

# Supporting Information

## Arsenic (III) Detection with Underpotential Deposition and Anodic Stripping Voltammetry

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## Section 1: Calculation of the coverage of Pt nanoparticles on the surface of a glassy carbon electrode (GCE)

To estimate the approximate coverage of nanoparticles in terms of monolayers deposited a cubic close packed arrangement was considered. The Pt nanoparticles as purchased from NanoComposix, have a diameter of ca 30 nm. Hence the area occupied by a single particle on the electrode is  $9 \times 10^{-16} \text{ m}^2$  (Figure S1). The particle concentration of the Pt nanoparticles used were  $1.8 \times 10^{11} \text{ particles mL}^{-1}$  [1] and there were 5  $\mu\text{L}$  of Pt nanoparticles suspension dropped onto the electrode. Thus, the number of particles that dropped onto the electrode can be estimated as  $9 \times 10^8$  particles.

For 5  $\mu\text{L}$  of Pt nanoparticles suspension, the covered/blocked area of particles by the nanoparticles is:

$$9 \times 10^{-16} \text{ m}^2 \times 9 \times 10^8 \text{ particles} = 0.008 \text{ cm}^2$$

The particles were drop casted on to a GCE with an area of  $0.07 \text{ cm}^2$  hence the approximate monolayer coverage is

$$\frac{0.008 \text{ cm}^2}{0.07 \text{ cm}^2} = 0.1$$

The number of moles of Pt nanoparticles on the surface of the GCE is

$$\frac{9 \times 10^8 \text{ particles}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 1.5 \times 10^{-15} \text{ mol}$$

Then the estimated surface coverage of Pt nanoparticles on GCE is

$$\frac{1.5 \times 10^{-15} \text{ mol}}{0.07 \text{ cm}^2} = 2 \times 10^{-14} \text{ mol cm}^{-2}$$

The surface area of each Pt nanoparticle was calculated assuming it is a sphere of radius 15 nm:

$$4 \times \pi \times 15 \text{ nm}^2 = 2.8 \times 10^3 \text{ nm}^2 = 2.8 \times 10^{-11} \text{ cm}^2$$

The surface area of each Pt nanoparticle was estimated assuming each particle to be a sphere with a roughness factor of  $4.4 \pm 1.1$  [2], the approximate surface area of each particle is  $1.2 \times 10^{-10} \text{ cm}^2$ .

The total surface area of the drop casted Pt nanoparticles was also calculated based on the number of particles times the surface area of each particle, which is:

$$9 \times 10^8 \text{ particles} \times 4 \times \pi \times 15 \text{ nm}^2 = 2.5 \times 10^{12} \text{ nm}^2 = 0.025 \text{ cm}^2$$

Recognising the roughness of the particles is characterised by a roughness factor of  $4.4 \pm 1.1$  [2], the approximate area of Pt available for As deposition is  $0.11 \text{ cm}^2$ .

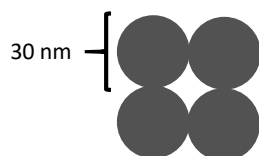


Figure S1. A scheme of possible distribution of Pt nanoparticles with a size of 30 nm on surface of GCE.

## Section 2: Optimization of the deposition potential

The deposition potential for the underpotential deposition was determined. The CV in Figure 2 in the main text shows no discernible feature for the deposition of As ad-atoms since this is likely obscured by the deposition of bulk As, peak 5. However the stripping peak of As ad-atoms was observed at ca +0.05 V in Figure 3 of the main text. The purpose of this section is to determine the potential of the ad-atom deposition by considering oxidative voltammograms following deposition at different cathodic limits. Figures S2a and b show voltammograms for bulk Pt and Pt nanoparticles respectively with deposition potentials between -0.6 and -0.8 V. It can be seen that peak 5' is absent when As is deposited at -0.6V but appears in both cases when more negative deposition potentials are used. It is inferred that the deposition potential of the As ad-atoms is ca  $-0.7\text{V} \pm 0.5\text{V}$ . If the deposition potential was more negative than -0.7 V, it would suffer the problem from solvent breakdown at both bulk Pt (Figure S2a) and Pt nanoparticles (Figure S2b). Thus, -0.7 V was used for the deposition potential.

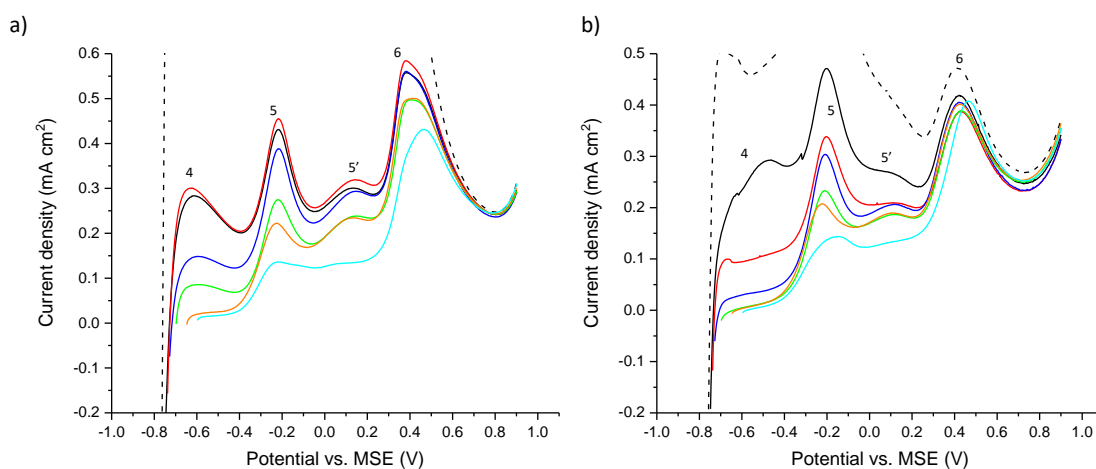


Figure S2. LSV curves of 50  $\mu\text{M}$  As(III) in 0.1 M  $\text{H}_2\text{SO}_4$  at a) Pt macroelectrode and b) Pt nanoparticle-modified GC electrode. LSV parameters: deposition for 210s at different potentials, scan rate was  $0.1\text{ V s}^{-1}$ . The deposition potentials are -0.8V (black dash line), -0.75V (black solid line), -0.74V (red), -0.73V (blue), -0.7V (green), -0.65V (orange) and -0.6V (cyan).

### Section 3: Optimization of the deposition time

Deposition time during the pre-concentration was also important and need to be determined. The purpose of this section is to determine the time of the ad-atom deposition by considering oxidative voltammograms following peak signal at different deposition time. Figures S3a and b illustrate the LSVs for bulk Pt and Pt nanoparticles respectively with deposition time from 60 s to 300 s. The deposition potential was -0.7 V for all experiments and the scan rate was  $0.1 \text{ V s}^{-1}$ . Three peaks were observed and labelled as 5, 5' and 6. Peaks 5 and 5' were observed at ca -0.2 V and ca +0.05 V, and represented oxidation peak of bulk As(0) and As ad-atoms, respectively [3]. Peak 6 at ca +0.4 V was ascribed to the oxidation of As(III) to As(V) [3, 4]. It can be seen in both cases that if the deposition time increased, the signal of peak 5' were enhanced until the deposition time reached to ca 240 s (Figures S3 c and d). Thus the deposition time was chosen to be 240 s for the rest of the study.

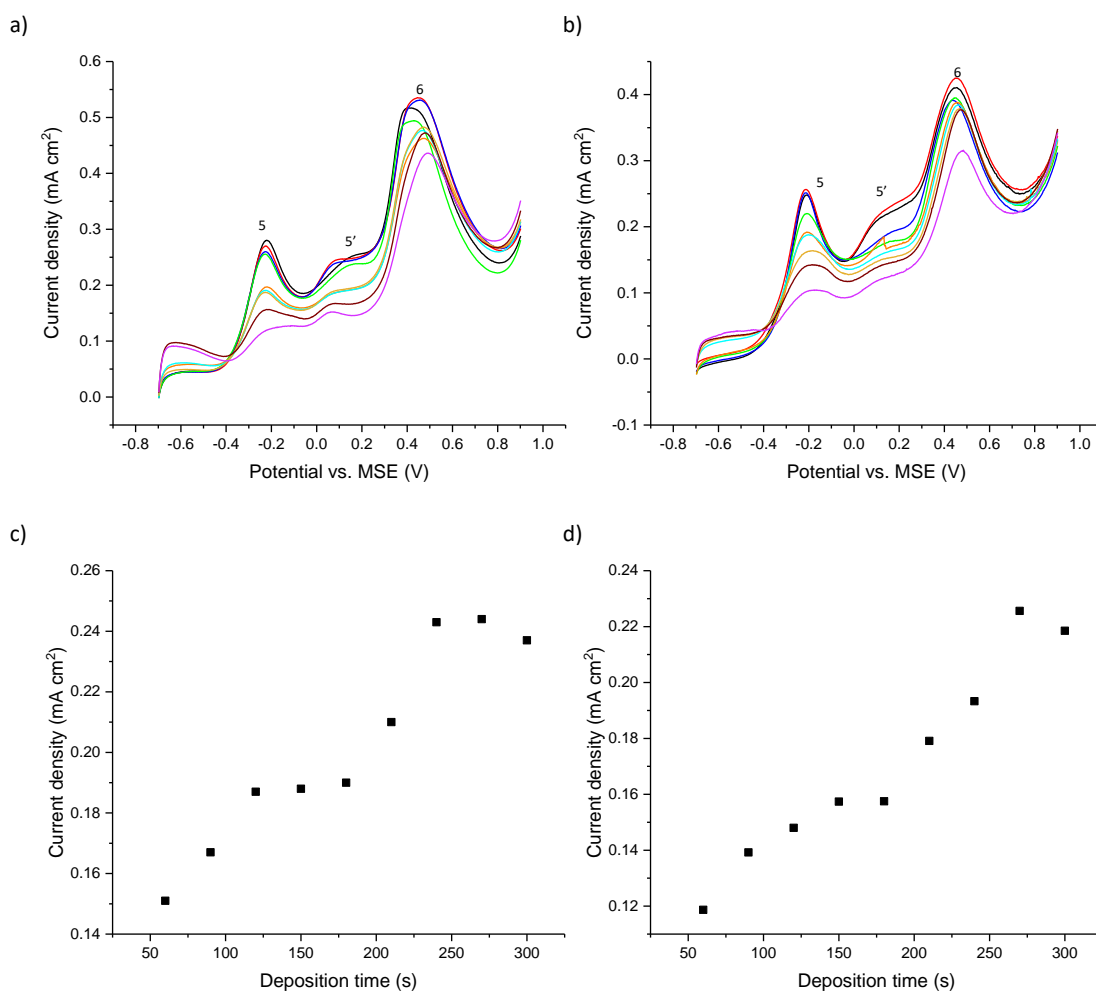


Figure S3. LSV curves of 50  $\mu\text{M}$  As(III) in 0.1 M  $\text{H}_2\text{SO}_4$  at a) Pt macroelectrode and b) Pt nanoparticle-modified GC electrode. LSV parameters: deposition at -0.7V for different time, scan rate was  $0.1 \text{ V s}^{-1}$ . The deposition times are 300s (black), 270s (red), 240s (blue), 210s (green), 180s (orange), 150s (cyan), 120s (yellow), 90s (purple) and 60s (pink). Plots of current densities of peak 5' vs. deposition time at c) Pt macroelectrode and d) Pt nanoparticle-modified GCE.

#### Section 4: Calculation of the surface coverage of As during pre-concentration on bulk Pt

The area of peak 5' can be calculated via 'Integrate' in Origin 2017. The area of the peak 5' of 2  $\mu\text{M}$  As(III) in 0.1 M  $\text{H}_2\text{SO}_4$  at Pt nanoparticle-modified GCE was  $9.4 \times 10^{-8}$  (Figure S4b). The charge (Q) of the peak then can be estimated as:

$$Q = \frac{\text{Area of peak}}{\text{Scan rate}} = 9.4 \times 10^{-7} \text{ C}$$

The corresponding number of electrons then was estimated as:

$$\frac{\text{Charge of peak 5'}}{\text{Elementary charge}} = \frac{9.4 \times 10^{-7} \text{ C}}{1.6 \times 10^{-19} \text{ C}} = 5.9 \times 10^{12}$$

The number of moles of electrons was calculated as:

$$\frac{\text{Number of electrons}}{\text{Avogadro constant}} = \frac{5.9 \times 10^{12}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 9.8 \times 10^{-12} \text{ mol}$$

Each As(III) ion has three electrons transferred during the electrochemical reaction. Thus, the number of moles of As can be estimated as:

$$\frac{\text{Moles of electrons}}{3} = \frac{9.8 \times 10^{-12} \text{ mol}}{3} = 3.3 \times 10^{-12} \text{ mol}$$

The surface area of Pt macroelectrode (with radius of 0.075 cm) is  $0.02 \text{ cm}^2$  or  $2 \times 10^{12} \text{ nm}^2$ . Hence, the estimated surface coverage of As on the surface of Pt could be obtained assuming As atoms were closely packed on the surface of electrode (Figure S4a):

$$\frac{\text{Moles of As}}{\text{Surface area of Pt macroelectrode}} = \frac{3.3 \times 10^{-12} \text{ mol}}{0.02 \text{ cm}^2} = 1.7 \times 10^{-10} \text{ mol cm}^2$$

The number of monolayers of As ad-atoms were also estimated. The radius of As atom is 185 pm [5] and diameter is 370 pm. The covered area of single As atom ( $d^2$ ) is calculated to be  $0.14 \text{ nm}^2$ .

The number of As deposited can be calculated from the number of moles of As and Avogadro constant, and it is:

$$\text{Moles of As} \times \text{Avogadro constant} = 3.3 \times 10^{-12} \text{ mol} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 2 \times 10^{12}$$



The number of one monolayer of As atoms on the surface of Pt electrode was estimated assuming As atoms were closely packed on Pt (Figure S4a):

$$\frac{\text{Surface area of Pt macroelectrode}}{\text{Covered area of single As atom}} = \frac{2 \times 10^{12} \text{ nm}^2}{0.14 \text{ nm}^2} = 1.4 \times 10^{13}$$

Therefore, the number of layers of As atoms on Pt is:

$$\frac{\text{Number of As atoms deposited}}{\text{Number of one monolayer of closely packed As atoms}} = \frac{2 \times 10^{12}}{1.4 \times 10^{13}} = 0.14$$

This corresponds to a sub-monolayer (ca 0.14 monolayers) of As atoms on the surface of Pt.

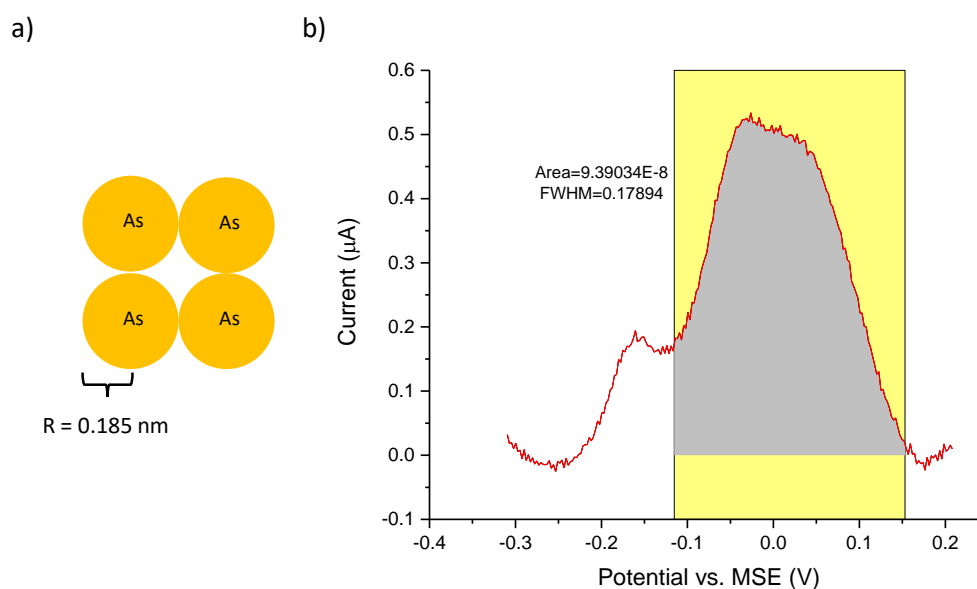


Figure S4. a) A scheme of As atoms closely packed at the surface of Pt. b) The baseline corrected LSV curves of peak 5' of  $2 \mu\text{M}$  As(III) in  $0.1 \text{ M H}_2\text{SO}_4$  at Pt macroelectrode. The grey areas are used for the integration. LSV parameters: deposition at  $-0.7 \text{ V}$  vs. MSE for 240s, potential scan rate  $0.1 \text{ V s}^{-1}$ , and baseline was modelled via polynomial method from  $-0.3 \text{ V}$  to  $+0.2 \text{ V}$  for peak 5'.

### Section 5: Calculation of the surface coverage of As after pre-concentration on Pt nanoparticles

The area of peak 5' was obtained via integration using Origin 2017. The peak was measured using 2  $\mu\text{M}$  As(III) in 0.1 M  $\text{H}_2\text{SO}_4$  at a Pt nanoparticle-modified GCE (Figure S5b) and gave a charge (Q) of  $9.2 \times 10^{-7}$  C.

The corresponding number of electrons was estimated as:

$$\frac{\text{Charge of peak 5'}}{\text{Elementary charge}} = \frac{9.2 \times 10^{-7} \text{ C}}{1.6 \times 10^{-19} \text{ C}} = 5.8 \times 10^{12}$$

The number of moles of electrons was calculated as:

$$\frac{\text{Number of electrons}}{\text{Avogadro constant}} = \frac{5.8 \times 10^{12}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 9.6 \times 10^{-12} \text{ mol}$$

Each As(III) ion has three electrons transferred during the electrochemical reaction. Thus, the number of moles of As can be estimated as:

$$\frac{\text{Moles of electrons}}{3} = \frac{9.6 \times 10^{-12} \text{ mol}}{3} = 3.2 \times 10^{-12} \text{ mol}$$

The estimated surface area of drop casted Pt nanoparticles was also calculated. It was assumed that each nanoparticle was spherical with a radius of 15 nm and a roughness factor of  $4.4 \pm 1.1$  [2]. The estimated surface area of the rough sphere is

$$\text{Roughness factor} \times \text{Number of particles} \times 4 \times \pi \times r^2 = 4.4 \times 9 \times 10^8 \text{ particles} \times 4 \times \pi \times 15 \text{ nm}^2 = 1.1 \times 10^{13} \text{ nm}^2 = 0.11 \text{ cm}^2$$

Then the estimated surface coverage of As on the surface of Pt nanoparticles can be:

$$\frac{\text{Moles of As}}{\text{Estimated surface area of Pt nanoparticles}} = \frac{3.2 \times 10^{-12} \text{ mol}}{0.11 \text{ cm}^2} = 2.9 \times 10^{-11} \text{ mol cm}^{-2}$$

The number of As atoms can be calculated from the moles of As and the Avogadro constant, is:

$$\text{Number of moles of As} \times \text{Avogadro constant} = 3.2 \times 10^{-12} \text{ mol} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 1.9 \times 10^{12}$$

The As atoms were assumed to be deposited on the surface of every single Pt nanoparticles as Figure S5a shows. The number of As atoms per nanoparticle were estimated based on the covered area of single As atom and the number of drop casted Pt nanoparticles:

$$\frac{\text{Number of As}}{\text{Number of Pt nanoparticles}} = \frac{1.9 \times 10^{12}}{9 \times 10^8} = 2100 \text{ atoms}$$

The surface area of each Pt nanoparticle was calculated to be  $1.2 \times 10^{-10} \text{ cm}^2$  assuming each particle to be a sphere of radius 15 nm with a roughness factor of  $4.4 \pm 1.1$  [2]. Then the area per As atoms on a single Pt nanoparticle can be calculated from the estimated surface area of the rough sphere particles and number of As atoms per Pt nanoparticle:

$$\frac{\text{Estimated surface area of each Pt nanoparticle}}{\text{Number of As atoms per nanoparticle}} = \frac{1.2 \times 10^{-10} \text{ cm}^2}{2100 \text{ atoms}} = 6 \times 10^{-14} \text{ cm}^2 = 6 \text{ nm}^2$$

This corresponds to ca 0.02 monolayers on the surface of a single nanoparticle.

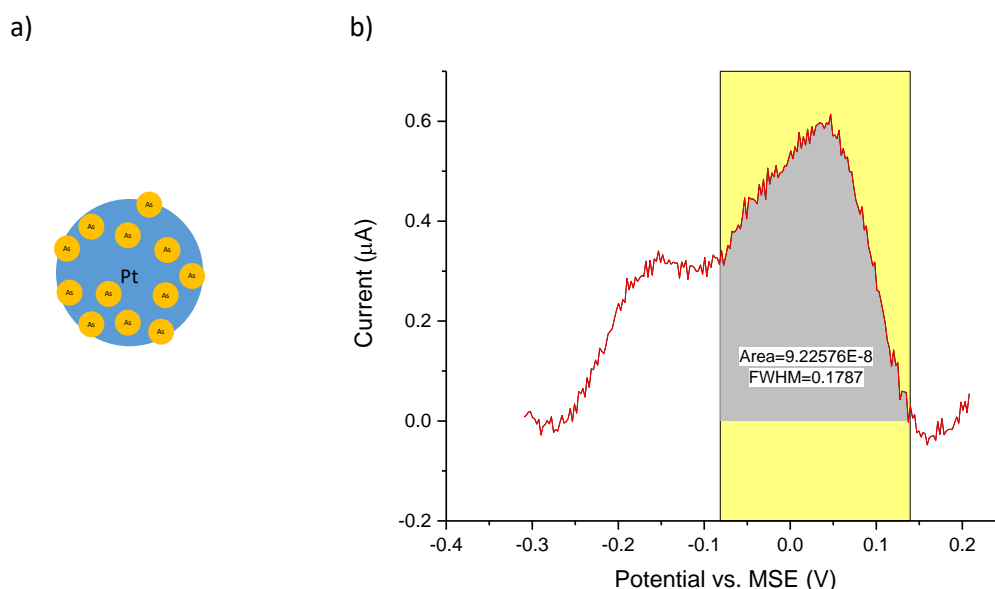


Figure S5. a) A scheme of As atoms deposited on the Pt nanoparticles. b) The baseline corrected LSV curves of peak 5' of 2  $\mu\text{M}$  As(III) in 0.1 M  $\text{H}_2\text{SO}_4$  at Pt nanoparticle-modified GCE. The grey areas in are used for the integration. LSV parameters: deposition at -0.7 V vs. MSE for 240s, potential scan rate  $0.1 \text{ V s}^{-1}$ , and baseline was modelled via polynomial method from -0.3 V to +0.2 V for peak 5'.

## Section 6: Baseline correction for peak 5'

The baseline was simulated via 'polynomial' method in Origin 2017. An example calculation of baseline correction of 1  $\mu\text{M}$  As(III) in 0.1 M  $\text{H}_2\text{SO}_4$  at Pt nanoparticles GCE is shown below.

At first, a LSV curve can be obtained from the electrochemical experiments and peak 5' can be seen at ca +0.05 V (Figure S6a). Then the LSV curve was zoomed in for the potential window from -0.3 V to +0.2 V because the peak 5' was in this range (black line in Figure S6b). The baseline of peak 5' was then simulated from ca -0.15 V to ca +0.1 V with a polynomial order of 7 (red line in Figure S6b). Finally, a baseline subtraction was accessed (black line subtract red line in Figure S6b) and a baseline corrected LSV was obtained (Figure S6c).

Similar baseline corrections were conducted to obtain baseline corrected LSVs at both bulk Pt and Pt nanoparticles in this study.

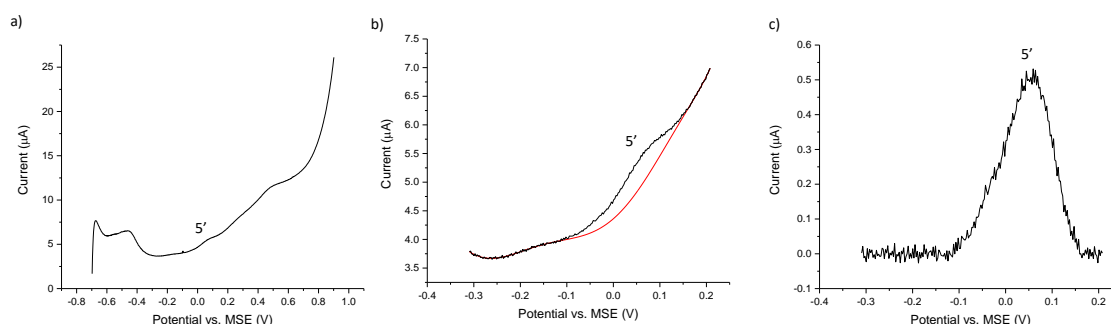


Figure S6. a) The original LSV curve of 1  $\mu\text{M}$  As(III) in 0.1 M  $\text{H}_2\text{SO}_4$  at Pt nanoparticles GCE. b) The LSV curve from -0.3 V to +0.2 V (black line) and simulated baseline (red line). c) The baseline corrected LSV curve from -0.3 V to +0.2 V. LSV parameters: deposition at -0.7 V vs. MSE for 240s, potential scan rate 0.1  $\text{V s}^{-1}$

### **Section 7: Linear response of peaks 5 and 6 of As(III) at low concentration**

The LSVs of 1 to 7.5  $\mu\text{M}$  at a Pt macroelectrode and Pt nanoparticle-modified GCE for various concentrations of As(III) in 0.1 M  $\text{H}_2\text{SO}_4$  after pre-concentration of As(0) are shown in Figures S7a and S7b, respectively. The plot of current densities of peak 5 observed at ca -0.2 V vs concentrations of As(III) on bulk Pt and Pt nanoparticles are shown in Figures S7c and S7d, respectively. The plot of peak 6 observed at ca +0.4 V are shown in Figures S7e and S7f. The peak current densities were calculated based on the geometric area of Pt macroelectrode, 0.02  $\text{cm}^2$  and Pt nanoparticles surface area, 0.11  $\text{cm}^2$  (calculations shown in SI section 1). Although a linear response can be observed from 1 (75 ppb) to 7.5  $\mu\text{M}$ , the detection limit is above the WHO limit for drinking water (10 ppb). Thus, peaks 5 or 6 were not chosen to be used analytically for As(III) detection.

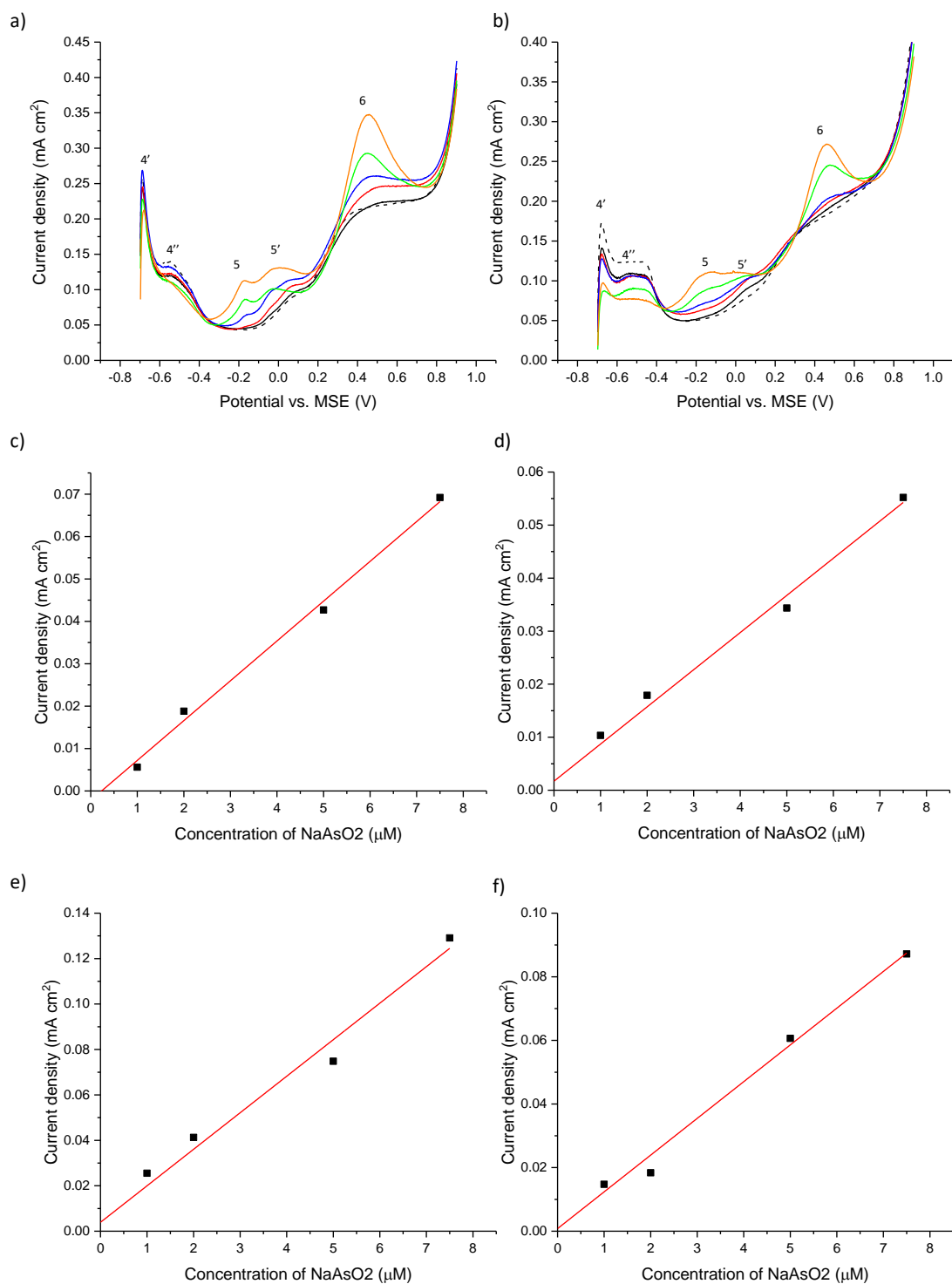


Figure S7. LSV curves of 1 to 7.5  $\mu\text{M}$  As(III) in 0.1 M  $\text{H}_2\text{SO}_4$  at a) Pt macroelectrode and b) Pt nanoparticle-modified GC electrode. LSV parameters: deposition at -0.7V for different time, scan rate was  $0.1 \text{ V s}^{-1}$ . The concentrations of As(III) were 0  $\mu\text{M}$  (black dash line), 0.5  $\mu\text{M}$  (black solid line), 1  $\mu\text{M}$  (red), 2  $\mu\text{M}$  (blue), 5  $\mu\text{M}$  (green) and 7.5  $\mu\text{M}$  (orange). Plots of current densities of peak 5 vs. As(III) concentrations at c) Pt macroelectrode and d) Pt nanoparticle-modified GCE, and of peak 6 vs. As(III) concentrations at e) Pt macroelectrode and f) Pt nanoparticle-modified GCE.

## Section 8: Detection of lowest signal

An example detection of lowest signal was shown in this section. The LSV curve of 0.05  $\mu\text{M}$  As(III) in 0.1 M  $\text{H}_2\text{SO}_4$  was obtained but the peak 5' at ca +0.05 V was not clear (Figure S8a). The LSV curve was zoomed in from -0.3 V to +0.2 V for the baseline subtraction (black line in Figure S8b). A baseline was then simulated with the method shown in section 5 (red line in Figure S8b). After the baseline subtraction, a corrected peak 5' was observed (Figure S8c).

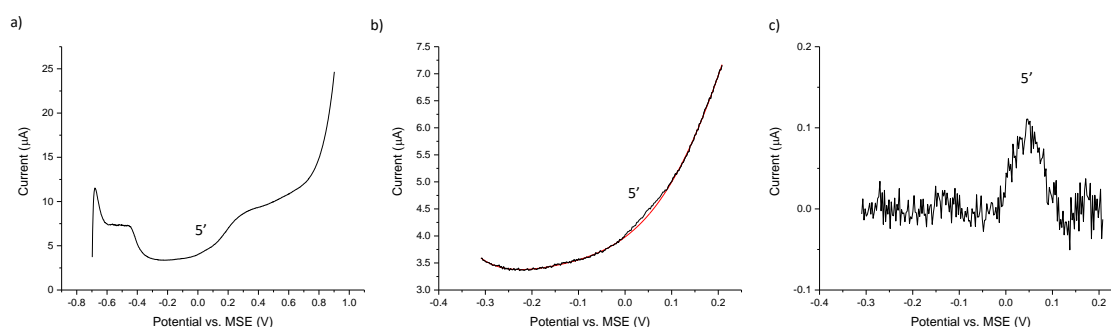


Figure S8. a) The original LSV curve of 0.05  $\mu\text{M}$  As(III) in 0.1 M  $\text{H}_2\text{SO}_4$  at Pt nanoparticles GCE. b) The LSV curve from -0.3 V to +0.2 V (black line) and simulated baseline (red line). c) The baseline corrected LSV curve from -0.3 V to +0.2 V. LSV parameters: deposition at -0.7 V vs. MSE for 240s, potential scan rate 0.1  $\text{V s}^{-1}$

## Section 9: Interference of Cu(II) in 50 $\mu\text{M}$ As(III)

The interference of high concentrations of Cu(II) was studied. Figure S9a illustrates the LSV curves of 50  $\mu\text{M}$  As(III) in 0.1 M  $\text{H}_2\text{SO}_4$  with additions of Cu(II) (50  $\mu\text{M}$  each) at Pt macroelectrode. Deposition was carried out at -0.7 V for 240 s and LSV was conducted from -0.7 V to +0.9 V at a scan rate of 0.1 V  $\text{s}^{-1}$ . Four peaks labelled as Cu, 5, 5' and 6 were observed at ca -0.35 V, ca -0.25 V, ca +0.05 V and ca +0.4 V, which represented the oxidation peak of Cu(0) to Cu(II), oxidation of bulk As(0), oxidation of As adatoms and oxidation of As(III) to As(V), respectively [3, 4]. It can be seen clearly that the Cu peak interfered with peak 5 and peak 5' due to the small difference of peak potential and the overlap of those peaks (Figure S9a). The Cu peak did not interfere with peak 6 because the peak did not overlap with each other.

Similarly, the electrochemical features at Pt nanoparticles were discerned (Figure S9b) and assigned to the same electrochemical reactions [3, 4]. Still, the Cu peak interfered with peaks 5 and 5' but not peak 6. One of the possible methods to reduce the interference from the Cu(II) is to dilute the solution and the Cu(II) will not interfere with peak 5', which is shown in Figure 5 in manuscript.

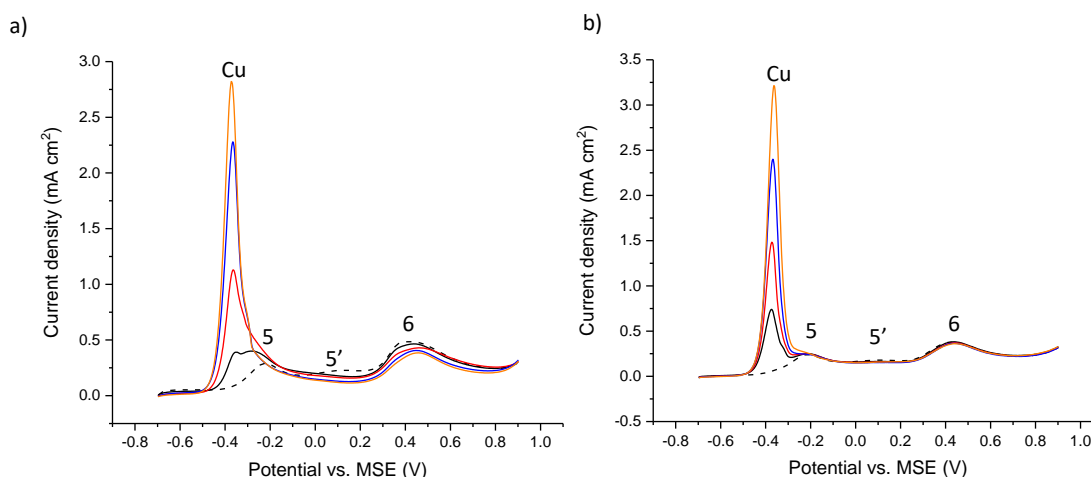


Figure S9. LSV curves of Cu(II) (50  $\mu\text{M}$  each) to 50  $\mu\text{M}$  As(III) in 0.1 M  $\text{H}_2\text{SO}_4$  in the potential range from -0.7 V to +0.9 V (vs. MSE) at a) Pt macroelectrode and b) Pt nanoparticle-modified GC electrode. LSV parameters: deposition at -0.7 V for 240s, scan rate was 0.1 V  $\text{s}^{-1}$ . Cu(II) concentration: 0  $\mu\text{M}$  (black dash line), 50  $\mu\text{M}$  (black solid line), 100  $\mu\text{M}$  (red), 150  $\mu\text{M}$  (blue) and 200  $\mu\text{M}$  (orange).



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