Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Materials for

Introducing thermo-mechanochemistry of lignin enabled high-quality low-cost carbon fiber

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This file includes the following:

Supplementary text

Analysis of CF Raman results

For calculating the I_D/I_G ratio of CFs, the broad D and G bands in the Raman spectra shown in Fig. 4b & 4c of the main text were deconvoluted into five bands using the Gaussian curve fitting. D_1 peak at 1360cm^{-1} and the D_2 peak at 1620cm^{-1} are disordered carbon in hexagonal carbon layers or at the edges of crystallites. D_3 (1500 cm^{-1}) between D_1 and G (1580 cm^{-1}) and D_4 (1200 cm^{-1}) at the left shoulder of the broad D band is derived from sp^2-boned amorphous carbon. The peak area sum of D_1 and D_2 divided by the peak area of G was used to calculate the I_D/I_G ratio, representing the disordered sp^2 attached to graphite structures. A lower I_D/I_G ratio represents a higher ordering and reduced structural defect.

Analysis of XRD results:

Before calculating crystalline parameters, Gaussian curve fitting was performed on the broad first band to deconvolute the 002 and γ bands. The Bragg and Scherrer formula was used to calculate crystalline parameters, including interlayer spacing (d_{002}), stacking height (L_c), and lateral length (L_a), as shown below:

$$d_{002}=\lambda/2\sin\theta$$

$$L=K\,\lambda/\beta\cos\theta$$

where θ is the Bragg angle of the corresponding peak. λ is the wavelength of the X-ray. The constant K is 0.89 for the (002) band and 1.84 for (100). β is the full width at half maximum intensity (FWHM) of the (002) peak and (100) peak. θ is the scattering angle of the corresponding peak. The (002) band measured from the parallel scan was used to calculate L_c, and the (100) band measured from the perpendicular scan was used to calculate L_a.

Analysis of SXAS results

The SAXS results (**Fig. S9**) were used to calculate average pore diameters of CF based on a modified form of the Kalliat model[1] for SXAS measurement by McDonald et al.[2] shown below:

$$I(q) = \rho^2 I_{OK}\left[\frac{A}{q^n} + \frac{C_{mi}}{(1 + b^2q^2)^2}\right] + bkg$$

$$the\ R = \sqrt{10b}$$

where *I(q)* is the scattering intensity of the fibers, ρ is the electronic density of graphite. I_{OK} is a parameter associated with the sample mass, the cross-section area of the sample, and the area of the X-ray beam penetrating the sample. q is the wave vector, and *A* is proportional to the surface area of pores. C_{mi} is proportional to the volume of pores, and *b* is the Debye autocorrelation length of the pores. *R* is the radius of the pores, and *bkg* is the background. *n* is set up as 3 in this study (for scattering from rough fractal surfaces). While CFs have a distribution of pore sizes, it has been proven that a single characteristic pore size is enough for a reasonable fit to the data instead of a distribution of pore sizes[1].

Table S1 Lignin characterizations after water purification

	Raw OL	Water washed OL	Raw KL	Water washed KL
M_w (g/mol)	2791	3091	4580	5505
Dispersity	4.39	3.8	4.82	4.53
T_g (°C)	95	74	198	156
T_d (°C)	178	196	269	280
Moisture content (%)	1.2	1.22	2.34	1.25
Ash content (%)	1.4	0.07	2.59	0.55
Fixed carbon (%)	37.4	38.7	38.80	39.2

T_d: temperature corresponding to 5% mass loss.

Table S2. Elemental composition of AF, NSF, and TSF

	C (%)	H (%)	N (%)	S (%)	O (%)
AF	67.403	5.063	0.253	0.044	27.236
NSF	64.890	3.293	0.297	0.078	31.442
TSF	64.990	3.366	0.350	0.051	31.243

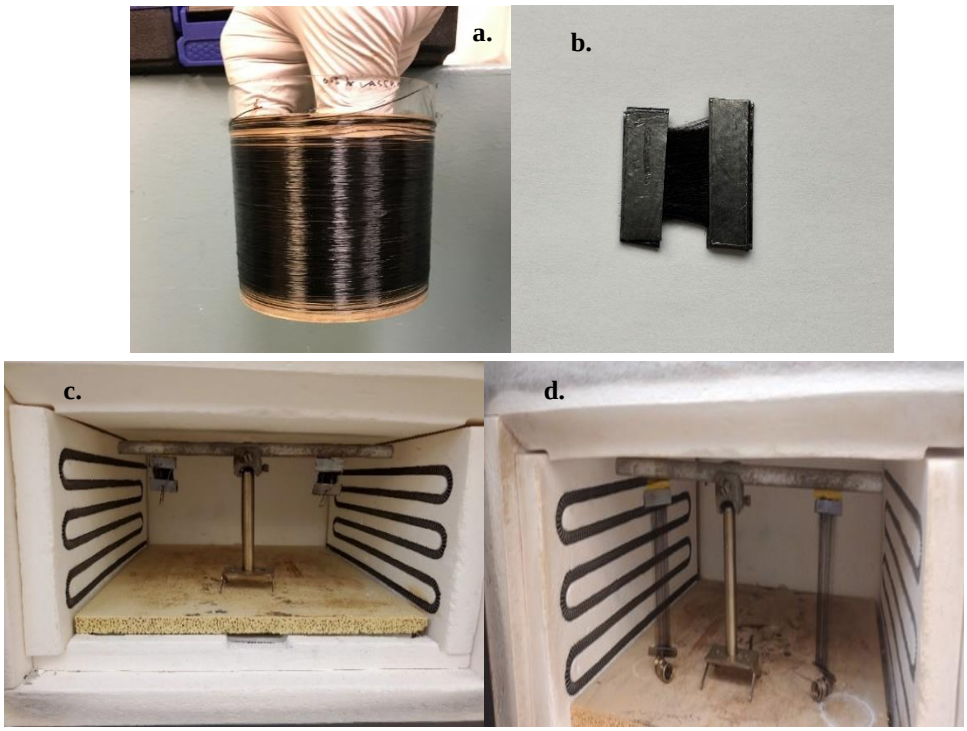


Figure S1. Stabilization of melt-spun fibers. **a**. As-spun fiber (AF) spool; **b**. AF fiber bundles prepared for stabilization; **c & d**. adjustable weights are attached to stretch the spun fibers during stabilization.

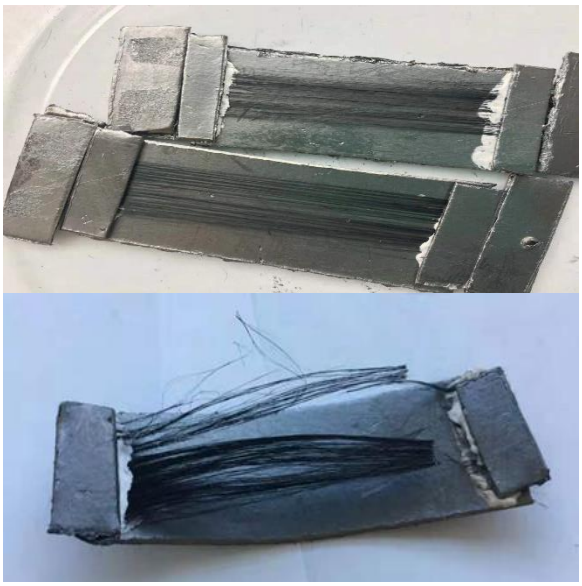


Figure S2. a. Stabilized fiber before carbonization; **b.** carbonizing at a constant heating rate of 7℃/min caused excessive fiber shrinkage to bend the graphene sheet and break the fibers.

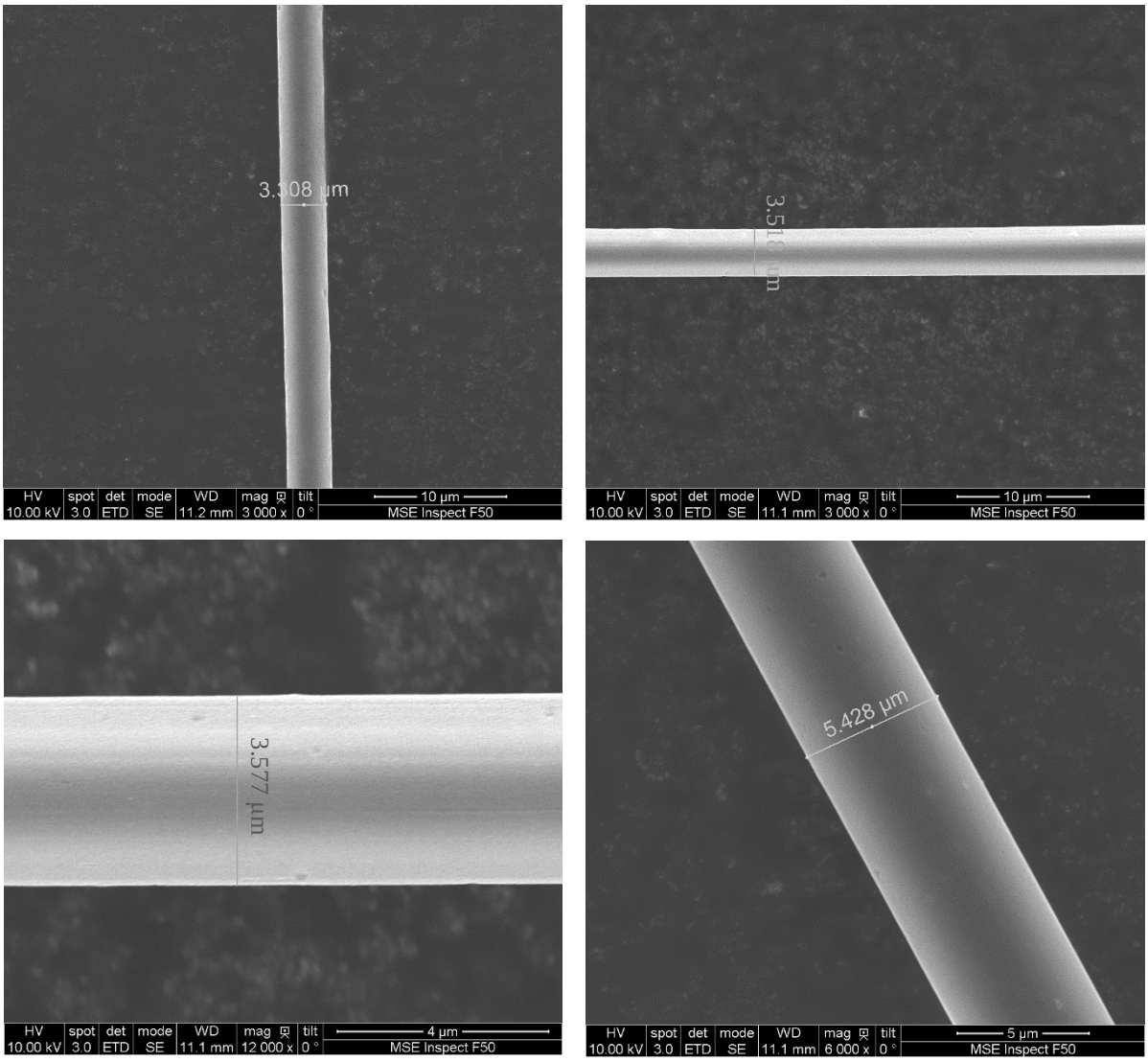


Figure S3. SEM images of representative CFs

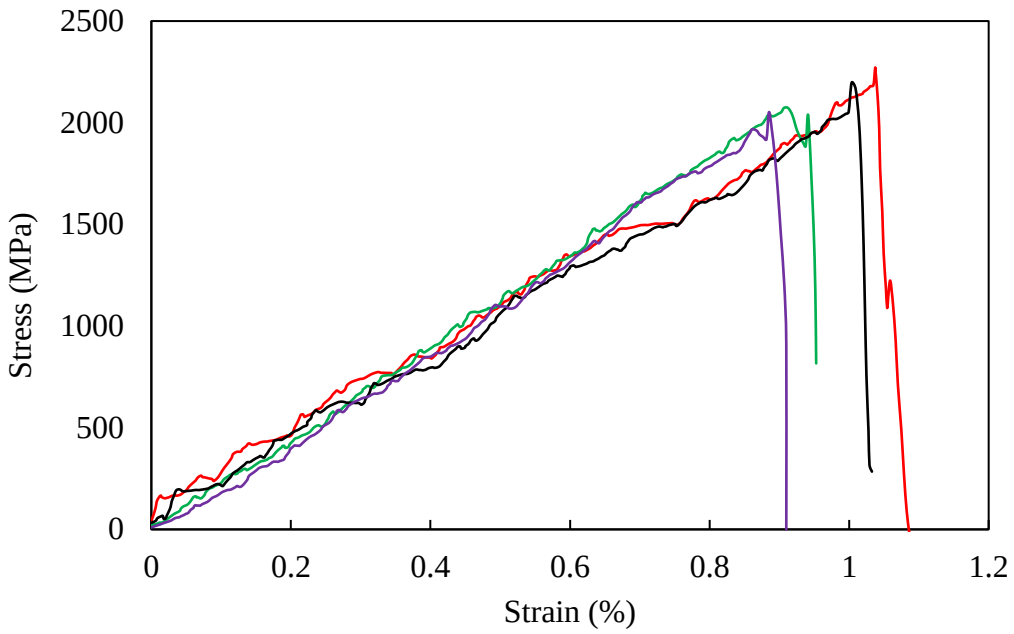


Figure S4. Strain-stress curve

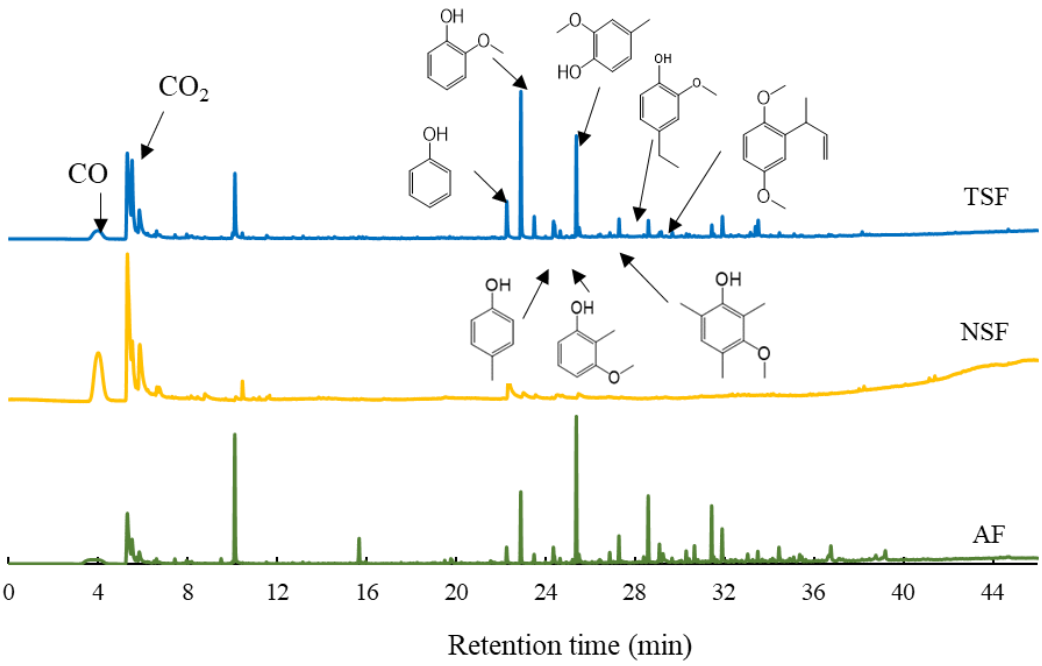


Figure S5. Pyrolysis-GC/MS chromatogram of AF, NSF, and TSF.

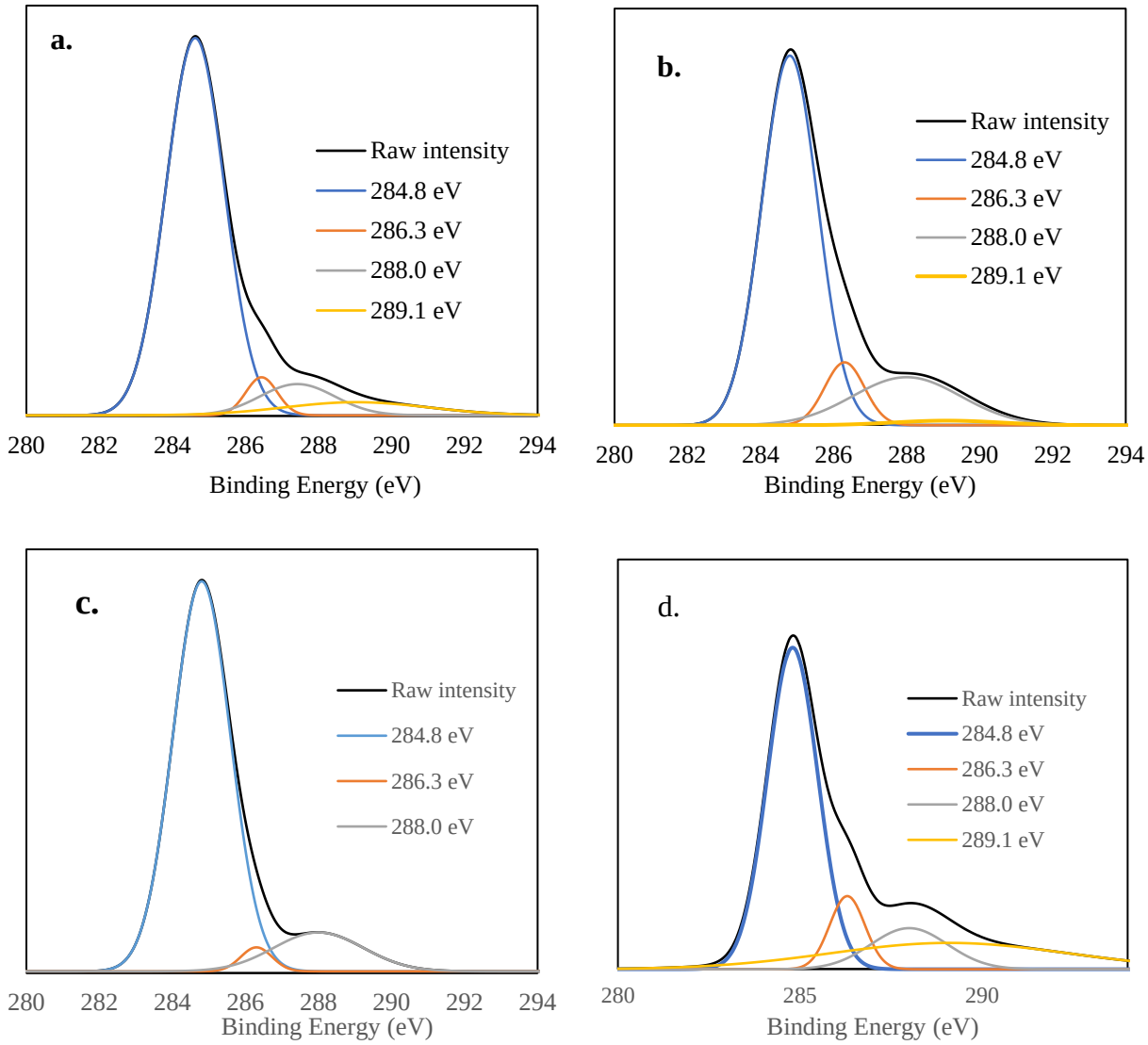
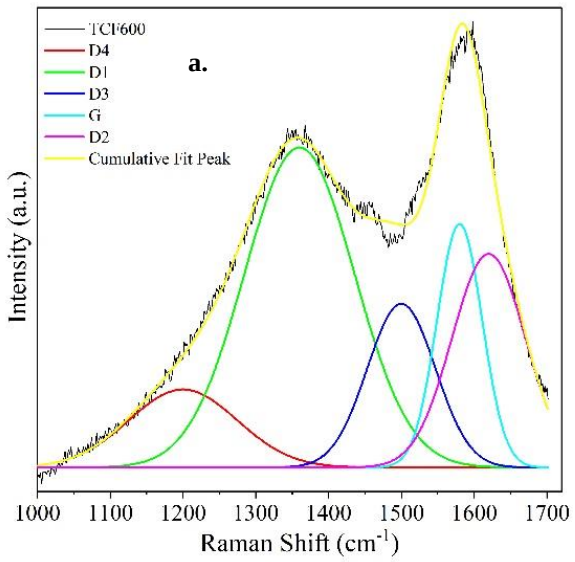
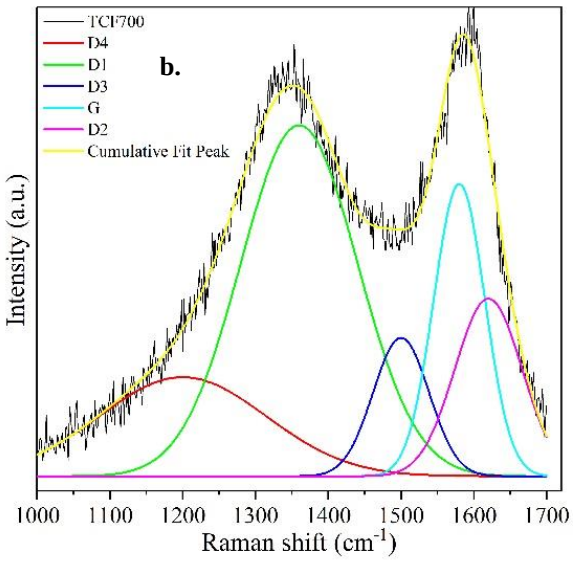
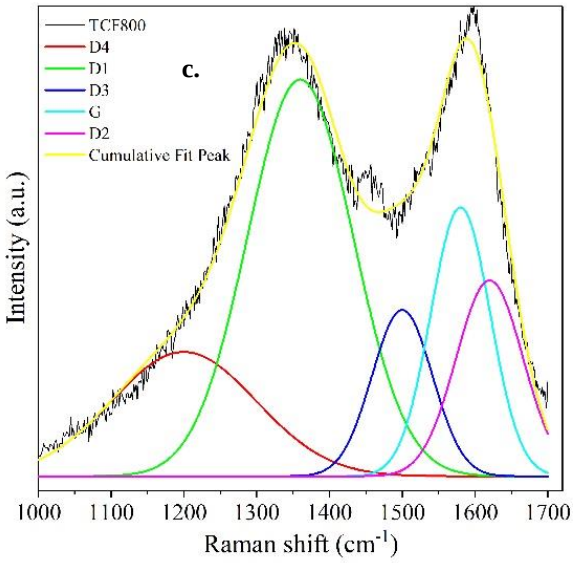
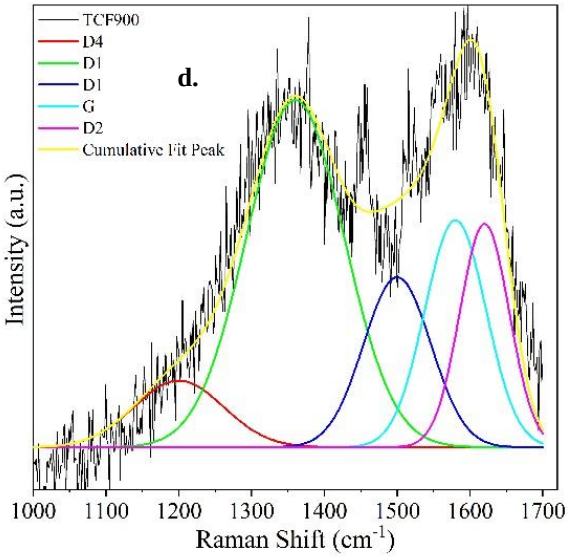


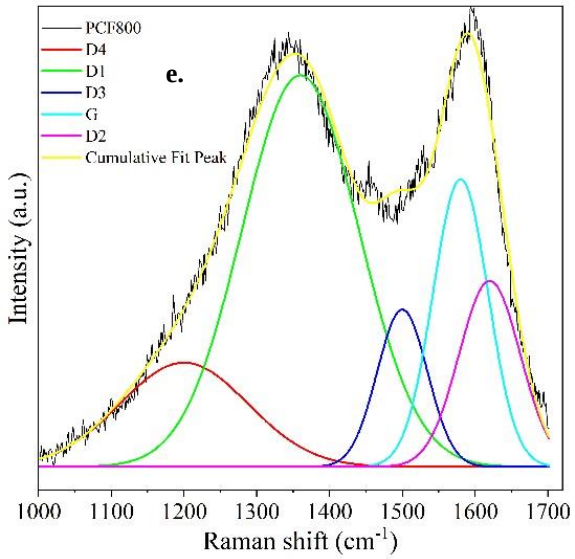
Figure S6. Gaussian fitting of XPS spectra of CFs. O. **a.** TCF700; **b.** TCF800; **c.**TCF900; **d.** NCF800. 284.8 eV: -C-C-, -C-H-: 286.3 eV: -C-O-; 288.0 eV: -C=O; 289.1 eV: -O-C=O.

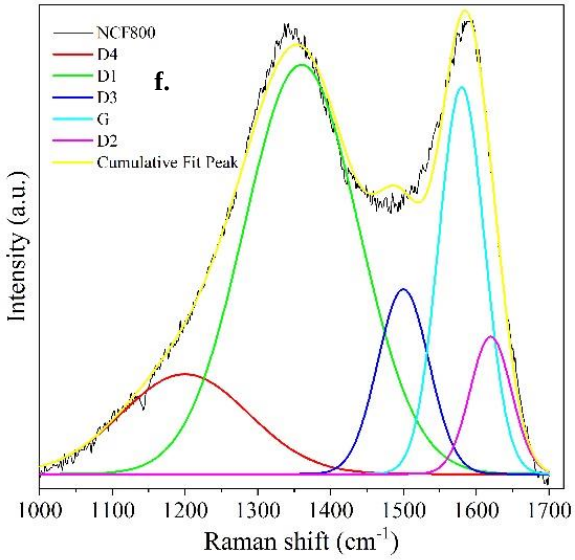

TCF600
D4
D1
D3
G
D2
Cumulative Fit Peak
a.
Intensity (a.u.)
1000 1100 1200 1300 1400 1500 1600 1700
Raman Shift (cm-1)

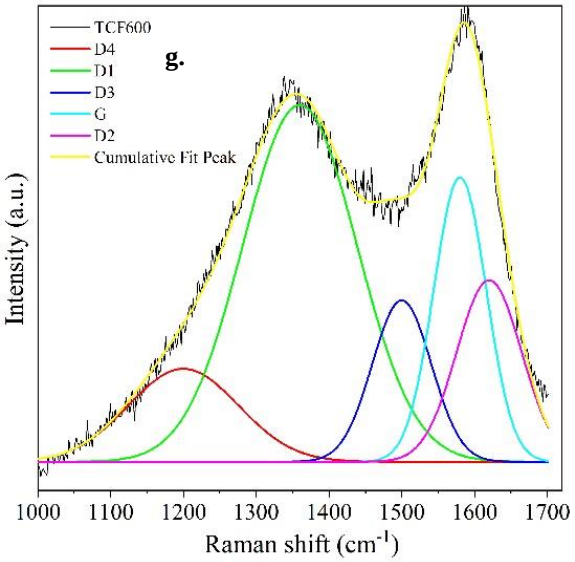

TCF700
D4
D1
D3
G
D2
Cumulative Fit Peak
b.
Intensity (a.u.)
1000 1100 1200 1300 1400 1500 1600 1700
Raman shift (cm-1)

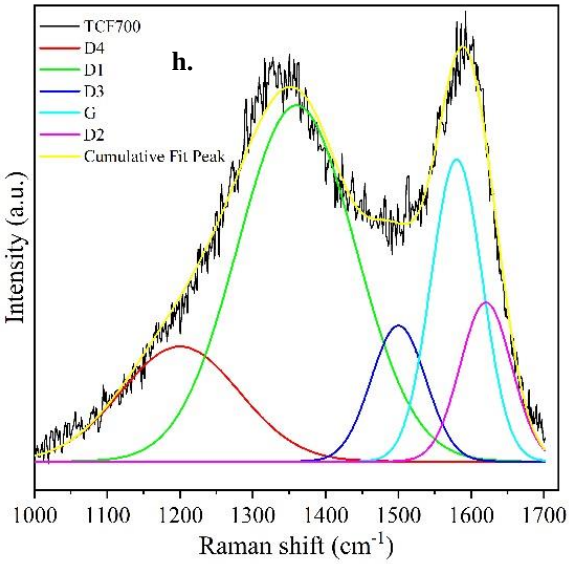

TCF800
D4
D1
D3
G
D2
Cumulative Fit Peak
c.
Intensity (a.u.)
1000 1100 1200 1300 1400 1500 1600 1700
Raman shift (cm-1)


TCF900
D4
D1
D1
G
D2
Cumulative Fit Peak
d.
Intensity (a.u.)
1000 1100 1200 1300 1400 1500 1600 1700
Raman Shift (cm-1)


PCF800
D4
D1
D3
G
D2
Cumulative Fit Peak
e.
Intensity (a.u.)
1000 1100 1200 1300 1400 1500 1600 1700
Raman shift (cm-1)


NCF800
D4
D1
D3
G
D2
Cumulative Fit Peak
f.
Intensity (a.u.)
1000 1100 1200 1300 1400 1500 1600 1700
Raman shift (cm-1)


TCF600
D4
D1
D3
G
D2
Cumulative Fit Peak
g.
Intensity (a.u.)
1000 1100 1200 1300 1400 1500 1600 1700
Raman shift (cm-1)


TCF700
D4
D1
D3
G
D2
Cumulative Fit Peak
h.
Intensity (a.u.)
1000 1100 1200 1300 1400 1500 1600 1700
Raman shift (cm-1)

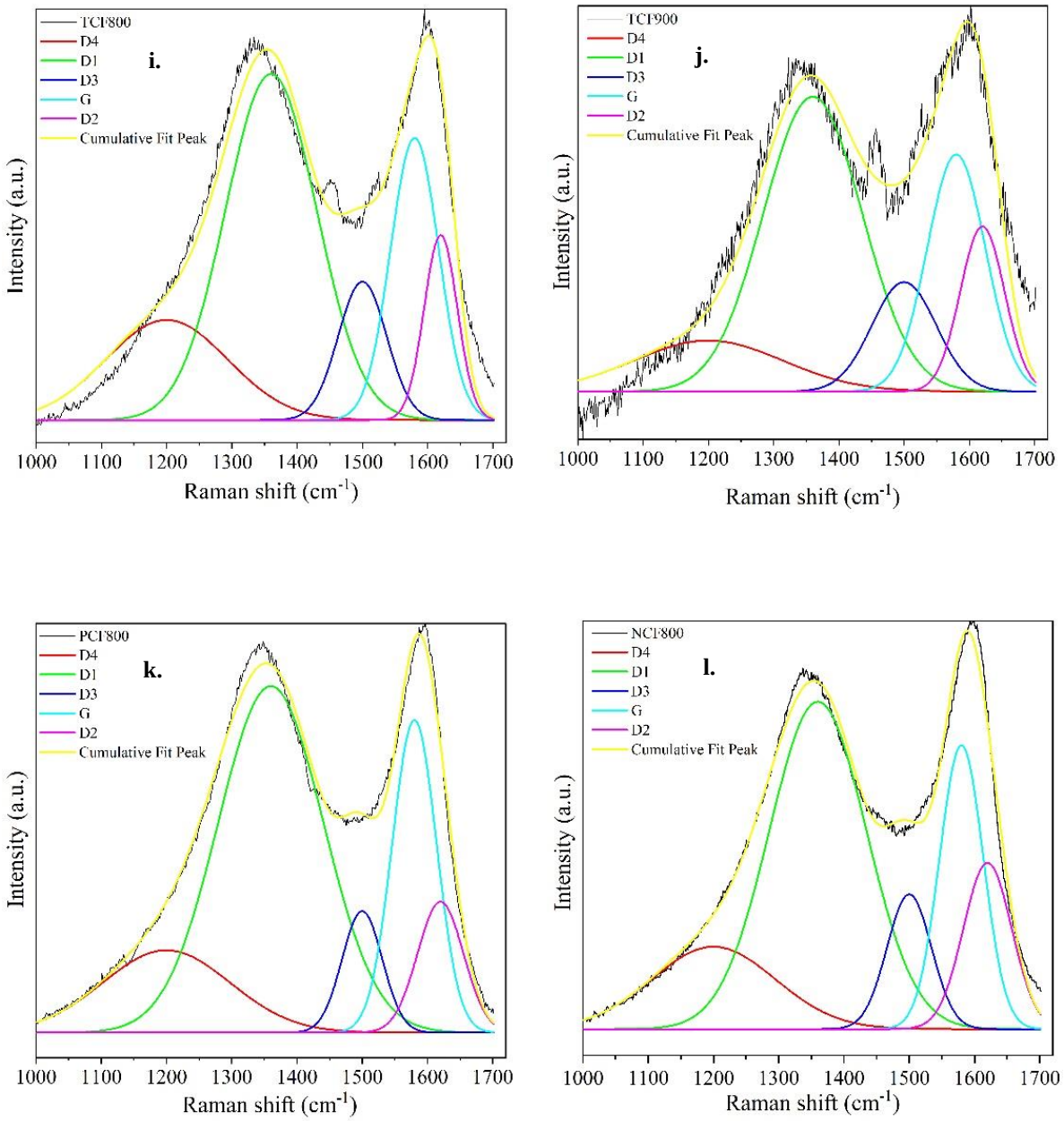
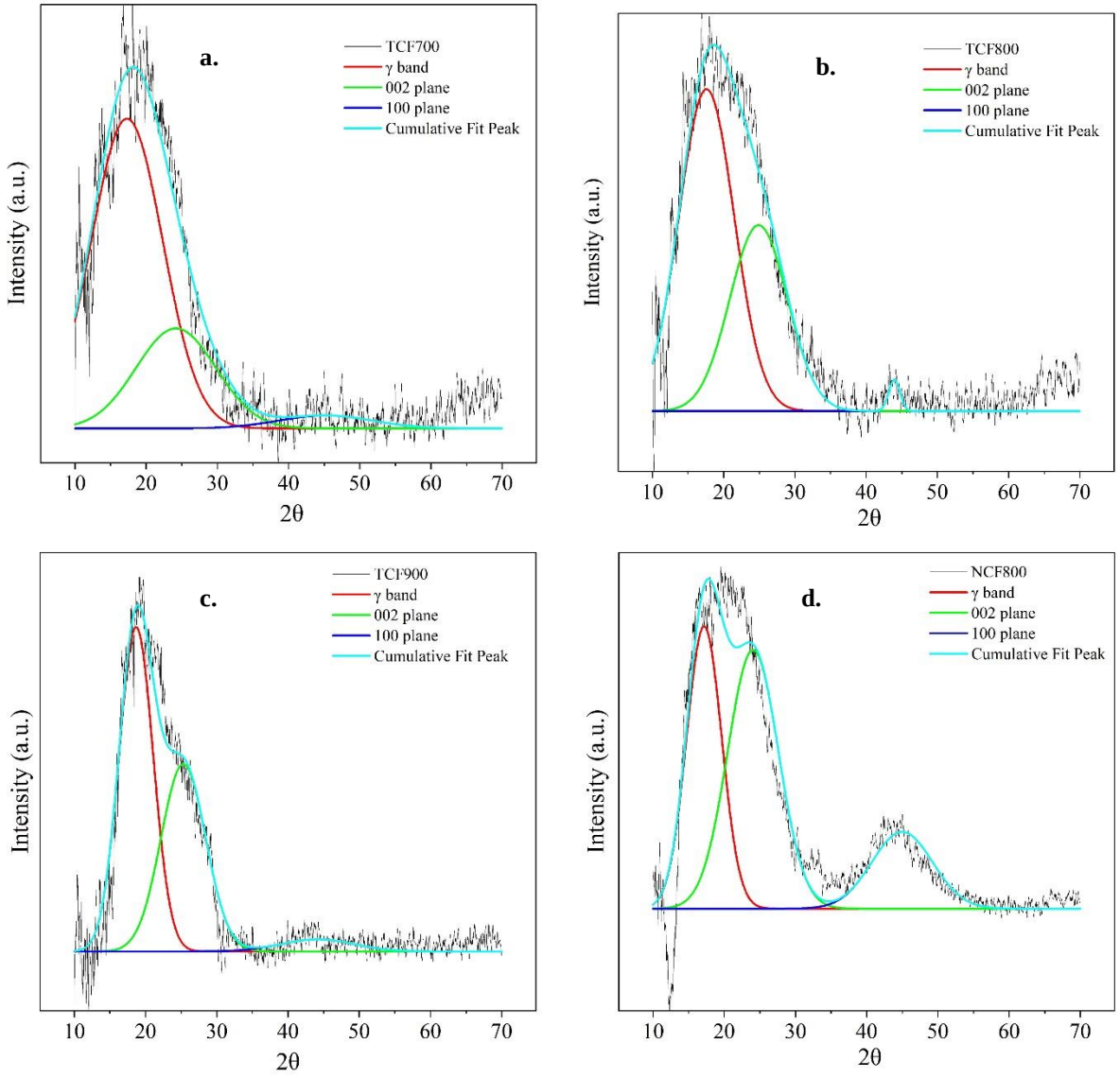


Figure S7. Gaussian fitting of Raman spectra of CFs. For the cross-section view spectra: **a.** TCF600; **b.** TCF700; **c.** TCF800; **d.** TCF900; **e.** PCF800; **f.** NCF800. For the top view spectra: **g.** TCF600; **h.** TCF700; **i.** TCF800; **j.** TCF900; **k.** PCF800; **i.** NCF800.


a.
TCF700
γ band
002 plane
100 plane
Cumulative Fit Peak
Intensity (a.u.)
2θ
b.
TCF800
γ band
002 plane
100 plane
Cumulative Fit Peak
Intensity (a.u.)
2θ
c.
TCF900
γ band
002 plane
100 plane
Cumulative Fit Peak
Intensity (a.u.)
2θ
d.
NCF800
γ band
002 plane
100 plane
Cumulative Fit Peak
Intensity (a.u.)
2θ

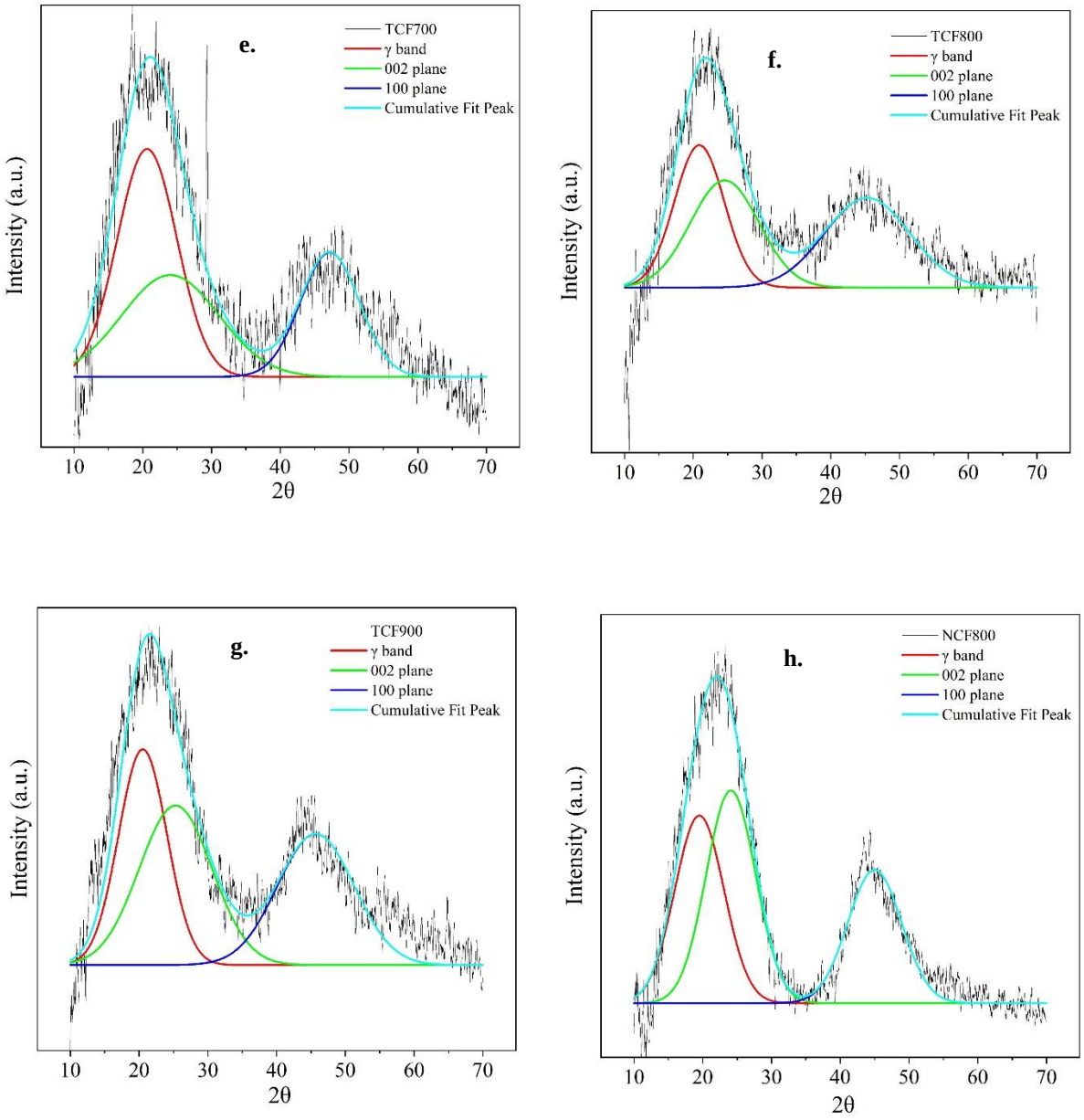


Figure S8. Gaussian fitting of XRD spectra of various CFs. For the parallel scan spectra: **a.** TCF700; **b.** TCF800; **c.** TCF900; **d.** NCF800. For the perpendicular scan spectra: **e.** TCF700; **f.** TCF800; **g.** TCF900; **h.** NCF800.

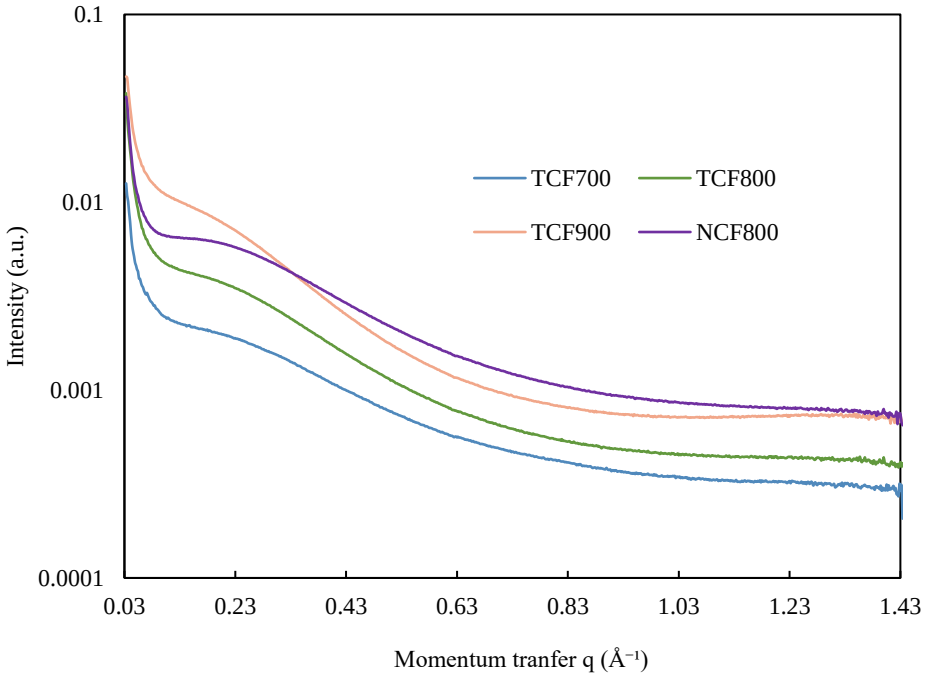


Figure S9. SAXR results of CFs.

Supplemental Material References:

1. M. Kalliat, C. Y. Kwak, and P. W. Schmidt, Small-angle X-ray investigation of the porosity in coals, *New Approaches in Coal Chemistry* Chapter 1, 3-22, *ACS Symposium Series* 169, ISBN13: 9780841206595 eISBN: 9780841208452, 1981.
2. M. J. McDonald, J. W. H. Smith, and J. R. Dahn, A study of small angle X-ray scattering from impregnated activated carbons, *Carbon* 2014, 68, 452–461, 2014.