Supporting Information

Three-Electrode 30–60 µL Mini-Cell for Ecologically Conscious Analytical Voltammetry with Common Macro- and Microelectrodes

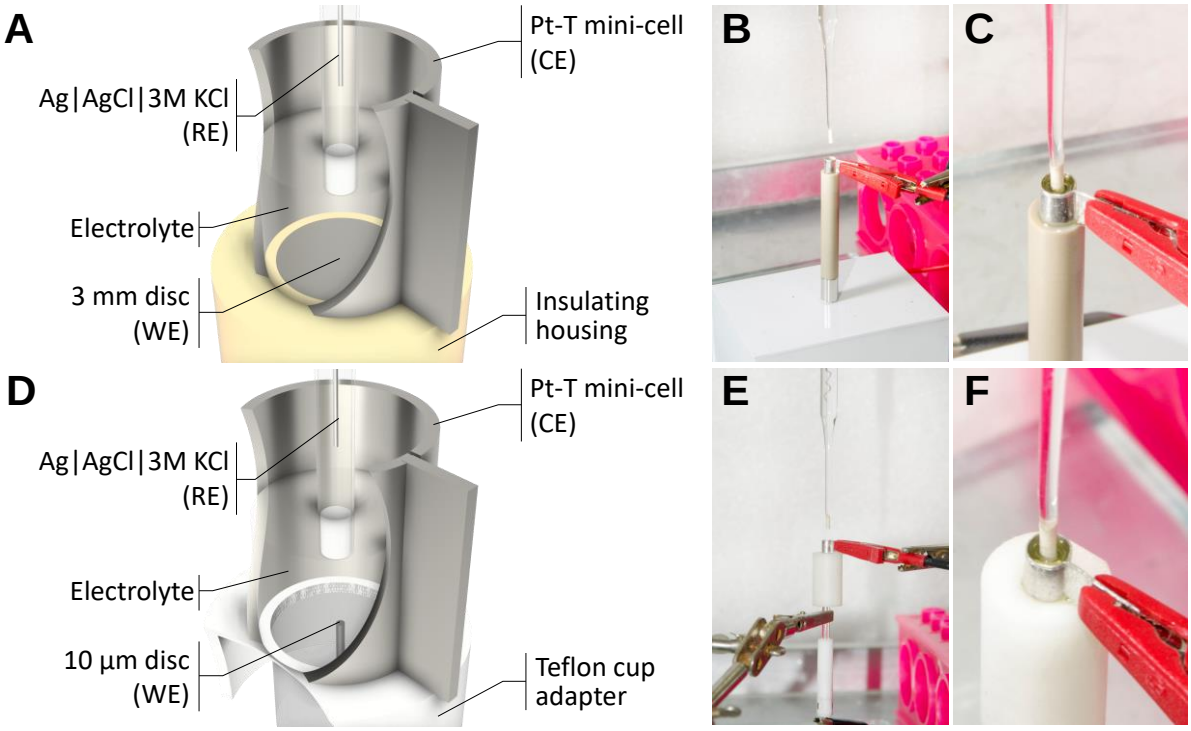
Wei Chung Sim,[†,§] *Nuttanun Kutrakul,*[‡] *Panida Khunkaewla*[†] *and Albert Schulte*[*,‡]

†Biochemistry and Electrochemistry Research Unit & School of Chemistry, Institute of Science, Suranaree University of Technology, 30000 Nakhon Ratchasima, Thailand.

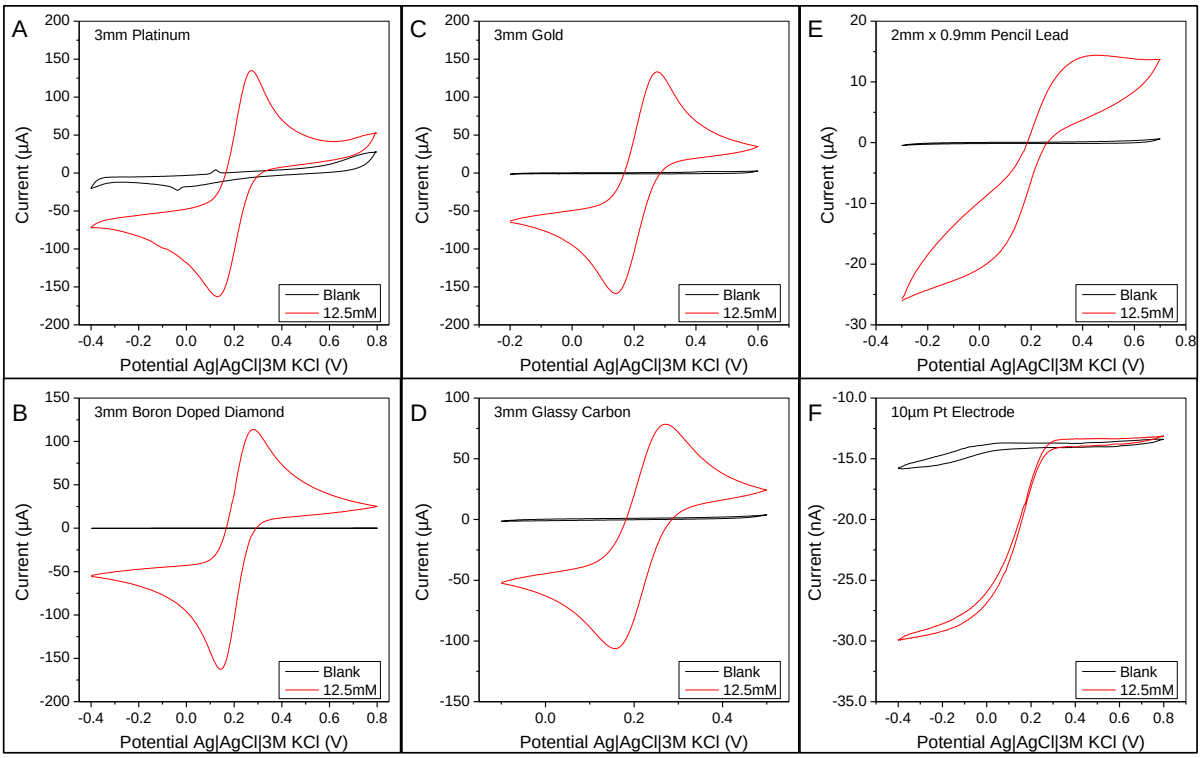
§ MARDILab Kota Kinabalu, Malaysian Agricultural Research and Development Institute, 88460 Kota Kinabalu, Sabah, Malaysia.

‡School of Biomolecular Science & Engineering, Vidyasirimedhi Institute of Science and Technology, 21210 Rayong, Thailand.

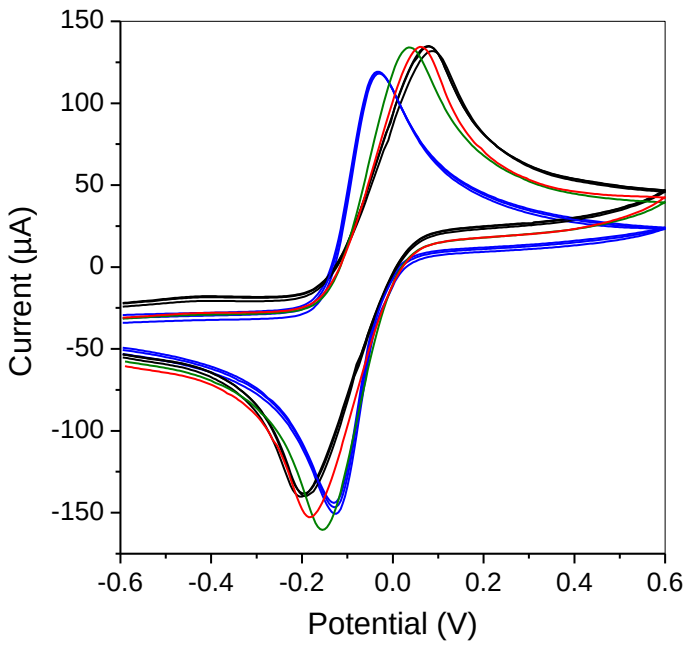
*Corresponding e-mail: albert.s@vistec.ac.th



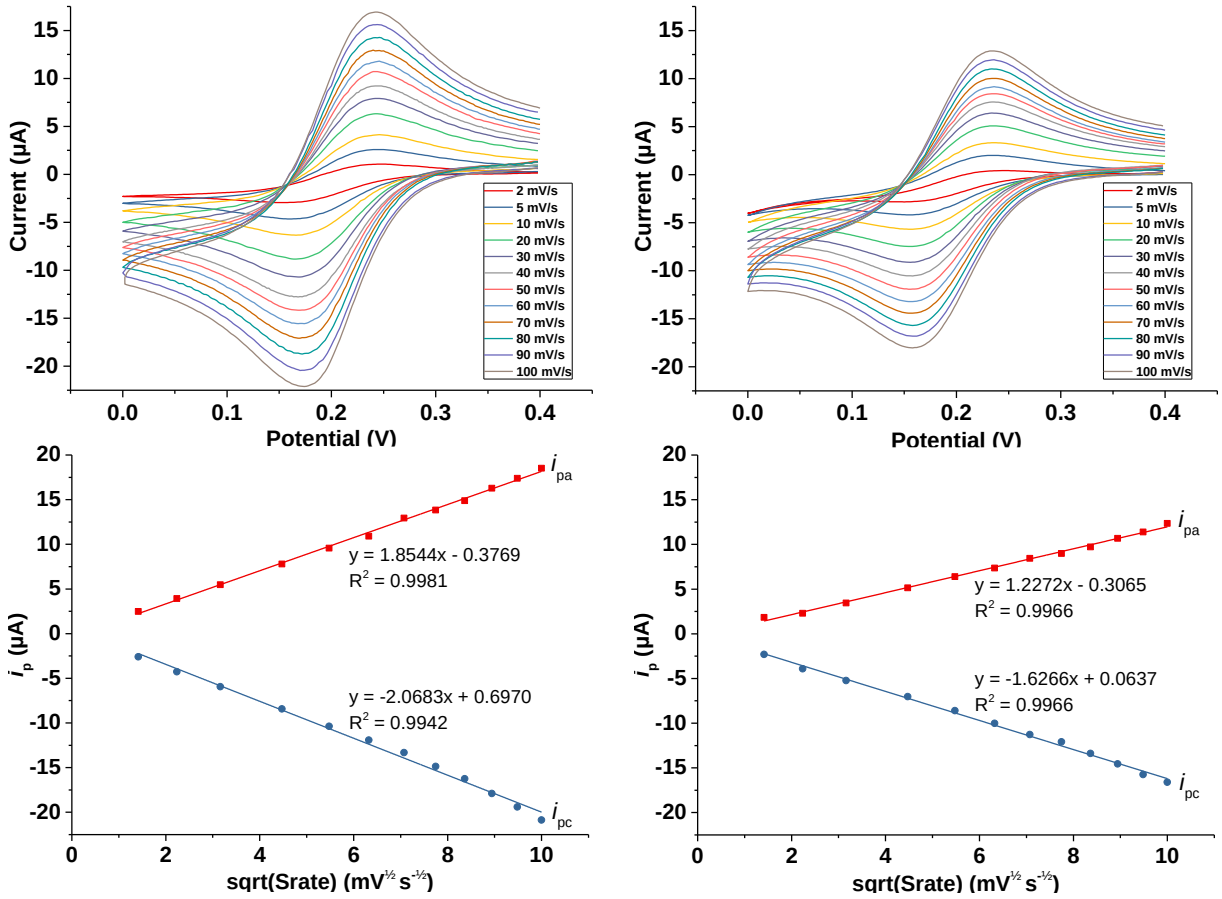
Supplementary Figure S1. The electrochemical cell setup: (A) Cutaway drawing illustrating the setup of the Pt-T mini-cell on a commercial macrodisc electrode. **(**B) and (C) show the actual arrangement of the Pt-T mini-cell on a 3 mm BDD disc electrode. (D) Cutaway drawing illustrating the Pt-T mini-cell on a commercial microdisc electrode. (E) and (F) show the actual arrangement of the Pt-T mini-cell on a commercial 10 µm Pt disc electrode with a special adapter.



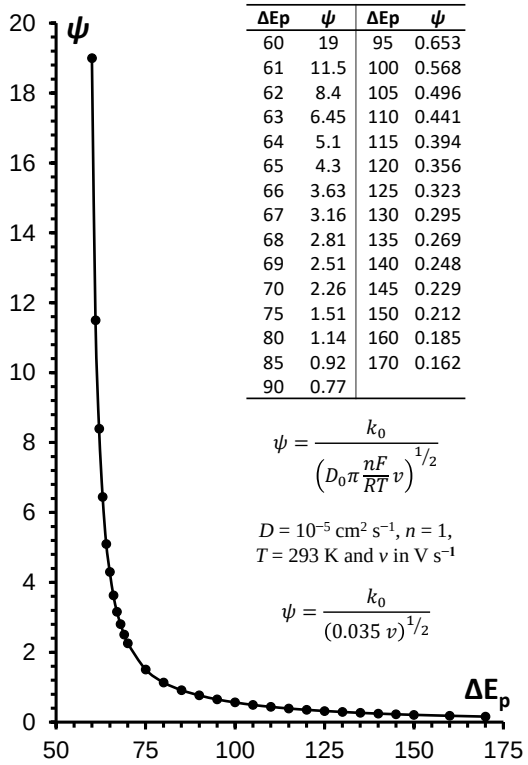
Supplementary Figure S2. CVs of 12.5 mM hexacyanoferrate(III) in 0.1 M phosphate buffer, pH 7.0 for (A) a 3 mm-diameter platinum disc electrode, (B) a 3 mm-diameter boron-doped diamond electrode, (C) a 3 mm-diameter gold disc electrode, (D) a 3 mm-diameter glassy carbon disc electrode, (E) a 2 mm-long 0.9 mm-diameter cylindrical pencil lead electrode and (F) a 10 µm-diameter Pt disc electrode. Black traces represent measurements in hexacyanoferrate(III)-free supporting electrolyte.



Supplementary Figure S3. Comparison of oxidation and reduction peaks of CVs of 10 mM hexaamminerutheniumIII) in 0.1 M phosphate buffer, pH 7.0, obtained with a BDD electrode in Pt-T mini-cell (blue lines: 3 scans in 3 cell reconstructions) and a normal beaker cell (black lines: 3 scans in one and the same single cell constructions, red and green lines: scans recorded in 2 cell reconstructions) at scan rate 100 mV s^{-1}.



Supplementary Figure S4. CVs of 1 mM hexacyanoferrate(III) in 0.1 M KCl in a Pt-T mini-cell (left panels) and a conventional 5 mL cell (right panels) at scan rates varying from 2 to 100 mV s^{-1} on a 3 mm Pt electrode.



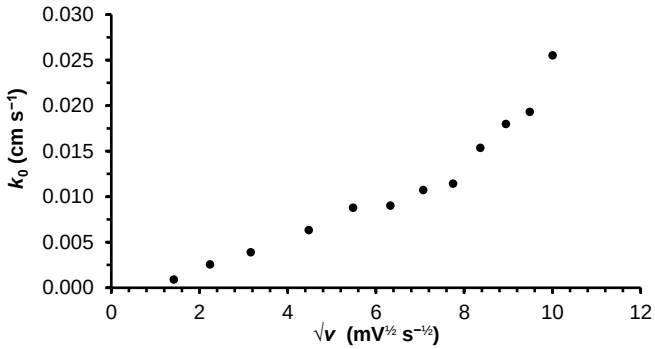
ΔEp	ψ	ΔEp	ψ
60	19	95	0.653
61	11.5	100	0.568
62	8.4	105	0.496
63	6.45	110	0.441
64	5.1	115	0.394
65	4.3	120	0.356
66	3.63	125	0.323
67	3.16	130	0.295
68	2.81	135	0.269
69	2.51	140	0.248
70	2.26	145	0.229
75	1.51	150	0.212
80	1.14	160	0.185
85	0.92	170	0.162
90	0.77		

$$\psi = \frac{k_0}{\left(D_0 \pi \frac{nF}{RT} v\right)^{1/2}}$$

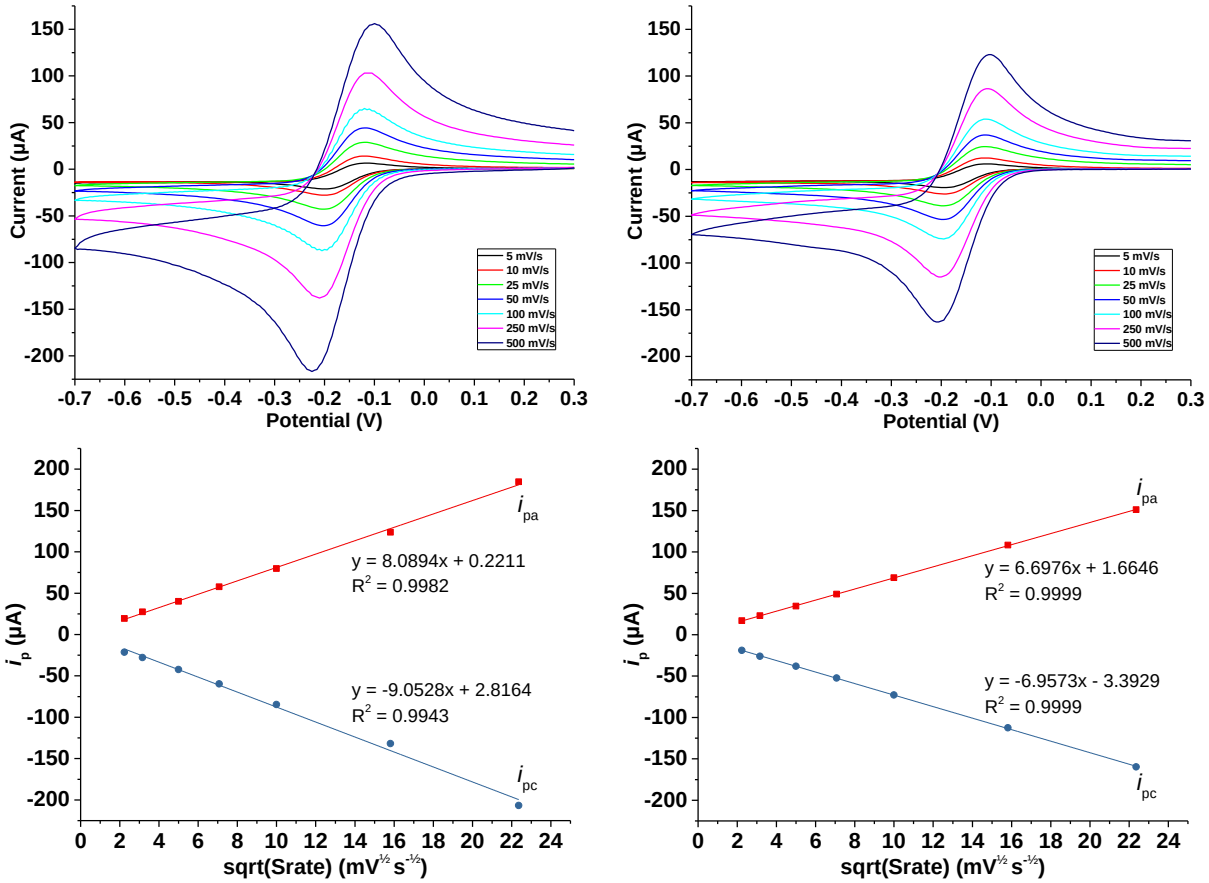
$D = 10^{-5}$ cm^2 s^{-1}, $n = 1$, $T = 293$ K and v in V s^{-1}

$$\psi = \frac{k_0}{(0.035\ v)^{1/2}}$$

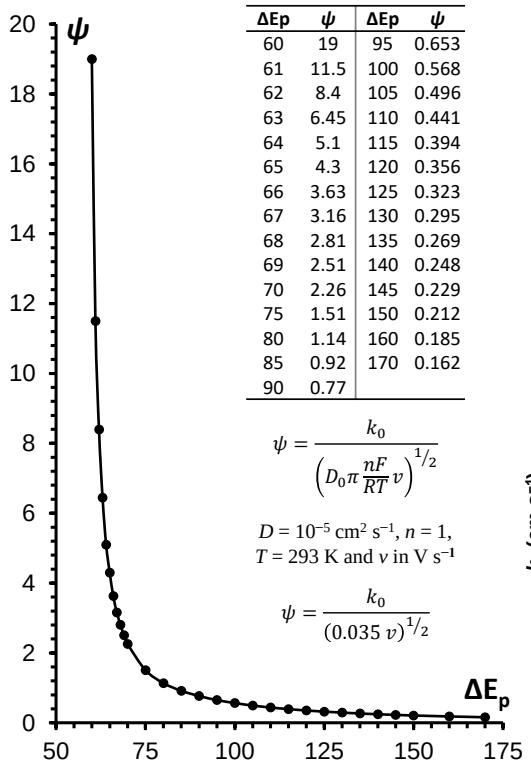
v (mV s^{-1})	$\sqrt{v}$ (mV$^{-1/2}$ s$^{-1/2}$)	ΔEp (mV)	ψ	k_0 (cm s^{-1})
5	2.2361	100.0	1.0344	2.560×10^{-3}
10	3.1623	82.4	1.1092	3.882×10^{-3}
20	4.4721	80.7	1.2806	6.339×10^{-3}
30	5.4772	78.1	1.4508	8.795×10^{-3}
40	6.3246	75.8	1.2880	9.016×10^{-3}
50	7.0711	78.0	1.3694	10.717×10^{-3}
60	7.7460	76.9	1.3324	11.423×10^{-3}
70	8.3666	77.4	1.6600	15.372×10^{-3}
80	8.9443	74.0	1.8160	17.977×10^{-3}
90	9.4868	72.0	1.8400	19.320×10^{-3}
100	10.0000	72.8	2.3050	25.512×10^{-3}



Supplementary Figure S5. Evaluation of rate of electron transfer of hexacyanoferrate(III) at a 3 mm Pt disc electrode using Pt-T mini-cell.



Supplementary Figure S6. CVs of 10 mM hexaamineruthenium(III) in 0.1 M KCl in a Pt-T mini-cell (left panels) and a conventional 5 mL cell (right panels) at scan rates varying from 5 to 500 mV s^{-1} on a 3 mm Pt electrode.



ΔEp	ψ	ΔEp	ψ
60	19	95	0.653
61	11.5	100	0.568
62	8.4	105	0.496
63	6.45	110	0.441
64	5.1	115	0.394
65	4.3	120	0.356
66	3.63	125	0.323
67	3.16	130	0.295
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70	2.26	145	0.229
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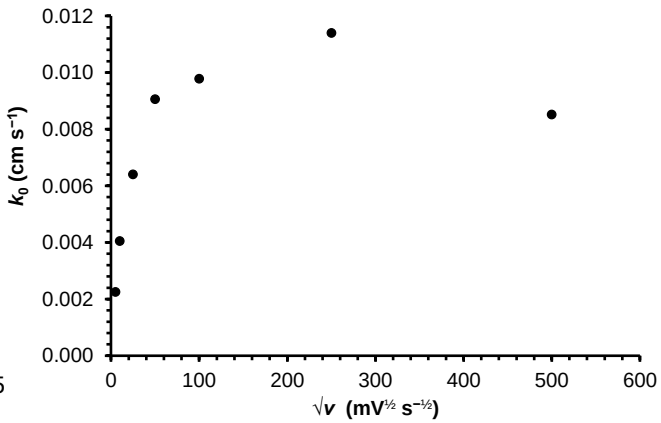
80	1.14	160	0.185
85	0.92	170	0.162
90	0.77		

$$\psi = \frac{k_0}{\left(D_0 \pi \frac{nF}{RT} v\right)^{1/2}}$$

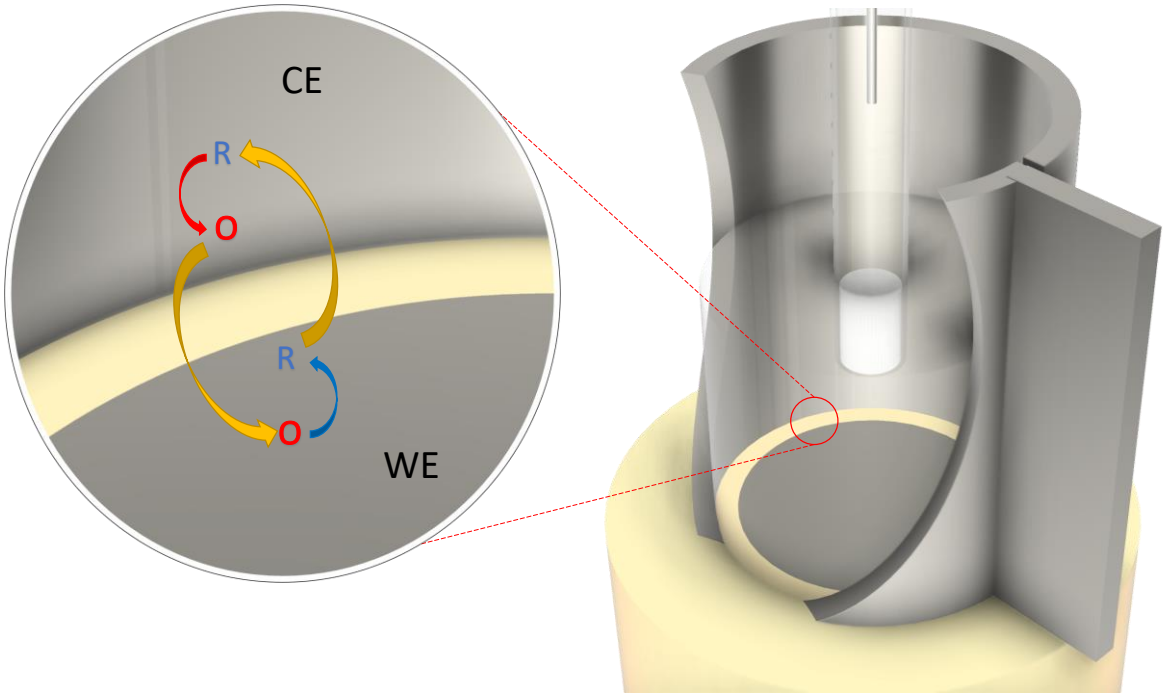
$D = 10^{-5}$ cm^2 s^{-1}, $n = 1$, $T = 293$ K and v in V s^{-1}

$$\psi = \frac{k_0}{(0.035\, v)^{1/2}}$$

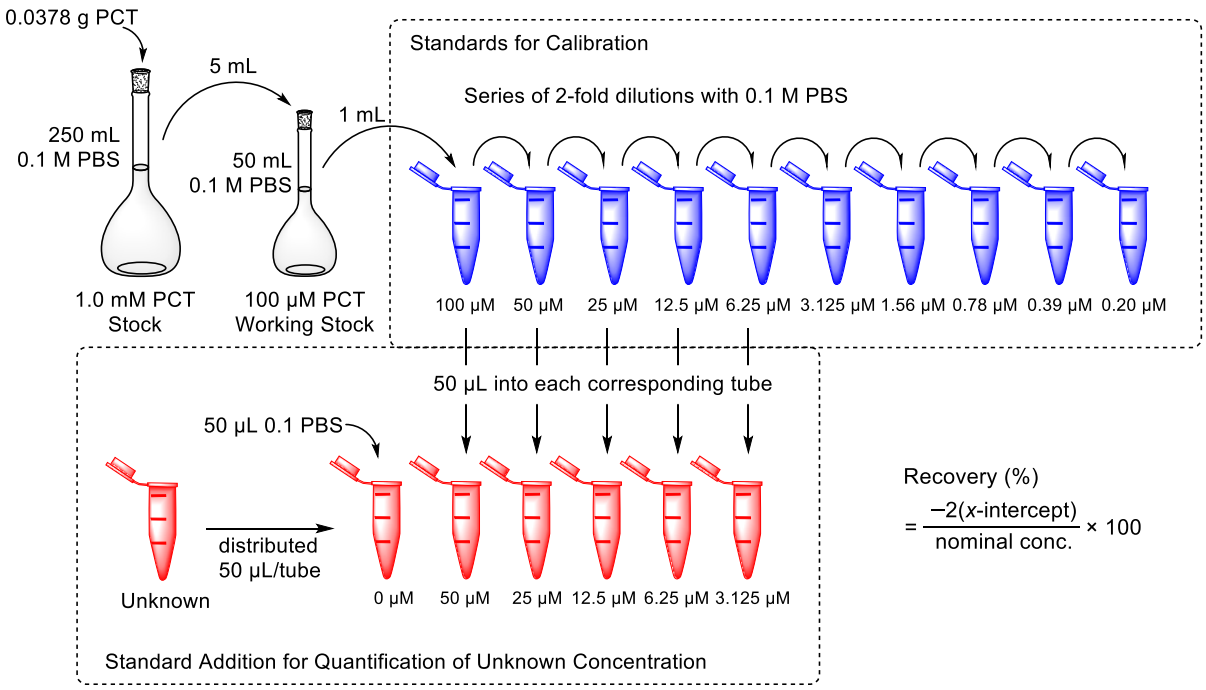
v (mV s^{-1})	$\sqrt{v}$ (mV$^{-1/2}$ s$^{-1/2}$)	ΔEp (mV)	ψ	k_0 (cm s^{-1})
5	2.2361	85.3	0.9110	2.255×10^{-3}
10	3.1623	79.9	1.1572	4.050×10^{-3}
25	5.0000	79.9	1.1572	6.404×10^{-3}
50	7.0711	79.9	1.1572	9.057×10^{-3}
100	10.0000	86.2	0.8840	9.784×10^{-3}
250	15.8114	95.1	0.6513	11.398×10^{-3}
500	22.3607	121.78	0.3443	8.520×10^{-3}



Supplementary Figure S7. Evaluation of rate of electron transfer of hexaamine-ruthenium(III) at a 3 mm Pt disc electrode using Pt-T mini-cell.



Supplementary Figure S8. Illustration of recycling effect of redox species between the disc working electrode (WE) and the edge of Pt-T mini-cell serving as the counter electrode (CE) which encompasses the disc WE. This leads to the current enhancing effect observed in Pt-T mini-cell in comparison to conventional beaker cell. R and O represent reduced and oxidised species, respectively.



Supplementary Figure S9. Schematic illustration of paracetamol standard solution preparation for calibration and standard addition for quantification of paracetamol in sample.

Supplementary Table S1. Electrochemical Parameter Settings for Figure 4

Experiment	Parameters
(A)	DPV E_{cond} −1.0 V 10 s; t_{equil} 10 s; E_{begin} -1.0 V E_{end} 1.5 V; S_{rate} 100 mV s^{-1}; E_{step} 5 mV; E_{pulse} 100 mV; t_{pulse} 10 ms.
(B)	DPV E_{cond} 0.0 V 10 s; t_{equil} 10 s; E_{begin} 0.2 V E_{end} 0.8 V; S_{rate} 100 mV s^{-1}; E_{step} 10 mV; E_{pulse} 25 mV; t_{pulse} 50 ms.
(C)	DPV E_{cond} 0.0 V 5 s; t_{equil} 5 s; E_{begin} 0.4 V E_{end} 1.2 V; S_{rate} 100 mV s^{-1}; E_{step} 5 mV; E_{pulse} 50 mV; t_{pulse} 10 ms.
(D)	CV E −0.5 to 1.0 V; S_{rate} 50 mV s^{-1}; E_{step} 10 mV.
(E)	CV E 0.2 to 1.2 V; S_{rate} 50 mV s^{-1}; E_{step} 10 mV.
(F)	Amperometry E +600 mV