Influence of Sulfuric Acid Concentration in the Simultaneous Voltammetric Determination of Uranium and Plutonium in Nuclear fuels

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1. Surface of PEDOT-PSS for different modified electrodes:

Three different PEDOT-PSS/GC electrodes are prepared and its response is recorded in 5 M H_2SO_4 and is shown in Figure S1a. The electrochemical response of the three modified electrode in blank exactly matches with each other which shows the surface of PEDOT-PSS is identical for every modified electrode. These is further confirmed by recording the CV response of three PEDOT-PSS/GC in 10 mM potassium ferricyanide ($K_3[Fe(CN)_6]$) in 0.1 M KCl at a scan rate of 10 mV s^{-1} (Figure S1b) and the electrochemically active surface area (A_e) of the electrodes are also calculated using the Randles-Sevcik equation. The CV responses of the different modified electrodes are exactly same and the A_e values of these electrodes are also close (0.1162, 0.1168 and 0.1200 cm^2, respectively). These confirm the surface of PEDOT-PSS is identical for every modified electrode.

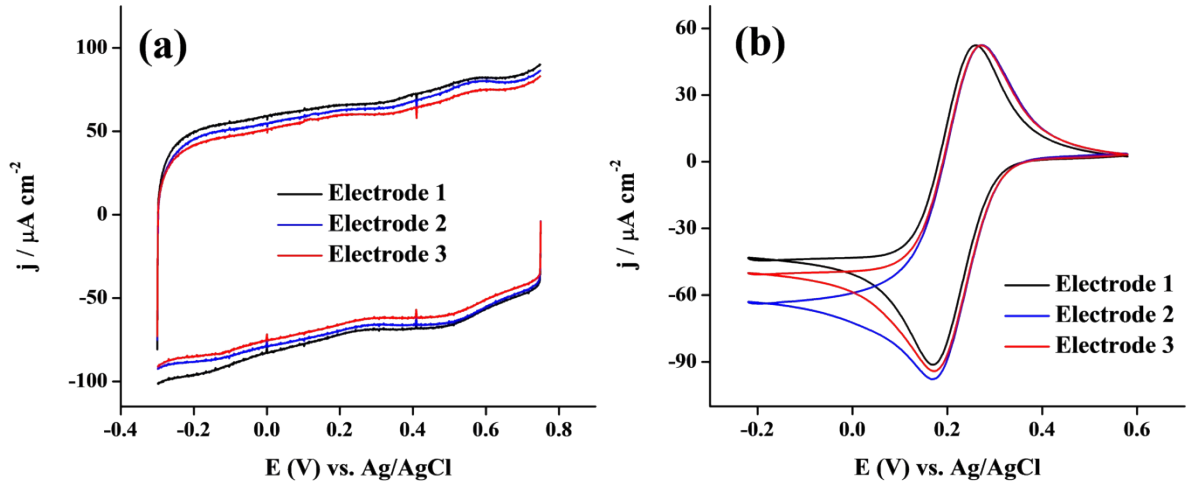

Figure S1. CVs of (a) blank (5 M H_2SO_4) at a scan rate of 50 mV s^{-1} and (b) $K_3[Fe(CN)_6]$ (10 mM) in 0.1 M KCl on three different modified PEDOT-PSS/GC at a scan rate of 10 mV s^{-1}.

2. Dissolution of (U, Pu)C and (U, Pu)O_2 samples:

Carbide samples ((U, Pu)C) get completely dissolved in 1:1 mixture of concentrated nitric and sulfuric acid by heating under reflux. But PuO_2 is difficult to dissolve in concentrated nitric acid alone. It gets quantitatively dissolved in presence of catalytic amount of HF. The more electronegative F^- will displace O from PuO_2 to form PuF_2^{2+} (surface reaction), which in turn dissociates in to Pu^{4+} and F^-. The liberated F^- again reacts with PuO_2 and the process of dissolution will continued. Since, F^- acts as a catalyst, so a little amount of HF is sufficient to

dissolve PuO_2 completely in concentrated nitric acid by heating under IR. The mechanism of dissolution is represented below:

$$PuO_2 + 2F^- + 2H^+ = PuOF_2 + H_2O$$

$$PuOF_2 + 2H^+ = PuF_2^{2+} + H_2O$$

$$PuF_2^{2+} = Pu^{4+} + 2F^-$$

$$Pu^{4+} + 6NO_3^- = [Pu(NO_3)_6]^{2-}$$

$$PuO_2 + 6NO_3^- + 4H^+ = [Pu(NO_3)_6]^{2-} + 2H_2O$$

Table S1. Isotopic composition (atom %) of U and Pu of FBTR fuel.

Nuclide	U (%)	Nuclide	Pu(%)
232	-	**238**	0.137
233	-	**239**	70.70
234	0.005	**240**	25.17
235	0.720	**241**	0.620
236	-	**242**	1.687
238	99.275	**244**	-

3. Coupled chemical reaction between U(IV) and Pu(IV):

The rate of coupled chemical reaction between U(IV) and Pu(IV) depends inversely upon the square of hydrogen ion concentration and is formulated as

$$-\frac{d[Pu(IV)]}{dt} = k[Pu^{4+}][U^{4+}][H^+]^{-2}$$

Where, k is the rate constant and it is given by

$$k = k'([H^+] + K_{Pu})([H^+] + K_U)$$

k' is called the apparent second order rate constant and K_{Pu} and K_U are the hydrolysis quotients for Pu(IV) and U(IV), respectively.[1]

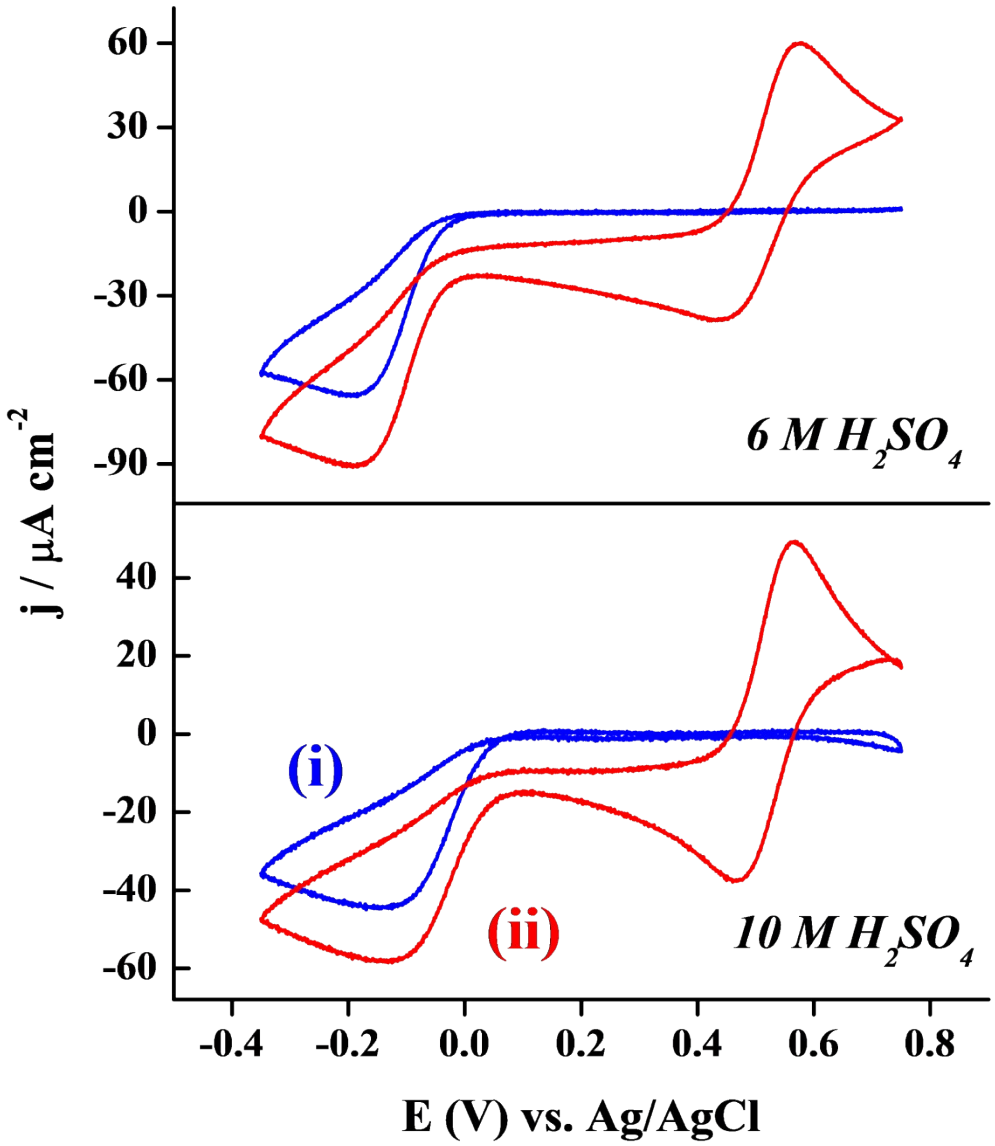

Figure S2. (a) CVs of PEDOT-PSS/GC in (i) U(VI) and (ii) U(VI) and Pu(IV) mixed solution in 6 and 10 M H_2SO_4. All CVs are recorded at a scan rate of 50 mV s^{-1}.

Table S2. Electrochemical parameters obtained from CV on PEDOT-PSS/GC in (U, Pu) mixed solution in different acid strength of H_2SO_4 at a scan rate of 100 mV s^{-1}.

	Pu			U
H_2SO_4 / M	**E_p^c / V**	**E_p^a / V**	**$E_0^{'}$ / V**	**E_p^c / V**
0.5	0.530	0.586	0.558	-0.177
1	0.513	0.582	0.548	-0.176
2	0.494	0.588	0.541	-0.173
3	0.493	0.582	0.536	-0.153
5	0.478	0.571	0.525	-0.144

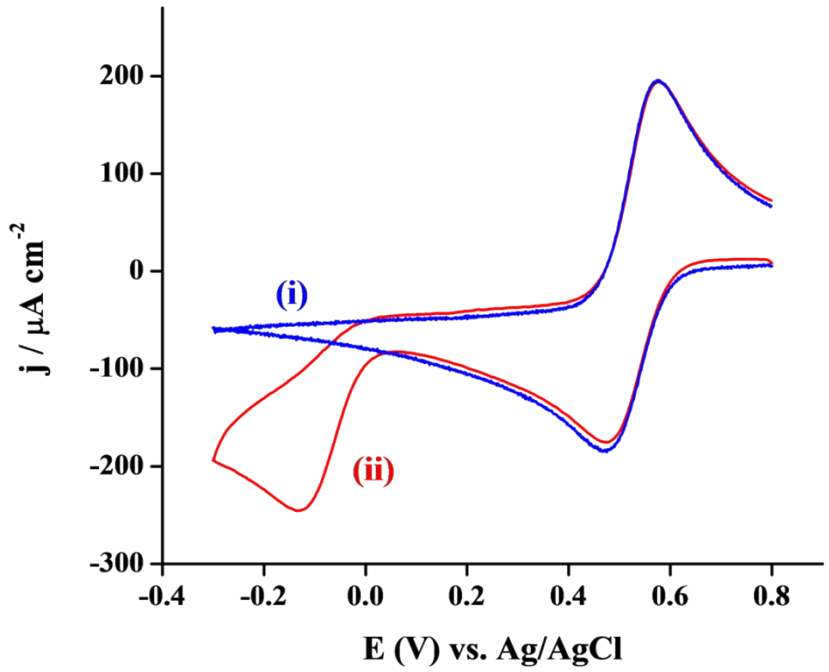

Figure S3. CVs of PEDOT-PSS/GC in (i) Pu(IV) (0.4581 mg g^{-1}) and (ii) U(VI) and Pu(IV) (0.2115 mg g^{-1} U and 0.4444 mg g^{-1} Pu) mixed solution in 5 M H_2SO_4 at a scan rate of 100 mV s^{-1}.

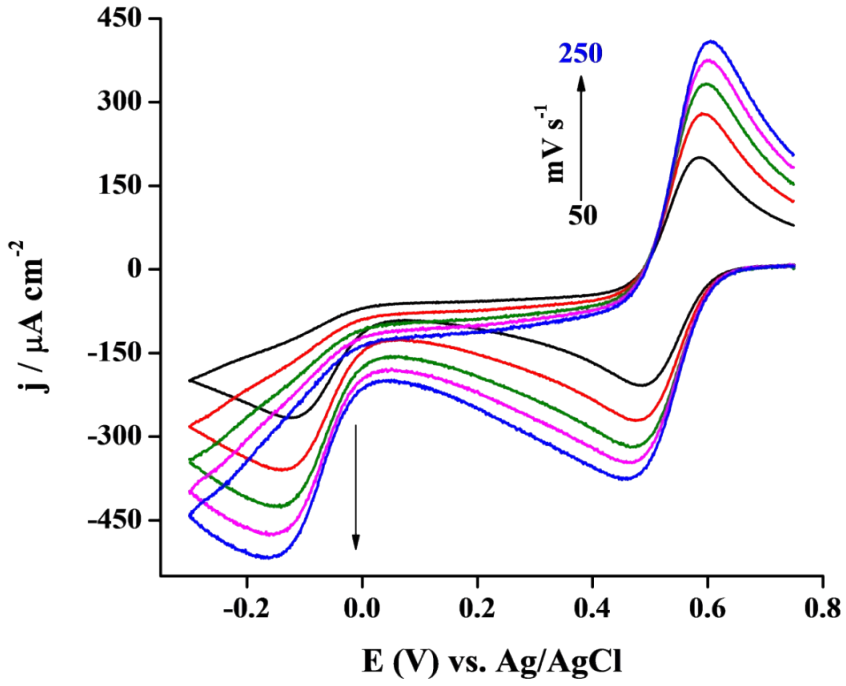

Figure S4. CVs of PEDOT-PSS/GC in U(VI) and Pu(IV) (0.2115 mg g^{-1} U and 0.4444 mg g^{-1} Pu) mixed solution in 5 M H_2SO_4 at different scan rates (50, 100, 150, 200 and 250 mV s^{-1}).

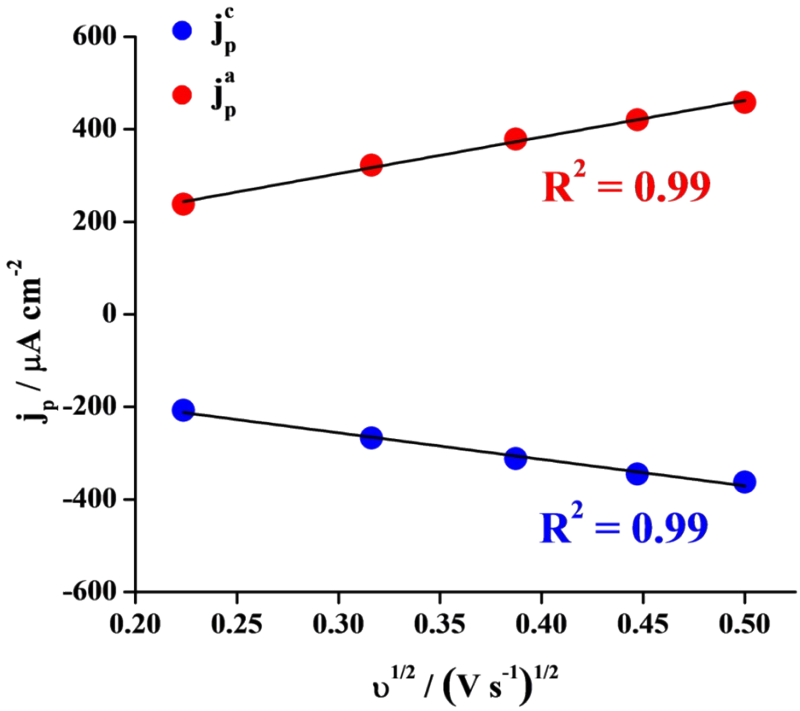

Figure S5. Plot of cathodic and anodic peak current density (j_p^c *and* j_p^a) of Pu(IV)/Pu(III) couple vs. square root of scan rate ($\upsilon^{1/2}$) (obtained from Fig. S4).

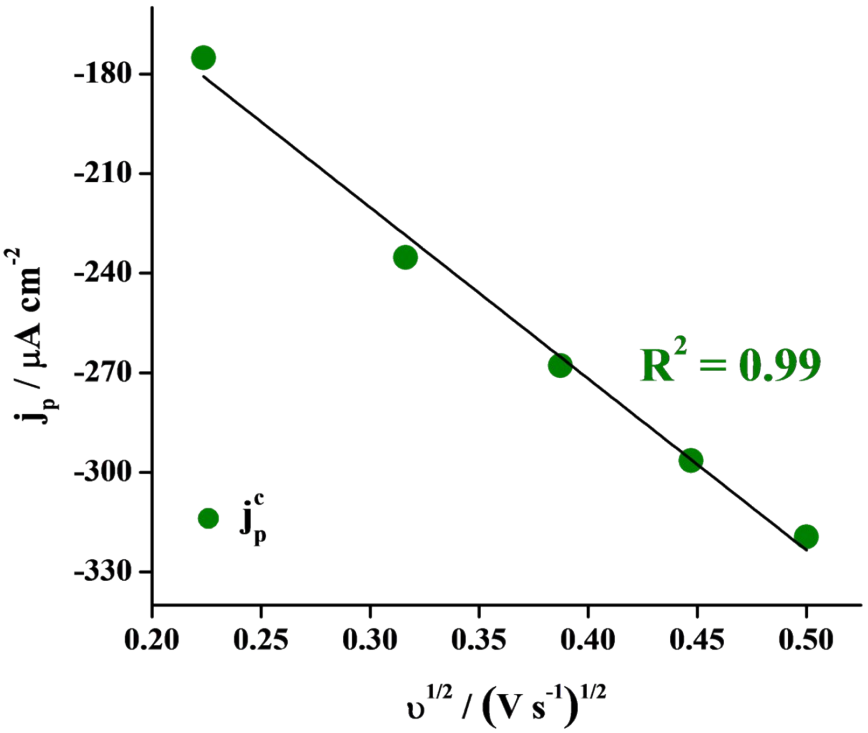

Figure S6. Plot of cathodic peak current density (j_p^c) of U(VI) reduction vs. square root of scan rate ($\upsilon^{1/2}$) (obtained from Fig. S4).

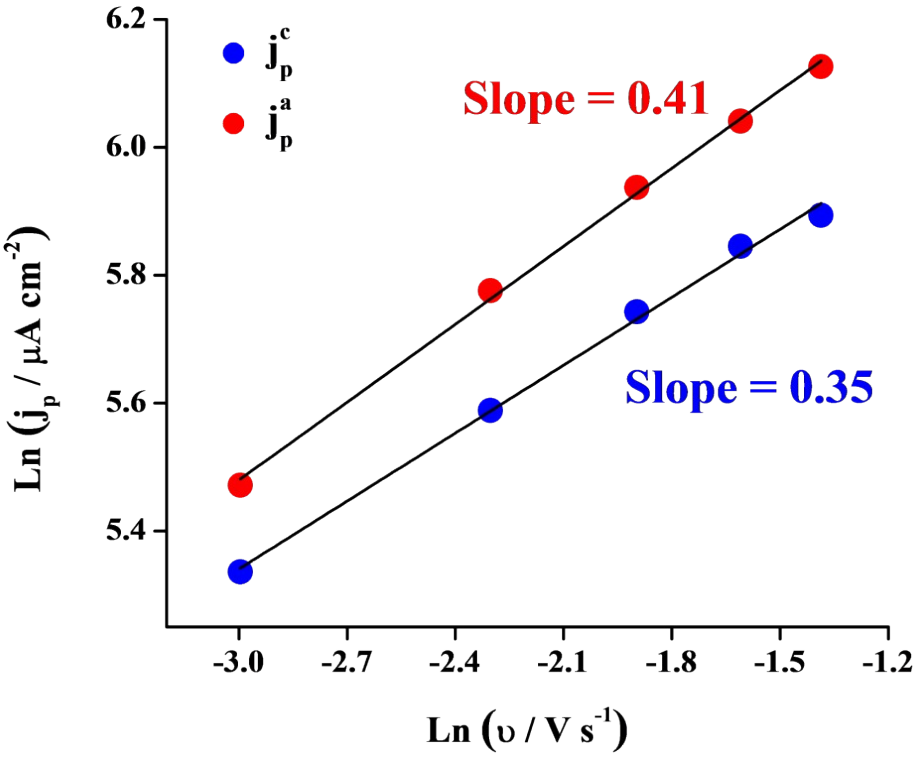

Figure S7. Plot of Ln$|-j_p^c \text{ and } j_p^a|$ of Pu(IV)/Pu(III) redox couple vs. Ln(ν) (obtained from Fig. S4).

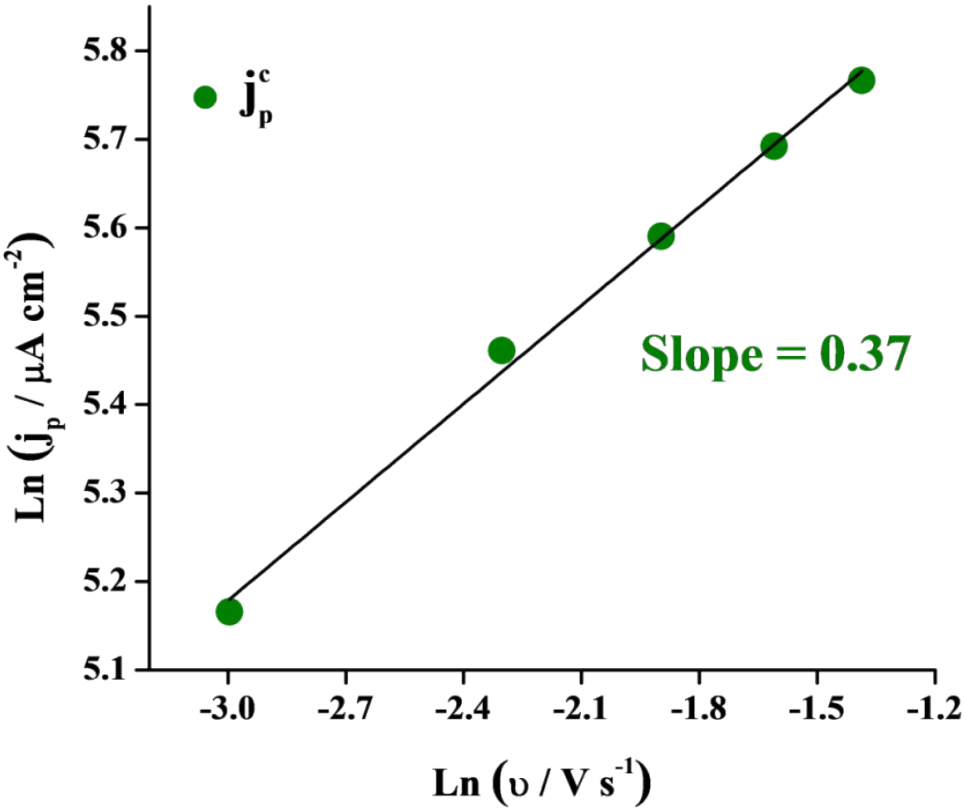

Figure S8. Plot of Ln$|-j_p^c|$ of U(VI) reduction vs. Ln(ν) (obtained from Fig. S4).

Table S3. Electrochemical parameters obtained from CV on PEDOT-PSS/GC in (U, Pu) mixed solution in 5 M H_2SO_4 at different scan rates.

	Pu					U	
v/ mV s^{-1}	**E_p^c/ V**	**E_p^a/ V**	**j_p^c/ µA cm^{-2}**	**j_p^a/ µA cm^{-2}**	**$E_0^{'}$/ V**	**E_p^c/ V**	**j_p^c/ µA cm^{-2}**
50	0.487	0.588	-208	238	0.538	-0.122	-175
100	0.474	0.589	-267	322	0.532	-0.139	-235
150	0.466	0.597	-312	379	0.532	-0.141	-268
200	0.460	0.603	-346	420	0.532	-0.161	-296
250	0.451	0.605	-363	458	0.528	-0.162	-319

4. CV response without blank subtraction:

CV of the modified electrode (PEDOT-PSS/GC) in 5 M H_2SO_4 in absence and presence of (U, Pu) is shown in Figure S9a. The same electrode is then rinsed in 5 M H_2SO_4 and then again CV is recorded in 5 M H_2SO_4 and shown in Figure S9b.

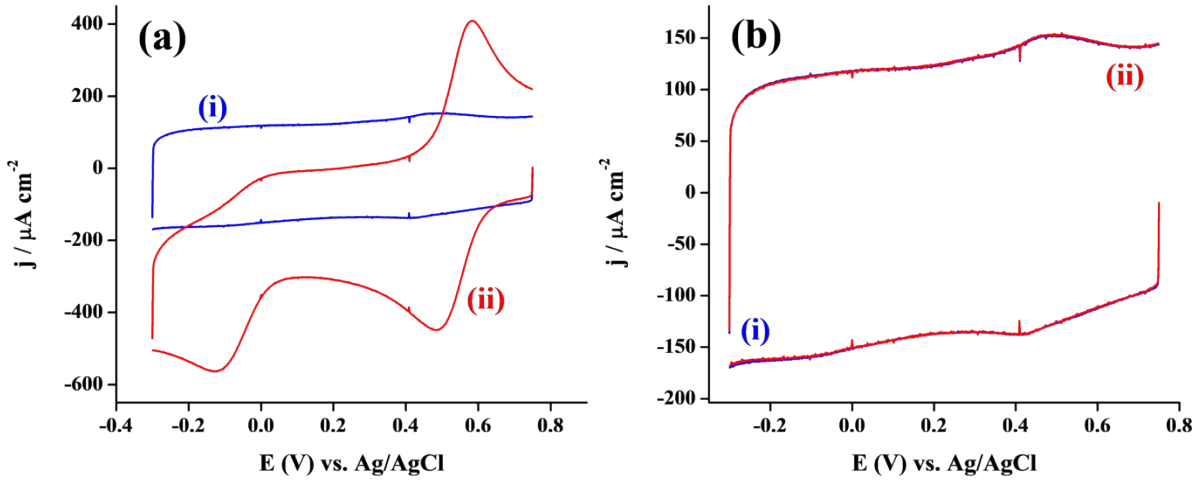

Figure S9. CVs of PEDOT-PSS/GC in 5 M H_2SO_4 in (i) absence and (ii) presence of (U, Pu) and (b) CV of PEDOT-PSS/GC in 5 M H_2SO_4 (i) before (U, Pu) analysis and (ii) after (U, Pu) analysis and rinsed with 5 M H_2SO_4. All the CVs are recorded at a scan rate of 50 mV s^{-1}.

Table S4. Accuracy and Precision of CV for analysis of (U, Pu) mixed solutions.

Element	Taken (mg)	CV (mg)	% Error	% RSD
U	3.6191	3.6399	0.57	0.17
Pu	5.5378	5.5138	0.43	0.31

Table S5. Comparison of atom % of U and Pu obtained from Biamperometry (BA) and Cyclic Voltammetry (CV) in PFBR samples.

Sample No.	BA (at %)	CV (at %)	CV/BA
U			
Sample-1	65.22 ± 0.01	65.56 ± 1.16	1.01
Sample-2	64.28 ± 0.04	65.51 ± 0.17	1.02
Sample-3	65.10 ± 0.04	66.49 ± 0.43	1.02
Sample-4	58.29 ± 0.02	61.07 ± 0.05	1.05
Sample-5	59.09 ± 0.06	59.46 ± 0.60	1.01
Sample-6	58.82 ± 0.08	57.97 ± 0.16	0.99
Pu			
Sample-1	17.75 ± 0.06	18.31 ± 1.36	1.03
Sample-2	18.42 ± 0.08	19.07 ± 1.67	1.04
Sample-3	17.56 ± 0.20	17.77 ± 0.04	1.01
Sample-4	24.22 ± 0.20	25.45 ± 0.02	1.05
Sample-5	23.93 ± 0.02	24.80 ± 0.24	1.04
Sample-6	23.80 ± 0.17	23.20 ± 0.95	0.97

Table S6. Comparison of atom % of U and Pu obtained from Biamperometry (BA) and Cyclic Voltammetry (CV) in FBTR samples.

Sample No.	BA (at %)	CV (at %)	CV/BA
U			
Sample-1	28.04 ± 0.30	26.33 ± 0.19	0.94
Sample-2	27.96 ± 0.00	27.98 ± 0.15	1.00
Sample-3	27.83 ± 0.07	27.46 ± 0.77	0.99
Sample-4	27.79 ± 0.20	28.42 ± 0.17	1.02
Sample-5	27.88 ± 0.00	28.76 ± 0.27	1.03
Sample-6	27.68 ± 0.30	27.78 ± 0.11	1.00
Sample-7	28.67 ± 0.20	28.63 ± 0.44	1.00
Sample-8	28.08 ± 0.17	27.86 ± 0.51	0.99
Sample-9	27.75 ± 0.05	27.80 ± 1.11	1.00
Sample-10	27.78 ± 0.13	27.36 ± 0.20	0.98
Pu			
Sample-1	66.46 ± 0.02	66.90 ± 0.22	1.01
Sample-2	66.97 ± 0.02	67.60 ± 0.23	1.01
Sample-3	67.10 ± 0.00	67.65 ± 0.03	1.01
Sample-4	67.49 ± 0.20	65.90 ± 0.00	0.98
Sample-5	66.92 ± 0.09	65.17 ± 0.05	0.97
Sample-6	67.15 ± 0.10	65.81 ± 0.03	0.98
Sample-7	66.31 ± 0.11	65.58 ± 0.01	0.99
Sample-8	67.06 ± 0.19	66.25 ± 0.06	0.99
Sample-9	67.56 ± 0.20	65.83 ± 0.44	0.97
Sample-10	67.37 ± 0.12	66.55 ± 0.55	0.99

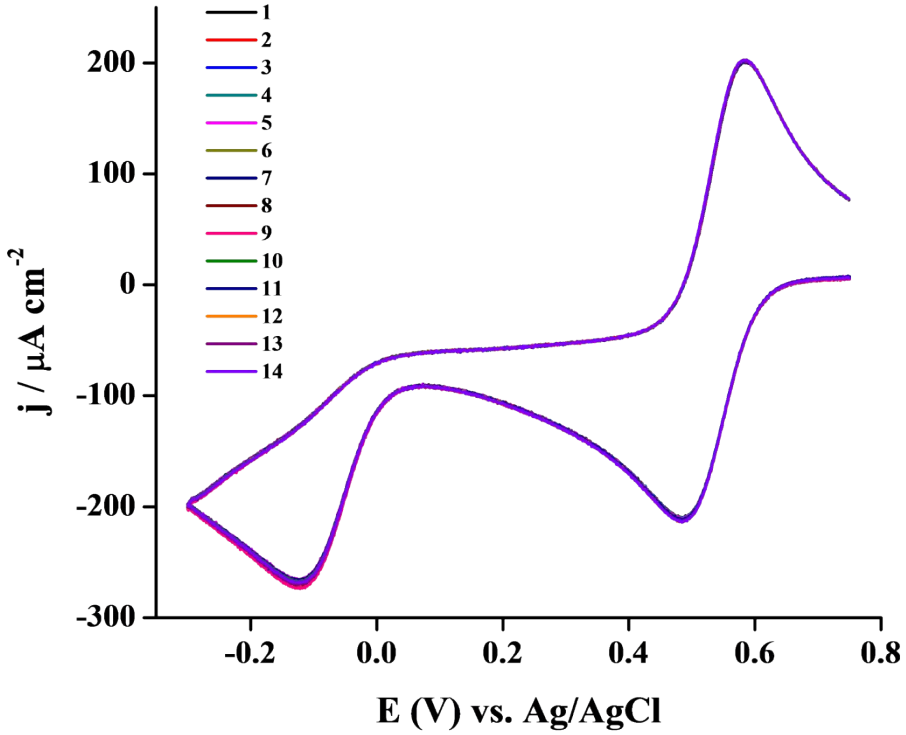

Figure S10. Fourteen repetitive CVs of PEDOT-PSS/GC in U(VI) and Pu(IV) (0.2115 mg g^{-1} U and 0.4444 mg g^{-1} Pu) mixed solution in 5 M H_2SO_4 at a scan rate of 50 mV s^{-1}.

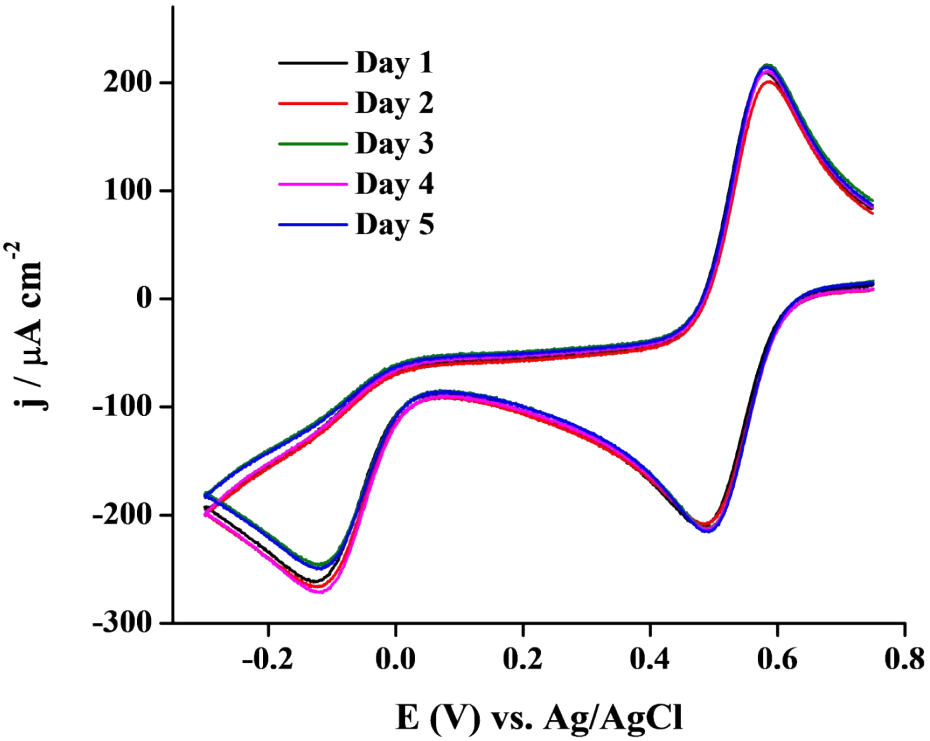

Figure S11. CVs of PEDOT-PSS/GC in U(VI) and Pu(IV) (0.2115 mg g^{-1} U and 0.4444 mg g^{-1} Pu) mixed solution in 5 M H_2SO_4 for five consecutive days at a scan rate of 50 mV s^{-1}.

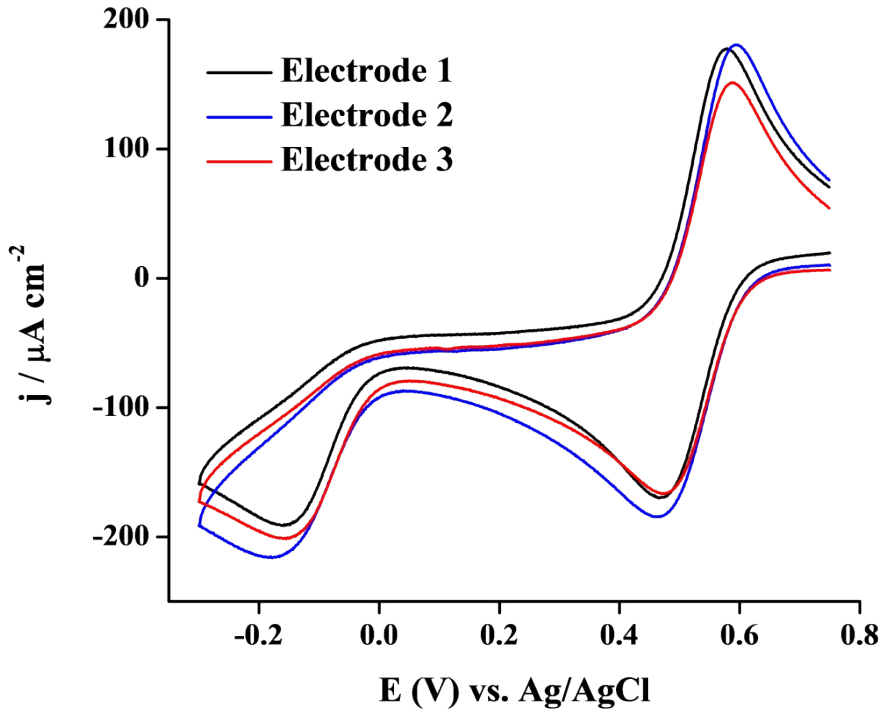

Figure S12. CVs of U(VI) and Pu(IV) mixed solution in 5 M H_2SO_4 on three different modified PEDOT-PSS/GC electrodes at a scan rate of 50 mV s^{-1}.

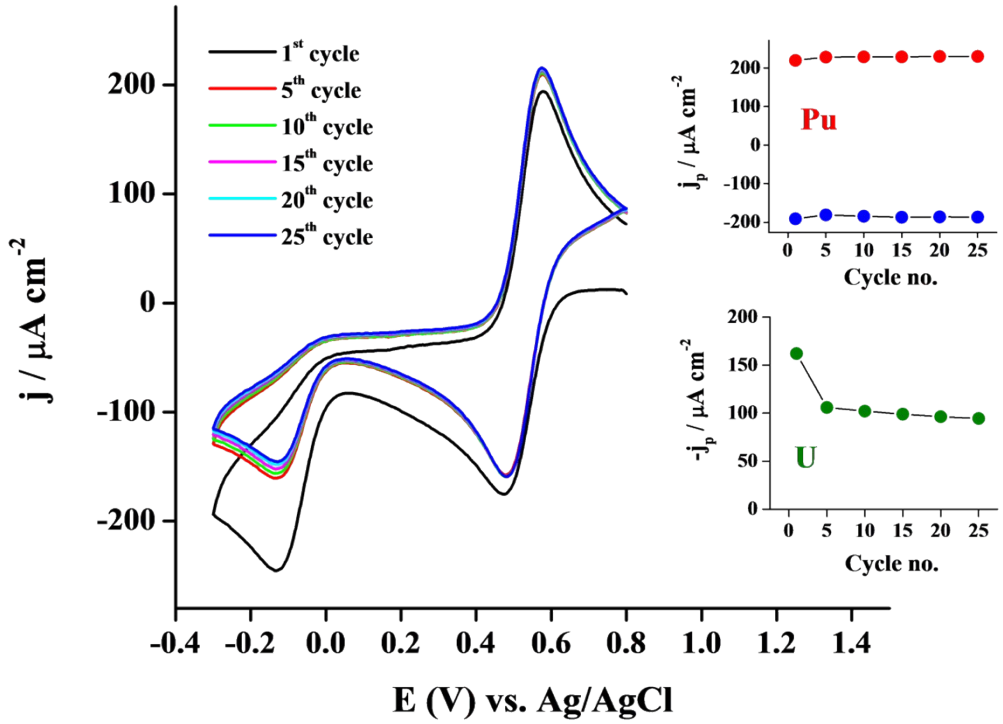

Figure S13. CVs of PEDOT-PSS/GC in U(VI) and Pu(IV) (0.2115 mg g^{-1} U and 0.4444 mg g^{-1} Pu) mixed solution in 5 M H_2SO_4 at a scan rate of 100 mV s^{-1} for successive 25 cycles. Only first cycle (black line), fifth cycle (red line), tenth cycle (green line), fifteenth cycle (magenta line), twentieth cycle (cyan line) and twenty-fifth cycles (blue line) is shown for simplicity. Inset shows the plot of corresponding peak current density of Pu(IV)/Pu(III) and U(VI)/U(IV) redox couples vs. CV cycle number.

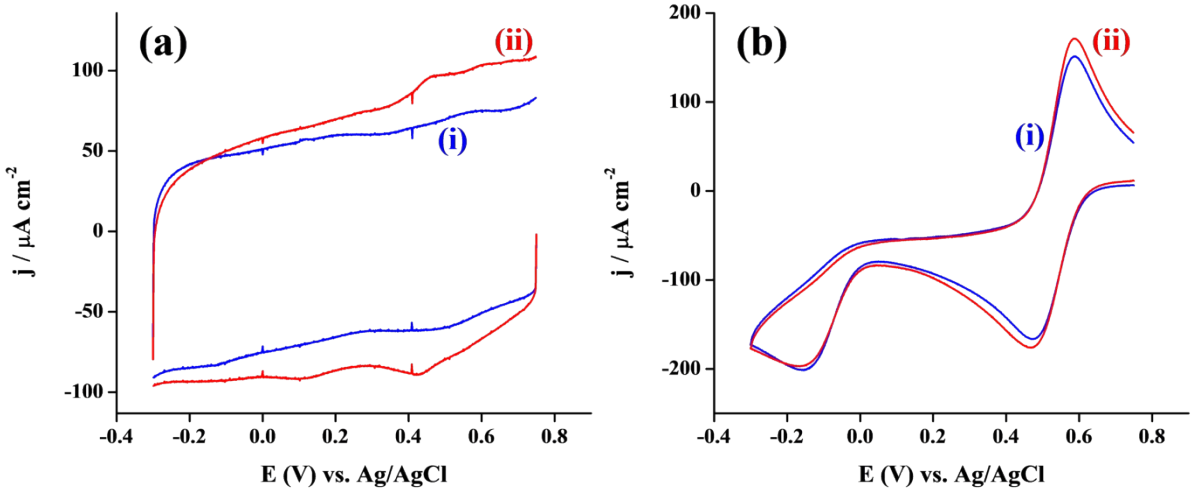

Figure S14. CVs of (a) blank and (b) U(VI) and Pu(IV) (0.2829 mg g^{-1} U and 0.6890 mg g^{-1} Pu) mixed solution on (i) un-irradiated and (ii) irradiated PEDOT-PSS/GC in 5 M H_2SO_4 at a scan rate of 50 mV s^{-1}.

5. Reusability of one single GC electrode to prepare different PEDOT-PSS/GC many times:

When we need to re-modify the same GC electrode, we follow the following five steps:

(i) At first, we record the CV response of bare GC in blank (Figure S15a(i));

(ii) Then the GC is modified with PEDOT-PSS and its response in blank is again recorded (Figure S15a(ii));

(iii) Next the modified electrode is used for (U, Pu) analysis and its response in one such (U, Pu) mixed solution is recorded (Figure S15a(iii));

(iv) The same Pu contaminated PEDOT-PSS/GC is rinsed in fresh acid and its response in blank is again recorded (Figure S15a(iv)). The response of PEDOT-PSS/GC before and after (U, Pu) analysis in blank matches exactly (Figure S15a (ii) and (iv)), which proves Pu is removed from the electrode surface.

(v) Now, the surface of this used electrode is gently rubbed on a tissue paper and its response is again recorded in blank which exactly matches with the response of bare GC (Figure S15a(v)). These confirm the complete removal of PEDOT-PSS layer from the GC and these GC can be reused again.

The same GC electrode is modified three times following the same five steps of Figure S15a and its response is recorded in the same (U, Pu) mixed solution and it is represented in Figure S15b. Precise peak current density of 124 ± 3 μA and 176 ± 5 μA cm^{-2} is obtained for U(VI) and Pu(IV) reduction reaction, respectively. These proves the reproducibility of the CV response of one single GC modified three times with PEDOT-PSS for (U, Pu) analysis. These results confirm the reusability of one single electrode many times.

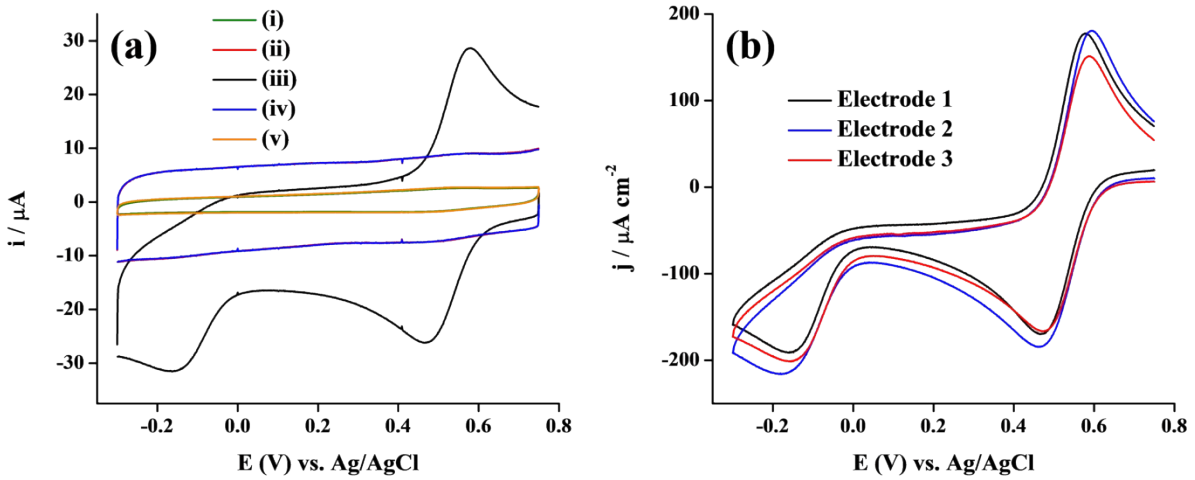

Figure S15. (a) CVs of (i) GC; (ii) PEDOT-PSS/GC; (iii) PEDOT-PSS/GC in (U, Pu) mixed solution; (iv) Pu-contaminated PEDOT-PSS/GC after rinsing in 5 M H_2SO_4 and (v) after removing PEDOT-PSS layer from GC surface with help of tissue paper in 5 M H_2SO_4 at a scan rate of 50 mV s^{-1} and (b) CVs (blank subtracted) of (U, Pu) mixed solution in 5 M H_2SO_4 on three different modified PEDOT-PSS/GC electrodes at a scan rate of 50 mV s^{-1}.

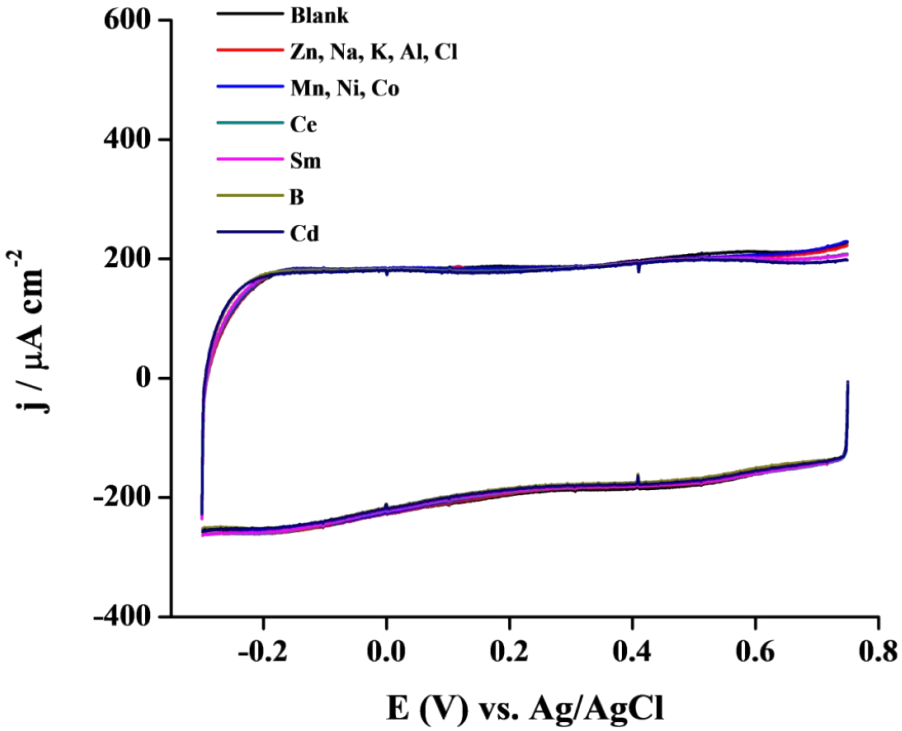

Figure S16. CVs of PEDOT-PSS/GC in presence and in absence of Zn(II), Na(I), K(I), Al(III), Cl(I), Mn(II), Ni(II), Co(II), Ce(IV), Sm(III), B(III) and Cd(II) (10 mM each) in 5 M H_2SO_4 at a scan rate of 50 mV s^{-1}.

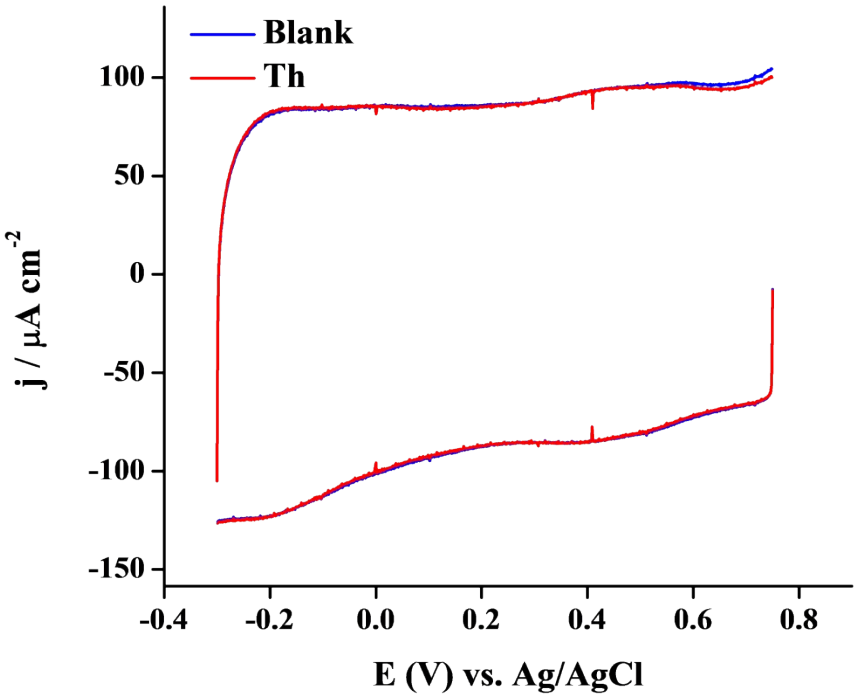

Figure S17. CVs of PEDOT-PSS/GC in 5 M H_2SO_4 in (i) absence and (ii) presence of 5 mM Th(IV) at a scan rate of 50 mV s^{-1}.

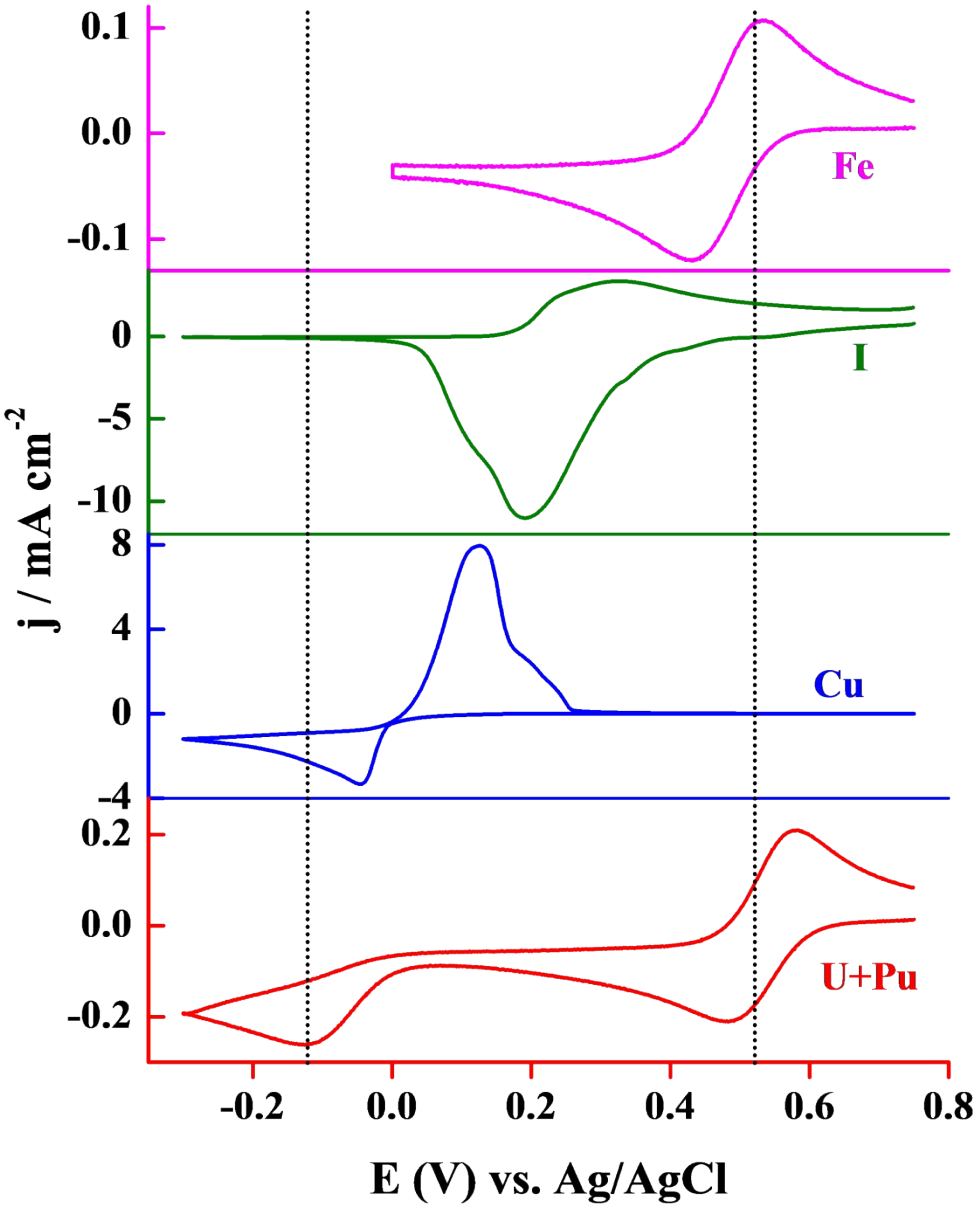

Figure S18. CVs of (i) 10 mM Fe(III), (ii) 10 mM I(I), (iii) 10 mM Cu(II) and (iv) 1.12 mM U(VI) and 2.35 mM Pu(IV) mixed solution in 5 M H_2SO_4 on PEDOT-PSS/GC at a scan rate of 50 mV s^{-1}.

Table 7. Specifications for MC pellets of FBTR.

Common Impurities	Concentration (ppm)
Al	500
B	2
Be	10
Ca+ Mg	200
Cd+Dy+Sm+Gd	20
Co	200
Cr	300
Cu	200
Fe	1000
Co+Mo+Mn+Cu+Zn	800
Mn	200
Mo	200
Na	100
Ni	500
Pb	200
Si	800
Sn	10
V	100
W	500
Zn	200
Total Impurities	≤ 3000

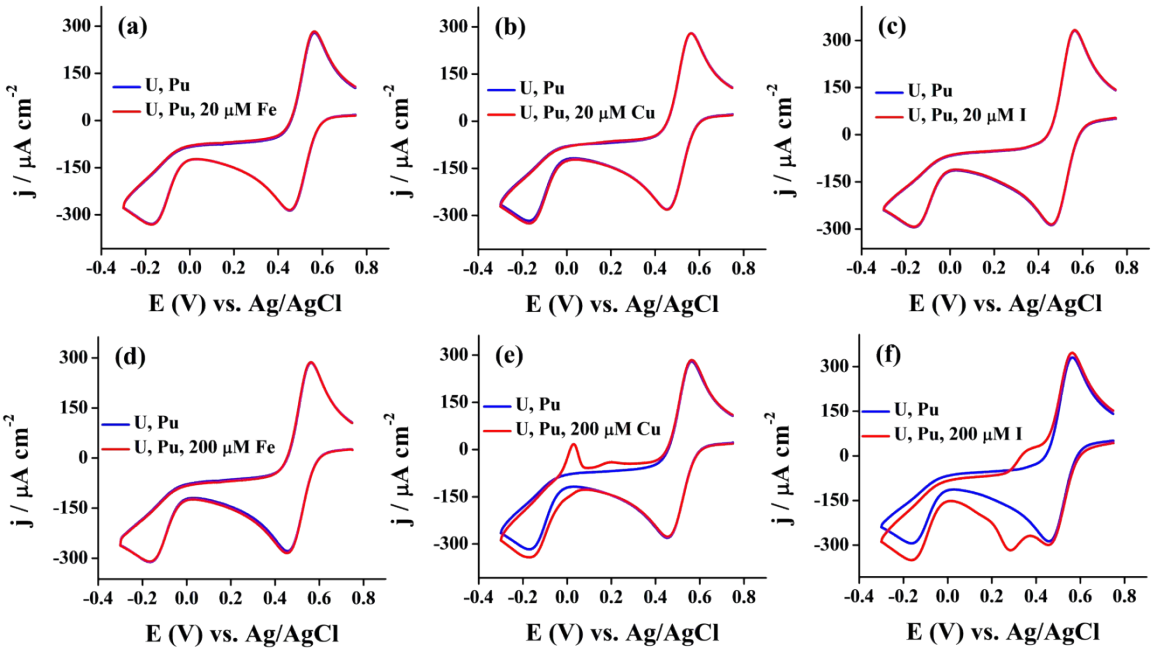

Figure S19. CVs of PEDOT-PSS/GC in absence and presence of (a) Fe(III) (20 µM), (b) Cu(II) (20 µM), I(I) (20 µM), (d) Fe(III) (200 µM), (e) Cu(II) (200 µM) and I(I) (200 µM) in U(VI) and Pu(IV) (1.5 mM U and 3.64 mM Pu) in 5 M H_2SO_4 at a scan rate of 50 mV s^{-1}.

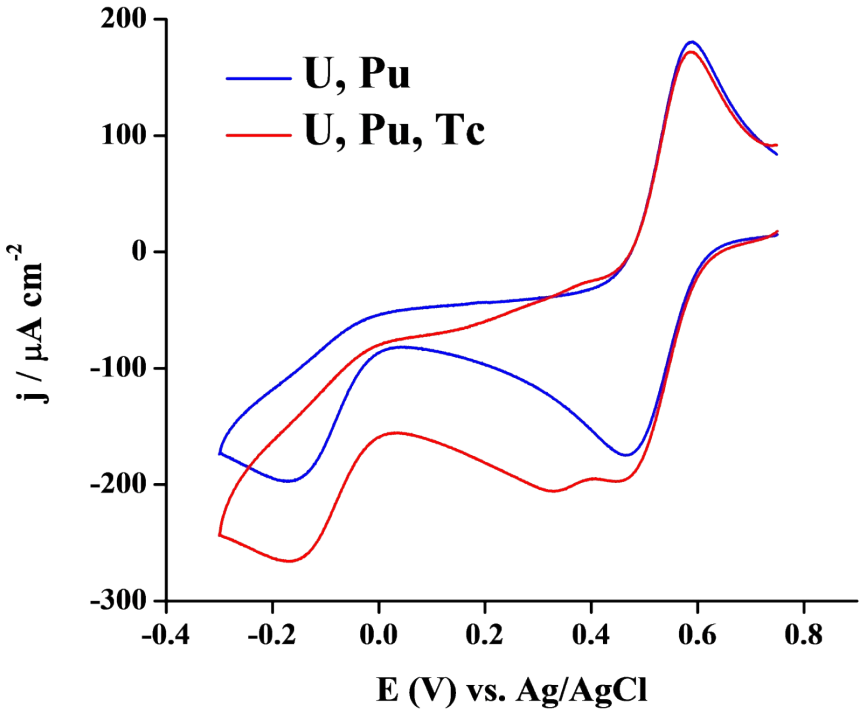

Figure S20. CVs of PEDOT-PSS/GC in absence and presence of 10 mM TcO_4^- in U(VI) and Pu(IV) (1.5 mM U and 3.64 mM Pu) in 5 M H_2SO_4 at a scan rate of 50 mV s^{-1}.

References:

1. T. W. Newton, *The Journal of Physical Chemistry*, 1959, **63**, 1493-1497.