

Deciphering the Role of Hydrothermal Pretreatment on Biomass Waste for Derived Hard Carbon with Superior Electrochemical Performance in Sodium-ion Battery

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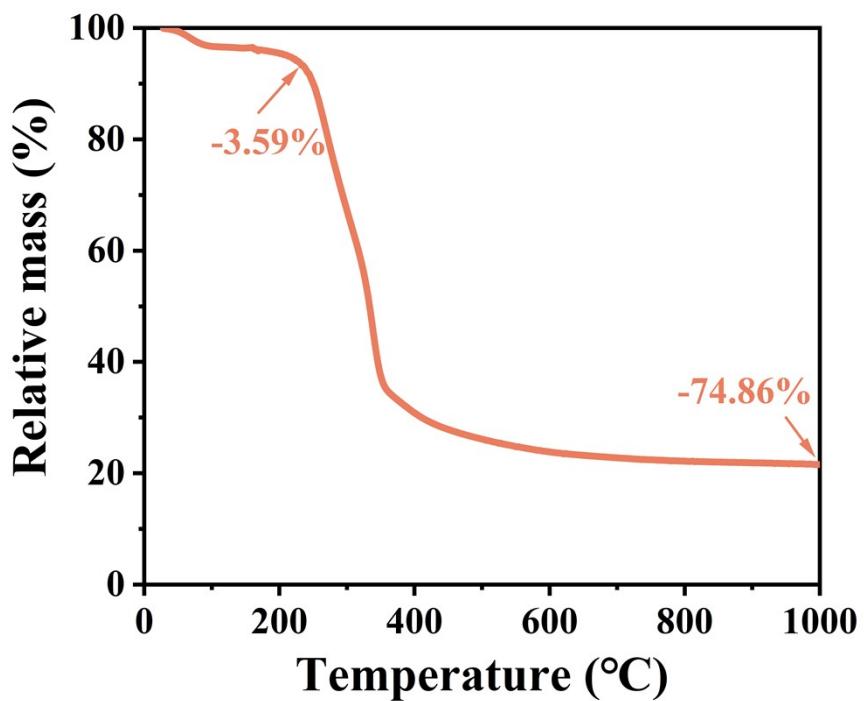


Fig. S1 TG curve of raw material.

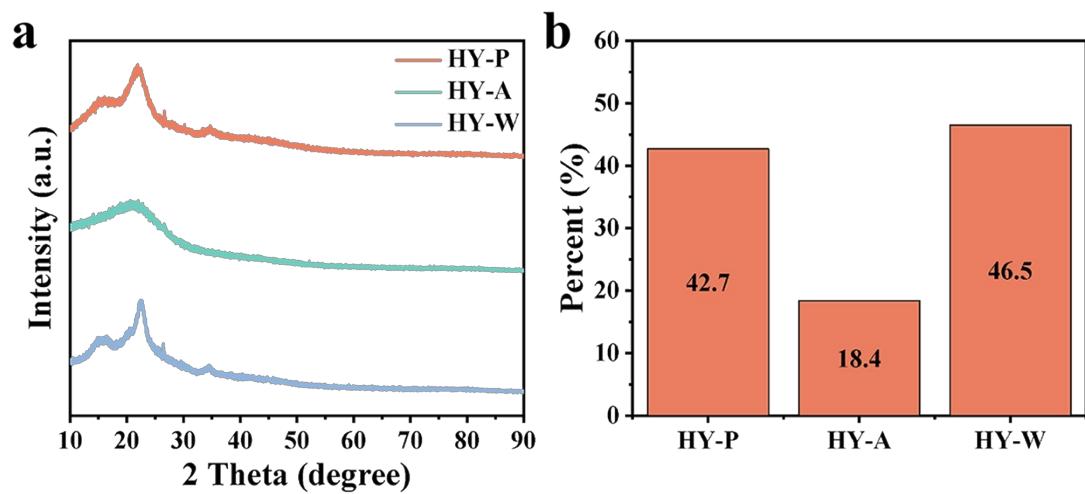


Fig. S2 (a) XRD patterns and (b) the relative crystallinity of HY-P, HY-A, HY-W.

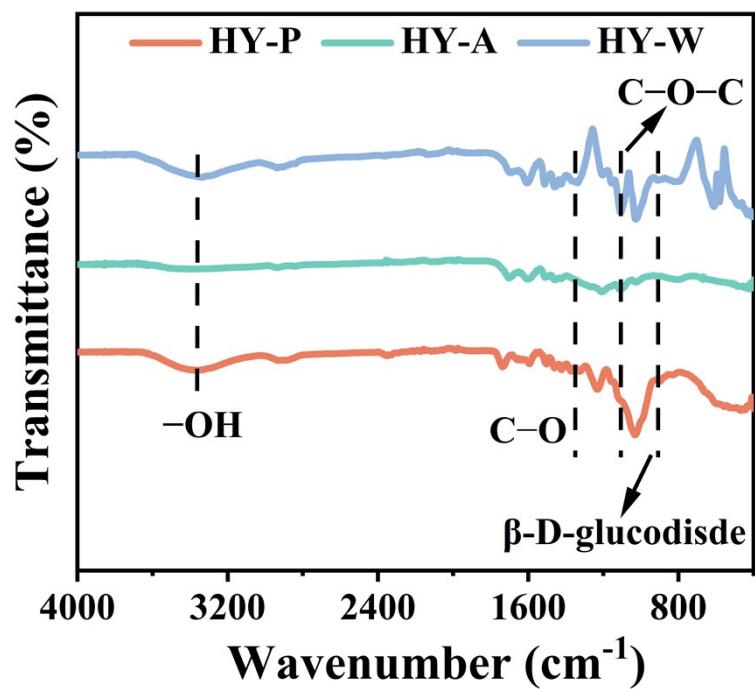


Fig. S3 Infrared spectra of HY-P, HY-A, HY-W.

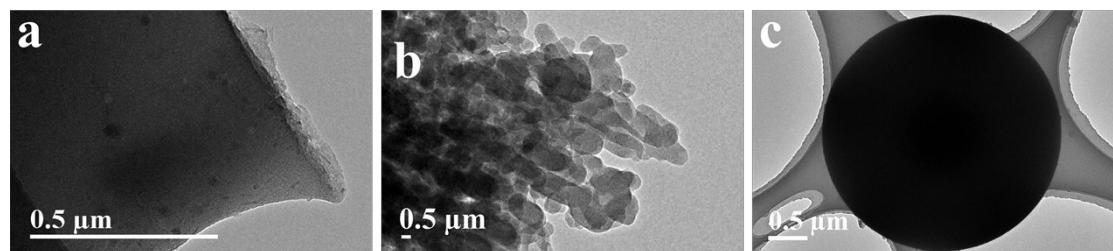


Fig. S4 TEM images of (a) HC-P, (b) HC-A, (c) HC-W.

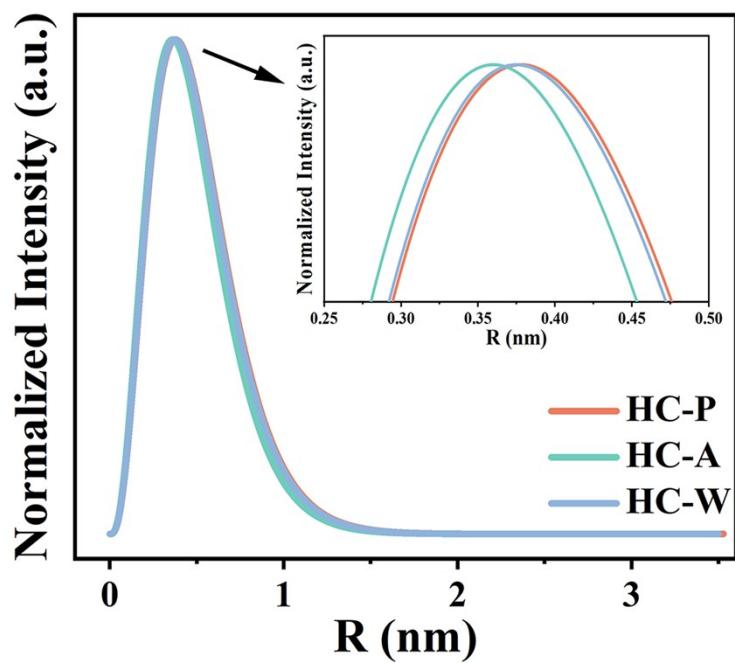


Fig. S5 Closed pore size distribution of HC-P, HC-A and HC-W.

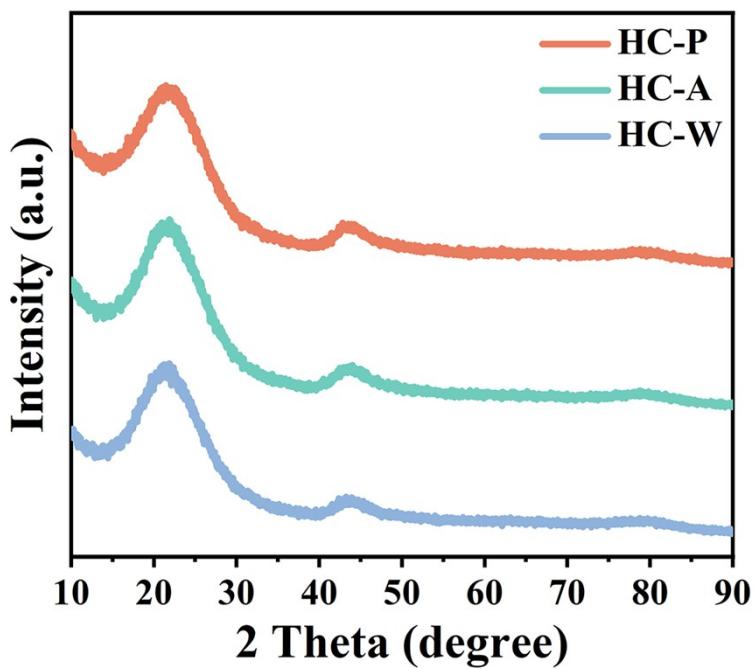


Fig. S6 XRD patterns of HC-P, HC-A and HC-W.

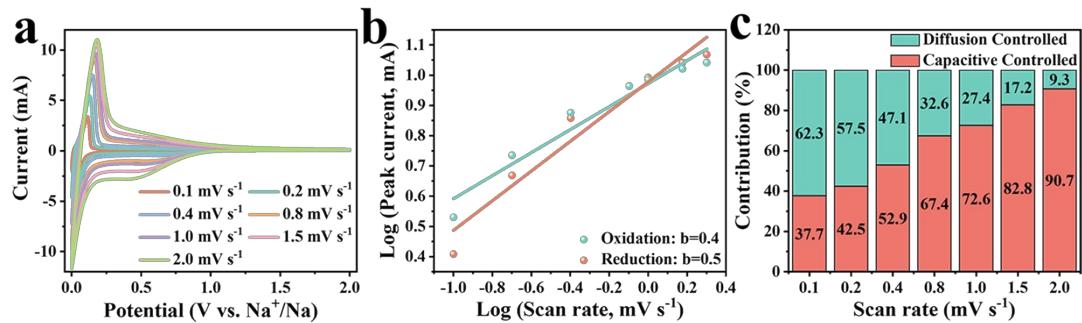


Fig. S7 (a) CV curves at different scan rates from 0.1 to 2.0 mV s⁻¹ and (b) b-values of HC-P. (c) Capacitive contribution at different scan rates of HC-P.

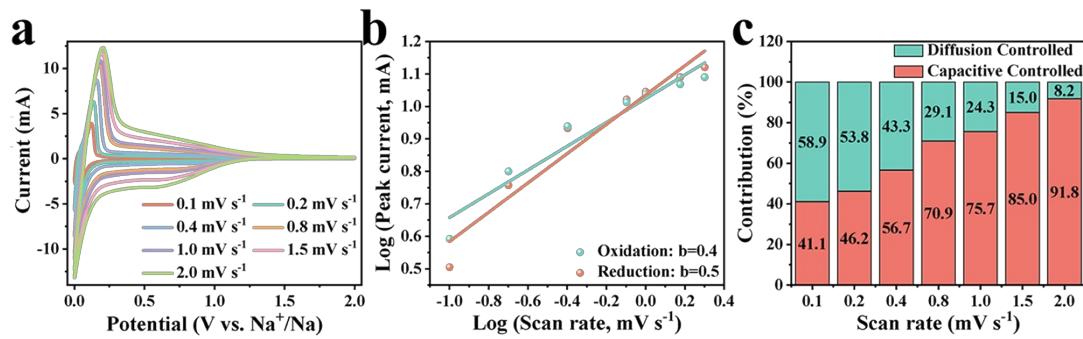


Fig. S8 (a) CV curves at different scan rates from 0.1 to 2.0 mV s⁻¹ and (b) b-values of HC-A. (c) Capacitive contribution at different scan rates of HC-A.

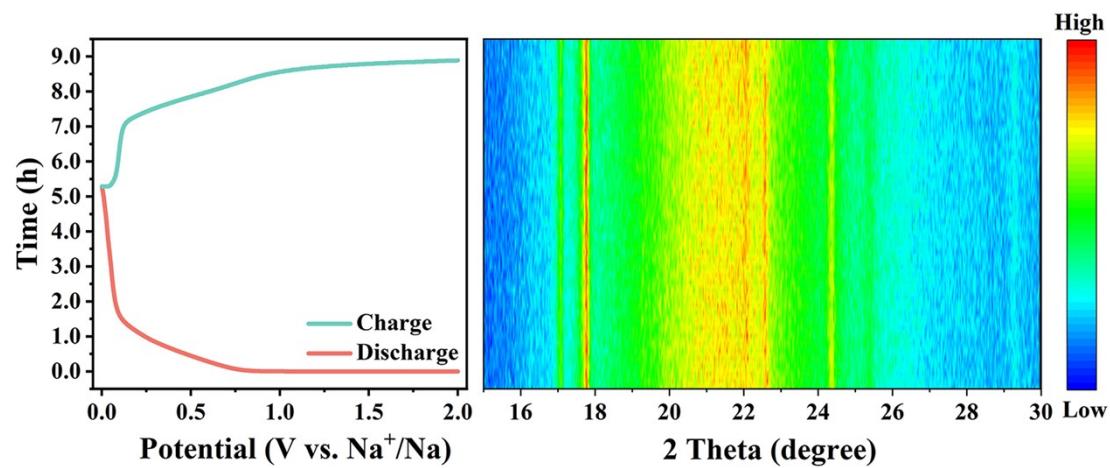


Fig. S9 The in-situ XRD curve of HC-P at 0.15 C.

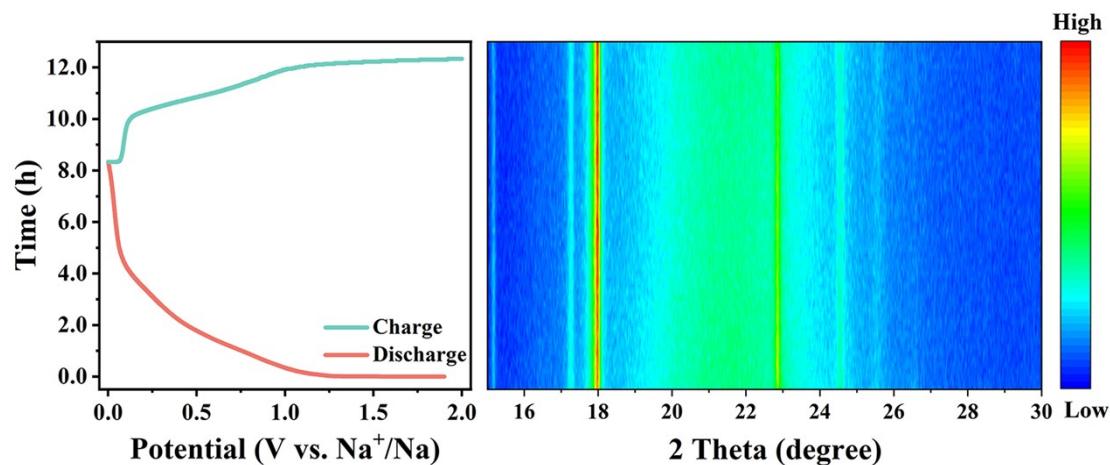


Fig. S10 The in-situ XRD curve of HC-A at 0.15 C.

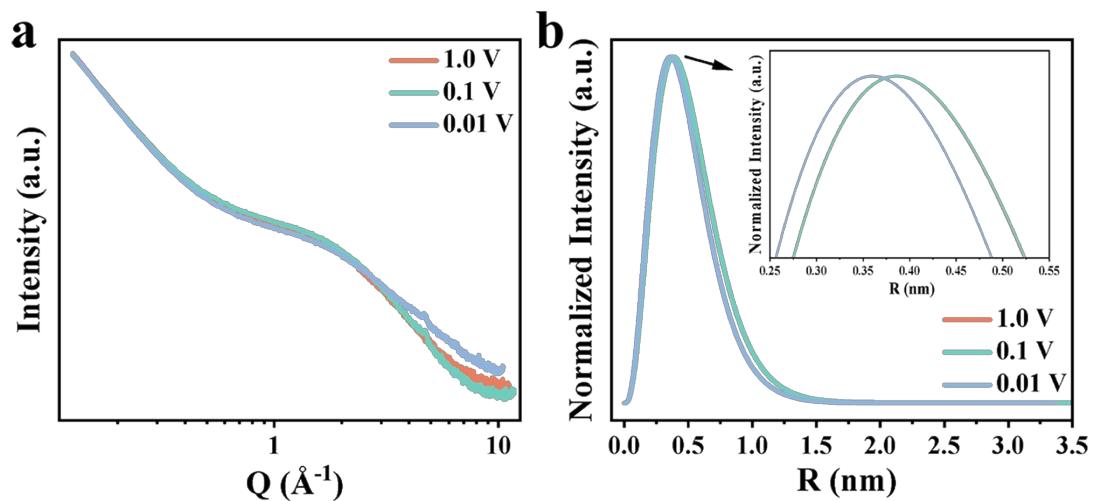


Fig. S11 (a) Ex-situ SAXS and (b) closed pore size distribution of HC-P at 1.0 V, 0.1 V and 0.01 V.

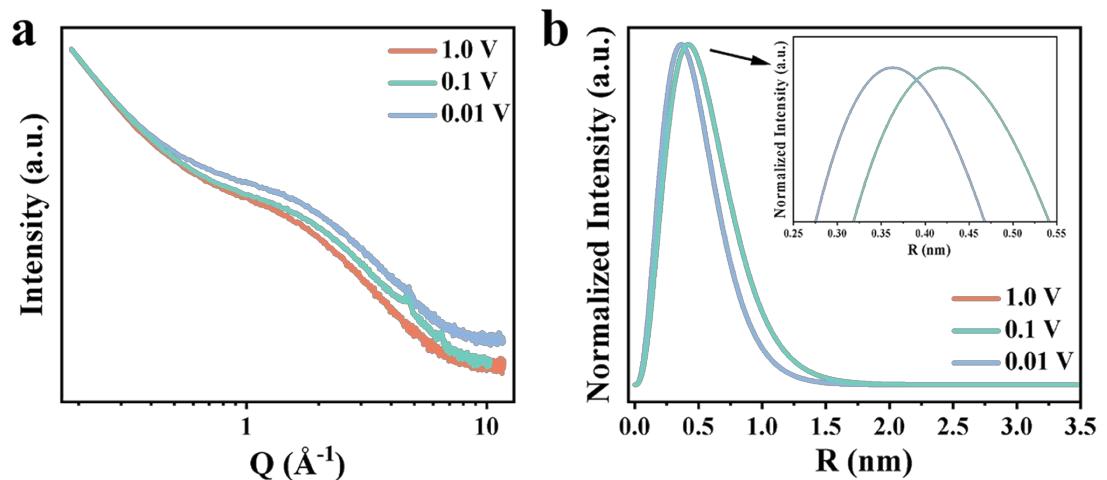


Fig. S12 (a) Ex-situ SAXS and (b) closed pore size distribution of HC-A at 1.0 V, 0.1 V and 0.01 V.

Table S1. Structure parameters of samples.

Samples	R _{SAXS} (Å)	d ₀₀₂ (nm)	L _a (nm)	L _c (nm)	FWHM (°)	A _D /A _G
HC-P	3.8	0.4	3.3	0.8	7.6	1.37
HC-A	3.6	0.4	3.2	0.7	7.4	1.31
HC-W	3.8	0.4	3.3	0.8	7.9	1.42

Table S2. Microcrystalline parameters of samples.

Band	Samples	Raman shift (cm ⁻¹)	Corresponding structure
G	HC-P	1581.7	Vibration of the graphite crystal
	HC-A	1590.0	
	HC-W	1586.9	
D(D1)	HC-P	1351.9	Disordered graphite lattice
	HC-A	1351.8	
	HC-W	1350.8	
D2	HC-P	1613.7	Layer-stacking arrangement of carbon atoms in graphene
	HC-A	1604.3	
	HC-W	1616.1	
D3	HC-P	1486.3	Amorphous carbon
	HC-A	1480.6	
	HC-W	1490.0	
D4	HC-P	1236.9	Disordered structure of sp ² -sp ³
	HC-A	1250.1	
	HC-W	1232.5	

Table S3. Comparison of the electrochemical performance with typical biomass-derived HC reported previously.

Precursors	Reversible capacity	Initial coulombic efficiency	Rate capacity	Capacity retention	Reference
Sunflower seed shells	287 mAh g ⁻¹ at 25 mA g ⁻¹	76%	135 mAh g ⁻¹ at 372 mA g ⁻¹	85% after 500 cycles at 372 mA g ⁻¹	¹
Aegle marmelos shell	224 mAh g ⁻¹ at 10 mA g ⁻¹	76%	78 mAh g ⁻¹ at 1 A g ⁻¹	66% after 2500 cycles at 1000 mA g ⁻¹	²
Peanut shell	204 mAh g ⁻¹ at 30 mA g ⁻¹	54%	99 mAh g ⁻¹ at 300 mA g ⁻¹	81% after 100 cycles at 300 mA g ⁻¹	³
Corncob	272 mAh g ⁻¹ at 30 mA g ⁻¹	67%	35 mAh g ⁻¹ at 2 A g ⁻¹	79% after 100 cycles at 30 mA g ⁻¹	⁴
Spartina alterniflora loisel	142 mAh g ⁻¹ at 50 mA g ⁻¹	42%	150 mAh g ⁻¹ at 500 mA g ⁻¹	42% after 1000 cycles at 200 mA g ⁻¹	⁵
Green peas pod	293 mAh g ⁻¹ at 30 mA g ⁻¹	74%	142 mAh g ⁻¹ at 300 mA g ⁻¹	74% after 100 cycles at 30 mA g ⁻¹	⁶

Sugarcane bagasse	300 mAh g^{-1} at 25 mA g^{-1}	57%	115 mAh g^{-1} at 1 A mA g^{-1}	67% after 300 cycles at 100 mA g^{-1}	7
Macadamia nutshell	118 mAh g^{-1} at 100 mA g^{-1}	54%	200 mAh g^{-1} at 200 mA g^{-1}	65% after 100 cycles at 20 mA g^{-1}	8
Rice husks	251 mAh g^{-1} at 25 mA g^{-1}	67%	111 mAh g^{-1} at 500 mA g^{-1}	85% after 500 cycles at 100 mA g^{-1}	9
Vine shoots	270 mAh g^{-1} at 30 mA g^{-1}	71%	110 mAh g^{-1} at 100 mA g^{-1}	97% after 315 cycles at 100 mA g^{-1}	10
Natural balsa	248 mAh g^{-1} at 100 mA g^{-1}	32%	100 mAh g^{-1} at 2 A g^{-1}	95% after 500 cycles at 2 A g^{-1}	11
Pomegranate peel	359 mAh g^{-1} at 30 mA g^{-1}	52%	84 mAh g^{-1} at 600 mA g^{-1}	68% after 200 cycles at 150 mA g^{-1}	12
Platanus flosses	260 mAh g^{-1} at 100 mA g^{-1}	80%	107 mAh g^{-1} at 2 A g^{-1}	80% after 1000 cycles at 500 mA g^{-1}	13
Waste hemp hurd	262 mAh g^{-1} at 30	73%	79 mAh g^{-1} at 1 A	96% after 300 cycles	14

	mA g^{-1}		g^{-1}	at 2 A	g^{-1}	
Coffee ground	225 mAh g^{-1} at 50 mA g^{-1}	62%	119 mAh g^{-1} at 2500 mA g^{-1}	92% after 250 cycles at 50 mA g^{-1}	15	
Almond shell	317 mAh g^{-1} at 37 mA g^{-1}	86%	267 mAh g^{-1} at 3720 mA g^{-1}	91% after 600 cycles at 372 mA g^{-1}	This work	

Table S4. Closed pore sizes of samples.

Samples	1.0 V (\AA)	0.1 V (\AA)	0.01 V (\AA)
HC-P	3.9	3.9	3.6
HC-A	4.2	4.2	3.6
HC-W	4.0	4.0	3.6

References:

- 1 N. Nieto, J. Porte, D. Saurel, L. Djuandhi, N. Sharma, A. Lopez-Urionabarrenechea, V. Palomares and T. Rojo, *ChemSusChem*, 2023, **16**, e202301053.
- 2 A. Patel, R. Mishra, R. K. Tiwari, A. Tiwari, D. Meghnani, S. K. Singh and R. K. Singh, *J. Energy Storage*, 2023, **72**, 108424.
- 3 B. T. Yan, C. Han, Y. M. Dai, M. Y. Li, Z. Y. Wu and X. P. Gao, *Fuel*, 2024, **371**, 132141.
- 4 N. J. Song, N. N. Guo, C. L. Ma, Y. Zhao, W. X. Li and B. Q. Li, *Molecules*, 2023, **28**, 3595.
- 5 H. Y. Wei, H. K. Cheng, N. Yao, G. Li, Z. Q. Du, R. X. Luo and Z. Zheng, *Chemosphere*, 2023, **343**, 140220.
- 6 M. Venkatesh, P. L. Mani Kanta, T. Thomas, R. Vijay, T. N. Rao and B. Das, *Biomass Bioenergy*, 2025, **194**, 107646.
- 7 B. Verma, H. Raj, H. Rajput and A. Sil, *Ionics*, 2023, **29**, 5205-5216.
- 8 U. Kumar, J. Wu, N. Sharma and V. Sahajwalla, *Energy Fuels*, 2021, **35**, 1820-1830.
- 9 W. Nie, X. L. Liu, Q. M. Xiao, L. X. Li, G. X. Chen, D. Li, M. Zeng and S. W. Zhong, *ChemElectroChem*, 2020, **7**, 631-641.
- 10 D. Alvira, D. Antorán, M. Vidal, V. Sebastian and J. J. Manyà, *Batteries Supercaps*, 2023, **6**, e202300233.
- 11 W. F. Jing, M. Wang, Y. Li, H. R. Li, H. N. Zhang, S. L. Hu, H. Q. Wang and Y. B. He, *Electrochim. Acta*, 2021, **391**, 139000.
- 12 Q. J. Wu, K. W. Shu, L. Zhao and J. M. Zhang, *Molecules*, 2024, **29**, 4639.
- 13 Z. D. Hou, D. Lei, M. W. Jiang, Y. Y. Gao, X. Zhang, Y. Zhang and J. G. Wang, *ACS Appl. Mater. Interfaces*, 2023, **15**, 1367-1375.
- 14 D. Antorán, D. Alvira, M. E. Peker, H. Malón, S. Irusta, V. Sebastián and J. J. Manyà, *Energy Fuels*, 2023, **37**, 9650-9661.

15 P. H. Chiang, S. F. Liu, Y. H. Hung, H. Tseng, C. H. Guo and H. Y. Chen, *Energy
Fuels*, 2020, **34**, 7666-7675.