

Supporting Information

Why Tail States Matter? Impact of Defect Types on the Electrochemical Kinetics of CF_x Cathodes

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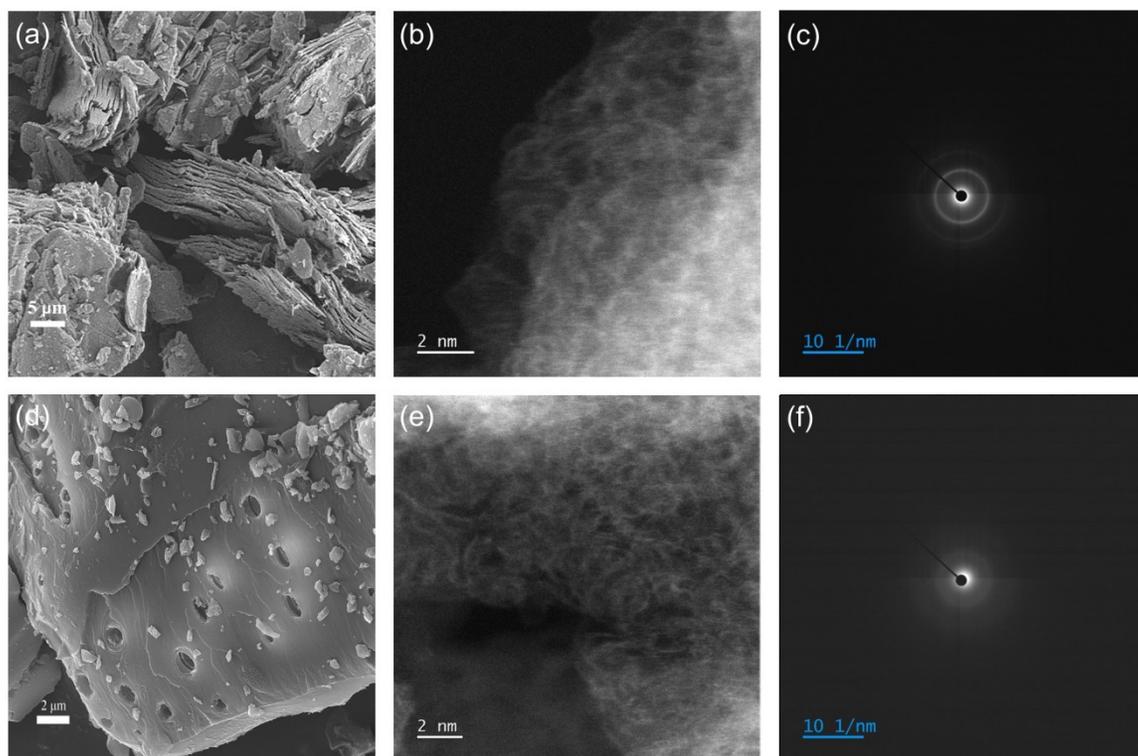


Figure S1. SEM image, Spherical AC-TEM image and corresponding SAED of FG (a-c) and FHC (d-f). For FHC, we choose a large particle for SEM imaging, clearly showing its sub-micron sized pore structure.

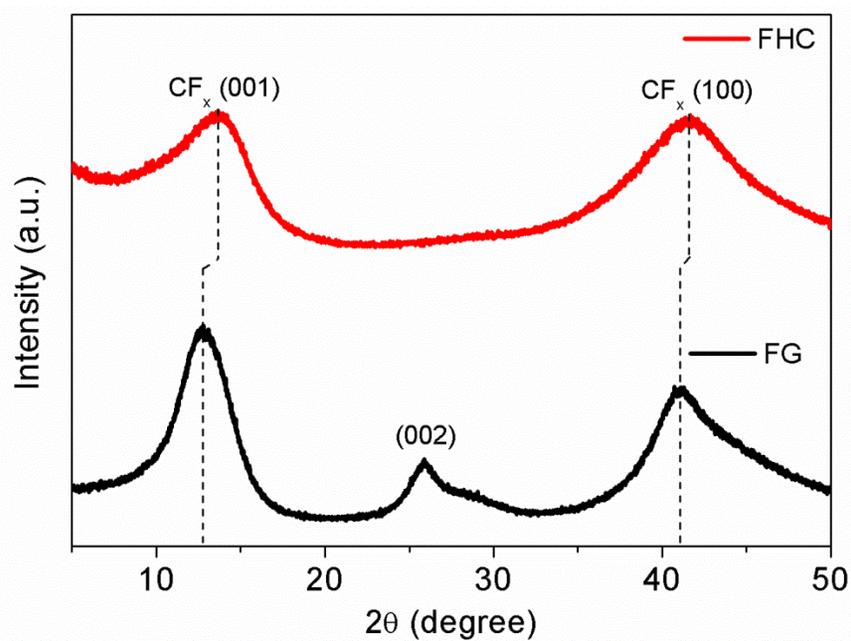


Figure S2. XRD patterns of FG and FHC powders measured at θ -2 θ configuration.

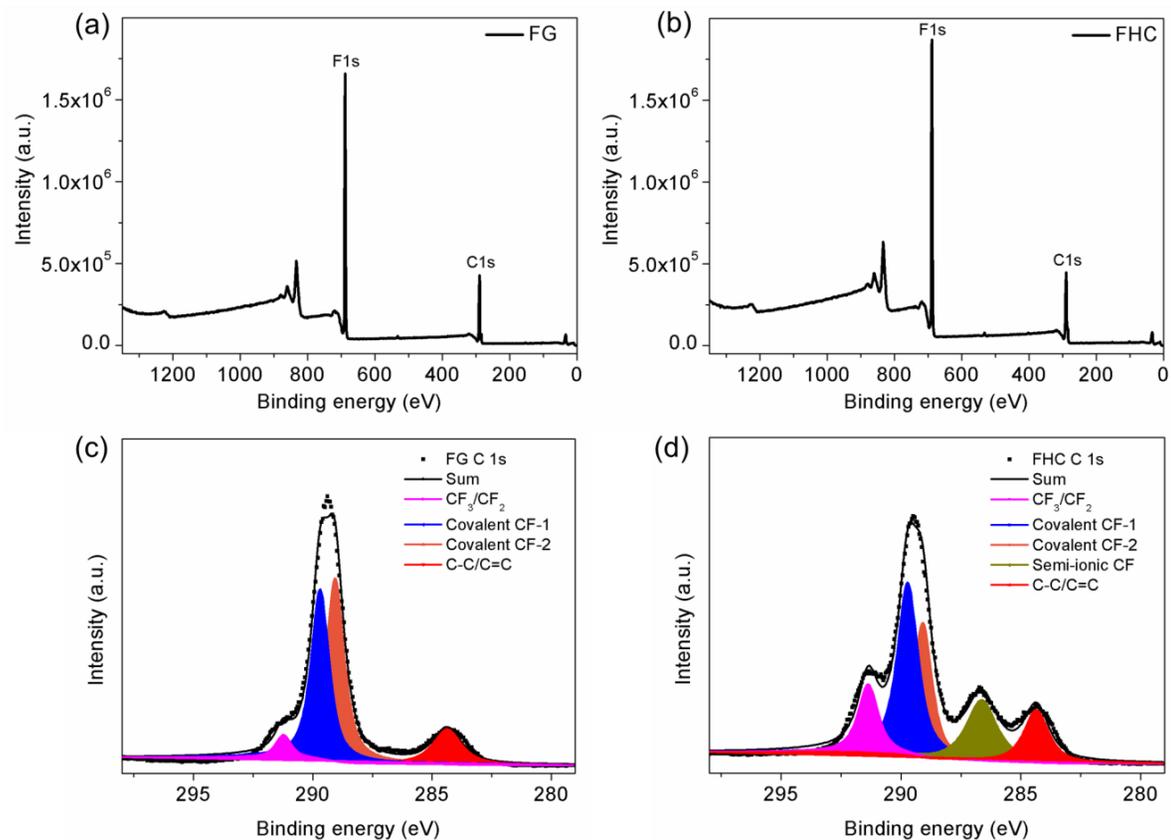


Figure S3. XPS full spectra of FG (a) and FHC (b); (c-d) C 1s spectrum of FG and FHC with fitting. Here 286.6 eV peak is attributed to be “semi-ionic” C-F bond, according to assignment in *Journal of Materials Chemistry A*, 2017, 5, 796.

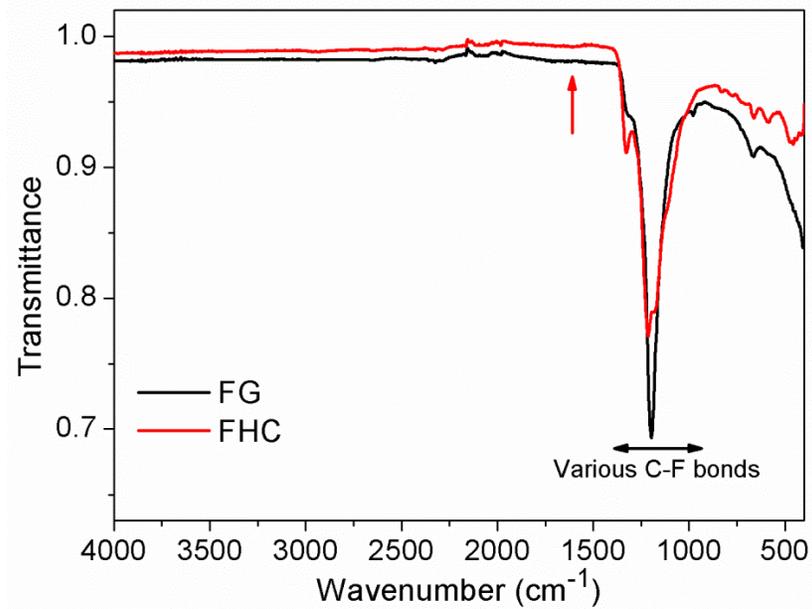


Figure S4. Original IR spectra of FG and FHC powders measured at transmission mode.

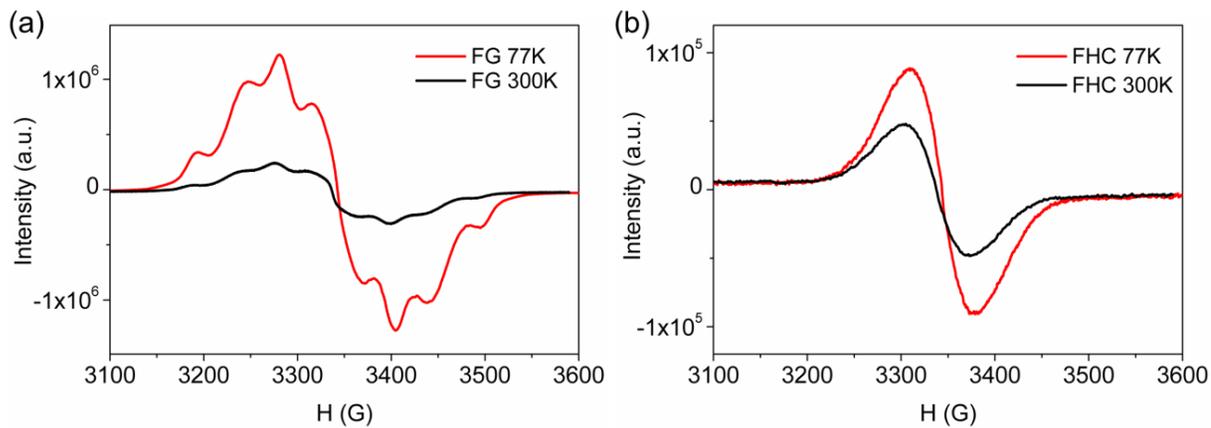


Figure S5. EPR spectra of FG (a) and FHC (b) powder at 77 K and 300 K.

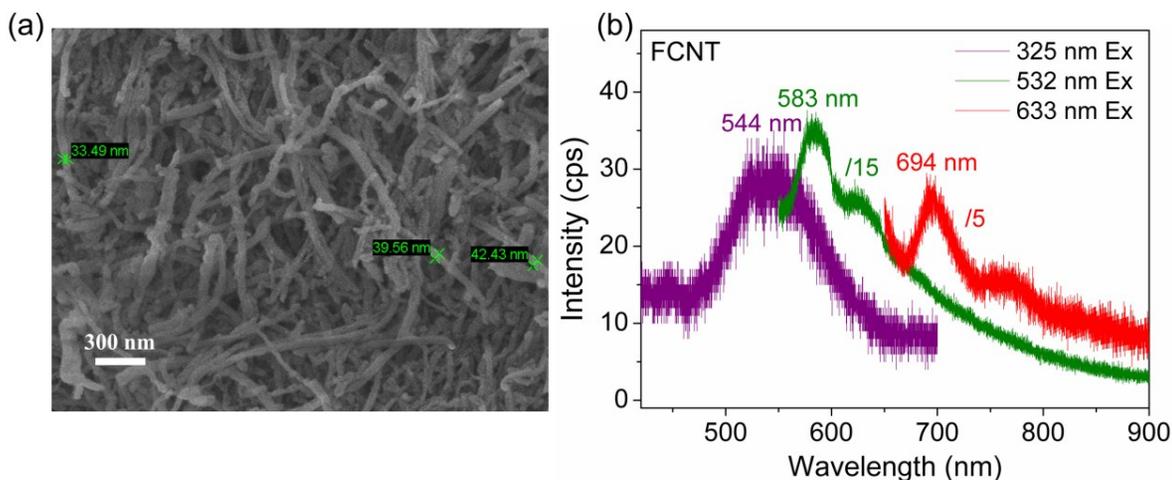


Figure S6. (a) SEM image of FCNT; (b) PL spectra of FCNT at different excitation wavelengths, with emission peaks labelled.

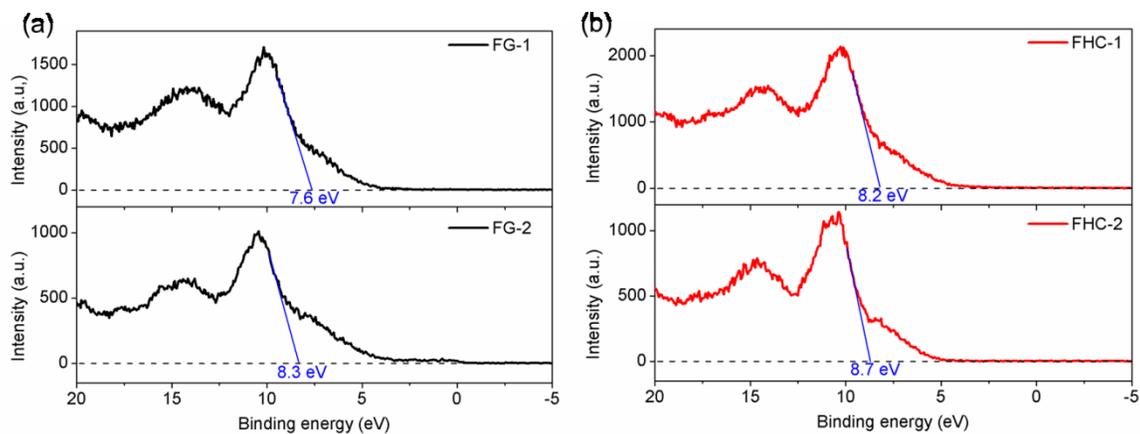


Figure S7. XPS valence band graph of FG (a) and FHC (b). For both samples, XPS-VB spectra were measured twice.

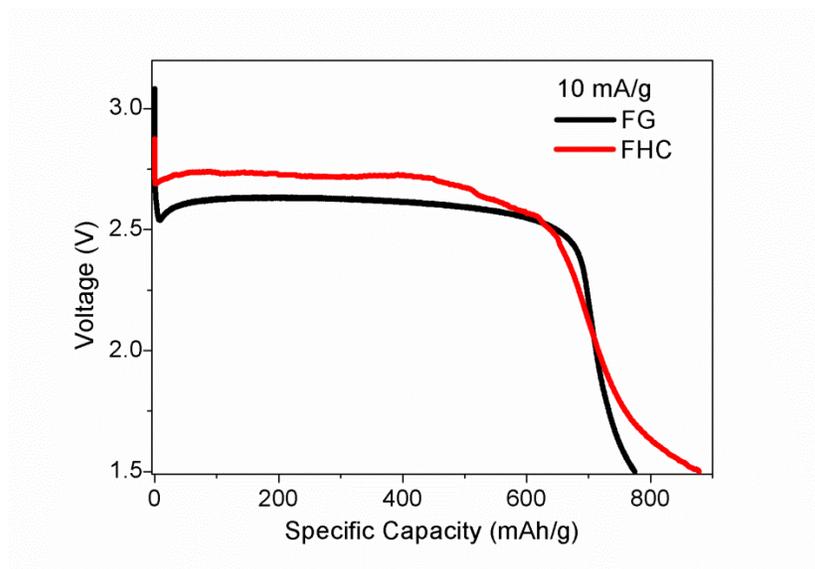


Figure S8. Constant-current discharge curves of FG and FHC based Li/CF_x coin cells under 10 mA/g discharge rate.

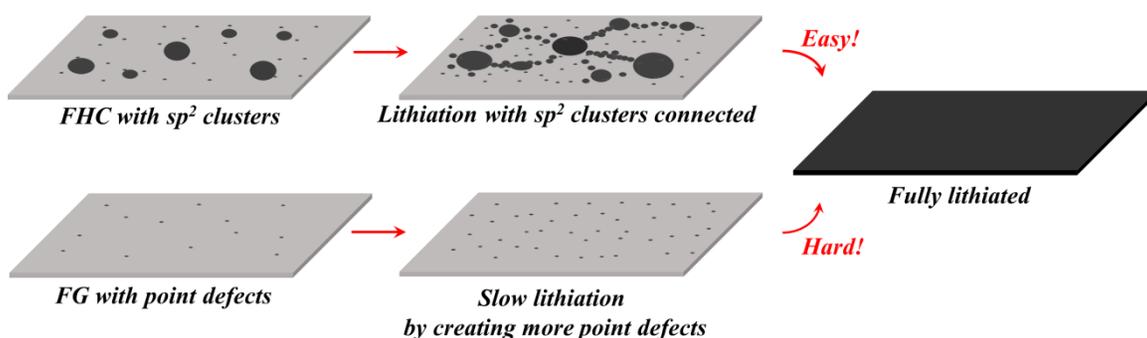


Figure S9. Schematic illustrations showing the lithiation process of FHC (top) and FG (bottom). The grey color represent unreacted CF_x and black means lithiated graphitic carbon phases, with smaller ones represent point defects and larger ones represent accumulated sp² carbon, respectively. Assuming the lithiation takes place at sp² carbon/CF_x interface, following edge propagation mechanism. -CF₂ group is not considered here due to its chemical inertness.

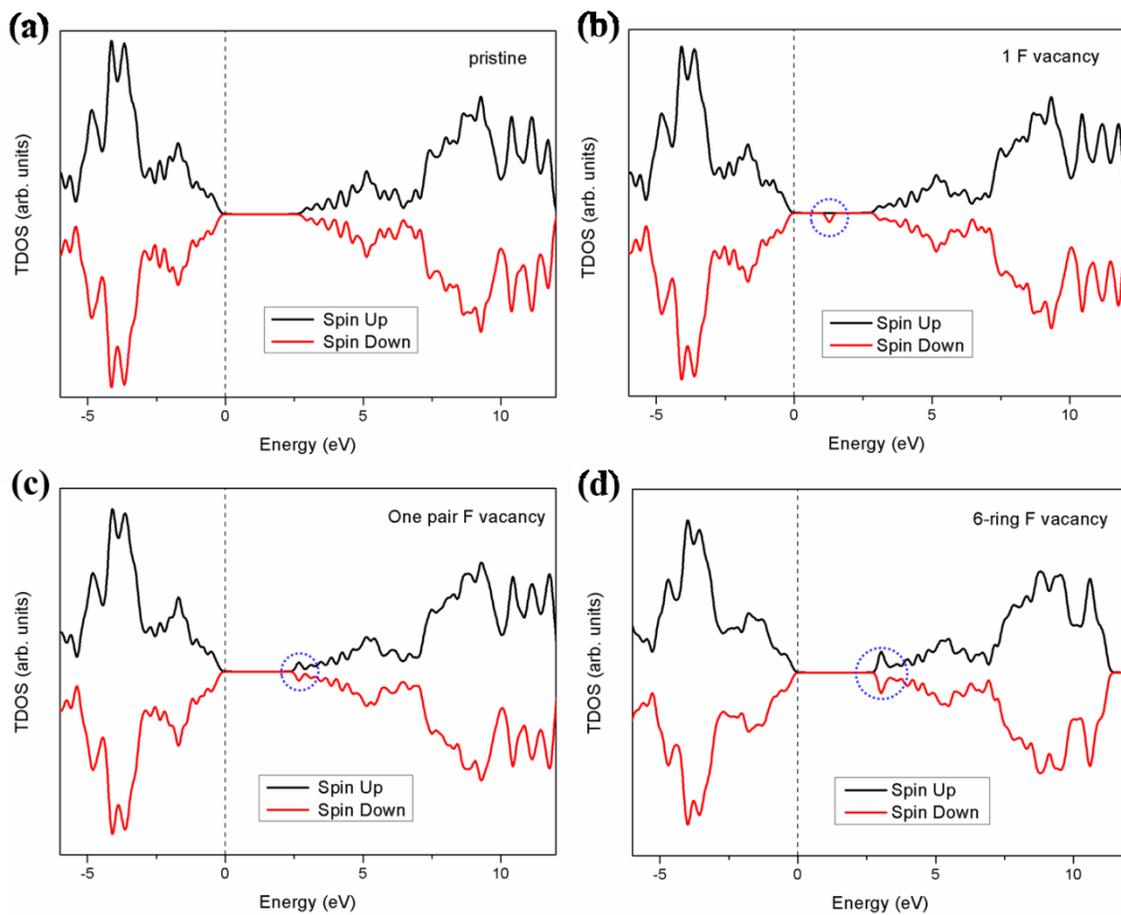


Figure S10. TDOS of pristine fluorinated graphite and defluorinated ones, corresponding to cases in Figure 6.

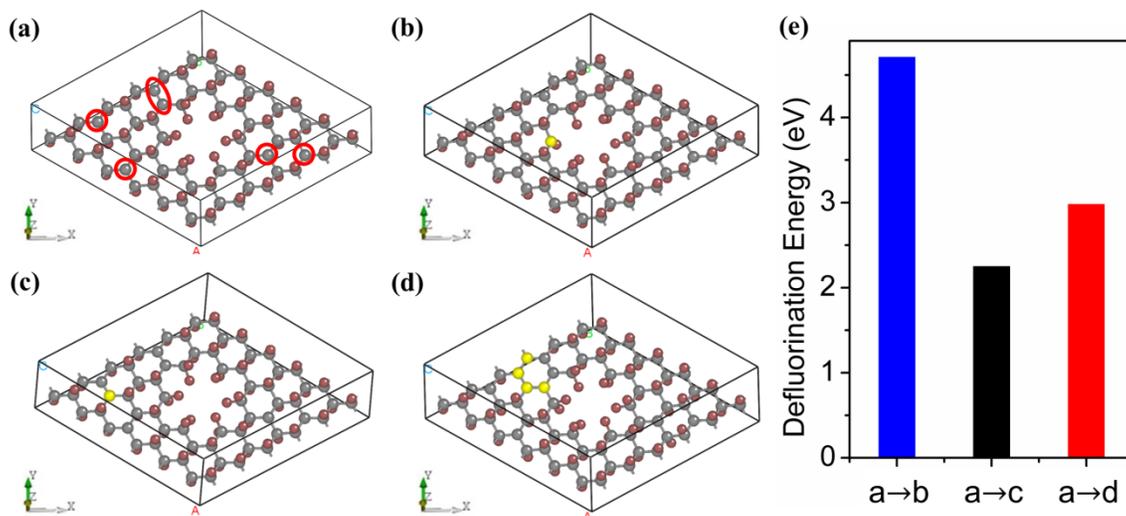


Figure S11. (a) Atomic structure of fluorinated hard carbon with $-CF_2$ group located around the middle pore, and sp^2 defluorinated carbons are indicated with red circles. The model contains 66 carbon atoms and 66 fluorine atoms. Grey: carbon atom; red: fluorine atom. (b) A single-fluorine vacancy close to the pore, which is indicated with yellow color. (c) One additional fluorine vacancy close to one sp^2 carbon, which is indicated with yellow color. (d) Removing 4 fluorine atoms near sp^2 carbon region, which is indicated with yellow. (e) Defluorination energy corresponding to different defluorination processes.

Table S1. EDX results of pristine FG and FHC, measured at different probing locations.

		Element	Line	Mass%	Atom%	x value in CF _x
FG	1	C	K	37.76±0.29	48.97±0.37	1.04
		F	K	62.24±0.80	51.03±0.66	
FG	2	C	K	40.64±0.24	51.98±0.31	0.92
		F	K	59.36±0.63	48.02±0.51	
FG	3	C	K	40.99±0.26	52.35±0.33	0.91
		F	K	59.01±0.68	47.65±0.55	
FHC	1	C	K	37.95±0.28	49.17±0.36	1.03
		F	K	62.05±0.76	50.83±0.63	
FHC	2	C	K	38.81±0.26	50.08±0.33	0.99
		F	K	61.19±0.69	49.92±0.57	
FHC	3	C	K	40.18±0.29	51.52±0.37	0.94
		F	K	59.82±0.76	48.48±0.62	

Table S2. Fluorine to carbon atomic ratio of FG and FHC, obtained from XPS results.

	Element	Atom%	x value in CF _x
FG	C	43.57	1.30
	F	56.43	
FHC	C	44.35	1.25
	F	55.65	

Table S3. Comparison of specific area, pore size and pore volume between FG and FHC powders (obtained from our previous work *ACS Appl. Mater. Interfaces* 2024, 16, 64898).

	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
FG	162	0.11	5.29
FHC	440	0.34	3.81