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## Supporting Information for

### Enhanced removal of perfluorooctanoic acid by VUV/sulfite/iodide: Efficiencies, influencing factors and decomposition mechanism

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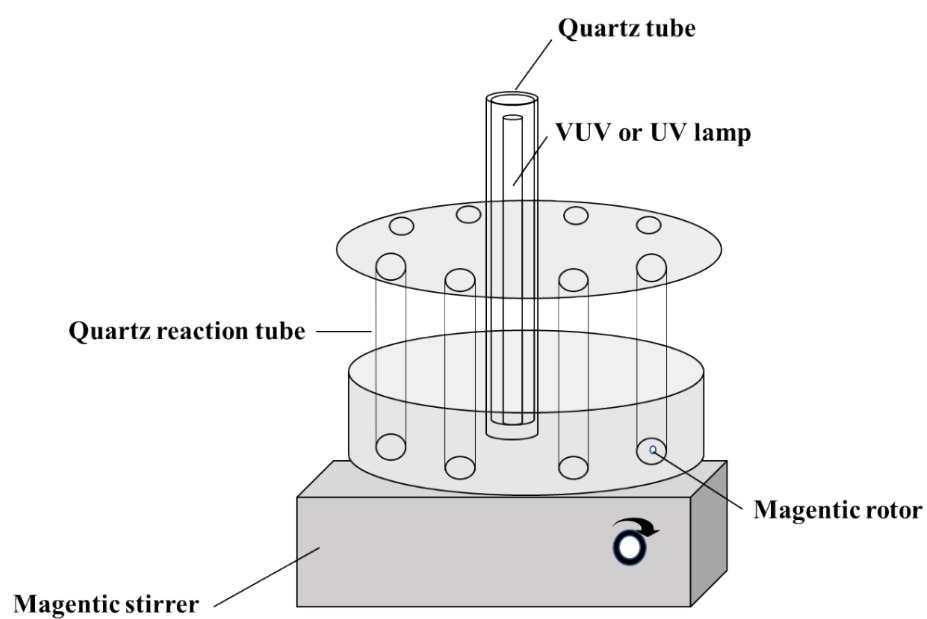
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19 **Text S1.** Chemicals and reagents

20 Sodium sulfite anhydrous ( $\geq 97.0\%$ ) was supplied by Tianjin Damao Chemical Reagent Co., Ltd,  
21 China. Sodium hydroxide ( $\geq 99.5\%$ ), Magnesium sulfate ( $\geq 99.0\%$ ), sodium chloride ( $\geq 99.5\%$ ),  
22 sodium bicarbonate ( $\geq 99.0\%$ ), sodium sulfate ( $\geq 99.5\%$ ), and copper sulfate pentahydrate ( $\geq$   
23  $99.0\%$ ) were all obtained from Sinopharm Chemical Reagent Co. Ltd., China. Tert-butyl alcohol  
24 and methanol were purchased from Sigma-Aldrich Co. Ltd., Germany. Sodium nitrate ( $\geq 99.0\%$ )  
25 was purchased from Tianjin Guangcheng Chemical Reagent Co., Ltd, China. Potassium iodide ( $\geq$   
26  $99.5\%$ ) and sodium nitrite ( $\geq 99.5\%$ ) were supplied from Tianjin Kemiou Chemical Reagent Co.,  
27 Ltd, China. Sulfuric acid was obtained from Suzhou Crystal Clear Chemical Co. Ltd., China.  
28 Ferric sulfate ( $\geq 99.0\%$ ) and humic acid (HA, No. 53680) were purchased from Aladdin (Shanghai,  
29 China). Perfluorooctanoic acid (PFOA,  $C_7F_{15}COOH$ , 98%) was supplied by J&K Scientific Inc.  
30 (Beijing, China). All solutions were prepared in Milli-Q ultrapure water ( $18.2 M\Omega \cdot cm$ , Millipore).



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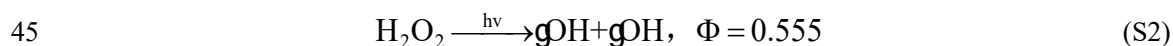
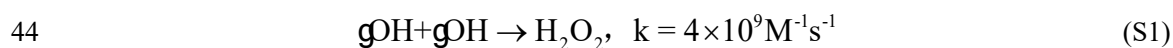
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**Fig. S1** Schematic diagram of the photochemical reactor

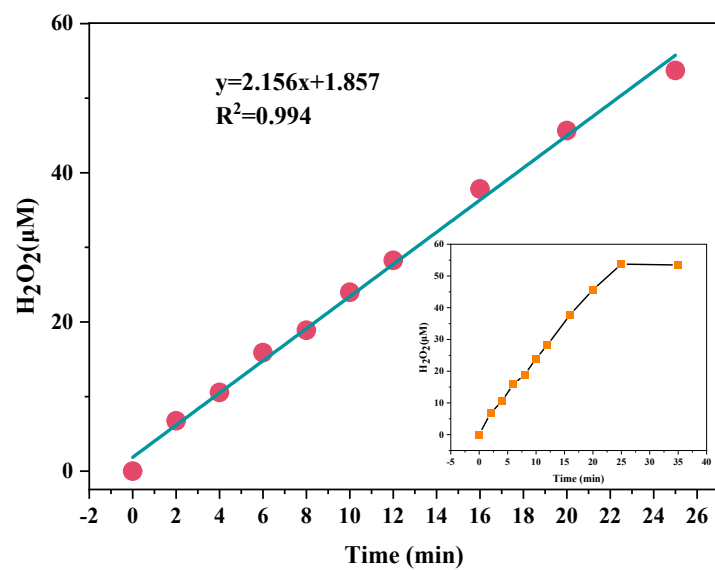
35 **Text S2.** VUV photonic intensity at 185 nm

36 To obtain VUV photonic intensity ( $I_{0,185\text{ nm}}$ ) at 185 nm, we explored the production rate of  $\text{H}_2\text{O}_2$  in  
37 ultrapure water by 185 nm VUV<sup>1</sup>. The concentration of  $\text{H}_2\text{O}_2$  increased with increasing reaction  
38 time until it reached a maximum value after 25 min exposure (Fig. S2). The quasi-stationary state  
39 was reached when the production rate of  $\text{H}_2\text{O}_2$  (Eq. (S1)) was equal to its consumption rate (Eqs.  
40 (S2) – (S3))<sup>2-4</sup>. As the  $\text{H}_2\text{O}_2$  production rate  $r_{\text{H}_2\text{O}_2}$  ( $\mu\text{M s}^{-1}$ ) followed a pseudo-zero-order reaction  
41 (Fig. S2), it would be proportional to the absorbed VUV photon flux.  $I_{0,185\text{ nm}}$  could be determined  
42 using Eq. (S4). Photonic intensity from the VUV source at 185 nm was determined to be  
43 approximately  $0.15 \mu\text{Einstein}\cdot\text{s}^{-1}$ .



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$$I_{0,185\text{ nm}} = \frac{r_{\text{H}_2\text{O}_2} V}{\Phi_{\text{H}_2\text{O}_2}} \quad (\text{S4})$$

48 where;  $\Phi_{\text{H}_2\text{O}_2}$  ( $25^\circ\text{C}$ ,  $0.024 \text{ M einstein}^{-1}$ ) is the apparent quantum yield for  $\text{H}_2\text{O}_2$  production, and  $V$   
49 is the reaction volume (L).



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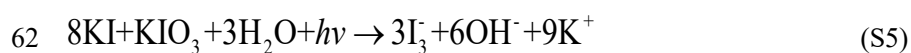
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Fig. S2  $\text{H}_2\text{O}_2$  production under VUV irradiation. Condition:  $T = 22 \pm 0.5 \text{ }^\circ\text{C}$

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53 **Text S3.** UV photonic intensity at 254 nm

54 The UV photonic intensity ( $I_{0,254\text{ nm}}$ ) at 254 nm was determined by the KI/KIO<sub>3</sub> method <sup>5</sup>. The  
55 mixed reaction solution in the presence of KI and KIO<sub>3</sub> will produce I<sub>3</sub><sup>-</sup> under the UV radiation of  
56 wavelength less than 290 nm (Eq.(S5)), and the concentration of I<sub>3</sub><sup>-</sup> will increase with time. The  
57 concentration of I<sub>3</sub><sup>-</sup> can be determined by a UV-vis spectrophotometer and the molar absorptivity  
58 of I<sub>3</sub><sup>-</sup> at 352 nm is 26400 M<sup>-1</sup>cm<sup>-1</sup>. Assuming that the reaction solution absorbed the light quantum  
59 radiated by UV<sub>254</sub> completely, the  $I_{0,254\text{ nm}}$  of the UV<sub>254</sub> system can be determined according to Eq.  
60 (S6). Photonic intensity from the VUV source and UV source at 254 nm was determined to be  
61 approximately 1.16 μEinstein•s<sup>-1</sup> and 1.27 μEinstein•s<sup>-1</sup>, respectively.



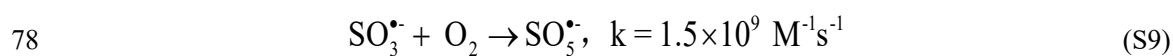
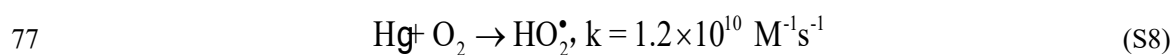
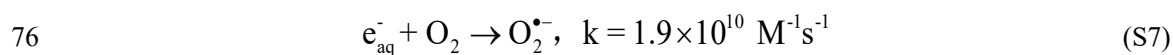
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$$I_{0,254\text{ nm}} = C_{\text{I}_3^-} \times V \times \frac{1}{\varphi_{\text{I}_3^-}} \times \frac{1}{t}$$
 (S6)

64 where  $C_{\text{I}_3^-}$  is the concentration of the formed I<sub>3</sub><sup>-</sup> (M), V is the volume of reaction solution (L),  
65  $\varphi_{\text{I}_3^-}$  (0.74 mol einstein<sup>-1</sup>, 20°C) is the quantum yield of formed I<sub>3</sub><sup>-</sup>, and  $t$  is reaction time (s).

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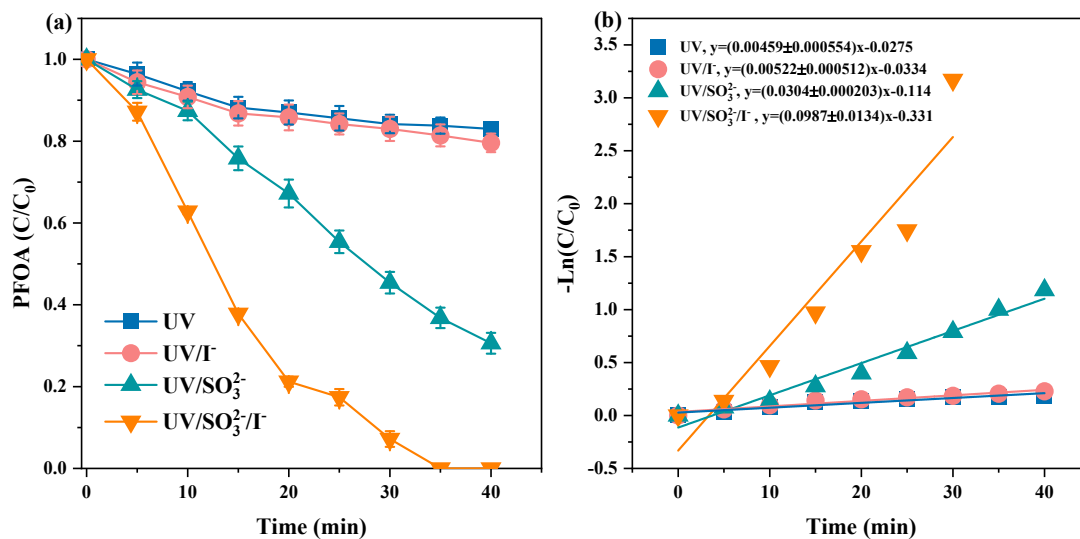
67 **Text S4.** The concentration of dissolved oxygen in different background solutions

68 As shown in Eqs. (S7) – (S9), plausible reactive species can be scavenged rapidly by dissolved  
69 oxygen (DO) <sup>6</sup>. Whereas, due to the inconsistent description concerning whether to control DO in  
70 some previous studies <sup>7,8</sup>. Thus, the effect of the reaction atmosphere on PFOA decomposition in  
71 the VUV/SO<sub>3</sub><sup>2-</sup>/I<sup>-</sup> system was investigated (Fig. S3). Since the initial DO was not instantaneously  
72 scavenged by SO<sub>3</sub><sup>2-</sup> (Fig. S4), PFOA degradation efficiency was slightly lower in the control  
73 atmosphere than in the nitrogen atmosphere. However, within 40 min, 10 mg·L<sup>-1</sup> PFOA was  
74 almost completely decomposed in both the nitrogen atmosphere and control atmosphere. DO  
75 could be neglected in the present system, which greatly benefits potential practical applications.



79 We investigated the concentration of dissolved oxygen (DO) in different background solutions.  
80 The initial concentration of DO was 9.38 mg·L<sup>-1</sup> in ultrapure water, which decreased to 5.87  
81 mg·L<sup>-1</sup> by introducing SO<sub>3</sub><sup>2-</sup> for 10 min of stabilization. It was found that the concentration of DO  
82 was below its detection limit (0.20 mg·L<sup>-1</sup>) by stirring for 10min. The concentration of DO was  
83 maintained at about 1.10 mg·L<sup>-1</sup> in PFOA/SO<sub>3</sub><sup>2-</sup> and PFOA/SO<sub>3</sub><sup>2-</sup>/I<sup>-</sup> systems continuously stirred  
84 for 10 min. The existence of PFOA reduced the quenching of DO by SO<sub>3</sub><sup>2-</sup>, which was speculated  
85 that PFOA as a surfactant may enhance the solubility of DO in water.

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88 **Fig. S3** (a) Degradation of PFOA and (b)  $k_{\text{obs}}$  in different systems under UV irradiation. Condition:  $[\text{PFOA}]_0 = 10$

89  $\text{mg}\cdot\text{L}^{-1}$ ,  $[\text{SO}_3^{2-}]_0 = 10 \text{ mM}$ ,  $[\text{I}^-]_0 = 1 \text{ mM}$ ,  $[\text{pH}] = \text{No adjusted}$ .

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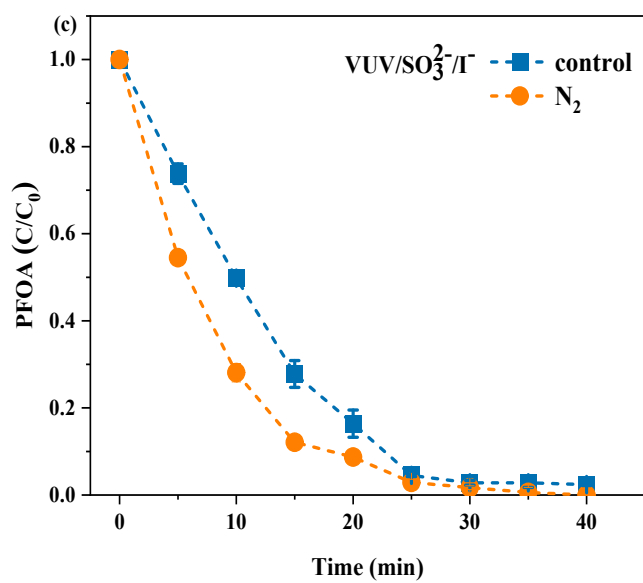
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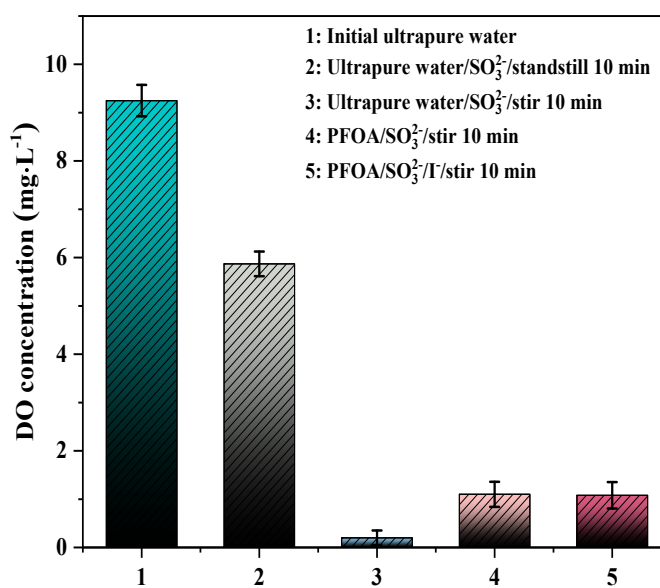




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100 **Fig.S4** The effect of reaction atmosphere on the degradation of PFOA in VUV/SO<sub>3</sub><sup>2-</sup>/I<sup>-</sup> system. Condition:

101 [PFOA]<sub>0</sub>=10 mg·L<sup>-1</sup>, [SO<sub>3</sub><sup>2-</sup>]<sub>0</sub> = 10 mM, [I<sup>-</sup>]<sub>0</sub> = 1 mM.



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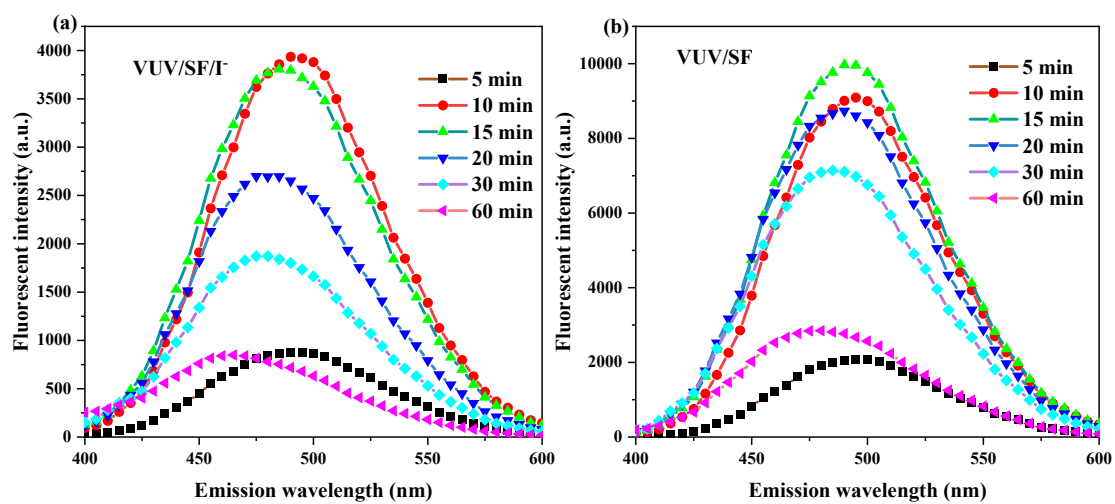
103 **Fig. S5** Concentrations of dissolved oxygen (DO) in different solution backgrounds. Condition: [PFOA]<sub>0</sub>=10

104 mg·L<sup>-1</sup>, [SO<sub>3</sub><sup>2-</sup>]<sub>0</sub> = 10 mM, [I<sup>-</sup>]<sub>0</sub> = 1 mM.

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**Table S1.** The second-order rate constants for reactions of reactive species and quenchers.

Reactive species	Reaction rate constants ( $M^{-1} s^{-1}$ )		Reactive species	Reaction rate constants ( $M^{-1} s^{-1}$ )
	MeOH <sup>4, 9-11</sup>	TBA <sup>10-12</sup>		NO <sub>2</sub> <sup>-13, 14</sup>
H•	$1 \times 10^5$	$1.15 \times 10^6$	H•	$7.1 \times 10^8$
OH•	$9.7 \times 10^8$	$6.0 \times 10^8$	e <sub>aq</sub> <sup>-</sup>	$4.1 \times 10^9$
SO <sub>4</sub> <sup>•-</sup>	$2.5 \times 10^7$	$8.4 \times 10^5$	/	
e <sub>aq</sub> <sup>-</sup>	$<10^4$	/		



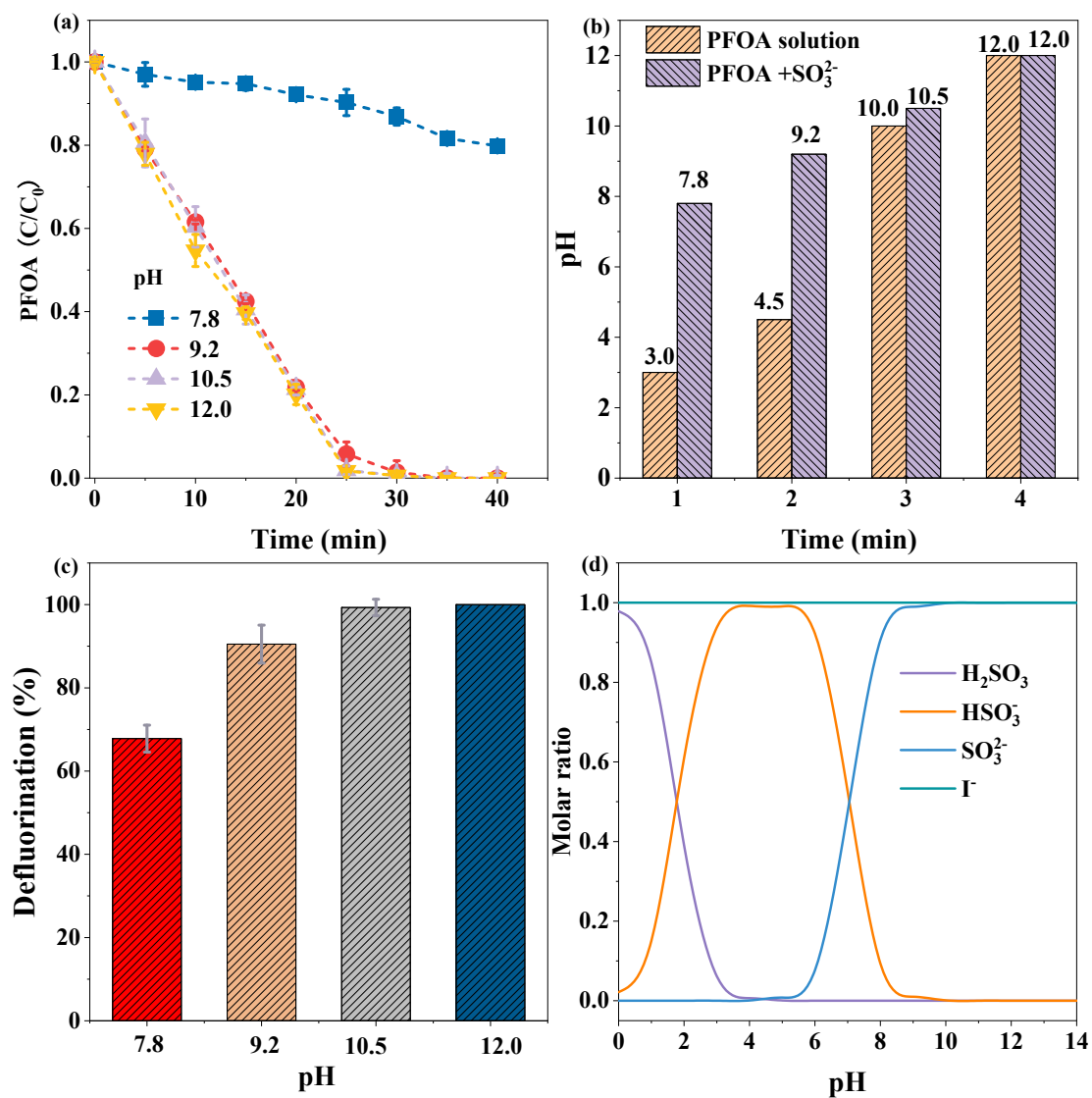
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109 **Fig. S6** Fluorescence intensity of 7-hydroxycoumarin at different reaction time in the (a) VUV/SO<sub>3</sub><sup>2-</sup>/I<sup>-</sup> and (b)

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VUV/SO<sub>3</sub><sup>2-</sup> processes. Condition: [SO<sub>3</sub><sup>2-</sup>]<sub>0</sub> = 10 mM, [I<sup>-</sup>]<sub>0</sub> = 1 mM, [Coumarin] = 1mM.

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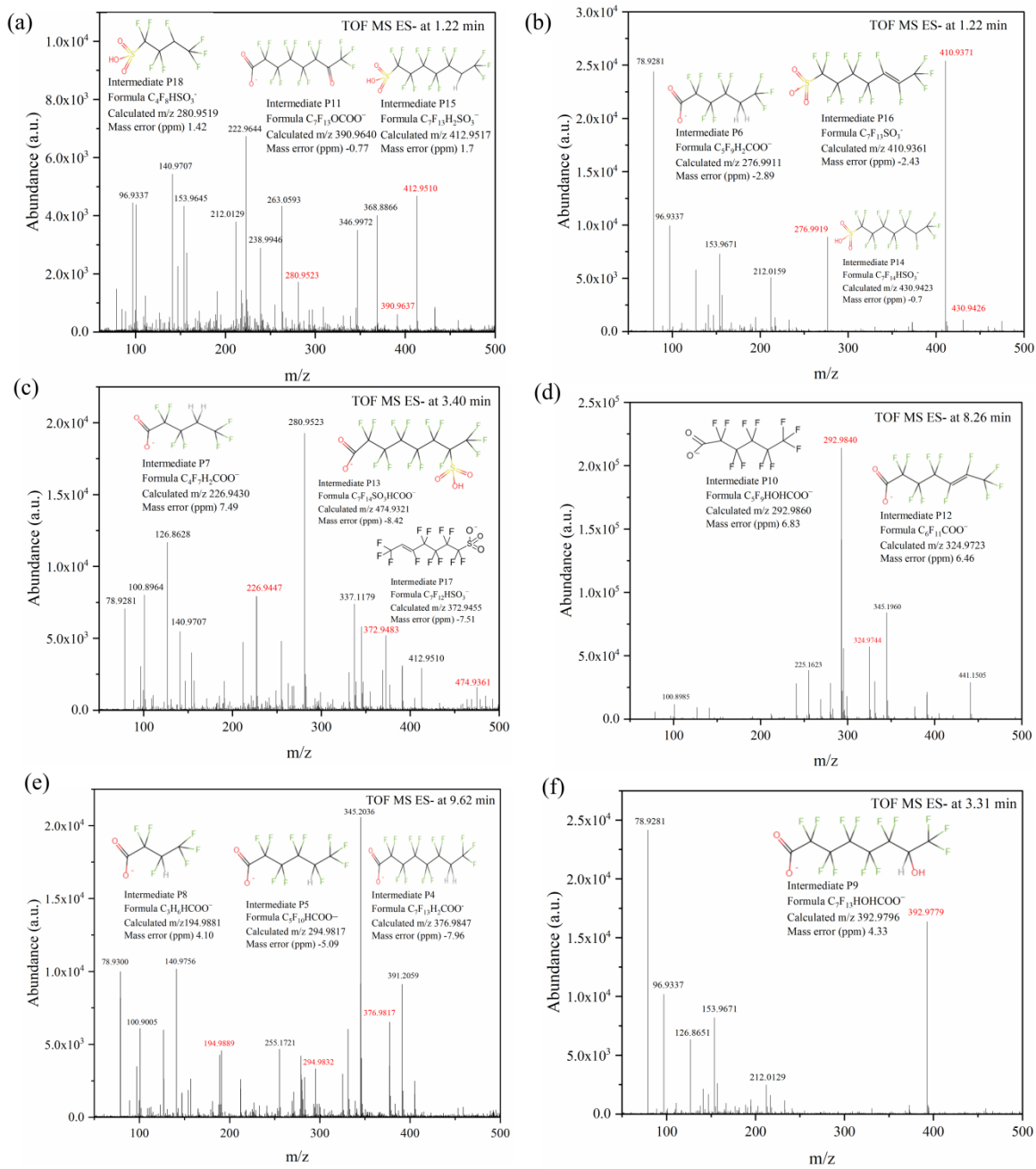
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113 **Fig. S7** Effect of initial pH on (a) the degradation of PFOA in the VUV/SO<sub>3</sub><sup>2-</sup>/I<sup>-</sup> system; (b) pH values in the

114 presence and absence of SO<sub>3</sub><sup>2-</sup> in PFOA solutions; (c) the defluorination of PFOA in the VUV/SO<sub>3</sub><sup>2-</sup>/I<sup>-</sup> system; (d)

115 the distribution and speciation of SO<sub>3</sub><sup>2-</sup> and I<sup>-</sup> species in pH from 0 to 14. Condition: [PFOA]<sub>0</sub> = 10 mg·L<sup>-1</sup>, [SO<sub>3</sub><sup>2-</sup>]<sub>0</sub>

116 = 10 mM, [I<sup>-</sup>]<sub>0</sub> = 1 mM.



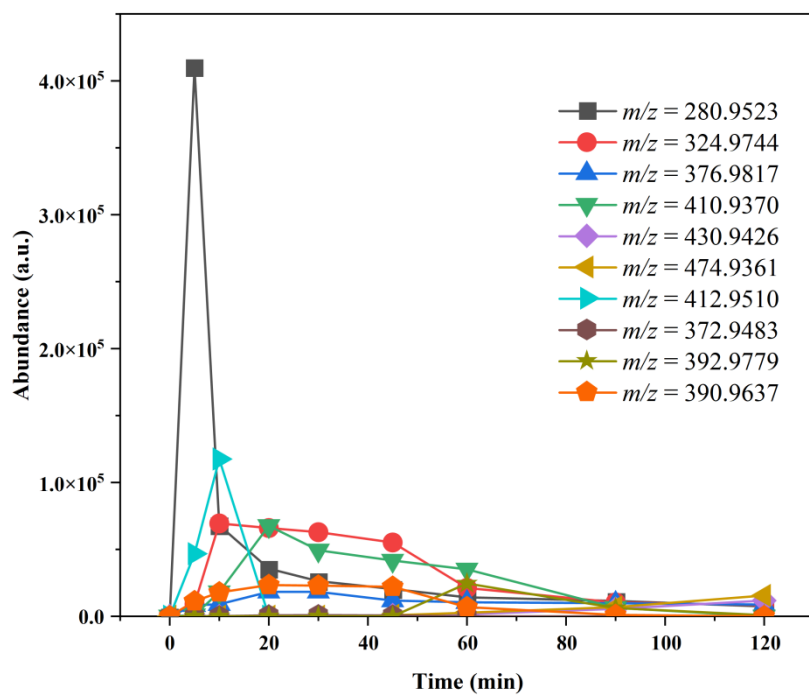
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**Fig. S8** Mass spectrometry of intermediates of PFOA degradation

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**Fig. S9** The evolution of intermediates of PFOA degradation in the VUV/SO<sub>3</sub><sup>2-</sup>/I<sup>-</sup> process

**Table S2.** Condensed  $f^+$  indices for PFOA anion

Atom	$q_N$	$q_{N+1}$	$f^+$
1(F)	-0.34571	-0.38227	0.03656
2(F)	-0.34571	-0.38227	0.03656
3(F)	-0.35079	-0.37734	0.02655
4(F)	-0.35079	-0.37734	0.02655
5(F)	-0.34486	-0.38869	0.04383
6(F)	-0.34486	-0.38869	0.04383
7(F)	-0.3493	-0.36671	0.01741
8(F)	-0.3493	-0.36671	0.01741
9(F)	-0.34091	-0.38687	0.04596
10(F)	-0.34091	-0.38687	0.04596
11(F)	-0.37005	-0.38132	0.01127
12(F)	-0.37005	-0.38132	0.01127
13(F)	-0.34823	-0.40822	0.05999
14(F)	-0.34814	-0.3832	0.03506
15(F)	-0.34814	-0.3832	0.03506
16(O)	-0.71014	-0.75801	0.04787
17(O)	-0.73221	-0.7523	0.02009
18(C)	0.67714	0.59607	0.08107
19(C)	0.67291	0.62214	0.05077
20(C)	0.67519	0.56512	0.11007
21(C)	0.67118	0.65432	0.01686
22(C)	0.64229	0.55802	0.08427
23(C)	0.63386	0.63119	0.00267
24(C)	1.06352	0.97068	0.09284
25(C)	0.65402	0.65918	-0.00516

Note:  $f^+ = q_N - q_{N+1}$  <sup>15</sup>

127 **Table S3.** The bond length of PFOA anion chemical bond calculated at B3LYP/6-31 G (d, p) level

<b>Chemical bond</b>	<b>Bond length(Å)</b>	<b>Chemical bond</b>	<b>Bond length(Å)</b>
13F-24C	1.34375	3F-19C	1.35817
14F-24C	1.33893	4F-19C	1.35817
15F-24C	1.33893	18C-19C	1.56478
22C-24C	1.55407	7F-21C	1.35904
9F-22C	1.35389	8F-21C	1.35904
10F-22C	1.35389	19C-21C	1.56513
5F-20C	1.35590	11F-23C	1.37713
6F-20C	1.35590	12F-23C	1.37713
20C-22C	1.55803	21C-23C	1.54951
1F-18C	1.35540	16O-25C	1.24586
2F-18C	1.35540	17O-25C	1.24524
18C-20C	1.56341	23C-25C	1.59795



**Table S4.** Condensed  $f^+$  indices for PFOA molecule

Atom	$q_N$	$q_{N+1}$	$f^+$
1(F)	-0.33326	-0.36092	0.02766
2(F)	-0.33326	-0.36092	0.02766
3(F)	-0.33673	-0.36257	0.02584
4(F)	-0.33673	-0.36257	0.02584
5(F)	-0.33423	-0.36431	0.03008
6(F)	-0.33423	-0.36431	0.03008
7(F)	-0.33007	-0.35731	0.02724
8(F)	-0.33007	-0.35731	0.02724
9(F)	-0.331	-0.35804	0.02704
10(F)	-0.331	-0.35804	0.02704
11(F)	-0.34746	-0.39711	0.04965
12(F)	-0.34746	-0.39711	0.04965
13(F)	-0.33539	-0.35351	0.01812
14(F)	-0.33852	-0.3531	0.01458
15(F)	-0.33852	-0.3531	0.01458
16(O)	-0.62029	-0.67507	0.05478
17(O)	-0.54857	-0.66209	0.11352
18(C)	0.667	0.62543	0.04157
19(C)	0.66645	0.62608	0.04037
20(C)	0.66314	0.6121	0.05104
21(C)	0.67464	0.64387	0.03077
22(C)	0.63739	0.58833	0.04906
23(C)	0.62663	0.54843	0.0782
24(C)	1.04089	1.02625	0.01464
25(C)	0.71255	0.62741	0.08514
26(H)	0.51809	0.49949	0.0186

132 **Table S5.** Predicted acute and chronic toxicity of 8:3FTCA and its intermediates by ECOSAR program

Compounds	acute toxicity (mg•L <sup>-1</sup> )			chronic toxicity (ChV) (mg•L <sup>-1</sup> )		
	Fish LC <sub>50</sub> /96h	Daphnia LC <sub>50</sub> /48h	Green algae EC <sub>50</sub> /96h	Fish	Daphnia	Green algae
PFOA	10.1	7.44	16.2	1.34	1.49	7.58
P1	35.4	24.5	41.4	4.37	4.15	16.9
P2	122	79.3	104	14.0	11.3	36.8
P3	409	250	254	43.6	30.0	78.4
P4	7.21	5.37	12.3	0.970	1.11	5.86
P5	118	76.9	100	13.6	10.9	35.4
P6	84.4	55.5	76.0	9.82	8.16	27.6
P7	276	171	181	29.9	21.1	57.4
P8	2.30E+3	1.29E+3	898	221	120	227
P9	181	117	148	20.6	16.3	51.7
P10	2.15E+3	1.23E+3	934	211	121	247
P11	518	319	333	55.8	39.1	105
P12	84.5	54.7	77.5	9.69	8.22	28.7
P13	1.20E+3	716	664	124	80.9	196
P14	83.9	56.3	83.8	9.99	8.75	31.8
P15	61.1	41.5	65.0	7.38	6.67	25.4
P16	109	72.4	102	12.8	10.8	37.5
P17	117	77.1	106	13.6	11.4	38.6
P18	3.48 E+3	1.94E+3	1.34E+3	330	180	337

133 Red: very toxic, LC<sub>50</sub> (EC<sub>50</sub>)/ChV < 1.0 mg•L<sup>-1</sup>; Pink: toxic, LC<sub>50</sub> (EC<sub>50</sub>)/ChV = 1.0–10.0 mg•L<sup>-1</sup>;

134 Blue: harmful, LC<sub>50</sub> (EC<sub>50</sub>)/ChV = 10.0–100.0 mg•L<sup>-1</sup>; Green: not harmful, LC<sub>50</sub> (EC<sub>50</sub>)/ChV > 100.0

135 mg•L<sup>-1</sup>.

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139 **References**

- 140 1. L. Yang, M. Li, W. Li, J. R. Bolton and Z. Qiang, A green method to determine VUV  
141 (185 nm) fluence rate based on hydrogen peroxide production in aqueous solution,  
142 *Photochem. Photobiol.*, 2018, **94**, 821-824.
- 143 2. K. Azrague, E. Bonnefille, V. Pradines, V. Pimienta, E. Oliveros, M.-T. Maurette and F.  
144 Benoit-Marquié, Hydrogen peroxide evolution during V-UV photolysis of water,  
145 *Photochem. Photobiol. Sci.*, 2005, **4**, 406-408.
- 146 3. S. Goldstein, D. Aschengrau, Y. Diamant and J. Rabani, Photolysis of aqueous H<sub>2</sub>O<sub>2</sub>:  
147 quantum yield and applications for polychromatic UV actinometry in photoreactors,  
148 *Environ. Sci. Technol.*, 2007, **41**, 7486-7490.
- 149 4. M. G. Gonzalez, E. Oliveros, M. Wörner and A. M. Braun, Vacuum-ultraviolet photolysis  
150 of aqueous reaction systems, *J. Photochem. Photobiol. C.*, 2004, **5**, 225-246.
- 151 5. R. O. Rahn, Potassium Iodide as a Chemical Actinometer for 254 nm Radiation: Use of  
152 Iodate as an Electron Scavenger, *Photochem. Photobiol.*, 1997, **66**, 450-455.
- 153 6. P. Neta, R. E. Huie and A. B. Ross, Rate constants for reactions of inorganic radicals in  
154 aqueous solution, *J. Phys. Chem. Ref. Data*, 1988, **17**, 1027-1284.
- 155 7. Z. F. Ren, U. Bergmann and T. Leiviskä, Reductive degradation of perfluorooctanoic acid  
156 in complex water matrices by using the UV/sulfite process, *Water Res.*, 2021, **205**,  
157 117676.
- 158 8. Y. R. Gu, T. Z. Liu, Q. Zhang and W. Y. Dong, Efficient decomposition of  
159 perfluorooctanoic acid by a high photon flux UV/sulfite process: Kinetics and associated  
160 toxicity, *Chem. Eng. J.*, 2017b, **326**, 1125-1133.

- 161 9. M. Anbar and E. J. Hart, The reactivity of aromatic compounds toward hydrated electrons,  
162 *J. Am. Chem. Soc.*, 1964, **86**, 5633-5637.
- 163 10. G. P. Anipsitakis and D. D. Dionysiou, Transition metal/UV-based advanced oxidation  
164 technologists for water decontamination, *Appl. Catal. B.*, 2004, **54**, 155-163.
- 165 11. G. Wu, Y. Katsumura and G. Chu, Photolytic and radiolytic studies of  $\text{SO}_4^{\cdot-}$  in neat  
166 organic solvents, *Phys. Chem. Chem. Phys.*, 2000, **2**, 5602-5605.
- 167 12. J. Criquet and N. K. V. Leitner, Degradation of acetic acid with sulfate radical generated  
168 by persulfate ions photolysis, *Chemosphere*, 2009, **77**, 194-200.
- 169 13. X. C. Li, J. Ma, G. F. Liu, J. Y. Fang, S. Y. Yue, Y. H. Guan, L. W. Chen and X. W. Liu,  
170 Efficient reductive dechlorination of monochloroacetic acid by sulfite/UV process,  
171 *Environ. Sci. Technol.* , 2012, **46**, 7342–7349.
- 172 14. G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, Critical review of rate  
173 constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals  
174 ( $\cdot\text{OH}/\cdot\text{O}^-$ ) in aqueous solution, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513–886.
- 175 15. Y. X. Bao, S. S. Deng, X. S. Jiang, Y. X. Qu, Y. He, L. Q. Liu, Q. W. Chai, M. Mumtaz,  
176 J. Huang, G. Cagnetta and G. Yu, Degradation of PFOA Substitute: GenX (HFPO–DA  
177 Ammonium Salt): Oxidation with UV/Persulfate or Reduction with UV/Sulfite? , *Environ.*  
178 *Sci. Technol.*, 2018, **52**, 11728-11734.
- 179