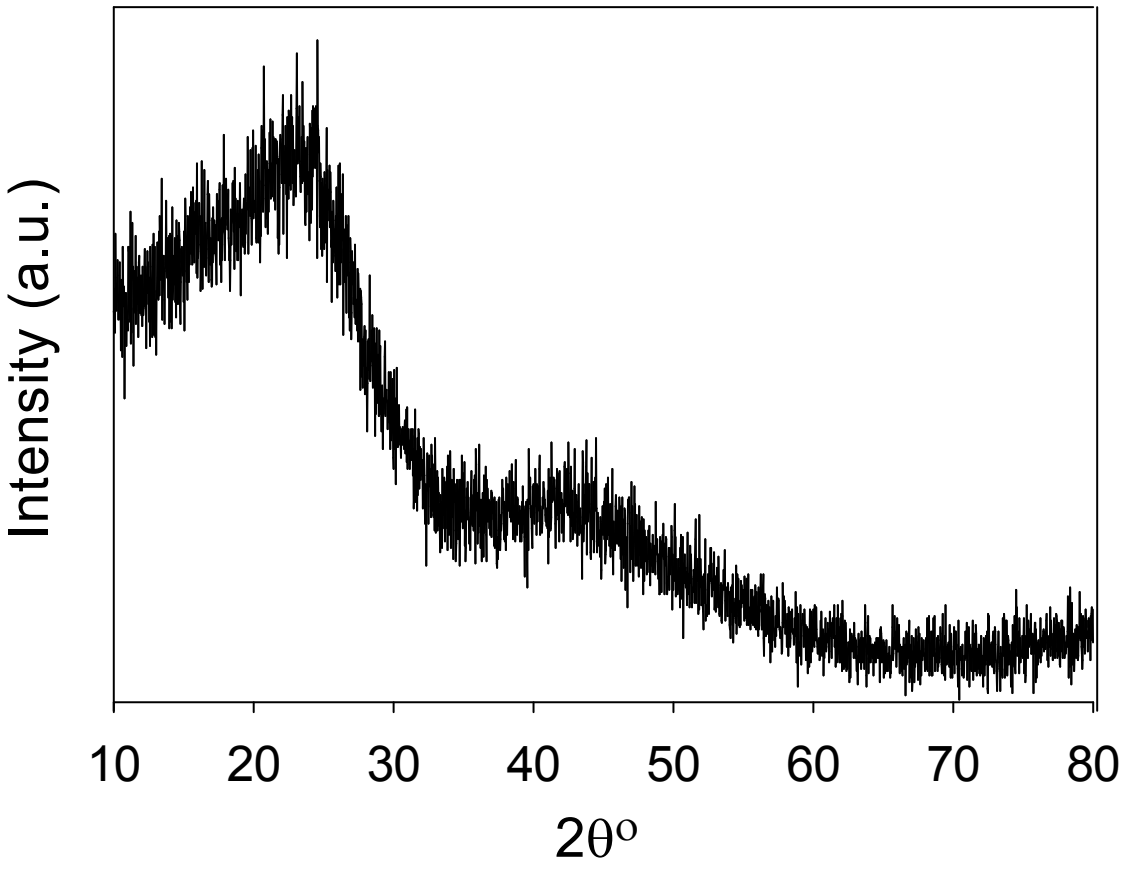
Sample	Pure CO_2 uptake[a] (mmol g^{-1})		Flue gas CO_2 uptake[b] (mmol g^{-1})	
	PSA	VSA	PSA	VSA
ACSD-2600	5.2	4.8	3.4	2.0
SD2600	3.7	4.5	3.1	2.0
CNL1-2600	3.2	3.7	2.4	1.7
ACSD-2700	6.1	5.3	3.7	2.1
SD2700	5.3	5.2	3.5	1.7
CNL1-2700	5.7	5.4	3.7	2.0
ACSD-2800	7.5	5.6	3.8	1.7
SD2800	7.4	4.5	3.0	1.3
CNL1-2800	6.3	5.2	3.5	1.8
ACSD-4800	8.3	5.0	5.3	1.5
SD4800	7.9	3.8	2.6	1.0
CNL1-4800	6.1	4.0	2.7	1.3

[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. Data for CNL1-xT samples is from reference 40.

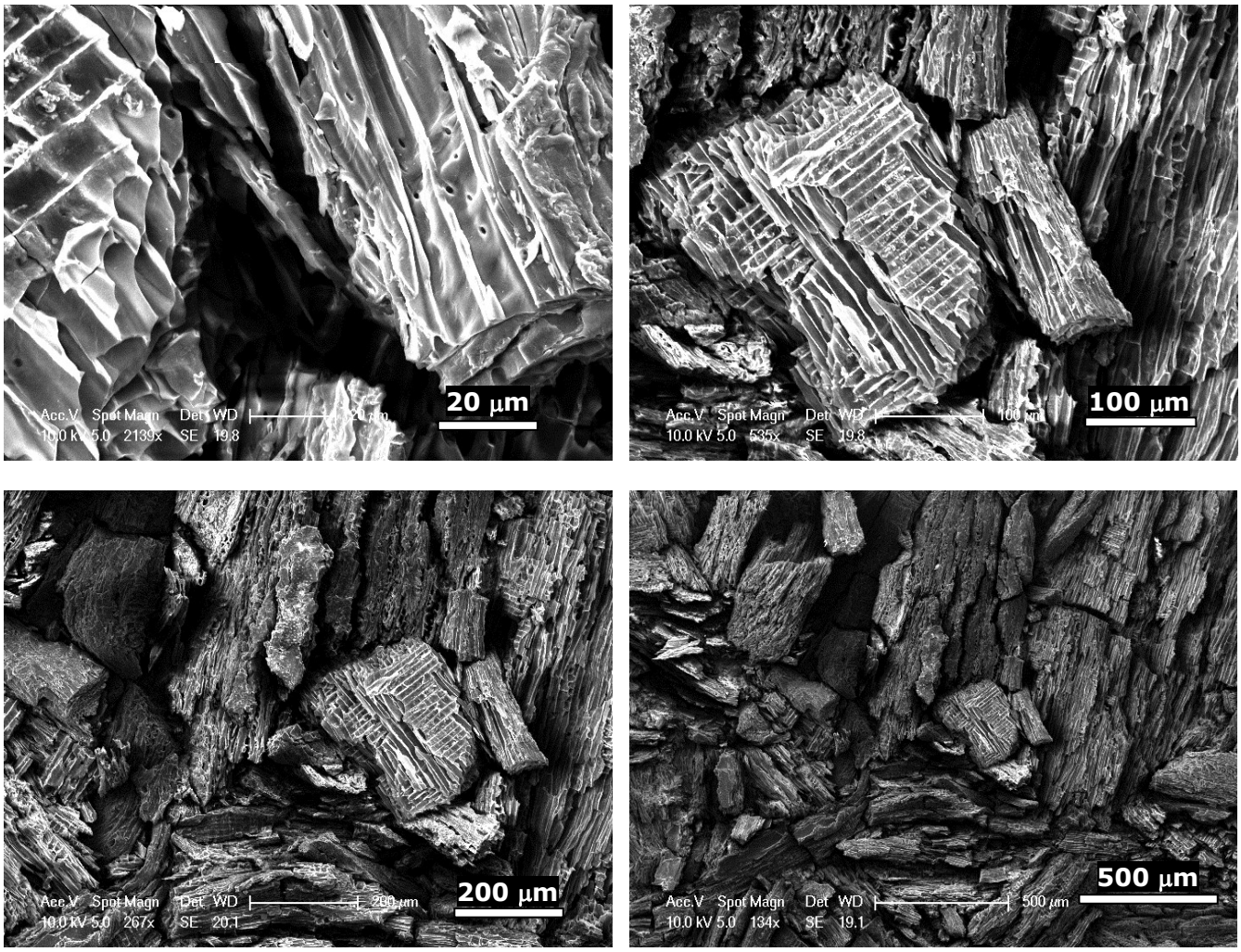
Table S8. Gravimetric and volumetric working capacity for pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) of CO_2 on ACSD-xT carbons compared to activated CNL1 carbons, and benchmark porous materials at 25 ^oC for a pure CO_2 gas stream and a 20% partial CO_2 pressure flue gas. The values in parentheses are volumetric uptake (in g l^{-1}).

Sample	Pure CO_2 uptake[a] (mmol g^{-1})		Flue gas CO_2 uptake[b] (mmol g^{-1})	
	PSA	VSA	PSA	VSA
ACSD-2600	5.2 (206)	4.8 (190)	3.4 (135)	2.0 (79)
CNL1-2600	3.2 (161)	3.7 (186)	2.4 (120)	1.7 (85)
ACSD-2700	6.1 (217)	5.3 (189)	3.7 (132)	2.1 (75)
CNL1-2700	5.7 (246)	5.4 (233)	3.7 (160)	2.0 (86)
ACSD-2800	7.5 (241)	5.6 (180)	3.8 (122)	1.7 (55)
CNL1-2800	6.3 (280)	5.2 (231)	3.5 (156)	1.8 (80)
ACSD-4800	8.3 (226)	5.0 (136)	5.3 (145)	1.5 (41)
CNL1-4800	6.1 (189)	4.0 (123)	2.7 (83)	1.3 (40)
HKUST-1[c]	7.8 (147)	6.4 (121)	4.5 (85)	1.6 (30)
Mg-MOF-74[d]	3.5 (63)	3.9 (70)	2.1 (38)	4.1 (74)
NaX[e]	1.6 (44)	2.8 (78)	1.8 (50)	2.5 (69)

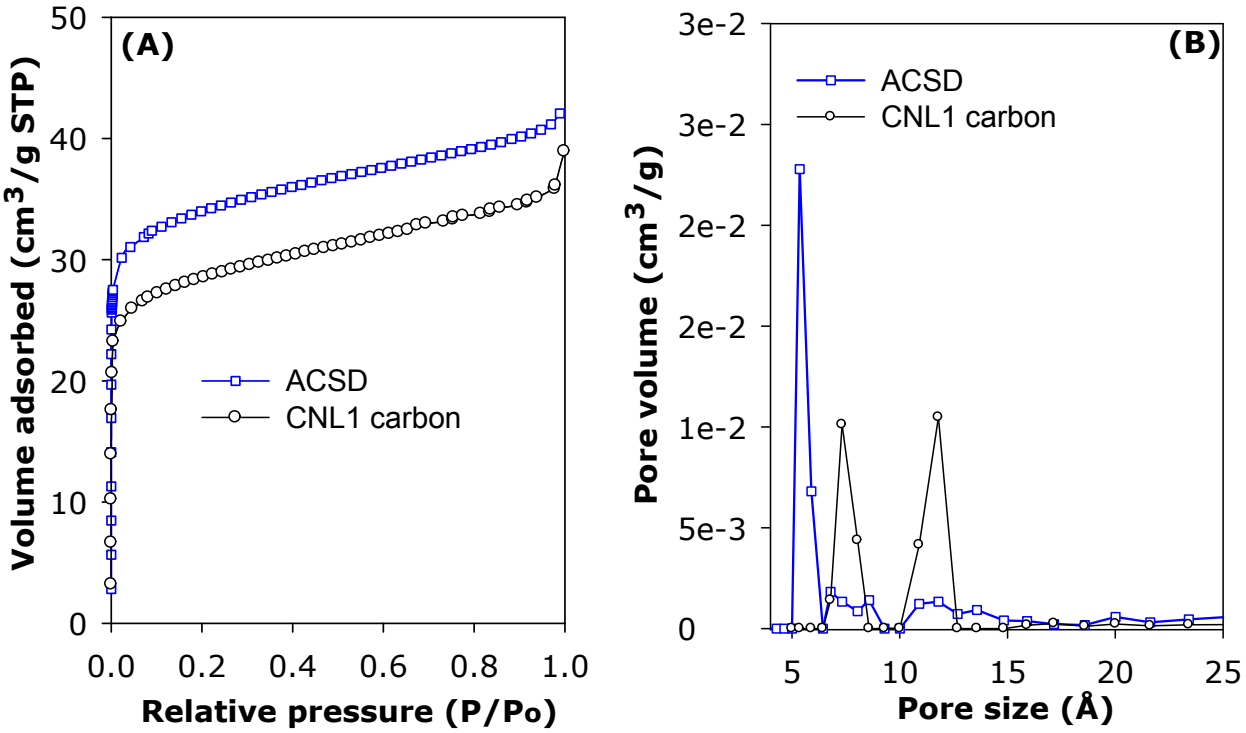
[a]1 bar to 6 bar for PSA; 0.05 bar to 1.5 bar for VSA. [b]0.2 bar to 1.2 bar for PSA; 0.01 bar to 0.3 bar for VSA. [c]Data from reference 78. [e]Data from reference 79. Data for CNL1-xT samples is from reference 40.



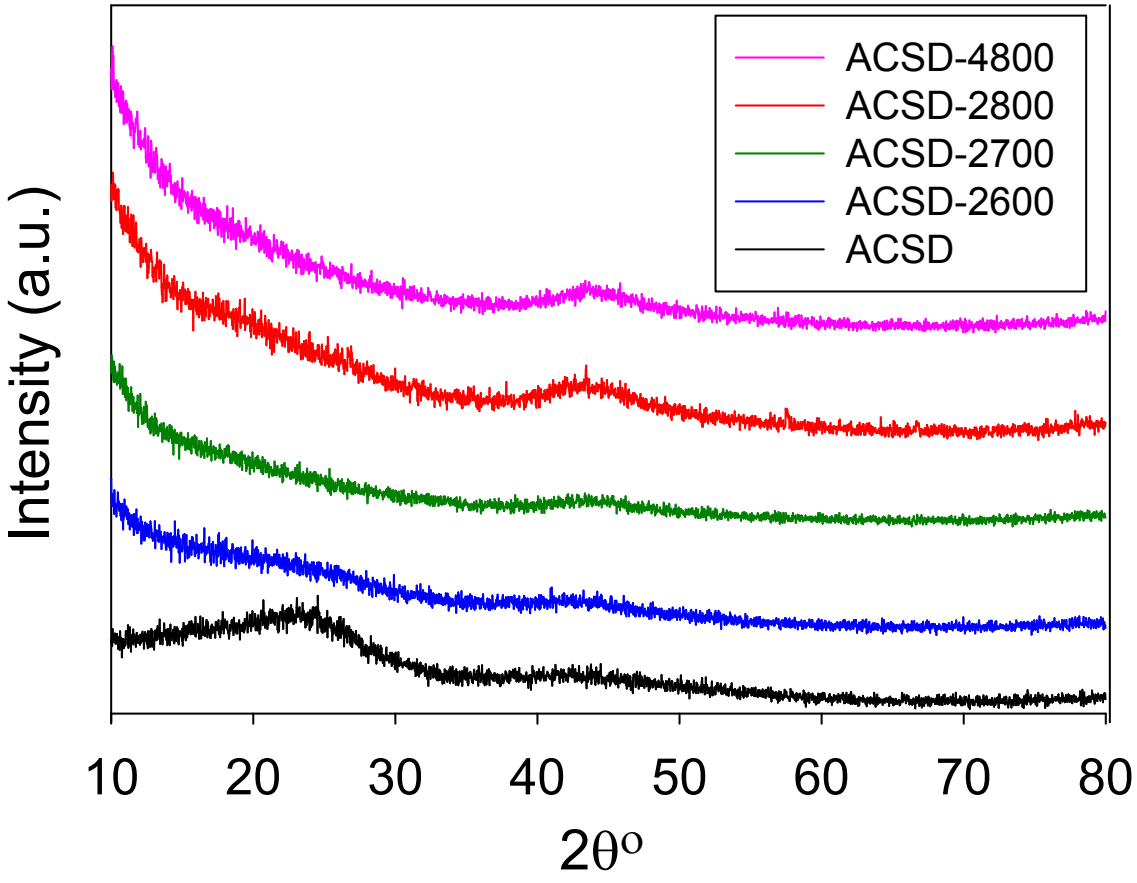
Supporting Figure S1. Powder XRD pattern of ACSD carbon.



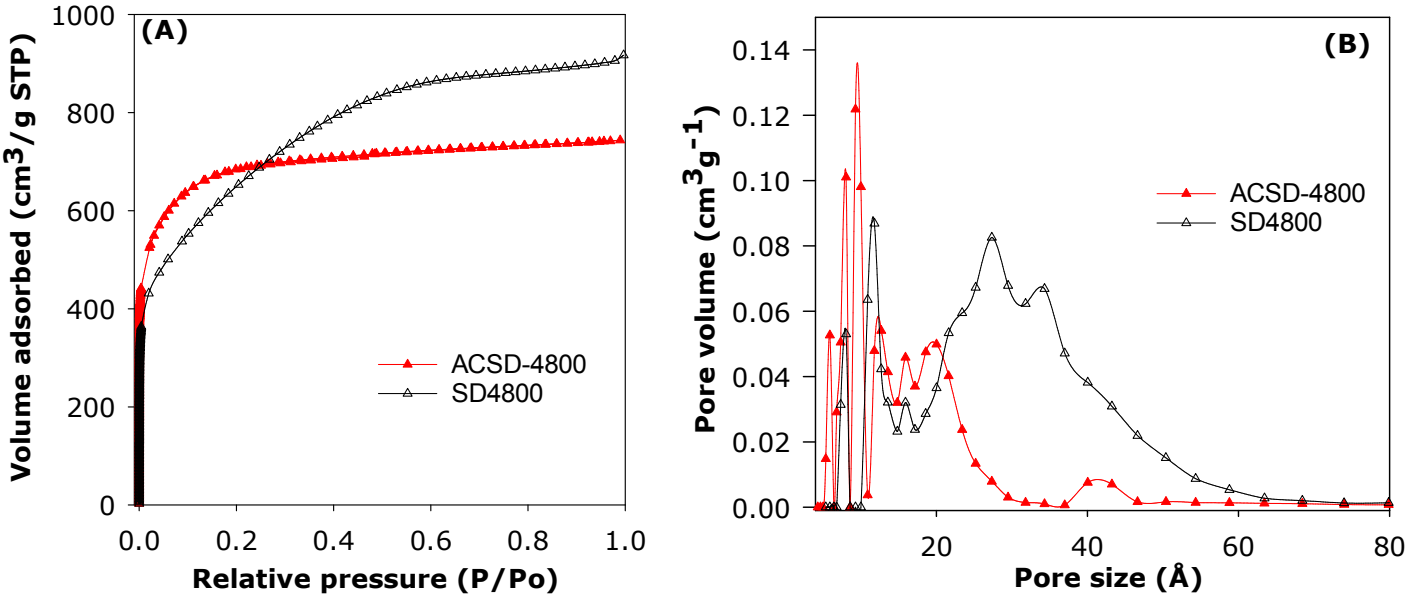
Supporting Figure S2. SEM images of ACSD carbon.



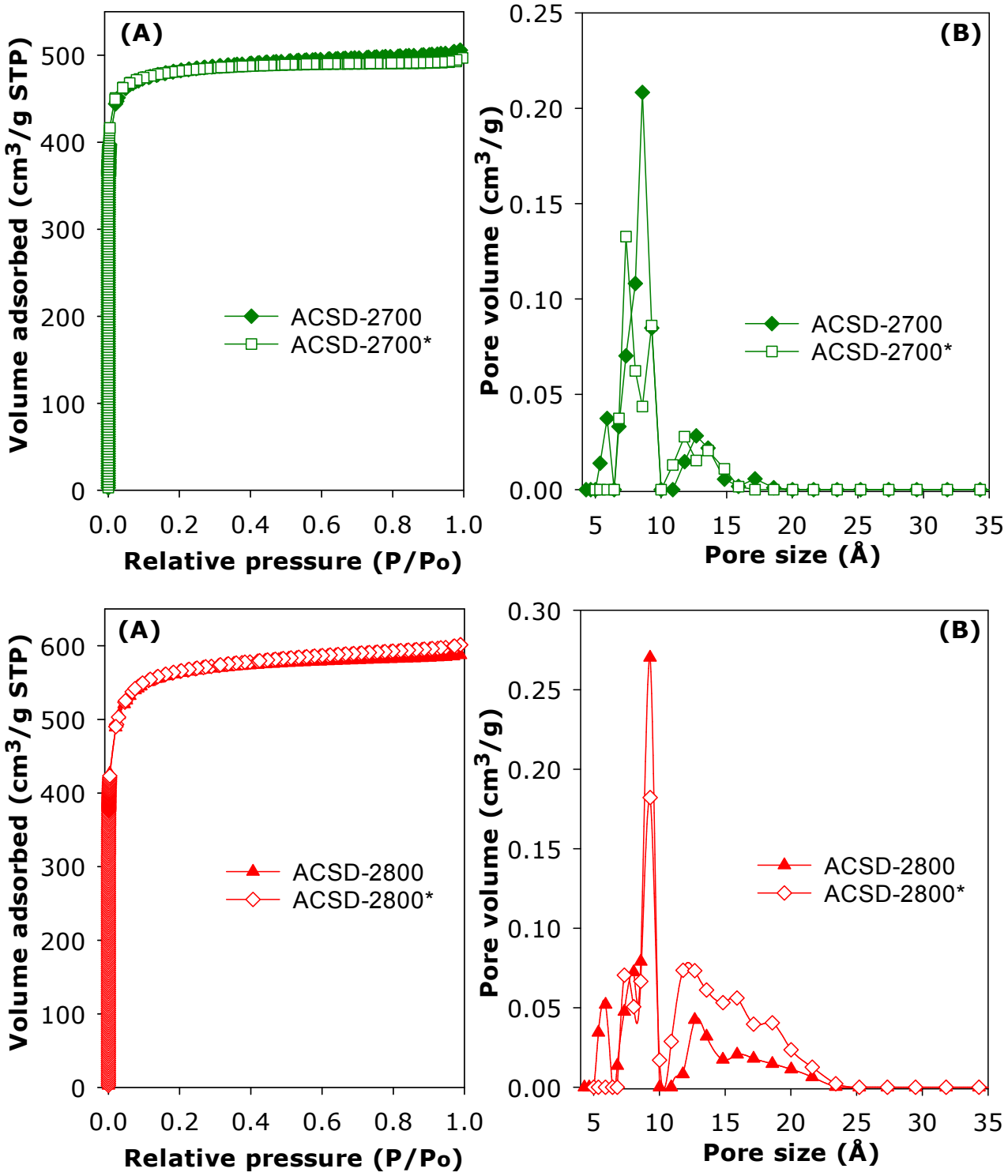
Supporting Figure S3. Nitrogen sorption isotherm (A) and pore size distribution curve (B) of ACSD carbon. We have compared the porosity of the ACSD carbon with that of so-called CNL1 carbon. Data for CNL1 carbon was obtained from reference 40 (E. Haffner-Staton, N. Balahmar and R. Mokaya, *J. Mater. Chem. A* 2016, **4**, 13324). Y-axis in (B) shows incremental pore volume.



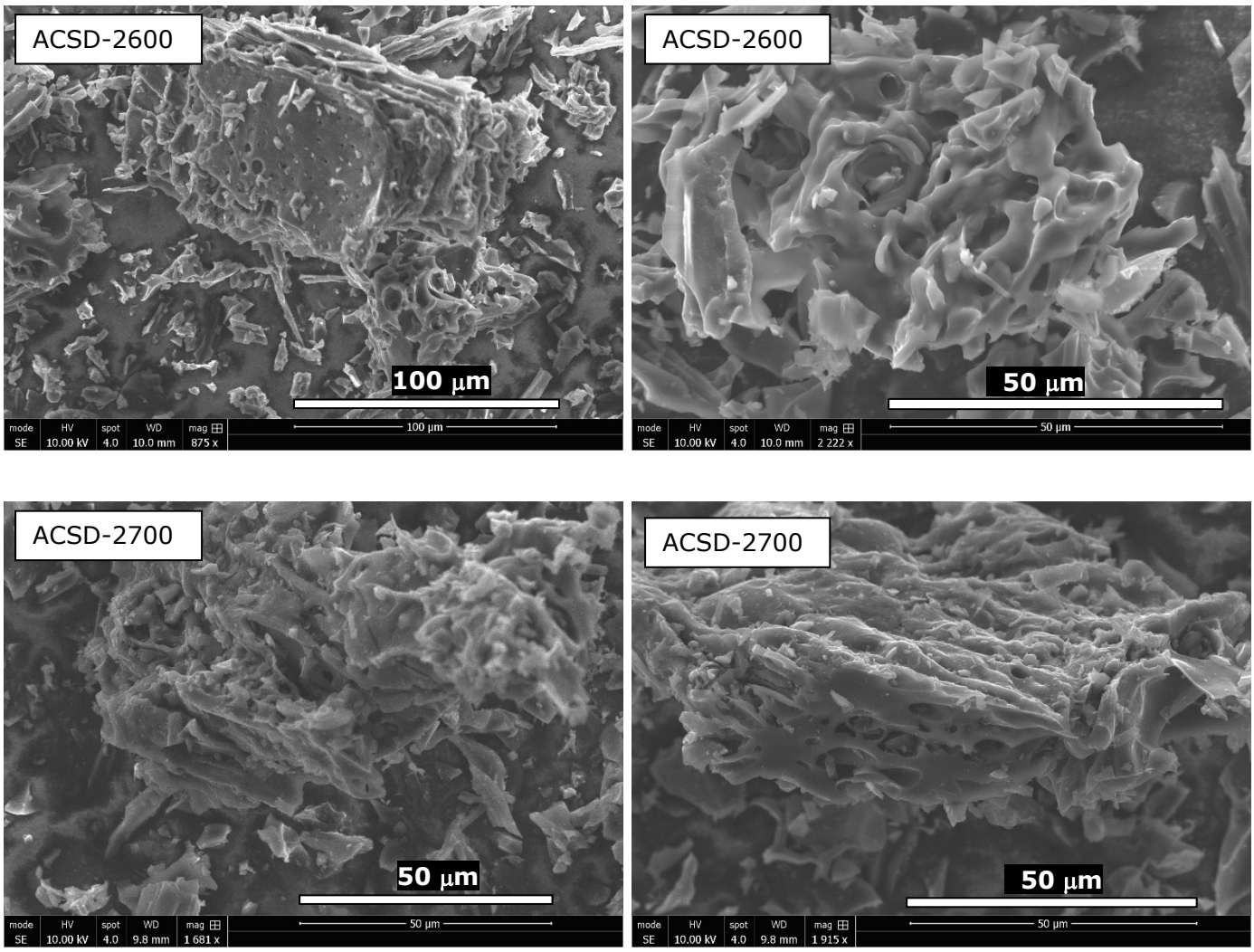
Supporting Figure S4. Powder XRD pattern of ACSD carbon, and activated ACSD-xT carbons.



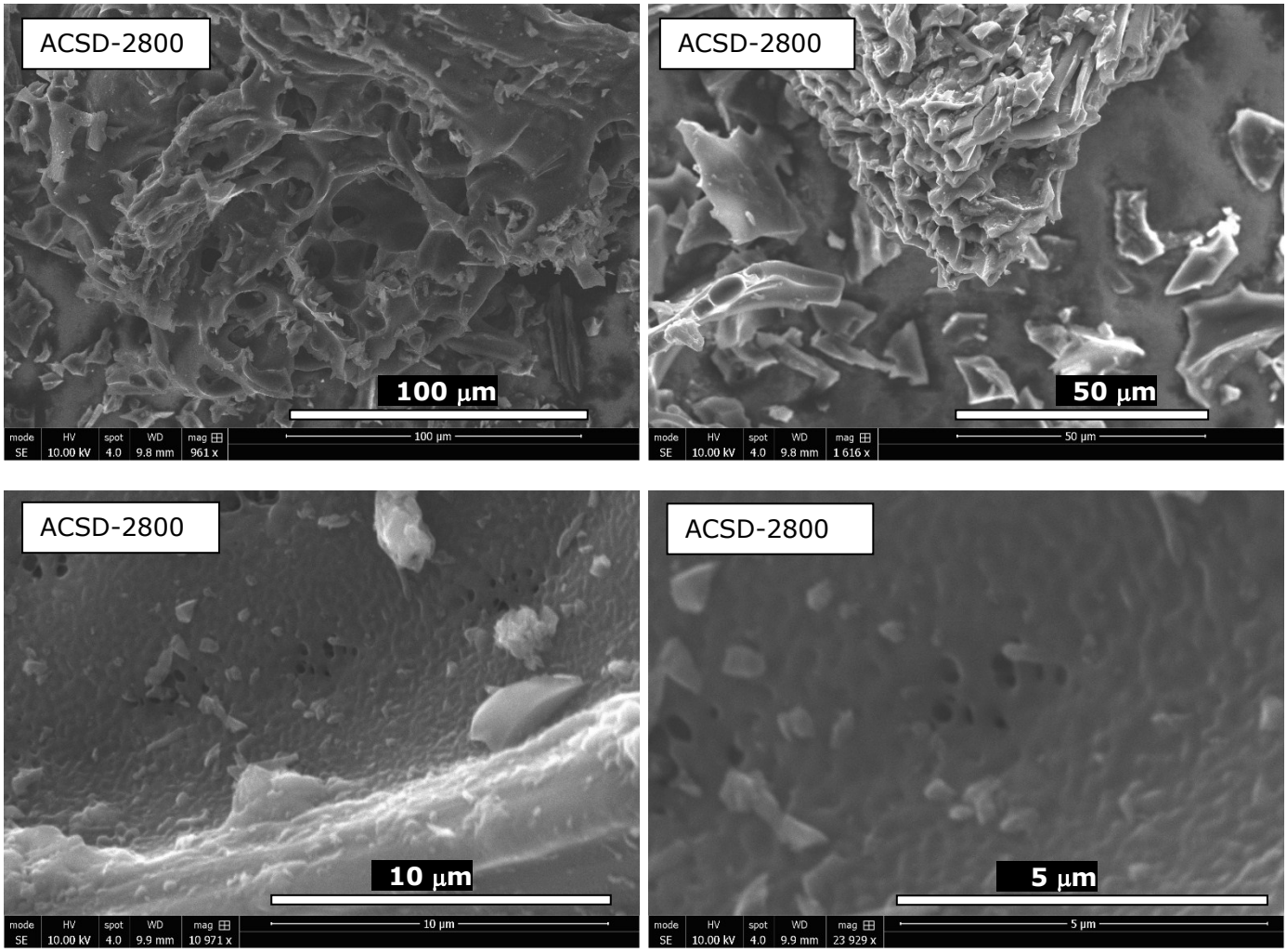
Supporting Figure S5. Comparison of (A) Nitrogen sorption isotherms and (B) pore size distribution (PSD) curves of sawdust-derived activated carbons prepared at KOH/carbon ratio of 4 and 800 °C via flash carbonization (ACSD-4800) or hydrothermal carbonisation (SD4800. Y-axis in (B) shows incremental pore volume.



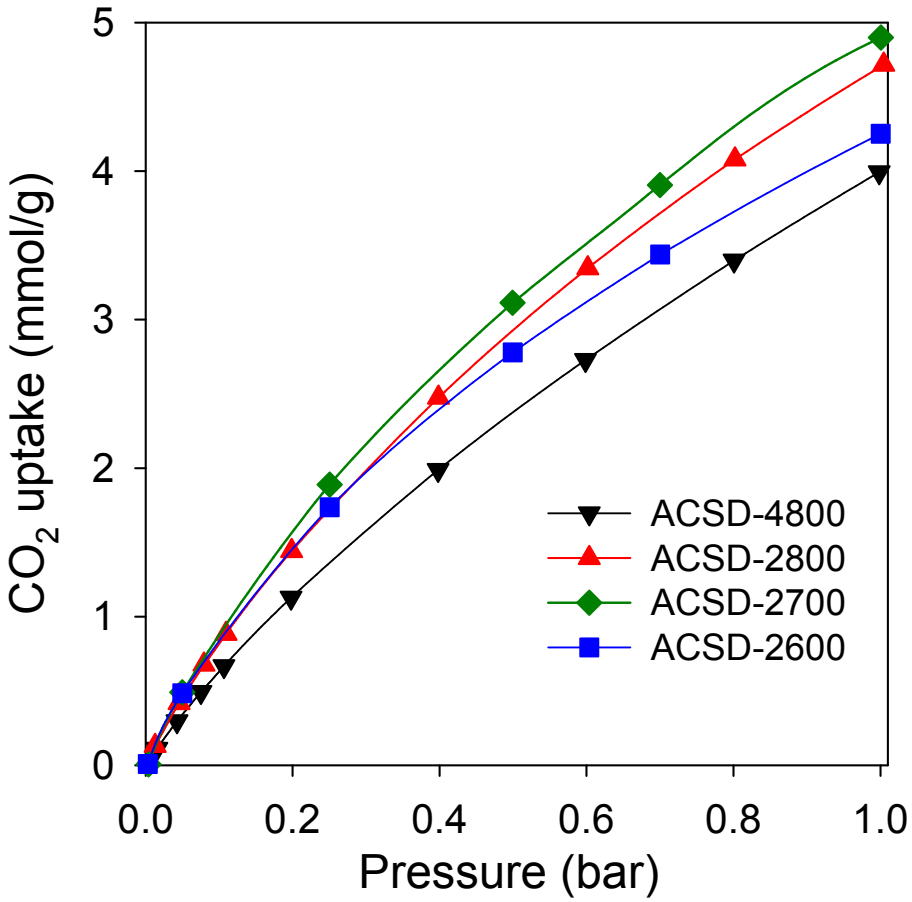
Supporting Figure S6. Comparison of (A) Nitrogen sorption isotherms and (B) pore size distribution (PSD) curves of flash carbonized activated ACSD-xT carbons from two separate preparations. Samples with an asterisk (i.e., ACSD-2700* and ACSD-2800* were prepared months later. The agreement in isotherms and PSD curves shows remarkable reproducibility. Y-axis in (B) shows incremental pore volume.



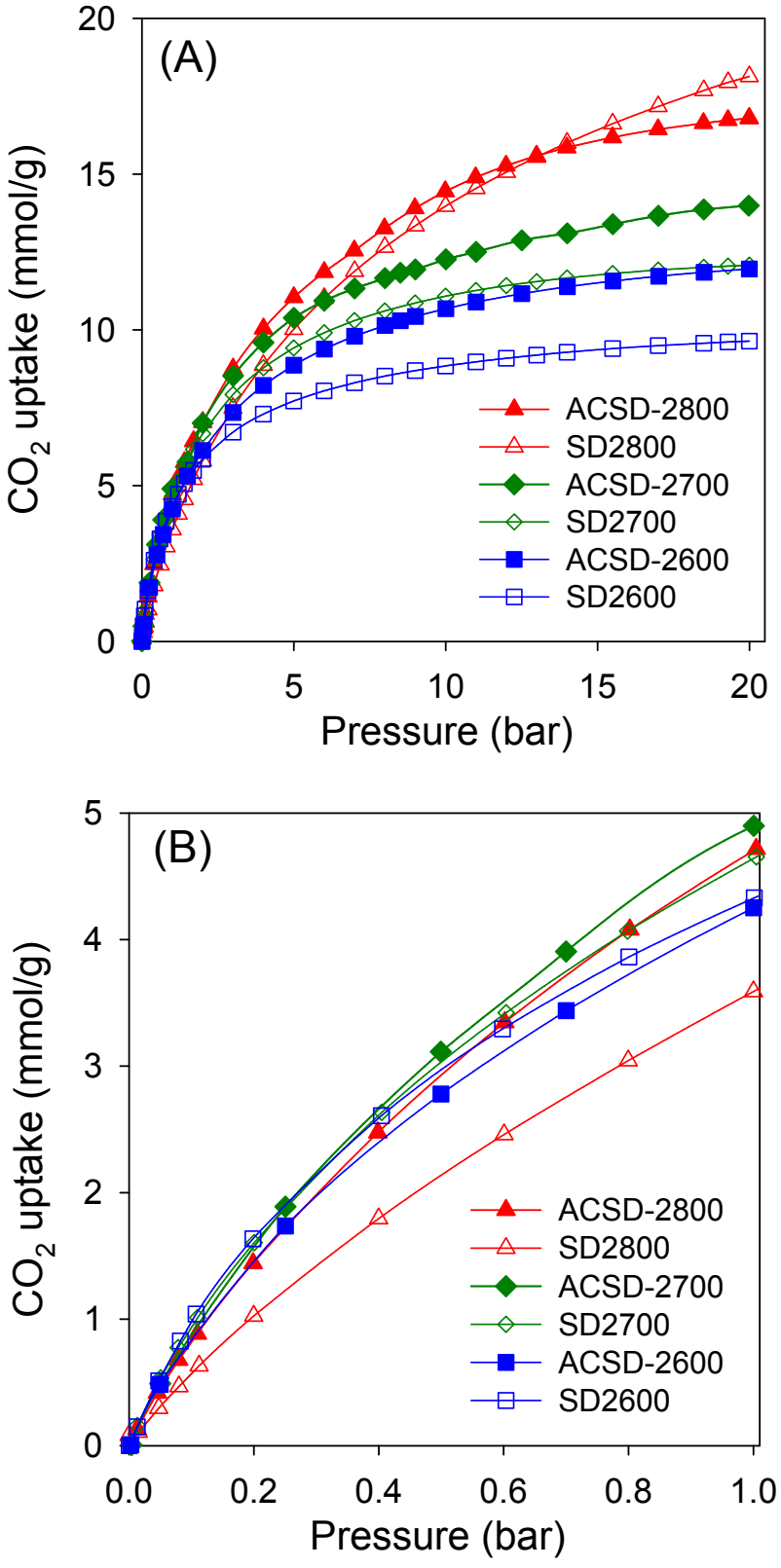
Supporting Figure S7. Representative SEM images of sawdust-derived flash carbonized activated ACSD-2T carbons prepared at KOH/carbon ratio of 2 at temperature (T) of 600 or 700 ^{o}C.



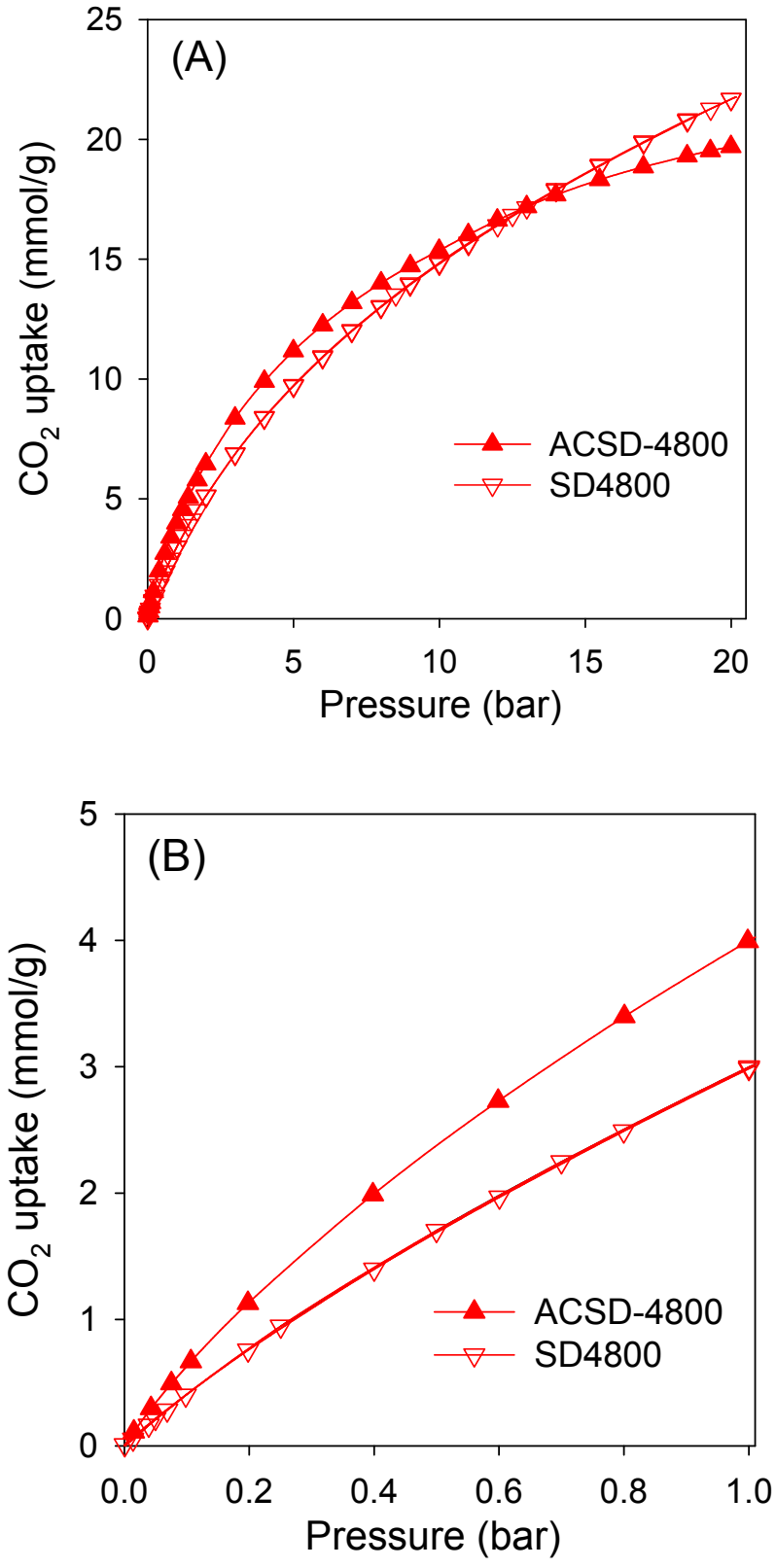
Supporting Figure S8. Representative SEM images of sawdust-derived flash carbonized activated ACSD-2T carbons prepared at KOH/carbon ratio of 2 at temperature (T) of 800 ^{o}C.



Supporting Figure S9. CO_2 uptake isotherms at 25 °C and 0 - 1 bar for sawdust-derived flash carbonized activated ACSD-xT carbons. See experimental section for sample designation.



Supporting Figure S10. CO_2 uptake isotherms at 25 °C and 0 - 1 bar for sawdust-derived flash carbonized activated ACSD-2T carbons compared to analogous activated carbons prepared from sawdust via hydrothermal carbonisation (SD2T).



Supporting Figure S11. CO_2 uptake isotherms at 25 °C and 0 - 1 bar for sawdust-derived flash carbonized activated ACSD-4800 sample compared to an analogous activated carbon (SD4800) prepared from sawdust via hydrothermal carbonisation.