Supplementary Information for:

UV light combined with nitrate for degradation of bisphenol A: kinetics, transformation pathways, and acute toxicity assessment

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Text S1 Details of LC/MS/MS test method.

The LC/MS/MS system was composed with Waters alliance 2695 XELC/MS/MS (Waters, Watford, UK), Zobax SB-C18 (5 μm, 4.6 mm × 250 mm, Agilent, USA). Separation was accomplished with a gradient mode: mobile phase A, water; mobile phase B, ACN; flow rate 0.3 mL/min, the ratio of A to B, 0~3 min, 70:30; 3~4 min, 70:30 to 95:5; 4~6 min, 95:5 to 100:0; 6~25 min, 100:0; 25~30 min, 100:0 to 70:30. This method utilized ESI-LC/MS/MS operating in MRM mode. The Waters alliance 2695 Quattro Premier XE was used in negative ion ESI. The ESI settings were the following: capillary voltage, 3.5 kV; cone voltage, 40 V; the flow of desolvation gas (Argon gas), 800 $L\cdot h^{-1}$; the flow of cone gas, 20 $L\cdot h^{-1}$; collision energy, 20 V.

Text S2 Details of the acute toxicity test method.

In terms of the acute toxicity test method, 75 μL osmotic pressure adjusting solution was added into 675 μL sample and then 250 μL resuscitated bacterial solution was added to each sample. Samples were mixed and measured after a certain interval of time. Note that methanol used in sample concentration for toxicity analysis was blown away and diluted in phosphate buffer.

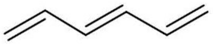
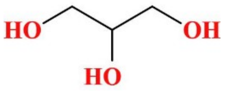
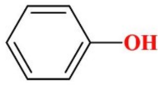
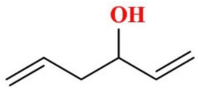
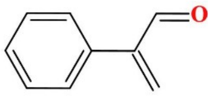
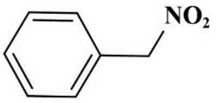
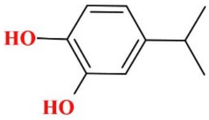
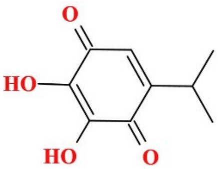
Table S1 Calculations of the contributions from UV, ·OH, and RNS in UV/NO_3^- process (Take control experiment as an example).

Time (s)	[BPA] (μM)	$k_{UV, BPA} \times \int_{t_{n-1}}^{t_n} [BPA]dt$	R_{UV} (μM)	$k_{\cdot OH, BPA}[\cdot OH] \times \int_{t_{n-1}}^{t_n} [BPA]dt$	$R_{\cdot OH}$ (μM)	R_{RNS} (μM)
0	30	0	0	0	0	0
300	29.03221	0.036898	0.036898	0.474755	0.474755	0.456137
600	27.63855	0.035422	0.072320	0.455764	0.930519	1.358611
1200	26.07389	0.067146	0.139466	0.863944	1.794463	1.992181
1800	24.79445	0.063591	0.203057	0.818198	2.612661	2.389833
2400	23.30352	0.060127	0.263184	0.773637	3.386298	3.046998
3000	22.00291	0.056638	0.319821	0.728737	4.115034	3.562234
3600	20.8828	0.053611	0.373433	0.689800	4.804835	3.938933

Table S2 $[\cdot OH]_{ss}$ at different concentrations of NO_3^- in UV/NO_3^- process.

NO_3^- (mM)	0	10	20	30	50
$k_{obs, NB}$ (s^{-1})	4.875×10^{-5}	5.095×10^{-5}	5.324×10^{-5}	6.925×10^{-5}	7.780×10^{-5}
R^2	0.991	0.998	0.980	0.998	0.998
$[\cdot OH]_{ss}$ (M)	-	5.64×10^{-16}	1.15×10^{-15}	5.26×10^{-15}	7.45×10^{-15}

Table S3 Detected intermediate products of bisphenol A in UV/NO_3^- process.

Compound	RT (time)	$[M-H]^-$		Chemical Formula	Proposed Structure
		Theoretical m/z	Observed m/z		
B_{79}	6.789	79.13	78.9	C_6H_8	
B_{92}	29.135	92.09	91.9	C_6H_5O	
B_{93}	29.135	93.1	93.0	C_6H_6O	
B_{97}	6.789	97.14	96.8	$C_6H_{10}O$	
B_{131}	7.428	131.16	131	C_9H_8O	
B_{135}	29.135	135.19	134.9	$C_9H_{12}O$	
B_{136}	29.135	136.14	135.9	$C_7H_7O_2N$	
B_{151}	6.789	151.19	151.1	$C_9H_{12}O_2$	
B_{181}	7.428	181.17	181.1	$C_9H_{10}O_4$	

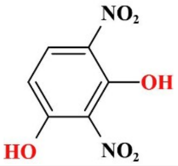
B_{199}	7.428	199.11	199.2	$C_6H_4O_6N_2$	

Table S4 Actual waters quality information.

actual waters	surface water	groundwater	drinking water	wastewater
TOC (mgC·L^{-1})	4.12	1.01	2.25	13.13
total alkalinity (mg $CaCO_3$·L^{-1})	230.63	252.41	154.01	110.39
NO_3^- (mg-N·L^{-1})	10.42	11.41	3.67	40.50
NO_2^- (mg-N·L^{-1})	0.10	nd	0.003	0.25
pH	7.81	7.61	8.21	7.45

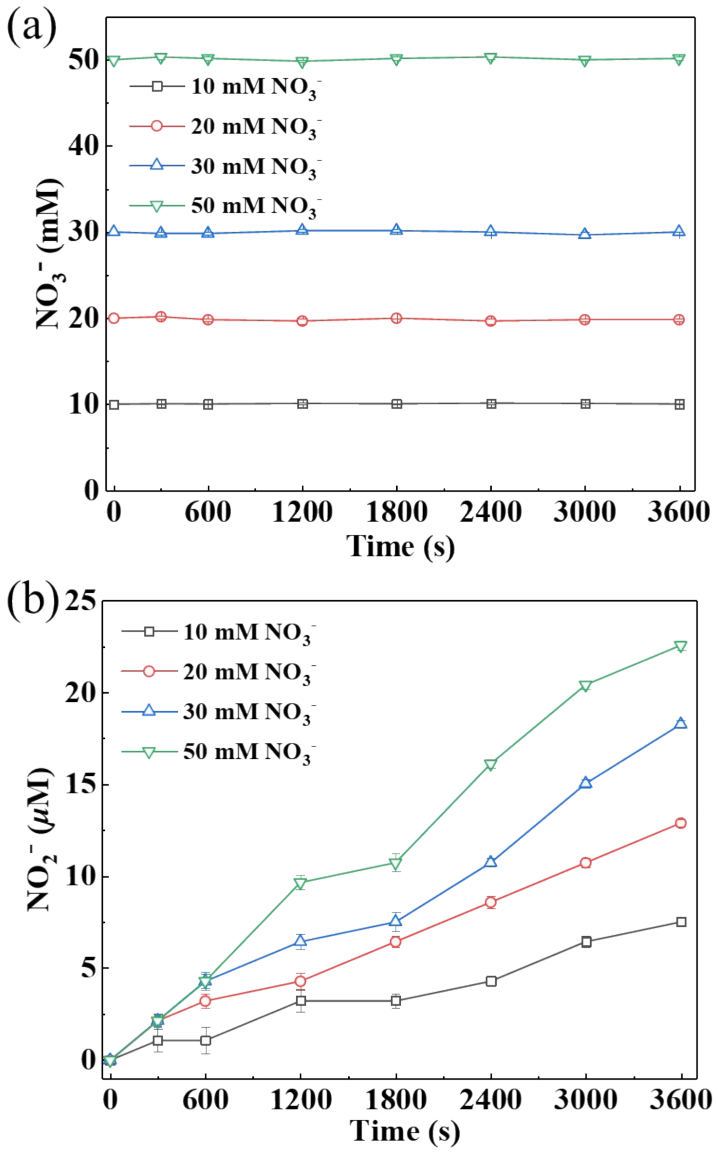
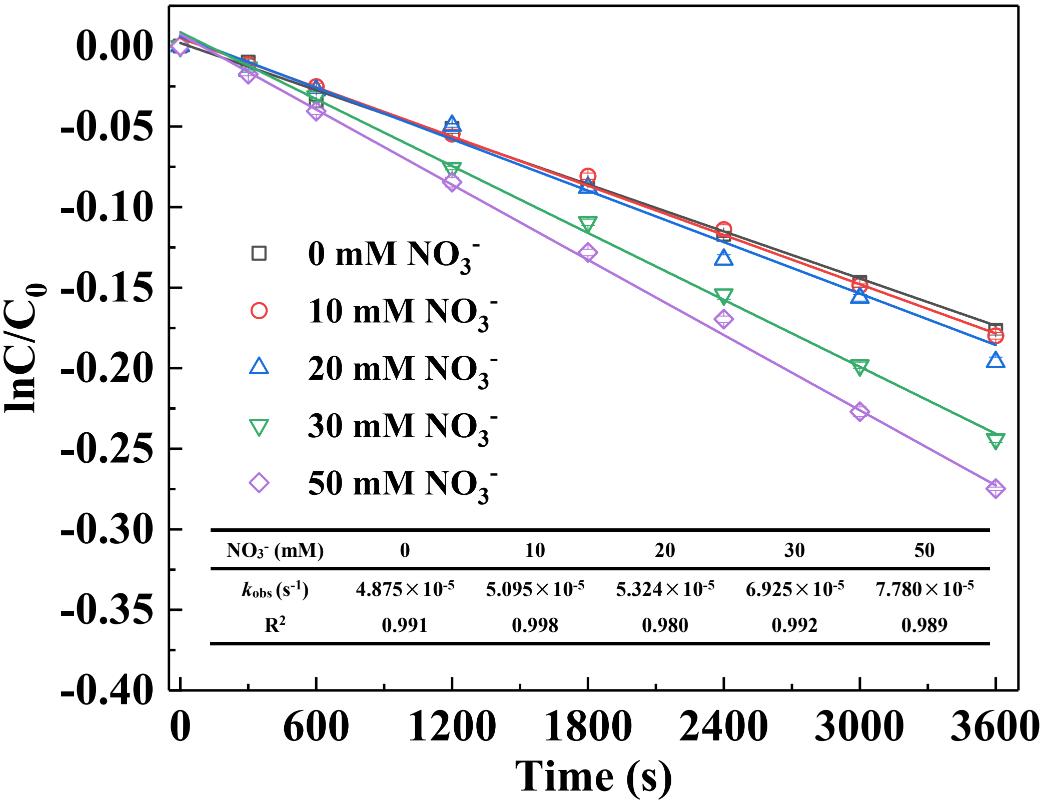


Fig. S1 (a) Changes of NO_3^- concentration in the UV/NO_3^- process. (b) Changes of NO_2^- concentration in UV/NO_3^- process. Experimental conditions: [BPA] = 30 μM, [NO_3^-] = 10~50 mM, pH = 7, [phosphate] = 5 mM, time = 3600 s, I = 0.172 mW·cm^{-2}.



NO_3^- (mM)	0	10	20	30	50
k_{obs} (s^{-1})	4.875×10^{-5}	5.095×10^{-5}	5.324×10^{-5}	6.925×10^{-5}	7.780×10^{-5}
R^2	0.991	0.998	0.980	0.992	0.989

Fig. S2 Degradation of NB in different concentrations of NO_3^-. Experimental conditions:[NB] = 50 μM, [BPA]= 30 μM, [NO_3^-] = 0~50 mM, pH = 7, [phosphate] = 5 mM, time = 3600 s, I = 0.172 mW·cm^{-2}.

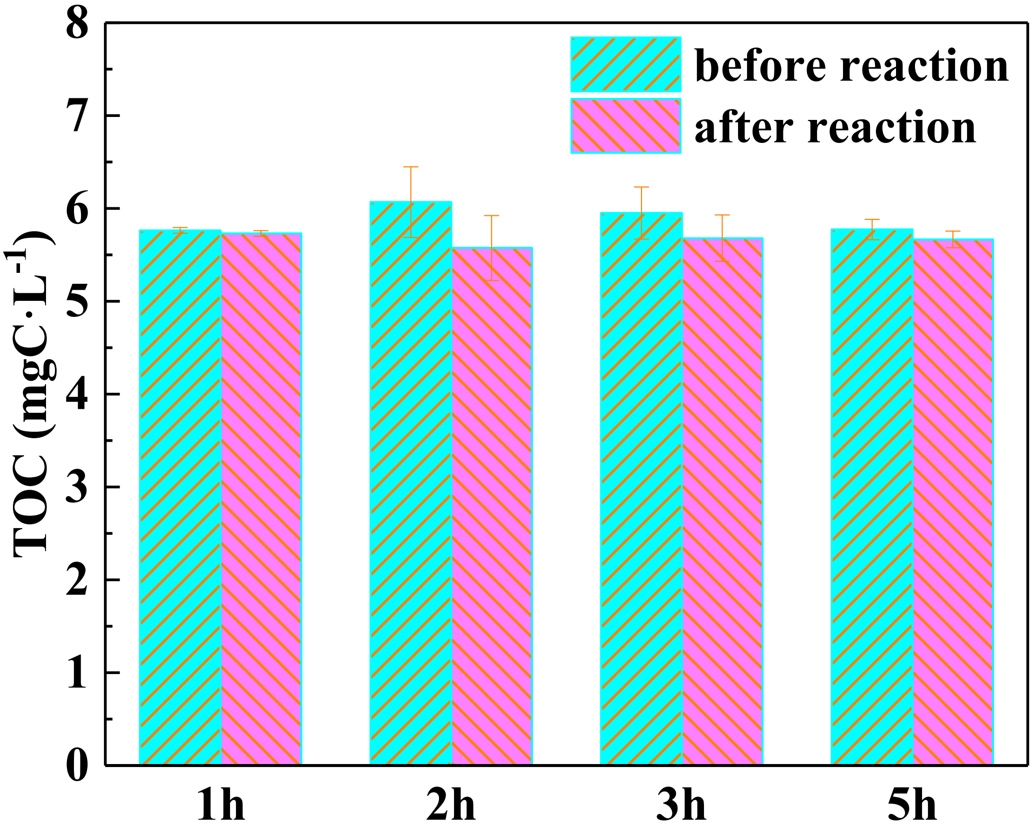
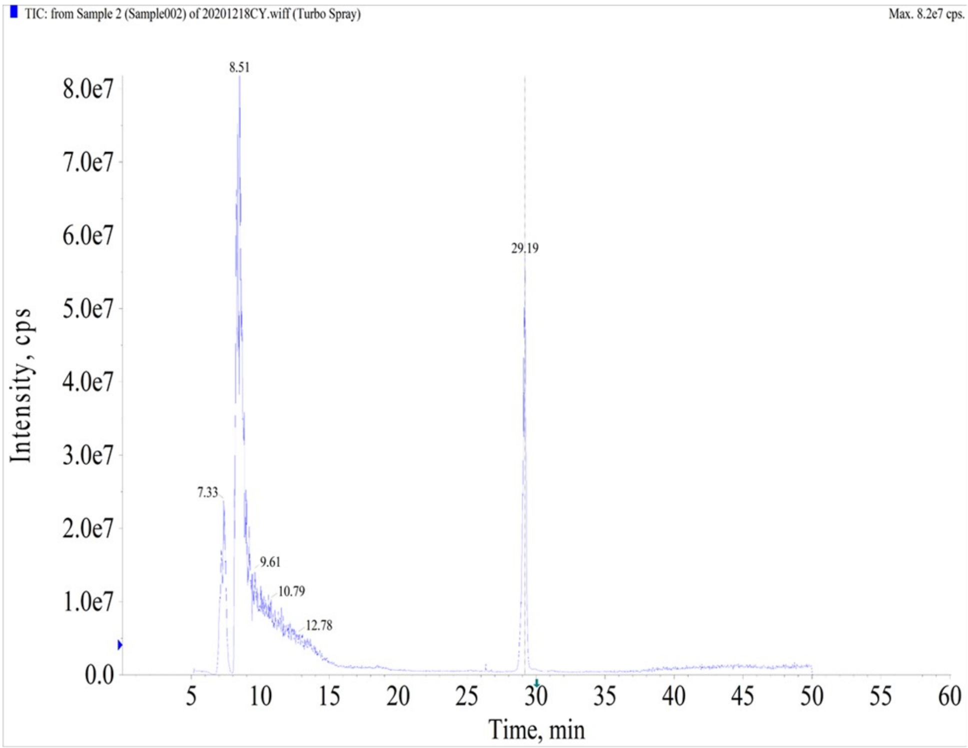
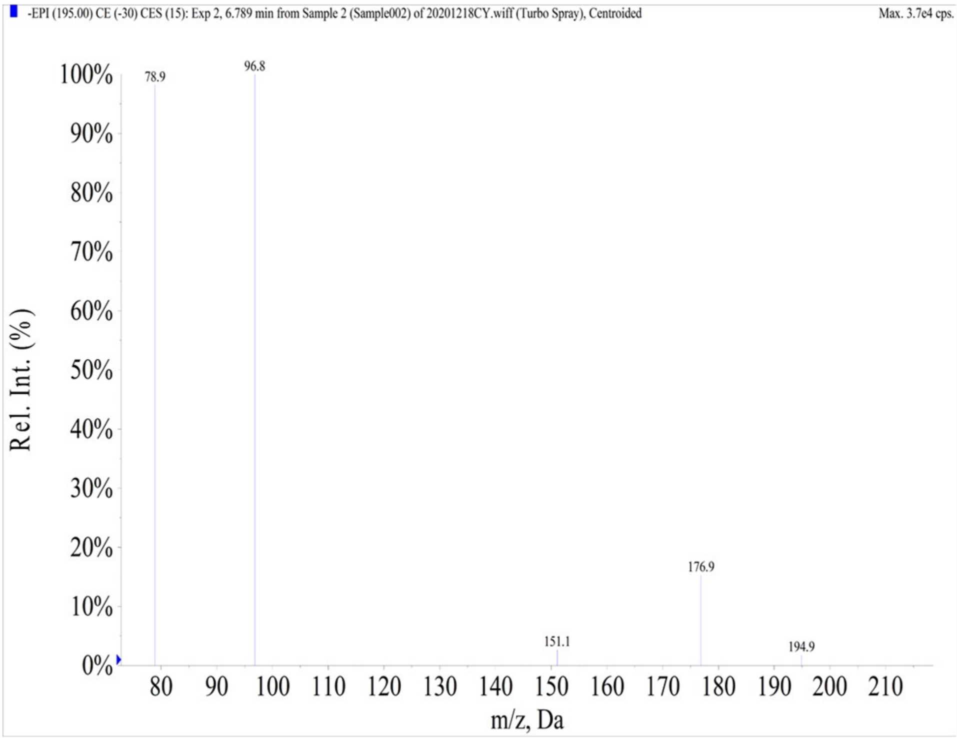


Fig. S3 Changes of TOC before and after reaction in UV/NO_3^- process. Experimental conditions:[BPA] = 30 μM, [NO_3^-] = 30 mM, pH = 7, [phosphate] = 5 mM, time = 3600 s, I = 0.172 mW·cm^{-2}.

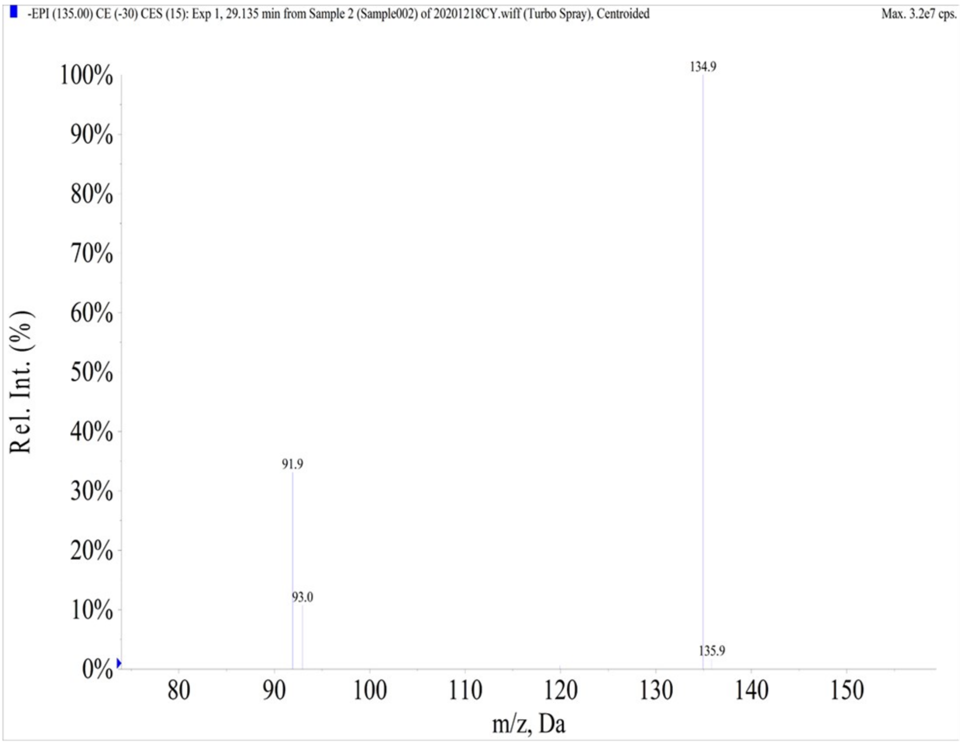
(a)


TIC: from Sample 2 (Sample002) of 20201218CY.wiff (Turbo Spray)
Max. 8.2e7 cps.
Intensity, cps
8.0e7
7.0e7
6.0e7
5.0e7
4.0e7
3.0e7
2.0e7
1.0e7
0.0
8.51
29.19
7.33
9.61
10.79
12.78
5
10
15
20
25
30
35
40
45
50
55
60
Time, min

(b)


-EPI (195.00) CE (-30) CES (15): Exp 2, 6.789 min from Sample 2 (Sample002) of 20201218CY.wiff (Turbo Spray), Centroided
Max. 3.7e4 cps.
Rel. Int. (%)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
78.9
96.8
151.1
176.9
194.9
80
90
100
110
120
130
140
150
160
170
180
190
200
210
m/z, Da

(c)


-EPI (135.00) CE (-30) CES (15): Exp 1, 29.135 min from Sample 2 (Sample002) of 20201218CY.wiff (Turbo Spray), Centroided
Max. 3.2e7 cps.
Rel. Int. (%)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
134.9
91.9
93.0
135.9
80
90
100
110
120
130
140
150
m/z, Da

(d)

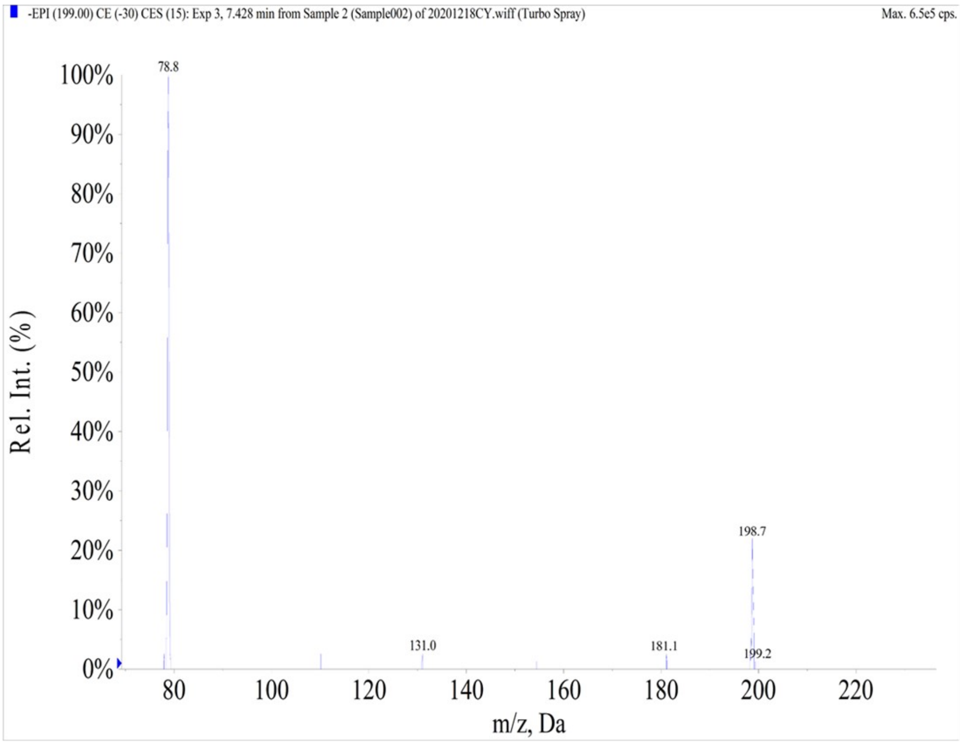

-EPI (199.00) CE (-30) CES (15): Exp 3, 7.428 min from Sample 2 (Sample002) of 20201218CY.wiff (Turbo Spray)
Max. 6.5e5 cps.
Rel. Int. (%)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
78.8
198.7
131.0
181.1
199.2
80
100
120
140
160
180
200
220
m/z, Da

Fig. S4 LC/MS/MS results of BPA degradation in UV/NO_3^- process. (a) LC chromatogram of BPA in UV/NO_3^- process. (b) The mass spectra of $B_{79,}$ $B_{97,}$ B_{151}. (c) The mass spectra of $B_{92,}$ B_{93}, $B_{135,}$ B_{136}. (d) The mass spectra of B_{131}, B_{181}, B_{199}.