

Supporting Information

Nitric Acid Concentration Strongly Influences Low Level Uranium

Determination on PEDOT-PSS Coated Glassy Carbon Electrode

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EXPERIMENTAL SECTION

Caution! ^{238}U ($t_{1/2} = 4.5 \times 10^9$ years) is a α -emitting radionuclide and hazardous. Due to its radiological and chemical toxicity, it should be handled in fume hoods and glove boxes in dedicated radioactive laboratories by trained personnel.

All the chemicals and reagents used were of analytical grade and all the solutions were prepared with Milli-Q water (18 M Ω cm) obtained from Milli-Q water purifier. PEDOT-PSS (1.3 wt% dispersion in water) was obtained from Sigma Aldrich. CHI 760D electrochemical workstation was used to perform all the electrochemical experiments at room temperature (T=298K) in a 10 ml electrochemical cell consisting of GC or PEDOT-PSS/GC working electrode, Pt wire counter electrode and Ag/AgCl/3 M KCl reference electrode. All the potential values mentioned in this manuscript are with respect to Ag/AgCl/3 M KCl only. High purity argon (Ar) gas was purged through the solution for 10 min before all electrochemical experiments to expel the dissolved O₂ and a constant Ar flow was maintained on the top of the solution during electrochemical experiments to avoid interference from atmospheric O₂. The GC electrode surface was cleaned by polishing with 1 to 0.05 μm alumina powder slurry on a polishing paper and then washed several times with Milli-Q water to remove any adhering alumina particles from the electrode surface. 10 μl of PEDOT-PSS was drop casted on the GC electrode ($\phi = 3$ mm) and then the electrode was dipped in ethanol to remove the excess PEDOT-PSS from the electrode surface and dried in open air for 1 h to obtain PEDOT-PSS/GC electrode. The electrochemically active surface area of (A_e) of PEDOT-PSS/GC is obtained as 0.1104 cm² by recording the CV of K₃[Fe(CN)₆] in 0.1 M KCl. If not stated otherwise, the peak-current densities were calculated using $A_e = 0.0707$ and 0.1104 cm² for GC and PEDOT-PSS/GC, respectively.

All Linear sweep voltammograms (LSVs) represented in this manuscript were blank subtracted, unless otherwise specified. A representative comparison of the actual LSV response and its blank subtracted response of 0.1 mM UO₂²⁺ in 0.05 M HNO₃ using the PEDOT-PSS/GC electrode was shown in Figure S1. All LSVs were recorded in the following three steps

- 1. conditioning:** a preconditioning potential (0.7 V) was applied for 300s in 0.05 M HNO₃ to remove any adsorbed UO₂²⁺ from the PEDOT-PSS/GC surface;
- 2. rest period:** then the electrode was dipped in UO₂²⁺ solution for 15 min to adsorb UO₂²⁺ and
- 3. LSV:** finally, LSV was recorded at a scan rate of 100 mV s⁻¹.

All the cathodic stripping voltammograms (CSVs) shown in the manuscript were blank subtracted and baseline corrected. A representative comparison of the actual CSV response and its response after blank subtraction and baseline correction for 10 μM UO₂²⁺ in 0.05 M HNO₃ using the PEDOT-PSS/GC electrode was shown in Figure S2. All CSVs for U determination were recorded in 4 steps,

- 1. conditioning:** a preconditioning potential (0.7 V) was applied for 300 s in 0.05 M HNO₃ to remove any adsorbed UO₂²⁺ from the PEDOT-PSS/GC surface;
- 2. deposition:** then a fixed deposition potential of -0.3 V was applied for a particular time under constant stirring to electrodeposit UO₂ on the electrode surface;
- 3. rest period:** then stirring was turned off and equilibration was done at 0.8 V for 10s in quiescent solution which oxidises the electrodeposited UO₂ to UO₂²⁺ at the electrode-solution interface and
- 4. Stripping:** finally the potential was scanned in the negative direction to reduce back the UO₂²⁺ to UO₂.

Adsorption of UO₂²⁺ on the electrode surface was characterized using Energy dispersive spectroscopy (EDS) which was recorded on tabletop SNE4500M SEM instrument with Bruker Nano GmbH Xflash detector 410-M (Berlin, Germany). Uranyl speciation in nitrate medium was constructed using Hyperquad Simulation and Speciation (HySS) programming.¹ The stability constant for formation of various uranyl-nitrate species were taken from NEA-TDB database.²

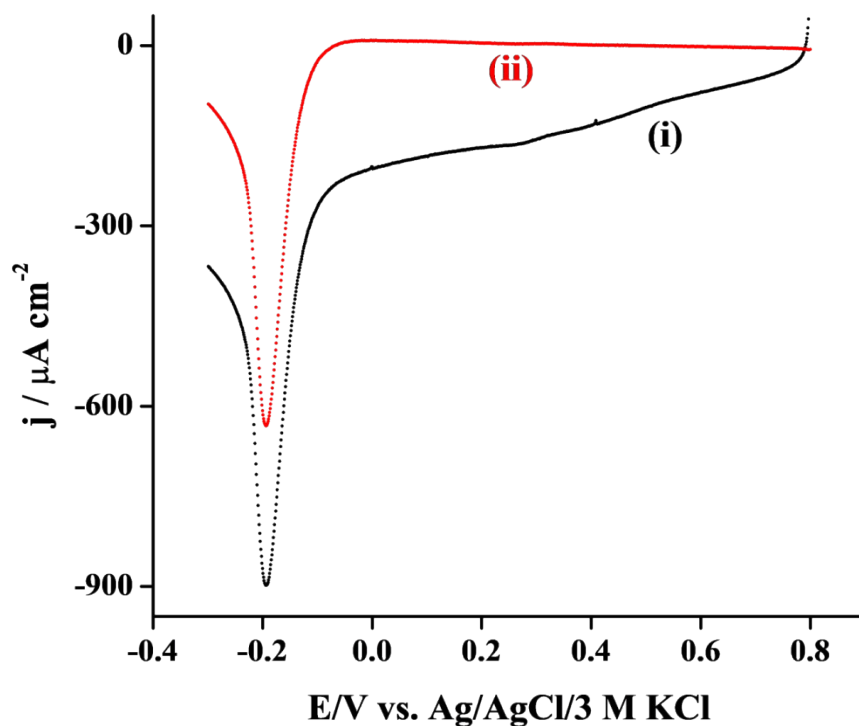


Figure S1. LSV of 0.1 mM UO_2^{2+} in 0.05 M HNO_3 recorded with PEDOT-PSS/GC electrode at a scan rate of 100 mV s^{-1} [(i) Actual signal (black) and (ii) after blank subtraction (red)].

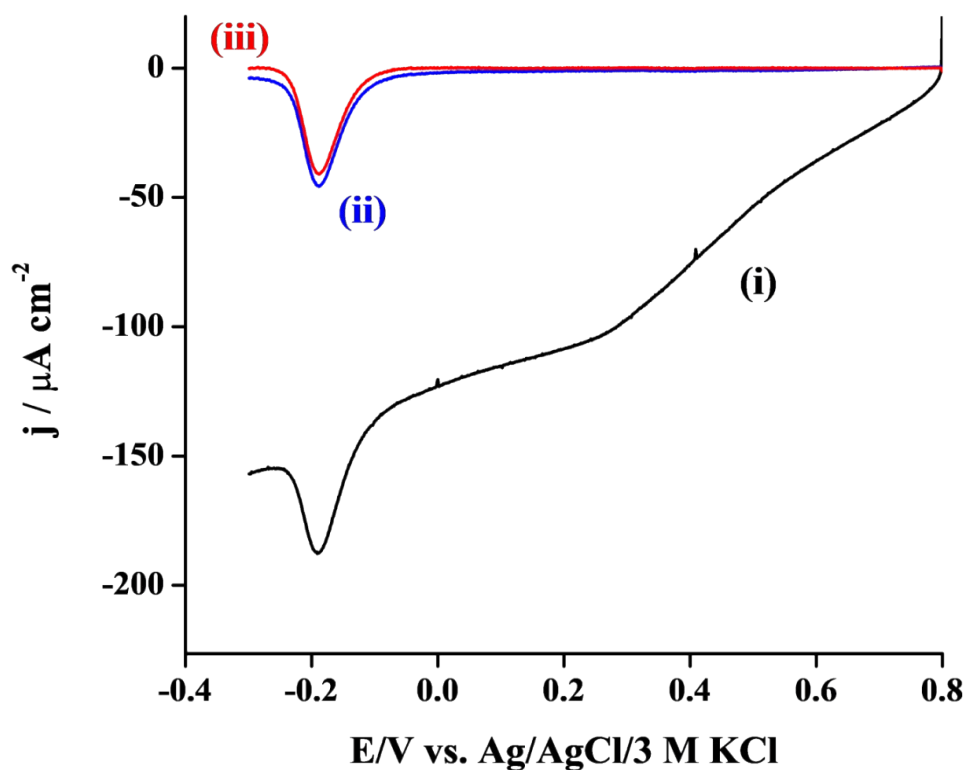


Figure S2. LSV of $10 \mu\text{M}$ UO_2^{2+} in 0.05 M HNO_3 recorded with PEDOT-PSS/GC electrode at a scan rate of 100 mV s^{-1} [(i) Actual signal (black); (ii) after blank subtraction (blue) and (iii) after baseline correction (red)].

Table T1: Binding energies and Gibbs free energies for formation of PEDOT-PSS- UO_2^{2+} , and PEDOT-PSS- $\text{UO}_2(\text{NO}_3)$, PEDOT-PSS- $\text{UO}_2(\text{NO}_3)_2$, PEDOT-PSS- $\text{UO}_2(\text{NO}_3)_3$ species.

Species	Gaseous Phase		Aqueous Phase	
	B. E (kJ/mol)	ΔG (kJ/mol)	B. E (kJ/mol)	ΔG (kJ/mol)
PEDOT-PSS- UO_2^{2+}	-1906.5	-750.7	-1825.3	-639.9
PEDOT-PSS- $\text{UO}_2(\text{NO}_3)$	-1479.7	-614.4	-1368.9	-503.6
PEDOT-PSS- $\text{UO}_2(\text{NO}_3)_2$	-899.5	-576.2	-769.2	-445.9
PEDOT-PSS- $\text{UO}_2(\text{NO}_3)_3$	-353.0	-430.1	-245.5	-322.5

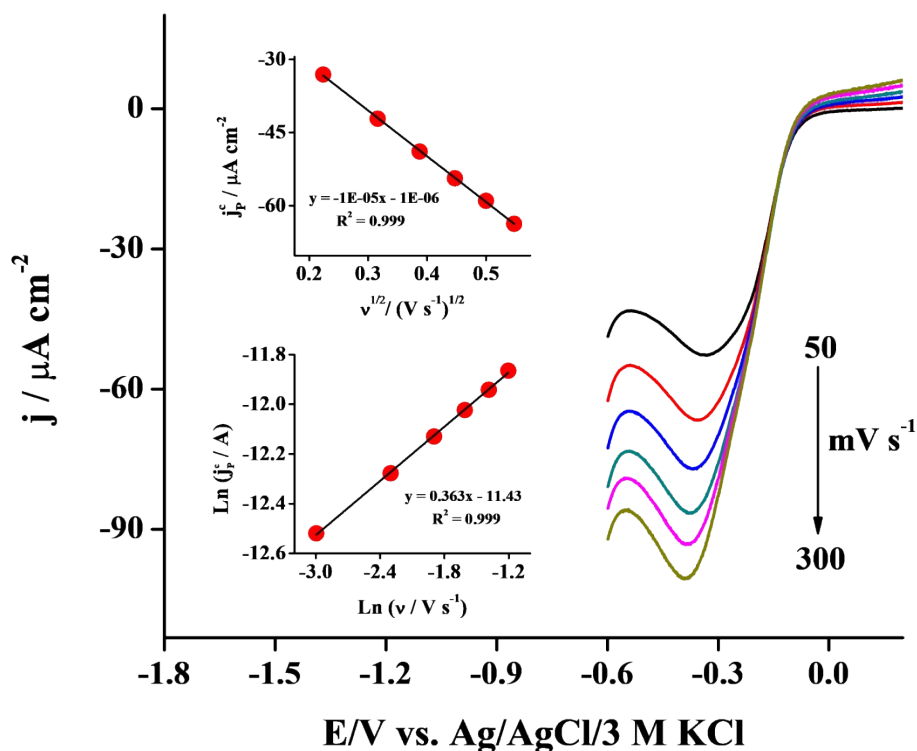


Figure S3. LSVs of 0.5 mM UO_2^{2+} in 1 M HNO_3 using GC electrode at different scan rates. Inset shows the plot of cathodic peak-current density (j_p^c) of UO_2^{2+} to U^{4+} reduction vs. square root of scan rate ($v^{1/2}$) and plot of $\text{Ln}|j_p^c|$ vs. $\text{Ln}(v)$.

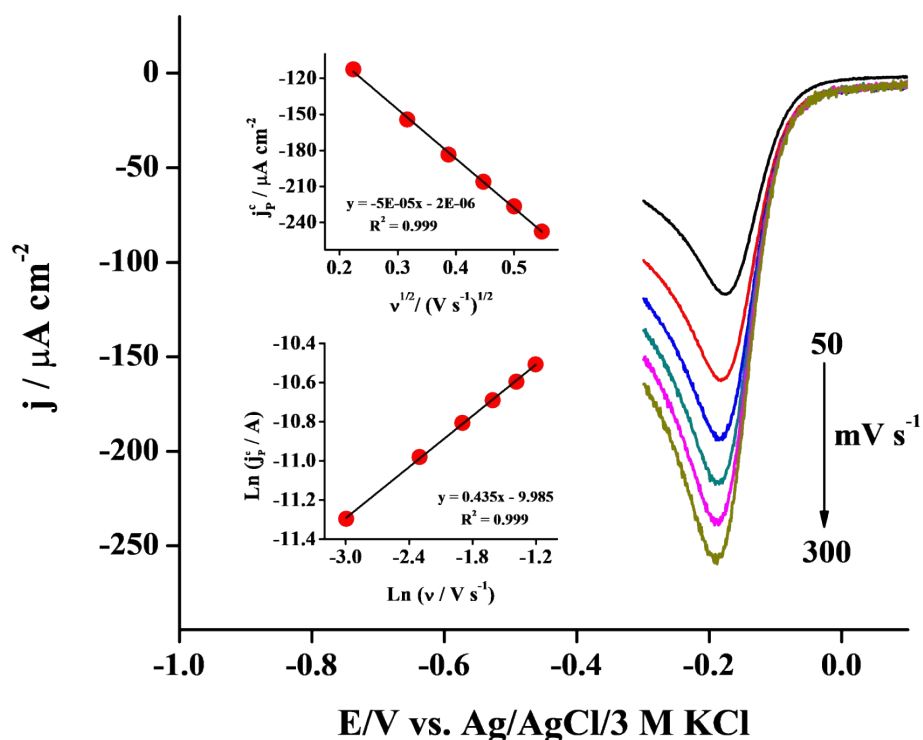


Figure S4. LSVs of 0.5 mM UO_2^{2+} in 1 M HNO_3 using PEDOT-PSS/GC electrode at different scan rates. Inset shows the plot of cathodic peak-current density (j_p^c) of UO_2^{2+} to U^{4+} reduction vs. square root of scan rate ($v^{1/2}$) and plot of $\text{Ln}|j_p^c|$ vs. $\text{Ln}(v)$.

LSV for U determination using GC in HNO_3 of different acid strength:

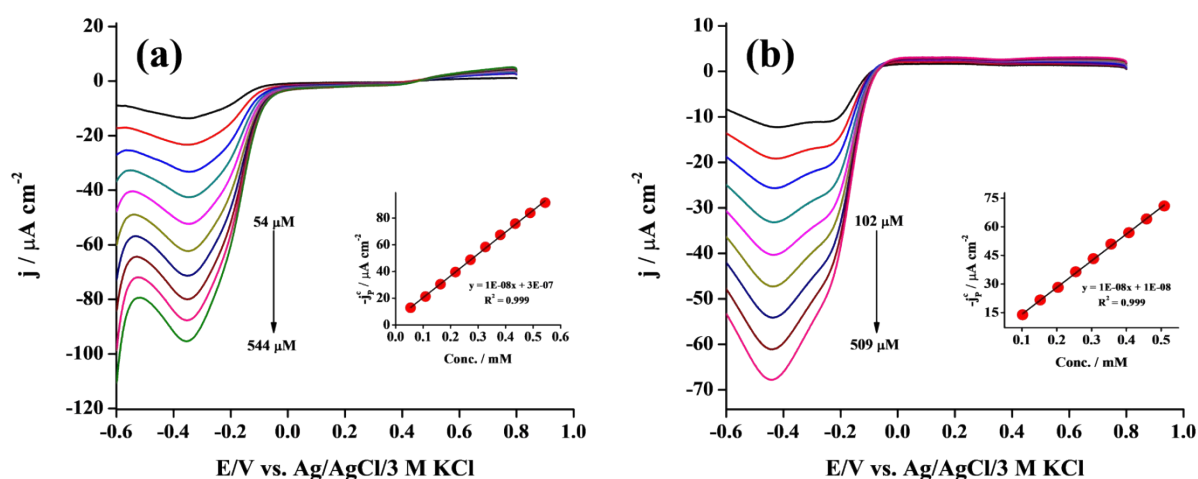


Figure S5. LSVs of different concentrations of UO_2^{2+} in (a) 1 M HNO_3 and (b) 0.05 M HNO_3 ; respectively using GC electrode at a scan rate of 100 mV s^{-1} . Inset shows the plot of corresponding cathodic peak current density (j_p^c) of $\text{U(VI)}/\text{U(IV)}$ couple versus U concentration.

Stability, repeatability and reproducibility of the PEDOT-PSS/GC electrode for determination of U in 0.05 M HNO₃:

Stability, repeatability and reproducibility are the key factors in evaluating the analytical method for application. The stability of the PEDOT-PSS/GC electrode was examined by recording CV of 0.1 mM UO₂²⁺ in 0.05 M HNO₃ for consecutive 25 cycles at a scan rate of 100 mV s⁻¹ (Figure S6). The peak-current density remains constant for successive CV cycling. The constancy in peak-current densities of UO₂²⁺ to UO₂ reduction up to 25 CV cycles confirms the stability of PEDOT-PSS/GC electrode in 0.05 M HNO₃ for U determination. The repeatability of the electrochemical response of the PEDOT-PSS/GC electrode for UO₂²⁺ to UO₂ reduction was confirmed by recording 6 repetitive LSVs of 0.1 mM UO₂²⁺ in 0.05 M HNO₃ at a scan rate of 100 mV s⁻¹ (Figure S7). A precise peak-current density (594 ± 5 μA cm⁻²) was observed. The reproducibility of the electrochemical response of the PEDOT-PSS/GC electrode for UO₂²⁺ to UO₂ reduction was confirmed by recording LSVs of 0.1 mM UO₂²⁺ in 0.05 M HNO₃ at a scan rate of 100 mV s⁻¹ using 3 different PEDOT-PSS/GC electrodes prepared by the same drop-casting procedure (Figure S8). A precise peak-current density (584 ± 13 μA cm⁻²) was observed. This confirms the electrochemical response of PEDOT-PSS is reproducible from one electrode to another.

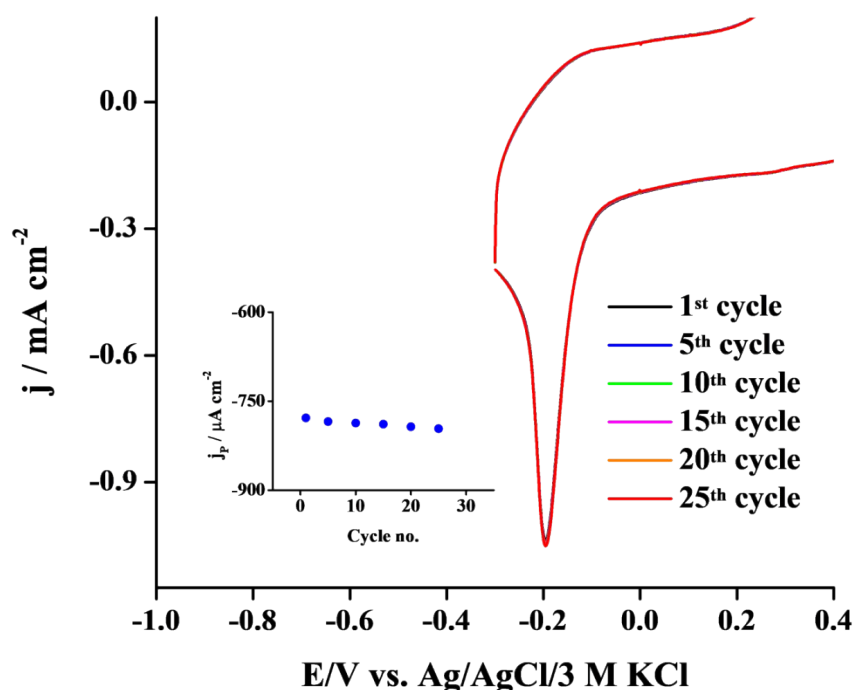


Figure S6. CVs (No blank subtraction) of 0.1 mM UO₂²⁺ in 0.05 M HNO₃ using PEDOT-PSS/GC electrode for consecutive 25 cycles at a scan rate of 100 mV s⁻¹. Only 1st, 5th, 10th, 15th, 20th, 25th cycles are shown for simplicity. Inset shows the plot of corresponding peak-current density (j_p^c) vs. CV cycle number.

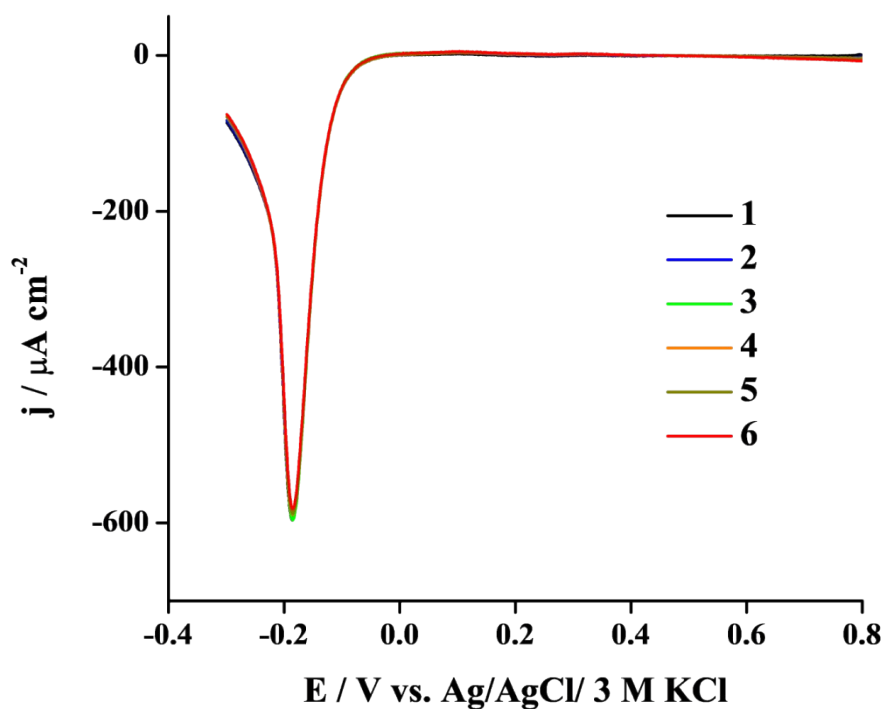


Figure S7. Repetitive CVs of 0.1 mM UO_2^{2+} in 0.05 M HNO_3 using PEDOT-PSS/GC electrode at a scan rate of 100 mV s^{-1} .

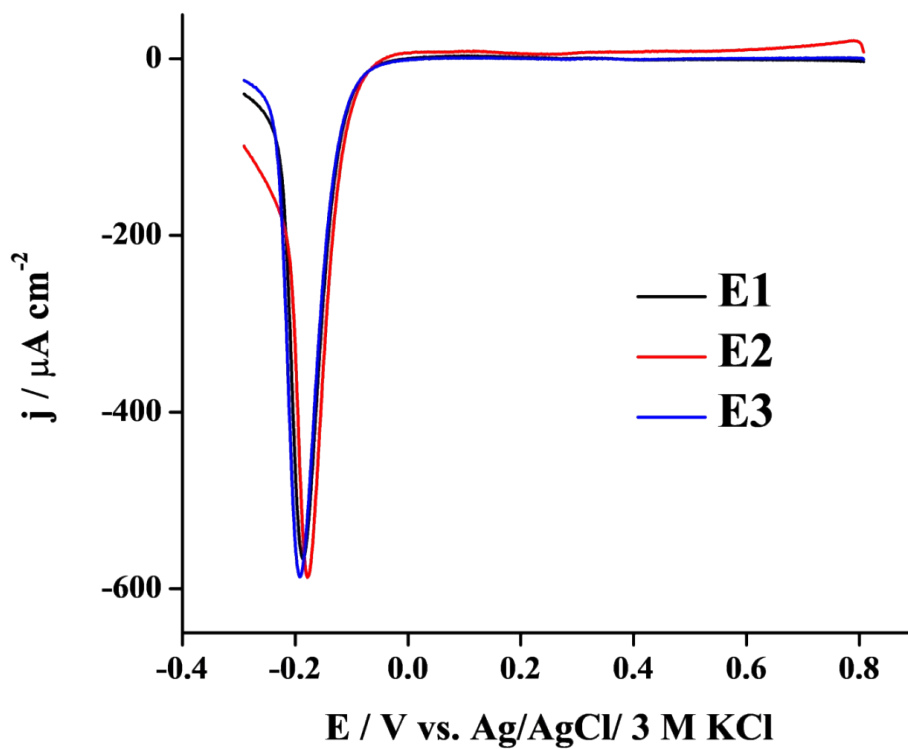


Figure S8. CVs of 0.1 mM UO_2^{2+} in 0.05 M HNO_3 using three different modified PEDOT-PSS/GC electrodes at a scan rate of 100 mV s^{-1} .

Interference study:

The interference of other elements in the cathodic stripping voltammetric determination of U was examined. CSVs of PEDOT-PSS/GC electrode in (i) absence and (ii) presence of Na^+ , K^+ , NH_4^+ , Ba^{2+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Hg^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} and Fe^{3+} ($10\ \mu\text{M}$ each) in $10\ \mu\text{M}$ UO_2^{2+} in $0.05\ \text{M}$ HNO_3 using a constant deposition potential ($-0.3\ \text{V}$) for $60\ \text{s}$ at a scan rate of $100\ \text{mV s}^{-1}$ (Figure S9) showed no change in peak current density of UO_2^{2+} to UO_2 reduction with appearance of two additional reduction peaks at $0.43\ \text{V}$ and $-0.09\ \text{V}$ corresponding to Fe(III)/Fe(II) and Cu(II)/Cu(0) reduction, respectively.^{3, 4} Unaltered peak current density of UO_2^{2+} to UO_2 reduction confirms the applicability of the present methodology for U determination in presence of most of the common cations such as Na^+ , K^+ , NH_4^+ , Ba^{2+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Hg^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} and Fe^{3+} ions in solution.

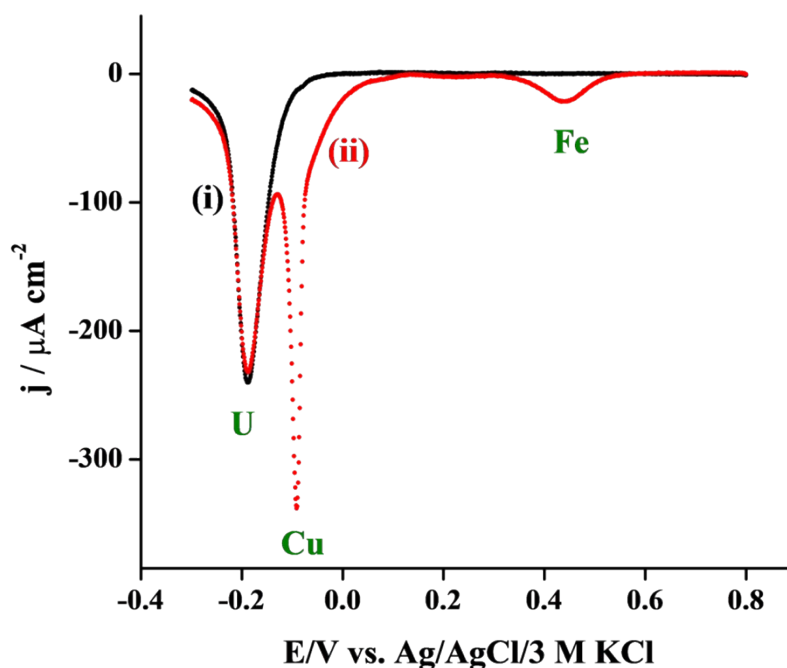


Figure S9. CSVs using constant deposition potential ($-0.3\ \text{V}$) for $60\ \text{s}$ in (i) $10\ \mu\text{M}$ UO_2^{2+} (black); (ii) mixed solution of UO_2^{2+} , Na^+ , K^+ , NH_4^+ , Ba^{2+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Hg^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} and Fe^{3+} ($10\ \mu\text{M}$ each) in $0.05\ \text{M}$ HNO_3 recorded with PEDOT-PSS/GC electrode at a scan rate of $100\ \text{mV s}^{-1}$.

LOD calculation:

$$LOD = \frac{3.3\sigma}{m}$$

Where, σ and m are the standard deviation of y-intercept of regression line and slope of the calibration plot, respectively.

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