Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

Predictable and targeted activation of biomass to carbons with high surface area density and enhanced methane storage capacity

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Table S1. Elemental composition and O/C atomic ratio of a range of activateable biomass precursors.

Biomass souce	C [%]	H [%]	O [%]	(O/C)[a]	Reference
Eucalyptus sawdust	46.4	5.8	47.8	0.773	1
Seaweed (*Sargassum fusiforme*)[b]	39.6	5.9	51.6	0.977	2
Palm leaves[c]	43.9	5.8	49.4	0.844	This work
Jujun grass	41.7	5.5	52.8	0.950	3
Camellia Japonica	46.2	5.4	48.4	0.786	3
Cellulose	44.4	6.2	49.4	0.830	1
Date seed (*Phoenix dactylifera*) [d]	49.0	7.0	42.4	0.649	This work

[a]Atomic ratio. [b]Seaweed contains 2.9 wt% N. [c]Palm leaves contain 0.9 wt% N. [d]Date seeds contain 1.6 wt% N.

Table S2. Elemental composition of flash air-carbonised activated ACDS carbon derived from date seed compared to other carbonaceous precursors, namely, flash air-carbonised sawdust (ACSD), CNL1 carbon (CNL1), raw sawdust (SDD), sawdust hydrochar (SD), lignin hydrochar (LAC), jujun grass hydrochar (ACGR), *Camelia Japonica* hydrochar (ACCA), cellulose hydrochar (C), cellulose acetate hydrochar (CA), starch hydrochar (S), fresh cigarette filter hydrochar (FF)), smoked cigarette filter hydrochar (SF), carbon nanotube composites (CN) and polypyrrole (Py).

Sample	C [%]	H [%]	O [%]	(O/C)[a]	Reference
Flash air carbonised date seed (ACDS)	78.5	4.0	16.3	0.156	This work
Flash air carbonised sawdust (ACSD)	72.4	3.2	24.2	0.251	4
CNL1 carbon (CNL1)	77.7	3.1	19.2	0.185	5
Raw sawdust (SDD)	46.4	5.8	47.8	0.773	2
Sawdust hydrochar (SD)	57.4	5.6	37.0	0.483	1,2,6
Lignin hydrochar (LAC)	66.6	5.1	28.3	0.319	7
Jujun grass hydrochar (AGGR)	55.8	5.7	38.5	0.517	3
Camellia Japonica hydrochar (ACCA)	49.1	5.2	45.7	0.698	3
Cellulose hydrochar (C)	69.5	6.2	24.4	0.263	1,8
Cellulose acetate hydrochar (CA)	66.2	3.9	29.9	0.339	8
Starch hydrochar (S)	68.8	6.6	24.6	0.269	1
Fresh cigarette filter hydrochar (FF)	63.6	4.2	32.2	0.380	9
Smoked cigarette filter hydrochar (SF)[b]	68.5	5.7	24.8	0.272	9
Carbon nanotube composites (CN)[c]	45.1	1.5	52.6	0.875	10
Polypyrrole (Py)[c,d]	44.5	3.0	39.9	0.672	11

[a]Atomic ratio. [b]Smoked cigarette filter hydrochar contains 1 wt% N. [c]The CNT composites contained 0.8 wt% N, and therefore a nominal O content of 52.6% obtained as O = 100-C-H-N, which gives O/C ratio of 0.875.[d]Polypyrrole contained 12.6 wt% N. [e]Polypyrrole has nominal O content of 39.9% obtained as O = 100-C-H-N, which gives O/C ratio of 0.672.

Table S3. Textural properties and surface area density of flash air-carbonised activated ACDSxT carbons derived from date seed at activation temperature of 800 ^{o}C (T) and KOH/carbon ratio (x) of 4 compared to similarly activated carbons derived from flash air-carbonised sawdust (ACSD-xT), CNL1 carbon (CNL1-xT), raw sawdust (SDxTD), sawdust hydrochar (SDxT), lignin hydrochar (LACxT), jujun grass hydrochar (ACGRxT), *Camelia Japonica* hydrochar (ACCAxT), cellulose hydrochar (C-xT), cellulose acetate hydrochar (CA-xT), fresh cigarette filter hydrochar (FF-xT), smoked cigarette filter hydrochar (SF-xT), carbon nanotube composites (CNxT) and polypyrrole (PyxT).

Sample	Surface area[a] (m^2 g^{-1})	Pore volume[b] (cm^3 g^{-1})	Surface area density (m^2 cm^{-3})	O/C ratio of precursor	Reference
ACDS4800	2609 (1825)	1.10 (0.70)	2372	0.156	This work
ACSD-4800	2610 (1892)	1.15 (0.74)	2270	0.251	4
CNL1-4800	2183 (1886)	1.05 (0.84)	2079	0.185	5
SD4800D	2980 (478)	2.10 (0.30)	1419	0.773	2
SD4800	2783 (694)	1.80 (0.36)	1546	0.483	2,6
LAC4800	3235 (1978)	1.77 (0.93)	1828	0.319	7
ACGR4800	2957 (1578)	1.72 (0.75)	1719	0.517	3
ACCA4800	3537 (2557)	1.85 (1.21)	1912	0.698	3
C-4800	2125 (1707)	0.98 (0.74)	2168	0.263	1,8
CA-4800	2864 (2662)	1.32 (1.17)	2170	0.339	8
FF-4800	4113 (2075)	1.87 (0.79)	2199	0.380	9
SF-4800	2393 (1810)	1.09 (0.70)	2195	0.272	9
CN4800	3802 (33)	2.98 (0.22)	1276	0.672	10
Py4800	3450 (1910)	2.57 (1.22)	1342	0.875	11

The values in the parenthesis refer to: [a]micropore surface area and [b]micropore volume.

Table S4. Textural properties and surface area density of flash air-carbonised activated ACDSxT carbons derived from date seed at activation temperature of 700 ^{o}C (T) and KOH/carbon ratio (x) of 4 compared to similarly activated carbons derived from sawdust hydrochar (SDxT), lignin hydrochar (LACxT), jujun grass hydrochar (ACGRxT), *Camelia Japonica* hydrochar (ACCAxT), cellulose hydrochar (C-xT), cellulose acetate hydrochar (CA-xT), starch hydrochar (SxT), fresh cigarette filter hydrochar (FF-xT), smoked cigarette filter hydrochar (SF-xT), carbon nanotube composites (CNxT) and polypyrrole (PyxT).

Sample	Surface area[a] (m^2 g^{-1})	Pore volume[b] (cm^3 g^{-1})	Surface area density (m^2 cm^{-3})	O/C ratio of precursor	Reference
ACDS4700	2192 (1871)	0.93 (0.74)	2357	0.156	This work
SD4700	2252 (2088)	1.03 (0.91)	2186	0.483	1,2,6
LAC4700	2038 (1832)	1.00 (0.84)	2028	0.319	7
ACGR4700	3144 (2753)	1.56 (1.23)	2015	0.517	3
ACCA4700	2983 (2500)	1.50 (1.14)	1987	0.698	3
C-4700	2370 (2201)	1.08 (0.94)	2194	0.263	1,8
CA-4700	3771 (3484)	1.75 (1.54)	2155	0.339	8
S4700	2194 (2082)	1.01 (0.92)	2172	0.269	1
FF-4700	2803 (1901)	1.23 (0.73)	2279	0.380	9
SF-4700	2512 (2019)	1.20 (0.91)	2093	0.272	9
CN4700	3202 (1106)	2.14 (0.20)	1496	0.672	10
Py4700	3568	2.46 (0.28)	1450	0.875	11

The values in the parenthesis refer to: [a]micropore surface area and [b]micropore volume.

Table S5. Textural properties and surface area density of flash air-carbonised activated ACDSxT carbons derived from date seed at activation temperature of 800 ^{o}C (T) and KOH/carbon ratio (x) of 2 compared to similarly activated carbons derived from flash air-carbonised sawdust (ACSD-xT), CNL1 carbon (CNL1-xT), raw sawdust (SDxTD), sawdust hydrochar (SDxT), lignin hydrochar (LACxT), jujun grass hydrochar (ACGRxT), *Camelia Japonica* hydrochar (ACCAxT), carbon nanotube composites (CNxT) and polypyrrole (PyxT).

Sample	Surface area[a] (m^2 g^{-1})	Pore volume[b] (cm^3 g^{-1})	Surface area density (m^2 cm^{-3})	O/C ratio of precursor	Reference
ACDS2800	2068 (1780)	0.88 (0.71)	2350	0.156	This work
ACSD-2800	2150 (1861)	0.91 (0.74)	2363	0.251	4
CNL1-2800	1326 (1263)	0.60 (0.55)	2210	0.185	5
SD2800D	2274 (1923)	1.20 (0.90)	1895	0.773	2
SD2800	2377 (1512)	1.40 (0.70)	1698	0.483	2,6
LAC2800	1924 (1839)	0.95 (0.87)	2025	0.319	7
ACGR2800	2735 (2083)	1.47 (0.94)	1861	0.517	3
ACCA2800	1917 (1691)	0.99 (0.75)	1936	0.698	3
CN2800	2925 (2538)	1.56 (1.18)	1875	0.672	9
Py2800	3410 (2530)	1.94 (1.21)	1758	0.875	10

The values in the parenthesis refer to: [a]micropore surface area and [b]micropore volume.

Table S6. Methane uptake at 25 ^{o}C and pressure of 35 bar for ACDS-derived activated carbons compared to the best performing porous carbons

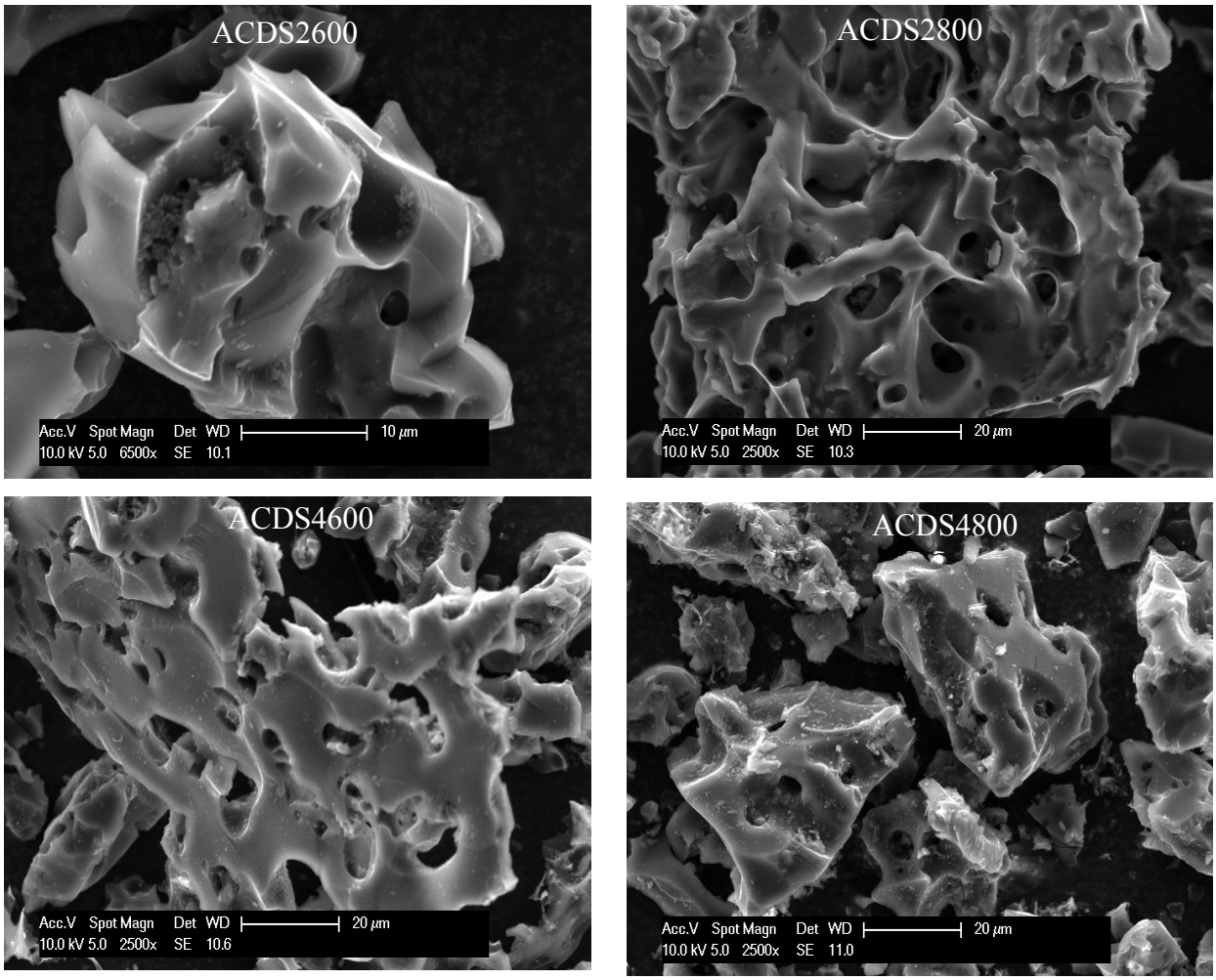
Sample	Excess uptake (35 bar) cm^3/cm^3	Total uptake (35 bar)[a] cm^3/cm^3	Reference
ACDS2800	184	208 (205)	This work
ACDS4700	196	222 (217)	This work
ACDS4800	176	201 (199)	This work
DO00-3:1_700	160	184	12
LMA738	142	165	13
BEA-ZTC	125	148	14
BEA-ZTC-873	142	165	14
AX-21		154	15

[a]Values in the parentheses are calculated using the equation; $V_{st} = V_{exc} + d_{CH4} (1 - \rho_{pd}/\rho_{He})$, where V_{st} (g/cm^3) is total storage inside a unit tank volume filled with an adsorbent, V_{exc} (g/cm^3) is the excess volumetric uptake per unit volume of an adsorbent, d_{CH4} is the methane gas density (g/cm^3) at 25^{o}C and 35 bar, ρ_{pd} is the packing density of the carbon, and ρ_{He} is the skeletal (or helium) density of the carbons, which was determined using helium pycnometry to be 2.1 g/cm^3.

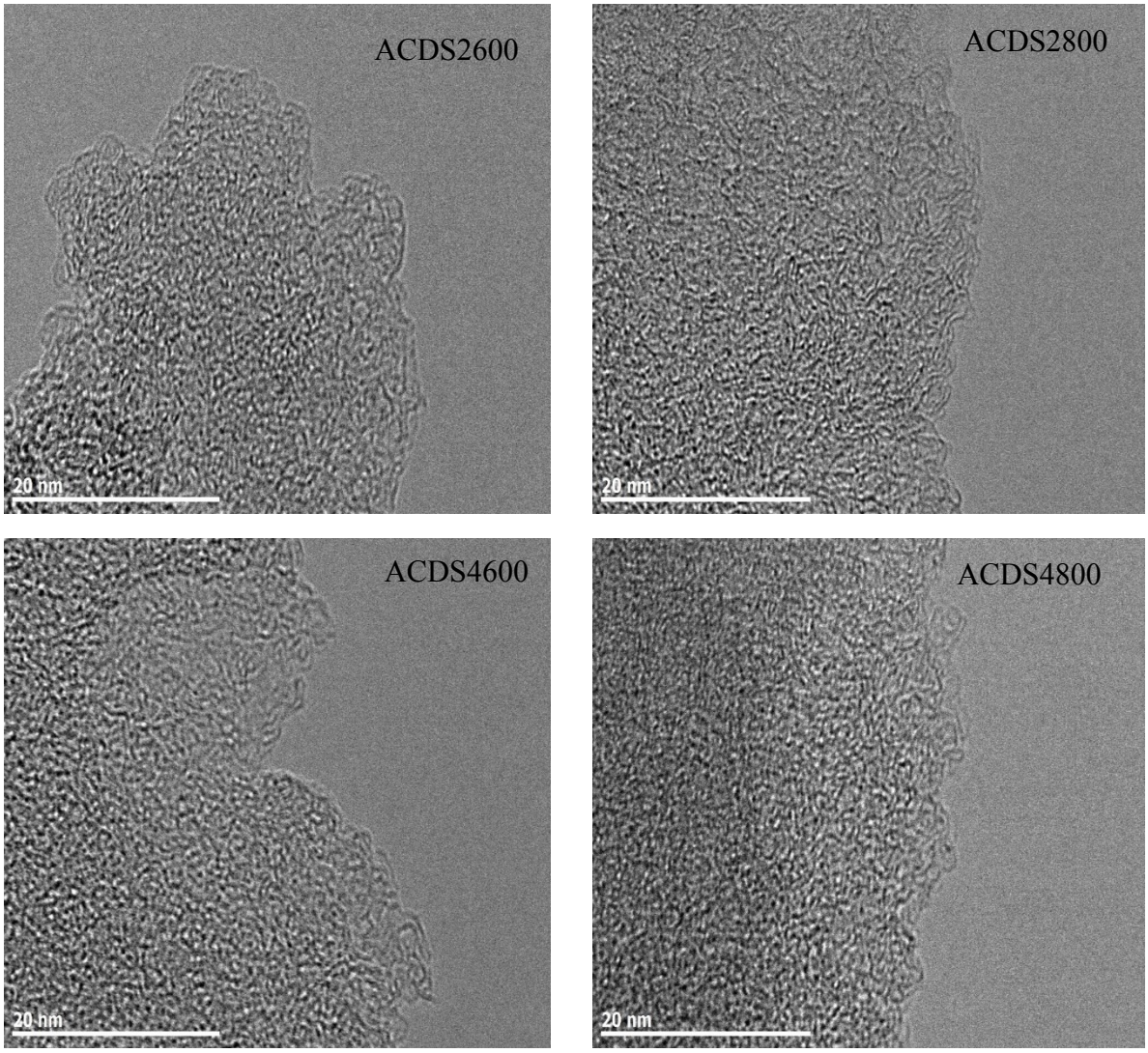
Table S7. Methane uptake and working capacity at 25 °C and pressure of 35 or 30 bar for ACDS-derived activated carbons compared to the best performing MOF, $_{mono}$HKUST-1

Sample	Excess uptake @ 35 (30) bar[a] cm^3/cm^3	Total uptake @ 35 (30) bar[b] cm^3/cm^3	Working capacity[c,d] cm^3/cm^3
ACDS2800	184 (177)	208 (198)	107 (97)
ACDS4700	196 (188)	222 (211)	128 (117)
ACDS4800	176 (168)	201 (190)	118 (107)
$_{mono}$HKUST-1[e]	205 (199)	224 (213)	137 (126)

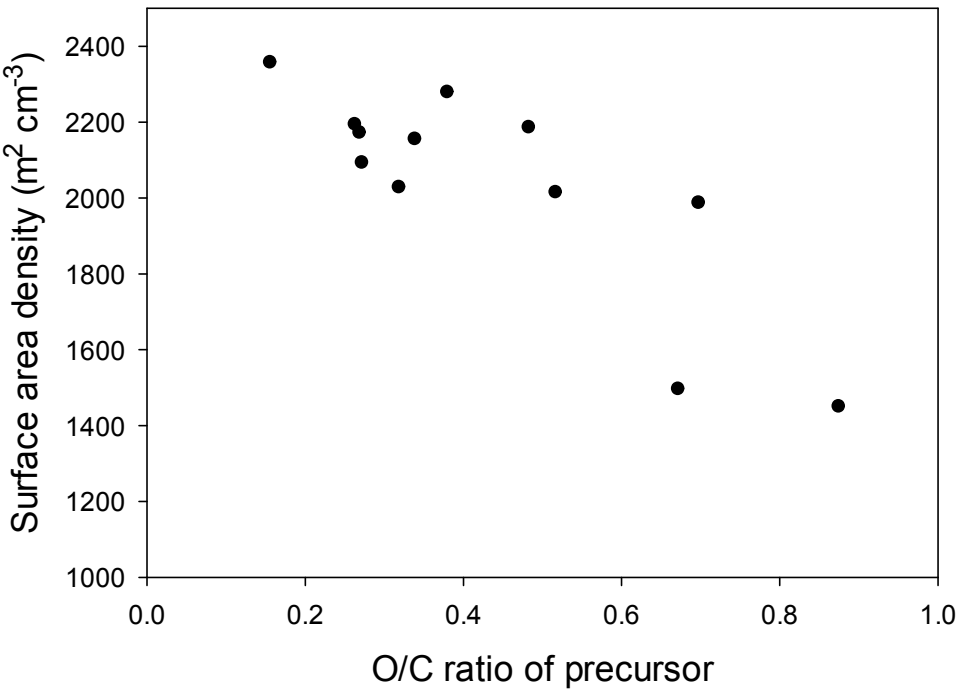
[a]Values in the parentheses are excess uptake at 30 bar. [a]Values in the parentheses are total uptake at 30 bar. [c]Working capacity is the difference in uptake between 35 bar and 5.8 bar. [d]The values in the parenthesis refer to working capacity as the difference in uptake between 30 bar and 5.8 bar.
[e]Values for $_{mono}$HKUST-1 are obtained from reference 16.



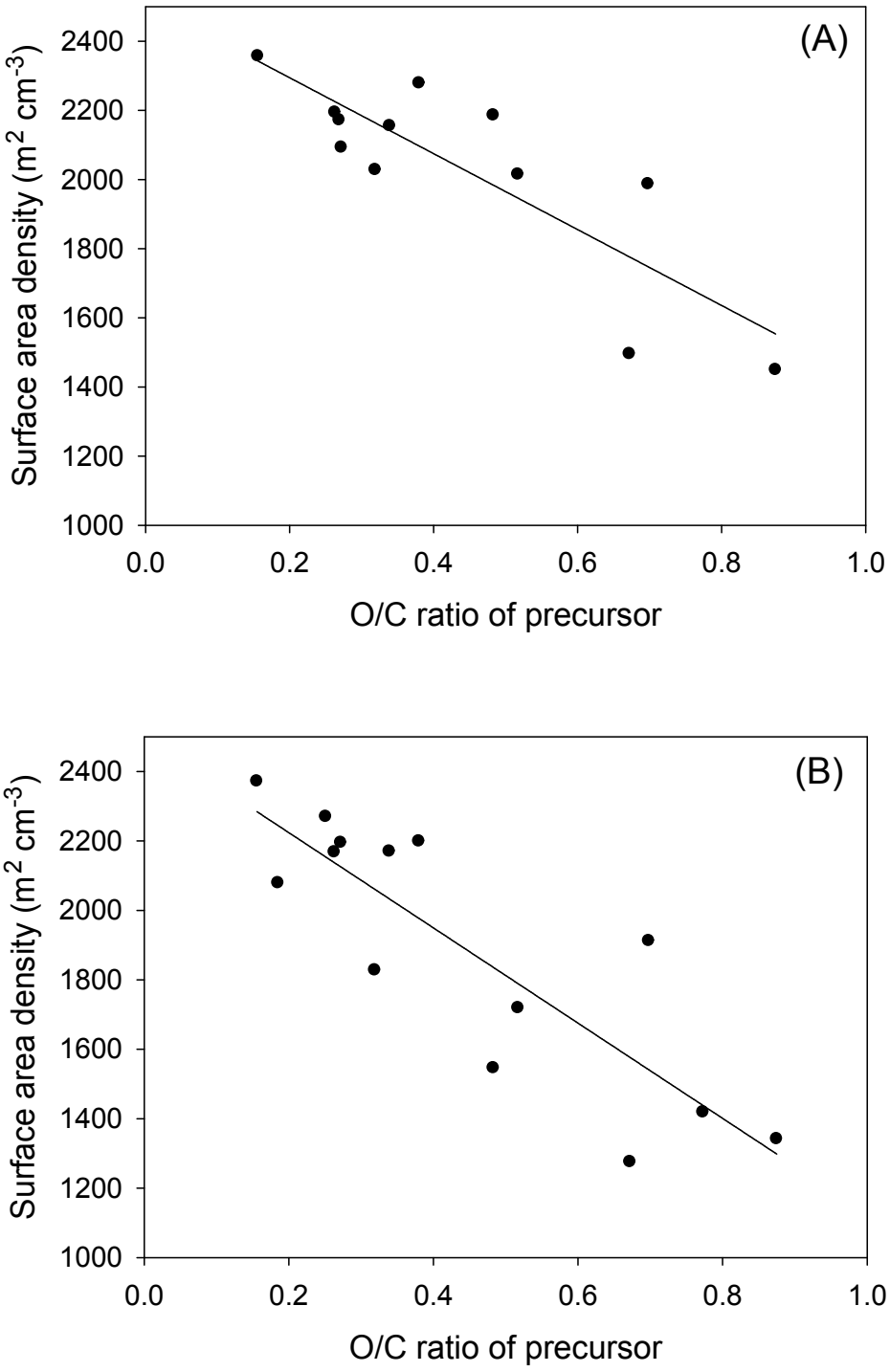
Supporting Figure S1. SEM images of air-carbonised activated date seed-derived carbons



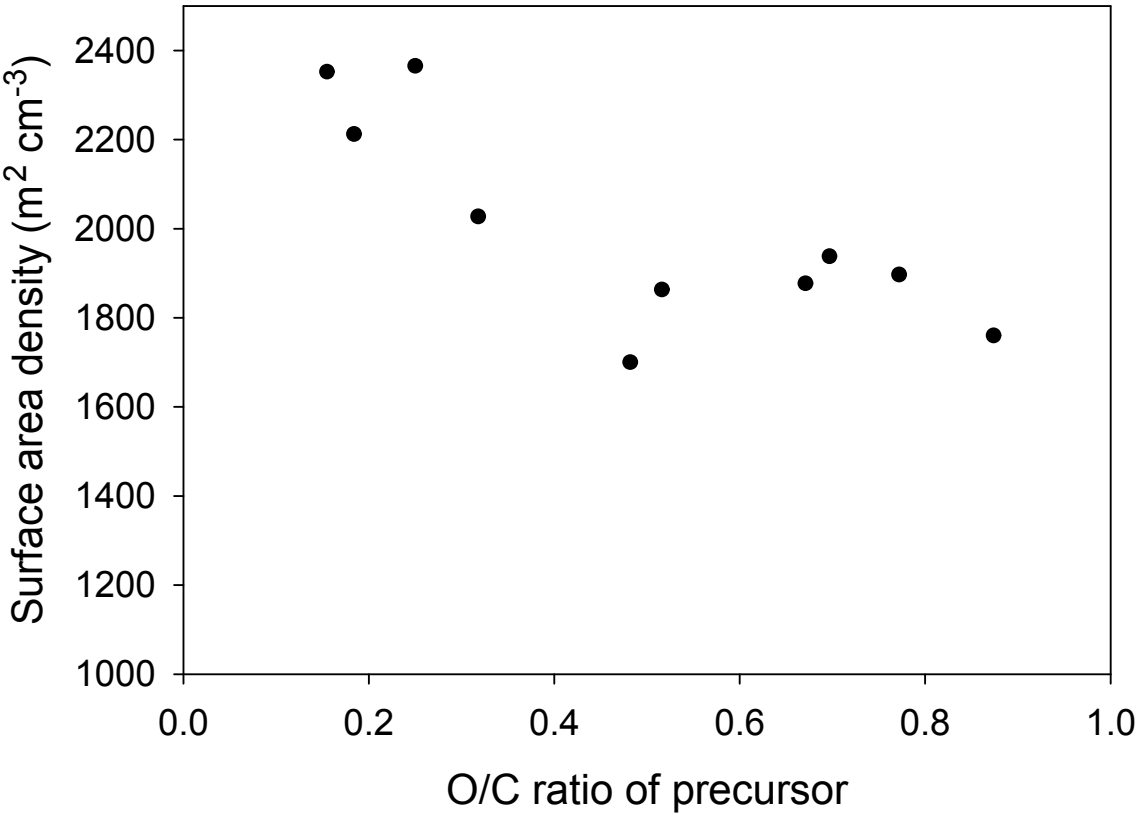
Supporting Figure S2. TEM images of air-carbonised activated date seed-derived carbons



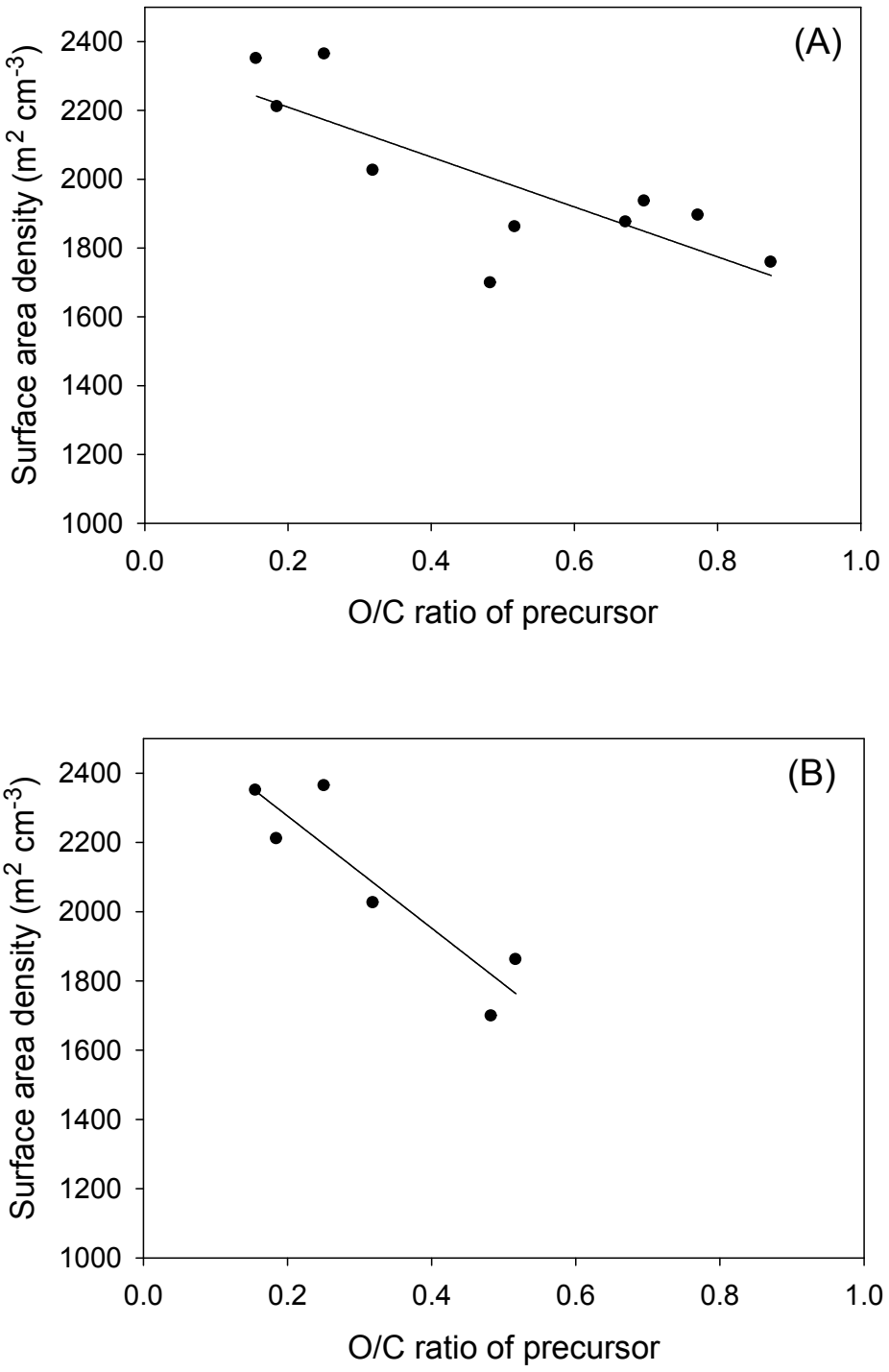
Supporting Figure S3. Surface area density of activated carbons as a function of the O/C ratio of the precursor carbonaceous matter. All activations were performed at 700 ^{o}C at the KOH/precursor ratio of 4.



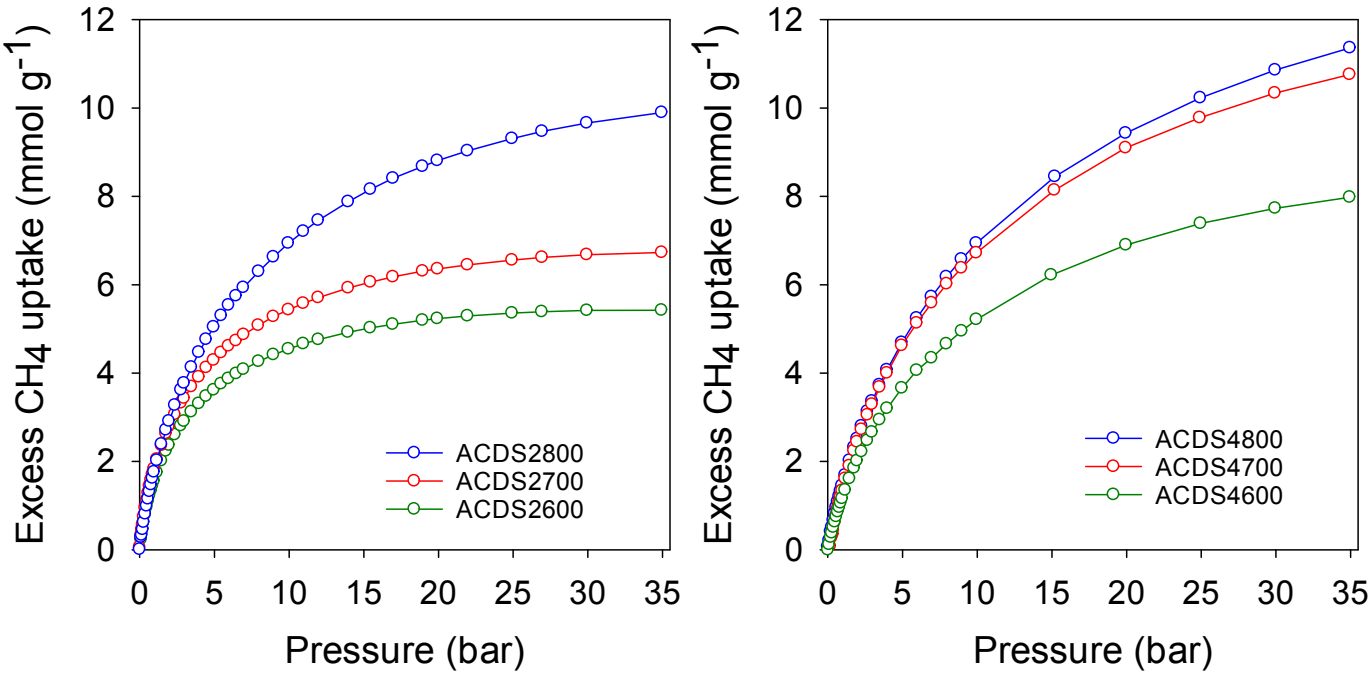
Supporting Figure S4. Linear regression analysis of the relationship between surface area density of activated carbons and the O/C ratio of precursor carbonaceous matter. The activations were performed at (A) 700 ^{o}C or (B) 800 ^{o}C, at the KOH/precursor ratio of 4. The analysis yields R value of 0.85 and 0.87 for activation at 700 ^{o}C and 800 ^{o}C, respectively.



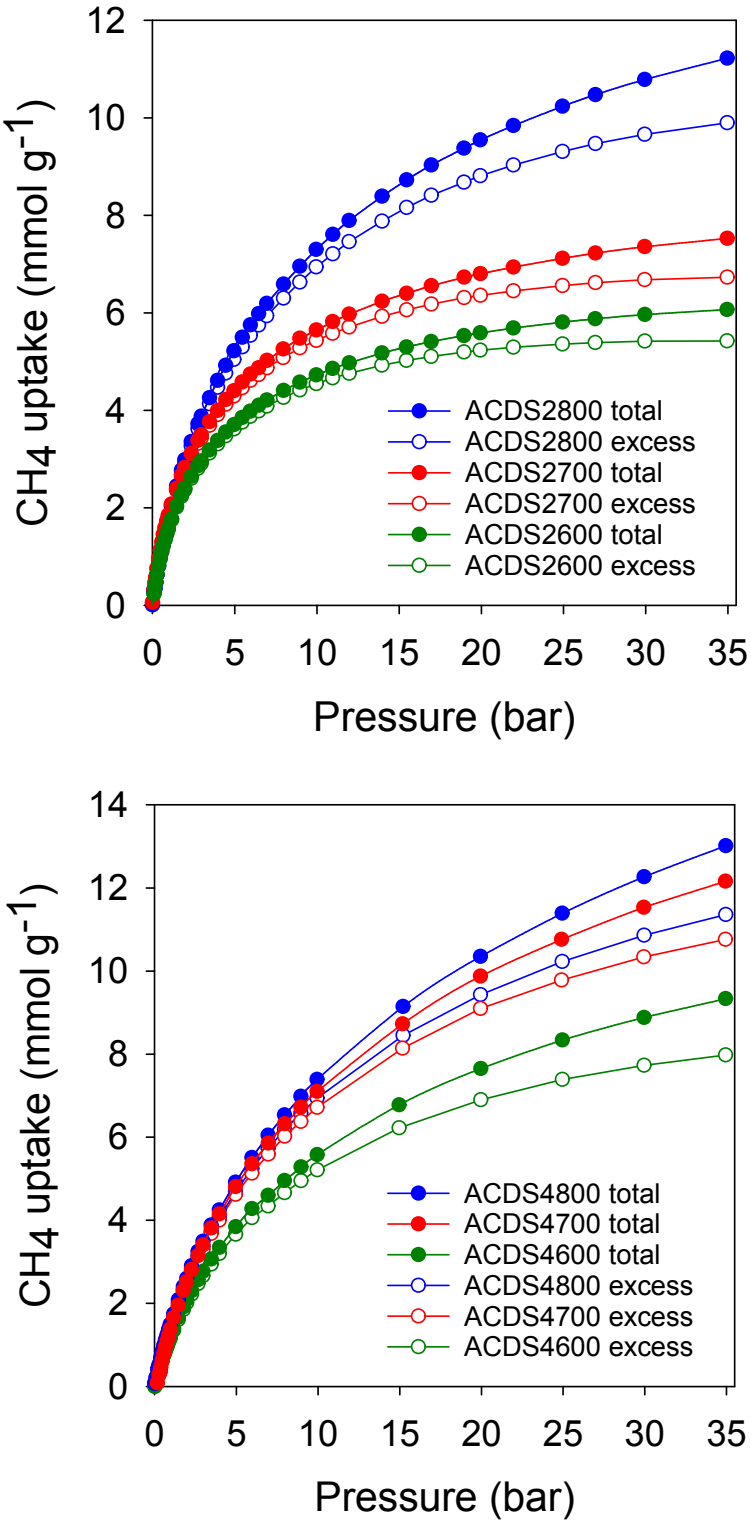
Supporting Figure S5. Surface area density of activated carbons as a function of the O/C ratio of the precursor carbonaceous matter. All activations were performed at 800 ^{o}C at the KOH/precursor ratio of 2.



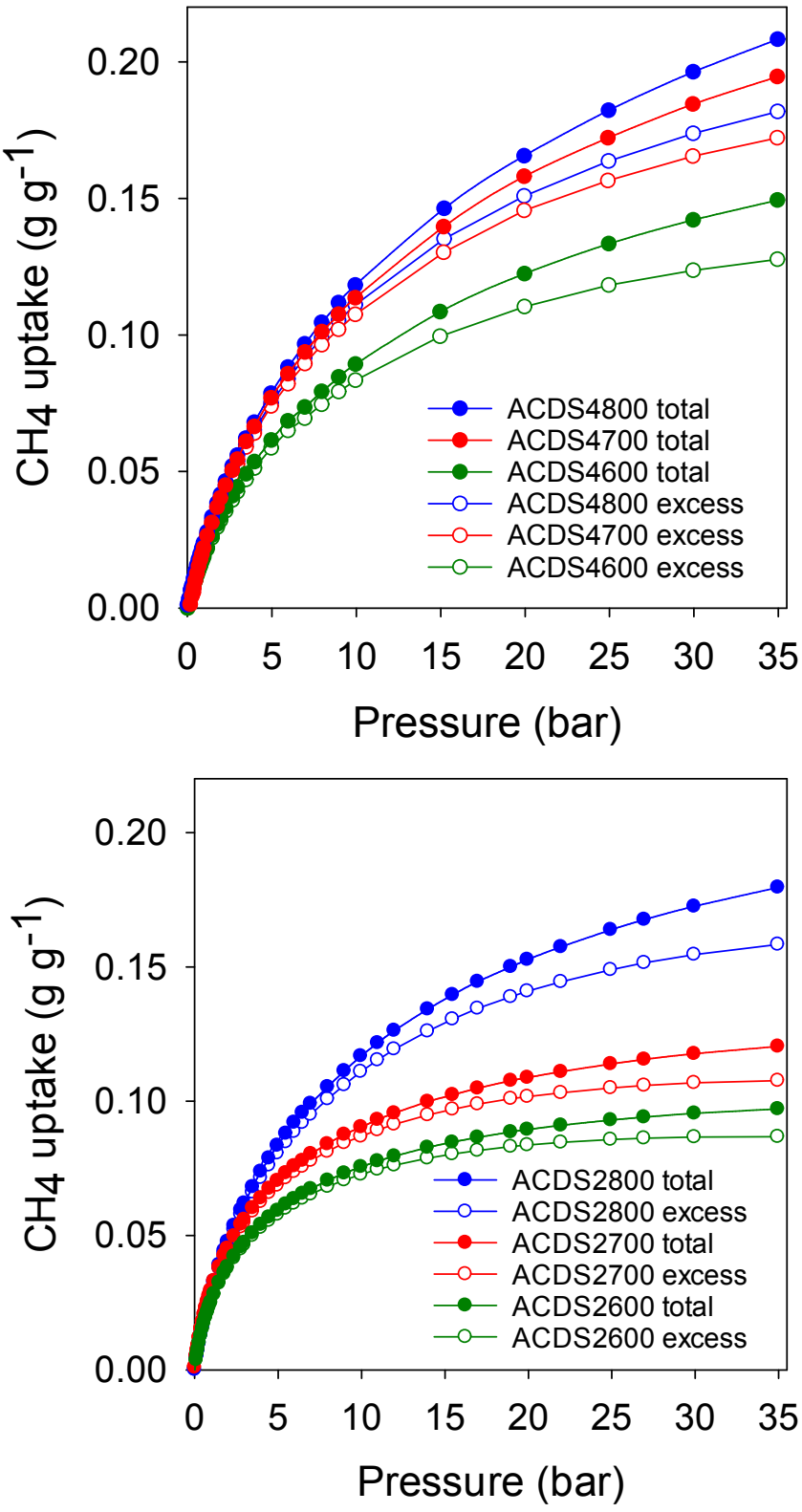
Supporting Figure S6. Linear regression analysis of the relationship between surface area density of activated carbons and the O/C ratio of precursor carbonaceous matter. All activations were performed at 800 ^{o}C at the KOH/precursor ratio of 2. The analysis yields R value of 0.80 for (A) and 0.92 for (B).



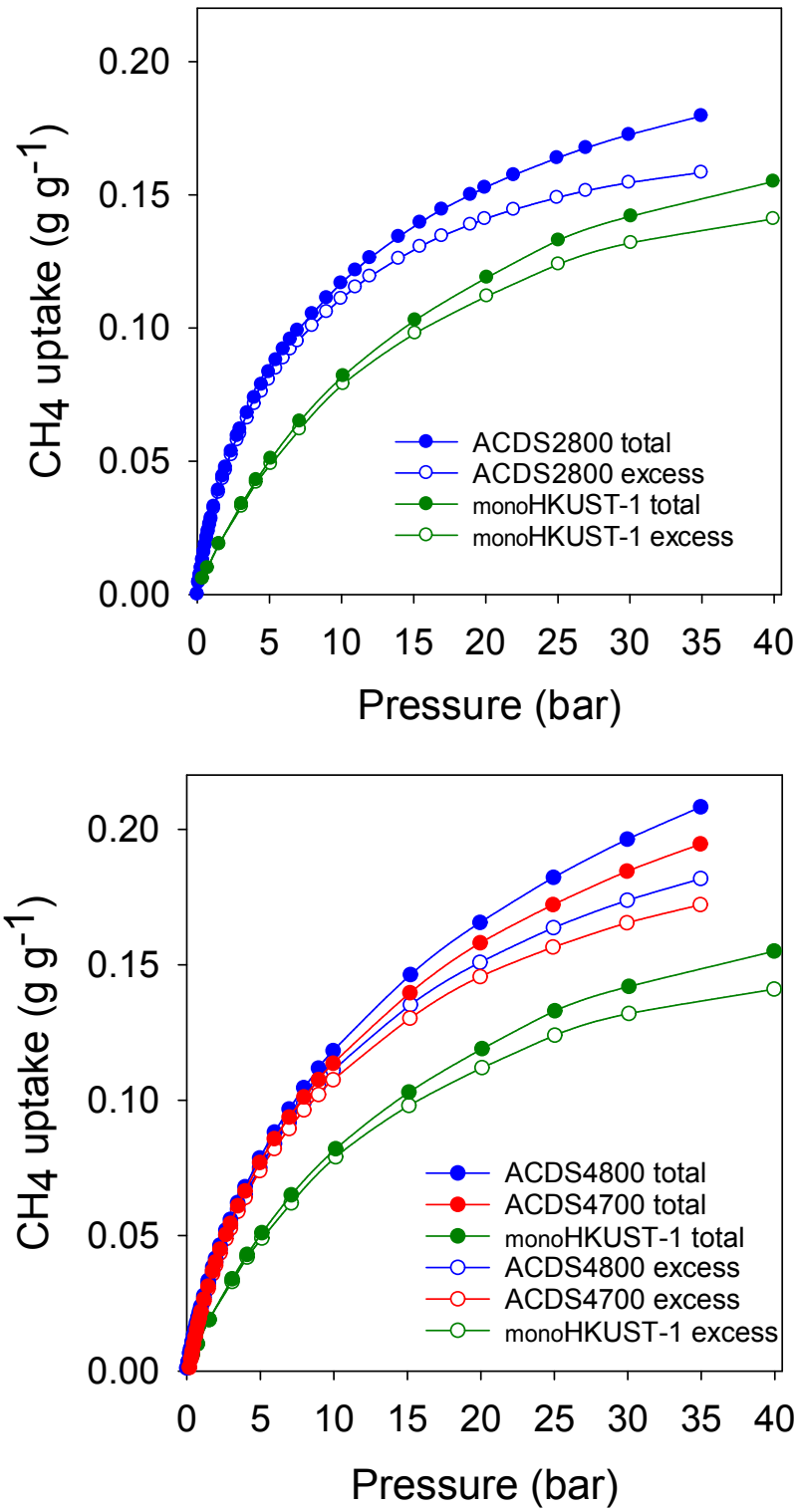
Supporting Figure S7. Excess gravimetric methane uptake at 25 °C of ACDS-derived activated carbons (ACDSxT), where x is KOH/ACDS ratio and T is activation temperature.



Supporting Figure S8. Total and excess gravimetric methane uptake at 25 °C of ACDS-derived activated carbons (ACDSxT), where x is KOH/ACDS ratio and T is activation temperature.



Supporting Figure S9. Total and excess gravimetric methane uptake at 25 °C of ACDS-derived activated carbons (ACDSxT), where x is KOH/ACDS ratio and T is activation temperature.



Supporting Figure S10. Total and excess gravimetric methane uptake at 25 °C of ACDS-derived activated carbons (ACDSxT) compared to the benchmark MOF, $_{mono}$HKUST-1. Data for $_{mono}$HKUST-1 obtained from reference 15.

References

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