
1 Supporting Information for

2 **Technical note: Intercomparison Study of the EC Radiocarbon**

3 **Analysis Methods Using Synthetic Known Samples**

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58 combustion, Pine wood combustion, Vehicle exhaust and Coal combustion.

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78 **1. Analytical Methods**

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80 **OC/EC and TOC analysis:**

81 The OC and EC in the three combustion source samples were analyzed by the TOT method,
82 performed with a laboratory OC/EC analyzer (Sunset Laboratory, USA) using the NIOSH2 thermal
83 protocol. (Salma et al., 2004; Maenhaut et al., 2005) Details regarding the method can be found in
84 the SI. The total organic carbon (TOC) concentration of the aerosols was also determined. For each
85 sample, 4 punches (4.8 mm diameter) were placed in precombusted Ag capsules, and the inorganic
86 carbon was removed by acidification, as described above. After drying, the TOC was quantified by
87 using a high-temperature catalytic CHN elemental analyzer.

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89 **Carbon isotope analysis** (Liu et al., 2013; Liu et al., 2017; Xu, et al., 2007):

90 The samples were analyzed for ^{13}C using a FLASH2000 Elemental Analyzer connected to a
91 Thermo MAT-253 isotope ratio mass spectrometer. The results are reported using standard delta
92 notation in permil units (‰): δ (‰) = $(R_{\text{sample}} - R_{\text{reference}})/R_{\text{reference}} \times 1000$, where δ (‰) stands for
93 $\delta^{13}\text{C}$ (‰), and R_{sample} and $R_{\text{reference}}$ are the isotopic ratios of the sample and reference material,
94 respectively. For carbon, the reference standard is Vienna Pee Dee Belemnite (VPDB). The
95 analytical precision for the international and in-house reference materials was generally better than
96 $\pm 0.5\%$ for $\delta^{13}\text{C}$. Replicate measurements of samples yielded similar standard deviations.

97 Preparation of graphite targets for accelerator mass spectrometry (AMS) analysis was
98 performed using the graphitization line at Guangzhou Institute of Geochemistry of the Chinese
99 Academy of Sciences (CAS) via the hydrogen and zinc reduction method (Xu et al., 2007). The
100 $^{14}\text{C}/^{12}\text{C}$ ratios in the graphite samples were determined using a compact AMS instrument (NEC,
101 National Electrostatics Corporation, USA) at the Guangzhou Institute of Geochemistry, CAS. AMS
102 calibration was performed using standards (Oxalic Acid Standards I and II) and blanks. The $\delta^{13}\text{C}$
103 value was obtained during AMS measurements and applied to correct the ^{14}C measurements for
104 isotopic fractionation. The fraction modern (f_m) was determined by comparing the measured $^{14}\text{C}/^{12}\text{C}$
105 ratio in a sample with that in a modern standard (NBS Oxalic Acid I in AD 1950). All of the reported
106 f_m values were corrected for $\delta^{13}\text{C}$ fractionation and for ^{14}C decay over the time period between 1950
107 and the year of measurement.

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109 **^{13}C solid state NMR experiments:**

110 All the ^{13}C solid state NMR experiments were performed using an AVANCE III 400-MHz NMR
111 spectrometer (Bruker, Billerica, MA, USA). The resonance frequency of ^{13}C is 100.613/MHz, and
112 glycine was used as a standard for chemical shift calibration. The selected samples were tested with
113 direct-polarization/magic-angle-spinning (DP/MAS) ^{13}C NMR experiments (Mao and Schmidt-
114 Rohr, 2004) using a Bruker 4-mm double-resonance probe head and a ZrO_2 rotor. DP/MAS ^{13}C
115 NMR experiments were run at a spinning speed of 14 kHz and the number of scans ranged from
116 4,000 to 40,000. The acquisition time was 5.12 μs , the spectral width was 100 kHz, and the 90° ^{13}C
117 pulse length was 4 μs . The recycle delay for DP/MAS ^{13}C NMR of the sample was based on
118 CP/T₁/TOSS experiments (Mao and Schmidt-Rohr, 2004). The data were processed with Bruker
119 Topspin 3.1 software.

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121 **Field emission scanning electron microscopy (FESEM):**

122 **FESEM** was used to observe the particle characteristics of typical carbon aerosol samples. The
123 field emission scanning electron microscope (Hitachi su8010, Hitachi, Japan) has higher resolution
124 than the traditional scanning electron microscope, and its resolution can be as high as 2 nanometers
125 under high voltage. It can be used to observe the micro surface morphology and composition
126 distribution of various material particles, and has higher imaging quality. The scanning electron
127 microscope was used to observe the morphology and particle size of amorphous organic matter in
128 carbonaceous aerosol samples, as well as the relationship between amorphous organic matter and
129 quartz membrane fiber under electron microscope. The low voltage mode (accelerating voltage of
130 about 1-2 kV, beam current of 10 μa , working distance of about 3-8 mm) was selected, or the
131 deceleration mode under low voltage condition (working distance less than 3 The backscattering
132 image was taken in a typical field of view with a magnification of 3000-100000 times.

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142 **2. Supplemental Tables:**

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144 **Table S1.** C%, OC/EC, EC/TC (TOT) %, $\delta^{13}\text{C}$ of the typical combustion samples.

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Sample	C% (± 3.0 %)	OC/EC	EC/TC(TOT)%	$\delta^{13}\text{C}$ ‰ (± 0.5 ‰)
Corn straw combustion	24.64	18.47	5.14	-14.02
Pine wood combustion	22.99	17.10	5.52	-24.41
Vehicle exhaust	14.49	2.42	29.21	-27.10
Coal combustion	11.60	3.85	20.62	-24.32

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172 **Table S2.** Composition ratio information (C% weight) of the six hybrid samples.

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Sampl e	C% (Corn straw combustion)	C% (Vehicl e exhaust)	C% (Coal combustion)	Sampl e	C% (Pine wood combustion)	C% (Vehicl e exhaust)	C% (Coal combustion)
S1	56.29	14.99	28.72	S4	56.27	15.02	28.71
S2	65.92	19.81	14.27	S5	65.93	19.74	14.34
S3	70.77	19.71	9.52	S6	70.80	19.69	9.50

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192 **Table S3.** The calculated and measured TC results of C% and $\delta^{13}\text{C}\text{‰}$, f_M for the six hybrid samples.
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Sample	C% (TC) (calculated)	C% (TC) (measured) ($\pm 3.0\%$)	$\delta^{13}\text{C}\text{‰}$ (TC) (calculated)	$\delta^{13}\text{C}\text{‰}$ (TC) (measured) ($\pm 0.5\%$)	f_M (TC) (calculated)	f_M (TC) (measured)
S1	17.26	17.70	-18.94	-18.71	0.5629	0.5930 \pm 0.0021
S2	18.97	19.10	-18.08	-17.74	0.6592	0.6831 \pm 0.0021
S3	19.79	19.39	-17.58	-17.40	0.7077	0.7220 \pm 0.0021
S4	17.76	18.18	-24.56	-24.66	0.5869	0.6117 \pm 0.0030
S5	19.17	19.31	-24.65	-24.67	0.6818	0.7157 \pm 0.0039
S6	19.82	20.08	-24.63	-24.63	0.7290	0.7705 \pm 0.0038

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216 **Table S4.**The EC/TC results of samples, including four combustion source samples and six
 217 synthetic known samples, isolated by four purification methods.

Sample	EC/TC(TOT) %	EC/TC(Hypy) %	EC/TC(CT O-375) %	EC/TC(EC _{He/} O ₂₋₄₇₅) %	EC/TC(EC _{LARA}) %
Corn straw	5.14	2.49	0.38	8.54	1.92
combustion	5.52	11.40	0.47	35.30	37.57
Pine wood					
combustion					
Vehicle	29.21	22.94	5.74	12.37	15.38
exhaust					
Coal	20.62	20.76	1.34	13.64	9.84
combustion					
S1	13.19	17.32	0.87	4.29	8.10
S2	12.11	14.16	0.52	3.86	8.44
S3	11.35	10.60	0.48	4.31	6.88
S4	14.09	16.68	0.09	29.00	23.59
S5	13.75	13.65	0.22	29.55	25.64
S6	12.56	11.52	0.18	28.32	27.87

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Table S5. Solid-state ^{13}C NMR structural parameters for Corn straw combustion, Pine wood combustion, Vehicle exhaust and Coal combustion.

Sample		fa	fa ^C	fa'	fa ^H	fa ^N	fa ^P	fa ^S	fa ^B	fal	fal ^H	fal*	fal ^O	C	FAA	FMA	Cn'	faC+ 0.5*(faP+ falO)* 100
Corn combustion	straw	0.48	0.03	0.46	0.21	0.25	0.05	0.08	0.32	0.52	0.22	0.14	0.22	64	0.28	0.27	6.5	13.53
Pine combustion	wood	0.51	0.01	0.50	0.22	0.28	0.04	0.1	0.35	0.49	0.18	0.16	0.2	68	0.28	0.33	4.9	12.01
Vehicle exhaust		0.41	0.03	0.38	0.09	0.29	0.03	0.07	0.28	0.59	0.3	0.15	0.18	86	0.26	0.25	8.43	10.53
Coal combustion		0.73	0.06	0.67	0.29	0.38	0.08	0.14	0.45	0.27	0.11	0.09	0.08	56	0.33	0.33	1.93	8.06

Structural parameter	Chemical shift range (ppm)	Carbon type	Parameter	Definition	Description
fa	90-240	Aromatic-carboxyl-carbonyl-amide	C		Average carbons per aromatic cluster ⁴⁹
fa ^C	165-240	Carboxyl-carbonyl-amide	FAA	$(fa^P + fa^S)/fa'$	Fraction of aromatic carbons with attachments
fa'	90-165	Aromatic	FMA	fal*/fal	Fraction of methyl in aliphatic
fa ^H	90-165	Protonated aromatic (w/o DD)	Cn'	fal/fa ^S	Average aliphatic carbon chain length
fa ^N	90-165	Non-protonated aromatic (w/ DD)		$fa^C + 0.5(fa^P + fal^O)*100$	A lower limit estimate for organic oxygen
fa ^P	150-165	Phenoxy-phenolic			
fa ^S	135-150	Alkyl-substituted aromatic			
fa ^B	90-135	Bridgehead aromatic			
fal	0-90	Aliphatic			
fal ^H	22-50	Methylene/methine			
fal*	0-22 & 50-60	Methyl/methoxy			
fal ^O	50-90	Alcohol/ether			

Table S6. The deviation between the results of different separation methods and the theoretical values, according to the ratio of herbaceous to woody combustion.

	Biomass*		Hypy	CTO-375	EC _{He/O2-475}	EC _{LARA}
	Herbaceous	Woody				
Africa	0.79	0.21	-37.38±1.36	93.88±20.79	57.85 ±6.84	14.80 ±6.84
Asia	0.55	0.45	-21.15±3.28	85.12±16.08	73.51 ±4.33	44.76 ±5.22
Australia/Oceania	0.91	0.09	-45.49±3.35	98.27±23.21	50.02 ±8.12	-0.19 ±7.74
Central America/Caribbean	0.10	0.90	9.27±11.26	68.68 ±8.61	102.88 ±1.97	100.94±3.90
Europe	0.27	0.73	-2.22±8.23	74.89±11.06	91.79 ±1.93	79.72 ±4.00
North America	0.10	0.90	9.27±11.26	68.68 ±8.61	102.88 ±1.97	100.94±3.90
South America	0.39	0.61	-10.34±6.10	79.27±13.11	83.96 ±2.80	64.74 ±4.40
Global average	0.58	0.42	-23.18±2.76	86.21±16.66	71.56 ±4.64	41.01 ±5.41

* The ratio of herbaceous and woody was calculated according to the reference (Bond et al., 2004; Zhang et al., 2004; Streets et al., 2003; Stevens et al., 2017)

Table S7. f_M and $\delta^{13}C$ measurements in SRM 1649 a/b.

Sample	f_M	M_C (μg)	$\delta^{13}C$ (‰ vs VPDB)	EC/TC	reference
1649b TC	0.525 \pm 0.002 (n = 1)	220	-25.6 \pm 0.5 (n = 2)	0.275 \pm 0.050	this work
1649a TC	0.522 \pm 0.018 (n = 5)	12–87	-25.5 \pm 0.6 (n = 2)	0.280 \pm 0.080	ref (Szidat et al., 2004)
1649a TC	0.510 \pm 0.011 (n = 3)	not given	-25.3 \pm 0.3 (n = 2)	0.080 \pm 0.010	ref (Reddy et al., 2002)
1649a TC	0.610 \pm 0.040	not given	not given	not given	ref (Currie et al., 2002)
1649a TC	0.505 \pm 0.003	not given	not given	0.458 \pm 0.025	ref (Currie et al., 2002)
1649a TC	0.517 \pm 0.004	not given	not given	not given	ref (Currie et al., 2002)
1649b EC	0.108 \pm 0.002 (n = 1)	270	-24.9 \pm 0.5 (n = 2)	0.275 \pm 0.050	this work
1649b EC	0.112 \pm 0.080* (n = 1)	~460	-24.9 \pm 0.5 (n = 2)	0.275 \pm 0.050	this work
1649a EC	0.066 \pm 0.020 (n = 4)	37–70	-24.8 \pm 0.5 (n = 4)	0.280 \pm 0.080	ref (Szidat et al., 2004)
1649a EC	0.065 \pm 0.014 (n = 3)	~2800	-26.55 \pm 0.04	0.080 \pm 0.010	ref (Reddy et al., 2002)
1649a EC	0.140 \pm 0.050 (n = 1)	459	not given	~0.280	ref (Liu et al., 2013)
1649a EC	0.150 \pm 0.080	not given	not given	not given	ref (Heal et al., 2011)
1649a EC	0.065 \pm 0.003 (n = 1)	not given	not given	0.077 \pm 0.002	ref (Currie et al., 2002)
1649a EC	0.153 \pm 0.002	not given	not given	0.458 \pm 0.025	ref (Currie et al., 2002)
1649a EC	0.038 \pm 0.012	not given	not given	0.109 \pm 0.005	ref (Currie et al., 2002)

* The same 1649b EC obtained by the Hypy method was sent to BETA for ^{14}C analysis.

3. Supplemental Figures:

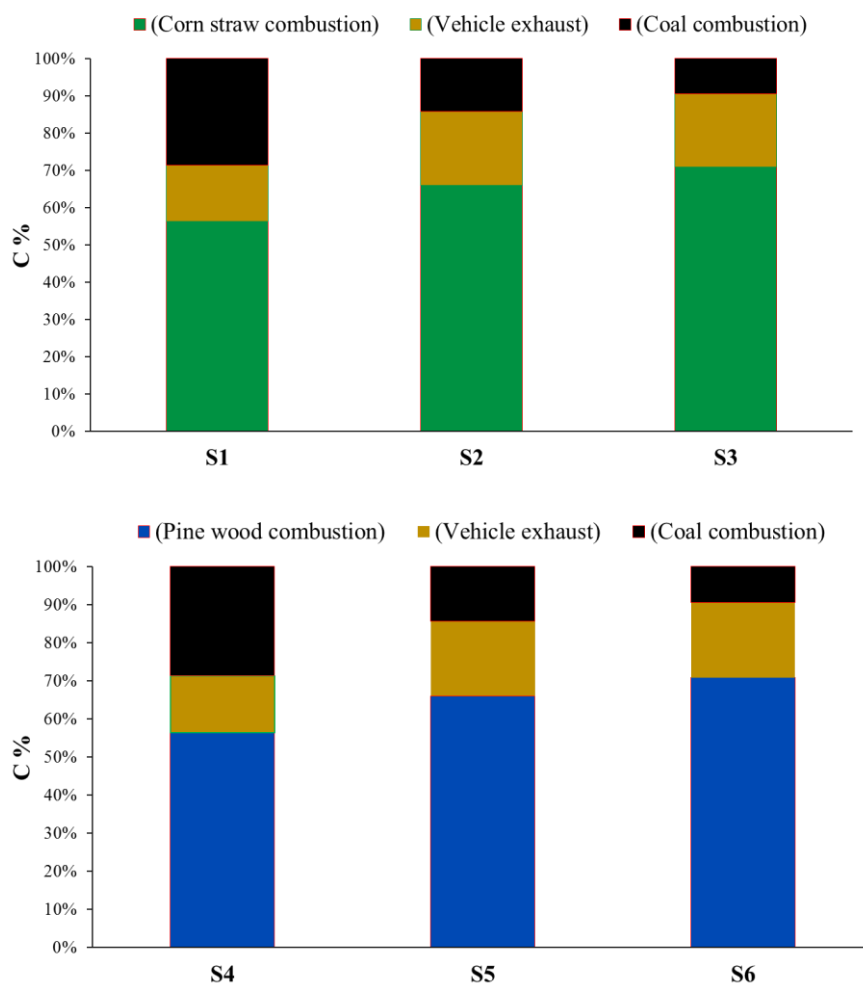


Figure S1. Composition ratio information (C% weight) of the six synthetic known samples.

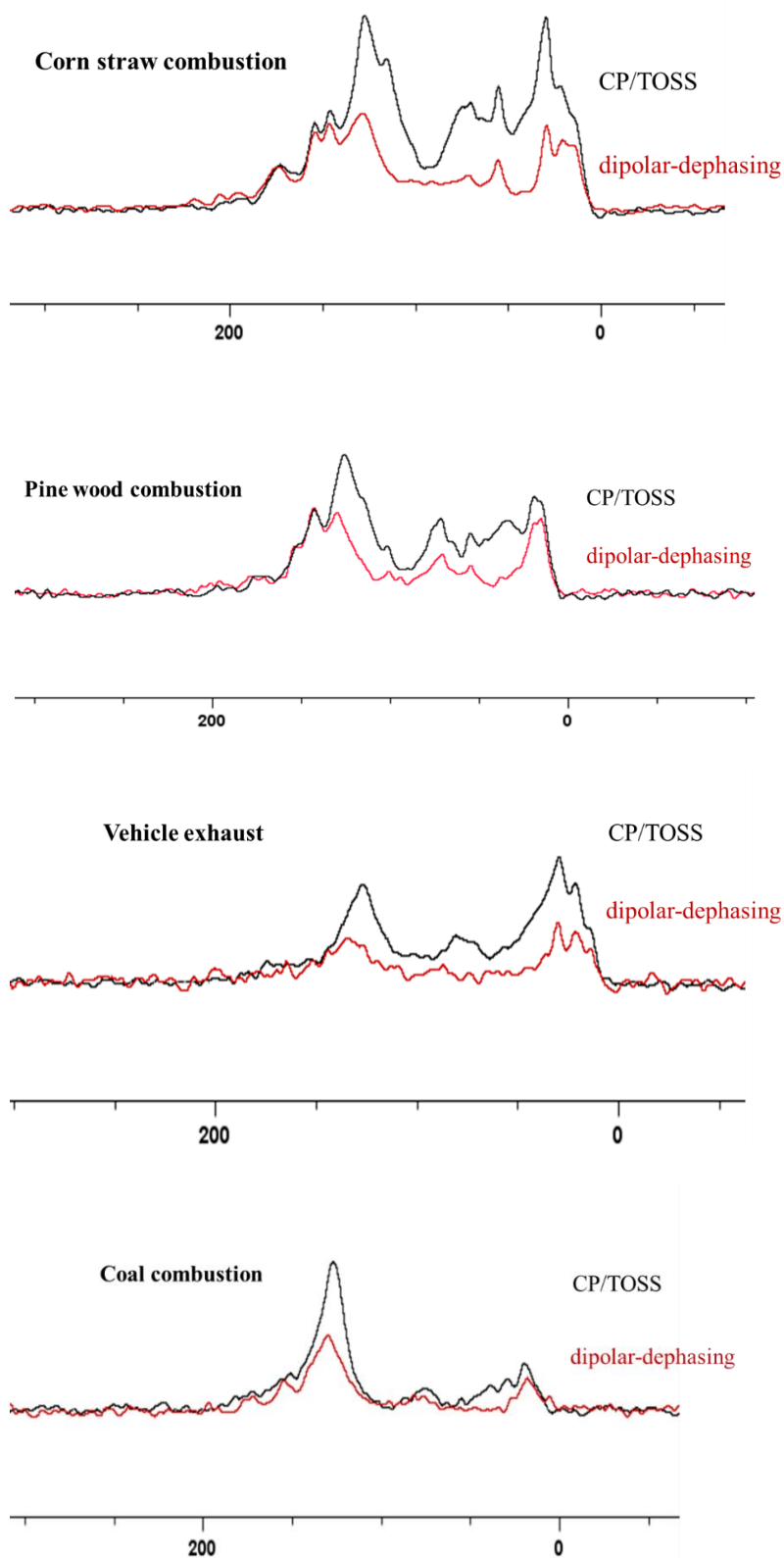
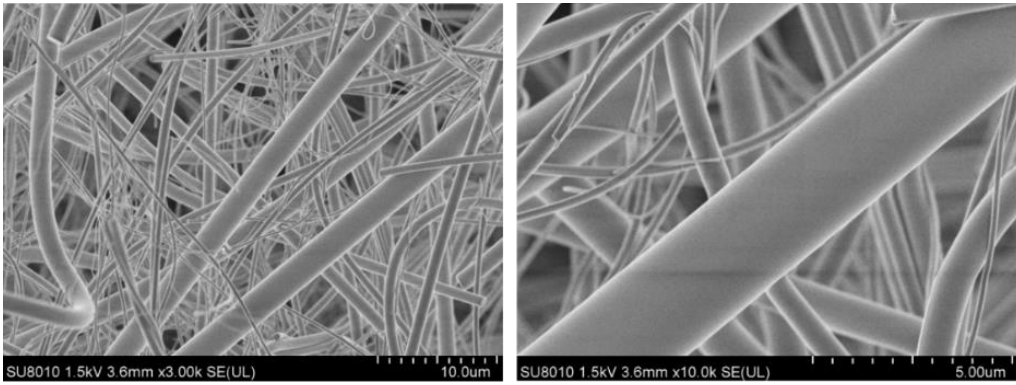
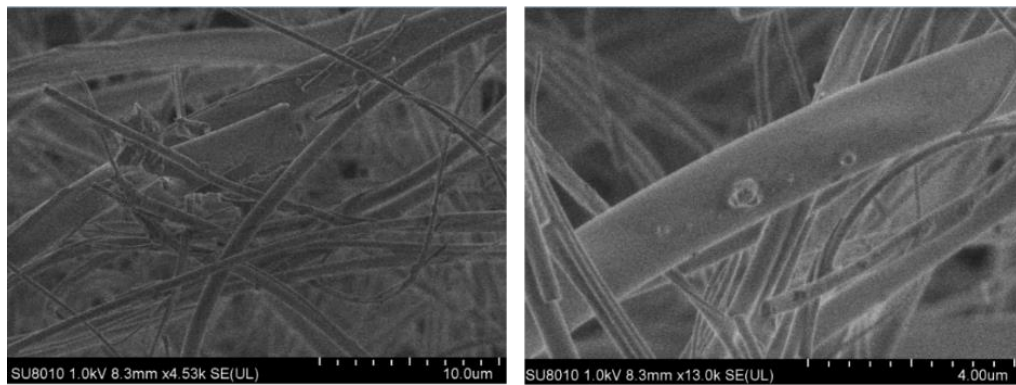


Figure S2. Solid-state ^{13}C NMR spectrum of Corn straw combustion, Pine wood combustion, Vehicle exhaust and Coal combustion.

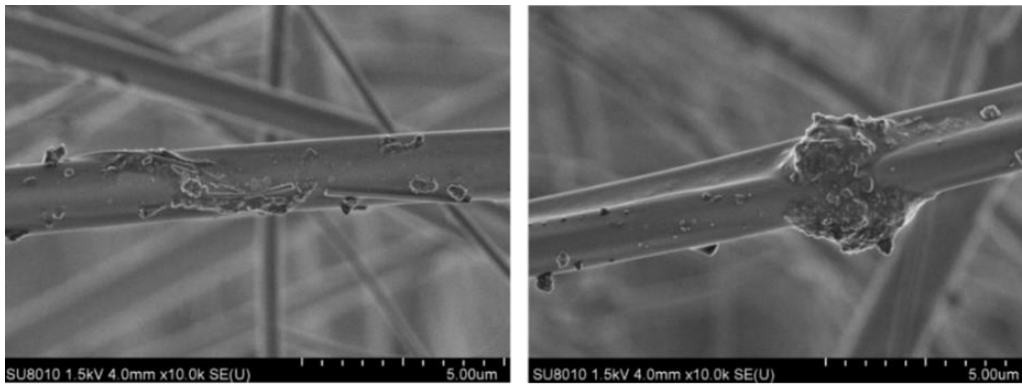
^{13}C CP/TOSS and CP/TOSS/DD NMR for the identification of functional groups in the samples. Black lines: CP/TOSS/DD NMR, unselective CP/TOSS spectra. Red lines: CP/TOSS/DD NMR, CP/TOSS with dipolar dephasing to select non-protonated carbons and mobile groups.



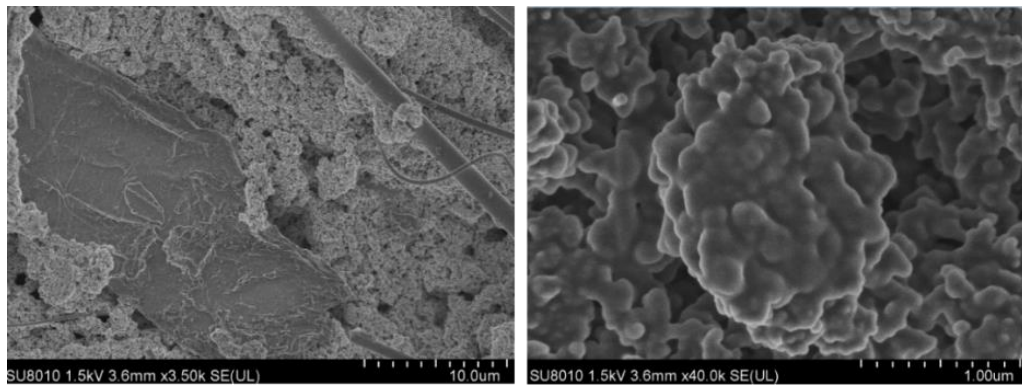
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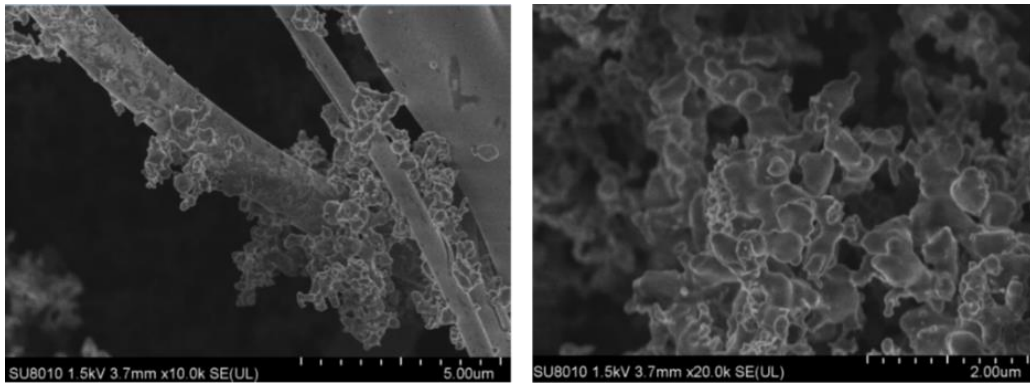
Corn stem combustion



Pine wood combustion



Vehicle exhaust



Coal combustion

Figure S3. The field emission scanning electron microscopy (FESEM) results of Corn straw combustion, Pine wood combustion, Vehicle exhaust and Coal combustion.

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