

**Preparation of novel TiO₂-RNTs/SnO₂-Sb/PbO₂-La
electrode and degradation of oily wastewater by pulse
electrochemical advanced oxidation process**

Yachao Han ^a, Yunlei Cen ^{a,b}, YuanYuan Zhou ^b, Ke Zheng ^a, Shaoqi Zhou ^{a,*}

^a College of Resources and Environmental Engineering, Guizhou University,
Guiyang 550025, China

^bKarst Key Laboratory of Geological Resources and Environment, Ministry of
Education, Guizhou University, Guiyang 550025, China

Corresponding E-mail address: Zhousq@gzu.edu.cn (Shaoqi Zhou)

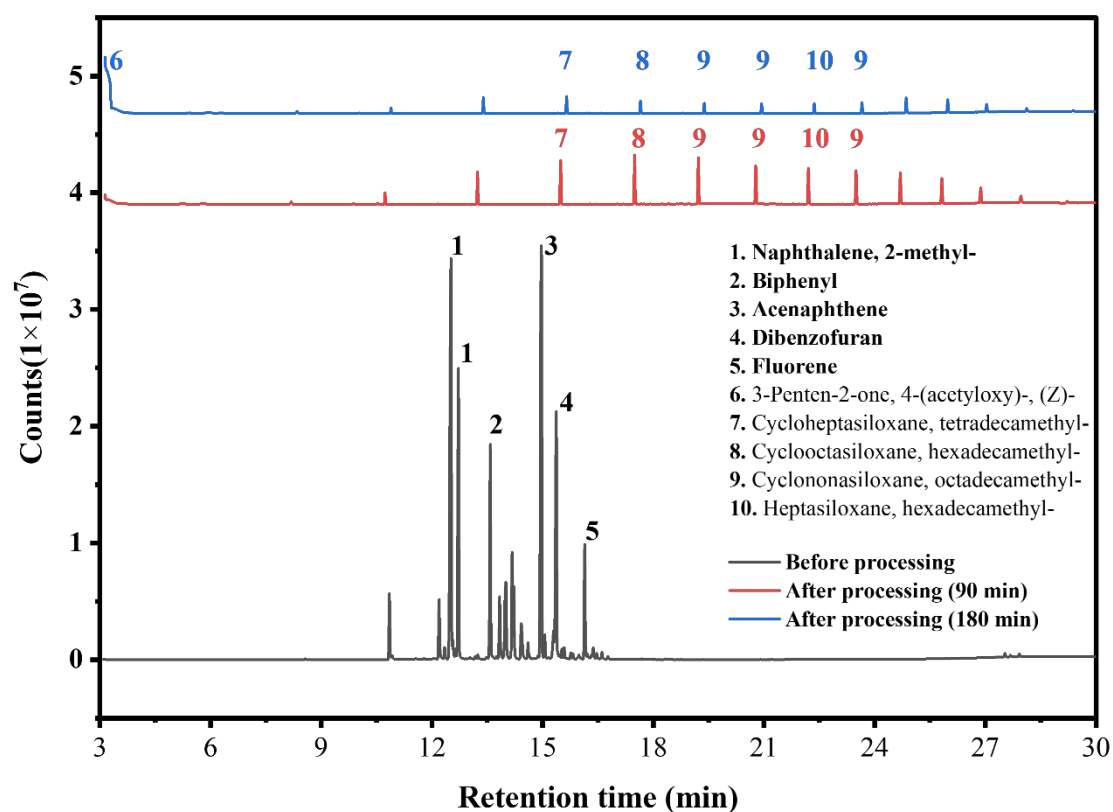


Fig S1. GC-MS superimposed chromatogram of the sample with an initial concentration of 50 mg L^{-1} after 0, 90, and 180 min of electrolysis.

Table S1.The compounds in the washing oil were detected by GC-MS.

	Retention time (min)	Name (Eight repetitions)	Molecular formula	Area (%)
1	14.966	Acenaphthene	C ₁₂ H ₁₀	20.79
2	12.516	Naphthalene, 2-methyl-	C ₁₁ H ₁₀	20.54
3	12.720	Naphthalene, 2-methyl-	C ₁₁ H ₁₀	10.30
4	15.367	Dibenzofuran	C ₁₂ H ₈ O	10.13
5	13.581	Biphenyl	C ₁₂ H ₁₀	7.20
6	14.003	Naphthalene, 1,6-dimethyl-	C ₁₂ H ₁₂	4.30
7	16.143	Fluorene	C ₁₃ H ₁₀	3.73
8	14.174	Naphthalene, 2,3-dimethyl-	C ₁₂ H ₁₂	3.40
9	14.217	Naphthalene, 2,6-dimethyl-	C ₁₂ H ₁₂	2.38
10	13.832	Naphthalene, 1-ethyl-	C ₁₂ H ₁₂	2.27
11	10.848	Naphthalene	C ₁₀ H ₈	2.07
12	12.195	Indole	C ₈ H ₇ N	2.05
13	14.421	Naphthalene, 1,2-dimethyl-	C ₁₂ H ₁₂	1.72
14	15.298	1-Isopropenylnaphthalene	C ₁₃ H ₁₂	1.35
15	15.057	1,1'-Biphenyl, 4-methyl-	C ₁₃ H ₁₂	0.83
16	12.565	Benzo[b]thiophene, 6-methyl-	C ₉ H ₈ S	0.67
17	14.602	Naphthalene, 1,2-dimethyl-	C ₁₂ H ₁₂	0.62
18	16.373	1,1'-Biphenyl, 4-methyl-	C ₁₃ H ₁₂	0.57
19	15.587	Naphthalene, 2,3,6-trimethyl-	C ₁₃ H ₁₄	0.44
20	12.340	Benzo[b]thiophene, 2-methyl-	C ₉ H ₈ S	0.37
21	12.639	Benzo[b]thiophene, 2-methyl-	C ₉ H ₈ S	0.35
22	15.522	Naphthalene, 2,3,6-trimethyl-	C ₁₃ H ₁₄	0.34
23	16.608	9H-Xanthene	C ₁₃ H ₁₀ O	0.27
24	16.464	1,1'-Biphenyl, 2-methyl-	C ₁₃ H ₁₂	0.27
25	16.212	4,4'-Dimethylbiphenyl	C ₁₄ H ₁₄	0.25
26	15.982	Naphthalene, 1,6,7-trimethyl-	C ₁₃ H ₁₄	0.22
27	15.768	Naphthalene, 1,6,7-trimethyl-	C ₁₃ H ₁₄	0.21
28	15.822	Naphthalene, 2,3,6-trimethyl-	C ₁₃ H ₁₄	0.18
29	15.458	Naphthalene, 2-(1-methylethyl)-	C ₁₃ H ₁₄	0.18
30	13.238	5-Ethynyl-1H-indole	C ₁₀ H ₇ N	0.18
31	10.923	Benzo[b]thiophene	C ₈ H ₆ S	0.17
32	14.870	1-Naphthalenecarbonitrile	C ₁₁ H ₇ N	0.17
33	27.530	Naphthalene, 2-ethenyl-	C ₁₂ H ₁₀	0.16
34	27.920	Acenaphthene	C ₁₂ H ₁₀	0.14
35	16.769	9H-Xanthene	C ₁₃ H ₁₀ O	0.12
36	16.309	1-Isopropenylnaphthalene	C ₁₃ H ₁₂	0.11
37	27.674	Naphthalene, 2-ethenyl-	C ₁₂ H ₁₀	0.10
38	13.169	Tryptamine	C ₁₀ H ₁₂ N ₂	0.10
39	15.159	Benzo[b]thiophene, 2,5,7-trimethyl-	C ₁₁ H ₁₂ S	0.10

40	13.752	Benzo[b]thiophene, 2,7-dimethyl-	C ₁₀ H ₁₀ S	0.09
41	13.485	1H-Indole, 2-methyl-	C ₉ H ₉ N	0.09
42	11.548	Isoquinoline	C ₉ H ₇ N	0.08
43	16.036	4-Ethylbiphenyl	C ₁₄ H ₁₄	0.05
44	14.736	Benzene, 1-methoxy-3-(methylthio)-	C ₈ H ₁₀ OS	0.05
45	13.035	Quinoline, 8-methyl-	C ₁₀ H ₉ N	0.05
46	11.789	Benzo[b]thiophene, 2,3-dihydro-	C ₈ H ₈ S	0.05
47	12.062	Phenol, 2,3,5-trimethyl-	C ₉ H ₁₂ O	0.05
48	18.320	Anthracene	C ₁₄ H ₁₀	0.04
49	8.569	Indane	C ₉ H ₁₀	0.03
50	17.694	Heptadecane	C ₁₇ H ₃₆	0.02
51	16.886	Bicyclo[4.2.1]nona-2,4,7-triene, 7-phenyl-	C ₁₅ H ₁₄	0.01
52	11.907	1H-Indene, 2,3-dihydro-4,7-dimethyl-	C ₁₁ H ₁₄	0.01
53	12.024	1H-Inden-1-one, 2,3-dihydro-	C ₉ H ₈ O	0.01
54	18.758	Carbonic acid, decyl tetradecyl ester	C ₂₅ H ₅₀ O ₃	0.01
55	25.941	Heptasiloxane, hexadecamethyl-	C ₁₆ H ₄₈ O ₆ Si ₇	0.01
56	17.624	2,3-Dihydroxybenzoic acid, 3TMS derivative	C ₁₆ H ₃₀ O ₄ Si ₃	0.01

Table S2. Compounds detected in the washing oil sample after 90 min of electrocatalytic oxidation by GC-MS.

	Retention time (min)	Name (Eight repetitions)	Molecular formula	Area (%)
1	17.651	Cyclooctasiloxane, hexadecamethyl-	C ₁₆ H ₄₈ O ₈ Si ₈	11.553
2	19.384	Cyclononasiloxane, octadecamethyl-	C ₁₈ H ₅₄ O ₉ Si ₉	10.798
3	15.646	Cycloheptasiloxane, tetradecamethyl-	C ₁₄ H ₄₂ O ₇ Si ₇	9.937
4	20.935	Octasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	C ₁₆ H ₅₀ O ₇ Si ₈	9.085
5	22.363	Heptasiloxane, hexadecamethyl-	C ₁₆ H ₄₈ O ₆ Si ₇	8.832
6	23.658	Cyclononasiloxane, octadecamethyl-	C ₁₈ H ₅₄ O ₉ Si ₉	8.561
7	24.856	1,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,17-icosamethylnonasiloxane	C ₂₀ H ₆₀ O ₈ Si ₉	7.832
8	13.394	Cyclohexasiloxane, dodecamethyl-	C ₁₂ H ₃₆ O ₆ Si ₆	7.045
9	25.979	1,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,17-icosamethylnonasiloxane	C ₂₀ H ₆₀ O ₈ Si ₉	6.491
10	27.038	1,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,17-icosamethylnonasiloxane	C ₂₀ H ₆₀ O ₈ Si ₉	4.327
11	10.891	Cyclopentasiloxane, decamethyl-	C ₁₀ H ₃₀ O ₅ Si ₅	2.536
12	28.124	1,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,19-docosamethyldecasiloxane	C ₂₂ H ₆₆ O ₉ Si ₁₀	2.195
13	3.659	Heptane	C ₇ H ₁₆	1.702
14	5.948	o-Xylene	C ₈ H ₁₀	1.219
15	5.414	Cyclotrisiloxane, hexamethyl-	C ₆ H ₁₈ O ₃ Si ₃	0.938
16	8.345	Cyclotetrasiloxane, octamethyl-	C ₈ H ₂₄ O ₄ Si ₄	0.857
17	29.386	1,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,15-octadecamethyloctasiloxane	C ₁₈ H ₅₄ O ₇ Si ₈	0.741
18	31.387	Heptasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl-	C ₁₄ H ₄₄ O ₆ Si ₇	0.724
19	10.029	Benzene, 1,2,4,5-tetramethyl-	C ₁₀ H ₁₄	0.305
20	30.911	1,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,15-octadecamethyloctasiloxane	C ₁₈ H ₅₄ O ₇ Si ₈	0.304
21	10.693	Cyclotetrasiloxane, octamethyl-	C ₈ H ₂₄ O ₄ Si ₄	0.285
22	32.804	Octasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	C ₁₆ H ₅₀ O ₇ Si ₈	0.238
23	6.312	Ethylbenzene	C ₈ H ₁₀	0.198
24	31.515	Octasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	C ₁₆ H ₅₀ O ₇ Si ₈	0.183
25	30.119	Cyclotetrasiloxane, octamethyl-	C ₈ H ₂₄ O ₄ Si ₄	0.174
26	30.499	Heptasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl-	C ₁₄ H ₄₄ O ₆ Si ₇	0.169
27	18.94	Octatriacontyl pentafluoropropionate	C ₄₁ H ₇₇ F ₅ O ₂	0.164
28	19.823	7-Methylimidazo[1,2-a]pyrimidin-5(1H)-one, TMS deriva	C ₁₀ H ₁₅ N ₃ O _{Si}	0.155

		tive		
29	16.25	Dodecanedioic acid, 2TBDMS derivative	C ₂₄ H ₅₀ O ₄ Si ₂	0.141
30	18.577	Cyclononasiloxane, octadecamethyl-	C ₁₈ H ₅₄ O ₉ Si ₉	0.132
31	15.367	Heptasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecame thyl-	C ₁₄ H ₄₄ O ₆ Si ₇	0.126
32	30.729	3-Ethoxy-1,1,1,5,5,5-hexamethyl-3-(trimethylsiloxy)trisilo xane	C ₁₁ H ₃₂ O ₄ Si ₄	0.121
33	6.264	Isonicotinic acid, 2-phenylethyl ester	C ₁₄ H ₁₃ NO ₂	0.113
34	17.186	Cyclooctasiloxane, hexadecamethyl-	C ₁₆ H ₄₈ O ₈ Si ₈	0.111
35	12.335	Cyclopentasiloxane, decamethyl-	C ₁₀ H ₃₀ O ₅ Si ₅	0.102
36	16.598	Hexadecane	C ₁₆ H ₃₄	0.098
37	31.665	Hexasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-	C ₁₂ H ₃₈ O ₅ Si ₆	0.096
38	17.726	Heptadecane	C ₁₇ H ₃₆	0.09
39	10.522	Benzene, 1-ethyl-3,5-dimethyl-	C ₁₀ H ₁₄	0.087
40	14.608	Cyclohexasiloxane, dodecamethyl-	C ₁₂ H ₃₆ O ₆ Si ₆	0.084
41	25.658	Heptasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecame thyl-	C ₁₄ H ₄₄ O ₆ Si ₇	0.081
42	11.388	Pentasiloxane, dodecamethyl-	C ₁₂ H ₃₆ O ₄ Si ₅	0.07
43	19.111	Heptasiloxane, hexadecamethyl-	C ₁₆ H ₄₈ O ₆ Si ₇	0.069
44	17.341	Heptasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecame thyl-	C ₁₄ H ₄₄ O ₆ Si ₇	0.068
45	21.454	2-(2',4',4',6',6',8',8'-Heptamethyltetrasiloxan-2'-yloxy)-2,4, 4,6,6,8,8,10,10-nonamethylcyclopentasiloxane	C ₁₆ H ₄₈ O ₁₀ Si ₉	0.067
46	27.386	Squalene	C ₃₀ H ₅₀	0.066
47	20.518	Heptasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecame thyl-	C ₁₄ H ₄₄ O ₆ Si ₇	0.062
48	23.171	Heptasiloxane, hexadecamethyl-	C ₁₆ H ₄₈ O ₆ Si ₇	0.061
49	17.839	Hexadecane, 2,6,10-trimethyl-	C ₁₉ H ₄₀	0.061
50	18.074	1,1,1,3,5,7,9,11,11,11-Decamethyl-5-(trimethylsiloxy)hexa siloxane	C ₁₃ H ₄₂ O ₆ Si ₇	0.06
51	21.417	Heptasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecame thyl-	C ₁₄ H ₄₄ O ₆ Si ₇	0.059
52	32.606	Hexasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-	C ₁₂ H ₃₈ O ₅ Si ₆	0.058
53	13.164	Cyclotetrasiloxane, octamethyl-	C ₈ H ₂₄ O ₄ Si ₄	0.055
54	16.443	3-Isopropoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsil oxy)tetrasiloxane	C ₁₈ H ₅₂ O ₇ Si ₇	0.054
55	20.716	Heptasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecame thyl-	C ₁₄ H ₄₄ O ₆ Si ₇	0.052
56	18.796	Octadecane	C ₁₈ H ₃₈	0.052
57	21.957	Heptasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecame thyl-	C ₁₄ H ₄₄ O ₆ Si ₇	0.045
58	17.908	Bis(pentamethylcyclotrisiloxy)tetramethyldisiloxane	C ₁₄ H ₄₂ O ₉ Si ₈	0.034
59	21.641	3,6-Dioxa-2,4,5,7-tetrasilaoctane, 2,2,4,4,5,5,7,7-octameth	C ₁₀ H ₃₀ O ₂ Si ₄	0.03

		yl-		
60	22.176	Heptasiloxane, hexadecamethyl-	C ₁₆ H ₄₈ O ₆ Si ₇	0.028
61	22.112	3,6-Dioxa-2,4,5,7-tetrasilaoctane, 2,2,4,4,5,5,7,7-octamethyl-	C ₁₀ H ₃₀ O ₂ Si ₄	0.023

Table S3. Compounds detected in the washing oil sample after 180 min of electrocatalytic oxidation by GC-MS.

	Retention time (min)	Name (Eight repetitions)	Molecular formula	Area (%)
1	3.386	3-Penten-2-one, 4-(acetyloxy)-, (Z)-	C ₇ H ₁₀ O ₃	13.094
2	24.856	1,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,15-octadecamethyl- ctasiloxane	C ₁₈ H ₅₄ O ₇ Si ₈	11.037
3	15.651	Cycloheptasiloxane, tetradecamethyl-	C ₁₄ H ₄₂ O ₇ Si ₇	10.943
4	13.394	Cyclohexasiloxane, dodecamethyl-	C ₁₂ H ₃₆ O ₆ Si ₆	9.832
5	25.979	1,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,17-icosameth ylnonasiloxane	C ₂₀ H ₆₀ O ₈ Si ₉	8.988
6	17.651	Cyclooctasiloxane, hexadecamethyl-	C ₁₆ H ₄₈ O ₈ Si ₈	7.437
7	23.658	Cyclononasiloxane, octadecamethyl-	C ₁₈ H ₅₄ O ₉ Si ₉	7.248
8	19.384	Cyclononasiloxane, octadecamethyl-	C ₁₈ H ₅₄ O ₉ Si ₉	6.637
9	22.363	Heptasiloxane, hexadecamethyl-	C ₁₆ H ₄₈ O ₆ Si ₇	6.568
10	20.935	Cyclononasiloxane, octadecamethyl-	C ₁₈ H ₅₄ O ₉ Si ₉	6.136
11	27.033	1,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,19-doco samethyldecasiloxane	C ₂₂ H ₆₆ O ₉ Si ₁₀	5.943
12	10.89	Cyclopentasiloxane, decamethyl-	C ₁₀ H ₃₀ O ₅ Si ₅	3.293
13	28.118	1,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,15-octadecamethyl- ctasiloxane	C ₁₈ H ₅₄ O ₇ Si ₈	2.844

Table S4. XPS data of different chemical states of Pb on different electrode surfaces.

	Binding energy (eV)		
	Pb ⁴⁺	Pb ²⁺	
Ti/SnO ₂ -Sb/PbO ₂ electrode	142.18, 137.47	143.08, 137.47	3.66
TiO ₂ -RNTs/SnO ₂ -Sb/PbO ₂ -La electrode	142.18, 137.45	143.28, 138.58	8.27

Table S5. ICP-MS test results.

Electrode	Pb/(ug/L)
Ti/SnO ₂ -Sb/PbO ₂	89.68
TiO ₂ -RNTs/SnO ₂ -Sb/PbO ₂ -La	31.74

Text S1. Pretreatment of Ti matrix and detailed preparation of TiO₂-RNTs

Pretreatment of Ti substrate surface: In order to remove the passivation oxide layer and fouling on the surface, firstly, the titanium plate (5×5×0.1 cm³) was polished with coarse and fine sandpaper, rinsed with a large amount of water and ultrasonically treated in ethanol for 10 min. Then, it was etched in 10% oxalic acid solution at 98°C for 2h, and finally rinsed with a large amount of water and ultrasonically removed the remaining impurities such as oxalic acid on the surface.

The intermediate layer of TiO₂ nanotubes: Reduced TiO₂ nanotubes, called TiO₂-RNTs, were prepared by using two anodic oxidations and one cathodic reduction. The pretreated Ti sheet was oxidized at a constant potential of 30 V for 1 hour in an ethylene glycol solution containing 0.5wt% NH₄F and 4vol% H₂O using a two-electrode system with etched titanium sheet as anode and graphite as cathode. The Ti sheet was ultrasonically treated in water for 15 minutes and subjected to a second anodization step (30 V, 1 h). Take out, and ultrasonically treat the Ti sheet in water for 15 minutes again. Finally, the crystal structure was obtained by heat treatment at 500°C for 2 h (heating rate of 5°C min⁻¹). Then the cathode oxidation was carried out in 1 mol L⁻¹ NaClO₄ solution at a current density of 5 mA cm⁻² for 5 minutes. The Ti sheet was ultrasonically treated in water for 15 minutes again.