Supplementary Information

Probing Photoreactions of Individual Suspended Carbonaceous Aerosols by Multi-Wavelength OT-SERS

Hang Zhong, ^a Jun Chen, ^{*a} Yi Hu, ^a Jun Chen, ^a Tao Shao, ^a and Junsheng Liao, ^{*b}

Affiliations:

^a Science and Technology on Surface Physics and Chemistry Laboratory, Jiangyou 621908, China

^b Institute of Materials, China Academy of Engineering Physics, Mianyang 621907, China

Corresponding Author

Jun Chen, E-mail: junchen76@163.com

Junsheng Liao, E-mail: jshliao64@163.com

Table S1

Plasmon resonance peak positions of AgNPs at different growth generations

generation	SPR dipolar (nm)	SPR quadrupolar (nm)
1	407	
2	413	
3	419	
4	423	
5	428	
6	431	
7	437	
8	439	
9	444	
10	447	
11	451	
12	455	
13	458	
14	464	
15	473	404
16	482	407
17	487	412
18	496	417
19	506	421
20	519	423
21	532	426
22	547	431
23	563	434
24	576	437
25	599	444
26	622	451
27	641	456

Table S2

4-N	MBA
Raman shift (cm ⁻¹)	Assignment
1078	v(CS) + v(CC)
1141	δ(CH)
1182	δ(CH)
1418	ν _s (COO ⁻)
1480	$\nu(CC) + \delta(CH)$
1584	v(CC)

The assignments of Raman peaks of 4-MBA¹⁻⁴

1. C. J. Orendorff, A. Gole, T. K. Sau and C. J. Murphy, Anal. Chem., 2005, 77, 3261.

 H. Yeasmin, M. Akteruzzaman, M. Motiur Rahaman Mazumder, S. Y. Alfaifi, R. H. Althomali and M. M. Rahman, J. Photoch. Photobio. A, 2024, 448.

3. T. Shao, J. Xu, H. Zhong, Y. Hu and J. Chen, Talanta, 2024, 274, 126008.

4. S. Zhu, C. Fan, J. Wang, J. He and E. Liang, Appl. Phys. A, 2014, 117, 1075.

Table S3

The optimized geometric structures and optimized coordinates of possible reaction products from DFT calculations.

Optimized geometric structures	Symbol	X	Y	Z
	С	-1.8418	0.013706	0.000001
	С	-1.13337	1.215551	-0.000004
	С	0.255585	1.204921	-0.000008
	С	0.962996	-0.002811	-0.000003
	С	0.248124	-1.201371	0.000007
	С	-1.14562	-1.194031	0.000005
9	S	2.752025	0.072117	0.000013
	0	-3.2105	0.085132	0.000004
	Н	-1.68034	2.150524	-0.00001
	Н	0.791542	2.147487	-0.000016
4 4 1 1	Н	0.768097	-2.152574	0.000017
4-mercaptophenol	Н	-1.6861	-2.136142	0.000011
	Н	2.966627	-1.257799	-0.000189
	Н	-3.58378	-0.802215	-0.000036
	С	-1.16531	1.0448	-0.00437
	С	0.225328	0.922212	0.002876
	С	0.82006	-0.35147	-0.00473
	С	-0.00112	-1.48294	0.013433
	С	-1.38312	-1.37141	0.005352
	С	-1.96083	-0.09735	-0.00503
	S	2.61017	-0.48358	0.073639
	0	-3.32446	-0.03154	-0.01163
	0	0.955221	2.063861	0.004266
	Н	-1.60052	2.038445	-0.00482
🥧 🔍 💆	Н	0.459462	-2.4634	0.0312
2.4 dihudrouuhanzanathial	Н	-2.02113	-2.24549	0.014095
2,4-diffydroxybenzenetmol	Н	2.859529	-0.53724	-1.25587
	Н	-3.60939	0.888452	-0.01055
	Н	1.893116	1.814891	0.06146
	С	0.691792	-1.591952	0.000005
	С	-0.687118	-1.383139	0.000015
	С	-1.193658	-0.081768	0.000008
	С	-0.314735	1.004849	-0.000017
	С	1.058936	0.792688	-0.000003
	С	1.564655	-0.513695	0.000002
	S	-2.971736	0.122157	-0.000033
	Ο	2.940675	-0.611642	0.000002
	О	1.900061	1.864386	-0.000006
	Н	1.083843	-2.60458	0.000011
	Н	-1.356833	-2.234498	0.000035
3 4-dihydroxybenzenethiol	Н	-0.67081	2.027944	-0.000041
5,4-uniyaroxy benzeneunoi	Н	-2.978071	1.469033	0.000497
	Н	3.2153	-1.533598	0.000026
	Н	2.809221	1.537338	-0.000025

Table S3 (continued)

The optimized geometric structures and optimized coordinates of possible reaction products from DFT calculations.

Optimized geometric	Symbol	Х	Y	Z
structures		2 010001	0.05025	0.00054
	C	2.018881	-0.0/03/	0.00254
	С	1.302635	-1.26053	-0.00345
A 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997	C	-0.08943	-1.20989	-0.00838
	С	-0.77671	0.021428	-0.00431
	С	-0.02627	1.204954	0.000088
	С	1.368107	1.167157	-0.00034
	S	-2.56245	0.02391	0.093964
	0	3.380728	-0.16618	0.005775
, <u> </u>	0	-0.75747	-2.38565	-0.02038
) - <u>- (</u>	0	-0.70841	2.384261	-0.0142
	Н	1.814066	-2.21317	-0.00594
2,4,6-trihydroxybenzenethiol	Н	1.939019	2.091386	-0.00759
	Н	-2.83268	0.317777	-1.19893
	Н	3.773384	0.712687	0.015746
	Н	-1.70966	-2.18576	-0.02285
	Н	-0.0871	3.118569	0.029668
	С	0.757293	-1.209746	0.000003
	С	-0.636736	-1.20017	0.000025
	С	-1.327758	0.009941	0.000014
	С	-0.629965	1.219195	-0.000027
	С	0.759422	1.202692	-0.00001
Q <u>Q</u> ==Q	С	1.464303	-0.007153	-0.000004
	S	-3.113996	-0.064155	-0.000034
	Ο	2.845558	0.131767	0.000005
)	О	1.435749	2.384887	-0.000011
	0	1.356498	-2.448117	-0.000005
	Н	-1.153106	-2.151756	0.000057
3,4,5-trihydroxybenzenethiol	Н	-1.132388	2.177749	-0.00006
	Н	-3.326438	1.265897	0.000553
	Н	3.314936	-0.705252	0.00018
	Н	2.383628	2.198327	-0.000008
	Н	2.315506	-2.395327	-0.000092
	С	0.703412	1.109135	-0.00383
	С	-0.67089	0.866855	0.001211
	С	-1.13816	-0.4497	-0.006202
	С	-0.2316	-1.5164	0.009341
	С	1.134655	-1.27102	-0.000668
	С	1.600512	0.048993	-0.005606
	S	-2.91255	-0.72354	0.076891
	0	2.954402	0.24626	-0.008306
	0	2.016268	-2.31459	0.00311
	Ο	1.225445	2.376442	-0.003102
	О	-1.47165	1.977181	-0.000086
	Н	-0.58542	-2.53858	0.026082
2.3.4.5-tetrahydroxybenzenethiol	Н	-3.15042	-0.82203	-1.251731
, , , , · · · · · · · · · · · · · · · ·	H	3.135863	1.194961	0.001796
	Н	2.914012	-1.95875	0.01048
	Н	0.497228	3.011005	0.016313
	Н	-2.3938	1.68054	0.068403

Table S3 (continued)

The optimized geometric structures and optimized coordinates of possible reaction products from DFT calculations.

Optimized geometric structures	Symbol	Х	Y	Z
	С	-1.69139	0.153482	-0.0111
	С	-0.90171	1.303633	0.007957
	С	0.487714	1.16113	0.027699
	С	1.109485	-0.09813	0.015323
	С	0.305814	-1.24418	-0.00181
	С	-1.07962	-1.10408	0.02622
	S	2.891726	-0.17612	-0.10357
	Ο	1.193461	2.328294	0.04848
? - 🤄 🎽 - 🌏	Ο	-1.49329	2.532911	-0.00332
	Ο	-3.04278	0.270812	-0.04729
	Ο	-1.88665	-2.24738	-0.02673
	Ο	0.876151	-2.48031	-0.01675
	Н	3.161314	-0.49645	1.183065
n antahu duauu h an zan athial	Н	2.140289	2.107355	0.040645
pentanyaroxybenzenetnioi	Н	-0.79268	3.197864	-0.00613
	Н	-3.40796	-0.60391	-0.23802
	Н	-2.10498	-2.53135	0.870413
	Н	0.179592	-3.12131	-0.21372

Reaction products frequencie s (cm ⁻¹) Reaction products frequencies (cm ⁻¹) 1076 1005 1005 1150 1125 1125 1150 1126 1281 1281 1316 1281 1316 134 1480 1576 134 1441 1631 1069 1031 108 1151 1281 1031 108 1143 1163 129 1228 1031 108 1143 1163 128 128 1031 108 129 118 129 128 1198 129 128 1208 129 128 1301 138 135 1338 1339 135 1466 1997 1601 1623 1062 1623 1621 1661 1696 1173 1221 125 1302 <th></th> <th>Vibrational</th> <th>action products from D110</th> <th>Vibrational</th>		Vibrational	action products from D110	Vibrational
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Reaction products	frequencie	Reaction products	frequencies
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	- F	$s(cm^{-1})$	L	(cm^{-1})
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		1076		1065
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		1150		1125
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Q 9	1163	a 🖉 🧶 🧶 🖉	1150
$\begin{bmatrix} 228 \\ 1268 \\ 1334 \\ 1480 \\ 1576 \\ 1595 \\ 3.4.5-trihydroxybenzenethiol \\ 1595 \\ 3.4.5-trihydroxybenzenethiol \\ 1050 \\ 1108 \\ 1151 \\ 1163 \\ 1198 \\ 1250 \\ 1301 \\ 1338 \\ 1577 \\ 1251 \\ 163 \\ 1198 \\ 1597 \\ 2.3.4.5-tetrahydroxybenzenethiol \\ 1466 \\ 149 \\ 149 \\ 1496 \\ 149 \\ 1496 \\ 1496 \\ 149 \\ 149 \\ 149 \\ 149 \\ 1$	<u>)</u> 3	1240	A state	1165
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		1281		1228
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		1316		1268
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	or ()) () () () () () () () () () () () (1480	<u>`````````````````````````````````````</u>	1334
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		1576		1444
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		1595		1481
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	4-mercaptophenol		3,4,5-trihydroxybenzenethiol	1588
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$				1609
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		1031		1050
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		1108		1143
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		1151		1161
$ \begin{array}{ c c c c c c c } \hline 1198 & 1229 & 1223 \\ 1301 & 1338 & 1439 & 1335 & 1335 \\ 1439 & 1472 & 2,3,4,5-tetrahydroxybenzenethiol & 1605 & 1623 & 1605 & 1624 & 1605 & 1624 & 1605 & 1625 & 1525 & 1525 & 1525 & 1525 & 1525 & 1525 & 1525 & 1526 &$		1163		1208
$\begin{array}{c} 1250\\ 1301\\ 1338\\ 1439\\ 2,4-dihydroxybenzenethiol\\ 2,4-dihydroxybenzenethiol\\ 2,4-dihydroxybenzenethiol\\ 3,4-dihydroxybenzenethiol\\ 2,4-dihydroxybenzenethiol\\ 3,4-dihydroxybenzenethiol\\ 2,4,6-trihydroxybenzenethiol\\ 2,4,6-trihydroxybenzenethiol\\ 1127\\ 1157\\ 1190\\ 1255\\ 1270\\ 1302\\ 1320\\ 1437\\ 1486\\ 1588\\ 1601\\ 101\\ 101\\ 101\\ 101\\ 101\\ 101\\ 10$		1198		1229
$\begin{array}{ c c c c c c c } \hline 1301 \\ 1338 \\ 1439 \\ 1472 \\ 1578 \\ 1472 \\ 1578 \\ 1597 \\ \hline \\ 1466 \\ 1496 \\ 1605 \\ 1623 \\ \hline \\ 1061 \\ 1190 \\ 1255 \\ 1270 \\ 1302 \\ 1320$		1250		1253
$\begin{array}{c} 1338\\ 1439\\ 2,4-dihydroxybenzenethiol\\ 2,4-dihydroxybenzenethiol\\ 2,4-dihydroxybenzenethiol\\ 2,4-dihydroxybenzenethiol\\ 3,4-dihydroxybenzenethiol\\ 2,4,6-trihydroxybenzenethiol\\ 2,4,6-trihydroxybenzenethiol\\ 2,4,6-trihydroxybenzenethiol\\ 1338\\ 1439\\ 2,3,4,5-tetrahydroxybenzenethiol\\ 1477\\ 1486\\ 1588\\ 1601\\ 1002\\ 1252\\ 1270\\ 1302\\ 1320\\ 1437\\ 1486\\ 1588\\ 1601\\ 1002\\ 1252\\ 1270\\ 1334\\ 1353\\ 1386\\ 1492\\ 1602\\ 125\\ 1270\\ 1334\\ 1353\\ 1386\\ 1492\\ 1602\\ 125\\ 127\\ 1157\\ 1190\\ 1205\\ 1344\\ 1352\\ 1$		1301		1282
$\begin{array}{c} 1439\\ 2,4-dihydroxybenzenethiol\\ 2,4-dihydroxybenzenethiol\\ 2,4-dihydroxybenzenethiol\\ 2,3,4,5-tetrahydroxybenzenethiol\\ 1496\\ 1406\\ 1496\\ 1605\\ 1623$		1338		1335
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	👘 🧉 🕌 The second sec	1439	🤞 🕘 🍼	1375
$\begin{array}{c} 2,4-\text{dihydroxybenzenethiol} \\ 1578 \\ 1597 \\ 1605 \\ 1623 \\ 1605 \\ 1623 \\ 1605 \\ 1623 \\ 1605 \\ 1623 \\ 1605 \\ 1623 \\ 1601 \\ 1061 \\ 1096 \\ 1167 \\ 1190 \\ 1255 \\ 1270 \\ 1304 \\ 1333 \\ 1304 \\ 1353 \\ 1386 \\ 1492 \\ 1601 \\ 1602 \\ 1602 \\ 1602 \\ 1602 \\ 1602 \\ 1602 \\ 1602 \\ 1601 \\$		1472		1466
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	2,4-dihydroxybenzenethiol	1578	2,3,4,5-tetrahydroxybenzenethiol	1496
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		1597		1605
$\begin{array}{c} 1062 \\ 1136 \\ 1173 \\ 1221 \\ 1261 \\ 1302 \\ 1320 \\ 1437 \\ 1486 \\ 1588 \\ 1601 \end{array} \qquad $				1623
$\begin{array}{c} 1136 \\ 1173 \\ 1221 \\ 1261 \\ 1302 \\ 1320 \\ 1437 \\ 1486 \\ 1588 \\ 1601 \end{array} \qquad $		1062		1061
$\begin{array}{c} 1173 \\ 1221 \\ 1261 \\ 1302 \\ 1320 \\ 1437 \\ 1486 \\ 1588 \\ 1601 \end{array} \qquad $		1136		1096
$\begin{array}{c} 1221 \\ 1261 \\ 1302 \\ 1320 \\ 1437 \\ 1486 \\ 1588 \\ 1601 \end{array} \qquad $	👝 🍸 🗩o	1173		1167
$\begin{array}{c} 1261 \\ 1302 \\ 1320 \\ 1437 \\ 1486 \\ 1588 \\ 1601 \end{array} \qquad $		1221		1190
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		1261		1255
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		1302		1270
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		1320	9 3	1304
$\begin{array}{c ccccc} 1486 & & & & 1386 \\ 1588 & & & pentahydroxybenzenethiol & 1492 \\ 1601 & & & 1602 \\ 1620 & & & 1620 \\ \hline \\ 1025 & & & 1052 \\ 1127 & & & 1157 \\ 1190 & & & 1205 \\ 1344 & & & 1352 \\ 1344 & & & 1352 \\ 1583 & & & 1607 \\ \hline \end{array}$		1437		1353
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		1486		1386
1601 pentalydroxybenzeneunor 1602 1620 1025 1052 1127 1157 1190 1205 1344 1352 1353 1607	3 4-dihydroxybenzenethiol	1588	nentahydroxybenzenethiol	1492
1620 1025 1052 1127 1157 1190 1205 1344 1352 1583 1607	5,uniyuroxybenzeneunbi	1601	pentanyaroxybenzeneunor	1602
1025 1052 1127 1157 1190 1205 1344 1352 1583 1607				1620
1052 1127 1157 1190 1205 1344 1352 1583 1607		1025		
1127 1157 1190 1205 1344 1352 1583 1607		1052		
1157 1190 1205 1344 1352 1583 1607		1127		
1190 1205 1344 1352 1583 1607	<u></u>	1157		
1205 1344 1352 1583 1607		1190		
1344 1352 1583 1607		1205		
1352 1583 2,4,6-trihydroxybenzenethiol		1344		
2,4,6-trihydroxybenzenethiol 1583 1607		1352		
2,4,6-trihydroxybenzenethiol		1583		
	2,4,6-trihydroxybenzenethiol	1607		

 Table S4

 The vibrational frequencies of possible reaction products from DFT calculation



Fig. S1. (a) Photographs and (b) UV-Vis absorption spectra of the different generations of AgNPs solutions.



Fig. S2. OT-Raman and optical images of 4-MB/C particles under trapping and excitation by lasers with wavelengths of 473 nm, 589 nm, and 671 nm. Scale bar: 10 μ m.



Fig. S3. (a-c) Temporal OT-SERS spectra and optical image of three 4-MBA/AgNPs/C particles under 473 nm laser irradiation. Scale bar: 10 μm.



Fig. S4. (a-c) Raman peak at 1078 cm⁻¹ of 4-MBA/AgNPs/C particle (from the corresponding panels of Fig. S3.a-S3.c) before and after 473 nm laser irradiation for 2 h.



Fig. S5. (a-c) Temporal OT-SERS spectra and optical image of three 4-MBA/AgNPs/C particles under 589 nm laser irradiation. Scale bar: 10 μm.



Fig. S6. (a-c) Raman peak at 1078 cm⁻¹ of 4-MBA/AgNPs/C particle (from the corresponding panels of Fig. S5.a-S5.c) before and after 589 nm laser irradiation for 2 h.



Fig. S7. (a-c) Temporal OT-SERS spectra and optical image of three 4-MBA/AgNPs/C particles under 671 nm laser irradiation. Scale bar: 10 μm.



Fig. **S8.** Calculated Raman spectra of (a) 4-mercaptophenol, (b) 2,4dihydroxybenzenethiol, 3,4-dihydroxybenzenethiol, (c) (d) 2,4,6-2,3,4,5trihydroxybenzenethiol, 3,4,5-trihydroxybenzenethiol, (e) (f) tetrahydroxybenzenethiol and (g) pentahydroxybenzenethiol.



Fig. S9. (a-d) Variation trend of peak intensities at 999, 1021 and 1428 cm⁻¹ of 4-MBA/AgNPs/C particle (from the corresponding panels of Fig. 5 and Fig. S5.a-S5.c) under 589 nm laser irradiation.



Fig. S10. (a-d) Variation trend of peak intensities at 999, 1021 and 1430 cm⁻¹ of 4-MBA/AgNPs/C particle (from the corresponding panels of Fig. 7 and Fig. S7.a-S7.c) under 671 nm laser irradiation.