Electronic Supplementary Information

Facile and Ultra-Sensitive Voltammetric Electrodetection of Hg²⁺ in Aqueous Media Using Electrodeposited AuPtNPs/ITO

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Figure S7. FESEM micrographs of bimetallic AuPtNPs/ITO electrodeposited by chronoamperometry at a constant overpotential of -300 mV_{SCE} for a duration of A) 150 sec., and B) 300 sec. Solution: 0.5 mM HAuCl₄ + 0.5 mM H₂PtCl₆.

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Figure S1. Bare ITO and ITO after modification with different types of NPS

Section S1. Repetitive Cyclic Voltammetric Electrodeposition of Au, Pt, and AuPt NPs on ITO

Fig. S1 (A-C) represents the successive CV deposition of AuNP, PtNP, and AuPtNPs on ITO substrates, respectively. Gold and platinum metallic complexes should move toward the electrode surface from bulk solution under an unstirred condition. The diffusion of the metallic complexes toward the surface leads to the formation of a concentration gradient adjacent to the electrode interface. Each characteristic peak in voltammograms is representative of an individual step (as depicted in Fig. S1) for an overall electrochemical reaction. Contrary to the organic electrolytes and ionic liquids, in aqueous solutions, the appearance of $AuCl_2^-$ species is thermodynamically less favorable.^{1,2} The most feasible reduction pathway for $AuCl_4^-$ to metallic gold occurs through a stepwise tow-then one-electron process, or an overall direct three-electron transfer process as follows:^{2, 3}

$$\operatorname{AuCl}_{4(aq)}^{-} + 3e^{-} \rightarrow \operatorname{Au}_{(s)}^{-} + 4\operatorname{Cl}_{(aq)}^{-}$$
(S1)

It is claimed that Reaction (S1) takes place through several steps, where $AuCl_4^-$ is firstly reduced according to the following Reaction (S2):

$$\operatorname{AuCl}_{4\,(\mathrm{aq})}^{-} \to \operatorname{AuCl}_{2\,(\mathrm{aq})}^{+} + 2\operatorname{Cl}_{(\mathrm{aq})}^{-} \tag{S2}$$

and subsequently, the process proceeds with two consecutive charge-transfer steps to the point where Au ad-atoms are electrodeposited on the electrode surface:¹

$$\operatorname{AuCl}_{2}_{(aq)}^{+} + 2e^{-} \to \operatorname{AuCl}_{2}_{(aq)}^{-}$$
(S3)

$$\operatorname{AuCl}_{2(aq)}^{-} + e^{-} \to \operatorname{Au}_{(s)}^{-} + 2\operatorname{Cl}_{(aq)}^{-}$$
(S4)

In other words, Reaction (S1) occurs via a two-step reaction as follows:²

$$\operatorname{AuCl}_{4}^{-} + 2e^{-} \to \operatorname{AuCl}_{2}^{-} + 2Cl^{-}$$
(S5)

$$AuCl_{2}^{-} + e^{-} \rightarrow Au_{(s)}^{-} + 2Cl^{-}$$
(S6)

The peaks that appeared in the potential range from -0.07 to +0.02 V in Fig. S1(A) are attributed to Reaction (S5), and those around -0.45 V correspond to the reduction of AuCl₄⁻ to AuCl₂⁻ through Reaction (S6)². With increasing the number of cycles from 1 to 6, the peak current is decreased due to the consumption of AuCl₄⁻ complexes in the diffusion

layer at the earlier scans⁴. The broad peak during the reverse scan at the potential of about +0.3 V may be due to the instability of the initial deposited Au clusters and their partial dissolution.³ It is important to maintain the appropriate pH condition of the aqueous gold solution to control the state of the metal precursor during the electrodeposition. The staircase CV of ITO in 1 mM H₂PtCl₆ at the scan rate of 50 mV.s⁻¹ is also illustrated in Fig. S1(B). The peak appeared between -0.33 to -0.42 mV corresponds to the reduction of Pt (IV) through the following Reaction (S7):⁵

$$PtCl_{6}^{2-} + 4e^{-} \rightarrow Pt + 6Cl^{-}$$
(S7)

It has been acknowledged elsewhere that Reaction (S7) corresponds to the reduction of platinum in the chloroplatinic acid electrolyte, which takes place through two consecutive steps as:^{6,7}

$$PtCl_{6}^{2-} + 2e^{-} \rightarrow PtCl_{4}^{2-} + 2Cl^{-}$$
(S8)

$$PtCl_4^2 + 2e^- \rightarrow Pt + 4Cl^-$$
(S9)

The broad peaks in more negative potentials around -0.5 V vs. SCE are primarily caused by the combined effect of the hydrogen reduction reaction on nucleated Pt clusters and partial reduction of PtCl₄⁻ to Pt ad-atoms.⁵ The desorption peak of H₂ evolution did not appear for AuNP, which indicates the much faster kinetics of H₂ evolution on platinum compared to gold.⁸ The consecutive cyclic scans for deposition of AuPtNPs on ITO in 0.5 mM HAuCl₄ +0.5 mM H₂PtCl₆ solution is depicted in Fig. S1(C). Three characteristic peaks were obtained during the reduction sweeping at the potentials of about +0.22 V, -0.29 V, and -0.65 V vs. SCE, which represent the reduction of AuCl₄⁻, and PtCl₆²⁻ complexes to Au and Pt, respectively, according to the pathways described in Fig. S1(C). The atomic ratio of Au/Pt in deposited AuPtNPs will not be 0.5/0.5 (as it is in the electrolyte), which is mainly ascribed to the difference reduction potentials of Au and Pt on ITO. There is a slight positive shift in the peak potentials by increasing the number of cycles from 1 to 6 because of the lower activation energy requirement when AuPtNPs gradually form on the substrate after each scan.⁹ AuNPs tend to crystallize at the surface of ITO first before PtNPs because of their lower reduction potential. The Au ad-atom nucleation can effectively prompt the deposition of Pt ad-atoms to assemble the bimetallic AuPtNPs during consecutive scans.^{10,11}



Figure S2. Successive CVs recorded for ITO electrode immersed in A) 1 mM HAuCl₄ B) 1 mM H₂PtCl₆, and C) 0.5 mM HAuCl₄ +0.5 mM H₂PtCl₆ solutions (solution volume = 50 mL), scan rate: 50 mV.s⁻¹.





Figure S3. |i|-t transients recorded during the electrodepositin of A) AuNPs on ITO in 1 mM HAuCl₄, and B) AuPtNPs on ITO in 0.5 mM HAuCl₄ + 0.5 mM H₂PtCl₆ solutions at different reduction overpotentials (solution volume = 50 mL).



Figure S4. FESEM micrographs of ITO glass before electrodeposition.

Figure S5



Figure S5. FESEM micrographs of bimetallic AuPtNPs modified ITO electrodes prepared by chronoamperometry from 0.5 mM HAuCl₄ + 0.5 mM H₂PtCl₆ solution during 150 s electrodeposition at overpotentials of A) –300, B) –350 and C) –450 mV vs. SCE.



Figure S6. FESEM micrographs of bimetallic AuPtNPs/ITO electrodeposited by repetitive CVs for A) 6, and B) 3 number of scans. Solution: $0.5 \text{ mM HAuCl}_4 + 0.5 \text{ mM H}_2\text{PtCl}_6$ (Scan rate 50 mV.s⁻¹).



Figure S7. FESEM micrographs of bimetallic AuPtNPs/ITO electrodeposited by chronoamperometry at a constant overpotential of -350 mV_{SCE} for a duration of A) 150 sec., and B) 300 sec. Solution: 0.5 mM HAuCl₄ + 0.5 mM H₂PtCl₆.



Figure S8. Successive CVs recorded during PtNPs deposition on ITO for A) 3, B) 6, and C) 10 cycles.

Section S2. References

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