Supporting Information for

Molecular characteristics of sulfonated biochar-derived organic matter

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Text S1 The detailed preparation procedure of the carbon materials

The rice husks were cleaned with tap water, washed with deionized water for three times and dried naturally in a ventilated area, then baked in a constant temperature oven at 80°C for 12 h, and then pulverized in a pulverizer and passed through a 60-mesh sieve.

(1) As previously reported,[1] sulfonated biochar were prepared as follows: the waste sulfuric acid of alkylated (WSAA) (100 g, 1 mol) was put into a 500-mL flask, and then the rice husk powder (20 g) was added. The reaction mixture was heated in flowing procedure. The mixture was slowly heated to 180 °C and held for 3 h. At the end of the reaction, cooled the reaction system to room temperature. The resulted substance was washed sequentially by dilute sulfuric acid of 30 wt.%, 15 wt.% and 5 wt.%. And, the final residue was washed repeatedly with boiled deionized water (>80°C) to obtain sulfonated biochar. The sulfonated biochar were dried at 80°C during 12 h.

(2) Pyrochars were prepared as follows: The20 g of rice husk powder was placed in a tube furnace (OTF-lnoX-S, HF-Kejing Company, China) under nitrogen atmosphere, heated up to 300°C at 5°C-min^{-1}, kept at a constant temperature of 300°C for 2 h, and then cooled down to room temperature.

(3) Hydrochars were prepared as follows: Approximate 20 g rice husk powder was placed in a 100 mL stainless steel reactor with a Lab Miniature Magnetic High Pressure Reactor (YZPR-100, Yanzheng Instrument Company, China) with following procedures: The mixture was slowly heated to 180 °C and held for 3 h at a pressure ranging from 2 to 3 MPa . At the end of the reaction, cooled the reaction system to room temperature. The aqueous solutions were filtered and the hydrochars were dried at 80°C during 12 h.

All prepared carbon materials, all of which were taken out for grinding and pass through 100-200-mesh (0.075-0.150 mm) sieves and stored in 500-mL amber glass bottles in 200-L desiccators.

Text S2 **FT-ICR MS data-related parameters integration**

From the molecular formula ($C_cH_hO_oN_nS_s$) assignments, the double bond equivalent (DBE) and modified aromaticity index (AI_{mod}) can be expressed as Eqs. (1) and (2).[2]

The overall DBE distribution can be described in terms of the intensity-weighted average DBE (DBE_{wa}), calculated according to Eqs. (3).

$$DBE = 1 + (2c - h + n)/2 \quad (1)$$

$$AI_{mod} = (1 + c - o/2 - h/2 - s)/(c - o/2 - n - s) \quad (2)$$

$$DBE_{wa} = \sum_i (I_i \times DBE_i) \Big/ \sum_i I_i \quad (3)$$

where c, h, n, o and s refer to the stoichiometric numbers of carbon, hydrogen, nitrogen, oxygen, and sulfur atoms per formula, respectively. I_i and DBE_i are the relative intensity and DBE value of peak i, respectively.

MLB_L% was calculated by dividing the sum of intensity of molecular formulas with H/C ⩾ 1.5 by the total intensity of molecular formulas.[2–4]

Carboxyl-rich alicyclic molecules (CRAMs) are usually related to refractory compounds.[5] CRAM% was calculated by dividing the sum of intensity of molecular formulas with DBE/C =0.3–0.68, DBE/H = 0.2–0.95, and DBE/O = 0.77–1.75 by the total intensity of molecular formulas.[6]

Tables

Table S1. The selected physicochemical properties of the carbon materials

Samples	C%	H%	O%	N%	S%	H/C	(N+O)/C	O/C	Ash%	Acidic groups (mmol/g)
Rice husk	39.12	5.42	44.37	0.66	＜0.1	1.66	0.87	0.85	15.98	-
Sulfonated biochar	47.90	4.29	33.57	0.58	6.34	1.07	0.54	0.53	25.09	4.01
Hydrochar	40.61	4.88	40.40	0.43	＜0.1	1.44	0.76	0.77	19.76	1.68
Pyrochar	48.77	4.02	32.48	0.72	＜0.1	0.99	0.52	0.50	8.01	1.69

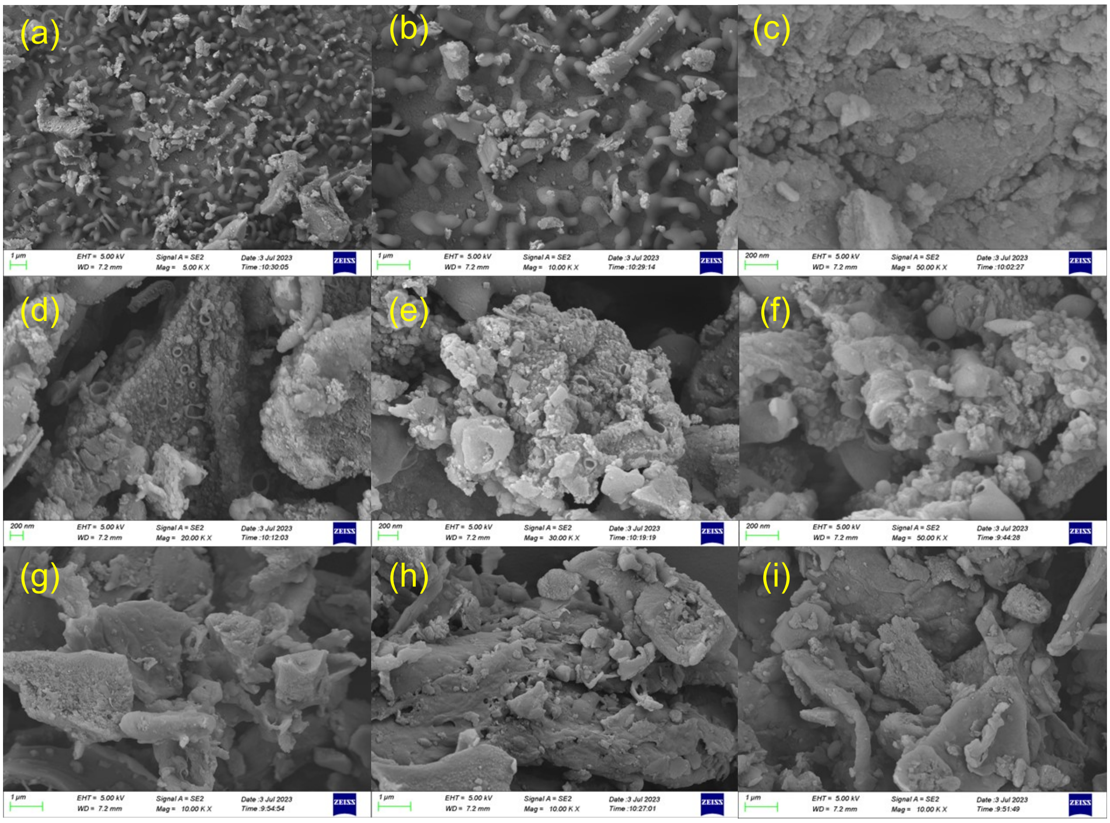
Table S2. BET of three carbon materials prepared from rice husk

Sample	Temperature ℃	BET surface area, m^2/g	Total pore volume, cm^3/g	Average pore diameter, nm
Sulfonated biochar	180	7.70	0.017	8.99
Hydrochar	180	8.90	0.033	14.86
Pyrochar	300	1.54	0.006	15.92

Table S3. Proportion of molecular formulas assigned to each compound class (calculated by molecular numbers).

Sample	RH	PYC	HYC	SBC
Polycyclic aromatic (%)	2.40 (138)	5.02 (246)	1.77 (87)	3.90 (139)
Highly aromatic compounds (%)	9.98 (574)	20.25 (992)	16.55 (813)	4.38 (156)
Highly unsaturated compounds (%)	53.82 (3095)	54.97 (2693)	62.79 (3085)	50.59 (1801)
Unsaturated aliphatic compounds (%)	15.60 (897)	7.70 (377)	4.54 (223)	22.47 (800)
Unsaturated aliphatic compounds (N) (%)	14.47 (832)	9.00 (441)	12.29 (604)	11.71 (417)
Carbohydrates (%)	0.00	0.00	0.00	0.25 (9)
lipids and saturated compounds (%)	3.15 (181)	2.08 (102)	1.55 (76)	6.49 (231)
Total number of molecules	(5751)	(4899)	(4913)	(3560)

Figures



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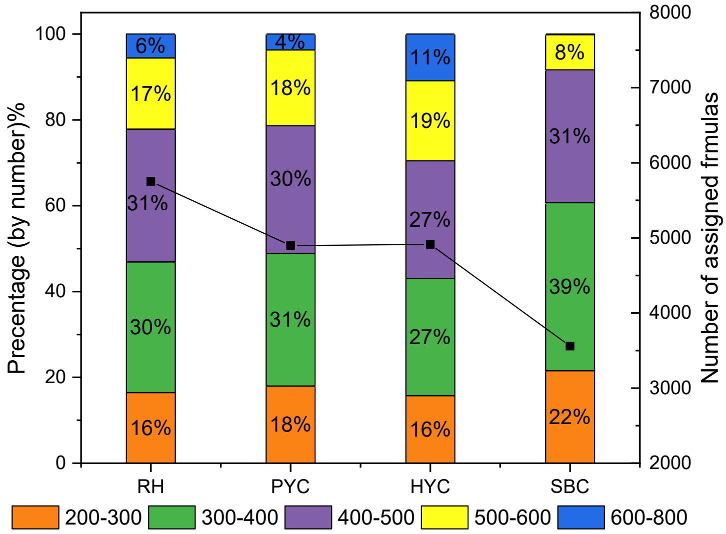

Figure S2. The number of formulas-assigned peaks, as determined from FT-ICR MS analysis, categorized according to *m/z*.

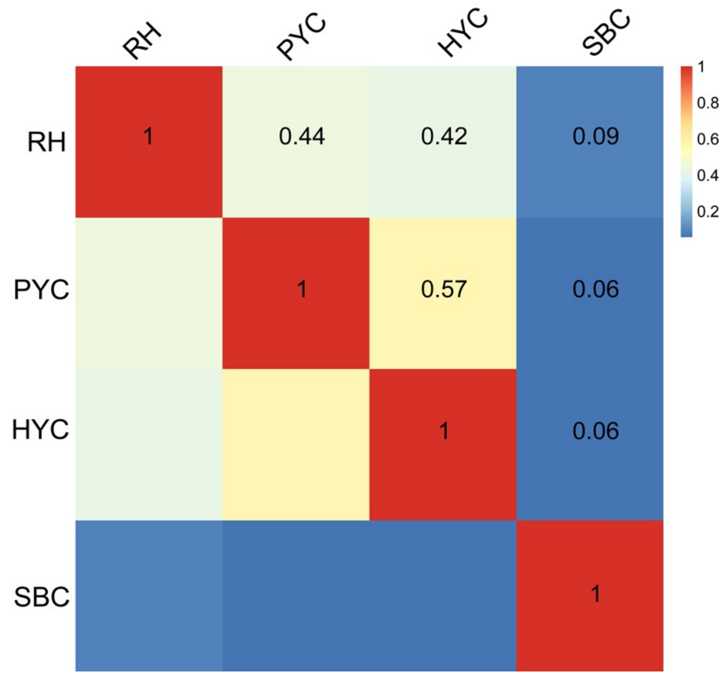

Figure S3. Percentage of same molecular formula among different samples (different colors represent the percentage of cross-identical molecular formulas in different samples).

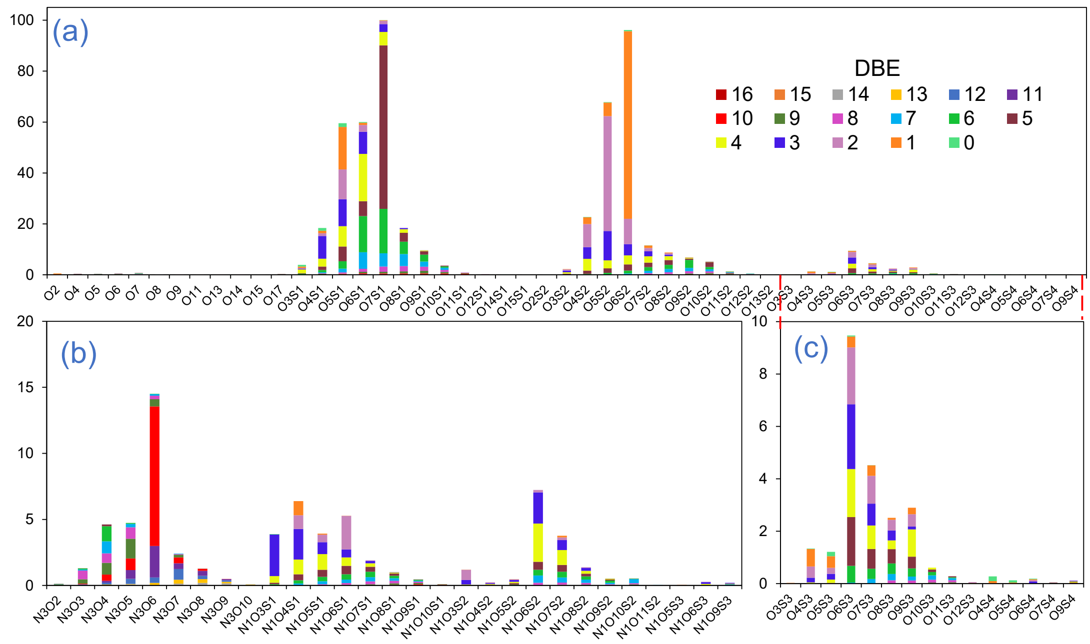

Figure S4. Relative abundance of heteroatom class species in sulfonated biochar DOM obtained by FT-ICR MS.

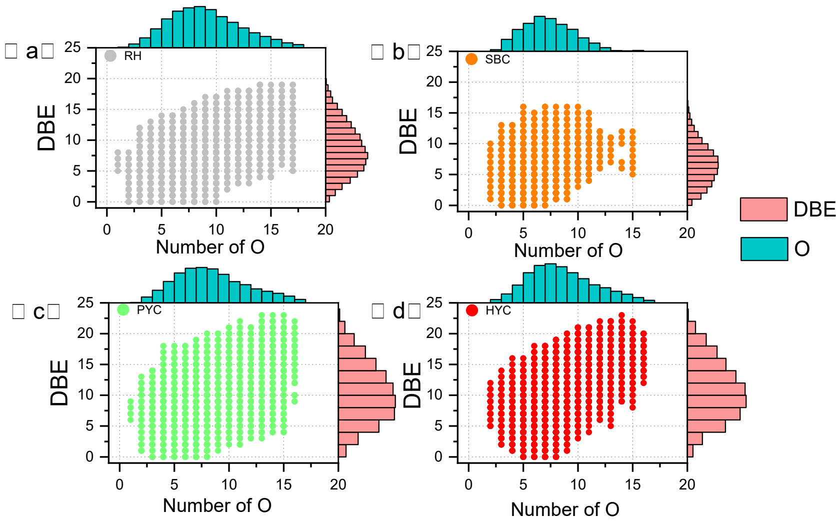

Figure S5. Plot of DBE versus the number of O atoms of DOM from different carbon materials.

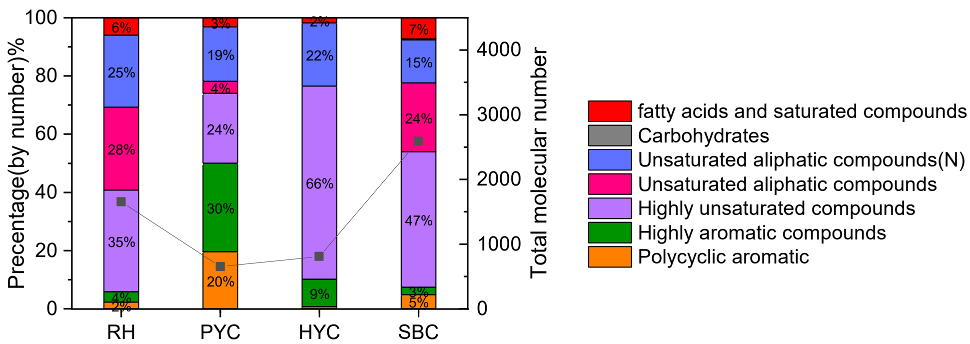

Figure S6. Classification of compounds with unique molecular formulas in all DOMs (calculated by molecular numbers).

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