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# Nitric acid concentration strongly influences low level uranium determination on PEDOT-PSS coated glassy carbon electrodes†

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Understanding the parametric optimization and addition of modifications in existing techniques are the keys to successful research in the analytical sciences. The present study reports an electro-analytical technique by modifying an electrode with PEDOT-PSS and adjusting the analyte solution to lower acidity (0.05 M) levels. The proposed methodology achieved a detection limit of 1.24 ppb of uranium, which is far below the available concentrations of uranium in seawater; the WHO permissible limit for uranium in drinking water; and the allowed disposal limit for uranium in radioactive waste solutions. Redox characteristics and speciation analysis supported by theoretical prediction helped to understand the basic mechanism which lay behind the achievement of such low detection limits. The technique was successfully employed for uranium determination in real water samples and the results were validated by another independent technique (ICP-MS).

Uranium is the most studied actinide element owing its extensive usage as a nuclear fuel material. The progress of nuclear energy is always associated with the challenges of handling, containing and concealing the radioactivity prior, during and after reactor operations. Uranium, being both a radiochemical and biological hazard, necessitates restricted release and high confinements. The concentration of uranium present or that could be disposed of depends on the primary source.<sup>1,2</sup> U reserves on land (~4.5 million tons) are scarce but abundant in sea water (~1000 times those on land), and this can be a rich U resource if we are able to efficiently extract U from sea

water. However, selective extraction of U from sea water is highly challenging owing to the ultralow of U concentration in sea water (3.3 ppb).<sup>3,4</sup> Thus it is of great importance to develop a sensitive method for trace level determination of U, to limit its exposure to aquatic and biological environments, for the selective extraction of U for the use of U as nuclear fuel in nuclear reactors, as well as to check that nuclear effluents to fall below the disposal limits.  $\alpha$ -Spectroscopy,<sup>5,6</sup> neutron activation analysis,<sup>7,8</sup> and inductively coupled mass spectrometry<sup>9,10</sup> are commonly employed to determine U at trace and ultra-trace levels. But these techniques are limited by their high-cost, requirements for specialized personnel, and non-portability outside of sophisticated laboratories. The electrochemical method with all these advantages offers a good choice for developing an analytical procedure to detect uranium.<sup>11</sup> Stripping voltammetry attains lower detection limits among the electroanalytical techniques owing to the added advantage of pre-concentration on the electrode prior to determination.

Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) is a widely used conducting polymer for the preparation of low-cost chemically-modified electrodes because of its high stability, aqueous processability, low cost, and high electrical conductivity.<sup>12</sup> PEDOT is water-insoluble and for aqueous processability, it is doped with the surfactant PSS.<sup>13</sup> Herein, we report the very low level of U determination down to ppb level using cathodic stripping voltammetry (CSV) using a PEDOT-PSS/glassy carbon (PEDOT-PSS/GC) electrode in aqueous medium. At first, the electrochemistry of U was explored in nitric acid using a PEDOT-PSS/GC electrode and it was observed that the height of the U(vi) to U(iv) reduction peak increases with decreases in nitric acid concentration.‡ Energy Dispersive Spectroscopy (EDS), a speciation study and Density Functional Theory (DFT) was used to understand the mechanism responsible for such nitric acid concentration dependence of the electrochemical response of the U(vi) to U(iv) reduction peak on the PEDOT-PSS/GC electrode. The large peak heights of the U(vi) to U(iv) reduction peak at low

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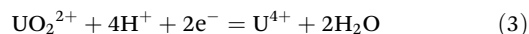
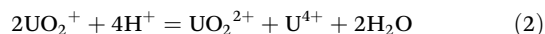
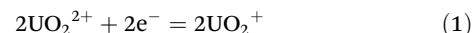
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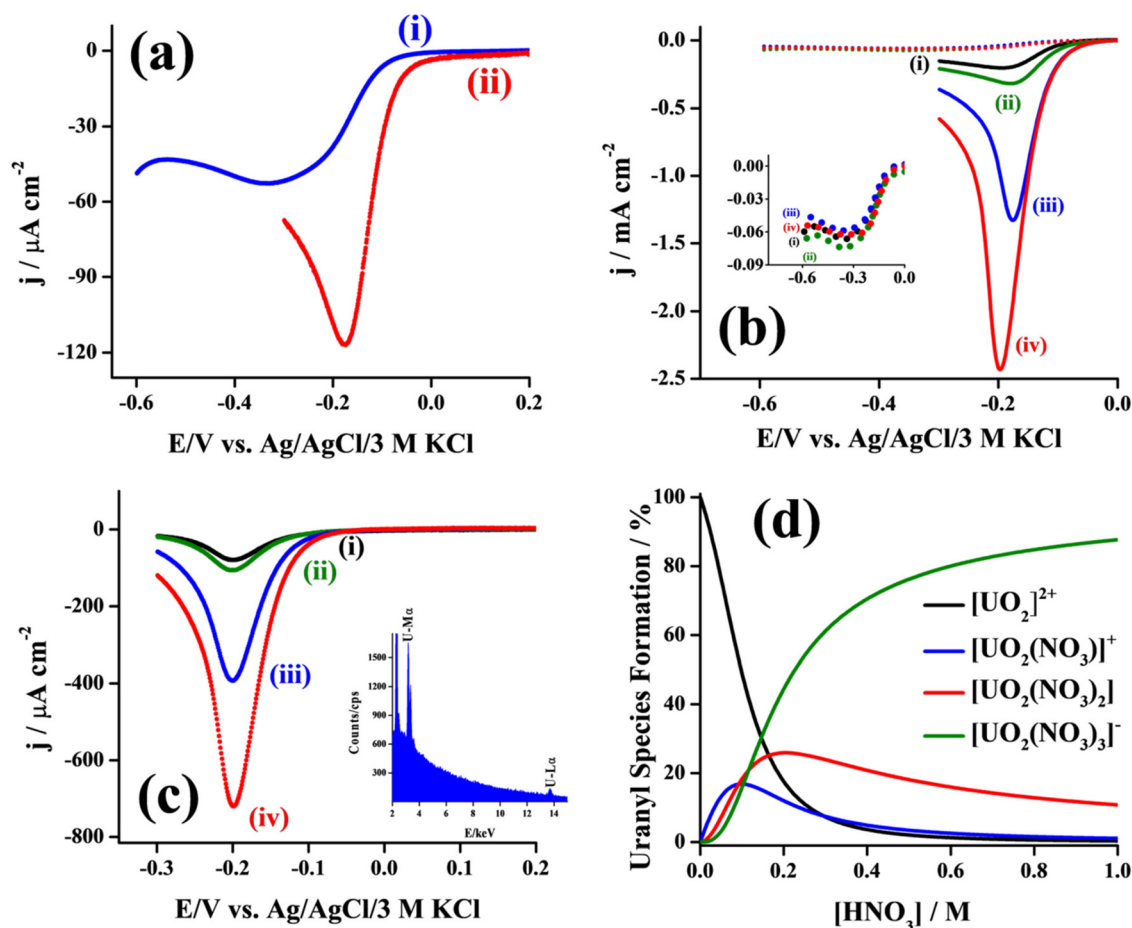
nitric acid molarity has analytical importance. Linear sweep voltammetry (LSV) results show a drastic improvement in the detection limit for U is observed with lowering the nitric acid concentration which facilitates more  $\text{UO}_2^{2+}$  ion adsorption on PEDOT-PSS and 0.05 M  $\text{HNO}_3$  is the preferred choice for trace level U determination in aqueous medium. To bring down the detection limit for U determination even further, the dual advantage of 0.05 M  $\text{HNO}_3$  is utilized in which the adsorbed  $\text{UO}_2^{2+}$  is electrochemically reduced to water insoluble  $\text{UO}_2$  which precipitates and pre-concentrates U at the PEDOT-PSS/GC electrode surface. Eventually, a detection limit of as low as 1.24 ppb of U was achieved using cathodic stripping voltammetry (CSV). The present methodology is evaluated with a real water sample and the results are also validated with inductively coupled plasma mass spectrometry (ICP-MS).

LSVs of 0.5 mM  $\text{UO}_2^{2+}$  in 1 M  $\text{HNO}_3$  using (i) GC and (ii) PEDOT-PSS/GC electrodes been recorded (Fig. 1a); wherein GC showed a cathodic peak at  $-0.330$  V with a peak current density of  $51.7 \mu\text{A cm}^{-2}$  ('i' in Fig. 1a) which corresponds to the reduction of  $\text{UO}_2^{2+}$  to  $\text{U}^{4+}$ . The reduction proceeds through

conversion of  $\text{UO}_2^{2+}$  to  $\text{UO}_2^+$  (eqn (1)); and the instantaneous disproportionation of  $\text{UO}_2^+$  into  $\text{UO}_2^{2+}$  and  $\text{U}^{4+}$  (eqn (2)).<sup>14,15</sup> Thus, all  $\text{UO}_2^{2+}$  reduces into  $\text{U}^{4+}$  at  $-0.330$  V as a result of fast disproportionation of  $\text{UO}_2^+$  in an acidic medium (eqn (3)).



The modification of the GC electrode by PEDOT-PSS shifted the  $\text{UO}_2^{2+}$  to  $\text{U}^{4+}$  reduction peak to  $-0.174$  V with an increased peak-current density ( $-112.5 \mu\text{A cm}^{-2}$ ) ('ii' in Fig. 1a). Thus, the energy barrier for electron transfer between the electrode and  $\text{UO}_2^{2+}$  centres is significantly reduced at PEDOT-PSS and shows enhanced electrochemical response as compared to GC.<sup>15</sup> The electrochemical response for  $\text{UO}_2^{2+}$  reduction at both GC and PEDOT-PSS/GC followed a linear variation in peak current with square root of scan rate ( $\sqrt{v}$ ) (Fig. S3 and S4†) and had slopes for  $\ln(j_p^c)$  ( $j_p^c$  = cathodic peak-current



**Fig. 1** (a) LSVs of 0.5 mM  $\text{UO}_2^{2+}$  in 1 M  $\text{HNO}_3$  using (i) GC (blue line) and (ii) PEDOT-PSS/GC (red line) at a scan rate of  $50 \text{ mV s}^{-1}$ . (b) LSVs of 0.5 mM  $\text{UO}_2^{2+}$  using GC (dotted line) and PEDOT-PSS/GC (solid line) at a scan rate of  $100 \text{ mV s}^{-1}$  at different acid strengths (i) 1 M, (ii) 0.5 M, (iii) 0.1 M and (iv) 0.05 M  $\text{HNO}_3$ ). Inset shows the zoomed portion of GC electrode. (c) LSVs of PEDOT-PSS/GC electrode in 0.05 M  $\text{HNO}_3$  at a scan rate of  $100 \text{ mV s}^{-1}$  after dipping the electrode in 0.5 mM  $\text{UO}_2^{2+}$  in (i) 1 M; (ii) 0.5 M; (iii) 0.1 M and; (iv) 0.05 M  $\text{HNO}_3$ , respectively for 10 minutes. Inset shows the EDS spectra of PEDOT-PSS/GC electrode after  $\text{UO}_2^{2+}$  adsorption. (d) Species distribution of  $\text{UO}_2^{2+}$  with variation in  $\text{HNO}_3$  acid concentration.

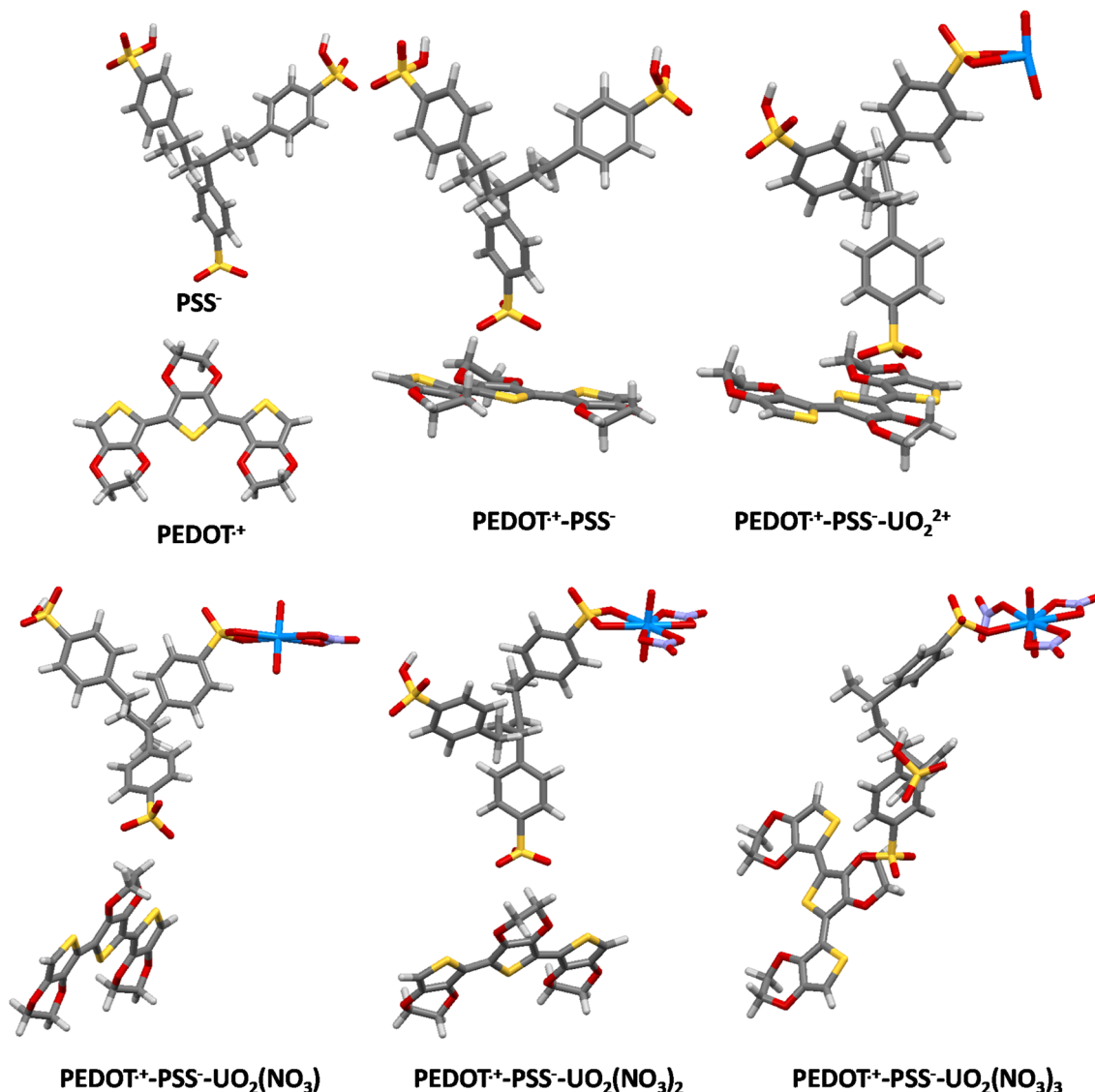
density) versus  $\ln(\theta)$  of 0.36 for GC, and 0.43 for PEDOT-PSS/GC, indicating a purely diffusion controlled process for  $\text{UO}_2^{2+}$  reduction at both the electrodes. LSVs of 0.5 mM  $\text{UO}_2^{2+}$  at various acid strengths of  $\text{HNO}_3$  (1 M to 0.05 M) using both GC (dotted line in Fig. 1b) and PEDOT-PSS/GC (solid line in Fig. 1b) electrodes at a scan rate of  $100 \text{ mV s}^{-1}$  were recorded to find out the effect of pH on the  $\text{UO}_2^{2+}/\text{U}^{4+}$  couple. The peak current density of  $\text{U(VI)}$  to  $\text{U(IV)}$  reduction is constant on GC but increases drastically on PEDOT-PSS/GC with a decrease in acid strength (concentration of  $\text{HNO}_3$ ). To get more insight, four different PEDOT-PSS/GC electrodes were dipped in 0.5 mM  $\text{UO}_2^{2+}$  in 1 M, 0.5 M, 0.1 M and 0.05 M  $\text{HNO}_3$ , respectively for 10 minutes, washed several times with Milli-Q water and then the LSV of each electrode was recorded in blank solution (0.05 M  $\text{HNO}_3$ ) at a scan rate of  $100 \text{ mV s}^{-1}$  (Fig. 1c). A reduction peak at  $-0.172 \text{ V}$  was observed in each case which signifies uranyl ion adsorption on PEDOT-PSS.<sup>16</sup> But the height of the  $\text{U(VI)}$  to  $\text{U(IV)}$  reduction peak current is greater at lower acidity (0.05 M  $\text{HNO}_3$ ) which signifies the amount of  $\text{UO}_2^{2+}$  ions adsorption on PEDOT-PSS/GC electrodes increases with a decrease in nitric acid strength. The same experiment was performed with bare GC electrode but no adsorption of  $\text{UO}_2^{2+}$  was observed. To further confirm uranyl adsorption on PEDOT-PSS, the PEDOT-PSS/GC electrode was dipped in 0.1 M  $\text{UO}_2^{2+}$  in 0.05 M  $\text{HNO}_3$  overnight, washed several times with Milli-Q water and the EDS spectrum of the electrode was recorded (inset of Fig. 1c). The EDS spectrum confirms  $\text{UO}_2^{2+}$  adsorption on PEDOT-PSS. Because of the  $\text{UO}_2^{2+}$  adsorption, the energy barrier for electron transfer between the electrode and  $\text{UO}_2^{2+}$  centres is significantly reduced at PEDOT-PSS and shows enhanced electrochemical response as compared to GC (Fig. 1a).

Speciation analysis depicting the percentage of free and complexed uranyl ions present in solution with variation in acid concentration (Fig. 1d) would be a useful tool to interpret the observation of high peak current densities at lower acidity.  $\text{UO}_2^{2+}$  ions get adsorbed on the surface of PEDOT-PSS/GC due to interaction with negatively charged  $\text{PSS}^-$ .<sup>17–20</sup>  $\text{UO}_2^{2+}$  is expected to form  $[\text{UO}_2(\text{NO}_3)]^+$ ,  $[\text{UO}_2(\text{NO}_3)_2]$  and  $[\text{UO}_2(\text{NO}_3)_3]^-$  species in solution. Thus, the free  $\text{UO}_2^{2+}$  and  $[\text{UO}_2(\text{NO}_3)]^+$  species possess high electrostatic attraction for  $\text{PSS}^-$  anions, while  $[\text{UO}_2(\text{NO}_3)_2]$  and  $[\text{UO}_2(\text{NO}_3)_3]^-$  species would be non-interacting with  $\text{PSS}^-$  anions and would remain in solution rather than getting adsorbed on the electrode. The speciation plot (Fig. 1d) shows that at lower acidity (0.05 M)  $\text{UO}_2^{2+}$  (~77%) and  $[\text{UO}_2(\text{NO}_3)]^+$  (~13%) are the dominant species, while at higher acidity (>0.3 M),  $[\text{UO}_2(\text{NO}_3)_2]$  and  $[\text{UO}_2(\text{NO}_3)_3]^-$  species amount to ~24% and ~61% of the species formation respectively. Thus, the lower acidity allows more  $\text{UO}_2^{2+}$  ions to get adsorbed on PEDOT-PSS/GC electrode, while the increase in acidity facilitates the formation of non-adsorbing  $[\text{UO}_2(\text{NO}_3)_2]$  and  $[\text{UO}_2(\text{NO}_3)_3]^-$  species, and thereby decreasing the peak current densities and hence the sensitivity (Fig. 1b).

A molecular-level understanding of the interaction of different species with the same substrate could shed light on key factors (energetics, bond distances, partial charges)

responsible for the differential binding of one species over another. Zotti *et al.* experimentally showed that a trimer of PEDOT possesses a mono-positive charge and PSS in mono-negative form interacts with PEDOT radical ions.<sup>21</sup> Thus, the present studies also employed the trimer units of PEDOT and PSS for optimization of PEDOT-PSS structures initially.  $\text{UO}_2^{2+}$  is expected to form  $[\text{UO}_2(\text{NO}_3)]^+$ ,  $[\text{UO}_2(\text{NO}_3)_2]$  and  $[\text{UO}_2(\text{NO}_3)_3]^-$  species in solution depending on the concentration of  $\text{HNO}_3$ . Thus, the optimized geometry was configured with  $\text{UO}_2^{2+}$  and its nitrate species on the other ends of the PSS moiety for geometry optimization of PEDOT-PSS- $\text{UO}_2^{2+}$ - $\text{NO}_3$  species. Geometry optimization by the combination of B3-LYP functional and def-SVP basis set followed by energetics calculations using the def-TZVP basis set using density functional theory (DFT) was found to be appropriate to interpret the uranyl speciation at molecular level.<sup>22–24</sup> Thus, the present studies also employed a similar protocol for geometry optimization and energetics estimation of PEDOT, PSS, PEDOT-PSS, PEDOT-PSS- $\text{UO}_2^{2+}$ , 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. Two C–O bonds formed by carbon atoms common to dioxy and thiophene rings in the centre monomer of the PEDOT trimer with the two oxygen atoms of sulphonate group of PSS, and an intermolecular hydrogen bonding (O–H) between hydrogen of  $\text{CH}_2$  from PEDOT and the third oxygen of PSS group results in the formation of the PEDOT-PSS species (Fig. 2). The sulphonate group on the opposite end to the PEDOT edge in PEDOT-PSS is attached with  $\text{UO}_2^{2+}/\text{UO}_2(\text{NO}_3)/\text{UO}_2(\text{NO}_3)_2/\text{UO}_2(\text{NO}_3)_3$  for geometry optimization of PEDOT-PSS- $\text{UO}_2^{2+}$ /its nitrate species. The binding energies as well as Gibbs free energies for the formation of PEDOT-PSS- $\text{UO}_2^{2+}$  species were found to be more negative than PEDOT-PSS- $\text{UO}_2^{2+}$ -nitrate species. Relatively more negative values (Table T1, ESI†) indicate the preferential binding of  $\text{UO}_2^{2+}$  to PEDOT-PSS over its nitrate species and the same is attributed to the experimentally observed higher peak currents for  $\text{UO}_2^{2+}$  at lower  $\text{HNO}_3$  concentrations (Fig. 1b). Further, to gain deeper insights, the bond distances and partial charges on binding moieties were also estimated using DFT at TZVP level. U and its nitrate species interact through the PSS moiety at the sulphonate group by U–O bond formation in the PEDOT-PSS interface. The calculated bond distances for the U–O bond are found to be shorter in PEDOT-PSS- $\text{UO}_2$  (2.21 Å, 2.22 Å) compared to PEDOT-PSS- $\text{UO}_2(\text{NO}_3)$  (2.38 Å, 2.39 Å) and PEDOT-PSS- $\text{UO}_2(\text{NO}_3)_2$  (2.51 Å, 2.51 Å), while in PEDOT-PSS- $\text{UO}_2(\text{NO}_3)_3$ , uranium binds through the single oxygen of sulphonate group, further affirming the preferential binding for  $\text{UO}_2^{2+}$  over its nitrate species by PEDOT-PSS.

The enhanced peak current of  $\text{U(VI)}$  to  $\text{U(IV)}$  reduction at lower nitric acid concentration signifies the analytical importance of the PEDOT-PSS/GC electrode for the determination of U at trace levels. Peak current densities measured by LSV at PEDOT-PSS/GC electrode showed a linear relation with  $\text{UO}_2^{2+}$  concentration at two different acidities (1 & 0.05 M  $\text{HNO}_3$ ; Fig. 3a & b). The limit of detection (LOD) of U on PEDOT-PSS/GC was estimated to be 9.97 and 0.32  $\mu\text{M}$  in 1 and 0.05 M

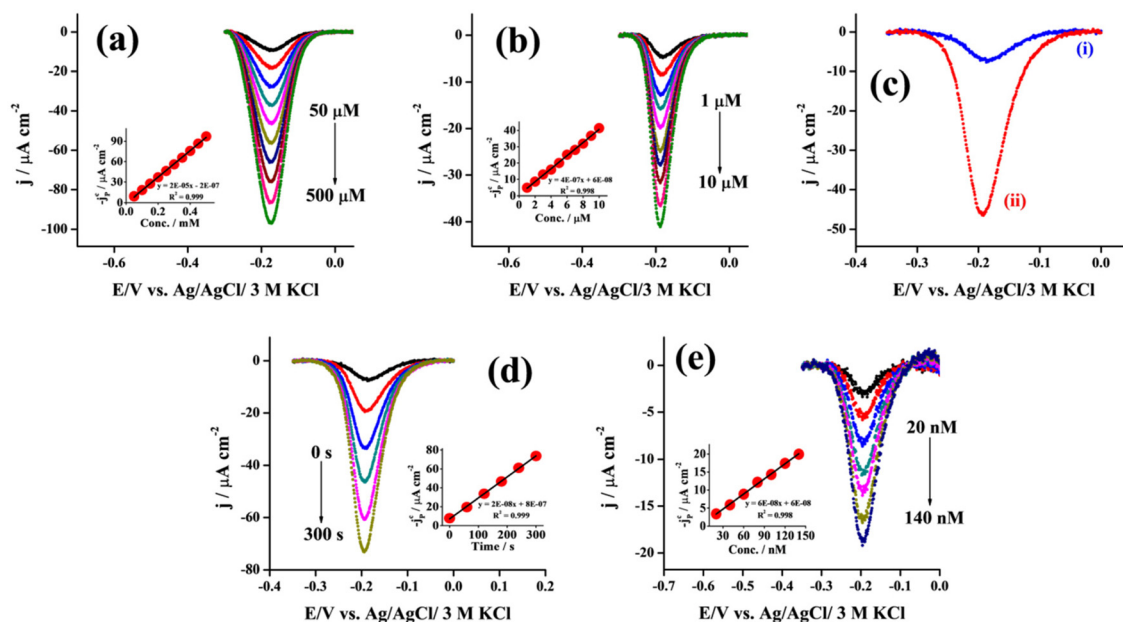


**Fig. 2** Optimized geometries for PEDOT, PSS, PEDOT-PSS, PEDOT-PSS- $\text{UO}_2$ , PEDOT-PSS- $\text{UO}_2(\text{NO}_3)$ , PEDOT-PSS- $\text{UO}_2(\text{NO}_3)_2$ , PEDOT-PSS- $\text{UO}_2(\text{NO}_3)_3$  species. Colour code: yellow – sulfur (S), red – oxygen (O), grey – carbon (C), white – hydrogen (H), blue – uranium (U).

$\text{HNO}_3$ , respectively. The improvement in LOD of U in 0.05 M  $\text{HNO}_3$  on PEDOT-PSS is ascribed to more  $\text{UO}_2^{2+}$  adsorption on PEDOT-PSS at lower acidity which results in an enhancement in the peak-current density. The LOD of U was also determined on bare GC electrode and is found to be 10  $\mu\text{M}$  of U irrespective of acid strength (Fig. S5†). Therefore, PEDOT-PSS/GC as the electrode and 0.05 M  $\text{HNO}_3$  as the solution medium are ideal choices for U determination at low levels. Besides, 0.05 M  $\text{HNO}_3$  as the solution medium has dual advantages. It not only results in more  $\text{UO}_2^{2+}$  adsorption on PEDOT-PSS but electrochemical reduction of the adsorbed  $\text{UO}_2^{2+}$  in 0.05 M  $\text{HNO}_3$  results in formation of neutral  $\text{UO}_2$  which is water insoluble and precipitates on the electrode surface. But the same in 1 M  $\text{HNO}_3$  results in the formation of water soluble  $\text{U}^{4+}$  which diffuses away from the electrode surface.<sup>1,25</sup> This can be further exploited as an efficient tool to pre-concentrate U as

$\text{UO}_2$  on the electrode surface by applying a constant negative potential (−0.3 V) followed by scanning towards negative potentials which results higher reduction currents. Hence, Cathodic Stripping Voltammetry (CSV) is exploited to further improve the LOD of U in 0.05 M  $\text{HNO}_3$  on PEDOT-PSS/GC. Fig. 3c shows the CSVs of 1  $\mu\text{M}$   $\text{UO}_2^{2+}$  (i) without and (ii) with pre-concentration of  $\text{UO}_2$  at a fixed deposition potential (−0.3 V) for 180 s which shows an enhancement in peak-current density of the  $\text{UO}_2^{2+}$  to  $\text{UO}_2$  reduction peak. Next, CSVs of 1  $\mu\text{M}$   $\text{UO}_2^{2+}$  were recorded for different deposition times at a constant negative potential of −0.3 V (Fig. 3d). They show a linear correlation of peak-current density *versus* deposition time. More  $\text{UO}_2$  gets precipitated at the electrode surface as deposition time increases and this results in a higher peak current. CSVs of different concentrations of  $\text{UO}_2^{2+}$  were recorded at a fixed deposition potential of −0.3 V for 300 s





**Fig. 3** LSVs of different concentrations of  $\text{UO}_2^{2+}$  in (a) 1 M  $\text{HNO}_3$  and (b) 0.05  $\text{HNO}_3$  using a PEDOT-PSS/GC electrode at a scan rate of  $100 \text{ mV s}^{-1}$ . Insets show the plot of peak-current density versus U concentration. CSVs of PEDOT-PSS/GC electrode in (c)  $1 \mu\text{M}$   $\text{UO}_2^{2+}$  in 0.05 M  $\text{HNO}_3$  (i) without and (ii) with pre-concentration of  $\text{UO}_2$  at a fixed deposition potential ( $-0.3 \text{ V}$ ) for 180 s; (d)  $1 \mu\text{M}$   $\text{UO}_2^{2+}$  in 0.05 M  $\text{HNO}_3$  at a fixed deposition potential ( $-0.3 \text{ V}$ ) for different deposition times; inset shows the plot of peak-current density versus deposition time; (e) different concentrations of  $\text{UO}_2^{2+}$  in 0.05  $\text{HNO}_3$  at a fixed deposition potential ( $-0.3 \text{ V}$ ) for 300 s. Inset shows the plot of peak-current density versus U concentration. All the CSVs are recorded at a scan rate of  $100 \text{ mV s}^{-1}$ .

using PEDOT-PSS/GC electrode (Fig. 3e), and it was observed that the peak-current density increases linearly with increase in U concentration. The LOD of U was found to be  $5.21 \text{ nM}$  ( $1.24 \text{ ppb}$ ) of U. The present methodology was tested to quantify U in a real water sample obtained from the Municipal Corporation of Greater Mumbai (MCGM). The water molarity was adjusted to 0.05 M  $\text{HNO}_3$  and U was not detected in MCGM supplied water and so it is spiked with a known quantity of  $\text{UO}_2^{2+}$  (20 nM). Initially, CSVs of the spiked water were recorded followed by standard solutions of  $\text{UO}_2^{2+}$  in 0.05 M  $\text{HNO}_3$  of varying concentrations. A linear correlation of peak currents versus U concentration was obtained. The amount of U present in spiked water is determined as  $19.24 \pm 0.19 \text{ nM}$  (repeatable measurements,  $n = 3$ ). The same sample was tested with ICP-MS and concentration of U was found out to be  $19.36 \pm 0.12 \text{ nM}$ .

The electrochemical response of the PEDOT-PSS/GC in  $\text{UO}_2^{2+}$  in 0.05 M  $\text{HNO}_3$  is found to be repeatable, reproducible and stable (Fig. S6–S8†) and also free from the interference of other metal ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$ ) present in aqueous medium (Fig. S9†).

In summary, the crucial role of nitric acid concentration for determining very low levels of U on a PEDOT-PSS/GC electrode is discussed in the manuscript. LSV, speciation and DFT studies shows that the preferential binding of free  $\text{UO}_2^{2+}$  to PEDOT-PSS over its nitrate species ( $[\text{UO}_2(\text{NO}_3)]^+$ ,  $[\text{UO}_2(\text{NO}_3)_2]$  and  $[\text{UO}_2(\text{NO}_3)_3]^-$ ) in low nitric acid strength is the main

reason for obtaining very low detection limits for  $\text{UO}_2^{2+}$  on a PEDOT-PSS coated GC electrode. The insolubility of  $\text{UO}_2$  in 0.05 M  $\text{HNO}_3$  is an added advantage to bring the LOD of U down to the ppb level.

## Author contributions

Rahul Agarwal: conceptualization, data curation, formal analysis, investigation, methodology, resources, validation, writing – original draft, writing – review & editing; Rama Mohana Rao Dumpala: data curation, methodology, validation, writing – review & editing and Manoj K Sharma: resources and supervision.

## Conflicts of interest

The authors declare no competing financial interest.

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## References

$^{238}\text{U}$  ( $t_{1/2} = 4.5 \times 10^9$  years) is a  $\alpha$ -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.

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