1 Supporting Information for:

2	Electrochemical Mineralization of Perfluorocarboxylic Acids (PFCAs) by Ce-doped Modified
3	Porous Nano-crystalline PbO ₂ Film Electrode
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11	This Supporting Information contains the detailed information on "Calibration conditions for the
12	quantification of perfluorinated acids (PFCAs, C ₂ ~C ₈) by HPLC-MS/MS", "The HPLC/MS/MS
13	chromatogram of standard perfluorocarboxylic acids bearing C ₂ ~C ₈ (every PFCA concentration
14	was 500ppb)", "Calibration conditions for the quantification of F by ion chromatography",
15	"Schematic diagram of the experimental apparatus, "Characterization of electrode", "Evaluation
16	of the anode surface", "Mass spectra with negative ESI of PFCA solutions (diluted 100 fold by
17	volume) after 45 min electrolysis", "The concentration of metals in the solution (electrolysis time:
18	90 min)", and "Comparison of previously reported techniques for degradation of PFOA".
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21	In total, there are five tables, eight figures, and the document length is twelve pages.
22	

25 **Table S1-** Calibration conditions for the quantification of perfluorocarboxylic acids (PFCAs, $C_2 \sim C_8$) by

analyte	m/z	Retention time (min)	Concentration range (µg/L)	Correlation coefficient (R ²)	LOD ^a (µg/L)	LOQ^{b} (µg/L)
C ₇ F ₁₅ COO ⁻	413>369	13.45	0~1000	0.993	0.12	0.25
C ₆ F ₁₃ COO ⁻	363>319	12.63	0~1000	0.996	0.54	2.18
C ₅ F ₁₁ COO ⁻	313>269	11.08	0~1000	0.989	0.24	0.75
C ₄ F ₉ COO ⁻	263>219	10.21	0~1000	0.999	0.15	0.39
C ₃ F ₇ COO ⁻	213>169	7.58	0~1000	0.997	0.09	0.20
$C_2F_5COO^2$	163>119	6.87	0~1000	0.994	0.58	2.55
CF ₃ COO ⁻	113>68	6.64	0~1000	0.991	0.83	3.96

26 HPLC-MS/MS.

^aLimit of detection (LOD) was calculated from the concentration of each perfluorocarboxylic acids that

28 yielded a signal-to-noise (S/N) ratio of higher than or equal to 3.

²⁹ ^bLimit of quantification (LOQ) was calculated from the concentration of each perfluorocarboxylic acids

30 that yielded a signal-to-noise (S/N) ratio of higher than or equal to 10.

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Figure S1 – The HPLC/MS/MS chromatogram of standard perfluorocarboxylic acids bearing C₂~C₈
 (every PFCA concentration was 500ppb).

Table S2- Calibration conditions for the quantification of F⁻ by ion chromatography.

	Retention time (min)	Concentration range (mg/L)	Correlation coefficient (R ²)	LOD ^a (mg/L)	LOQ ^b (mg/L)
-	4.09	0~5	0.999	0.002	0.02
	3		1 0 1		

³⁹ ^aLimit of detection (LOD) was calculated from the concentration of F⁻ that yielded a signal-to-noise

40 (S/N) ratio of higher than or equal to 3.

41 ^bLimit of quantification (LOQ) was calculated from the concentration of F⁻ that yielded a signal-to-noise

42 (S/N) ratio of higher than or equal to 10.





45 Figure S2 – Schematic diagram of the experimental apparatus (1. dc power, 2. electrolytic cell, 3. wire
46 terminal, 4. air drain, 5. cathode, 6. anode).

48 **Characterization of electrode**

49 Figure S3 shows the images of Ti/SnO₂-Sb/Ce-PbO₂ (a, b), Ti/SnO₂-Sb/PbO₂ (c, d), and Ti/SnO₂-Sb electrodes surface. The surface of Ti/SnO₂-Sb/PbO₂ electrode is compact and homogeneous 50 (Figure S3c) and has a pyramid morphology (Figure S3d). The PbO₂ crystal particles of the 51 Ti/SnO₂-Sb/PbO₂ electrode surface are mostly a few microns, and there are cracks on the crystals 52 surface. There are obvious differences in the morphology of the Ti/SnO₂-Sb/Ce-PbO₂ electrode (Figure 53 S3a, b). The Ti/SnO₂-Sb/Ce-PbO₂ electrode has a rough and porous surface (Figure S3a) and has an oval 54 morphology (Figure S3b). The PbO₂ crystal particles of the Ti/SnO₂-Sb/Ce-PbO₂ electrode surface are 55 nanoscale, the majority of the crystal particles are hundreds of nanometers. Figure S3b shows that the 56 PbO₂ crystals are dense and no cracks, indicating the deposition of PbO₂ changed on addition Ce and the 57 internal stress of the crystal significantly reduced. Porous and nano-structures can effectively increase 58 59 the electrode area and reactivity point, which are conductive to improving the electrode performance.





electrodes. Images of the Ti/SnO₂-Sb/Ce-PbO₂ (a) and Ti/SnO₂-Sb/PbO₂ (c) electrodes.



69 **Figure S4** – Linear sweep voltammetry (LSV) of the Ti/SnO₂-Sb/PbO₂ electrode and 70 Ti/SnO₂-Sb/Ce-PbO₂ electrode in 0.5 mol L⁻¹ H₂SO₄ solution. Scan rate: 10 mV s⁻¹; sensitivity: 0.01 a 71 V^{-1} .

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73 Evaluation of the anode surface

The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out in three-electrode electrochemical cells driven by a CHI 66D electrochemical workstation (Shanghai Chenhua instrument Co, Ltd., China). The Ce-doped modified porous nano-crystalline PbO₂ film electrode (Ce-PbO₂) served as the work elected (1 cm \times 2 cm), a platinum wire and saturated calomel electrode (SCE) served as the counter electrode and the reference electrode, respectively. X-ray photoelectron spectroscopy (XPS) was measured by ESCALAB 250Xi (Thermo Scientific Ltd), using a monochromatic Al K α source.

It has been reported that BDD surface could be fluorinated by electrolysis in PFOA solution (1, 2). The electron transfer for $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ has been considered to be extremely sensitive to surface properties of the electrodes. Figure S5 shows the cyclic voltammograms for 10 mM K₃Fe(CN)₆ in 0.5 M KNO₃ solution at the Ce-PbO₂ surface. The scan range is from 0.2V *vs.* SCE to 0.7V *vs.* SCE. The

cyclic voltammetry curves of Ce-PbO₂ before and after electrolysis have no significant change, the 85 separations between the anodic and the cathodic peak (ΔE_P) were 175 mV and 179 mV at the scan rate 86 of 25 mV S⁻¹, respectively, suggesting the Ce-PbO₂ surface is not fluorinated by PFOA. Figure S6 87 shows EIS plots for 3.5% NaCl at the Ce-PbO₂ surface at 0.6V vs. SCE and 1.6V vs. SCE open circuit 88 89 potential. The frequency range is $0.1 \sim 100,000$ Hz. The Nyquist plots of Ce-PbO₂ before and after 90 electrolysis have no significant change, implying the Ce-PbO₂ surface is not fluorinated modification 91 after electrolysis in PFOA solution. Figure S7 shows the X-ray photoelectron spectra (XPS) of the Ce-PbO₂ surface before and after electrolysis. Both surfaces existed trace amount of fluorine. XPS 92 93 analysis also revealed the atomic concentrations of fluorine were 1.53% (A) and 1.45% (B). As the 94 electrodeposition solution contains NaF, the trace amount of fluorine at the Ce-PbO₂ surface came from 95 NaF rather than PFOA. On the other hand, high recoveries of fluoride $(86.6\% \pm 9.4)$ and carbon (95.5% \pm 6.7) for PFOA after 90 min electrolysis were achieved, suggesting that PFOA was completely 96 mineralized. The above analysis shows that the Ce-PbO₂ surface is not fluorinated modification after 97 98 electrolysis in PFOA solution.



Figure S5 –Cyclic voltammograms for 10 mM $K_3Fe(CN)_6$ in 0.5 M KNO₃ solution at the Ce-PbO₂ surface: (A) before electrolysis; (B) after electrolysis of 100 mg L⁻¹ PFOA at 20 mA cm⁻² for 90 min. The potential sweep rate was 25 mV S⁻¹.



Figure S6 –Electrochemical impedance spectroscopy for 3.5% NaCl solution at the Ce-PbO₂
 surface: (A) before electrolysis; (B) after electrolysis of 100 mg L⁻¹ PFOA at 20 mA cm⁻² for 90 min.
 The AC amplitude signal: 10 mV. Left: Nyquist; Right: Bode.



Figure S7 –XPS spectra of the Ce-PbO₂ surface: (A) before electrolysis; (B) after electrolysis of 100
mg L⁻¹ PFOA at 20 mA cm⁻² for 90 min.



Figure S8 – Mass spectra with negative ESI of PFCAs solutions (diluted 100 fold by volume) after 45
min electrolysis: PFBA (a), PFPeA (b), PFHxA (c), PFHpA (d), and PFOA (e).

Table S3- The ion peaks of different m/z correspond to immediate produces from Figure S5.

m/z	113	119	163	169	201
Correspond ions	CF ₃ COO ⁻	$[C_2F_5]^-$	$C_2F_5COO^2$	$[C_3F_7]^{-1}$	$[C_3F_7OO]^-$
m/z	213	219	220	223	263
Correspond ions	C ₃ F ₇ COO ⁻	$[C_4F_9]^-$	Fragment ions	Fragment ions	C ₄ F ₉ COO ⁻
m/z	313	319	363	369	413
Correspond ions	C ₅ F ₁₁ COO ⁻	$[C_6F_{13}]^-$	C ₆ F ₁₃ COO ⁻	$[C_7F_{15}]^-$	C ₇ F ₁₅ COO ⁻

Table S4 – The concentration of metals in the solution (electrolysis time: 90 min).

Concentra	tion (mg L^{-1})	Sn	Sb	Ce	Pb	Ti
	Before electrolysis	ND	ND	ND	ND	ND
PFBA	After electrolysis	ND	ND	ND	ND	0.051
	Before electrolysis	ND	ND	ND	ND	ND
PFPeA	After electrolysis	ND	ND	ND	0.005	0.085
	Before electrolysis	ND	ND	ND	ND	ND
μεμαχά	After electrolysis	ND	ND	ND	ND	0.093
	Before electrolysis	ND	ND	ND	ND	ND
РГПРА	After electrolysis	ND	ND	ND	0.007	0.065
DEOA	Before electrolysis	ND	ND	ND	ND	ND
PPUA	After electrolysis	ND	ND	ND	0.008	0.054

Treatment Technique	PFCA	$C_0 \pmod{(\text{mg L}^{-1})}$	Experimental conditions	Products	Energy (Wh L^{-1}) (50% gradation)/ $t_{1/2}$	Ref
UV/S ₂ O ₈ ²⁻	PFOA	559	$50 \text{ mM } \text{S}_2 \text{O}_8^{2-},$ O ₂ (0.48MPa), pH=3.0 200 W XM-LP (200nm-600nm)	59.1% F ⁻ 49.8% CO ₂ (4h)	9091/58 min ^a	3
UV/KI	PFOA	10	0.3 mM KI, N ₂ 15 W LP-Hg 254 nm pH=9.0	98% F ⁻ (14h)	32/95 min ^a	4
Sonolysis	PFOA	91	<i>f</i> =354 KHz	-	2129/511 min ^b	5
VUV	PFOA	41	pH=3.7, 40°C, N ₂ 15W LP-Hg 185nm	17.1% F ⁻ (2h)	29/92 min ^a	6
UV/In ₂ O ₃	PFOA	41	0.5 g L ⁻¹ In ₂ O ₃ , 25°C 23 W LP-Hg 254 nm	33.7% F ⁻ (2h)	105/110 min ^a	7
UV/TiO ₂	PFOA	1035	1.5wt% P25 100 W MPUV 254 nm	-	2160/648 min ^a	8
UV/TiO ₂ + Electrolysis (BDD)	PFOA	1035	1.5wt% P25 100 W MPUV 254 nm d=10 mm <i>i</i> =0.6 mA cm ⁻²	-	1031/309 min ^a	8
Electrolysis (Ti/SnO ₂ -Sb-Bi)	PFOA	41	d=10 mm $i=22 \text{ mA cm}^{-2}$	63.8% F ⁻ (3h)	48/21.5 min ^a	9
Electrolysis	PFOA	100	$d=10 \text{ mm}, 25^{\circ}\text{C}$ $i=20 \text{ mA cm}^{-2}$	81.7% F ⁻ 91.7 CO ₂ (1.5h)	45/18.7 min ^a	this work

^a Pesudo-first order; ^b Pesudo-zero order.

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149 Literature Cited

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