Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology. This journal is © The Royal Society of Chemistry 2019

1	
2	Supporting Information for
3	Electrochemical degradation of perfluoroalkyl acids by titanium suboxide anodes
4	
5	Yaye Wang ^{a, †} , Randall "David" Pierce, Jr. ^{a, †} , Huanhuan Shi ^{a,b} , Chenguang Li ^{a,b} , Qingguo Huang ^{a,*}
6 7 8	^a College of Agricultural and Environmental Sciences, Department of Crop and Soil Sciences, University of Georgia, Griffin, GA 30223, United States.
9 10	^b State Key Laboratory of Pollution Control and Resources Reuses, School of the Environment, Nanjing University, Nanjing 210023, P. R. China
11	[†] These authors contributed equally to this study.
12	* Corresponding author, E-mail: <u>qhuang@uga.edu</u> .
13	
14	
15	
16	
17	
18	
19	
20	
21	
22	
23	
24	
25	
26	
27	
28	
29	
30	
31	

32 Text S1

- 33 Based on the data of a substrate concentration collected over time, pseudo-first-order kinetic rate constant
- k of the substrate degradation was calculated for each reaction condition according to the following
- 35 equation (1):

$$k = -\ln \frac{C_t}{C_0} \times \frac{1}{t} \tag{1}$$

37 where C_0 is the substrate concentration at time zero (mol/L); C_t is the substrate concentration (mol·L⁻¹) at 38 time t (s). To enable comparison between different electrodes, the surface area normalized reaction rate

39 constant (k_{SA}) was calculated by the following equation (2)¹:

$$k_{SA} = k \times \frac{V}{S} \tag{2}$$

41 where *V* is the volume of the reaction solution (m³); *S* the effective electroactive surface area of the anode 42 (m²).

43

36

44 Text S2

Geometric surface area does not reflect the active sites that are accessible to electrolytes where 45 electrochemical reaction can occur². So effective electroactive surface area (EESA) was introduced to 46 describe the surface area where electrochemical reaction may occur. To this end, cyclic voltammetry (CV) 47 was obtained at different scan rate (Figure S7). Voltammetric charge q^* was then obtained by integrating 48 the area encloded in the CV (Figure S8), and it is a measure of electroactive sites of the anode, which is 49 dependent on the scan rate, because more electroactive sites become accessible at slower scan rate. Total 50 voltammetric charge q_T^* which represents the total effective surface area (ESA) of anode can be divided 51 into two parts, the 'outer' q_0^* (more accessible in the electrochemical reaction) and 'inner' q_1^* (less 52 accessible in the electrochemical reaction). q_T^* , q_0^* and q_I^* can be calculated via equation (3) and (4)³⁻⁵, 53 $q^* = q_0^* + k_1 v^{-1/2}$ 54 (3)

55
$$(q^*)^{-1} = (q_T^*)^{-1} + k_2 v^{1/2}$$
 (4)

where, v is scan rate, k_1 and k_2 are constants (Figure S8). Roughness factor (RF) is the ratio of actual ESA 56 per geometric surface area. It can be calculated by dividing determined capacitance of the anode by the 57 average double-layer capacitance of an oxide electrode (60 μ F cm⁻²). The q_T^* , q_O^* , q_I^* , RF, total ESA and 58 EESA of the TSO anode are summarized in Table S4. As an additional note, there could be potential drop 59 in the pores of TSO that may reduce the EESA for PFAS reaction. Such effect can be evaluated by an 60 approach provided by Lasia⁶, using a calculated parameter $v{Lasia, 1997 \#10}{Lasia, 1997 \#10}$. When v is 61 much samller than 1 V, the effect of potential drop on the electrochemical process in pores can be 62 neglected⁶. In our case (TSO anode in 100 mM Na₂SO₄), v was calculated to be 0.153 V, lower than 1 V 63 but not significantly lower. Therefore, the potential drop in pores may have some effect on the EESA 64 in this study, albeit not significant. However, since the pore size is not uniform in the TSO anode 65 used in this study, the potential drop cannot be accurately calculated and thus not addressed in this 66 study. 67 68

69 Text S3

- 70 A standard addition approach⁷ was used to measure F⁻ concentration using a F⁻ ion selective electrode
- 71 (ISE) (Thermo ScientificTM OrionTM). 5 mL pH-adjusted sample solution were pipetted into 10 mL
- volumetric tubes. Exactly 0, 0.05, 0.10, 0.15 or 0.25 mL of a standard solution (cs) containing 100 ppm of
- 73 F⁻ was added to each. After dilution to volume, the meter response S for each of the five solution were
- 74 measured by the F^{-} ISE.

75 For example, the data collected for the sample from 8-hour electrooxidation of 2 µM PFAAs in 100 mM

- 76 Na₂SO₄ on TSO anode at 15 mA \cdot cm⁻² are shown in Figure S9.
- 77 Based on the fluoride concentration, a defluorination ratio (dF) was calculated by dividing the released F-
- 78 concentration by the total fluorine in the PFAA that has been removed from the system as shown in 79 equation 4:
- 79 equation 4:

$$dF = \frac{[F^{-}]_{t} - [F^{-}]_{0}}{\sum n([PFAA]_{0} - [PFAA]_{t})} \times 100\%$$
(4)

81 Where $[F^-]_0$ and $[F^-]_t$ are the fluoride concentration at time 0 and t, respectively. $[PFAA]_0$ and $[PFAA]_t$ are

- 82 PFAA concentrations at time 0 and t, respectively, and n is the number of fluorine contained in the PFAA.
- 83

84 Text S4

The limiting current technology was used to measure the mass transfer rate constant of each PFAA on the TSO anode. 10 mM $K_4Fe(CN)_6$ and 10 mM $K_3Fe(CN)_6$ were dissolved in 100 mM KH_2PO_4 solution which worked as the supporting electrolyte. A linear sweep potential was applied at a slow scan rate (10 mV·s⁻¹) to the cell, and the corresponding current was measured (Figure S10). The current first increased along with the cell voltage, and then remained stable when the current reached the limiting current. After hydrogen started to evolve, the current began to increase again. The mass transfer rate constant of $Fe(CN)_6^{4-}$ to the anode can be calculated by the following equation:

$$k_{m,Fe(CN)}^{4^-} = \frac{I_{lim}}{nFAC}$$
(6)

where I_{lim} is the limiting current (A); n = 1; F is the Faraday constant (96485 C·mol⁻¹); A is the geometric surface area of the anode (m²); C is the concentration of Fe(CN)₆⁴⁻ in bulk solution (mol m⁻³). Equation (7) can be sued to estimate mass transfer rate constant of PFAA based on that of K₄Fe(CN)₆^{8,9}:

$$k_{m, PFOS} = k_{m, Fe^{2} +} \times (\frac{D_{PFAA}}{D_{Fe(CN)}^{4}})^{\frac{2}{3}}$$
96 (7)

97 where D_{PFAA} and $D_{Fe(CN)}^{4-6}$ are the diffusion coefficient of each PFAA or Fe(CN)₆⁴⁻ (7.43 × 10⁻¹⁰ m² s⁻¹).

98 The diffusion coefficient of each PFAA can be calculated by Hayduk-Laudie correlation⁹:

$$D_{PFAA} = \frac{13.26 \times 10^{-9}}{(\mu_l)^{1.14} (V_b)^{0.589}}$$
(8)

100 where μ_l is the viscosity of water (0.89 cP at 25 °C); V_b is the molar volume of each PFAA at normal boiling 101 point (cm³·mol⁻¹) The diffusion coefficient and mass transfer rate on the TSO anode for each PFAA are 102 summarized in Table S5.

103

104 **Table S1** The flow rate and the gradient condition of UPLC program.

0.3	60	40
0.3	20	80
0.3	60	40
	0.3	0.3 20 0.3 60

107 Table S2 Analyte-specific mass spectrometer parameters for PFAAs.

PFCs	MRM	Cone (V)	Collision (eV)	Dwell (s)
PFBS	298.90>79.9	56.0	26	0.007
PFHxS	399.00>80.00	52.0	30	0.007
PFBA	213.00>169.00	15.0	10	0.007
PFPeA	263.00>219.00	15.0	9.0	0.007
PFHxA	313.00>269.00	15.0	8.0	0.007
PFHpA	363.00>319.00	15.0	7.0	0.007
PFOA	412.86>368.80	16.0	8.0	0.007
M8PFOA	420.6>375.80	16.0	8.0	0.007

PFOS	498.70>98.80	60.0	35	0.007
M8PFOS	506.70>98.80	60.0	45	0.007
108				

Table S3. Fluoride concentration measured for the fluoride recovery rate

Current Density (mA/cm ²)	Total Possible Defluorination based on Degradation (ppm)	Fluoride Recovery (ppm)	Fluoride Release Ratio (%)
1	2.55	0.07 ± 0.0038	3.0 ± 0.14
2	2.69	0.14 ± 0.0021	5.0 ± 0.08
5	2.92	1.08 ± 0.0042	37 ± 0.17
7.5	3.06	1.50 ± 0.0083	49 ± 0.27
10	3.25	2.96 ± 0.0090	91 ± 0.28
15	3.57	3.41 ± 0.0030	96 ± 0.08

116 Table S4. Total, outer, inner charge values, RF, total ESA and EESA of the TSO anode

		q_T^* (mC·cm ⁻²)	<i>q</i> [*] ₀ (mC·cm ⁻²)	<i>q</i> [*] ₁ (mC·cm ⁻²)	RF	Total ESA (m²)	EESA (m ²)	
	TSO anode	25.91±3.70	0.45±0.01	25.46	345.00±29.43	2.691	0.046	
0								

120 Table S5. Diffusion coefficient and mass transfer rate on the TSO anode for each PFAA

	Diffusion coefficient (m ² ·s ⁻¹)	Mass transfer rate (m·s ⁻¹)
PFBA	8.14×10^{-10}	5.93×10^{-5}
PFPeA	7.22×10^{-10}	5.47×10^{-5}
PFHxA	6.54×10^{-10}	5.12×10^{-5}
PFHpA	6.00×10^{-10}	4.84×10^{-5}
PFOA	5.58×10^{-10}	2.23×10^{-5}
L-PFBS	6.81×10^{-10}	5.27×10^{-5}
L-PFHxS	5.75×10^{-10}	4.70×10^{-5}





125 Figure S1. Photos of the electrochemical reactor: side view (left) and top view (right).







Figure S3. The profile of L-PFOS (A) and B-PFOS (B) concentration during electrooxidation with TSO anode in 100 mM Na₂SO₄ solution. Initial PFOS concentration = 2.0μ M, current density = $5.0 \text{ mA} \cdot \text{cm}^{-2}$.









solution with TSO anode. Initial concentration = 2.0 μ M (828 ppb for PFOA), current density = 5.0 mA·cm⁻².

150

146





- 152 Figure S6. Profiles of linear sweep voltammetry (LSV) at a scan rate of 50 mV s⁻¹ in 100-mM Na₂SO₄
- 153 solution with TSO anode

0.15 20 mV s⁻¹ 25 mV s⁻¹ 30 mV s⁻¹ 0.10 35 mV s⁻¹ 40 mV s⁻¹ 0.05 45 mV s⁻¹ Current (A) 50 mV s⁻¹ 0.00 -0.05 -0.10 -0.15 1.8 1.2 0.8 1.6 1.4 1.0 Potential (V vs. SHE) 157



0.6

159

155

156





161 **Figure S8.** (A) Voltammetric charge (q^*) vs. the reciprocal square root of scan rate $(v^{-1/2})$; (b) Reciprocal 162 voltammetric charge quantity $(1/q^*)$ vs. the square root of scan rate $(v^{1/2})$. Data obtained from the cyclic

163 voltammograms (Figure S7) at various scan rates in $100 \text{ mM Na}_2\text{SO}_4$ solution.



166 Figure S9. Plot of ISE response versus the volume of added standard solution for F⁻ concentration167 measurement.

165

169



170

- 171 Figure S10. Linear sweep voltammogram of 10 mM K₄Fe(CN)₆ on TSO anode in 100 mM KH₂PO₄
- 172 solution.

173

174 Reference

- L. Valentine Richard and H. C. A. Wang, Iron Oxide Surface Catalyzed Oxidation of Quinoline by
 Hydrogen Peroxide, *Journal of Environmental Engineering*, 1998, **124**, 31-38.
- W. Zhao, J. Xing, D. Chen, Z. Bai and Y. Xia, Study on the performance of an improved
 Ti/SnO2DDSb2O3/PbO2 based on porous titanium substrate compared with planar titanium
 substrate, *RSC Advances*, 2015, **5**, 26530-26539.
- 1803.S. Ardizzone, G. Fregonara and S. Trasatti, "DInner"DD and "DD outer"DD active surface of RuO2181electrodes, *Electrochimica Acta*, 1990, **35**, 263-267.

- 1824.H. Lin, J. Niu, S. Liang, C. Wang, Y. Wang, F. Jin, Q. Luo and Q. Huang, Development of183macroporous Magn@ll phase Ti4O7 ceramic materials: As an efficient anode for mineralization
- 184 of poly- and perfluoroalkyl substances, *Chemical Engineering Journal*, 2018, **354**, 1058-1067.
- 185 5. L. Xu and J. D. Scantlebury, Electrochemical Surface Characterization of IrO2 2- Ta2 O 5 Coated
 186 Titanium Electrodes in Na2 SO 4 Solution, 2003, **150**, B288-B293.
- 1876.A. Lasia, Porous electrodes in the presence of a concentration gradient, Journal of188Electroanalytical Chemistry, 1997, **428**, 155-164.
- 189 7. D. A. Skoog, F. J. Holler and T. A. Nieman, *Principles of instrumental analysis*, Belmont (Calif.):
 190 Brooks/Cole, 5th ed. / edn., 1998.
- A. Donaghue and B. P. Chaplin, Effect of Select Organic Compounds on Perchlorate Formation at
 Boron-doped Diamond Film Anodes, *Environmental Science & Technology*, 2013, 47, 12391 12399.
- 1949.J. C. Crittenden, R. R. Trussell, D. W. Hand, K. J. Howe and G. Tchobanoglous, *MWH's Water*195treatment : principles and design, John Wiley and Sons, Inc. , 2012.