Anodic Stripping Voltammetry of Arsenic(III) Using Gold Nanoparticle-Modified Electrodes

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Anodic Stripping Voltammetry of Arsenic(III) Using Gold Nanoparticle-Modified Electrodes

Xuan Dai, Olga Nekrassova, Michael E. Hyde, and Richard G. Compton*

Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, United Kingdom

A novel method for the detection of arsenic(III) in 1 M HCl at a gold nanoparticle-modified glassy carbon electrode has been developed. The gold nanoparticles were electrodeposited onto the glassy carbon electrode via a potential step from +1.055 to −0.045 V vs SCE for 15 s from 0.5 M H_2SO_4 containing 0.1 mM $HAuCl_4$. The resulting electrode surfaces were characterized with both AFM and cyclic voltammetry. Anodic stripping voltammetry of arsenic(III) on the modified electrode was performed. After optimization, a LOD of 0.0096 ppb was obtained with LSV.

Arsenic is highly toxic. Exposure to arsenic can cause a variety of adverse health effects, including dermal changes and respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic, and carcinogenic effects.[1] Contamination of groundwater by arsenic has been reported in 20 countries where arsenic levels in drinking water are above the World Health Organization's arsenic guideline value of 10 μg L^{-1}.[2] Many detection methods have been developed for determination of such levels of arsenic, as summarized in recent reviews.[3–6] These include inductively coupled plasma mass spectrometry (ICPMS),[7] graphite furnace atomic absorption spectrometry,[8] and high-performance liquid chromatography with ICPMS.[9] However, the most reliable techniques are more suitable for laboratory conditions only and are, additionally, time-consuming. They cannot thus be used for routine in-field monitoring of a large number of samples. Therefore, a sensor needs to be developed to solve these problems. Electrochemical techniques provide a possible means to this end since they are both rapid and portable.

Voltammetric stripping techniques provide accurate measurements of low concentrations of metal ions at the ppb levels with rapid analysis times and low-cost instrumentation. Electrochemical methods for the determination of As(III) involve cathodic (CSV) or anodic stripping voltammetry (ASV). CSV analysis of As(III) is carried out using a hanging mercury drop electrode.[10] However, due to the potential toxicity of mercury together with operational limitations, portable sensors utilizing mercury electrodes were subsequently replaced by solid substrates. Forsberg et al.[11] investigated in detail the determination of arsenic by ASV and differential pulse anodic stripping voltammetry (DPASV) at various electrode materials (Hg, Pt, Au). Au provides a more sensitive response toward arsenic oxidation than the other electrode materials studied and has a higher hydrogen overvoltage than platinum. The arsenic stripping peak appears as a shoulder on the oxidation waves of Hg and Ag. Thus, these metals are not suitable as electrodes for arsenic determination via ASV.[11] Accordingly, gold was found to be the superior substrate for the working electrode among the substrates considered to date. There have been several reports about arsenic detection on gold or gold film electrodes (Table 1). Using DPASV, Forsberg et al.[11] found a limit of detection (LOD) of 0.02 ppb for As(III) in 1 M perchloric acid with 10-min (sic) predeposition. Hua et al.[12] determined total arsenic in seawater on a gold ultramicroelectrode (25 μm) using ASV and achieved a LOD of 0.2 ppb. Kopanica and Novotny[13] performed the determination of As(III) in aqueous solutions by DPASV and obtained a LOD of 0.15 ppb. Simm et al.[14] investigated the sonoelectroanalytical arsenic detection on a gold electrode giving a LOD of 0.75 ppb. In addition to solid gold electrodes, gold film electrodes have also been used. Hamilton and Ellis[15] used a gold film electrode to determine arsenic and antimony in electrolytic copper samples and obtained a LOD of 0.56 ppb. The renewal of the gold film before each measurement improved the reproducibility. However, hydrogen bubbles forming during the deposition period caused poor reproducibility. Accordingly, Bodewig et al.[16] and Sun et al.[17] investigated the arsenic determination on gold rotating electrodes to remove the hydrogen bubbles mechanically. The LODs were 0.2 and 0.19 ppb, respectively. In the most sensitive detection to date, Feeney and Kounaves[18,19] developed a rapid method of the determination of arsenic in

* To whom correspondence should be addressed. Tel: 00441865 275413. Fax: 00441865 275410. E-mail: richard.compton@chemistry.ox.ac.uk.

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Table 1. Summary of Different Methods Developed for Arsenic Detection

authors	electrode material	method	deposition time/s	LOD/ppb
Forsberg et al.[11]	gold disk	DPASV	600	0.02
Hua et al.[12]	gold ultramicroelectrode	CCSV	240 (flow)	0.20
Kopanica and Novotny[13]	gold disk	DPASV	300	0.15
Simm et al.[14]	gold disk	sonoelectro-chemical SWV	120	0.75
Hamilton and Ellis[15]	gold film modified on glassy carbon	ASV	200	0.56
Bodewing et al.[16]	rotating gold disk	DPASV	240	0.20
Sun et al.[17]	rotating gold disk	DPASV	240	0.19
Feeney and Kounaves[18,19]	gold ultromicroelectrode array	SWV	300	0.013

DPASV: differential pulse anodic stripping voltammetry; CCS: constant current stripping voltammetry; SWV: square wave voltammetry. LOD: limit of detection.

aqueous solution on 564 gold ultramicroelectrode disk arrays (AuUMEA) using square wave voltammetry (SWV). These arrays were microlithographic fabricated using electron beam evaporation. Each ultramicroelectrode was circular and 12 μm in diameter with center-to-center spacing of 58 μm. AuUMEA could amplify the signal of arsenic with a low noise level while keeping the ultramicroelectrode behavior. A limit of detection of 0.013 ppb (statistical approach, 95% confidence) was obtained with 300-s predeposition. A portable battery-powered device was constructed to demonstrate rapid on-site arsenic analysis.

Recently, materials in the nanometer range have shown superior or advantageous functional properties for a wide range of technological applications, including catalysis, optics, microelectronics, and chemical/biological sensors. Metal nanoparticles provide three important functions for electroanalysis: the roughening of the conductive sensing interface, catalytic properties, and conductivity properties.[4] Several works have been based on gold nanoparticles. Gold nanoparticles can be made by chemical synthesis,[20] UV light or electron beam irradiation,[21] or electrochemical methods.[22,23] The former two methods are either time or cost consuming. In contrast, electrochemical deposition provides an easy and rapid alternative for the preparation of gold nanoparticle electrodes in a short time. Most gold nanoparticle-based electrodes are utilized as gas sensors and for the analysis of biological samples. However, the application of gold nanoparticle-modified electrodes for stripping voltammetry is, to the best of our knowledge, unexplored.

It was noted above that the microdisk array approach of Kounaves et al. represents the present state of the art in respect to arsenic detection via ASV using gold electrodes. The alternative use of an array of gold nanoparticles is investigated in this paper with the aim of an improved analytical performance (lower LOD, shorter deposition time, or both) reflecting increased rates of deposition arising from the large local rates of mass transport to the nanoparticles comprising the array.

The current study presents the first ever electrochemical detection of As(III) at a gold nanoparticle-modified glassy carbon

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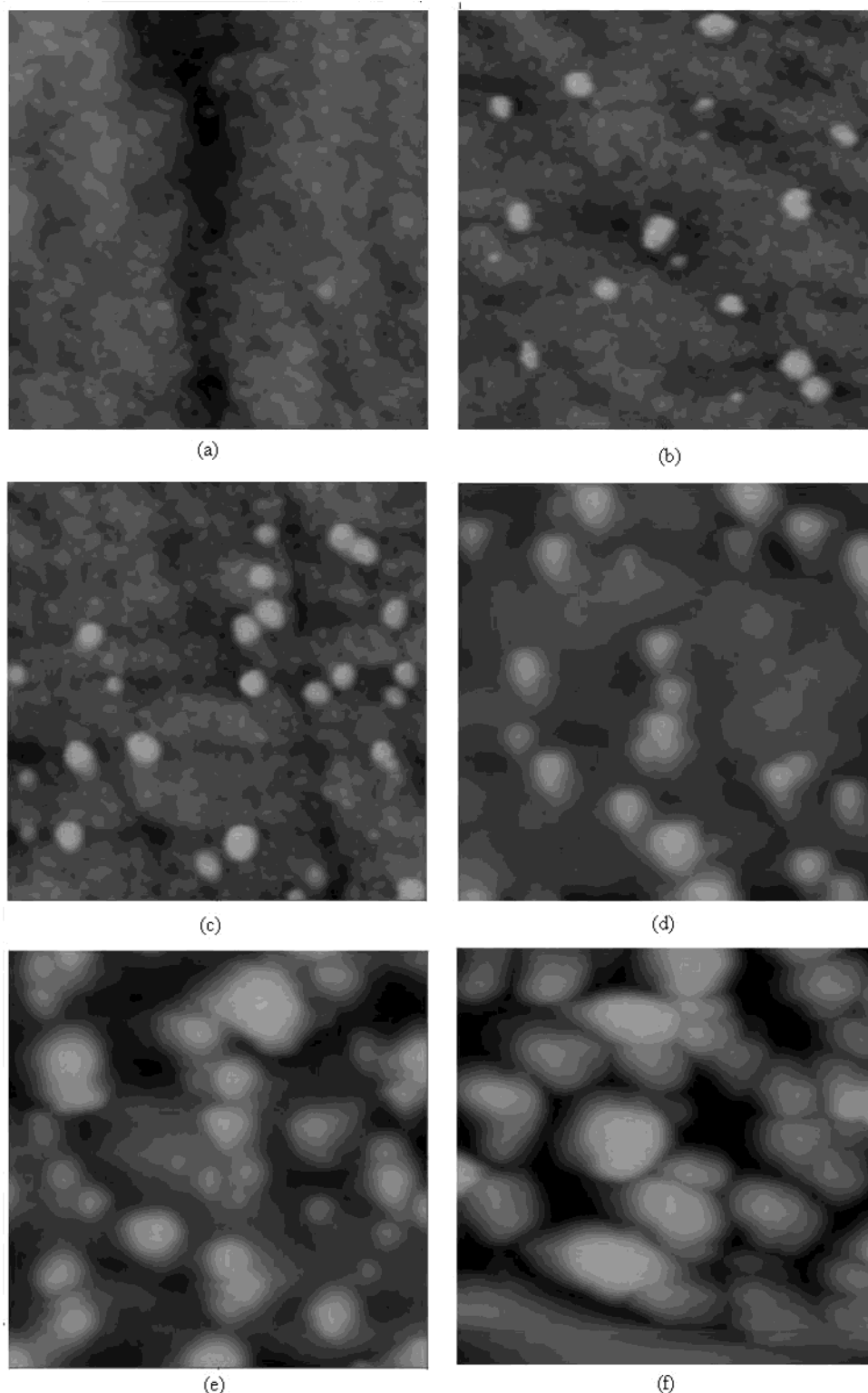(23) El-Deab, M. S.; Okajima, T.; Ohsaka, T. *J. Electrochem. Soc.* **2003**, *150*, A851.

(GC) electrode. First, the electrochemical deposition of Au nanoparticles onto GC was examined under various experimental conditions. Next the responses of As(III) on Au nanoparticle-modified GC were compared by using differential pulse voltammetry (DPV), linear sweep voltammetry (LSV), and square wave voltammetry. SWV was found to produce the most sensitive signal. Thus, other parameters were optimized further by using SWV. High sensitivity and large linear range were achieved using SWV. Low values for the LOD of ~0.01 ppb were obtained using either SWV or LSV.

EXPERIMENTAL SECTION

Chemical Reagents. All reagents were obtained from Aldrich were the highest grade available and used without further purification. All solutions and subsequent dilutions were prepared using deionized water from Vivendi UHQ grade water system (Vivendi) with a resistivity of not less than 18 MΩ cm. As(III) stock solution (10 mM) was prepared from As_2O_3: 0.009892 g of As_2O_3 was dissolved in the minimal amount of concentrated NaOH; the pH adjusted to 3.0 with concentrated HCl and diluted to 10 mL with deionized water.[11]

Instrumentation. Electrochemical measurements were recorded using an Autolab PGSTAT 30 computer-controlled potentiostat (EcoChemie) with a standard three-electrode system. A gold nanoparticle-modified GC electrode (geometric area of 0.07 cm^2, BAS Technicol) served as a working electrode; a platinum wire was used as a counter electrode with a saturated calomel reference electrode (SCE, Radiometer, Copenhagen, Denmark) completing the cell assembly. Between each modification, the GC electrode was polished with alumina Micropolish II (Buehler) using decreasing particle sizes from 1 to 0.3 μm. The electrode was sonicated for 10 min in deionized water after each stage of polishing. All experiments were carried at a temperature of 20 $\pm$ 2 °C.

The AFM measurements were performed using a Digital Instruments Multimode SPM, operating in ex situ contact mode. A model J scanner was used having a lateral range of 125 $\times$ 125 μm and a vertical range of 5 μm. Standard silicon nitride probes (type NP, Digital Instruments Multimode SPM), having a force constant of ~0.58 N m^{-1}, were used.

Preparation of Gold Nanoparticle-Modified Electrodes. The procedure for the deposition of gold nanoparticles at GC was adapted from previously published reports.[22,23] The polished GC

Figure 1. AFM images (500-nm scale) of various gold nanoparticle-modified GC: (a) bare GC, gold nanoparticles electrodeposited GC prepared from 0.5 M H_2SO_4 solution containing various concentration of $AuCl_4^-$ via different times of potential step from 1.055 to -0.045 V vs SCE, (b) 0.1 mM $AuCl_4^-$/5 s, (c) 0.1 mM $AuCl_4^-$/15 s, (d) 0.1 mM $AuCl_4^-$/30 s, (e) 0.1 mM $AuCl_4^-$/150 s, and (f) 1.0 mM $AuCl_4^-$/15 s.

(see above) was immersed into solutions of $AuCl_4^-$ in 0.5 M H_2SO_4 (see Results and Discussion for details) and a potential step from +1.055 V (vs SCE) to a selected potential (-0.245, -0.045, $+0.155$, or $+0.355$ V vs SCE) was applied for a fixed time (5, 15, 30, or 150 s). All solutions were degassed with a N_2 stream prior each measurement for at least 10 min.

RESULTS AND DISCUSSION

Characterization of Au Deposition. Typical AFM images of electrode surfaces formed under different formation conditions (deposition time and $AuCl_4^-$ concentration) for the electrodeposition of Au nanoparticles onto GC are shown in Figure 1. First, images of clean glassy carbon surfaces was taken (e.g.,

Table 2. Characterization of the Gold Nanoparticles Electrodeposited on GC under Various Deposition Conditions and As(III) Responses on These Electrodes

$AuCl_4^-$ concn/mM deposn time/s potential step end/V	charge of reductn peak/μC	Au surface area/ 10^{-3} cm^2	% geometric area	sensitivity $\mu A/\mu M$	LOD/ μM
0.1/5/−0.045	1.7	4.2	6.0	0.27	0.25
0.1/15/−0.045	3.0	7.4	10	1.0	0.042
0.1/30/−0.045	3.6	8.9	13	1.5	0.077
0.01/15/−0.045	0.34	0.86	1.2	0.02	0.13
1/15/−0.045	11	26	37	2.0	0.14
0.1/15/−0.245[a]	2.9	7.2	10	1.0	0.12
0.1/15/0.155	2.7	6.7	9.4	0.57	0.11

[a] Poor reproducibility.

Figure 1a). Then, the surfaces of different gold nanoparticle-modified glassy carbon electrodes were scanned (Figure 1b−f). The $AuCl_4^-$ concentration was 0.1 mM while the deposition time was 5, 15, 30, and 150 s, respectively, for Figure 1b−e. The conditions for Figure 1f were a 1.0 mM $AuCl_4^-$ solution and 15 s of deposition time. Clear small deposits can be seen in Figure 1b, while there are no such features seen on clean GC surfaces (Figure 1a). This shows that visible Au nanoparticles are first generated within just 5 s of deposition. It can be seen that an increase in the deposition time results in the enhancement of the average particle size of the Au nanoparticles (Figure 1 b−e). The mean radius of the Au nanoparticles is 9.5 nm for Figure 1b and 11 nm for Figure 1c. For growth from 0.1 mM $AuCl_4^-$, increasing the deposition time up to or beyond 30 s (Figure 1d) causes the formation of a gold film on the electrode surface as opposed to discrete nanoparticles. The longer the deposition time, the more gold film is formed (Figure 1d and f). Comparing Figure 1c and f, it can be seen that increasing the concentration of $AuCl_4^-$ solution also causes an increased tendency toward gold film formation (Figure 1f). To get as many Au nanoparticles as possible while not forming a continuous gold film, 15 s was chosen as the optimum deposition time and the optimal $AuCl_4^-$ concentration as 0.1 mM. Under the optimal deposition conditions, the number density of Au nanoparticles is ∼75 μm^{-2} and the mean radius is 11 nm.

To get surface information about the electrodeposited Au nanoparticles on glassy carbon, cyclic voltammetric profiles of each electrode under various formation conditions were next recorded in 0.05 M H_2SO_4 in the potential range from 0 to 1.5 V (vs SCE) with the scan rate of 100 mV s^{-1}. The corresponding curves are shown in Figure 2. Curve a is for clean glassy carbon. No peak is observed in either the forward or backward scan. The deposition time for formation of gold nanoparticles used to modify the electrode prior to recording curves b, d, and f is 15 s. The $AuCl_4^-$ concentrations used are 0.01, 0.1, and 1.0 mM, respectively, for curves b, d, and f. The $AuCl_4^-$ concentration for curves c−e is 0.1 mM while the deposition time varied from 5 to 15 s and then to 30 s. Thus, curves b, d and f show the effect of $AuCl_4^-$ concentration, while curves c−e show that of the deposition time. Analogous voltammetric profiles are observed for $AuCl_4^-$ concentrations up to 0.1 mM with a single reduction peak at + 0.85 V (vs SCE) which attributes to the reduction of gold surface oxide.[22,23] The magnitude of the reduction peak current is found to increase with the increase of either $AuCl_4^-$ concentration
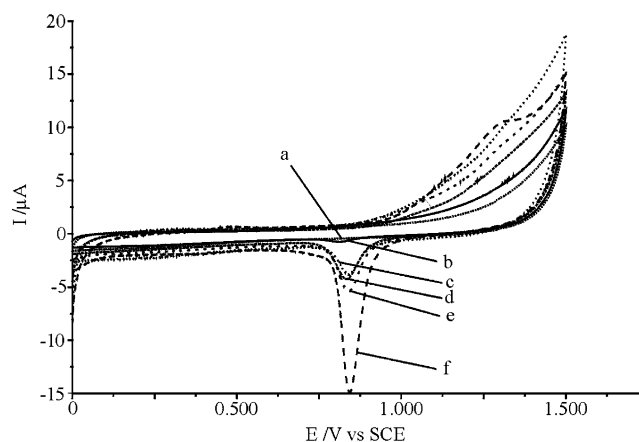

Figure 2. CV curves in N_2-saturated 0.05 M H_2SO_4, for gold nanoparticles electrodeposited on GCs prepared from 0.5 M H_2SO_4 solutions containing various concentrations of $AuCl_4^-$ via different times of potential step from 1.055 to −0.045 V vs SCE: (a) clean glassy carbon, (b) 0.01 mM $AuCl_4^-$/15 s, (c) 0.1 mM $AuCl_4^-$/5 s, (d) 0.1 mM $AuCl_4^-$/15 s, (e) 0.1 mM $AuCl_4^-$/30 s, and (f) 1.0 mM $AuCl_4^-$/ 15 s. Potential scan rate 100 mV s^{-1}.

(curves b, d, f) or the deposition time (curves c−e). This suggests that the increase of the total amount of gold nanoparticles loaded on the glassy carbon surface results from the increase in either the $AuCl_4^-$ concentration or the deposition time, in an agreement with the observations from the AFM images (Figure 1 b−f). No obvious oxidation process is found for the gold nanoparticle-modified electrodes deposited from solutions containing 0.01 and 0.1 mM $AuCl_4^-$. In contrast, a single oxidation peak at + 1.3 V (vs SCE) (curve f) is registered for the electrode constructed from 1.0 mM $AuCl_4^-$ solution along with the reduction peak at + 0.85 V (vs SCE) analogous to others. The presence of the oxidation peak suggests a gold "macro"electrode behavior,[20] which corresponds to the presence of the partial gold film in the AFM image (Figure 1f).

Based on the cyclic voltammetric curves outlined in Figure 2, the real surface area of the Au nanoparticles loading on GC was estimated. This was conducted based on the amount of charge consumed during the reduction of the Au surface oxide monolayer and a reported value of 400 μC cm^{-2} was used for the calculation.[24,25] Table 2 summarizes the characteristic information of the

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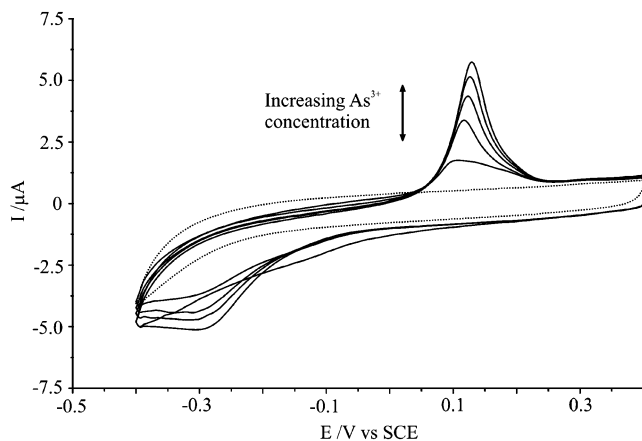
Figure 3. CV response of As(III) on gold nanoparticles electrode-posited on GC prepared from 0.5 M H_2SO_4 containing 0.1 mM $AuCl_4^-$ via 15-s potential step from 1.055 to -0.045 V vs SCE. Potential scan rate 100 mV s^{-1}.

gold surface area for the Au nanoparticles electrodeposited on GC under various experimental conditions. This confirms the observations made based on AFM and cyclic voltammetric measurements: The area of the gold surface is correlated to concentration of the $AuCl_4^-$ solution and deposition time. Increasing the concentration from 0.01 to 0.1 mM results in the increase of Au surface area from 8.6×10^{-4} to 7.4×10^{-3} cm^2, a nearly 10-fold increase. The increase of $AuCl_4^-$ concentration from 0.1 to 1.0 mM causes a nearly 4-fold increase of the Au surface area. Increasing the deposition time from 5 to 15 s, the Au surface area is increased from 4.2×10^{-3} to 7.4×10^{-3} cm^2. However, changing the deposition time from 15 to 30 s causes only a little increase of the surface area. The $AuCl_4^-$ concentration affects the Au nanoparticles deposition significantly. It can be seen that the deposition potential only slightly affects the amount of the gold surface area formed. However, it does affect the response of the constructed electrode toward the electrolysis of arsenic, which will be discussed next.

Electrochemical Response of As(III) on Gold Nanoparticle-Modified Electrodes. (1) Cyclic Voltammetry. To examine the electroanalytical performance of gold nanoparticle-modified electrodes, cyclic voltammetry was employed first. Figure 3 illustrates typical cyclic voltammetric responses in the range from -0.4 to $+0.4$ V (vs SCE, 100 mV s^{-1}) of a gold nanoparticle-modified electrode (stepped from 1.055 to -0.045 V for 15 s from 0.5 M H_2SO_4 containing 0.1 mM $AuCl_4^-$) in 1 M HCl. It can be seen that no redox processes were registered in the potential range studied (dashed line in Figure 3). However, a new reduction wave emerges at -0.29 V (vs SCE) upon the addition of 1 μM As(III) and can be attributed to the three-electron reduction of As(III) to As(0).[26] On the reversal anodic scan, an oxidation wave at $+0.13$ V (vs SCE) was observed. This process is ascribed to the subsequent reoxidation of As(0) to the parent As(III) species. Both waves were found to increase linearly with further additions of As(III) up to total concentration of 10 μM. The sensitivities and LODs calculated from the response of various gold nanoparticle-modified electrodes toward As(0) oxidation are summarized

in Table 2. It can be seen that the responses obtained at the electrode stepped to the more positive potential produces the lowest sensitivity, possibly due to the poor adhesion of gold nanoparticles to the glassy carbon surface. Increasing the Au deposited on GC by either using higher concentrations of $AuCl_4^-$ or prolonging the deposition time subject to not forming gold film leads to an increase of sensitivity. The best analytical parameters and reproducible signal were obtained for gold nanoparticles deposited under the same conditions as the optimal conditions from AFM experiments. Thus, these conditions were used for further electrochemical analysis of As(III).

(2) Stripping Voltammetry. Several supporting electrolytes were compared in respect of the response toward As(III) on the gold nanoparticle-modified electrodes using linear sweep voltammetry. The electrolyte solutions included 0.1, 1.0, and 2.0 M HCl, 0.5, 1.0, and 2.0 M H_2SO_4, and 1.0 M HNO_3. Among these, only HCl provided approximate *G*aussian-shaped and reproducible arsenic stripping peaks. The 2 M HCl gave the highest sensitivity (16 μA/μM), but not much higher than 1 M HCl (14 μA/μM); however, poor reproducibility was observed. The 1 M HCl supplied the best linear calibration plots and still gave a high sensitivity among the tested electrolytes. Thus, 1 M HCl was chosen as the supporting electrolyte in the following electrochemical experiments.

Different deposition times of 30, 60, 120, and 180 s were examined using LS V with standard additions of As(III) to 1 M HCl. With the increase of deposition time, the peak heights increased linearly. For the detection of low concentrations of As-(III), longer deposition time can be applied. For high concentrations of As(III), short deposition time can be used to avoid the saturation of the electrode surface. A scan rate of 100 mV s^{-1} (optimized) was used for the following experiments.

Linear sweep voltammetry and square wave voltammetry were compared, with 1 M HCl serving as the supporting electrolyte. In the two methods, the arsenic stripping peaks were seen between $+0.1$ and $+0.2$ V. Under the selected parameters, SWV gave the highest sensitivity but the noise of the baseline increased at the same time, which resulted in a higher LOD (S/N = 3), LSV (scan rate 100 mV s^{-1}) supplied a bigger linear range than SWV and the lowest LOD. Figure 4 shows the comparison of electrochemical curves of arsenic on gold nanoparticles electrodes in LSV and SWV. The calculated results for LSV and SWV are summarized in Table 3.

Then the SWV parameters of frequency and amplitude were optimized by examining the arsenic response at a gold nanoparticle-modified electrode in 1 M HCl. The SWV frequency from 25 to 110 Hz was examined. The frequency of 75 Hz gave an optimal signal-to-noise ratio and was used in the following experiments.

The pulse amplitudes of 25, 50, and 75 mV were tested. With an increase of pulse amplitude, the stripping peak potential shifted to more negative value and the peak heights increased. However, with the increase of the peak height, the reproducibility became worse. 25-mV amplitude gave out the best linear calibration plots and the lowest LOD among these three pulse amplitudes. The pulse amplitude of 25 mV was selected for all subsequent analyses.

Calibration and LOD. Calibration plots were made using gold nanoparticle-modified electrodes with the optimal deposition conditions (potential stepped from $+1.055$ to -0.045 V vs SCE

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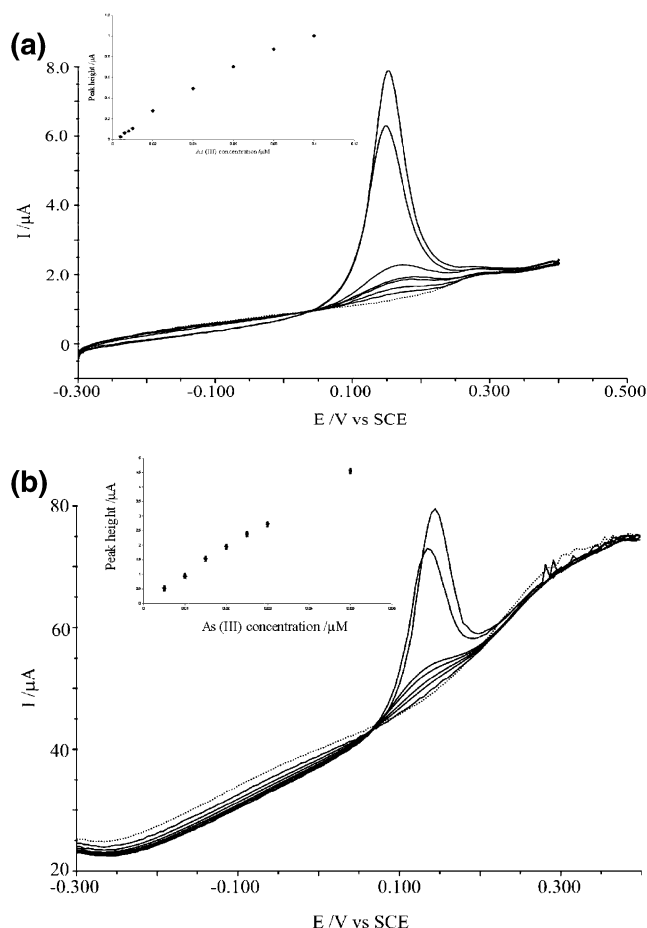
(a)

(b)

Figure 4. LSV and SWV curves of As(III) in 1 M HCl on gold nanoparticles electrodeposited on GC prepared the same as in Figure 3. LSV parameters: predeposition at −0.3 V vs SCE for 60 s, potential scan rate 100 mV s^{-1}. SWV parameters: predeposition at −0.3 V vs SCE for 60s, f = 75 Hz, E_{sw} = 25 mV, ΔE_s = 5 mV. Inset: plot peak height vs arsenic concentration.

Table 3. Comparison of LSV, SWV, and DPV of As(III) Response on Gold Nanoparticle-Modified GC

	LSV	SWV
sensitivity/μA/μM	14.2	71.7
LOD/μM	0.001	0.002
LOD/ppb	0.075	0.15

in 0.5 M H$_2$SO$_4$ containing 0.1 mM AuCl$_4^-$) in 1 M HCl with standard additions of As(III). Calibration experiments were performed using both LSV and SWV with 180-s deposition of As(III) at −0.3 V vs SCE. In LSV, a calibration slope of 18 μA/μM was obtained and the LOD was 0.000 13 μM (0.0096 ppb). In SWV under the optimal parameters, the calibration slope was 95 μA/μM and the LOD was 0.000 19 μM and 0.014 ppb. Both of the methods supplied a LOD or even lower LOD comparable to that obtained for gold ultramicroelectrode arrays.[11,12] It is interesting that the LSV response is similar to, or superior than, that from SWV, this likely reflects the shape (breadth) of the voltammetry response.

Application to a Real Matrix. Then this method was investigated on the detection of As(III) in spiked river water
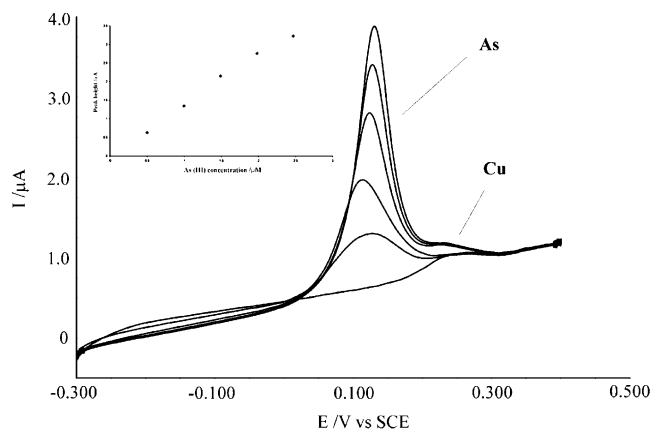

Figure 5. LSV voltammetry responses of standard additions of As-(III) to a 1:1 diluted river sample. Predeposition at −0.3 V vs SCE for 180 s, potential scan rate 100 mV s^{-1}. Inset: plot peak height vs added arsenic concentration.

samples which also contained copper ($\sim$1 μM). A river water sample (River Cherwell, Oxford) was taken and diluted with 2 M HCl (1:1). Standard additions of As(III) were performed in the diluted sample. Figure 5 showed the electrochemical curves and the corresponding calibration plots. No obvious As(III) stripping could be found in the curve of the water sample itself. There was a second peak at $\sim$+0.25 V (vs SCE) that was due to copper.[14] With the standard additions of As(III), linear plots were obtained and used for the calculation of As(III) concentration in the river water sample. The value of As(III) in the water sample was found to be 0.035 μM.

CONCLUSION

This study demonstrates a fast and easy way to detect arsenic-(III) on gold nanoparticles electrodeposited on GC electrode. The entire analytical procedure from the electrode preparation to the detection can be completed in several minutes. A high sensitivity of 95 μA/μM is obtained using SWV. LODs of 0.0096 ppb using LSV and 0.014 ppb using SWV are achieved. These provide the possibility of applying this method for the detection of arsenic in natural water samples. Further studies will focus on the application of this method for the field screening of arsenic in natural waters, noting Cu(II)[10,18] as the only likely interference. As with other electrochemical methods for As, it is anticipated that it will be to possible to determine total As, if As(V) is chemically reduced to As(III).[11,16] The method offers considerable simplicity and economy of electrode preparation as compared to the present state-of-the-art[18,19] electrochemical methods for As with likely similar rapidity.