1 Physicochemical property changes during oxidation process for
2 diesel PM sampled at different tailpipe positions

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16 **Abstract**

17 Diesel particulate matter (PM) samples were collected at different tailpipe positions where sampling
18 temperature differed greatly. All the samples were pre-heated in air at high temperature until 40%
19 mass was burnt out. Physicochemical properties of diesel PM both before and after partial oxidation
20 were analyzed, and to further figure out the reasons of oxidation activity changes in the oxidation
21 process. The results showed that ignition temperature of PM whose sampling temperature was
22 higher than 208 °C differed greatly from PM sampled below that temperature. After partial
23 oxidation, sample 3 presented the hugest oxidation activity decreasing with burn out temperature
24 increasing by 14.7 °C. Primary particle size distribution shifted to smaller diameter direction after
25 partial oxidation, and particle stacking degree decreased evidently. Nanostructures of diesel PM
26 transferred from onion like structures with randomly arranged crystallite to core-shell like structures
27 with void inner cores. Oxygen-containing functional groups (carbonyl and hydroxy) decreased
28 evidently after PM partial oxidation that was obtained from Fourier transform infrared spectroscopy
29 (FTIR) spectra, it was consistent with the results of Raman parameter I_{D3}/I_G .

30 **Keywords:** diesel PM; sampling temperature; partial oxidation; physicochemical properties

31 **1. Introduction**

32 Soot emitted by diesel engines has brought about huge environmental and health problems [1, 2] so
33 that an urgent necessity is needed to decrease diesel PM. Diesel PM is complicated compounds that
34 mainly contain soot, organic compounds, sulphur compounds and metal [3]. Diesel particulate filter
35 (DPF) is considered to be the most successful technology to remove diesel PM while DPF
36 encounters regeneration problem. Diesel PM captured on DPF should be oxidized periodically to
37 keep excellent performance. The oxidation behaviors of diesel PM are closely related to engine

operation conditions, fuel properties, cylinder combustion and sampling conditions [4-9]. The factors mentioned above lead to the differences of diesel PM physicochemical properties that are considered to be fundamental factors causing the distinctions of oxidation activity.

PM accumulation consists of many spherical-like particles at the function of organic compounds and bridge forces [10]. The morphology of diesel PM shows chain shape with many particles overlapping [11]. Nanostructures of some diesel PM present onion like structures that are with short and randomly arranged crystallite, and others present void cores with core-shell like structures [12-14]. The effect of fuel on PM oxidation activity and nanostructures was performed [15]. Nanostructures of PM obtained from biodiesel engine are more densely arranged compared with diesel PM. Nanostructures are considered to be vital factors contributing to the differences in PM oxidation activity [10]. However, Song et. al [15] pointed that oxygen functional groups were more important for PM oxidation. This opinion was verified by the fact that biodiesel soot is 5 times more oxidative reactive than diesel soot though biodiesel soot is more orderly arranged. The oxygen-containing functional groups provide active sites that are necessary to form active surface areas conducting to PM oxidation. Biodiesel soot presents higher absorbance intensity at wave number 2928 cm^{-1} and 2856 cm^{-1} in FTIR where aliphatic hydrocarbon is indicated [16]. The nanostructures observed by high resolution transmission electron microscopy (HRTEM) figures are mutually complementary with Raman spectra. Crystallite size calculated using Raman parameters shows consistency with HRTEM results [8]. Raman spectra present information about vibration and rotation of molecules crystal lattice, which is reflected by amorphous carbon and graphitized carbon [17-19] that are closely related to PM oxidation activity, however, the relations of Raman spectra and PM oxidation activity are still in debated [7, 8, 20, 21]. The amorphous carbon is caused by

oxygen-containing functional groups [22, 23].

Meng et. al [24] put forward a PM oxidation model that volatile substance evaporated at the beginning, then the amorphous carbon oxidation, graphitization and combustion. During the oxidation process, physicochemical properties change greatly with nanostructures of diesel PM presenting onion like structures, void core-shell like structures and densely arranged bands [4]. Also, oxygen content decreases greatly due to the volatilization of volatile organic compounds (VOC) and amorphous carbon oxidation. The decrease is evident after 40% mass loss for biodiesel PM while it is 20% for diesel PM, and the content dropped to zero when more than 80% mass was burnt out [25]. In the oxidation process, average primary particle diameter decreases, also the void cores are enlarged. Raman parameter I_D/I_G (intensity ratio of D band to G band) decreases from 1.65 to 1.12 continuously that indicates high graphitization of diesel PM. Markus and Vander [14, 26] observed the similar phenomenon that crystallite arranged more orderly and the void cores became huger.

Reference [27] investigated the particle mode evolution process in diesel tailpipe that particle size distribution and particle number were tested along the tailpipe. The nucleation mode particles and total particle number increase greatly due to the temperature drop along the tailpipe. While the number of accumulation mode particles remains almost the same. The literatures about the differences of diesel PM physicochemical properties along the tailpipe are scarce to date and many questions about PM physicochemical property changes after partial oxidation remain to be addressed. In this paper, diesel PM samples were collected at different tailpipe positions where the temperature differed greatly. The physicochemical property differences were analyzed for samples collected at different tailpipe positions, which was useful for further analyze particle mode evolution in tailpipe. Also physicochemical property changes were investigated after PM partial

82 oxidation, which showed closely related to DPF regeneration.

83 2. Experimental section

84 2.1 The test engine

85 The engine was the power of a diesel generator that the specifications of the diesel engine are listed
86 in Tab. 1. The load of the diesel engine can be adjusted by the power output of the generator, and
87 the engine load was adjusted as 60% when the samples were collected. The experiment lay-out is
88 shown in Fig. 1. The distances of the exhaust valve and the sampling positions were about 0.5 m,
89 1.0 m, 1.5 m and 2.0 m in which the temperature was 253 °C, 231 °C, 208 °C and 185 °C, and the
90 samples were designated as sample 1, sample 2, sample 3 and sample 4 respectively. The
91 fundamental properties of diesel fuel used in the experiments are shown in Tab. 2.

92 Tab. 1 Diesel engine specifications

Specification	Value
Displacement	0.418 L
Bore	86 mm
Stroke	72 mm
Speed	3000 rpm
Injection type	Direct injection
Injector valve opening pressure	21 MPa
Compression ratio	19
Intake valve opening	16° BTDC
Intake valve closing	44° ABDC
Exhaust valve opening	48° BBDC

Exhaust valve closing	12° ATDC
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93 BTDC, before top dead center; ABDC, after bottom dead center; BBDC, before bottom dead center; ATDC, after
 94 top dead center.

Fig. 1 Experiment lay-out

Tab. 2 Fundamental properties of diesel fuel

Property	Value
Density	850 kg/m ³
H/C ratio	0.156
S content	0.0042wt%
Viscosity (20 °C)	4.1 mm ² /s
Cetane number	52
95% distillation points	340 °C
50% distillation points	290 °C

98 2.2 The instruments used for physicochemical properties testing

99 Oxidation activity of diesel PM was tested using thermogravimetry analysis (TGA) device (DTG-60)
 100 that was made by Shimadzu, and the technical specifications are shown in Tab. 3. In order to
 101 decrease the experimental error, vacant combustion in air was performed to remove the residual.

102 The duplicate tests of TGA experiments are shown in Fig. S1. As can be seen, the repeatability of
 103 the TGA experiments is excellent. The flow rate of carry gas and ramp rate of TGA experiments in
 104 the paper are 100 mL/min and 5 °C/min respectively. PM samples were collected at different
 105 tailpipe positions (raw PM), and all the samples were pre-treated at high temperature in air.
 106 Procedure of the pre-treatment using TGA device was as following: samples were heated in air from
 107 ambient temperature at ramp rate of 5 °C/min, until 40 % mass loss, then, the carry gas was
 108 switched as N₂, and temperature dropped to room temperature. Raw PM and pre-treated PM were
 109 packaged with silver paper. The oxidation activity of PM both before and after pre-treatment was
 110 tested.

111 Tab. 3 Technical specifications of TGA device

TGA	Technical specifications
Balance	Horizontal differential type
Weight capacity	200 mg
Signal resolution	0.001 μ g
Temperature range	Ambient to 1100 °C
Ramp rate	0.001 to 100 °C/min
Air flow rate	0 to 1000 mL/min
Crucible	Alumina

112

113 The morphology and nanostructures of diesel PM were observed by transmission electron
 114 microscope (JEM-2100), the applied magnifications were set as 40, 000 $\times$ and 500, 000 $\times$. Before the
 115 tests, the suspensions were created by ultrasonication of soot within acetone. One drop of the

suspension was deposited on a lacey C/Cu transmission electron microscopy (TEM) grid, then, the TEM grid was dried under accent light to remove the acetone. The point-to-point resolution of TEM images was 0.19 nm. Low resolution TEM figures were used to obtain the primary particle diameter distributions. The particle number for diameter statistics was more than 300. The functional groups of diesel PM were investigated using FTIR device (Shimadzu IRAffinity-1s). The scope of FTIR spectrum was $500 \sim 4000 \text{ cm}^{-1}$. Due to the antivacuum of FTIR spectroscopy, the absorption peak of H_2O and CO_2 was observed at $\sim 3300 \text{ cm}^{-1}$ and $\sim 2349 \text{ cm}^{-1}$. A Invia Raman spectra with an Ar-ion laser source (633 nm) was used to obtain the Raman spectra of diesel PM both before and after pre-treatment. The Raman spectra were used to analysis the vibration and rotation of the molecule, further, to investigate the molecular structures. The Raman spectra of diesel PM indicate the defects of crystallites and carbon graphitization. Raman shifts of the first order Raman spectra were $700 \text{ cm}^{-1} \sim 2000 \text{ cm}^{-1}$. Double peaks of the first order Raman spectra were observed, and the Raman shifts were corresponding to 1350 cm^{-1} and 1580 cm^{-1} respectively. The D (1350 cm^{-1}) and G (1580 cm^{-1}) peaks show closely relations to oxidation activity of diesel PM.

3. Results and discussion

Diesel PM sampled at different tailpipe positions owns different physicochemical properties [27]. The differences may be smaller compared with PM samples collected at different engine loads and speeds, especially for the nanostructures. The formation conditions of diesel PM sampled at different tailpipe positions are identical, physicochemical property differences are mainly caused by the sampling temperature that is lower than $300 \text{ }^\circ\text{C}$. The most evident difference is particle mode that some gas phase hydrocarbons (HC) is transferred to nucleation mode particles. The

138 transformation lead to the changes of particle size distributions that was evidenced by the reference
139 [27]. Sampling positions have a significant effect on the nucleation mode particles but limited effect
140 on accumulation mode particles. The physicochemical property differences lead to the distinctions
141 of diesel PM oxidation activity. Oxidation activity mentioned in the section was mainly referred to
142 ignition temperature and burn out temperature. Some part of the physicochemical property changes
143 after partial oxidation were discussed in reference [28].

144 Fig. 2 presents oxidation profiles of diesel PM both before and after partial oxidation. As shown in
145 the figure that oxidation profiles differed slightly for samples 1, 2 and 3 before pre-treatment. Due
146 to the lowest sampling temperature for sample 4, mass loss was remarkable when temperature was
147 lower than 400 °C and with the lowest ignition temperature (207.8 °C). Much gaseous HC
148 condensed on the surface of diesel PM in the process of PM being emitted to the atmosphere. The
149 burn out temperature showed limited differences (Tab. 4) that was smaller than diesel PM sampled
150 at different engine operation conditions [3, 7]. The heat-treatment temperature in air for the four
151 samples was around 520 °C (~40% mass loss) that also can be known from TGA profiles of raw PM.
152 The ignition temperature and burn out temperature increased compared with raw PM. Mass of
153 partially oxidized PM dropped gradually when the temperature was higher than 400 °C. Partial
154 oxidation led to the decrease of active surface area, and the carbon graphitization was aggravated.
155 The reasons mentioned above may cause the oxidation activity decrease for partially oxidized diesel
156 PM. The increase of burn out temperature for sample 3 was 14.7 °C that was much higher than
157 other PM samples. The reasons contributing to the phenomenon may be the hugest changes of
158 physicochemical properties for sample 3, and it was further explored in the following sections.

Fig. 2 Oxidation profiles of diesel PM

Tab. 4 Characteristic temperature of diesel PM

Sample	$T_{5\%}$	$T_{10\%}$	$T_{90\%}$	$T_{95\%}$
	°C			
1	411.7	457.8	615.2	627.0
2	418.3	459.1	622.9	630.6
3	417.8	455.2	612.8	623.2
4	207.8	267.3	620.3	631.5
1-40% loss	472.1	496.5	623.5	632.6
2-40% loss	488.3	514.2	626.1	633.8
3-40% loss	481.5	506.7	628.7	637.9
4-40% loss	480.3	503.1	626.1	634.9

$T_{5\%}$: ignition temperature, 5% mass loss; $T_{10\%}$: 10% mass loss; $T_{90\%}$: 90% mass loss; $T_{95\%}$: burn out temperature, 95% mass loss.

The morphology of diesel PM obtained using TEM device is shown in Fig. 3 that it presented the branch-like structures and the particles were seriously stacked, the same phenomenon was observed

166 in references [10, 29]. Morphology of diesel PM sampled at different tailpipe positions was similar
 167 that soot particles were spherical-like in shape, and aggregated to form the accumulation structures.
 168 The agglomerates of diesel PM was caused by the adsorption force of liquid and solid. The particle
 169 stacking was the most serious for sample 4 that was caused by the highest HC content, as can be
 170 seen from Fig. 2 and 2. Soewono et. al [30] demonstrated that aggregation degree of diesel PM
 171 sampled at low engine load was more serious than it collected at high engine load that was caused
 172 by high HC content. After partial oxidation, the accumulation of diesel PM decreased, and the
 173 particle size diminishing was observed qualitatively.

174 Fig. 3 Morphology of diesel PM: upper panel, raw PM; bottom panel, partially oxidized PM
 175 Primary particle size was obtained by measuring PM outlines in TEM figures, and the count used
 176 for diameter statistic was more than 300. Diameter distribution obtained from TEM figures is
 177 different from those in references [31, 32] where the diameter is the aerodynamic diameter
 178 calculated using relative dynamical equations, however, the diameter in the paper is the physical

179 diameter. The aerodynamic diameter takes the liquid HC into consideration.

180 The primary particle size distributions both before and after pre-treatment are shown in Fig. 4. The

181 shapes of primary particle size distributions were similar for PM samples collected at different

182 tailpipe positions that indicated limited effect of sampling temperature (lower than 300 °C) on

183 primary particle diameter. Particle size distribution moved slightly to left compared with other

184 reference [10], and the peak positions was around 40 nm that was huger than Qu' results [10].

185 Particle size distribution moved toward to left evidently after partial oxidation, the peak positions

186 were smaller than 40 nm with small particles increasing. The change of average particle size was

187 the most evident for sample 3 that the particle size decreased to 27.1 nm (Tab. 5). The percentage of

188 particles smaller than 25 nm was more than 40%, and almost no particles huger than 80 nm were

189 observed. During the oxidation process, the surface oxidation happened firstly due to many active

190 sites adhering on PM surfaces that led to the diameter decreases of primary particles. The hugest

191 changes of diesel particle diameter may partially explain the maximum drop of burn out

192 temperature for sample 3.

193

194 Fig. 4 Diameter distributions of diesel primary particles

195 Tab. 5 Average diameter of primary particles

Sample	Average diameter / nm
1	49.2
2	48.6
3	48.9
4	41.1
1-40% loss	38.2
2-40% loss	38.8
3-40% loss	27.1
4-40% loss	33.9

196 For diesel PM sampled at different engine conditions, it presents onion like structures with
197 randomly arranged crystallites, or the core-shell like structures that owns orderly arranged shells
198 and void cores [26, 33, 34]. PM formed at high temperature tends to be void core structures, as
199 shown in references [35-38]. Sampling temperature difference presents little effect on PM
200 nanostructure that all raw diesel PM showed onion like structures with short and randomly arranged
201 crystallites, as shown in Fig. 5. Some amorphous carbons were also observed on the surface of raw
202 diesel PM. For the partially oxidized diesel PM, the inner cores became void and the shell became
203 partially or completely closed. More orderly arranged crystallite indicated more seriously
204 graphitization of diesel PM. Many oxygen-containing functional groups adhered on diesel PM
205 surface, oxidation activity of PM surface was more active than the cores that led to the preferential
206 oxidation of PM surfaces. With the proceeding of surface oxidation, graphitization aggravated and
207 oxidation activity decreased for surface, then, the oxidation transferred into inner cores. Further, the
208 cores were gradually oxidized that caused the void inner cores [4]. For partially oxidized PM (50%

209 mass loss), large areas of void cores were observed in reference [13]. Due to the decrease of active
 210 surfaces and serious graphitization, the ignition temperature and burn out temperature of partially
 211 oxidized PM increased. Pawlyta et. al [39] observed the same phenomenon that PM samples with
 212 onion like structures transferred into evident void cores and orderly arranged shells after PM was
 213 pre-treated at high temperature.

214 Fig. 5 Nanostructure of diesel PM: up panel, raw PM; bottom panel, partially oxidized PM

215 FTIR spectroscopy was used to test functional groups, and the amorphous carbon was caused by
 216 oxygen-containing functional groups. The amorphous carbon conducted to PM oxidation that
 217 partially led to the differences of PM oxidation activity. Fig. 6 shows FTIR spectra of diesel PM
 218 both before and after partial oxidation. Absorbance intensity of sample 1 was the weakest among
 219 the four raw PM samples that was caused by the highest sampling temperature. The absorbance
 220 intensity was strong at wavenumber $1450\text{ cm}^{-1} \sim 1750\text{ cm}^{-1}$ that was corresponding to methyl,
 221 methylene and carbonyl, as shown in the figure. Diesel PM contained much methyne, except for

sample 1. Due to the prior oxidation of organic compounds in the oxidation process, the absorbance intensity of functional groups was weak compared with raw PM. Intensity changes of sample 3 were the hugest after partial oxidation that may partially explained the maximum increase of burn out temperature. Oxygen-containing functional groups (carbonyl and hydroxy) contained in diesel PM provided active surfaces for PM oxidation, and the content decreased greatly after 40% mass loss. Reference [25] indicated that oxygen content dropped to zero when 80% sample was burnt out.

Fig. 6 FTIR spectra of diesel PM

Raman spectra indicated crystallite defects and carbon graphitization that was around 1350 cm^{-1} and 1580 cm^{-1} respectively. Raman spectra presented closely related to PM oxidation activity, while it was still in debate [7, 8, 39]. Fig. 7 shows Raman spectra of diesel PM both before and after partial oxidation. The changes of Raman parameter I_D/I_G were different after partial oxidation, while it

234 decreased continuously during the whole oxidation process in reference [25]. The phenomenon can
 235 be explained by the theory raised by Livneh et. al [40], the tendency of Raman parameter I_D/I_G
 236 changes depended on the initial degree of PM graphitization. For some diesel PM, Raman shift of D
 237 and G peaks changed slightly that was caused by H-C changes in diesel PM [41]. Meng et. al [24]
 238 also found that the value I_D/I_G decreased after volatilization of VOC and partial oxidation.

Fig. 7 Raman spectra of diesel PM: (a) raw PM; (b) partially oxidized PM

241 The three-curve-fitting method was used to process the original Raman spectra, as shown in Fig. 8.
 242 The correlation coefficients of the curve-fitting results were more than 0.98. Raman shifts of D1,
 243 D3 and G bands were corresponding to $\sim 1350 \text{ cm}^{-1}$, $\sim 1500 \text{ cm}^{-1}$ and $\sim 1580 \text{ cm}^{-1}$ respectively. D1
 244 and G bands were caused by crystallite defects and carbon graphitization respectively, and D3 band
 245 was caused by amorphous carbon that referred to the oxygen-containing functional groups. Raman
 246 parameters obtained by three-curve-fitting method are listed in Tab. 6. Full width at half maximum
 247 (FWHM) indicated the anisotropy of diesel PM. Raman spectra showed no obvious tendency with
 248 sampling positions for raw PM. Raman parameter I_{D3}/I_G decreased after diesel PM partially
 249 oxidized that was caused by the oxidation of oxygen-containing functional groups. Reference [39]

250 also demonstrated that Raman parameter I_{D3}/I_G decreased with increasing soot formation
 251 temperature that was caused by less oxygen-containing functional groups. Lapuerta et. al [42]
 252 reported that Raman parameters I_{D1}/I_G and I_{D3}/I_G decreased slightly with increasing engine load. D1
 253 band FWHM decreased seriously after partial oxidation, while the change was reverse for D3 band.
 254 That indicated different changes of anisotropy in D1 and D3 bands. Zhao et. al [43] showed that D3
 255 band FWHM of biodiesel PM increased with biodiesel content. D1 band FWHM, I_{D1}/I_G and A_{D1}/A_G
 256 showed reverse relations with $t_{50\%}$ (time corresponding to 50% mass loss) for soot from different
 257 sources, and G FWHM was almost the same [21]. However, D1 FWHM was almost the same in the
 258 oxidation process for PM sampled from different engines [26] that suggested less correlations of D1
 259 band FWHM with oxidation activity.

Fig. 8 Three-curve-fitting method

Tab. 6 Raman parameters obtained using three-curve-fitting method

Samples		1	2	3	4	1-40% loss	2-40% loss	3-40%	4-40%
								loss	loss
FWHM /	D1	247.7±9.6	270.3±11.7	240.6±5.4	262.1±17.3	233.7±12.3	219.7±10.8	224.3±8.6	224.5±9.7
cm⁻¹	D3	85.5±4.1	74.4±8.1	89.3±9.3	91.2±4.8	122.0±3.6	102.7±8.5	130.3±5.8	110.3±7.1

	G	76.76±3.5	77.6±7.6	75.3±5.1	77.0±4.6	79.8±3.9	79.9±8.2	73.1±4.2	74.9±12.5
Intensity	I_{D1}/I_G	1.01±0.04	1.02±0.11	1.01±0.09	1.02±0.03	1.06±0.15	1.08±0.08	0.94±0.03	1.09±0.05
ratio	I_{D3}/I_G	0.14±0.02	0.15±0.02	0.14±0.01	0.13±0.02	0.11±0.01	0.13±0.02	0.13±0.02	0.12±0.01
Area ratio	A_{D1}/A_G	3.25±0.29	3.53±0.17	3.24±0.35	3.46±0.28	3.11±0.52	3.02±0.31	2.88±0.42	3.14±0.29
	A_{D3}/A_G	0.10±0.01	0.08±0.01	0.11±0.01	0.10±0.01	0.12±0.01	0.12±0.01	0.16±0.01	0.12±0.01

263 I_{D1}/I_G : intensity ratio of D1 band to G band; A_{D1}/A_G : area ratio of D1 band to G band; I_{D3}/I_G : intensity ratio of D1
264 band to G band; A_{D3}/A_G : area ratio of D1 band to G band. Error being smaller than 0.01 was thought to be 0.01.

265 4. Conclusion

266 Physicochemical properties change greatly in the process of PM oxidation, which is closely related
267 to DPF regeneration, and particle mode evolutions also happen during PM emitting from cylinder to
268 atmosphere. In this paper, four diesel PM samples were collected at different tailpipe positions
269 where sampling temperature differed greatly. The samples were pre-heated in air at high
270 temperature until 40% mass was burnt out. The physicochemical properties of these PM samples
271 both before and after partial oxidation were tested to analyze the effect of sampling temperature and
272 partial oxidation on PM physicochemical properties. The main conclusions obtained in this paper
273 are as following:

274 (1) Sampling temperature showed small effect on oxidation behaviors of raw diesel PM that
275 ignition temperature and burn out temperatures presented small difference for PM sampled at
276 different tail pipe positions, except for sample 4 owning the lowest sampling temperature and the
277 highest VOC content. For partial oxidized PM, the ignition temperature was more than 470 °C.
278 Ignition temperature and burn out temperature increased after partial oxidation that indicated the
279 oxidation activity drop. The oxidation activity drop was further evidenced by FTIR and Raman

280 spectra.

281 (2) Sampling temperature presented limited effect on morphology of raw diesel PM that it showed
282 spherical-like in shape with particles seriously stacked. After partial oxidation, the stacking degree
283 decreased greatly, and particle size distribution moved toward to smaller diameter direction. Raw
284 PM sampled at different tailpipe positions showed onion like structures with randomly arranged
285 crystallites while it presented core-shell like structures with void cores after partial oxidation.

286 (3) FTIR spectra of diesel PM sampled at the position where temperature is the highest showed the
287 weakest absorbance intensity that meant the least content of organic compounds.
288 Oxygen-containing functional groups decreased greatly after partial oxidation, which dominated the
289 oxidation activity drop. The drop of oxygen-containing functional groups was the maximum for
290 sample 3 that partially illustrated to the maximum increase of burn out temperature. Raman
291 parameter I_{D3}/I_G decreased after partial oxidation that was consistent with FTIR phenomenon.

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295 **Supplementary information**

296 Provide the information of duplicate tests of TGA experiments.

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