Electronic Supplementary Material (ESI) for Analyst.

Supporting information for

Time-resolved *in situ* Monitoring of Photocatalytic Reactions by Probe Electrospray Ionization Mass Spectrometry

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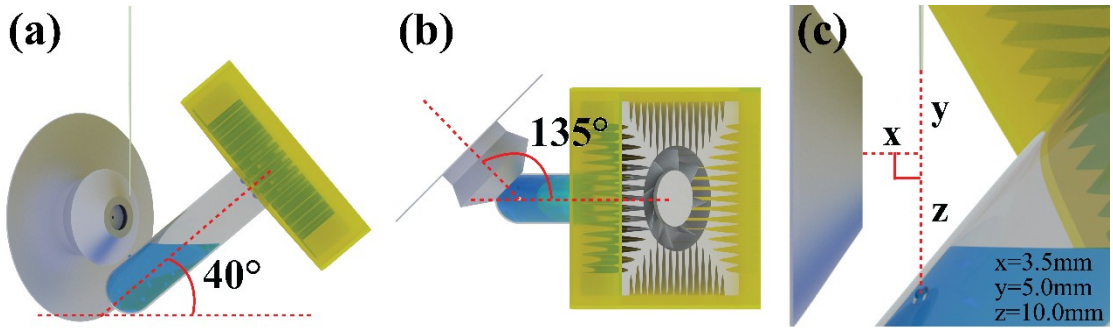


Figure S1 The front view (a) and the top view (b) of the reaction unit which was located in front of the ion sampling orifice of the mass spectrometer. The distance between the axis of the ion sampling orifice to the probe tip, to the sampling hole of the reaction unit and to the center of the ion sampling orifice were shown in (c).

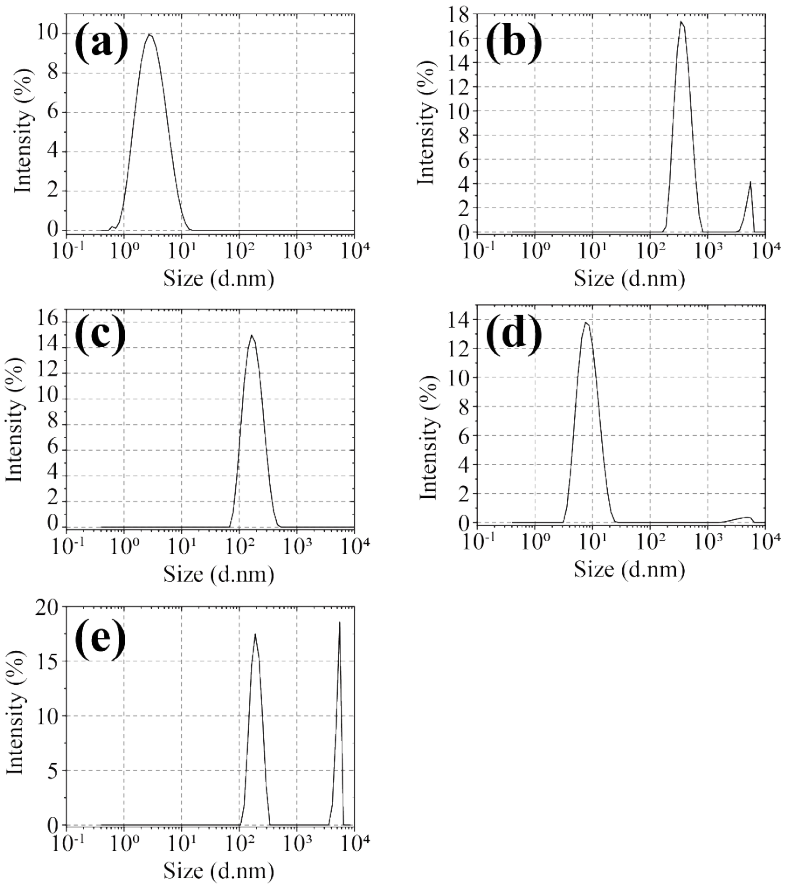


Figure S2 Intensity-based size distribution of (a) TiO_2, (b) SnO_2, (c) WO_3, (d) SiC and (e) ZnS at the concentration of 0.001 g /mL in ultrapure water, respectively. All data were measured by using a Nano-ZS90 Zetasizer instrument (Malvern Instruments, Worcestershire, UK) at a fixed detector angle of 90°.

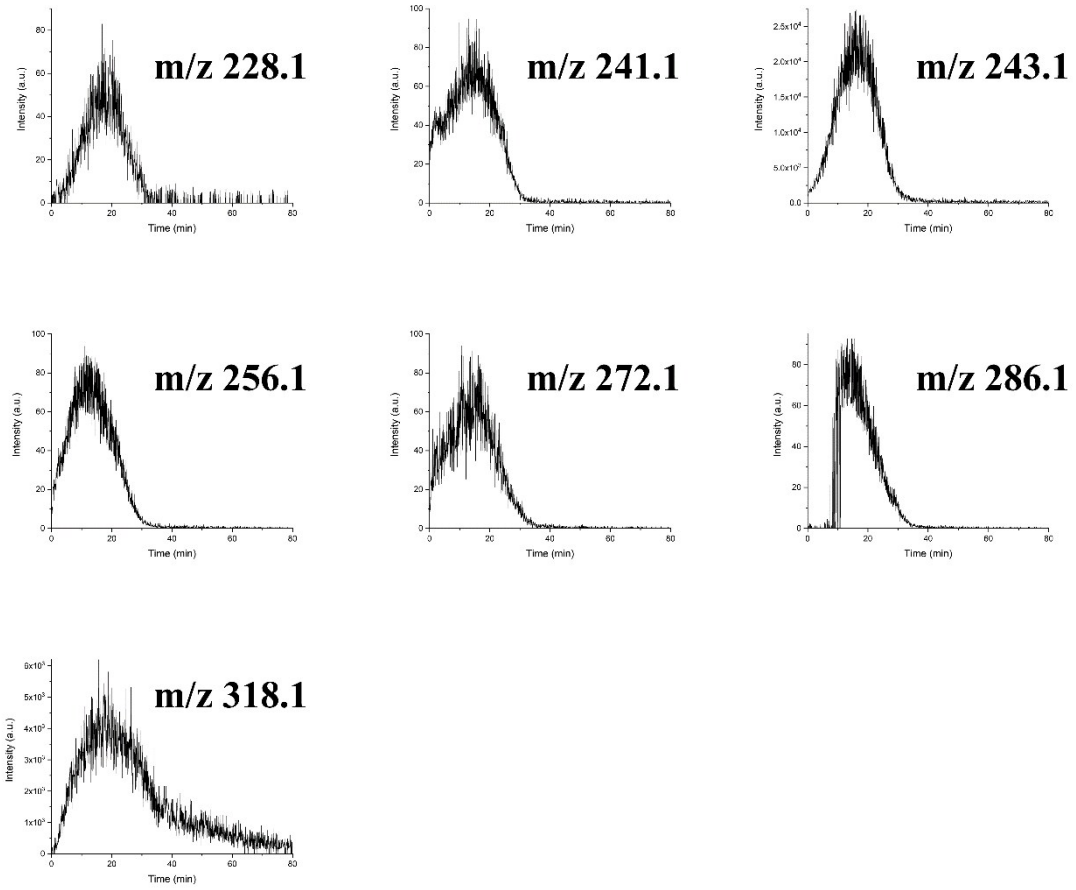
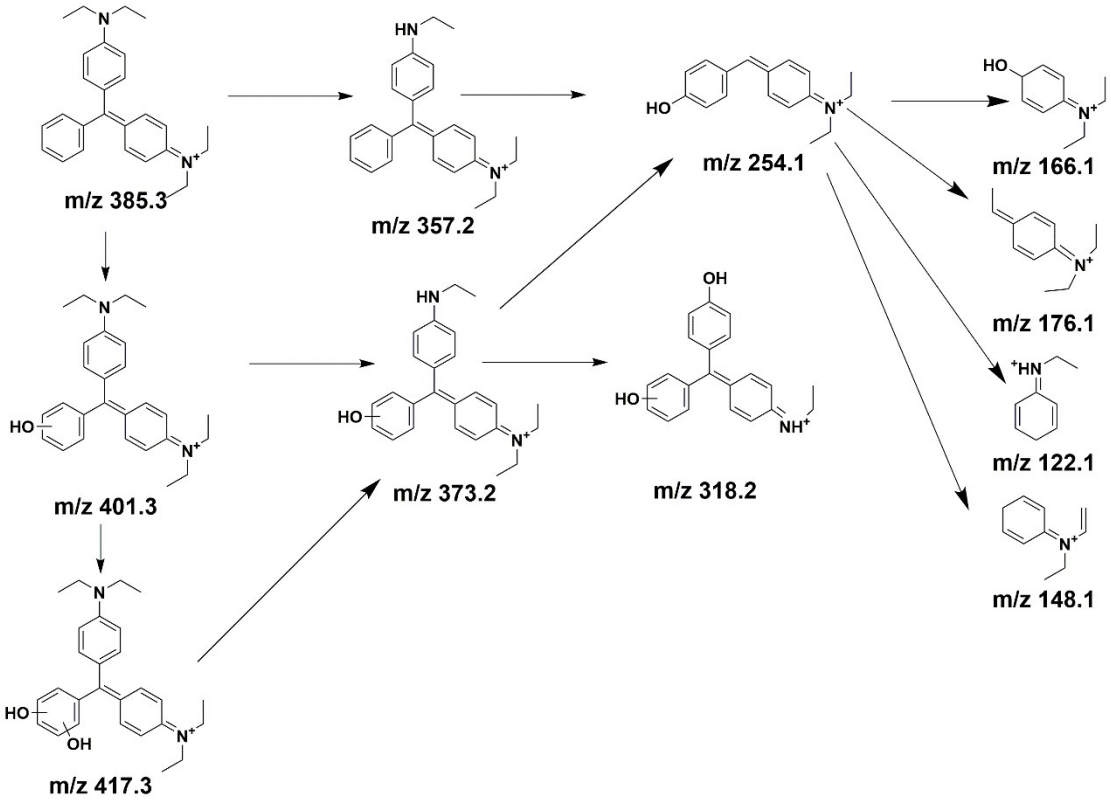


Figure S3 Extracted ion chromatograms of intermediate ions at *m*/*z* 228.1, 241.1, 243.1, 256.1, 272.1, 286.1, and 318.1 from *in situ* monitoring of photocatalytic reaction of methylene blue by TiO_2 under UV radiation.



Scheme S1 Proposed degradation mechanism of brilliant green under UV irradiation in 45% ethanol WO_3 dispersions followed by the identification of several intermediates by PESI-MS.

Table S1 Intermediates detected in the *in situ* monitoring of photocatalytic reaction of methylene blue by TiO_2, WO_3, ZnS, SiC and SnO_2 under UV radiation by PESI-MS.

ID	Intermediate ion (m/z)	Photocatalysts				
		TiO_2	WO_3	ZnS	SiC	SnO_2
1	330.0		✓			
2	328.1	✓	✓			✓
3	318.3		✓		✓	✓
4	318.1	✓				
5	316.1		✓			
6	301.0	✓	✓			✓
7	300.1	✓	✓			
8	286.1	✓	✓	✓	✓	✓
9	277.0	✓	✓			
10	274.0					✓
11	273.0	✓	✓			
12	272.1	✓	✓	✓	✓	✓
13	271.1			✓		
14	270.0	✓	✓			
15	270.1			✓	✓	
16	269.0		✓	✓		
17	265.0	✓				
18	263.0		✓			
19	261.0	✓	✓			
20	260.0		✓			
21	259.0	✓	✓			
22	257.0	✓	✓	✓	✓	✓
23	256.1	✓	✓	✓		✓
24	256.2					✓
25	255.0			✓		
26	254.0		✓	✓	✓	
27	251.0	✓				
28	249.0	✓	✓			
29	247.0	✓	✓			
30	246.7			✓		
31	245.0		✓			
32	244.7			✓		
33	243.1	✓	✓	✓	✓	✓
34	243.0	✓	✓			
35	242.7			✓		
36	242.0		✓			
37	241.1	✓	✓	✓	✓	✓
38	240.8			✓		
39	239.0			✓		
40	235.0	✓				

41	233.0	✓	✓			
42	231.0	✓	✓			✓
43	230.2					✓
44	229.0	✓	✓			
45	228.1	✓	✓	✓	✓	✓
46	227.0			✓	✓	
47	225.0			✓		
48	221.0	✓	✓			
49	219.0	✓	✓			
50	217.0	✓	✓			
51	215.0	✓	✓			
52	214.0		✓		✓	
53	209.0	✓	✓			
54	208.8			✓		
55	207.0	✓	✓			
56	206.8			✓		
57	205.0	✓	✓			
58	204.8			✓		
59	203.0		✓			
60	202.7			✓		
61	195.0		✓			
62	191.0	✓	✓			
63	188.8			✓		
64	188.0	✓	✓			
65	179.8			✓		
66	177.8			✓		
67	177.0	✓	✓			
68	175.8			✓		
69	166.8			✓		
70	166.0	✓	✓			
71	165.0	✓	✓			
72	164.0	✓	✓			
73	164.8			✓		
74	163.0	✓	✓			
75	162.8			✓		
76	160.8			✓		
77	152.0	✓	✓			
78	150.0		✓			
79	149.0			✓		
80	133.0	✓	✓			
81	122.0		✓			
82	121.0			✓		
83	120.0	✓	✓			
84	119.0	✓				✓

85	112.8	✓	
86	112.0		✓
87	110.9		✓
88	109.9		✓
89	108.3		✓
90	107.9		✓

Note: The checkmark "✓" indicates the intermediate ion can be detected when the analyst was used for the *in situ* monitoring of photocatalytic degradation of methylene blue under UV radiation by PESI-MS.

Table S2 Intermediates detected in the *in situ* monitoring of photocatalytic reaction of brilliant green by TiO_2, WO_3, ZnS, SiC and SnO_2 under UV radiation by PESI-MS.

ID	Intermediate ion (m/z)	Photocatalysts				
		TiO_2	WO_3	ZnS	SiC	SnO_2
1	417.3	✓	✓			
2	401.3	✓	✓		✓	
3	373.2	✓				
4	362.2		✓			
5	357.2		✓	✓	✓	✓
6	346.6		✓			
7	344.2			✓		
8	338.3			✓		
9	329.1		✓			
10	328.2	✓				
11	325.2	✓	✓			
12	323.2					✓
13	318.2		✓	✓	✓	✓
14	302.3		✓			
15	301.1	✓	✓			✓
16	296.1		✓			
17	281.1		✓			
18	276.1	✓				
19	274.2		✓	✓	✓	✓
20	270.1	✓				
21	256.2		✓	✓	✓	
22	254.1	✓	✓	✓	✓	✓
23	230.2		✓		✓	
24	226.1					✓
25	225.1	✓	✓	✓		✓
26	224.1			✓		
27	210.0	✓	✓	✓		✓
28	206.8			✓		
29	204.8			✓		
30	202.8			✓		
31	176.1	✓	✓	✓	✓	✓
32	166.1	✓	✓			
33	160.8			✓		
34	157.0	✓				
35	148.0	✓	✓	✓		✓
36	137.0	✓	✓	✓		
37	135.0				✓	✓
38	134.0		✓			
39	124.1			✓		
40	122.0	✓	✓	✓		✓

41	120.0		✓	✓		
42	118.9	✓				
43	109.0	✓	✓	✓		
44	108.0			✓		
45	105.0	✓	✓	✓	✓	✓

Note: The checkmark "✓ " indicates the intermediate ion can be detected when the analyst was used for the *in situ* monitoring of photocatalytic degradation of brilliant green under UV radiation by PESI-MS.