

GLASSY CARBON ELECTRODE MODIFIED WITH *ex-in-situ* GOLD FILM – A SIMPLE AND EFFECTIVE WORKING ELECTRODE FOR As(III) DETERMINATION BY USING DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

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Abstract. An easy-to-make new working electrode, an *ex-in-situ* AuF/GCE, was developed for trace As(III) detection. A gold film electrode prepared *ex-situ* was re-plated *in-situ* during each arsenic deposition step by adding Au(III) into the analyte solution. The factors affecting arsenic stripping response, namely, gold film preparation conditions, electrolyte concentration, electrode cleaning potential, cleaning time, deposition potential, and deposition time, were investigated. Compared with the traditional gold film electrodes prepared *ex-situ*, the new electrode has better precision and linearity of arsenic differential pulse anodic stripping voltammetry responses. For a deposition time of 90 s at –200 mV, the new electrode exhibits a sensitivity, a limit of detection (3-Sigma), a limit of quantitation of 0.103 $\mu\text{A}\cdot\text{L}\cdot\mu\text{g}^{-1}$, 0.4 $\mu\text{g}\cdot\text{L}^{-1}$, and 1.3 $\mu\text{g}\cdot\text{L}^{-1}$, respectively.

Keywords: arsenic, As(III), arsenic determination, anodic stripping voltammetry, gold film

1 Introduction

Inorganic arsenic contamination in drinking water is a serious worldwide threat to human health. Long-term exposure to inorganic arsenic in drinking water is causally related to increased cancer risks in the skin, lungs, bladder, kidney, and other skin changes, such as hyperkeratosis and pigmentation changes [1]. Therefore, WHO's maximum contaminant level of arsenic in drinking water is limited to 10 $\mu\text{g}\cdot\text{L}^{-1}$ [2].

Some analytical methods are often used to determine arsenic, such as flameless atomic absorption spectroscopy using graphite furnaces (GF-AAS), hydride generation- atomic absorption spectroscopy (HG-AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS). These methods were

reported to provide detection limits under the maximum contaminant level regulated by WHO and numerous countries. Their use for arsenic detection, however, causes several issues such as high cost of the instrument, the need for highly trained operators, and extensive sample preparations [3].

As good alternatives, electrochemical methods can provide low-cost and highly sensitive detection for arsenic determination. Anodic stripping voltammetry (ASV) is the most popular electrochemical method due to its good detection capabilities and simple operations [4]. The anodic stripping voltammetry technique for trace arsenic analysis was established by Kaplan et al., which is based on the deposition of metallic arsenic on the electrode surface with subsequent anodic stripping [5]. The excellent electrochemical performance, such as sensitivity, the limit of

detection, and the anti-interference of arsenic detection, was achieved at noble-metal nanoparticles (such as Au, Pt, and Ag) modified electrodes. Glassy carbon modified with gold film (AuF/GCE) is common for trace arsenic determination. However, the response of arsenic at this electrode is unstable and strongly dependent on the past history, pretreatment, and formation of the oxide film [5, 6]. Several attempts were carried out to overcome these problems. An *ex-situ* re-plated gold film electrode before each measurement [7] was found to ensure good precision. Unfortunately, the idea of re-plating the gold film could not be implemented on all voltammetric equipment. Moreover, this process also makes the analysis more complex and time-consuming.

This paper describes a new and simply fabricated AuF/GCE for differential pulse anodic stripping voltammetric (DP-ASV) determination of As(III), which can significantly improve the precision of the arsenic stripping response.

2 Experimental

2.1 Chemical reagents

The As(III) stock solution (1000 ppm) was prepared from As₂O₃ (EQP Panreac, Spain). HAuCl₄·3H₂O, 37% HCl, ≥65% HNO₃ were purchased from Sigma–Aldrich (Singapore). Ascorbic acid was from Merck (Germany).

All glassware was thoroughly cleaned by soaking into a 1:2 (v/v) HNO₃/H₂O solution for 4–6 h and rinsed with double-distilled water (DD water) before use. All solutions and subsequent dilutions were prepared with DD water.

2.2 Instrumentation

Differential pulse anodic stripping voltammetric determination measurements were performed on a 797 VA Computrace (Metrohm,

Switzerland) with a 50 mL glass electrochemical cell and a system of three electrodes, consisting of an AuF/GCE as working electrodes, an Ag/AgCl (3 M KCl) as a reference electrode, and a platinum rod as a counter electrode.

2.3 Preparation of *ex-situ* AuF/GCE

A glassy carbon electrode (3.0 mm diameter) was thoroughly polished with a slurry of Al₂O₃ powder (grain size of 0.6 μm), then washed with 2 M NaOH and DD water. Then, the electrode was submerged into a plating solution of 5 mM Au(III) in 1 M HCl (purged with pure nitrogen for 2 min) and applied at a plating potential of –100 mV (E_{pla}) for 120 s (t_{pla}). The potential was then stepped to a potential of +500 mV ($E_{\text{clean-1}}$) for 30 s ($t_{\text{clean-1}}$) to remove easily oxidizable co-deposited impurities. After this step, the electrode was taken out of the plating solution and washed carefully with DD water before use. The gold film electrode prepared by this procedure was named *ex-situ* AuF/GCE.

After about 15 serial measurements, the gold film of the AuF/GCE was removed by applying a piece of filter paper onto the surface of a rotating electrode. Then a new *ex-situ* AuF/GCE was fabricated by plating another new gold film onto the surface of the cleaned glassy carbon electrode.

2.4 Differential pulse anodic stripping voltammetry of As(III)

The working electrode (*ex-situ* AuF/GCE), reference electrode, and counter electrode were immersed into an electrochemical cell with 10 mL solution containing As(III), HCl, and ascorbic acid (AA).

The deposition step was conducted at a potential of –200 mV (E_{dep}) for 90 s (t_{dep}). In this step, the working electrode rotates at 2000 rpm. After deposition, the rotation was turned off to

make the solution quiescent at -200 mV for 15 s. In the deposition step, As(III) in the solution is electrochemically reduced to elemental arsenic As(0), deposited on the gold film of the electrode surface (Eq. 1).



The subsequent stripping step was carried out in a differential pulse mode starting from a potential of -200 mV (E_{start}) to $+300$ mV (E_{end}) at a scan rate of 20 mV·s⁻¹. In this step, elemental arsenic is re-oxidized to As(III) and stripped out of the surface of the electrode (Eq. 2).



The stripping peak of arsenic appears on the voltammogram at a potential of about $+100$ mV (E_p). The stripping peak current (I_p) was utilized for arsenic determination.

At the end of each measurement, a $+600$ mV ($E_{\text{clean-2}}$) cleaning potential was applied to the working electrode for 5 s ($t_{\text{clean-2}}$).

3 Results and discussion

3.1 Differential pulse voltammetry parameters

Rising the pulse amplitude from 10 to 100 mV or the scan rate from 10 to 60 mV·s⁻¹ causes the stripping peak current of arsenic to increase. However, with the increase of I_p , the slope of the voltammogram backgrounds also increases, reducing the peak resolution. This could make it difficult to identify peak of the analyte and increase the likelihood of the effects of impurities having adjacent stripping peaks. For achieving satisfactory stripping peak currents and resolutions, a pulse amplitude of 50 mV and a scan rate of 20 mV·s⁻¹ were chosen as a compromise.

The highest I_p of arsenic was obtained at an electrode rotation rate of 2000 rpm.

3.2 Au(III) concentration for preparation of *ex-in-situ* AuF/GCE

In reality, sometimes stripping peaks of arsenic do not appear when using *ex-situ* AuF/GCE with appropriately selected analysis conditions. Moreover, the stripping peak currents of arsenic recorded on *ex-situ* AuF/GCE often decrease continuously in repeated measurements, as shown in Fig. 1a. These drawbacks of gold and gold film electrodes make it difficult to utilize them for arsenic determination in practice and have been notified and discussed by several authors [5, 7, 8, 9]. Some reasonable causes have been given, such as

1. the formation of H₂ bubbles that adhere to the electrode surface during the electrolyzing stage to enrich arsenic in the acid medium [5];
2. the gold film on the electrode may partly dissolve because of the complex formation between Au(III) and the Cl⁻ ion [7];
3. only part of the arsenic plated on the electrode surface is dissolved during the anodic scan, while the rest will be stripped by holding the electrode at $+0.7$ V [8].

The insoluble arsenic remaining after each measurement may occupy some parts of the electrode surface, thus reducing the number of active centres on the gold film. Consequently, the amount of arsenic accumulated on the electrode likely decreases between repeated measurements in the same solution, resulting in a significant decline in I_p .

For reactivating the AuF/GCE surface, a tiny amount of Au(III) is added to the solution. In the subsequent deposition step, under an electrolysis potential of -200 mV, a small amount of gold was accumulated on the surface of the *ex-situ* AuF/GCE together with arsenic. Under these conditions, the number of active centres at the electrode surface is recovered after each

measurement, improving the sensitivity and the repeatability (Fig. 1b). The suitable added concentration of Au(III) is approximately 50 μM . The replicated differential pulse anodic stripping voltammograms of a 5 $\mu\text{g}\cdot\text{L}^{-1}$ As(III) solution, containing 0.7 M HCl, 0.5 mM AA, and 50 μM Au(III) are shown in Fig. 1b.

In this case, *ex-situ* AuF/GCE was *in-situ* “made up” during the deposition step in an analyte solution containing Au(III). The electrodes prepared this way are named *ex-in-situ* AuF/GCE.

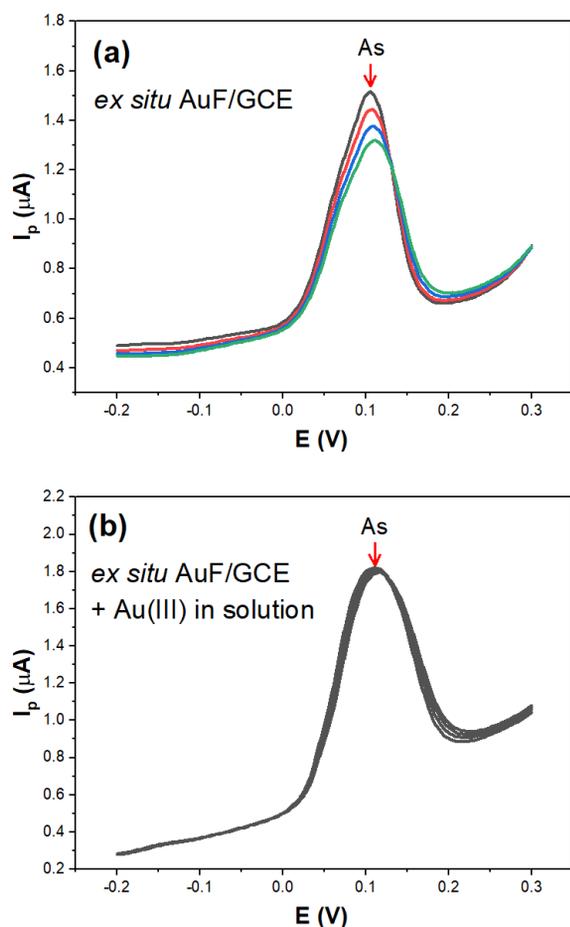


Fig. 1. Replicated differential pulse stripping anodic voltammograms ($n = 4$) of 5 $\mu\text{g}\cdot\text{L}^{-1}$ As(III) solutions (a) in the absence and (b) in the presence of Au(III) at *ex-situ* AuF/GCE

3.3 Supporting electrolytes

HCl concentration

Among the acids tested, namely H_2SO_4 , HNO_3 , HCl, and HClO_4 , HCl allows to obtain a better differential pulse anodic stripping peak current and repeatability. When increasing the concentration of HCl (C_{HCl}) in the solution from 0.1 to 1.5 M, the I_p of arsenic started to increase, but then declined gradually. Sun [7] suggested that As(III) exists in a solution containing Cl^- ions in various forms, of which $\text{As}(\text{OH})_2\text{Cl}$ and $\text{As}(\text{OH})\text{Cl}_2$ are considered electronic transporting species at the electrode surface. Thus, when the concentration of Cl^- in the solution increases, the concentration of $\text{As}(\text{OH})_2\text{Cl}$ and $\text{As}(\text{OH})\text{Cl}_2$ also increases, therefore enhancing the effectiveness of arsenic deposition on the electrode surface. However, when C_{HCl} is relatively high, the gold film may be corroded because Au(III) can form AuCl_4^- complex, leading to the decline of arsenic I_p . The HCl concentration of 1 M was found to be suitable for achieving high I_p and good repeatability.

Ascorbic acid concentration

Ascorbic acid (AA) is often added to the solution for As(III) detection. Ascorbic acid is believed to prevent the oxidation of As(III) in a solution to As(V), an electrochemically inactive species reducing arsenic I_p [10]. Ascorbic acid does not increase the I_p but significantly improves the repeatability in measuring I_p . The appropriate AA concentration (C_{AA}) of 0.5 mM was selected for the following experiments.

3.4 Electrode cleaning potential and cleaning time

For dissolving the remaining As(0) after each measurement, the electrode surface needs to be cleaned by applying a sufficiently positive potential ($E_{\text{clean-2}}$) for an appropriate time ($t_{\text{clean-2}}$).

Investigation results show that cleaning the electrode does not significantly increase the sensitivity but improves the repeatability of the measurements. After stripping out most of the arsenic residues, active centres on the electrode surface might be restored, resulting in enhanced arsenic deposition, preventing I_p to decrease between successive measurements. However, if the cleaning time is prolonged, a portion of the gold film may dissolve, reducing the I_p of arsenic and thus the sensitivity. As a compromise between improving repeatability and not reducing sensitivity, an $E_{\text{clean-2}}$ of +600 mV and a $t_{\text{clean-2}}$ of 5 s were selected for arsenic detection. The obtained I_p has very good repeatability (RSD = 1.9%, $n = 4$).

3.5 Deposition potential and deposition time

As shown in Table 1, at the deposition potentials more positive than -100 mV, the efficiency of arsenic accumulation is low, resulting in a low I_p of arsenic. At the negative potentials lower than -100 mV, I_p tends to increase slowly. The more negative the deposition potential is, the greater the risk of contamination of electrode surface due to possibly existing metal impurities in the analyte solution. Therefore, a deposition potential of -200 mV was selected for further experiments.

Table 1. Influence of deposition potential on I_p of arsenic at *ex-in-situ* AuF/GCE

E_{dep} (mV)	I_p (nA)	RSD (% , $n = 4$)
-50	820	7.1
-100	956	7.3
-150	975	1.8
-200	990	2.2
-250	985	0.5
-300	1007	0.7

Conditions: Electrolyte solution: 5 $\mu\text{g}\cdot\text{L}^{-1}$ As(III), 1 M HCl, 0.5 mM AA, 50 μM Au(III). DP-ASV mode. $t_{\text{dep}} = 90$ s.

Experiment results show a notable difference in the effect of the deposition time (t_{dep}) on the I_p of arsenic when using two different types of AuF/GCE, as described in Fig. 2. For *ex-situ* AuF/GCE, I_p only proportionally increases to the t_{dep} less than 90 s. After 90 s, the signal becomes almost independent of the deposition time, suggesting a saturation of the electrode surface.

Wang [8] suggested that prolonged deposition can form a layer of poorly conductive As(0) on the electrode surface, preventing the effective arsenic accumulation, so I_p does not increase even further. However, with the *ex-in-situ* AuF/GCE, increasing the deposition time to 150 s does not cause the I_p saturation. A gold film on the *ex-in-situ* AuF/GCE might constantly be "refreshed". More active centres appear for arsenic deposition, thus limiting the formation of a less conductive layer, as mentioned above. As a compromise between reasonable analysis time and the I_p , 90 s was selected as the most appropriate deposition time for further applications.

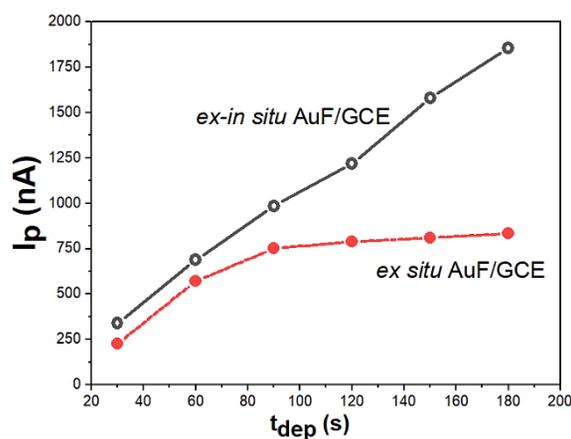


Fig. 2. Influence of deposition time on I_p of arsenic at *ex-in-situ* AuF/GCE and *ex-situ* AuF/GCE

Conditions: Electrolyte solution of 5 $\mu\text{g}\cdot\text{L}^{-1}$ As(III), 1 M HCl, 0.5 mM AA, 50 μM Au(III) (in the case of *ex-in-situ* AuF/GCE). DP-ASV mode. $E_{\text{dep}} = -200$ mV.

3.6 Repeatability, linear range, and limit of detection

Repeatability

The obtained differential pulse anodic stripping voltammograms (DP-ASVs) of repeated measurements of a $5 \mu\text{g}\cdot\text{L}^{-1}$ As(III) solution with an *ex-in* AuF/GCE (Fig. 3b) show a significant improvement in the stripping peak current values and the repeatability compared with the *ex-situ* AuF/GCE (Fig. 3a).

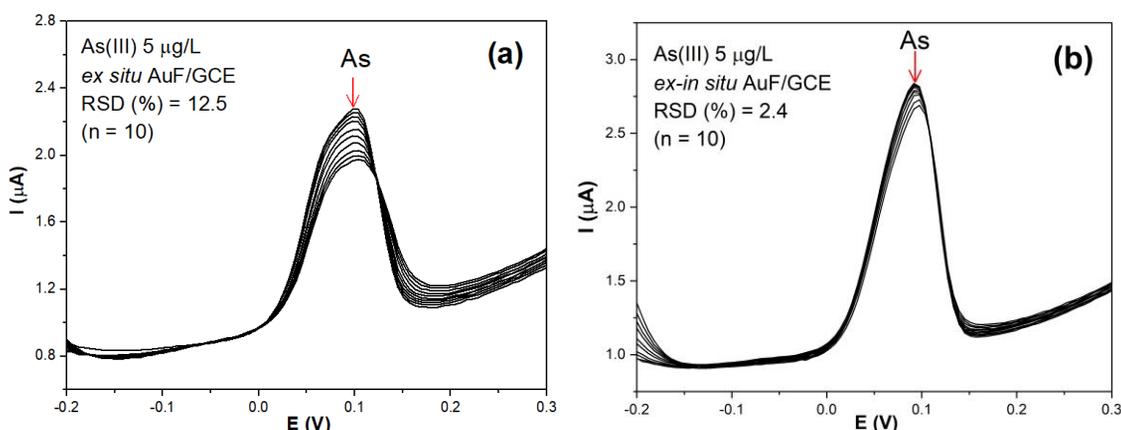


Fig. 3. DP-ASVs of $5 \mu\text{g}\cdot\text{L}^{-1}$ As(III) solution at (a) *ex-situ* AuF/GCE and (b) *ex-in-situ* AuF/GCE. Conditions: $t_{\text{dep}} = 90 \text{ s}$; other conditions are as in Fig. 2

Linear range and limit of detection

As shown in Fig. 4 and Fig. 5, compared with the *ex-situ* AuF/GCE, the *ex-in-situ* AuF/GCE allows to obtain a much wider $I_p-C_{\text{As(III)}}$ linear range with R^2 being 0.9991. The sensitivity is $0.103 \mu\text{A}\cdot\text{L}\cdot\mu\text{g}^{-1}$ (Fig. 5). With a deposition time of 90 s, the limit of detection (LOD), calculated according to the 3-Sigma method, is $0.4 \mu\text{g}\cdot\text{L}^{-1}$. The corresponding limit of quantitation (LOQ) is $1.3 \mu\text{g}\cdot\text{L}^{-1}$. These LOD and LOQ values are much lower than the maximum allowable concentration of arsenic in drinking water ($10 \mu\text{g}\cdot\text{L}^{-1}$) under the current WHO guideline [2]. Therefore, the *ex-in* AuF/GCEs could be used to develop a DP-ASV method to quantify trace As(III) in water samples.

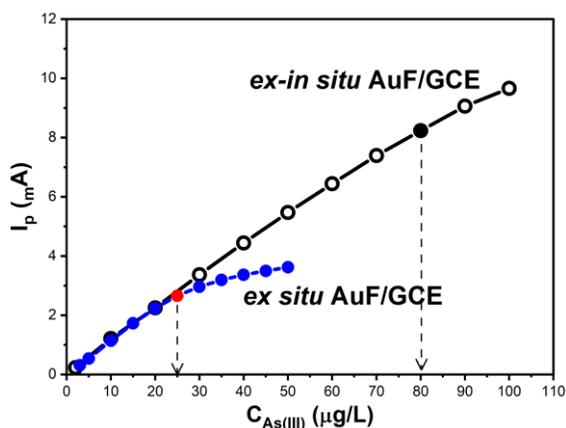


Fig. 4. Dependence between I_p and $C_{\text{As(III)}}$ at *ex-situ* AuF/GCE and *ex-in-situ* AuF/GCE at *ex-in-situ* AuF/GCE and *ex-situ* AuF/GCE. Conditions: $E_{\text{dep}} = -200 \text{ mV}$, $t_{\text{dep}} = 90 \text{ s}$; other conditions as in Fig. 2

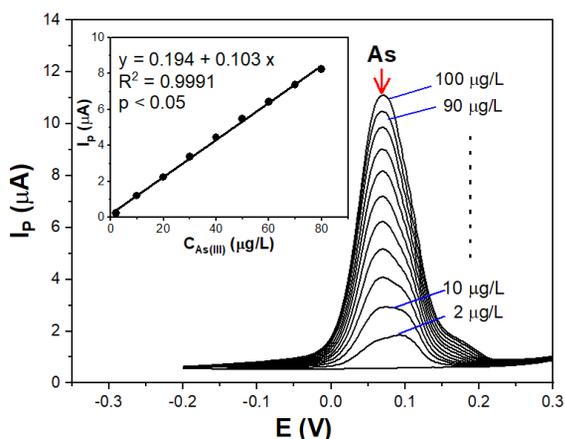


Fig. 5. DP-ASVs of As(III) at an *ex-in-situ* AuF/GCE in solutions containing 1 M HCl, 0.5 mM AA, 50 µM Au(III). Inset: Linear relationship of I_p versus $C_{As(III)}$. Conditions: $E_{dep} = -200$ mV; $t_{dep} = 90$ s

4 Conclusion

An easy-to-make new gold film working electrode was developed for trace As(III) detection. This electrode was prepared by combining *ex-situ* and *in-situ* gold film deposition techniques on a glassy carbon based electrode. Compared with a traditional gold film electrode, this new electrode allows to achieve better arsenic stripping peak currents, wider linear intervals, better sensitivity (lower LOD) and repeatability, and is suitable for developing DP-ASV methods for determining arsenic traces in water samples.

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