Supporting Information

Low temperature synthesized carbon nanotube superstructures with superior CO_2 and hydrogen storage capacity

Beatrice Adeniran and Robert Mokaya*

University of Nottingham, University Park, Nottingham NG7 2RD, U. K.
E-mail: r.mokaya@nottingham.ac.uk (R. Mokaya)

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:

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

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

Supporting Table S1. Textural properties and CO_2 uptake at 25 ^oC and 1 bar for activated CN2T samples prepared between 500 and 700 ^oC.

Sample	Surface area ($m^2\ g^{-1}$)	Micropore surface area ($m^2\ g^{-1}$)[a]	Pore volume ($cm^3\ g^{-1}$)	Micropore volume ($cm^3\ g^{-1}$)[b]	Pore size[c] (Å)	CO_2 uptake at 25 ^oC and 1 bar (mmol g^{-1})
CN2500	1026	940 (92%)	0.56	0.41 (73%)	5.5/7	3.7
CN2550	1175	1091 (93%)	0.63	0.48 (76%)	5.5/7	4.2
CN2600	1479	1400 (95%)	0.83	0.67 (81%)	6/9/11	4.5
CN2650	1628	1577 (97%)	0.83	0.69 (83%)	7/8/9.5/12	4.8
CN2700	2102	1987 (95%)	1.18	0.95 (81%)	6/9/13	4.0

Supporting Table S2. CO_2 uptake at 0 ^oC of activated CNxT samples.

Sample	CO_2 uptake at 0 ^oC (mmol g^{-1})			
	1 bar	5 bar	10 bar	20 bar
CN2600	6.1	10.3	11.6	12.4
CN2650	8.4	13.4	14.8	15.5
CN2700	6.4	13.8	16.4	17.8
CN2800	4.6	13.9	19.8	25.4
CN2900	3.8	11.8	17.5	25.7
CN4800	3.3	11.0	16.8	26.4

Table S3. Total gravimetric hydrogen uptake for sample CN4800 under cryogenic (-196 ^{o}C) or room temperature conditions.

Pressure (bar)	Hydrogen uptake	
	Cryogenic (wt%)	Room temperature (wt%)
1	2.7	0.12
2	3.6	0.16
4	4.5	0.23
8	5.6	0.37
10	6.0	0.44
20	7.5	0.80
30	8.7	1.13
40	9.7	1.45
50	10.6	1.76
60	11.3	2.08
70	11.9	2.36
80	12.5	2.65
90	13.0	2.92
100	13.4	3.20
110	13.8	3.45
120	14.1	3.70
130	14.5	3.95
140	14.7	4.20
150	14.9	4.43

Table S4. Surface area, pore volume and hydrogen storage (at -196 ^{o}C) for sample CN4800 compared to the best benchmark metal organic frameworks (MOFs).

Sample	Surface area (m^2 g^{-1})	Pore Volume (cm^3 g^{-1})	Gravimetric H_2 uptake (wt%) Excess[a]	Total[b]	Reference
CN4800	3802	2.98	6.0	12.5 (14.9)[c]	This work
MOF-5	3800	1.55	7.1	9.6 (11.1)[c]	1
MOF-177	4740	1.89	7.1	11.3	2
NOTT-112	3800	1.62	7.1	10.0	3
NU-100	6143	2.82	9.2	16.4	4
MOF-210	6240	3.60	8.3	17.6	5

[a]Excess H_2 uptake at ca. 40 bar. [b]Total H_2 uptake at 80 bar. [c]Values in parenthesis are total H_2 uptake at 150 bar.

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Table S5. Surface area, pore volume and hydrogen storage at room temperature (25 °C) for sample CN4800 compared to the best benchmark carbon and metal organic frameworks (MOFs).

Sample	Surface area (m^2/g)	Pore Volume (cm^3/g)	H_2 uptake (wt%) Excess	Total[a]	Reference
CN4800	3802	2.98	1.3	4.4	This work
Carbon KUA5	3183	1.25	1.0	2.7	1,2
ZTC	3800	1.70	1.2	2.9	3
ZTC	3600	1.66	1.3	2.8	4
MOF-5	3800	1.55	0.7	2.1	5
MOF-210	6240	3.60	0.5[b]	2.7[b]	6,7

[a]Total H_2 uptake at 25 °C and 150 bar. [b]uptake at 80 bar.

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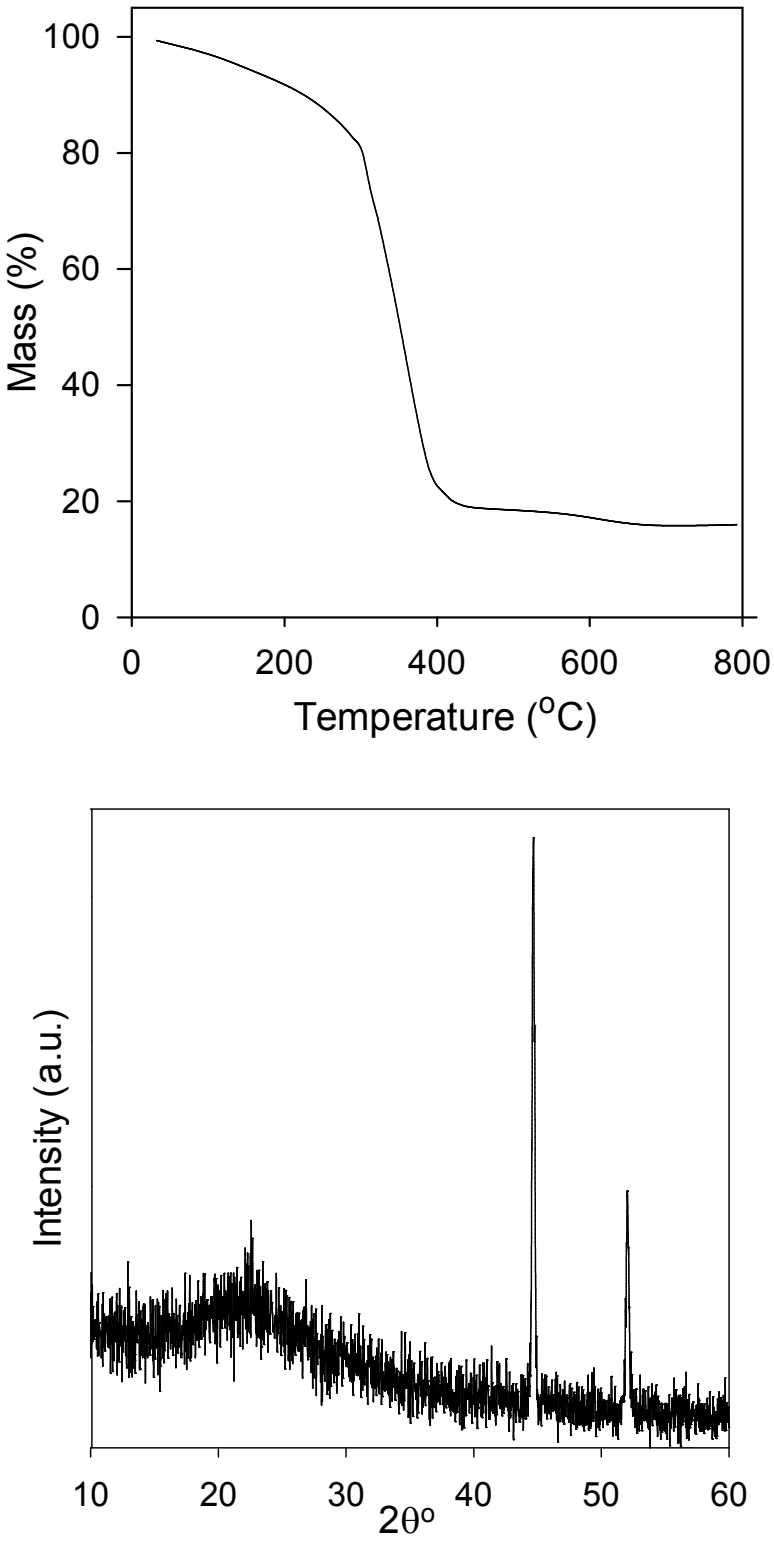
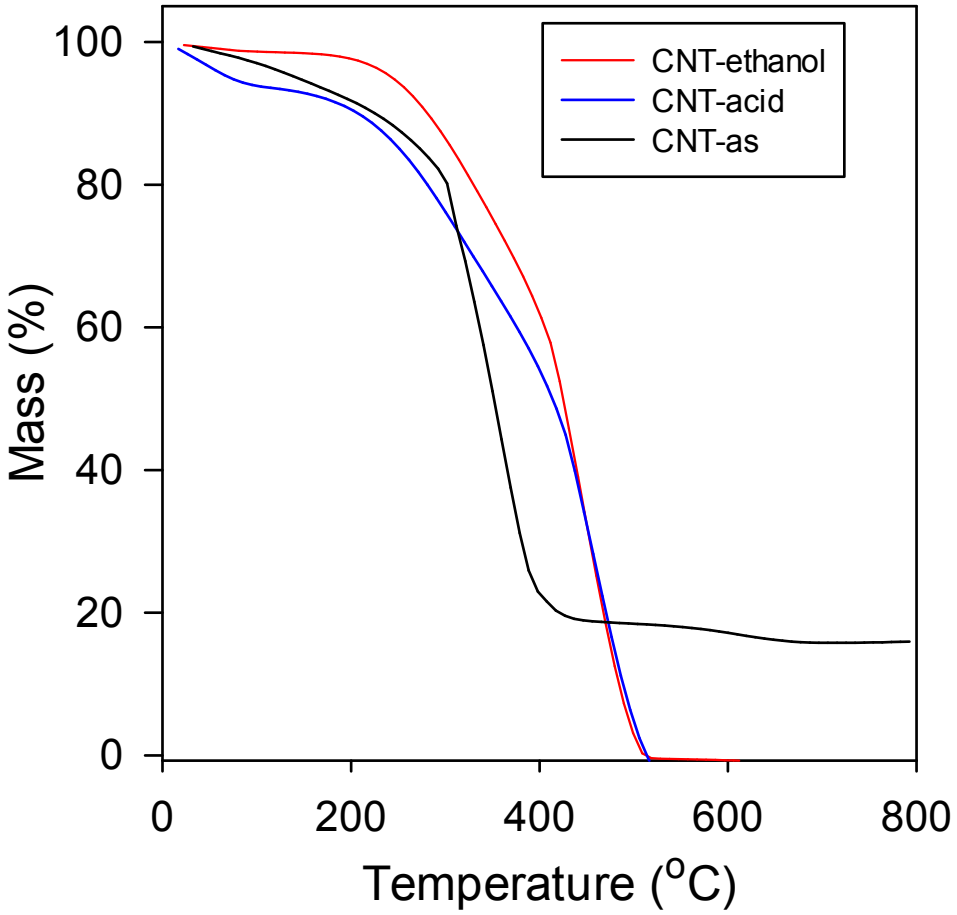
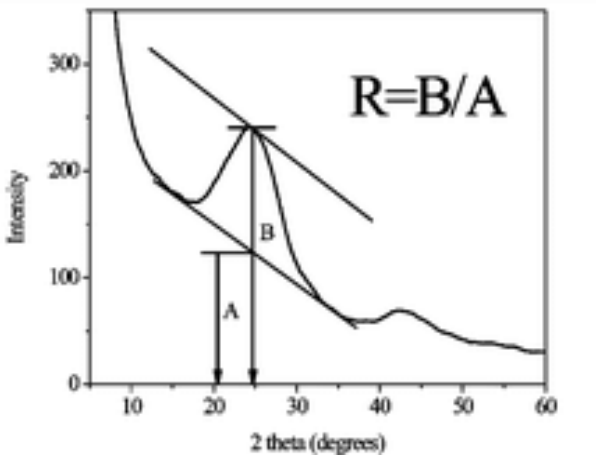


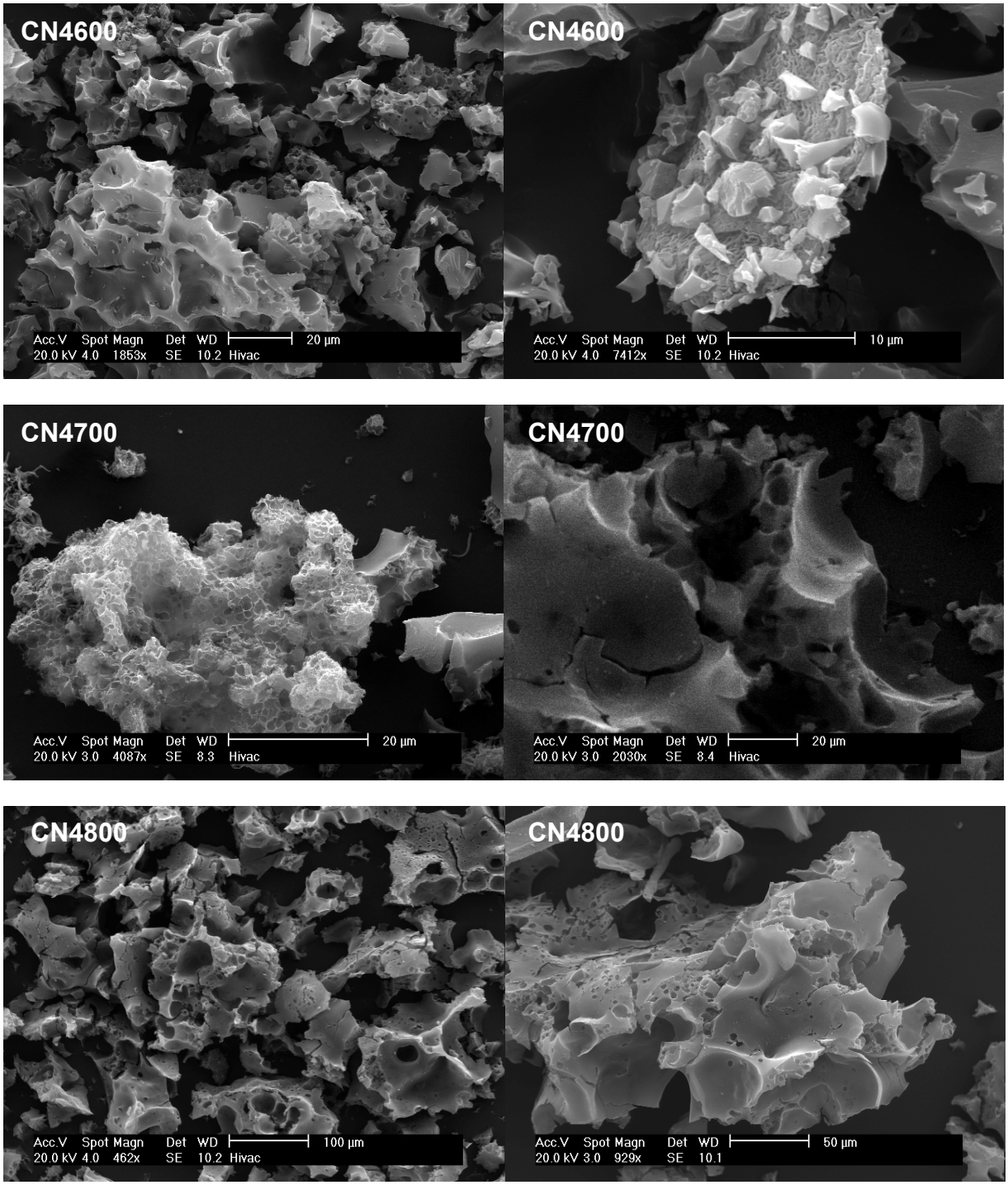
Supporting Figure S1. Thermogravimetric analysis (TGA) curve (top) and XRD pattern (bottom) of as-synthesised (CNT-as) sample.



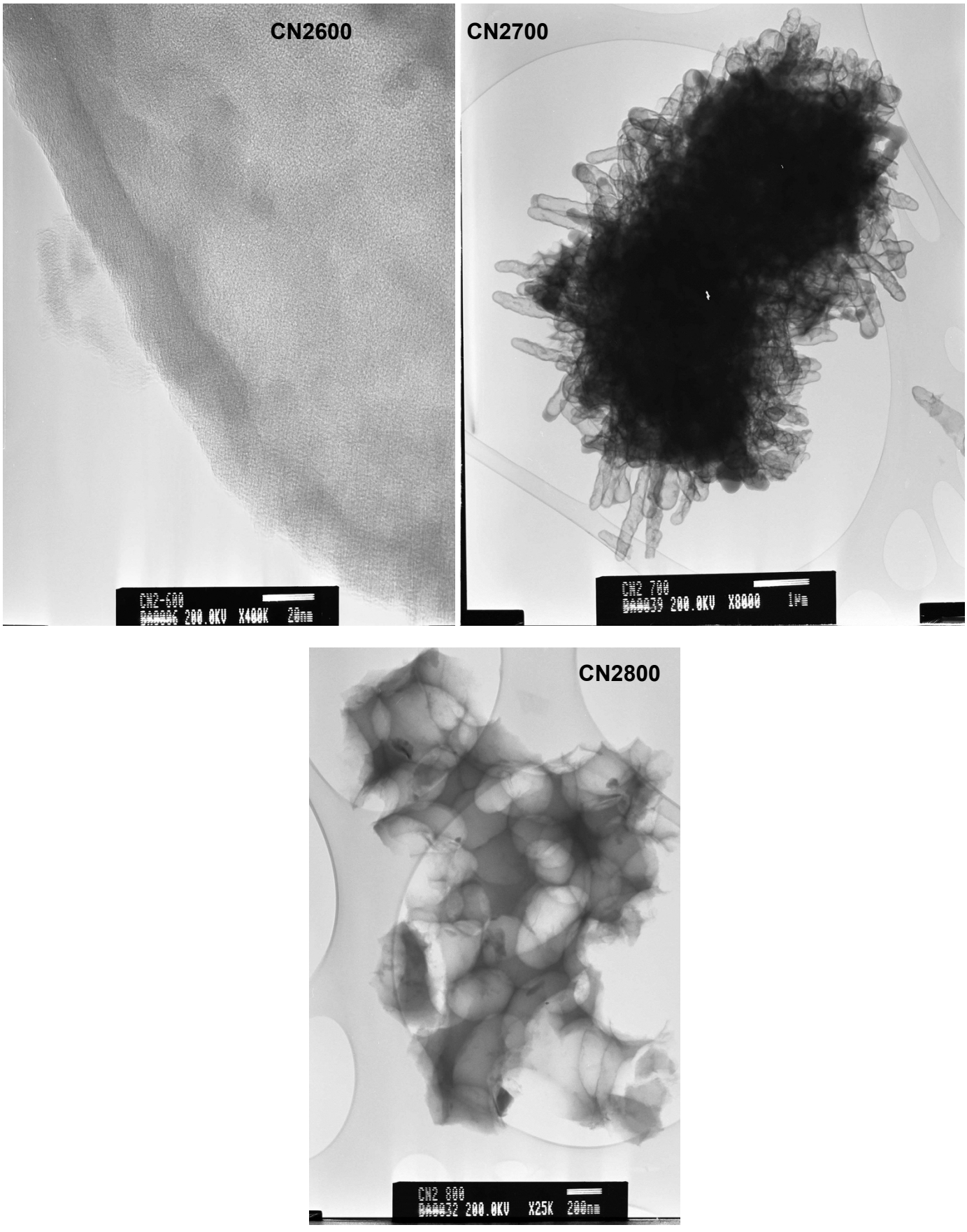
Supporting Figure S2. Thermogravimetric analysis curves of as-synthesised (CNT-as) sample, and after purification via washing in acid (CNT-acid) or ethanol (CNT-ethanol).



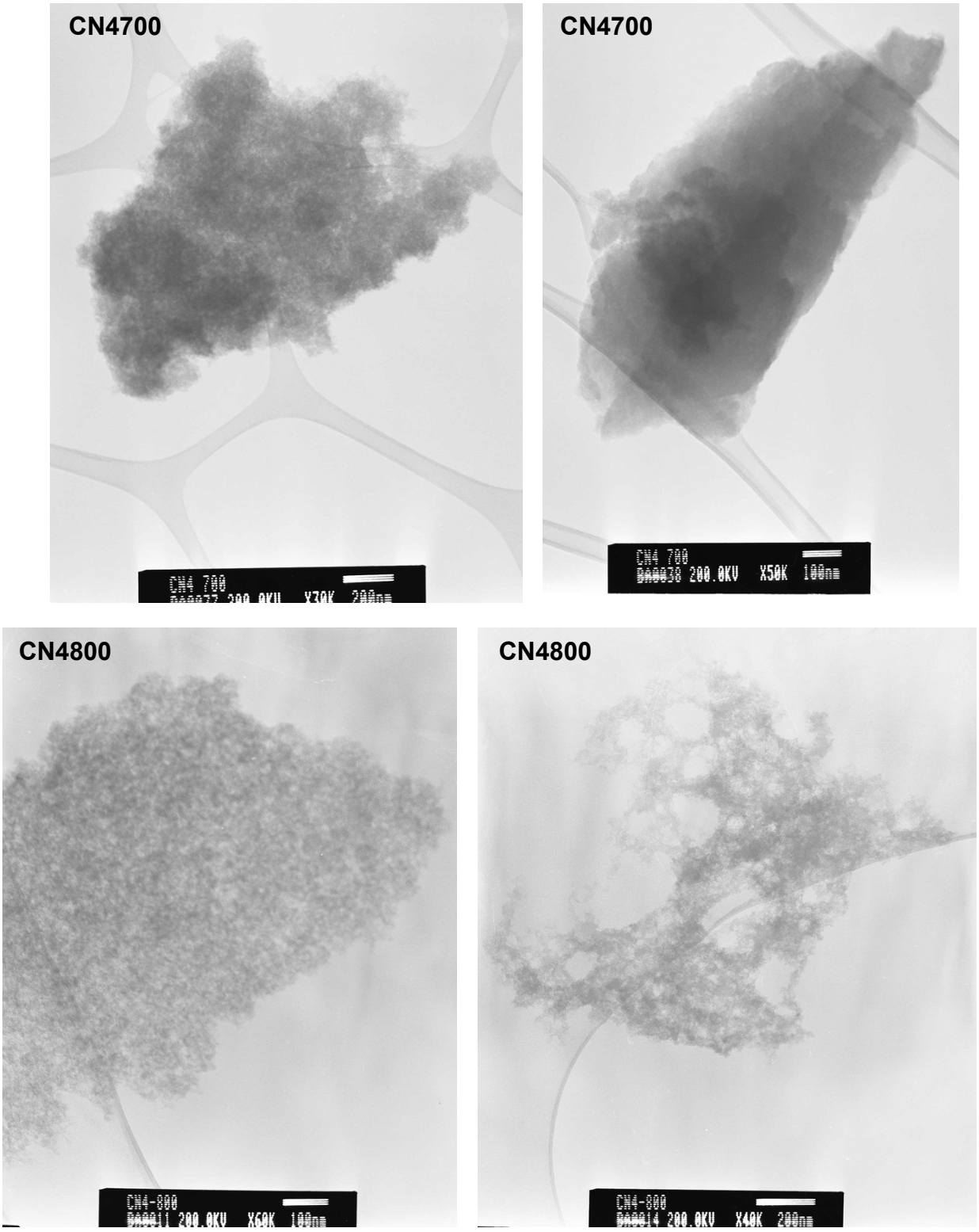
Supporting Figure S3. Illustration of calculating the R value from XRD patterns. Adapted from ref. 37.



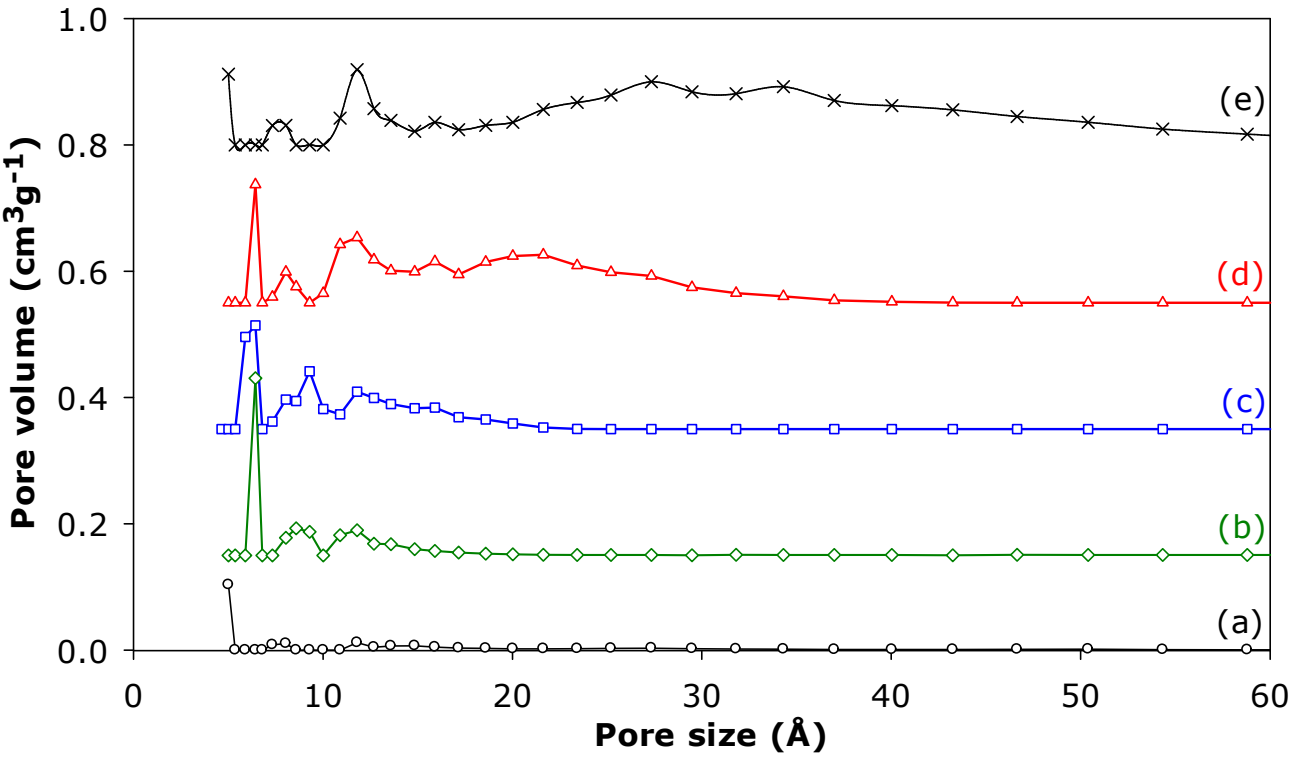
Supporting Figure S4. SEM images of activated CNT samples prepared at KOH/carbon ratio of 4 at various temperatures.



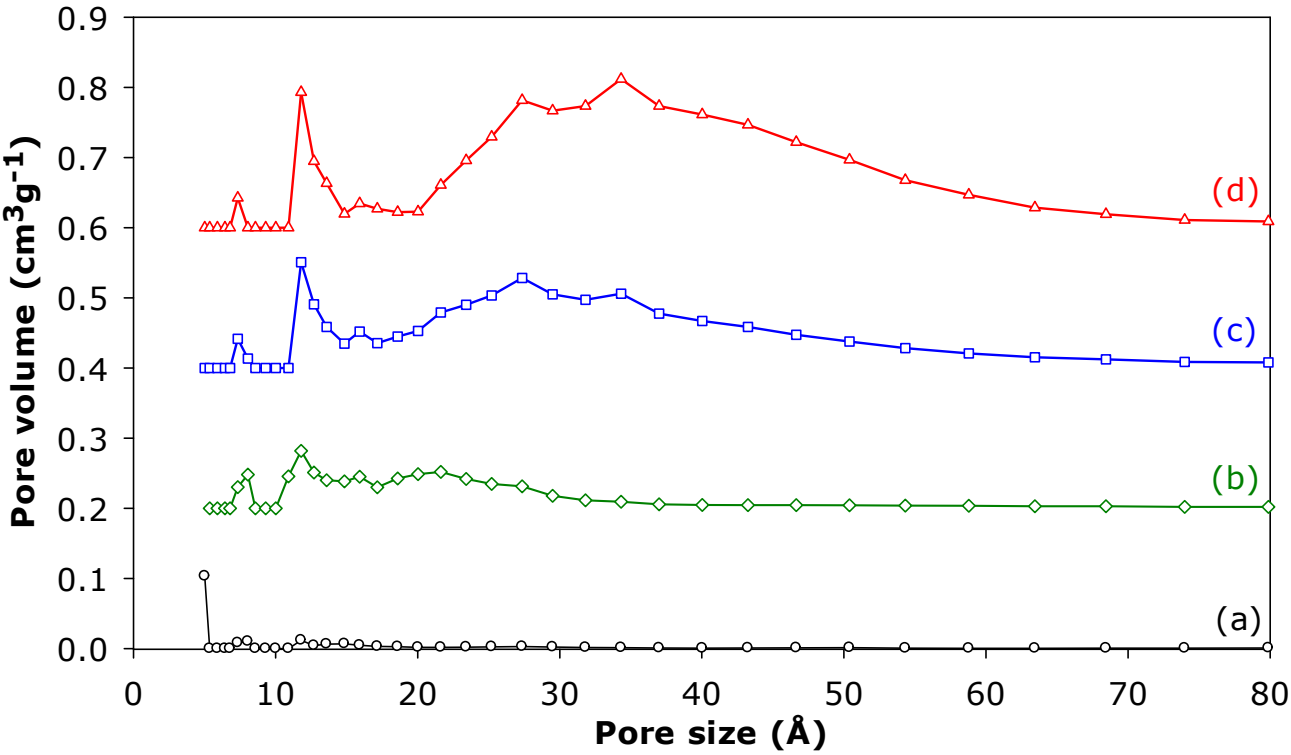
Supporting Figure S5. TEM images of activated CN2T samples.



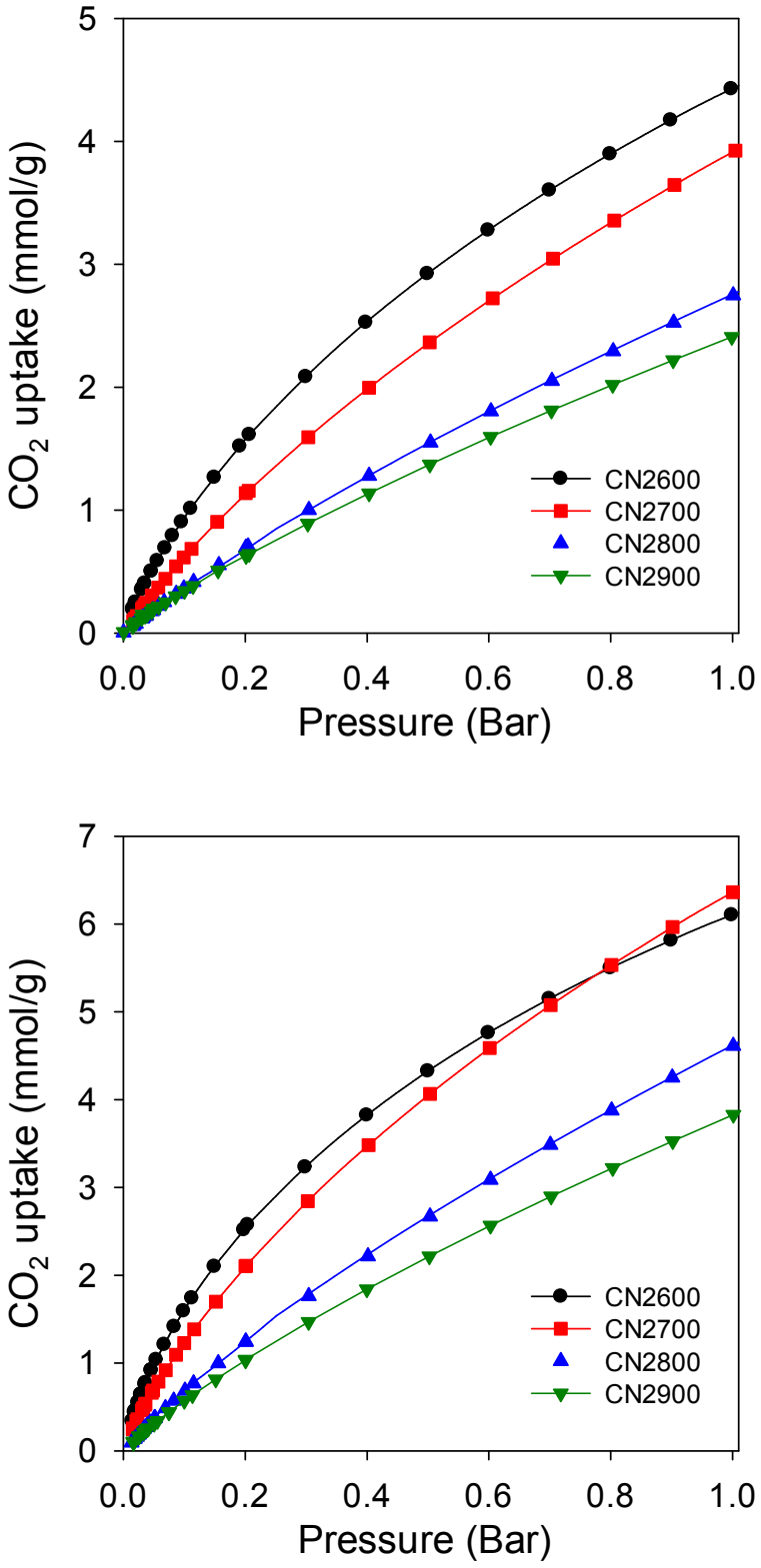
Supporting Figure S6. TEM images of activated CN4T samples.



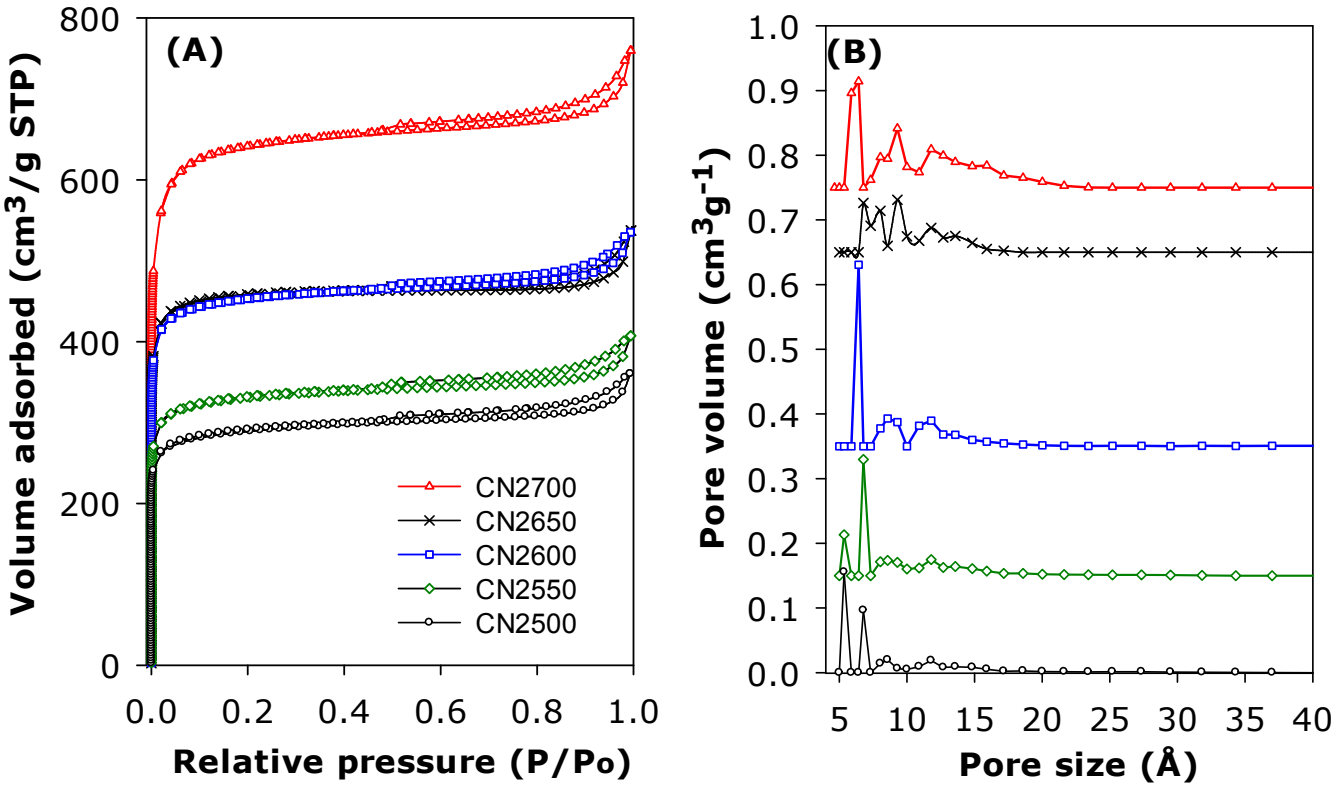
Supporting Figure S7. Pore size distribution curves of (a) pristine (CNT-as) sample, and activated CN2T samples; (b) CN2600, (c) CN2700, (d) CN2800 and (e) CN2900.



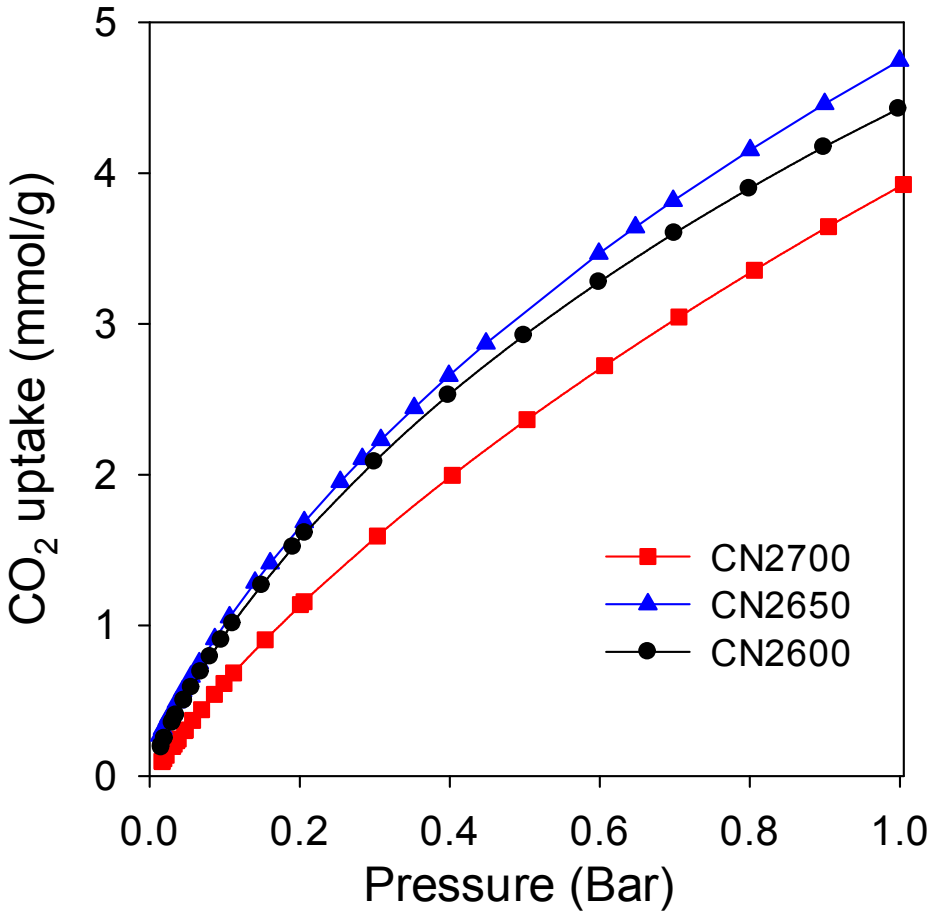
Supporting Figure S8. Pore size distribution curves of (a) pristine (CNT-as) sample and activated CN4T samples; (b) CN4600, (c) CN4700 and (d) CN4800.



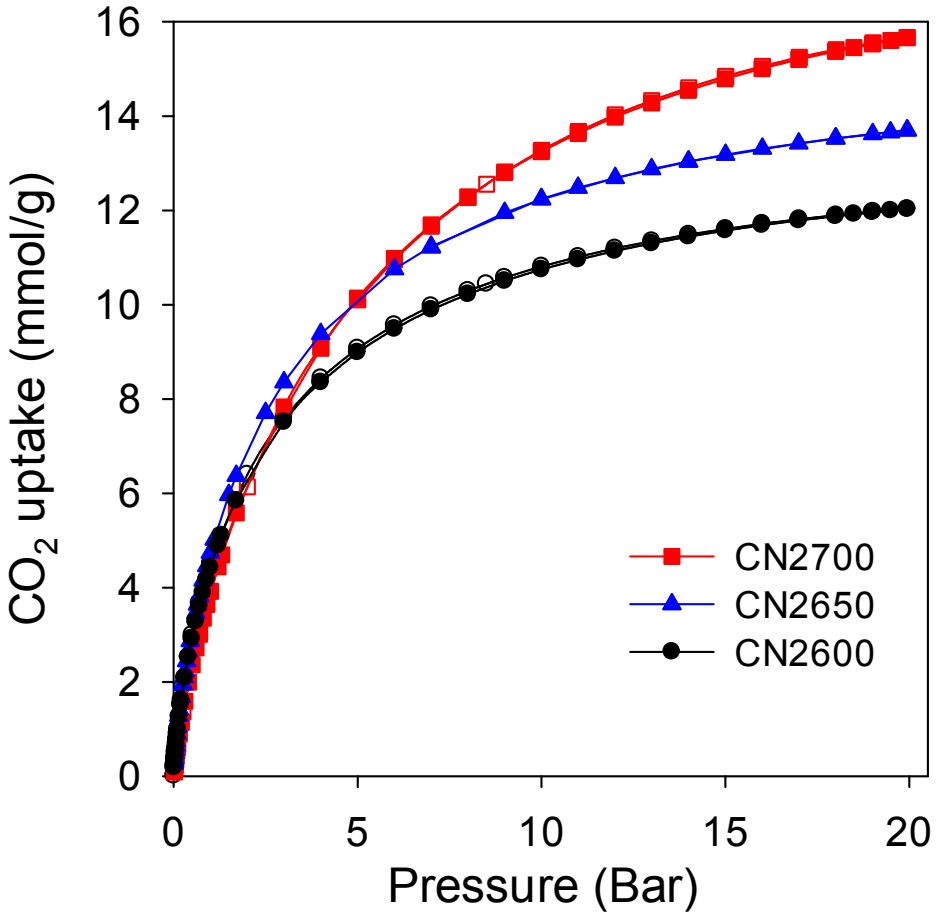
Supporting Figure S9. Low pressure CO_2 uptake isotherms for activated CN2T carbons at 25 °C (top panel) and 0 °C (bottom panel) in the pressure range 0 - 1 bar.



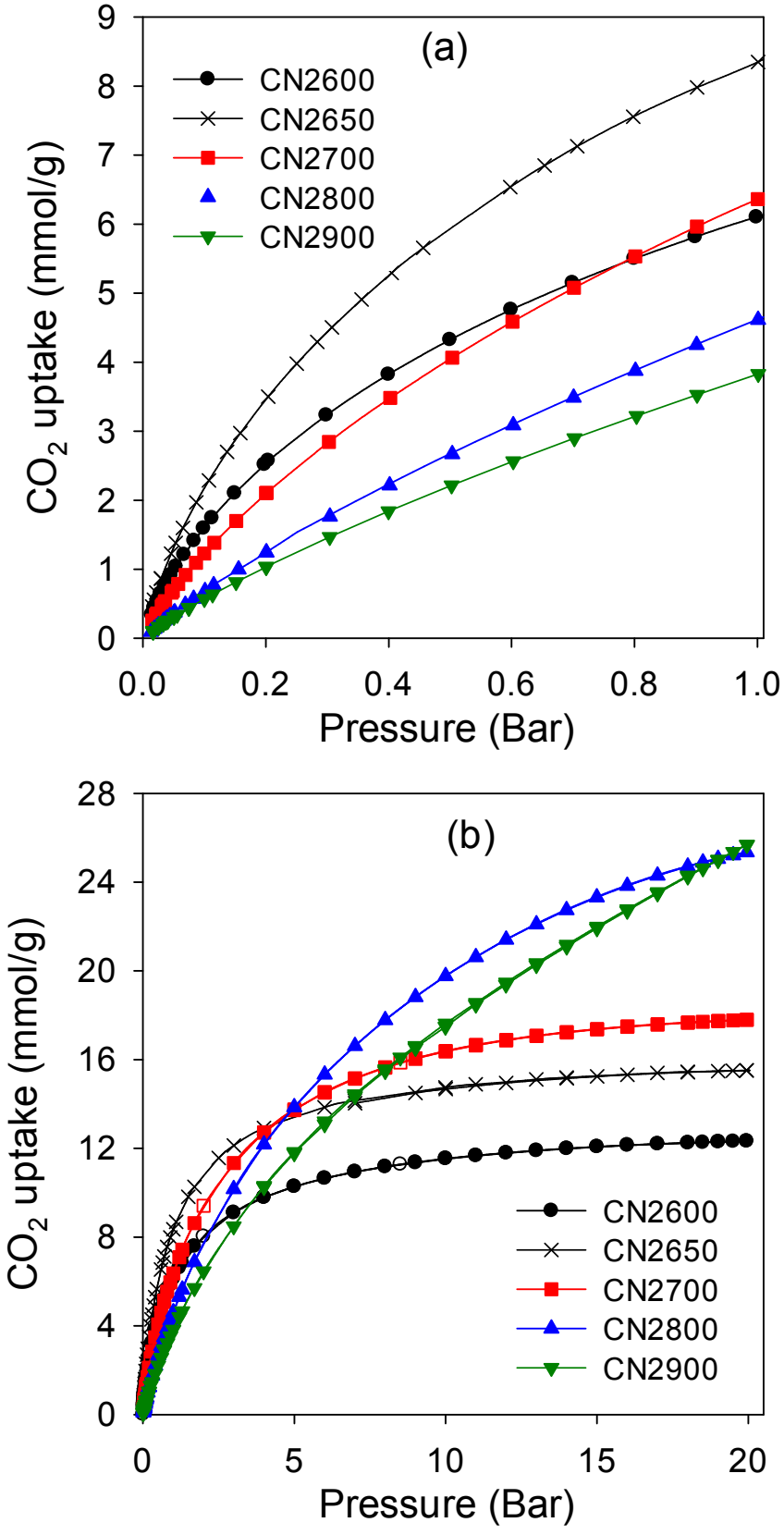
Supporting Figure S10. Nitrogen sorption isotherms (A) and pore size distribution curves (B) of activated CN2T samples prepared between 500 and 700 °C.



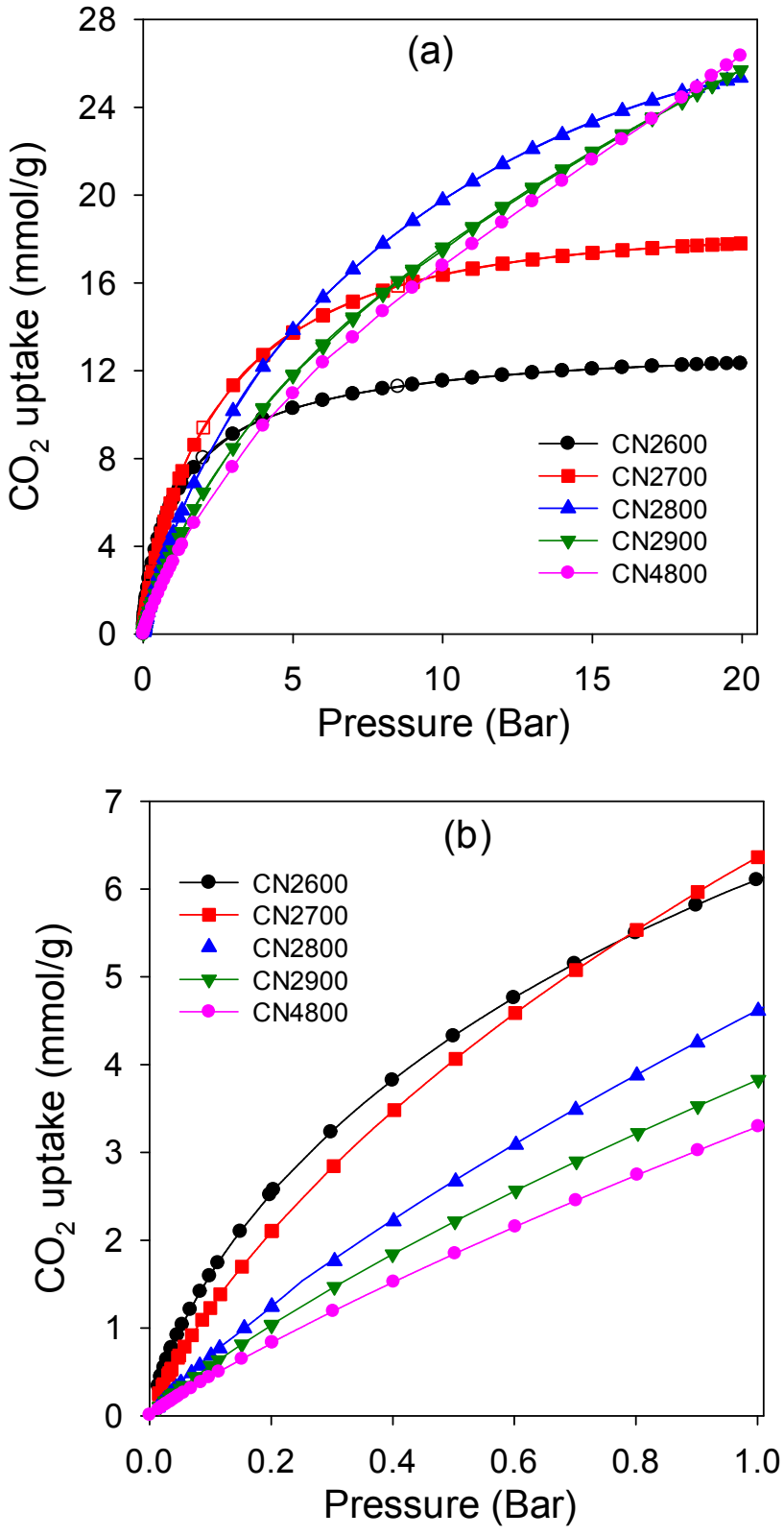
Supporting Figure S11. Low pressure CO_2 uptake isotherms at 25 ^oC for activated CN2T samples for T = 600, 650 and 700 ^oC.



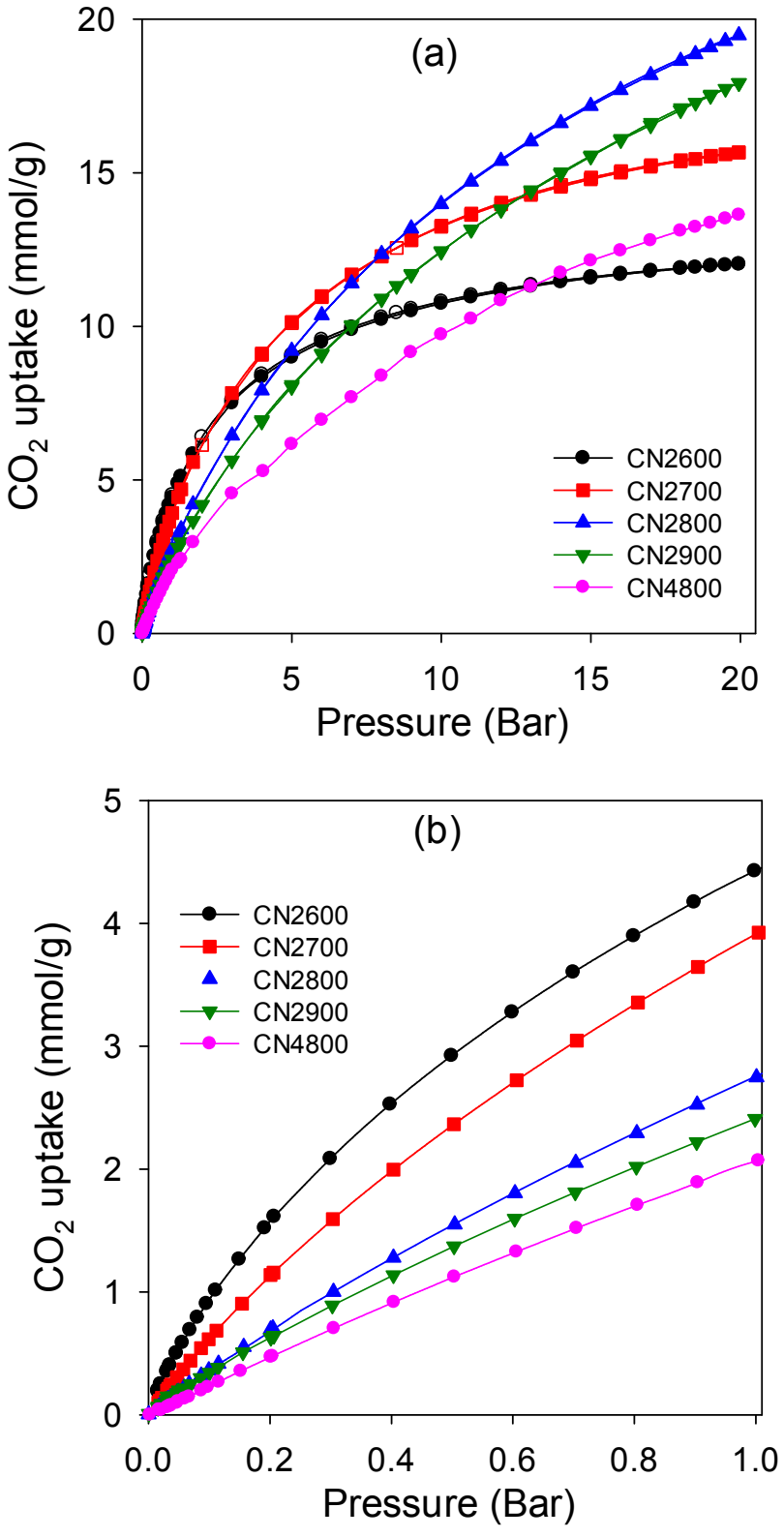
Supporting Figure S12. CO_2 uptake isotherms at 25 °C and 0 – 20 bar for activated CN2T samples for T = 600, 650 and 700 °C.



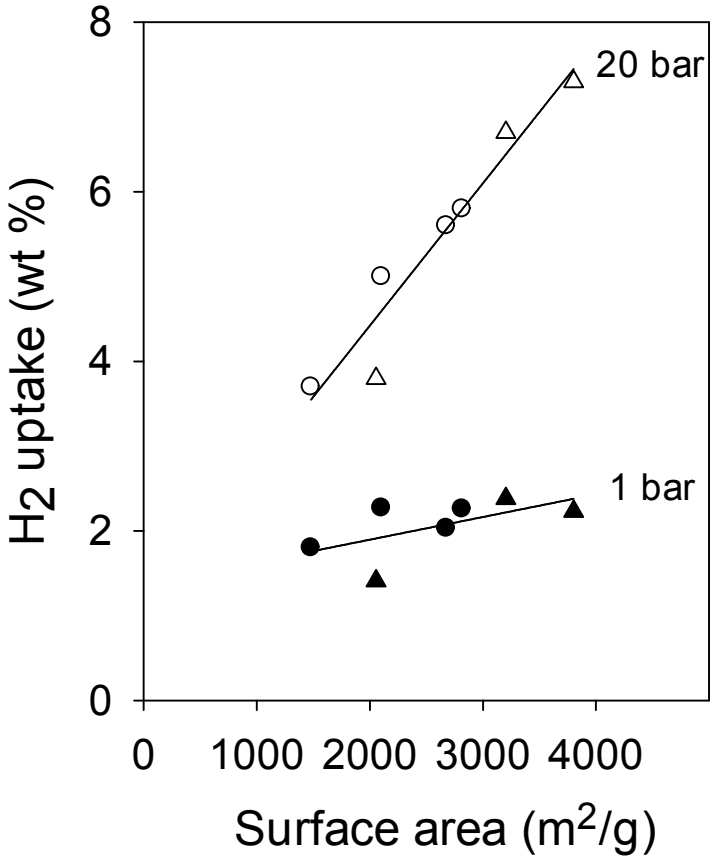
Supporting Figure S13. CO_2 uptake isotherms for activated CN2T samples at 0 ^oC and (a) low pressure (0 – 1 bar) and (b) 0 – 20 bar.



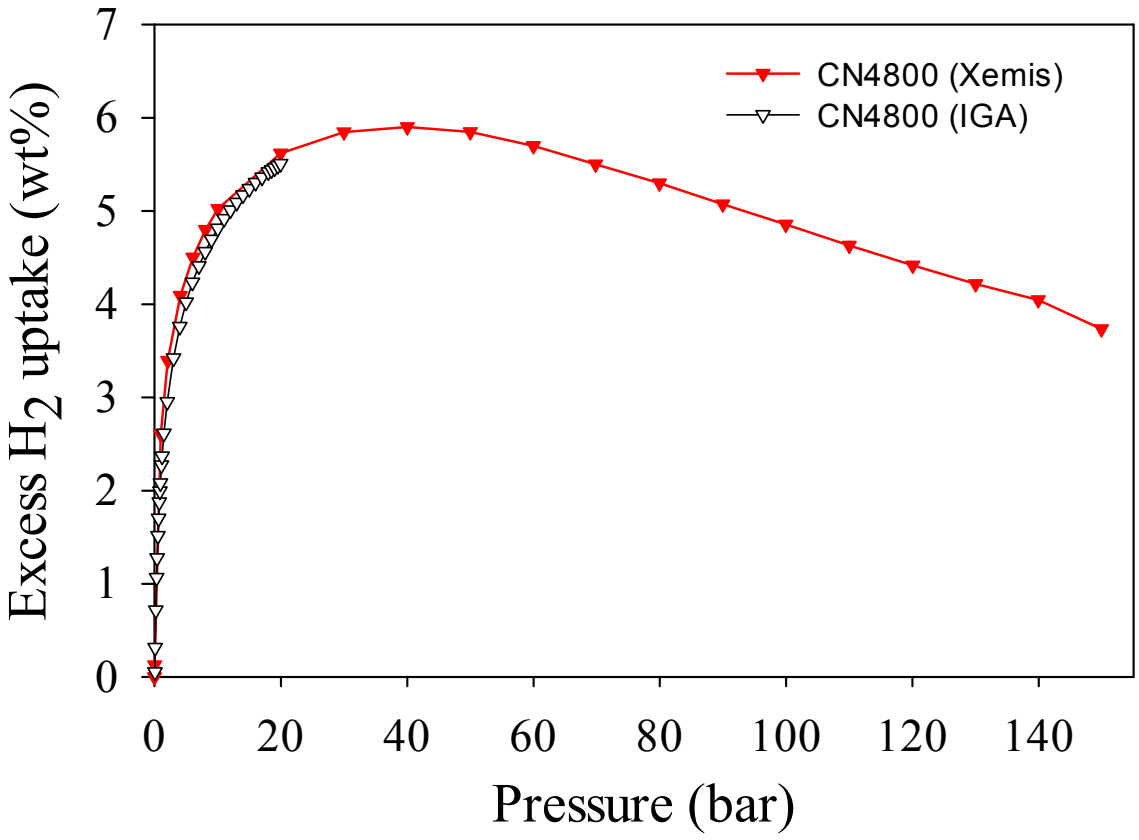
Supporting Figure S14. CO_2 uptake isotherms at 0 °C for sample CN4800 compared to CN2T samples; (a) 0 – 20 bar and (a) low pressure (0 – 1 bar).



Supporting Figure S15. CO_2 uptake isotherms at 25 °C for sample CN4800 compared to CN2T samples; (a) 0 – 20 bar and (a) low pressure (0 – 1 bar).



Supporting Figure S16. Plot of hydrogen uptake of CN2T (○,●) and CN4T (△,▲) samples, at 1 bar and 20 bar, as a function of surface area.



Supporting Figure S17. Excess hydrogen uptake data for sample CN4800 at -196 °C obtained on a Hiden IGA compared to that obtained on a Hiden Xemis analyser. There is close agreement between hydrogen uptake data from IGA and Xemis analysers in the range 0 – 20 bar.