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Supporting Information

Pre-mixed precursors for modulating the porosity of carbons for enhanced hydrogen storage: Towards predicting the activation behaviour of carbonaceous matter

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Excess and total hydrogen uptake

Our measurements provided the excess hydrogen uptake, which is the amount of hydrogen adsorbed in the carbons above that which would have been stored in the pores under similar conditions (temperature and pressure) assuming that there is zero energy of interaction between the hydrogen and the carbon pore walls. The total uptake is calculated from the excess storage by taking into account the amount of hydrogen compressed into the carbon pore volume space. Our gravimetric methods measured the excess hydrogen uptake (θ_{Exc}) from which the total storage (θ_T) was calculated from the equation:

$$\theta_T = \theta_{Exc} + \frac{100 \text{ x } d_{H2} \text{ x } V_T}{(1 + d_{H2} \text{ x } V_T)}$$

Where;

θ_T = total hydrogen uptake (wt%)

θ_{Exc} = excess hydrogen uptake (wt%)

d_{H2} = density (g cm^{-3}) of compressed hydrogen gas at the relevant temperature and pressure. The density was obtained from the National Institute of Standards and Technology (NIST) website (http://www.nist.gov/)

V_T = Pore volume (cm^3 g^{-1}) of the carbon from nitrogen sorption analysis

The excess volumetric uptake capacity ($v\theta_{Exc}$), in g l^{-1}, was obtained using the equation;

$v\theta_{Exc} = \theta_{Exc} \times d_{carbon}$

where, d_{carbon} = packing density of the carbon

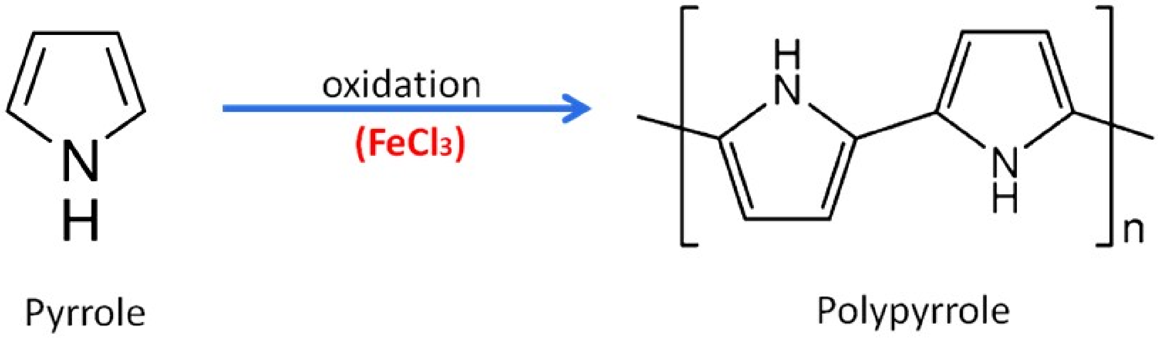
The total volumetric uptake capacity ($v\theta_T$), in g l^{-1}, was obtained using the equation;

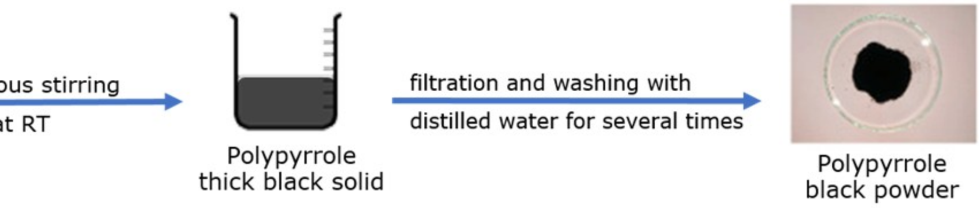
$V\theta_T = \theta_T \times d_{carbon}$

Where, d_{carbon} = packing density of the carbon

The packing density of powder samples was determined by pressing a given amount of carbon in a 1.3 cm die at pressure of 7 MPa for 5 min. Alternatively, relatively similar values are obtained using the general equation; $d_{carbon} = (1/\rho_s + V_T)^{-1}$, where ρ_s is skeletal density and V_T is total pore volume.

Synthesis of polypyrrole





Scheme 1. Scheme showing the synthesis of polypyrrole from pyrrole.

Table S1. Textural properties of activated carbons derived from single precursors (polypyrrole, raw sawdust and sawdust-derived hydrochar) or pre-mixed mixtures of the precursors.

Sample	Surface area[a] (m^2g^{-1})	Pore volume[b] (cm^3g^{-1})	V_{mes}[c] (%)	Packing density (gcm^{-3})	Pore size[a] (Å)
PPY-4800	2965 (287)	2.34 (0.18)	92	0.35	12/30
SD-4800D	2980 (478)	2.10 (0.30)	86	0.39	12/29
SD-4800	2783 (694)	1.80 (0.36)	80	0.44	11/27
PPYSD134800	2739 (1562)	1.31 (0.62)	53	0.56	8/11/21
PPYSD124800	3477 (1356)	1.78 (0.62)	65	0.44	8/12/25
PPYSD114800	3279 (1015)	1.70 (0.39)	77	0.46	8/11/22
PPYSD214800	3085 (452)	1.76 (0.18)	90	0.45	8/12/22
PPYH134800	1828 (1468)	0.83 (0.59)	29	0.77	9/13
PPYH124800	2227 (1569)	1.04 (0.62)	40	0.66	8/12
PPYH114800	3815 (1377)	2.18 (0.66)	70	0.38	8/12/25
PPYH214800	3583 (887)	1.97 (0.35)	82	0.41	7/12/22

[a]The values in the parenthesis are micropore surface area. [b]The values in the parenthesis are micropore volume. [c]Proportion of pore volume arising from mesopores.

Table S2. Elemental composition of polypyrrole, raw sawdust and sawdust hydrochar compared to hydrochars of lignin and Jujun grass, and carbonaceous matter obtained from biomass via carbonisation in the presence of air (i.e., via flash carbonisation in air or burning).

Sample	C [%]	H [%]	O [%]	(O/C)[a]
Polypyrrole[b,c]	44.5	3.0		
Raw sawdust	46.4	5.8	47.8	0.773
Sawdust hydrochar	57.4	5.6	37.0	0.483
CNL1 carbon	77.7	3.1	19.2	0.185
Flash carbonised sawdust	72.4	3.2	24.2	0.251
Lignin hydrochar	66.6	5.1	28.3	0.319
Jujun grass hydrochar	55.8	5.7	38.5	0.517

[a] Atomic ratio. [b] Polypyrrole contains 12.6 wt% N. [c] 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 O/C ratio of activated carbons derived from polypyrrole (PPY-4800), raw sawdust SD-4800D), sawdust hydrochar (SD-4800), CNL1 carbon (CNL1-4800), flash air carbonized sawdust (ACSD-4800), lignin hydrochar (LAC-4800) and Jujun grass hydrochar (ACGR-4800). All the activated carbons were prepared at activation temperature of 800 ^{o}C and KOH/precursor ratio of 4.

Sample	Precursor O/C ratio	Surface area^{a} (m^2 g^{-1})	*Meso* SA (%)	Pore volume^{b} (cm^3 g^{-1})	*Meso* PV (%)	Pore size^{c} (Å)
PPY-4800	0.672	2965 (287)	90	2.34 (0.18)	92	12/30
SD-4800D	0.773	2980 (478)	84	2.10 (0.30)	86	12/29
SD-4800	0.483	2783 (694)	75	1.80 (0.36)	80	11/27
CNL1-4800	0.185	2183 (1886)	14	1.05 (0.84)	20	6.5/8.5/16
ACSD-4800	0.251	2610 (1892)	28	1.15 (0.74)	36	6/8/10/16
LAC-4800	0.319	3235 (1978)	39	1.77 (0.93)	47	8/11/27
ACGR-4800	0.519	2957 (1578)	47	1.72 (0.75)	56	8/12/27

The values in the parenthesis refer to: ^{a}micropore surface area and ^{b}micropore volume. ^{c}pore size distribution maxima obtained from NLDFT analysis. *Meso* SA and *Meso* PV are proportion (%) of surface area and pore volume, respectively, arising from mesopores.

Table S4. Surface area, pore volume hydrogen storage (at -196 °C) for activated carbons (PPYH114800 and PPYSD124800) derived from pre-mixed precursor containing polypyrrole and sawdust hydrochar or raw sawdust compared to the best performing metal organic frameworks (MOFs); NOTT-112, NU-100, and MOF-210.

Sample	Surface area (m^2 g^{-1})	Pore Volume (cm^3 g^{-1})	Gravimetric H_2 uptake (wt%)[a]		Volumetric H_2 uptake (g l^{-1})[c]		Reference
			20 bar	40 bar	20 bar	40 bar	
PPYH114800	3815	2.18	8.1	10.0	30.8	38.0	This work
PPYSD124800	3477	1.78	7.5	8.9	32.6	39.0	This work
NOTT-112[b]	3800	1.62	7.8	9.2	17.9	21.2	1
NU-100[b]	6143	2.82	8.5	10.5	12.8 (25.6)	15.8 (31.6)	2
MOF-210[b]	6240	3.60	8.4	11.0	10.5 (21.0)	13.8 (27.6)	3

[a]Total gravimetric H_2 uptake at -196 °C and 20 or 20 bar. [b]Packing density values (g cm^{-3}) used are: 0.23 (NOTT-112), 0.15 (NU-100) and 0.125 (MOF-210) according to reference 83 in main manuscript (Y. Peng, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha and T. Yildirim, *J. Am. Chem. Soc*. 2013, **135**, 11887). The packing density values are based on experimental data (reference 83) that shows that the actual "tapped density" of MOFs is roughly one-half of the 'ideal' crystal density. [c]Values in parenthesis were obtained using 'idea' crystal density (0.25 g cm^{-3} for MOF-210 and 0.30 g cm^{-3} for NU-100).[2,3]

References

1. Y. Yan, X. Lin, S. Yang, A. J. Blake, A. Dailly, N. R. Champness, P. Hubberstey and M. Schroder, *Chem. Commun*., 2009, 1025.
2. O. K. Farha, A. O. Yazaydın, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *Nat. Chem*., 2010, **2**, 944.
3. H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. O. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim and O. M. Yaghi, *Science*, 2010, **329**, 424.

Table S5. Deliverable gravimetric and volumetric hydrogen capacity based on pressure swing (100 bar to 5 bar at 77 K) adsorption conditions for activated carbons derived pre-mixed precursors containing polypyrrole and sawdust or sawdust hydrochar compared to benchmark metal organic frameworks.

Sample	Surface area (m^2 g^{-1})	ΔH_2 100 bar to 5 bar[a]		ΔH_2 100 to 5 bar[b]
		wt%	g l^{-1}	g l^{-1}
PPYH114800	3815	7.1	27	
PPYH214800	3583	6.1	25	
PPYSD124800	3477	5.7	25	
PPYSD114800	3279	5.3	25	
PPYSD214800	3085	5.4	24	
NOTT-112[h]	3800	5.3	24	18 (12)
HKUST-1	1980	2.0	17	13 (9)
NU-125	3230	4.1	24	18 (12)
CYCU-3-Al	2450	5.2	30	23 (15)
NU-1000	2200	5.5	27	20 (14)
NU-1101	4340	6.1	30	23 (15)
NU-1102	3720	6.9	31	23 (16)
NU-1103	6245	10.1	33	25 (17)
PPYSD114900	3563	8.4	28	
PPYH114900	3592	7.5	28	
PPYSD115800	3458	6.1	25	

[a] Volumetric uptake of MOFs determined using crystal density. [a] Volumetric uptake of MOFs adjusted by taking into account a 25% loss in capacity due to packing density (according to reference 86). [a] Volumetric uptake of MOFs determined using a value of 50% of crystal density as the packing density.

Data for the MOFs is taken from reference 76 in main manuscript (P. García-Holley, B. Schweitzer, T. Islamoglu, Y.Liu, L. Lin, S. Rodriguez, M. H. Weston, J. T. Hupp, D. A. Gómez-Gualdrón, T. Yildirim, and O. K. Farha, *ACS Energy Lett*. 2018, **3**, 748.)

Table S6. Deliverable gravimetric and volumetric hydrogen capacity based on pressure swing (100 bar to 5 bar at 77 K) adsorption conditions for activated carbons derived pre-mixed precursors containing polypyrrole and sawdust or sawdust hydrochar.

Sample	Surface area (m^2 g^{-1})	ΔH_2 100 bar to 5 bar[a] wt%	g l^{-1}
PPYSD114900	3563	8.4	28
PPYH114900	3592	7.5	28
PPYSD115800	3458	6.1	25

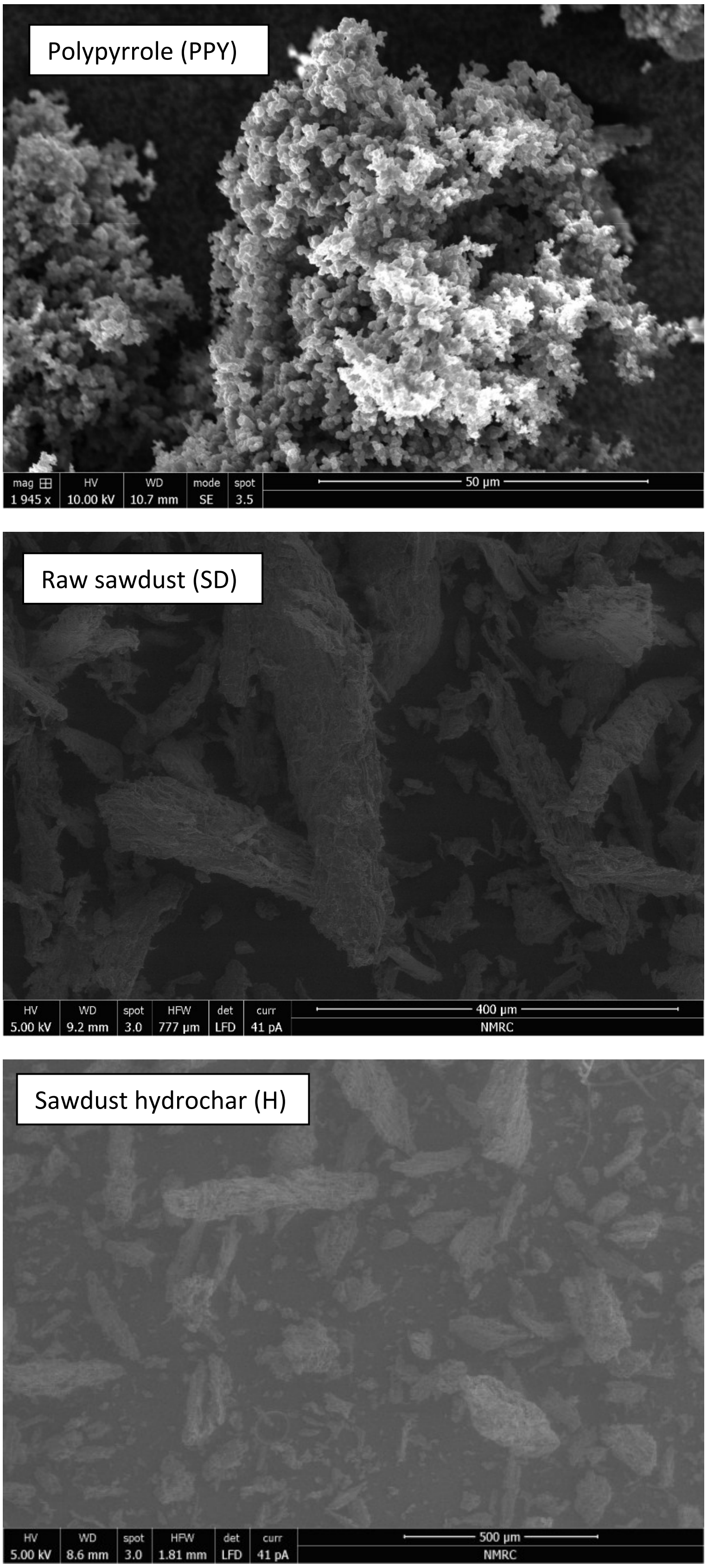


Figure S1. SEM images of polypyrrole, raw sawdust and sawdust hydrochar

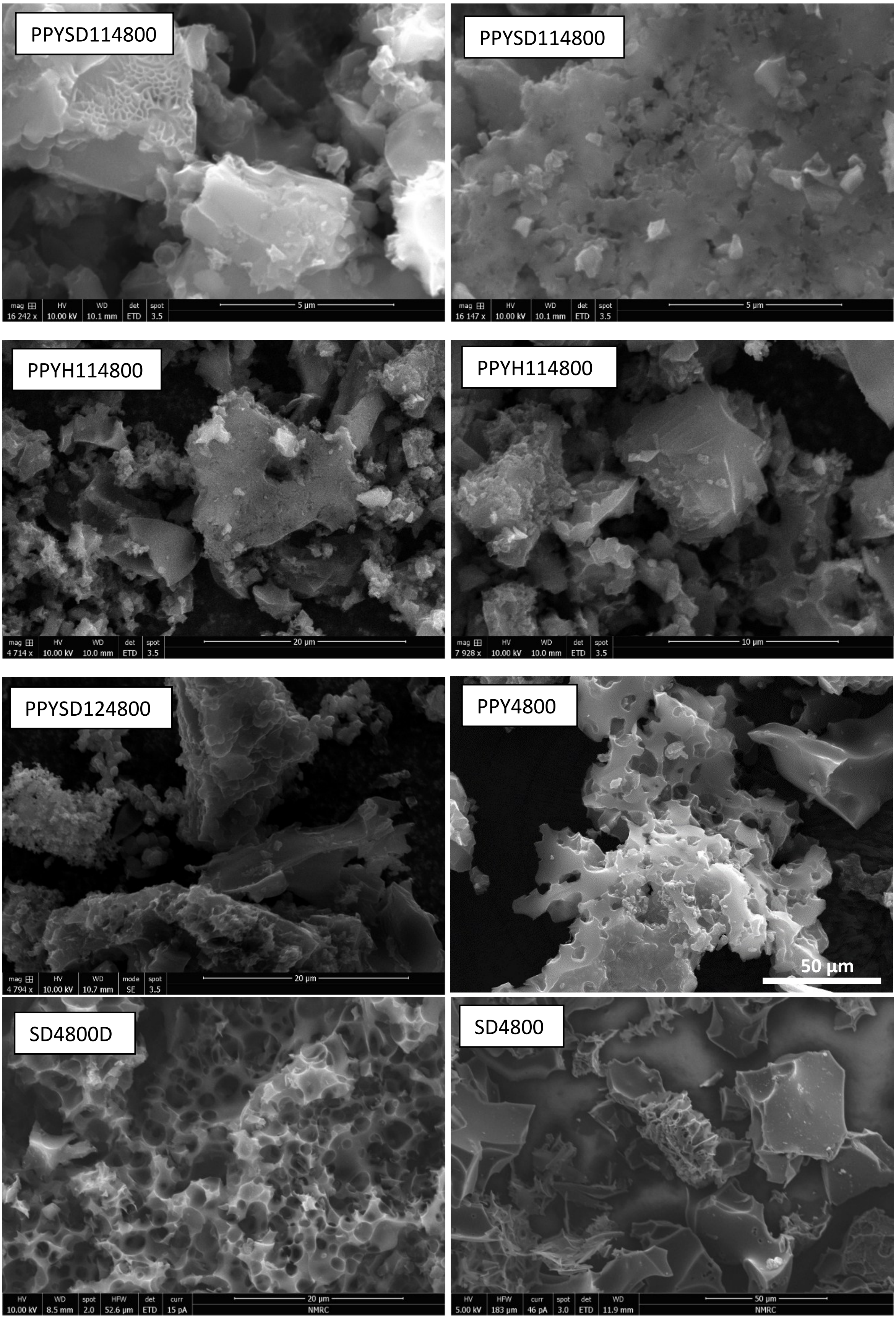


Figure S2. SEM images of activated carbons derived from single precursors (PPY4800, SD4800 and SD4800) or from pre-mixed mixtures of the precursors (polypyrrole, raw sawdust or sawdust hydrochar).

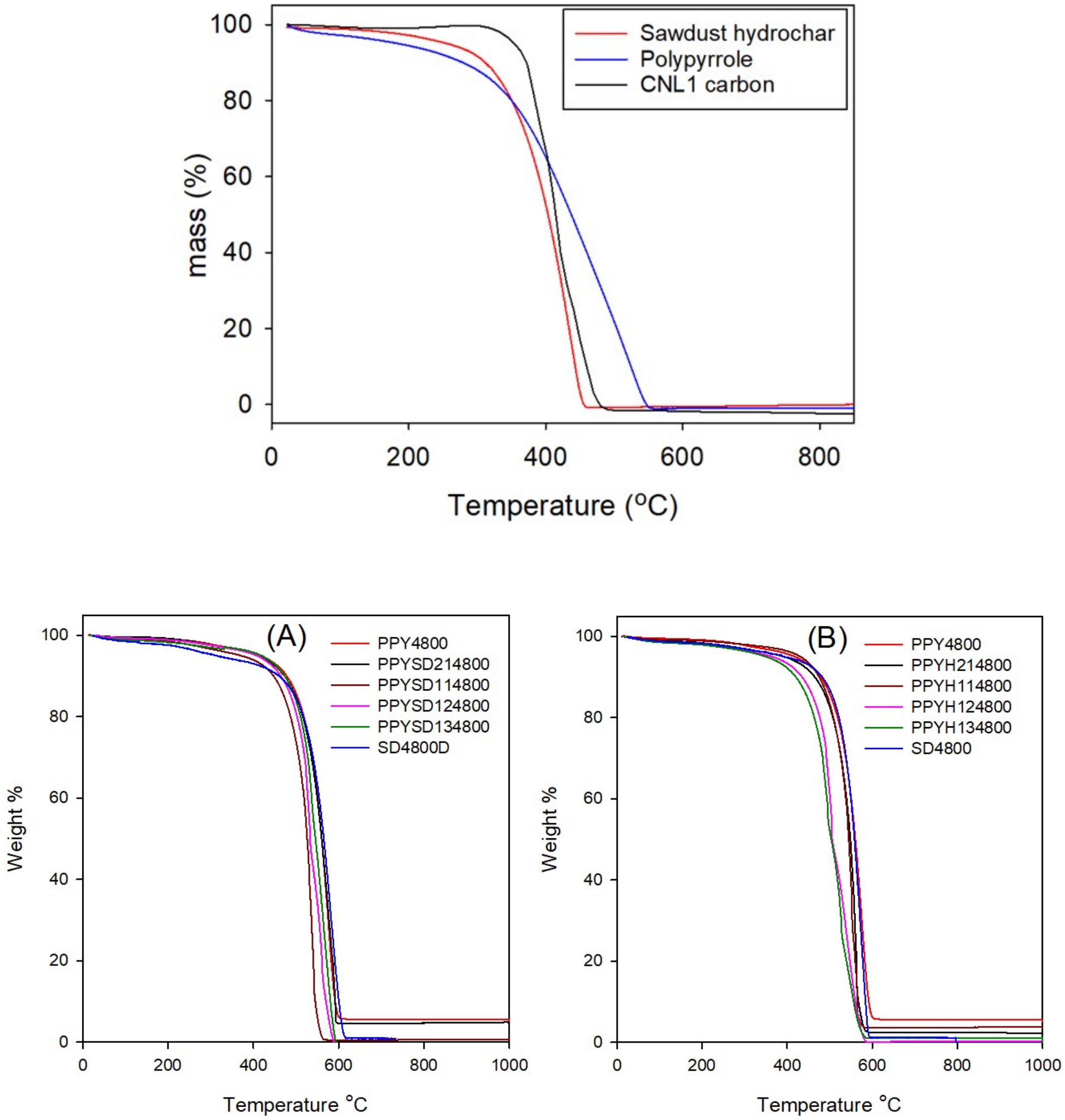


Figure S3. Thermogravimetric analysis (TGA) curves of (top panel) sawdust hydrochar, polypyrrole and CNL1 carbon precursor materials, and (bottom panels) activated carbons derived from single precursors (PPY4800, SD4800 and SD4800) or from pre-mixed mixtures of the precursors (polypyrrole, raw sawdust or sawdust hydrochar).

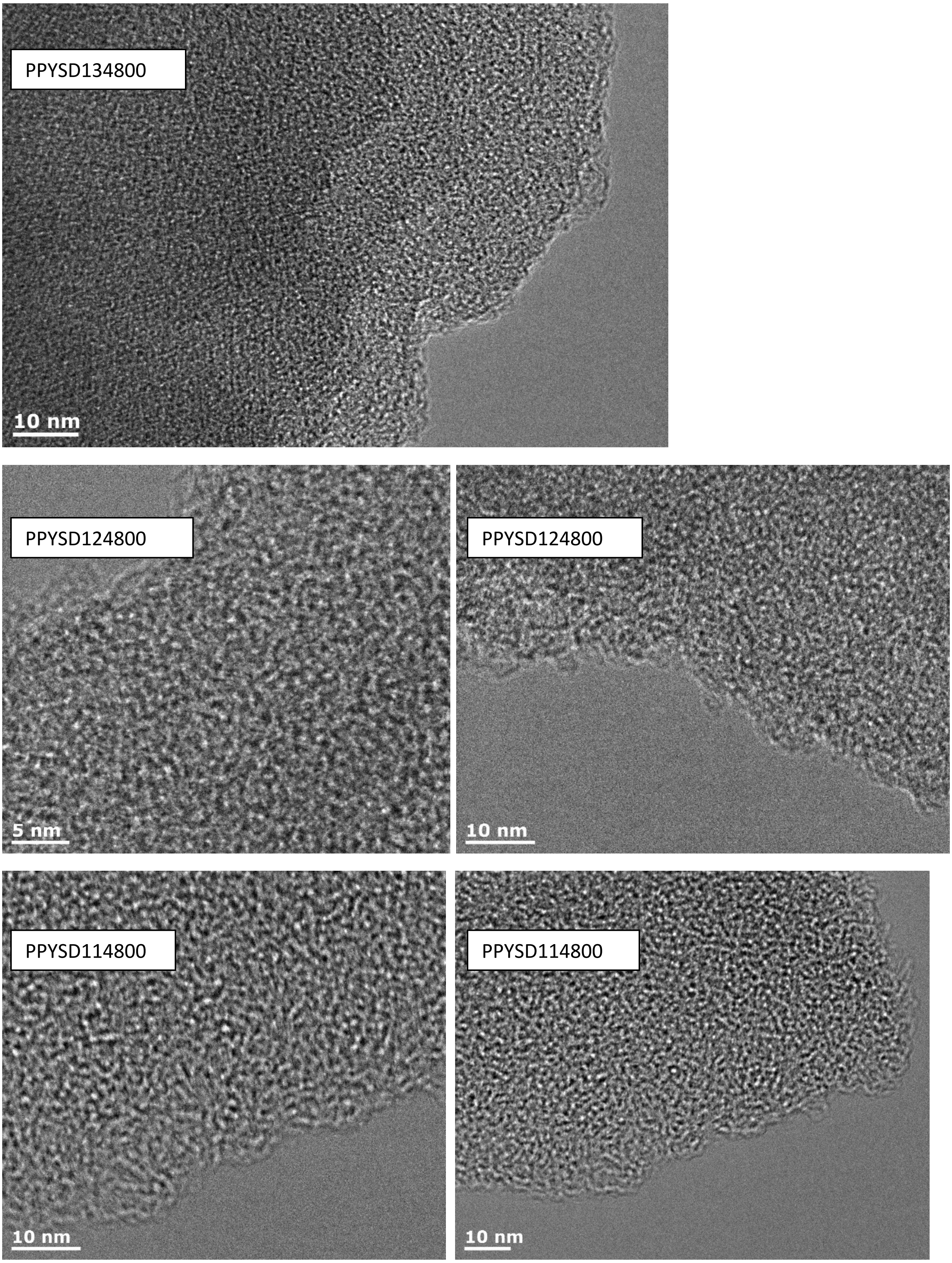


Figure S4. TEM images of activated carbons derived from pre-mixed mixtures of polypyrrole (PPY) and raw sawdust (SD).

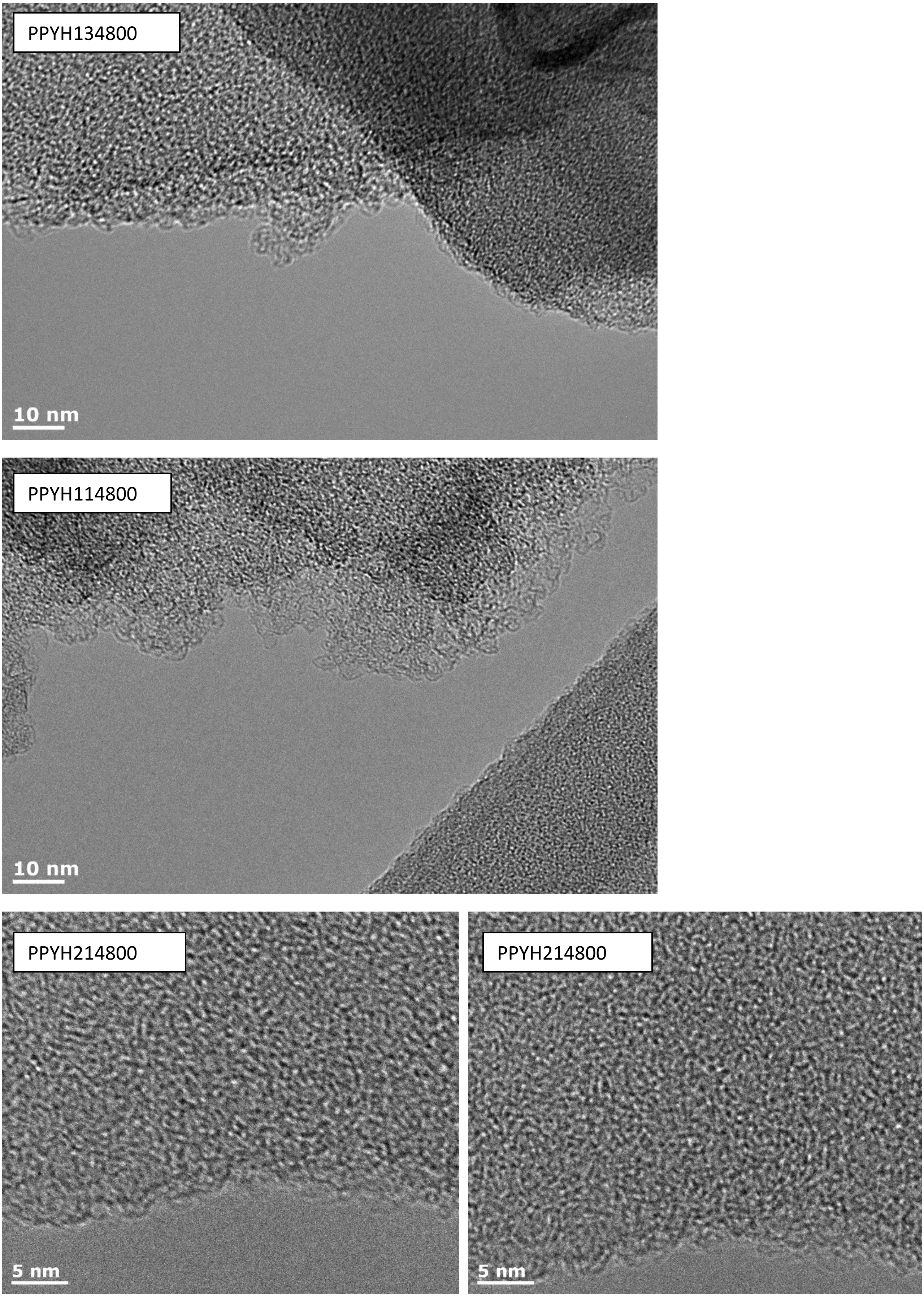


Figure S5. TEM images of activated carbons derived from pre-mixed mixtures of polypyrrole (PPY) and sawdust hydrochar (H).

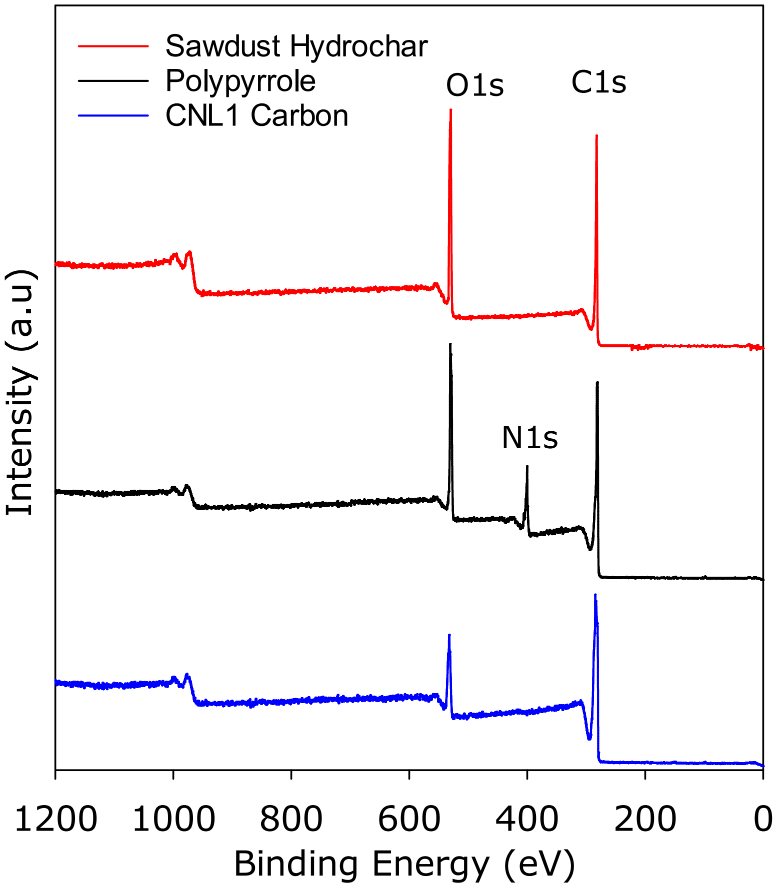


Figure S6. X-ray photoelectron spectroscopy (XPS) spectra of sawdust hydrochar, polypyrrole and CNL1 carbon precursor materials.

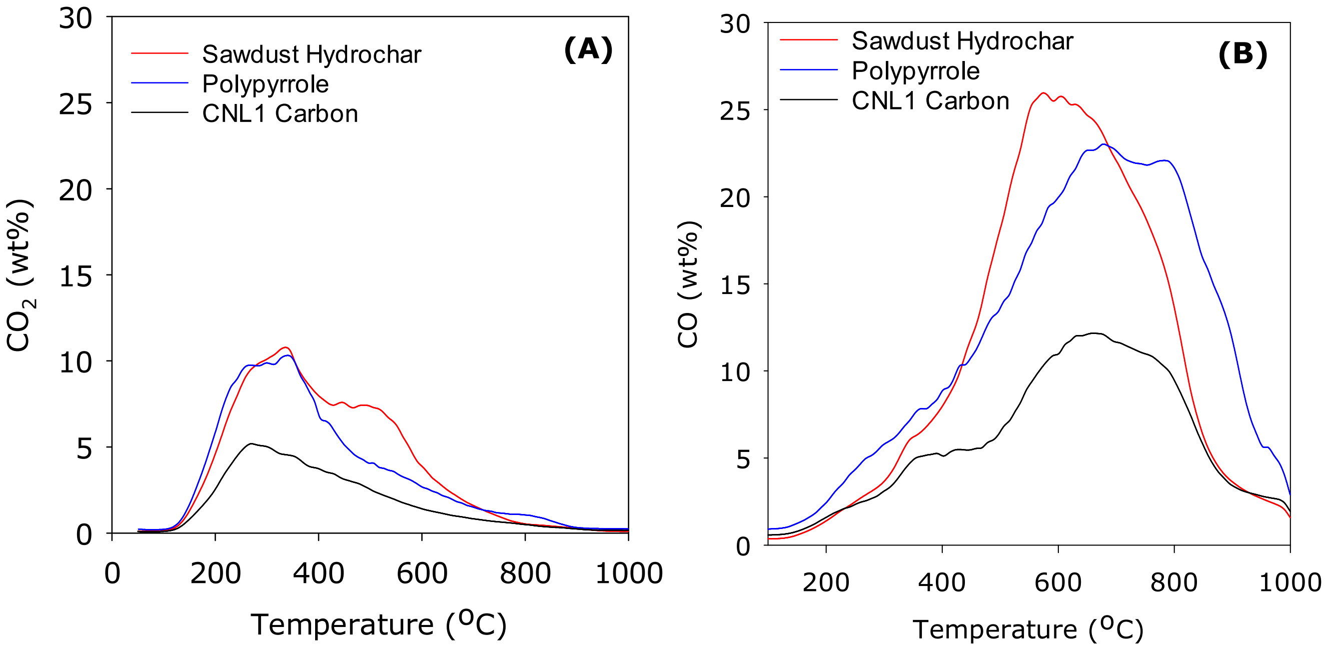


Figure S7. Temperature programmed desorption (TPD) of sawdust hydrochar, polypyrrole and CNL1 carbon precursor materials.

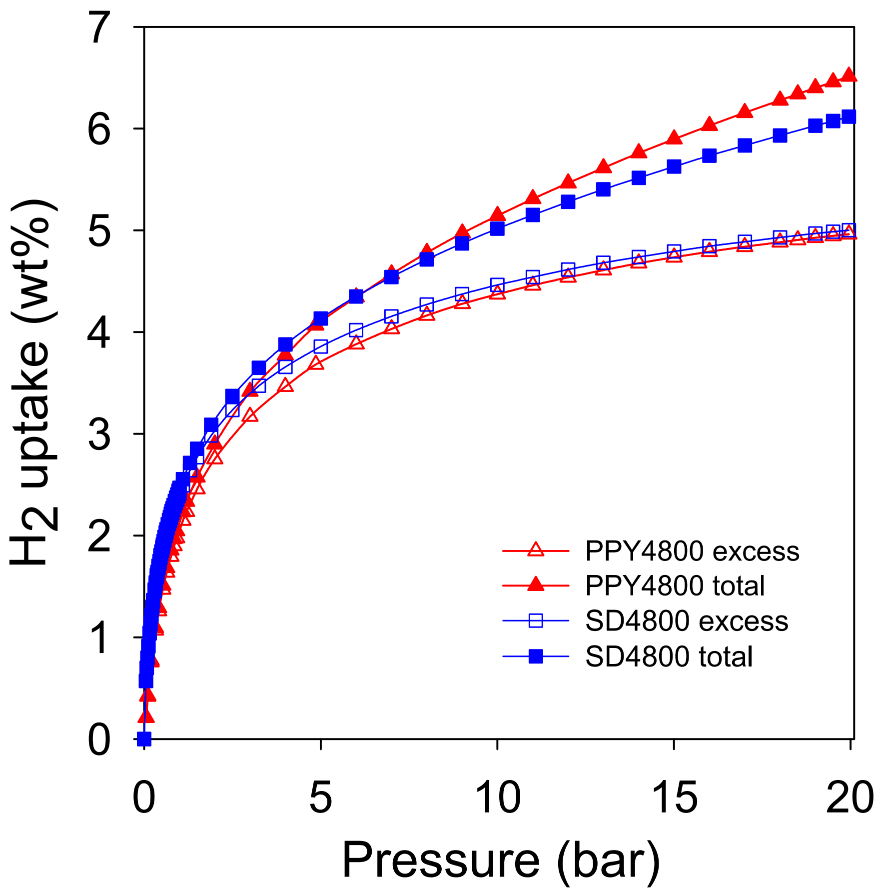


Figure S8. Hydrogen uptake isotherms of activated carbons derived from single precursor; PPY4800 (polypyrole, PPY) or SD4800 (sawdust hydrochar, H).

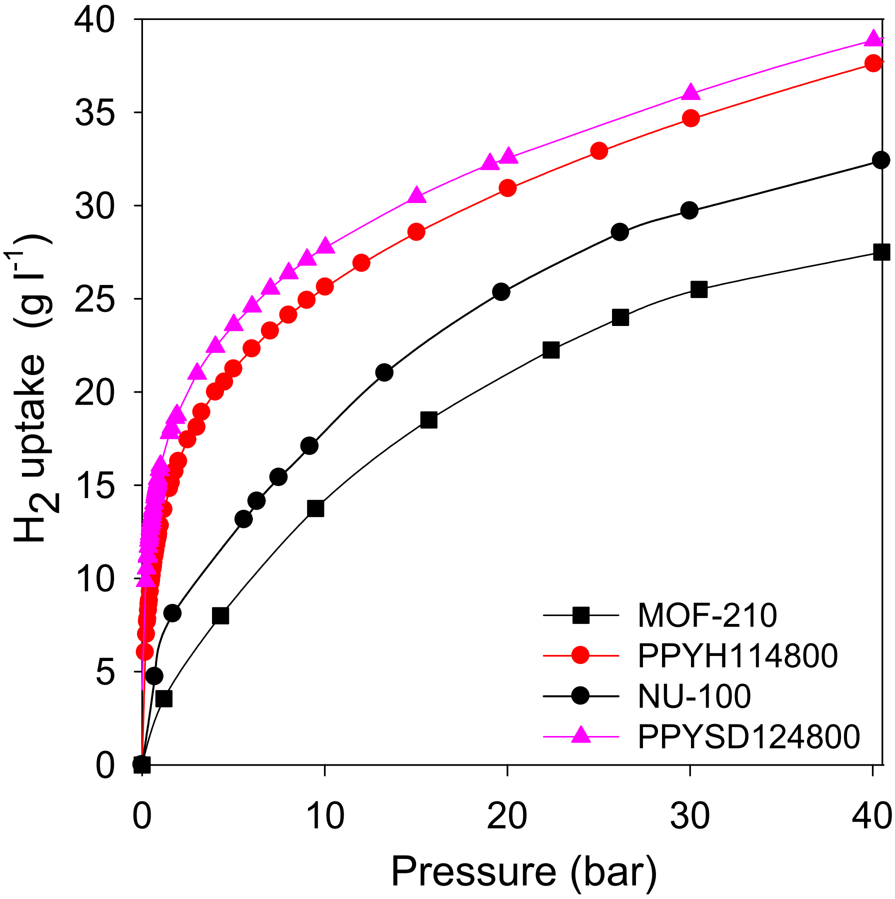


Figure S9. Volumetric hydrogen storage capacity of activated carbons (PPYH114800 and PPYSD124800) derived from pre-mixed precursors containing polypyrrole and sawdust hydrochar or raw sawdust compared to the best performing metal organic frameworks (MOFs); NU-100,[22] and MOF-210.[24] The crystal density (rather than packing density) was used to compute the volumetric uptake of the MOFs.

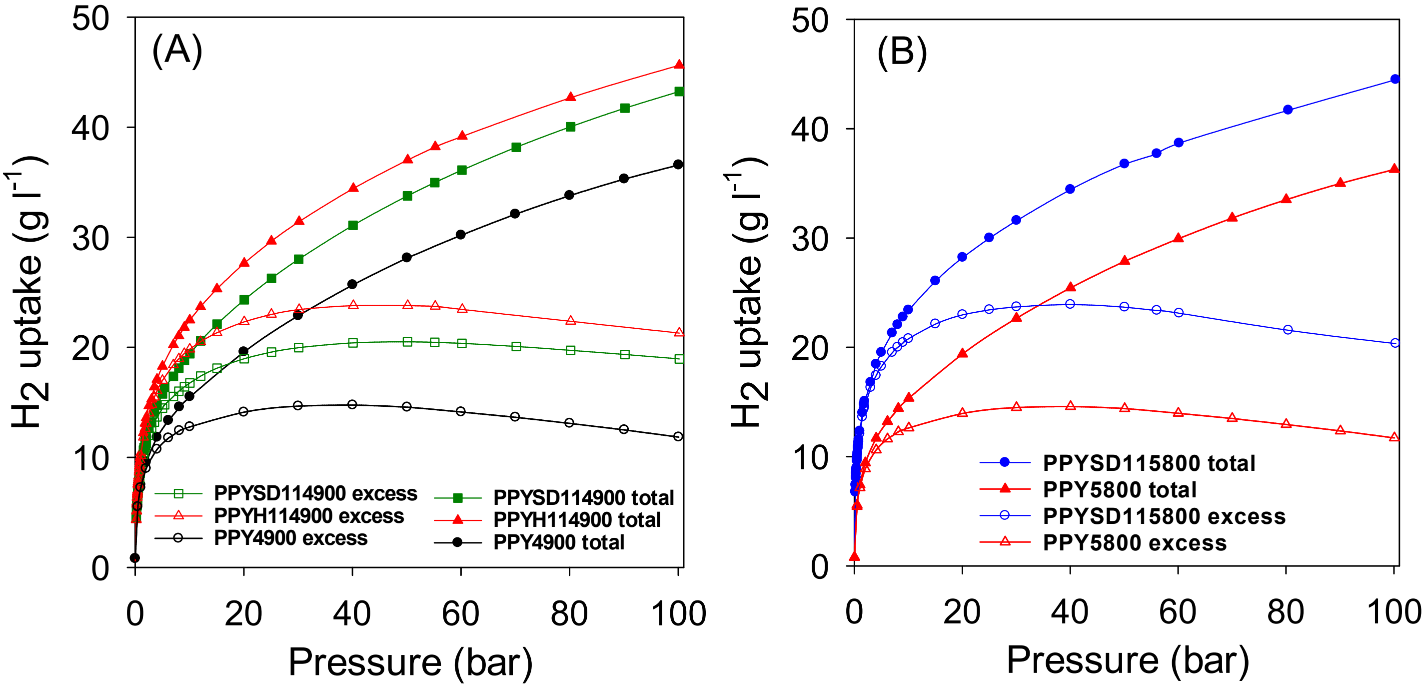


Figure S10. Volumetric hydrogen uptake isotherms of activated carbons derived from polypyrrole only (PPY5800 and PPY4900) or pre-mixed precursors containing polypyrrole and raw sawdust (A) or polypyrrole and sawdust-derived hydrochar (B).