

Supporting Information

Synthesis of Perfectly Ordered Mesoporous Carbons by Water-assisted Mechanochemical Self-assembly of Tannin

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Table S1. Pore texture parameters, calculated from N₂ and CO₂ adsorption isotherms, of carbon materials: (i) prepared with various amounts of Pluronic® F127 and water, and used as references; (ii) obtained after various milling times; and (iii) synthesized with 2 g of aqueous HCl solutions with different pH values.

	Milling time [min]	S_{NLDFT} [m ² g ⁻¹]	A_{BET} [m ² g ⁻¹]	$V_{0.97,N_2}$ [cm ³ g ⁻¹]	$V_{\mu,NLDFT}$ [cm ³ g ⁻¹]	V_{meso} [cm ³ g ⁻¹]	F_{meso} [%]
(i) References							
CT2P0W0_60	60	829	578	0.25	0.23	0.02	8
CT2P0W2_60	60	503	231	0.10	0.11	--	--
CT2P2W0_60	60	672	466	0.36	0.17	0.19	53
(ii) Milling time							
CT2P2W2_30	30	735	543	0.46	0.18	0.28	60
CT2P2W2_45	45	683	497	0.46	0.16	0.30	64
CT2P2W2_60	60	695	522	0.47	0.16	0.30	65
CT2P2W2_75	75	703	521	0.44	0.17	0.27	61
CT2P2W2_90	90	709	538	0.46	0.18	0.28	61
CT2P2W2_120	120	663	484	0.40	0.16	0.24	60
(iii) pH							
CT2P2pH0_60	60	775	591	0.43	0.20	0.23	53
CT2P2pH1_60	60	713	533	0.51	0.17	0.34	67
CT2P2pH2_60	60	696	522	0.45	0.17	0.28	61
CT2P2pH3_60	60	713	528	0.44	0.18	0.26	60
CT2P2pH4_60	60	698	524	0.45	0.17	0.28	62

S_{NLDFT} and A_{BET} : specific surface areas calculated by applying NLDFT and BET models, respectively; $V_{0.97,N_2}$: total single point pore volume at relative pressure of 0.97; $V_{\mu,NLDFT}$: micropore volume from NLDFT model; $V_{meso} = V_{0.97,N_2} - V_{\mu,NLDFT}$: mesopore volume; $F_{meso} = V_{meso}/V_{0.97,N_2}$: mesopore fraction.

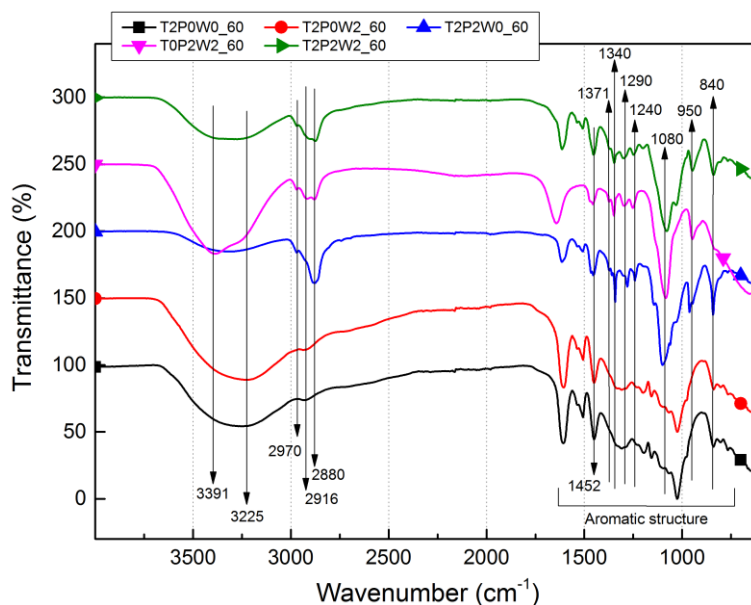


Figure S1. FTIR spectra of T2P2W2_60 and reference samples. The data were normalized with respect to a common peak (1452 cm^{-1}) and, for easier viewing, the spectra were shifted with respect to each other by 50% of transmittance.

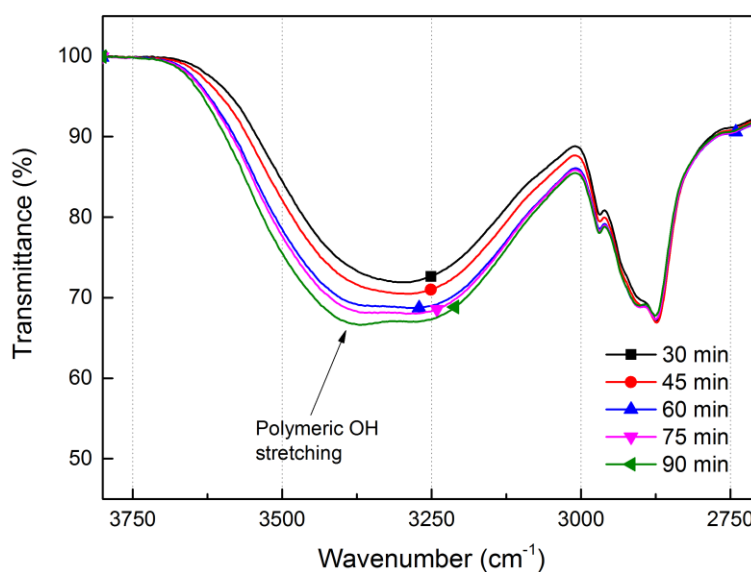


Figure S2. Detailed view of the FTIR spectra of samples T2P2W2_t synthesized during different milling times t, ranging from 30 to 90 min. For comparison, the data were normalized with respect to a common peak (1452 cm^{-1}).

Table S2. Peak assignment of FTIR spectra presented in Figure S1 and Figure S2.^{29–31}

Aromatic structure of mimosa tannin	
Wavenumber [cm ⁻¹]	Assignment
1606 ^{a)} , 1533, 1507	C=C stretching in pyrogallol-like B ring
1450 ^{b)}	C-C stretching in pyrogallol-like B ring
1200	C-O stretching of aromatic rings
1157 ^{c)}	Vibrations of resorcinol-like A ring
1025 ^{c)}	Overlapping stretching of C-O, C-C, C-OH, C-H bonds
766	Torsion of resorcinol-like A ring

Triblock copolymer Pluronic® F127	
Wavenumber [cm ⁻¹]	Assignment
3391	Polymeric OH stretching
2970, 2916, 2880, 1371, 1340, 950, 840	C-H bonds
1290, 1240, 1080	C-O bonds

^{a)} Some authors assigned this peak to OH bending or C=O stretching ^[29], explaining why a peak around 1640 cm⁻¹ also appears in TOP2W2_60 spectrum.

^{b)} This peak appears also in TOP2W2_60 spectrum because of the C-C bonds; however, the intensity is lower in comparison with the samples containing tannin.

^{c)} Low-intensity peak. For samples containing P, this peak overlaps the strong peak at 1080 cm⁻¹ due to the C-O bonds.

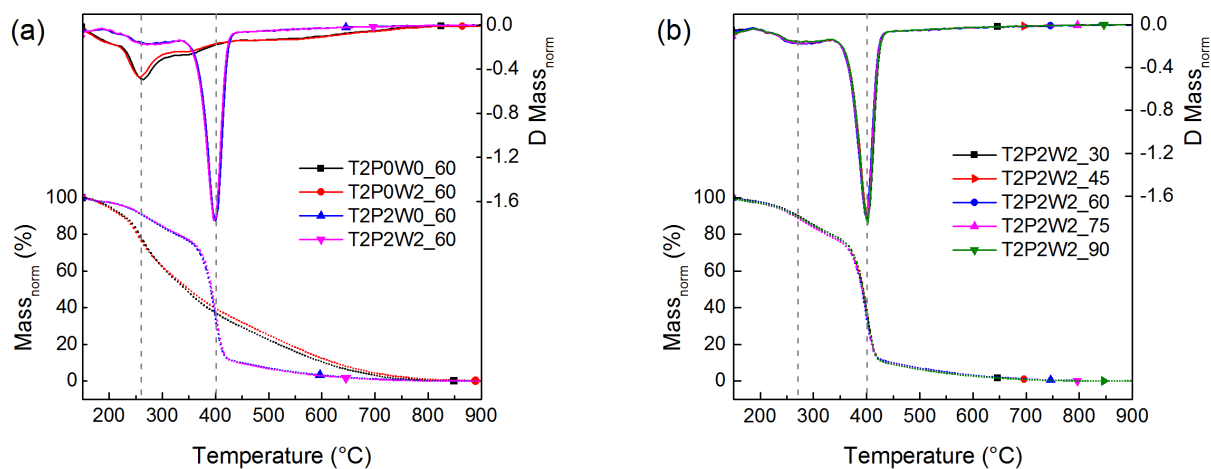


Figure S3. Absolute (left scale) and differential (right scale) normalized mass losses of: (a) T2P2W2_60 and reference samples; and (b) samples T2P2W2_t prepared at various milling times *t*, ranging from 30 to 90 min. The normalization was performed after removing the mass loss attributed to the evaporation of water.

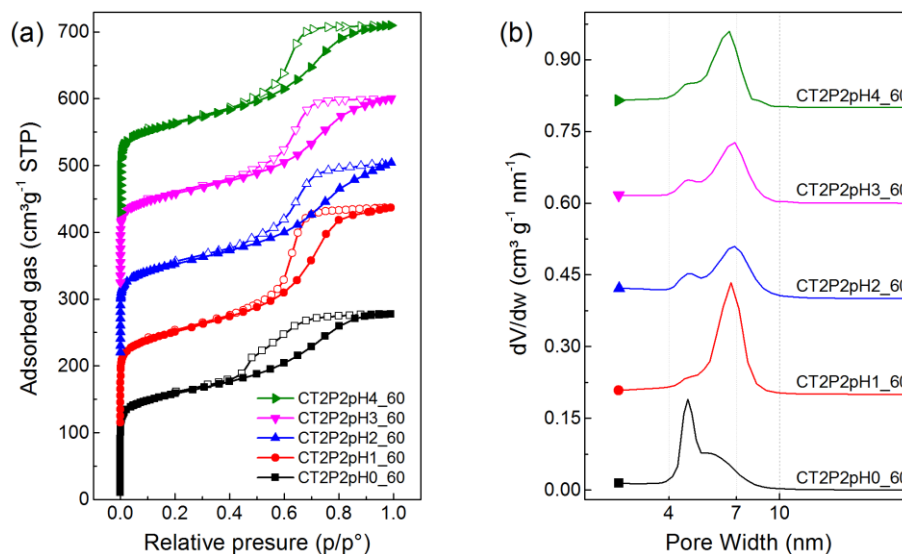


Figure S4. (a) N_2 adsorption-desorption isotherms and (b) corresponding PSDs of carbon materials CT2P2pH_x_60, synthesized by using aqueous solutions of HCl at pH ranging from 0 to 4 instead of water, and a milling time of 60 min. For easier viewing, the curves were shifted with respect to each other by 105 cm³ g⁻¹ STP for isotherms and by 0.2 cm³ g⁻¹ nm⁻¹ for PSDs.

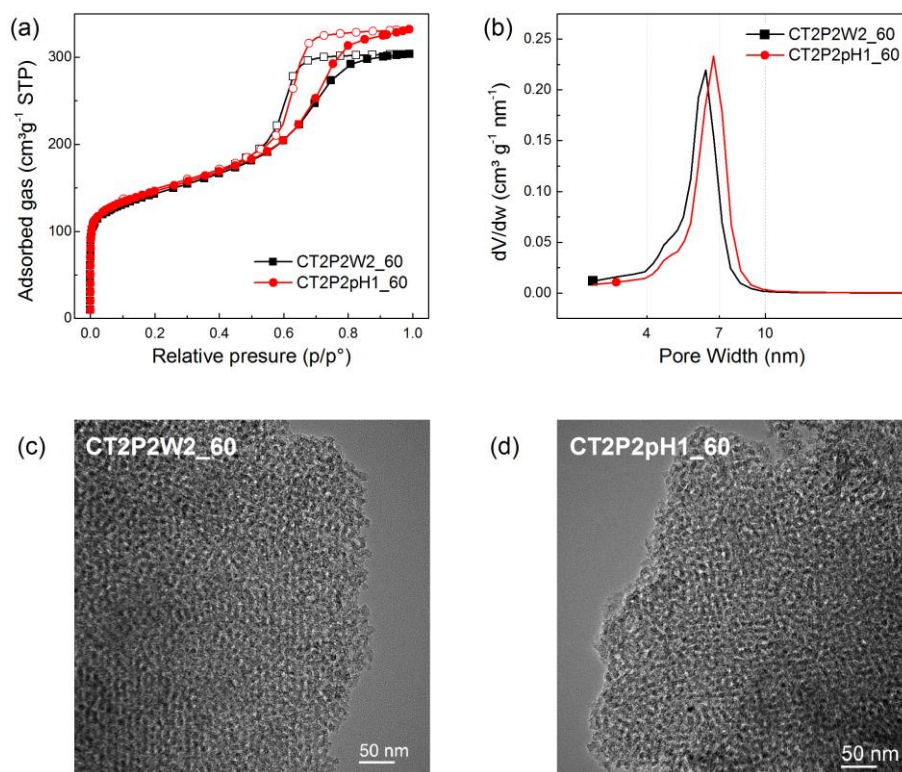


Figure S5. Comparison between CT2P2W2_60 and CT2P2pH1_60: (a) N_2 adsorption-desorption isotherms; (b) PSDs; and (c,d) TEM images.

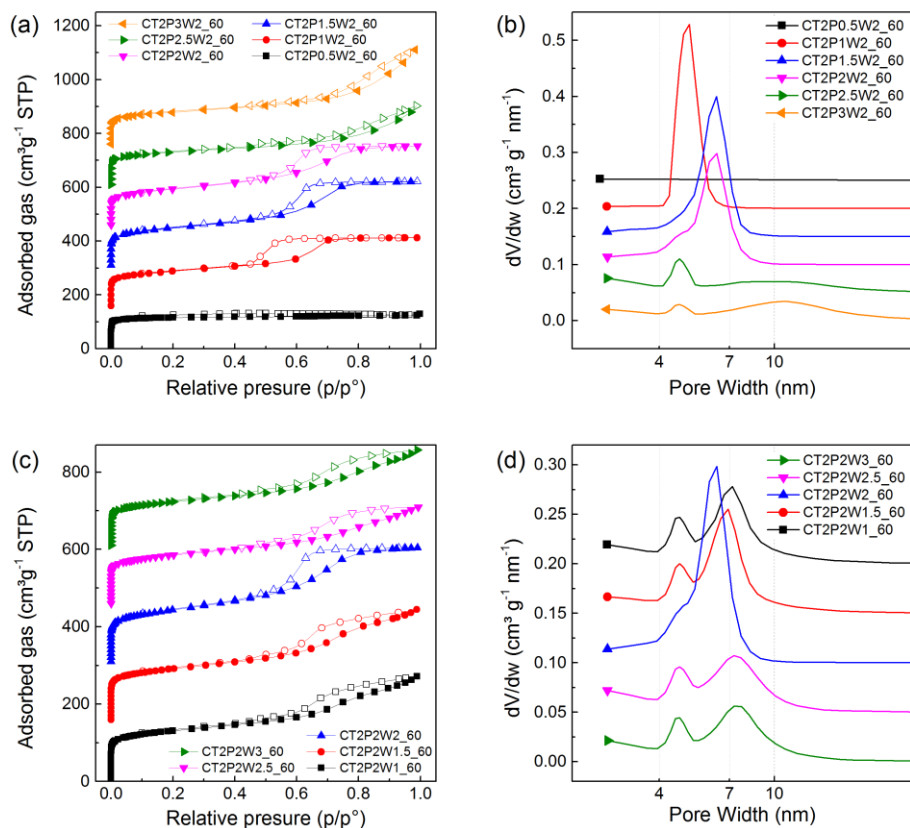


Figure S6. (a,c) N₂ adsorption-desorption isotherms and (b,d) corresponding PSDs of carbon materials synthesized using 60 min of milling and various P:W weight ratios. For easier viewing, the curves were shifted with respect to each other by 150 cm³ g⁻¹ STP for isotherms and by 0.05 cm³ g⁻¹ nm⁻¹ for PSDs.

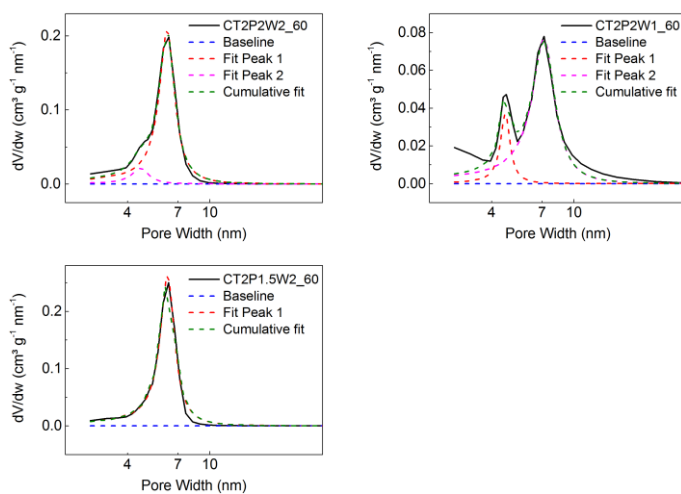


Figure S7. Examples of deconvolution into Lorentzian contributions performed on the PSDs of CT2P2W2_60, CT2P2W1_60 and CT2P1.5W2_60 samples.

Table S3. Characteristics of the main peaks in the PSDs of carbon materials synthesized using 60 min of milling and various P:W weight ratios.

	Maximum height (M) [cm ³ g ⁻¹ nm ⁻¹]	FWHM [nm]	M / FWHM	Peak position [nm]
CT2P0W2_60	0.0	--	0.0	--
CT20.5W2_60	0.0	--	0.0	--
CT2P1W2_60	0.37	0.73	0.50	5.0
CT2P1.5W2_60	0.26	1.24	0.21	6.2
CT2P2W2_60	0.02 0.23	1.13 1.20	0.02 0.19	4.7 6.2
CT2P2.5W2_60	0.05 0.02	0.51 17.22	0.10 0.001	4.7 10.3
CT2P3W2_60	0.02 0.03	0.48 10.65	0.03 0.003	4.7 11.3
CT2P2W0_60	0.03 0.03	0.44 7.40	0.06 0.004	4.7 7.0
CT2P2W1_60	0.04 0.08	0.61 2.21	0.06 0.03	4.7 7.1
CT2P2W1.5_60	0.04 0.11	0.59 1.84	0.06 0.06	4.7 6.8
CT2P2W2.5_60	0.03 0.06	0.63 3.42	0.05 0.02	4.7 7.4
CT2P2W3_60	0.03 0.06	0.58 3.37	0.06 0.02	4.6 7.6
CT2P0.5W1_60	0.0	--	0.0	--
CT2P0.5W1.5_60	0.09	0.71	0.12	4.1
CT2P0.75W1.25_60	0.25	0.54	0.46	4.4
CT2P0.75W1.5_60	0.44	0.37	1.20	4.5
CT2P0.75W1.75_60	0.56	0.32	1.77	4.6
CT2P1W1_60	0.31	0.87	0.35	4.7
CT2P1W1.25_60	0.34	0.82	0.42	5.0
CT2P1W1.5_60	0.47	0.60	0.78	4.9
CT2P1W1.75_60	0.31	0.94	0.33	5.2
CT2P1.25W1.25_60	0.29	0.99	0.29	5.9
CT2P1.25W1.5_60	0.25	1.21	0.21	6.0
CT2P1.25W1.75_60	0.23	1.26	0.18	5.9
CT2P1.5W1_60	0.27	1.21	0.22	6.2
CT2P1.5W1.25_60	0.25	1.35	0.18	6.1
CT2P1.5W1.5_60	0.31	1.04	0.30	6.2
CT2P1.5W1.75_60	0.30	1.11	0.27	6.1

Table S4. Pore texture parameters of samples synthesized with different P:W initial ratios and obtained after 60 min of ball-milling, calculated from N₂ and CO₂ isotherms.

	S_{NLDFT} (m ² g ⁻¹)	A_{BET} (m ² g ⁻¹)	$V_{0.97,N_2}$ (cm ³ g ⁻¹)	$V_{\mu,NLDFT}$ (cm ³ g ⁻¹)	V_{meso} (cm ³ g ⁻¹)	F_{meso} (%)
CT2P0.5W1_60	566	304	0.12	0.13	--	--
CT2P0.5W1.5_60	732	529	0.25	0.20	0.05	18
CT2P0.5W2_60	657	457	0.19	0.18	0.01	3
CT2P0.75W1.25_60	659	477	0.30	0.17	0.12	41
CT2P0.75W1.5_60	731	537	0.35	0.19	0.15	44
CT2P0.75W1.75_60	761	567	0.36	0.20	0.16	44
CT2P1W1_60	733	546	0.42	0.18	0.24	57
CT2P1W1.25_60	755	568	0.44	0.19	0.25	57
CT2P1W1.5_60	750	556	0.44	0.19	0.25	58
CT2P1W1.75_60	784	587	0.47	0.19	0.28	59
CT2P1W2_60	712	508	0.41	0.17	0.24	58
CT2P1.25W1.25_60	713	532	0.46	0.17	0.29	63
CT2P1.25W1.5_60	732	547	0.49	0.17	0.31	64
CT2P1.25W1.75_60	696	527	0.45	0.17	0.28	62
CT2P1.5W1_60	742	565	0.51	0.18	0.34	66
CT2P1.5W1.25_60	715	539	0.49	0.17	0.32	66
CT2P1.5W1.5_60	767	588	0.52	0.18	0.34	65
CT2P1.5W1.75_60	750	577	0.53	0.18	0.35	66
CT2P1.5W2_60	726	541	0.50	0.17	0.33	66
CT2P2W1_60	689	486	0.40	0.17	0.23	58
CT2P2W1.5_60	721	524	0.44	0.18	0.26	60
CT2P2W2_60	695	522	0.47	0.16	0.30	65
CT2P2W2.5_60	696	503	0.39	0.18	0.21	54
CT2P2W3_60	641	454	0.38	0.16	0.22	59
CT2P2.5W2_60	686	486	0.43	0.17	0.26	60
CT2P3W2_60	638	476	0.53	0.16	0.37	70

S_{NLDFT} and A_{BET} : specific surface areas calculated by applying NLDFT and BET models, respectively; $V_{0.97,N_2}$: total single point pore volume at relative pressure of 0.97; $V_{\mu,NLDFT}$: micropore volume from NLDFT model; $V_{meso} = V_{0.97,N_2} - V_{\mu,NLDFT}$: mesopore volume; $F_{meso} = V_{meso}/V_{0.97,N_2}$: mesopore fraction.

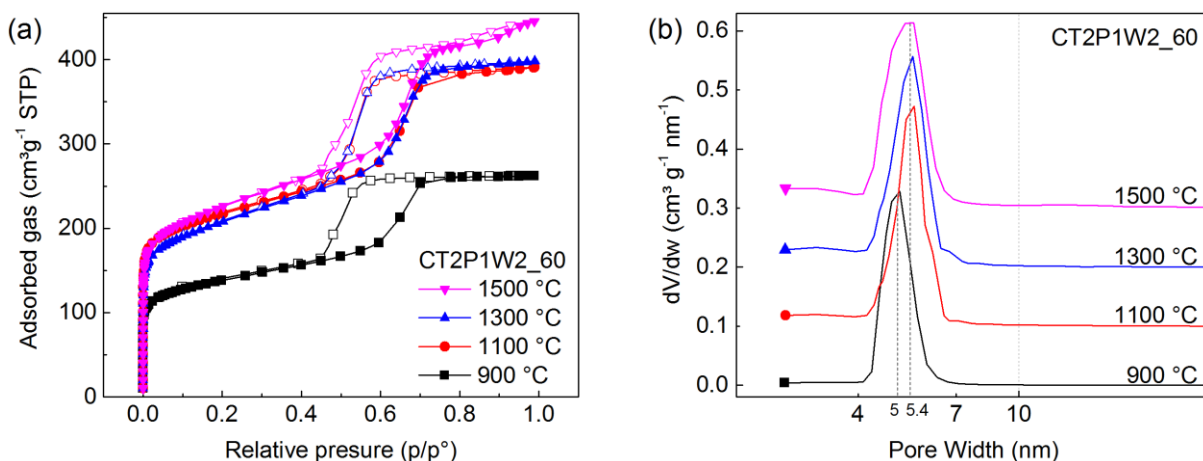


Figure S8. (a) N₂ adsorption-desorption isotherms and (b) corresponding PSDs for CT2P1W2_60 pyrolyzed at different temperatures. For easier viewing, the PSDs curves were shifted with respect to each other by 0.1 cm³ g⁻¹ nm⁻¹.

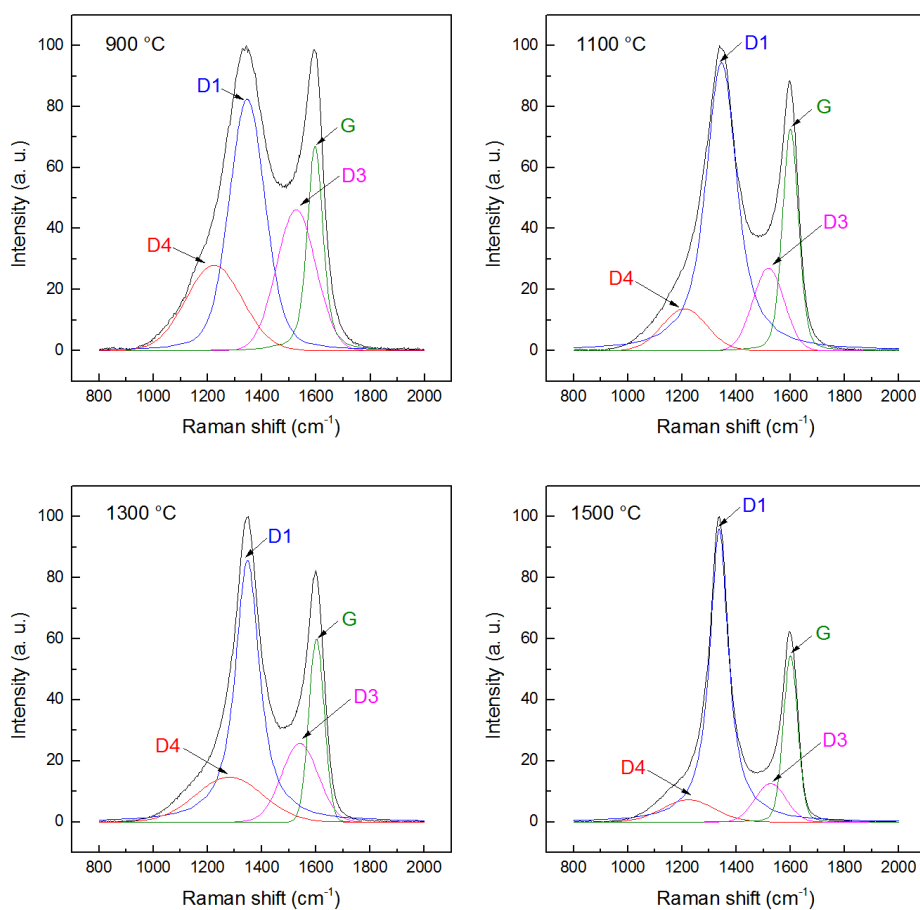


Figure S9. Raman spectra of CT2P1W2_60 pyrolyzed at different temperatures, and corresponding D₁, D₃, D₄ and G bands.

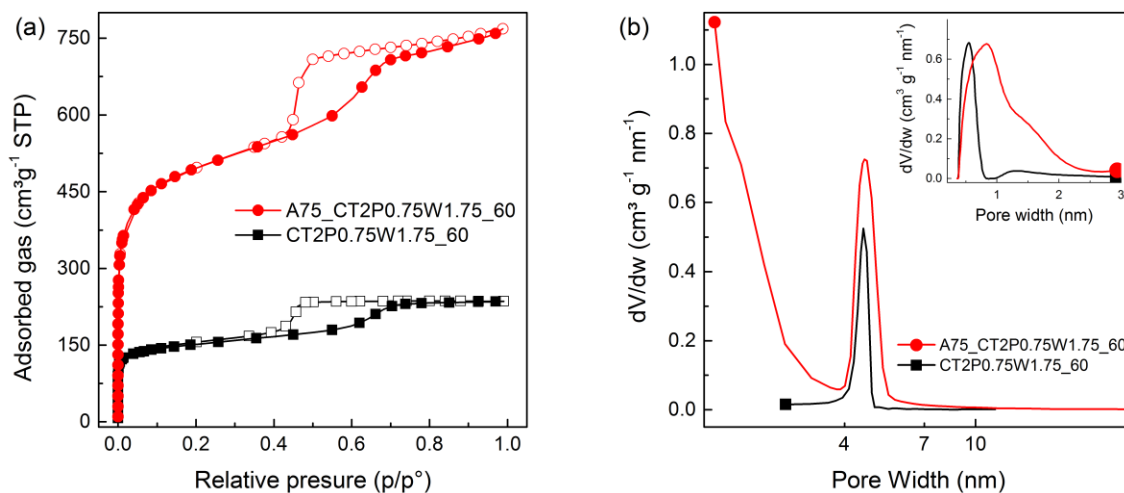


Figure S10. (a) N₂ adsorption-desorption isotherms, and (b) corresponding PSD for one OMC before (CT2P0.75W1.75_60) and after (A75_CT2P0.75W1.75_60) activation with CO₂ for 75 min at 900°C. The inset in (b) shows the DFT PSD in the micropore range for both materials.

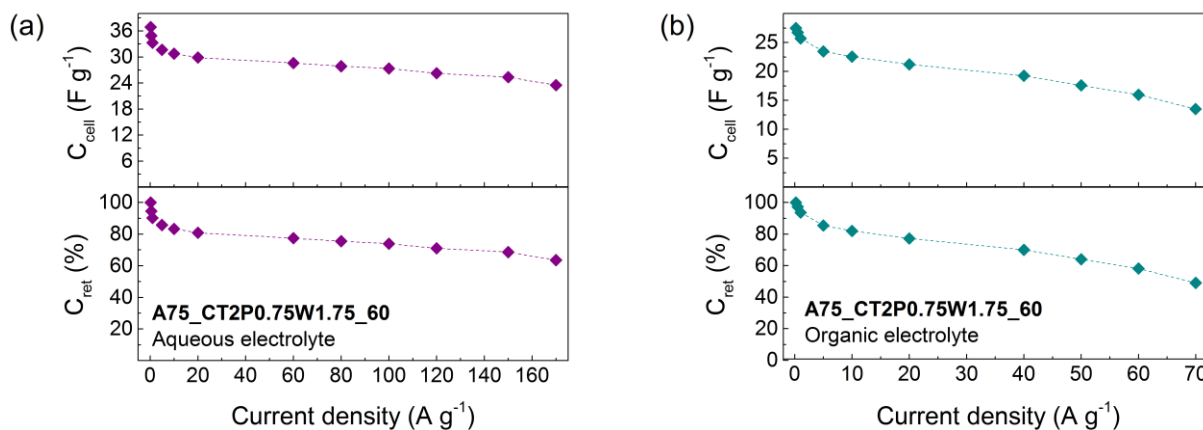


Figure S11. Evolution of cell capacitance (C_{cell}) and capacitance retention (C_{ret}) with current density for A75_CT2P0.75W1.75_60 in (a) aqueous and (b) organic electrolyte.

Table S5. Electrochemical performances of different carbon materials reported in the literature.

Carbon precursor/ Synthesis method	Carbon material	Electrolyte (cell voltage)	Capacitance [F g ⁻¹]	Current density [A g ⁻¹]	Energy density [Wh kg ⁻¹]	Power density [kW kg ⁻¹]	Ref.
Polyphenols: Phloroglucinol, gallic acid, catechin, and mimosa tannin/ Hard-templating (SBA-15); carbonization	OMCs: 2D-Hexagonal.	1 M H ₂ SO ₄ (0.8 V)	~196	0.1	2.27 – 4.08	6.83 – 0.06	62
			~127	12	2.46 – 4.46	5.97 – 0.05	
					1.31 – 4.18	5.17 – 0.01	
					1.91 – 4.62	6.56 – 0.06	
Sugarcane molasses/ HTC; carbonization	Oxygen rich carbons.	1 M H ₂ SO ₄ (0.7 V)	32	0.1	~0.04 – ~1.8	3 – ~0.15	63
			13	1	~0.35 – ~6.9	~5.5 – 0.5	
					~0.03 – ~0.6	~4.5 – ~0.15	
					~0.45 – ~6.9	~5 – ~0.13	
Mesoporous SiC/ Si etching	Microporous nanorods	1 M H ₂ SO ₄ (0.6 V)	~150 – ~190 ~130 – 150	0.1 15.5	-	-	64
Willow catkins/ Carbonization; KOH activation	Hollow fibrous structure.	6 M KOH (1 V)	333 ^a 209 ^a	0.1 10	5 – 8.8	5 – 0.05	65
Sucrose/ Hard-templating (MCM-48 and SBA-15); carbonization	OMCs: 3D cubic, 2D hexagonal rods and 2D hexagonal pipes.	30 wt.% KOH (0.9 V)	-	-	~4 – ~6	~0.8 – ~0.1	66
					~4.7 – ~5.4	~0.95 – ~0.1	
					~5.4 – ~5.9	~1.05 – ~0.1	
Seaweed/ Carbonization; KOH activation	Micro-mesoporous carbon with egg-box structure	1 M H ₂ SO ₄ (1 V)	425 280	0.1 100	-	-	67
		1M TEABF ₄ /AN (2.5 V)	210 156	0.1 50	25 – 42	29 – 0.39	

Table S5 (Continued). Electrochemical performances of different carbon materials reported in the literature.

Carbon precursor/ Synthesis method	Carbon material	Electrolyte (cell voltage)	Capacitance [F g ⁻¹]	Current density [A g ⁻¹]	Energy density [Wh kg ⁻¹]	Power density [kW kg ⁻¹]	Ref.
Sodium gluconate/ Carbonization	Micro-mesoporous carbon nanosheets	1 M H ₂ SO ₄ (1 V)	175 – 220 80 – 140	0.05 150	~1 – ~6 ~1.5 – ~6 ~3 – ~8	~20 – ~0.02 ~20 – ~0.02 ~30 – 0.02	59
		1M TEABF ₄ /AN (2.7 V)	100 – 135 50 – 100	0.05 120	~7 – 23 ~13 – ~33 16 – ~26	~90 – ~0.07 110 – ~0.07 110 – ~0.07	
Furfuryl alcohol/ Hard templating (Silica)	OMCs: 3D cubic; 3D low ordered. Worwhole-like pores.	1M TEABF ₄ /AN (2 V)	~95	~0.06	~3.5 – ~13	~5.7 – ~0.04	68
Peanut shell and rice husk/ ZnCl ₂ activation	Disordered mesoporous carbons	1M TEABF ₄ /PC (2.7 V)	99 79	0.05 3	19.3 – 26.6	1.01 – ~0.07	69
Resol and Pluronic/ Two-step template synthesis: latex spheres and silica hard template Thermosetting; carbonization; HF washing.	Ordered mesoporous carbon sphere arrays	1M TEABF ₄ /PC (3 V)	84	0.1	-	-	70

^a Capacitance values calculated from galvanostatic charge-discharge in a three-electrode cell.

Calculation of electrochemical properties

The specific cell capacitances (C_{cell} , F g⁻¹) were calculated from CV data through Equation S1:

$$C_{cell} = \frac{\int I dV}{s \Delta V m} \quad (1)$$

where I is the current (A), s is the scan rate (V s⁻¹), ΔV is the potential window (V), and m is the mass of active material in the two electrodes (g).

GCD curves were used to calculate the specific capacitances of the cell (C_{cell} , F g⁻¹), the energy densities (E , Wh kg⁻¹) and the power densities (P , W kg⁻¹) by application of Equation S2, S3 and S4, respectively:

$$C_{cell} = \frac{I \Delta t}{m(\Delta V - iR)} \quad (2)$$

$$E = \frac{1}{2} C_{cell} (\Delta V - iR)^2 \quad (3)$$

$$P = \frac{E}{\Delta t} \quad (4)$$

where I is the discharge current (A); Δt is the discharge time (s), and iR is the potential drop due to inner resistance.

The single electrode specific capacitances, C_e , can be estimated by Equation S5:

$$C_e \approx 4 C_{cell} \quad (5)$$