

Supporting information

Roles of Surface Chemistry and Texture of Nanoporous Activated Carbons in CO₂ Capture

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SUMMARY

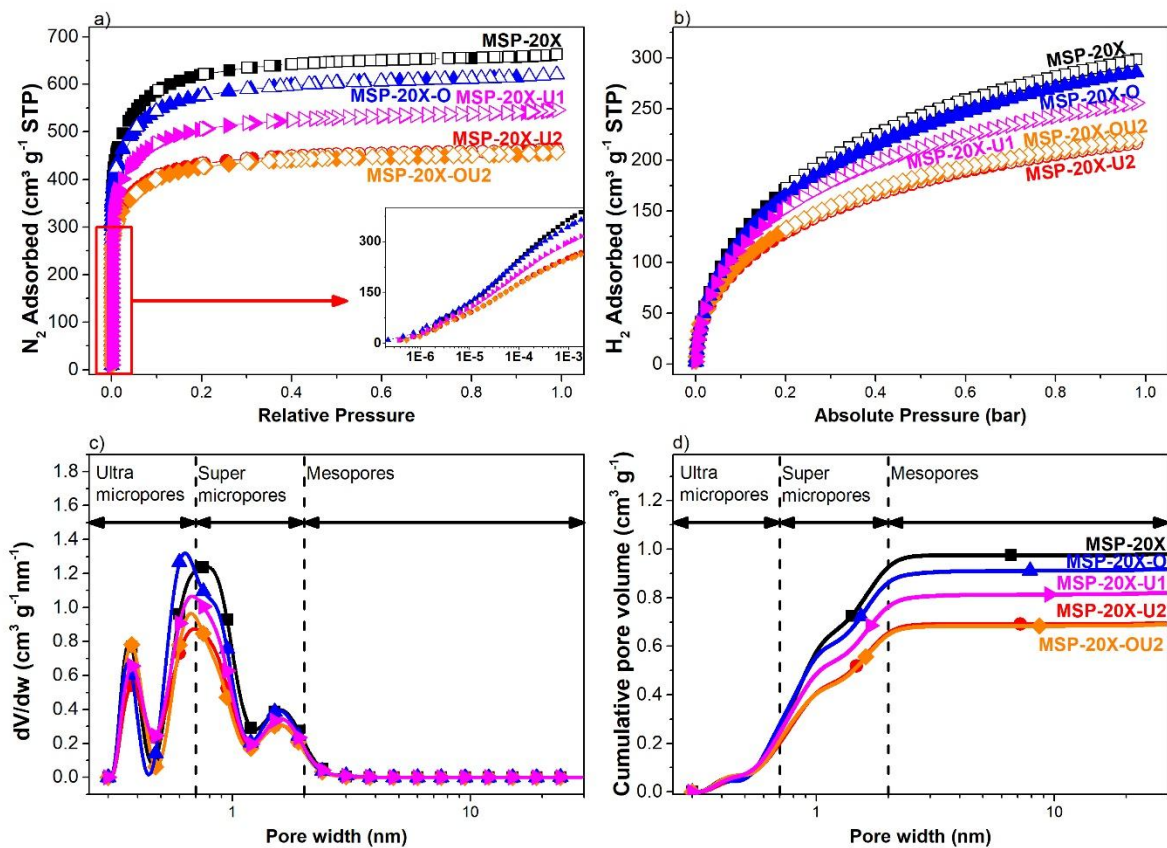
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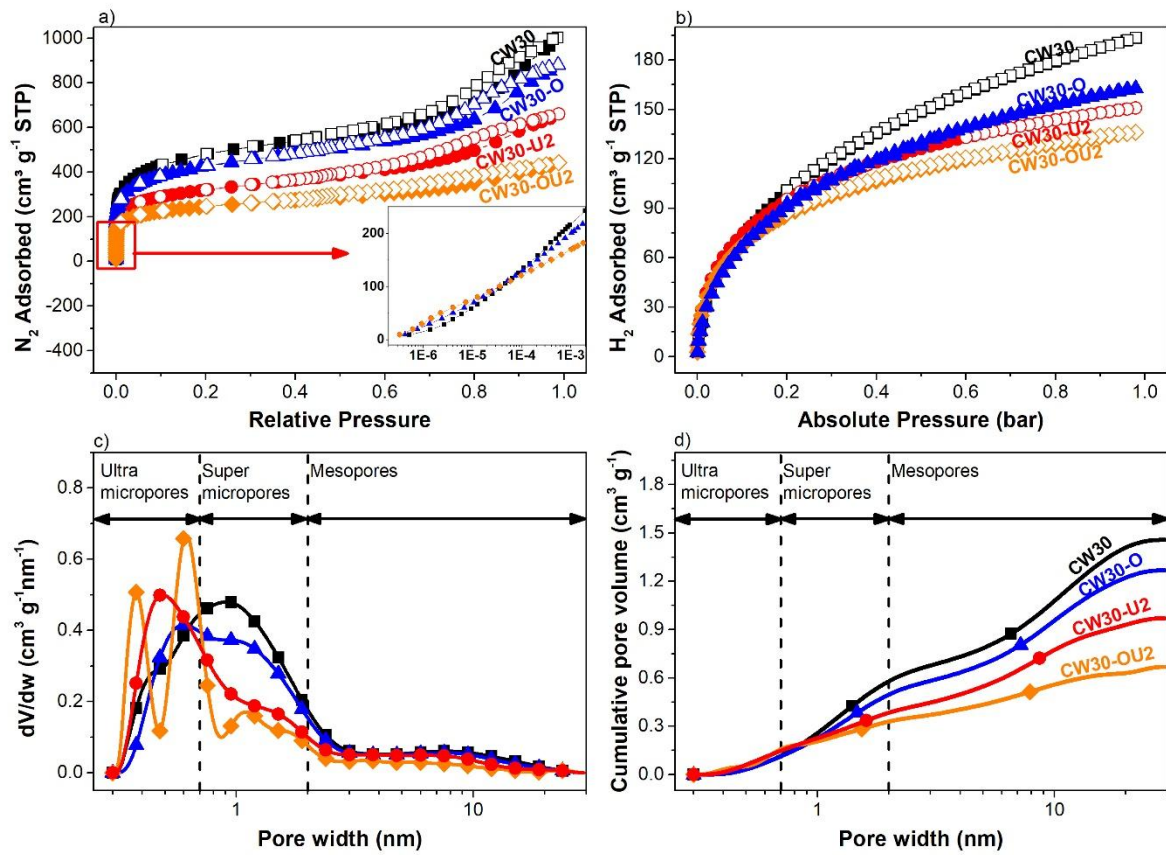
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SI 1. Textural properties calculated from N₂ and H₂ adsorption isotherms for all materials in this study.

Carbon Material	Textural Properties														
	A_{BET} [m ² /g]	S_{NLDFT} [m ² /g]	$V_{\mu\text{-DRN2}}$ [cm ³ /g]	V_{T} [cm ³ /g]	V_{MES} [cm ³ /g]	$V_{\text{ult-micro}}$ [cm ³ /g]	$X_{\text{ult-micro}}$ [%]	$V_{\text{sup-micro}}$ [cm ³ /g]	V_{micro} [cm ³ /g]	X_{micro} [%]	L_0 ult-micro [nm]	L_0 sup-micro [nm]	L_0 micro [nm]	L_0 meso [nm]	L_0 [nm]
MSP-20X	2344	2284	0.87	0.98	0.05	0.25	27	0.68	0.93	95	0.56	1.16	1.00	3.95	1.16
MSP-20X-U1	1901	1948	0.69	0.82	0.06	0.24	32	0.52	0.76	93	0.56	1.18	0.98	4.50	1.22
MSP-20X-U2	1630	1650	0.58	0.70	0.04	0.20	31	0.45	0.65	93	0.56	1.19	0.99	4.31	1.19
MSP-20X-O	2178	2170	0.78	0.92	0.06	0.28	33	0.58	0.86	93	0.57	1.17	0.98	5.02	1.22
MSP-20X-OU2	1600	1668	0.57	0.69	0.04	0.21	32	0.44	0.65	94	0.55	1.20	0.99	4.86	1.22
MSC-30	3200	2522	1.18	1.65	0.66	0.12	12	0.88	1.00	61	0.54	1.29	1.20	2.89	1.87
MSC-30-U1	2661	1918	0.90	1.31	0.50	0.07	9	0.74	0.80	61	0.64	1.28	1.23	2.90	1.87
MSC-30-U2	2230	2029	0.77	1.13	0.37	0.19	25	0.57	0.76	67	0.54	1.33	1.13	2.88	1.70
MSC-30-O	2982	2357	1.02	1.50	0.56	0.15	16	0.79	0.93	62	0.58	1.31	1.20	2.90	1.83
MSC-30-OU2	1981	1722	0.67	0.98	0.30	0.16	24	0.51	0.67	68	0.56	1.32	1.14	3.10	1.75
CW30	1736	1521	0.63	1.46	0.88	0.12	21	0.46	0.58	40	0.55	1.24	1.11	9.77	6.32
CW30-U2	1157	1192	0.42	0.97	0.59	0.15	39	0.24	0.38	39	0.53	1.24	0.97	9.04	5.84
CW30-O	1540	1325	0.54	1.27	0.77	0.11	22	0.38	0.50	39	0.56	1.26	1.10	9.57	6.25
CW30-OU2	898	1032	0.32	0.67	0.34	0.16	48	0.17	0.33	49	0.54	1.26	0.92	9.17	5.10



SI 2. Adsorption (full symbols) and desorption (empty symbols) isotherms at 77K of: (a) nitrogen, and (b) hydrogen; (c) pore size distributions; and (d) cumulative pore volumes calculated by the 2D-NLDFT model for pristine MSP-20X and MSP-20X-doped ACs. The insert in (a) shows nitrogen isotherms up to relative pressures of 10^{-3} .



SI 3. Same as Fig. SI 2 but for the pristine CW30 and CW30-doped ACs.

SI 4. Bulk composition measured by elemental analysis (EA).

Carbon Material	Elemental content				
	C [wt. %]	H [wt. %]	O [wt. %]	N [wt. %]	O+N [wt. %]
MSP-20X	95.5	0.25	3.37	0.11	3.48
MSP-20X-U1	86.2	1.23	8.02	6.87	14.9
MSP-20X-U2	85.8	1.07	6.95	10.5	13.8
MSP-20X-O	86.8	1.25	12.9	0.04	12.9
MSP-20X-OU2	80.4	1.45	9.50	13.2	22.7
MSC-30	95.0	0.55	3.99	0.30	4.29
MSC-30-U1	82.8	1.42	8.51	7.68	16.2
MSC-30-U2	79.0	1.63	8.09	12.0	20.0
MSC-30-O	87.6	1.33	13.7	0.16	13.8
MSC-30-OU2	79.9	1.36	8.98	12.9	21.9
CW30	77.5	3.21	19.5	0.22	19.8
CW30-U2	69.2	2.99	21.2	15.1	36.3
CW30-O	73.9	3.33	28.0	0.22	28.3
CW30-OU2	68.0	3.17	18.0	16.5	34.5

SI 5. Surface composition measured by X-ray Photoelectron Spectroscopy (XPS).

Carbon Material	Element content*			
	C [wt. %]	O [wt. %]	N [wt. %]	O+N [wt. %]
MSP-20X	93.2	6.8	0.0	6.8
MSP-20X-U1	89.2	3.5	8.2	11.8
MSP-20X-U2	89.0	4.1	8.0	12.0
MSP-20X-O	90.6	9.4	0.0	9.4
MSP-20X-OU2	86.8	3.3	11.3	14.6
MSC-30	96.3	3.7	0.0	3.7
MSC-30-U1	91.7	3.3	5.8	9.1
MSC-30-U2	86.8	3.0	11.6	14.6
MSC-30-O	92.5	7.5	0.0	7.5
MSC-30-OU2	87.1	3.4	10.8	14.2
CW30	93.9	6.1	0.0	6.1
CW30-U2	80.2	7.7	13.9	21.6
CW30-O	85.9	14.1	0.0	14.1
CW30-OU2	79.5	7.7	14.6	22.3

* Atomic percentages were converted to weight percentages in order to directly compare XPS results with those from elemental analysis

SI 6. Relative contribution of the different surface oxygen groups of the materials in this study, measured by XPS.

Carbon Material	Oxygen groups			
	OI ¹ [%]	OII ² [%]	OIII ³ [%]	OIV ⁴ [%]
MSP-20X	28.5	69.3	2.2	0.0
MSP-20X-U1	52.0	43.5	2.2	2.3
MSP-20X-U2	50.2	43.6	6.2	0.0
MSP-20X-O	28.7	71.3	0.0	0.0
MSP-20X-OU2	63.5	30.6	6.0	0.0
MSC-30	25.5	63.5	7.8	3.2
MSC-30-U1	41.7	51.2	2.7	4.3
MSC-30-U2	48.0	43.4	5.2	3.3
MSC-30-O	15.5	75.0	7.2	2.3
MSC-30-OU2	56.1	36.8	4.7	2.4
CW30	45.5	34.9	10.3	9.4
CW30-U2	46.9	34.3	11.0	7.8
CW30-O	26.0	67.4	0.9	5.7
CW30-OU2	46.5	34.9	9.6	8.9

¹- quinonic carbonyl oxygen groups;

²- carbonyl oxygen groups in esters, anhydrides and hydroxyls;

³- non-carbonyl oxygen (ether type) groups in esters and anhydrides;

⁴- oxygen contained in carboxylic acids.

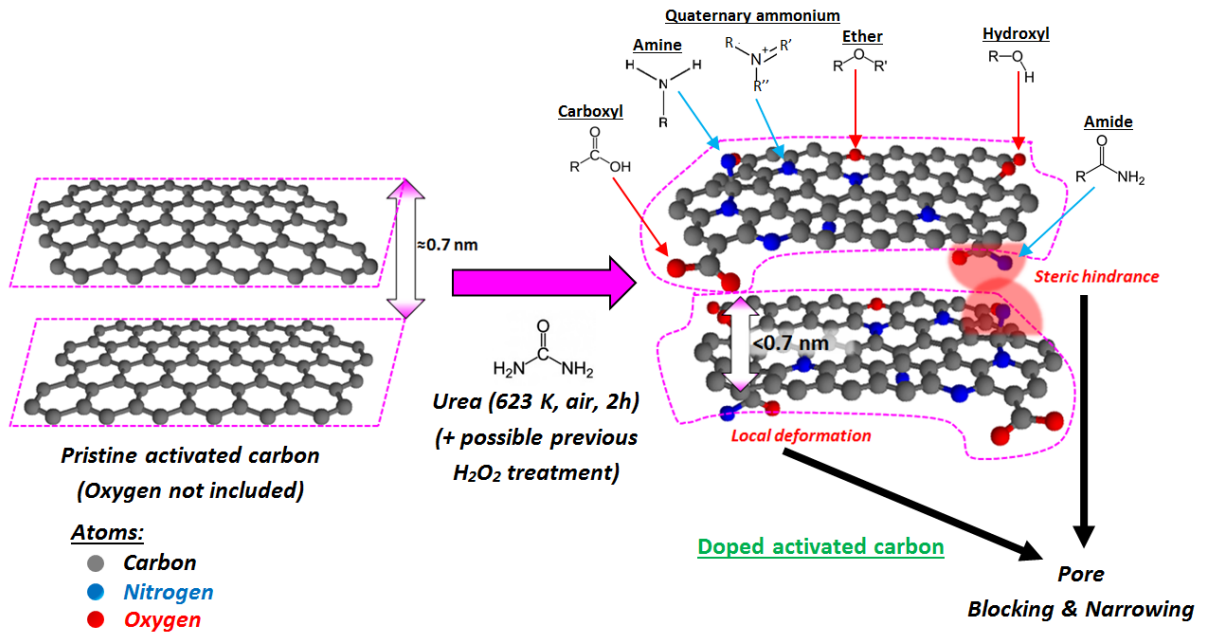
SI 7. Same as SI 6, but for nitrogen groups.

Carbon Material	Nitrogen groups		
	N5 ¹ [%]	N6 ² [%]	NQ ³ [%]
MSP-20X	-	-	-
MSP-20X-U1	56.6	34.6	10.8
MSP-20X-U2	52.5	34.4	13.1
MSP-20X-O	-	-	-
MSP-20X-OU2	53.3	37.5	9.2
MSC-30	-	-	-
MSC-30-U1	53.2	34.8	12
MSC-30-U2	46.3	39.9	13.7
MSC-30-O	-	-	-
MSC-30-OU2	47.4	41.7	10.9
CW30	51.3	33.5	14.9
CW30-U2	58.6	38.2	3.2
CW30-O	-	-	-
CW30-OU2	54	37.3	8.9

¹- pyrrolic groups;

²- pyridinic groups;

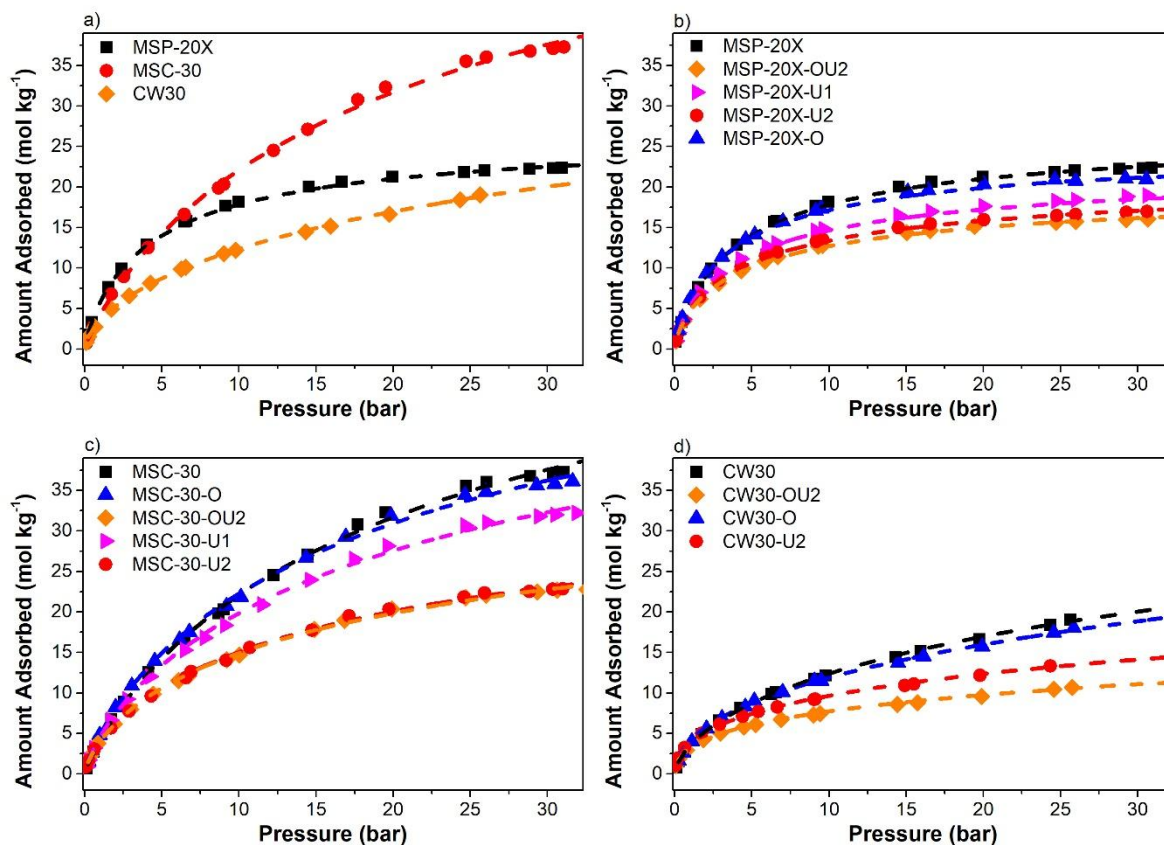
³- quaternary nitrogen groups.



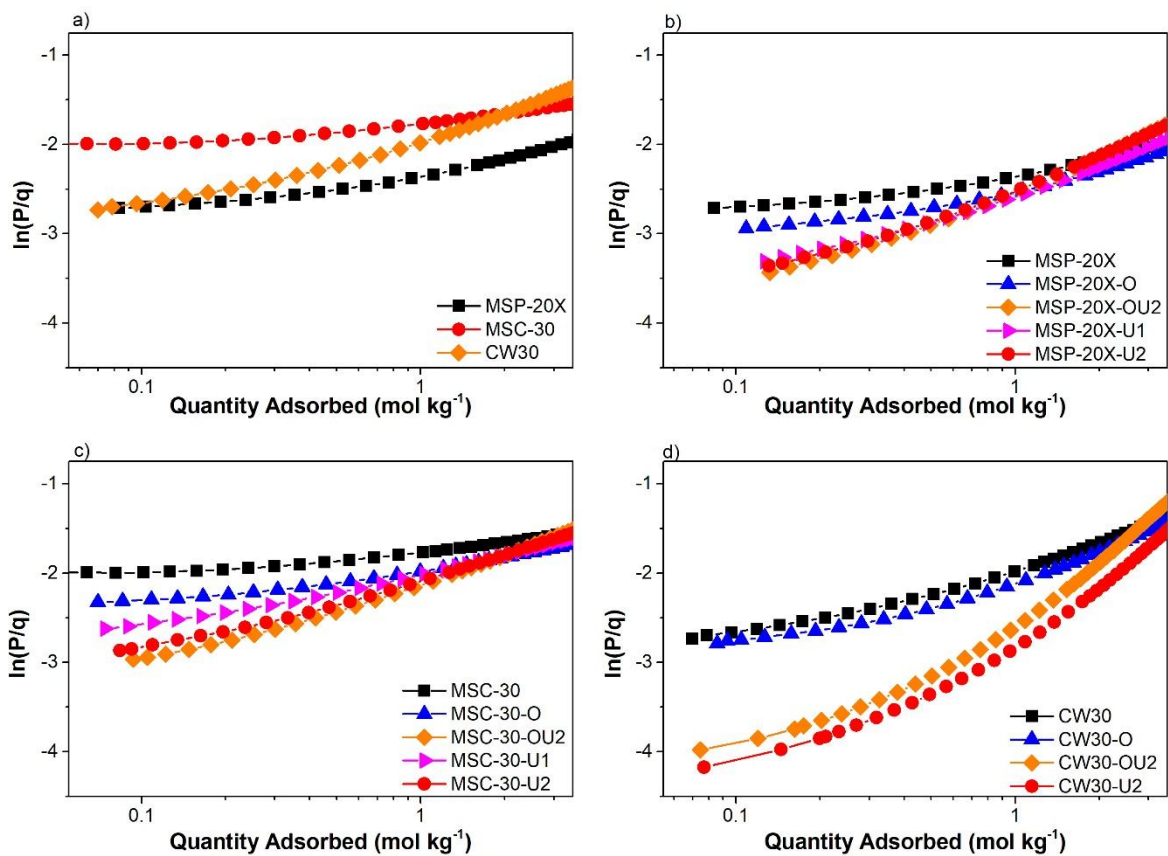
SI 8. Simplified pore narrowing and blocking mechanism due to the incorporation of N- and O- functional groups.

SI 9. Determination coefficients (R^2) between textural and chemical properties. A color gradient from red to green was used to differentiate the smallest (red) and the largest (green) values in the same row.

		XPS			EA			Textural Properties													
		O	N	O+N	O	N	O+N	A_{BET}	$S_{2D-NLDFT}$	V_T	V_{MES}	$V_{ult-μ}$	$X_{ult-μ}$	$V_{sup-μ}$	$V_{μ}$	$X_{μ}$	$L_0_{ult-μ}$	$L_0_{sup-μ}$	$L_0_{μ}$	L_0_{meso}	L_0
Elemental	O		0.10	0.05	0.65	0.18	0.10	0.09	0.12	0.02	0.15	0.01	0.03	0.11	0.12	0.20	0.01	0.02	0.04	0.47	0.42
	N	0.10		0.73	0.04	0.59	0.44	0.44	0.46	0.17	0.00	0.01	0.24	0.46	0.49	0.07	0.10	0.02	0.11	0.15	0.13
	O+N	0.05	0.73		0.41	0.31	0.73	0.73	0.79	0.12	0.07	0.03	0.35	0.78	0.83	0.27	0.14	0.00	0.20	0.61	0.54
XPS	O	0.65	0.04	0.41		0.00	0.54	0.32	0.50	0.01	0.35	0.14	0.06	0.39	0.51	0.53	0.02	0.01	0.02	0.74	0.79
	N	0.18	0.59	0.31	0.00		0.45	0.36	0.35	0.42	0.08	0.00	0.34	0.39	0.37	0.00	0.05	0.02	0.15	0.01	0.00
	O+N	0.10	0.44	0.73	0.54	0.45		0.68	0.85	0.14	0.06	0.08	0.34	0.78	0.89	0.31	0.07	0.04	0.14	0.48	0.47
Textural Properties	A_{BET}	0.09	0.44	0.73	0.32	0.36	0.68		0.86	0.48	0.01	0.02	0.68	0.98	0.87	0.04	0.17	0.09	0.58	0.58	0.32
	$S_{2D-NLDFT}$	0.12	0.46	0.79	0.50	0.35	0.85	0.86		0.21	0.04	0.06	0.37	0.88	0.98	0.24	0.06	0.00	0.24	0.65	0.54
	V_T	0.02	0.17	0.12	0.01	0.42	0.14	0.48	0.21		0.61	0.39	0.70	0.41	0.19	0.27	0.05	0.30	0.72	0.01	0.04
	V_{MES}	0.15	0.00	0.07	0.35	0.08	0.06	0.01	0.04	0.61		0.71	0.21	0.00	0.04	0.85	0.00	0.36	0.33	0.19	0.53
	V_{ult}	0.01	0.01	0.03	0.14	0.00	0.08	0.02	0.06	0.39	0.71		0.28	0.00	0.05	0.65	0.09	0.44	0.42	0.05	0.28
	$X_{ult-μ}$	0.03	0.24	0.35	0.06	0.34	0.34	0.68	0.37	0.70	0.21	0.28		0.68	0.42	0.02	0.31	0.19	0.87	0.23	0.04
	$V_{sup-μ}$	0.11	0.46	0.78	0.39	0.39	0.78	0.98	0.88	0.41	0.00	0.00	0.68		0.91	0.08	0.19	0.04	0.51	0.60	0.37
	$V_{μ}$	0.12	0.49	0.83	0.51	0.37	0.89	0.87	0.98	0.19	0.04	0.05	0.42	0.91		0.27	0.11	0.00	0.26	0.67	0.57
	$X_{μ}$	0.20	0.07	0.27	0.53	0.00	0.31	0.04	0.24	0.27	0.85	0.65	0.02	0.08	0.27		0.01	0.36	0.10	0.37	0.75
	$L_0_{ult-μ}$	0.01	0.10	0.14	0.02	0.05	0.07	0.17	0.06	0.05	0.00	0.09	0.31	0.19	0.11	0.01		0.01	0.23	0.13	0.07
	$L_0_{sup-μ}$	0.02	0.02	0.00	0.01	0.02	0.04	0.09	0.00	0.30	0.36	0.44	0.19	0.04	0.00	0.36	0.01		0.53	0.03	0.03
	$L_0_{μ}$	0.04	0.11	0.20	0.02	0.15	0.14	0.58	0.24	0.72	0.33	0.42	0.87	0.51	0.26	0.10	0.23	0.53		0.21	0.01
	L_0_{meso}	0.47	0.15	0.61	0.74	0.01	0.48	0.58	0.65	0.01	0.19	0.05	0.23	0.60	0.67	0.37	0.13	0.03	0.21		0.85
	L_0	0.42	0.13	0.54	0.79	0.00	0.47	0.32	0.54	0.04	0.53	0.28	0.04	0.37	0.57	0.75	0.07	0.03	0.01	0.85	



SI 10. CO₂ adsorption isotherms at 273K and up to 10 bar on: (a) pristine commercial carbons; (b) MSP-20X series; (c) MSC-30 series; and (d) CW30 series. The solid lines are fits to the Sips adsorption model.



SI 11. Relative Virial plot for low-pressure CO₂ adsorption isotherms at 273K on: (a) pristine commercial carbons; (b) MSP-20X series; (c) MSC-30 series; and (d) CW30 series.

SI 12. Parameters obtained by applying the Sips model to the carbon dioxide adsorption isotherms.

Carbon Material	Sips adsorption model				
	q_s [mol kg ⁻¹]	k_s [bar ⁻¹]	n_s	R ² H. P. ^a	R ² L. P. ^b
MSP-20X	27.15	0.27	1.18	1.000	1.000
MSP-20X-U1	23.25	0.30	1.33	1.000	1.000
MSP-20X-U2	22.05	0.29	1.37	1.000	0.998
MSP-20X-O	25.12	0.32	1.22	1.000	0.998
MSP-20X-OU2	20.94	0.29	1.39	1.000	1.000
MSC-30	62.91	0.07	1.20	1.000	0.998
MSC-30-U1	55.27	0.09	1.33	1.000	0.996
MSC-30-U2	47.48	0.09	1.48	0.999	0.996
MSC-30-O	50.70	0.11	1.21	1.000	0.999
MSC-30-OU2	38.21	0.12	1.44	1.000	1.000
CW30	32.72	0.12	1.47	1.000	0.993
CW30-U2	29.45	0.15	2.07	1.000	0.996
CW30-O	27.59	0.16	1.52	0.999	0.998
CW30-OU2	16.72	0.25	1.96	1.000	0.997

^a Using the CO₂ isotherm data at high pressure measured in an HPVA II;

^b Using the CO₂ isotherm data at low pressure measured in an ASAP 2420.

SI 13. Determination coefficients (R^2) between the Sips parameters and textural and chemical properties. A color gradient from red to green was used to differentiate the smallest (red) and the largest (green) values in the same row.

	XPS			Elemental			Textural Properties													
	O	N	O+N	O	N	O+N	A_{BET}	$S_{2\text{D-NLDFT}}$	V_{T}	V_{MES}	$V_{\text{ult-micro}}$	$X_{\text{ult-micro}}$	$V_{\text{sup-micro}}$	V_{micro}	X_{micro}	$L_0_{\text{ult-micro}}$	$L_0_{\text{sup-micro}}$	L_0_{micro}	L_0_{meso}	L_0
q_s	0.10	0.11	0.26	0.10	0.09	0.19	0.69	0.36	0.68	0.24	0.31	0.71	0.59	0.34	0.07	0.11	0.49	0.84	0.30	0.04
k_s	0.01	0.00	0.00	0.01	0.01	0.00	0.19	0.02	0.65	0.64	0.64	0.45	0.13	0.01	0.48	0.02	0.76	0.71	0.01	0.08
n_s	0.06	0.48	0.71	0.37	0.46	0.83	0.62	0.74	0.11	0.07	0.07	0.41	0.72	0.82	0.35	0.16	0.02	0.20	0.49	0.50

SI 14. Experimental data set used to analyze the joint effect of surface textural and chemical characteristics.

Materials	Experimental CO ₂ uptake in mmol g ⁻¹ and wt. % (between brackets) at different pressures and 273K				
	0.1 bar	1 bar	5 bar	10 bar	25 bar
MSP-20X	1.0 (4.4)	5.5 (24.2)	14.0 (61.6)	18.0 (79.2)	21.9 (96.4)
MSP-20X-U1	1.2 (5.3)	5.1 (22.4)	11.7 (51.5)	14.9 (65.6)	18.3 (80.5)
MSP-20X-U2	1.2 (5.3)	4.7 (20.7)	10.7 (47.1)	13.5 (59.4)	16.5 (72.6)
MSP-20X-O	1.5 (6.6)	6.2 (27.3)	13.9 (61.2)	17.5 (77.0)	20.9 (91.9)
MSP-20X-OU2	1.1 (4.8)	4.5 (19.8)	10.2 (44.9)	12.9 (56.8)	15.7 (69.1)
MSC-30	0.6 (2.6)	4.2 (18.5)	14.1 (62.0)	21.5 (94.6)	35.6 (156.6)
MSC-30-U1	0.8 (3.5)	4.5 (19.8)	13.1 (57.6)	19.3 (84.9)	30.7 (135.1)
MSC-30-U2	0.9 (4.0)	4.0 (17.6)	10.3 (45.3)	14.6 (64.2)	21.9 (96.4)
MSC-30-O	0.9 (4.0)	4.9 (21.6)	14.7 (64.7)	21.7 (95.5)	34.5 (151.8)
MSC-30-OU2	1.0 (4.4)	4.1 (18.0)	10.4 (45.8)	14.6 (64.2)	21.8 (95.9)
CW30	0.8 (3.5)	3.4 (15.0)	8.7 (38.3)	12.2 (53.7)	18.7 (82.3)
CW30-U2	1.3 (5.7)	3.8 (16.7)	7.4 (32.6)	9.5 (41.8)	13.6 (59.8)
CW30-O	1.1 (4.8)	3.8 (16.7)	8.6 (37.8)	11.7 (51.5)	17.6 (77.4)