

Electrochemical Determination of As(III) at Nanoporous Gold Electrodes with Controlled Surface Area

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ABSTRACT. Because arsenic (As) is a chemical substance toxic to humans, there have been extensive investigations on the development of As detection methods. In this study, the electrochemical determination of As on nanoporous gold (NPG) electrodes was investigated using anodic stripping voltammetry. The electrochemical surface area of the NPG electrodes was controlled by changing the reaction times during the anodization of Au for NPG preparation, and its effect on the electrochemical behavior during As detection was examined. The detection efficiency of the NPG electrodes improved as the roughness factor of the NPG electrodes increased up to around 100. A further increase in the surface area of the NPG electrodes resulted in a decrease of the detection efficiency due to high background current levels. The most efficient As detection efficiency was obtained on the NPG electrodes prepared with an anodization time of 50 s. The effects of the detection parameters and of the Cu interference in As detection were investigated and the NPG electrode was compared to flat Au electrodes.

Keywords: Nanoporous gold, Roughness factor, As detection, Anodic stripping voltammetry

INTRODUCTION

Arsenic (As) is a toxic substance that causes various health problems such as respiratory, mutagenic, and carcinogenic effects as well as dermal changes when exposed to the human body.^{1,2} As species exist in the form of As(III) or As(V); As(III) is 40–70 times more toxic than As(V).³ Therefore, there have been extensive investigations on the development of sensitive, selective, and fast analytical methods for the detection of As(III).⁴ Mass spectrometry, atomic emission spectrometry, high-performance liquid chromatography, and X-ray fluorescence methods have been developed for the detection of As. However, these methods require expensive equipment and highly skilled operators.⁵ In contrast, electrochemical methods, especially stripping voltammetry, provide an alternative route for As detection that has advantages such as low cost, simple operation, excellent sensitivity, and easy portability.^{4,6}

Various electrode materials based on Pt, Ag, and Au have been investigated for the electrochemical detection of As. A Pt-nanoparticle-modified glassy carbon electrode exhibited better sensitivity than a macro Pt electrode.⁷ Ag-based electrodes showed good performance for As detection in nitric acid electrolytes.⁸ Among the various electrode materials, Au-based electrodes have been widely investigated as highly sensitive electrode materials for electrochemical detection of As.^{9,6,10} Au-nanoparticle-modified

glassy carbon electrodes and Au nanoelectrode ensemble electrodes were effectively utilized for sensitive and selective electrochemical detection of As.^{9,11} Au(111)-like polycrystalline gold electrodes can selectively detect As in the presence of interference by high concentrations of Cu(II).⁶

Nanoporous gold (NPG) has received considerable attention as an electrode material because of its large surface area and electrocatalytic properties.¹² There have been several investigations on the electrochemical determination of As using the NPG electrodes. NPG-modified glassy carbon electrodes showed improved sensitivity for As detection due to their large surface area.^{4,13} NPG-based microelectrodes were fabricated for the electrochemical determination of As.^{5,10} However, most of the previous studies focused on the sensitivity enhancement of the NPG electrodes compared to that of flat Au electrodes. In this study, we investigated the electrochemical determination of As on the NPG electrodes depending on the surface area of the NPG electrodes. The effect of the surface roughness of NPG electrodes on the electrochemical detection of As has not been investigated in a detailed way. The surface area of the NPG electrodes can be controlled straightforwardly using the anodization of Au in Cl⁻-containing solutions.^{12,14} The electrochemical behavior of the NPG electrodes with different surface areas was examined for As detection using anodic stripping square wave voltammetry (SWV). The experimental parameters were

optimized to determine the NPG electrodes with the best As detection performance, and the Cu(II) interference effect was investigated.

EXPERIMENTAL

All solutions were prepared using purified water (Milli-Q, 18.2 M Ω cm). HCl and H₂SO₄ were purchased from Merck, and other chemicals were purchased from Aldrich. A 5 mM As(III) stock solution was prepared as follows: 1) As₂O₃ was dissolved in a minimal amount of NaOH solution, 2) HCl was added to the solution to adjust the pH to 3, and 3) the solution was diluted to total volume with Milli-Q water.¹⁵ Electrochemical measurements were performed using a CHI 660D electrochemical workstation (CH instrument). Ag/AgCl electrodes (3 M NaCl) and Pt wire were used as reference and counter electrodes, respectively. The NPG electrodes were fabricated by the anodization of Au rod electrodes (CH Instruments, 2 mm in diameter) in phosphate buffer solution (pH 8) containing 1 M KCl, as reported in our previous studies.^{12,14} Before anodization, the Au rod electrodes were mechanically polished with alumina powder and sonicated in water. The surface areas of the NPG electrodes were controlled by adjusting the anodizing reaction time. The roughness factor (R_f , electrochemical surface area divided by geometric area) of the NPG electrodes increased with increasing reaction time (Fig. S1). The NPG electrodes fabricated with the designated reaction times are named 'NPG (reaction time)'; for example, the NPG electrodes fabricated in 50 s are named 'NPG (50 s)'. Electrochemical detection of As(III) on the NPG electrodes was performed in 1 M HCl using anodic stripping SWV. As(III) was first accumulated on the NPG electrode surface in the form of As(0) at a deposition potential of -0.2 V for 150 s of deposition time. SWV was then performed to strip the As(0) to As(III) with typical parameters of increment $E = 0.004$ V, amplitude = 25 mV, and frequency = 15 Hz.

RESULTS AND DISCUSSION

We first examined the effect of an increase in the surface area of the NPG electrodes on As(III) detection compared with a flat Au electrode. Fig. 1 shows the SWV of flat Au and NPG (50 s) obtained in the presence of 3 μ M As(III). On both of these electrodes, anodic stripping peaks of As(III) occur, indicating that the As(III) can be electrochemically detected. The peak current on NPG (50 s) was 47.8 μ A, significantly higher than that on a flat Au

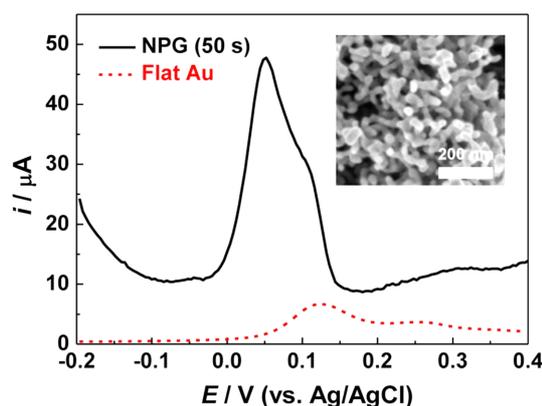


Figure 1. SWV responses on flat Au and NPG (50 s) electrodes in 3 μ M As(III) + 1.0 M HCl. Inset: Typical SEM image of NPG electrode.

electrode (6.7 μ A). This demonstrates that As(III) can be more easily detected on an NPG electrode compared to a flat Au electrode because of the large NPG electrode surface area. The potential of the stripping peak on the NPG electrode shifts to a more negative value compared to the flat Au. This is probably due to the large surface area and the large number of catalytic active sites originating from the porous structure of the NPG electrode.^{4,13}

We next investigated the effect of variation in surface area of NPG on the SWV response during anodic stripping of As(III). The NPG electrodes with different surface areas were prepared by adjusting the reaction time, and their SWV behavior in the presence of 3 μ M As(III) is compared in Fig. 2. Fig. 2(a) shows that the stripping current increases continuously as the reaction time increases from 25 s up to 100 s, implying that the increase in surface area of NPG results in an increase of the efficiency of As(III) detection. When the reaction time increases to values longer than 150 s, the NPG electrodes exhibit broad anodic waves at around 0.27 V (Fig. 2(b)). The stripping current for As detection on these NPG electrodes was less clearly observed because of the broad waves at 0.27 V. The dependence of the stripping peak current corrected for the background current on the reaction time for NPG preparation is plotted in Fig. 2(c). The stripping current peak increases sharply as the reaction time increases up to 50 s. The stripping current for the NPG (100 s) electrode is similar to that of the NPG (50 s) electrode. A further increase in the reaction time results in a decrease in stripping current, and the stripping of As can hardly be detected for the NPG (300 s) electrode.

These results suggest that the NPG (50 s) electrode can be regarded as the best one for As detection. The NPG (50 s)

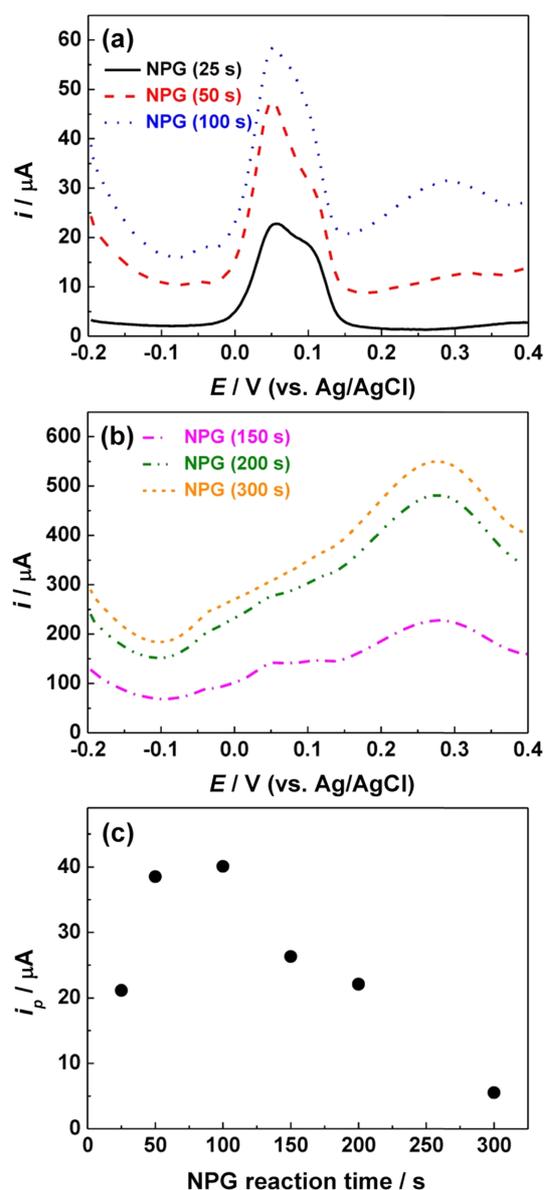


Figure 2. (a) and (b) SWV responses on NPG electrodes with different surface areas in $3 \mu M$ As(III) + $1.0 M$ HCl. (c) Dependence of the As(III) stripping peak current on the NPG reaction time.

electrode typically shows a roughness factor of ~ 100 (refer to Fig. S1(b)). A higher stripping current can be obtained with a larger surface area of NPG; however, further improvement in As detection efficiency was not achieved when the roughness factor of NPG became higher than ~ 100 . Fig. 3 shows the background SWV response of the NPG electrodes in $1.0 M$ HCl in the absence of As(III). Broad anodic waves at $0.27 V$ observed in Fig. 2(b) were also measured in the background SWV in the absence of As(III), indicating that these waves originate from NPG surfaces with high surface roughness in the blank electrolyte. The

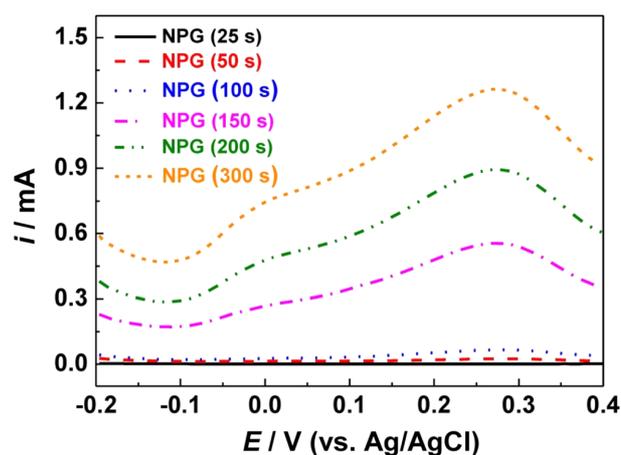


Figure 3. Comparison of background SWV response of NPG electrodes in $1.0 M$ HCl in the absence of As(III).

increase of the As stripping current on the NPG electrodes with moderate surface roughness is discernable from the blank response. However, the As stripping current on the NPG electrodes with high surface area (reaction times longer than $150 s$) is buried by the high background current. Therefore, the NPG electrodes with reaction times longer than $150 s$ cannot be used for the electrochemical detection of As from a practical perspective.

We speculate that the broad wave at $0.27 V$ is due to the adsorption of Cl^- ion on the NPG electrode surface with high surface roughness in the HCl electrolyte. Control experiments of As detection were performed in $1.0 M H_2SO_4$ electrolytes (Fig. S2). The electrochemical behavior obtained in H_2SO_4 electrolytes were similar to those observed in the HCl electrolytes. The background currents abruptly increased on the NPG ($150 s$) electrode, and broad anodic waves appeared at $0.25 V$ in the H_2SO_4 electrolytes. The stripping current increased as the reaction time of NPG increased from $25 s$ up to $100 s$; however, a further increase in the stripping current could not be achieved. The change in the background response including broad waves is not due to adsorption of Cl^- . Although the exact explanation is not available at this stage, the NPG electrodes with higher surface area than a certain level are not useful for the electrochemical detection of As.

In order to find optimal conditions for As detection, the effect of the potential for pre-deposition of As(III) in the form of As(0) on the peak current for As stripping was examined using the NPG ($50 s$) electrode (Fig. S3). In the potential range $-0.1 V$ to $-0.3 V$, a maximum stripping current was obtained at $-0.2 V$. A pre-deposition potential of $-0.1 V$ is not sufficiently negative to reduce As(III) to As(0) compared to the pre-deposition at $-0.2 V$. The strip-

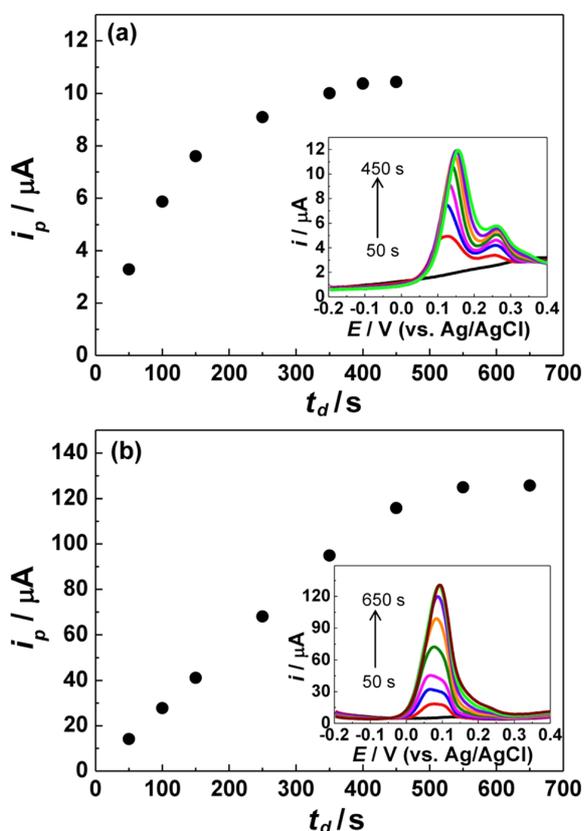


Figure 4. Dependence of stripping current on pre-deposition times obtained on (a) flat Au and (b) NPG (50 s) electrodes in 5 mM As(III) + 1.0 M HCl.

ping current significantly decreases at -0.3 V, at which potential hydrogen evolution reactions occur rather than the reduction of As(III).^{15,16} We applied a pre-deposition potential of -0.2 V throughout the present investigation.

We next investigated the effect of the pre-deposition time on the efficiency of As detection. Fig. 4 shows the dependence of stripping current for As detection on the pre-deposition times used for the flat Au and NPG electrodes. The stripping peak current increased as the pre-deposition time increased both on the flat Au and NPG electrodes. The stripping current on the flat Au electrodes increased sharply with pre-deposition times up to 150 s, after which the stripping current gradually increased to a saturated value at 350 s. On the other hand, the stripping current on the NPG electrodes continued to increase with pre-deposition times up to 450 s, indicating that a higher stripping current is obtained on the NPG electrodes at longer pre-deposition times compared to the flat Au electrodes. It is known that the As(0) layers deposited on Au surfaces have insulating properties,¹⁵ which prohibit further deposition of As(0) from As(III). Because the NPG electrodes have

more abundant active sites for As deposition than the flat Au electrodes have, due to their large surface area, a higher stripping current can be obtained at longer pre-deposition times.

According to the results shown in Fig. 4, we expect that the electroanalytical efficiency for As detection on the NPG electrodes would be improved over flat Au electrodes as the pre-deposition time increases. SWVs for As detection with different pre-deposition times were obtained on the NPG electrodes (Fig. 5(a)), from which calibration curves for As detection are presented in Fig. 5(b). As the pre-deposition time increases, the sensitivity of the calibration curves significantly increases. Calibration curves obtained on flat Au electrodes with different pre-deposition times were also constructed from the SWVs (Fig. S4) and are compared in Fig. 5(b). On flat Au electrodes, the sensitivity becomes higher when the pre-deposition increases from 50 s to 150 s; however, no further sensitivity increase is observed at a pre-deposition time of 400 s.

The degree of sensitivity enhancement between NPG and flat Au electrodes depending on pre-deposition times was compared using the sensitivity ratios between the two electrodes (Table S1). The sensitivity ratio of NPG over flat Au electrode increases as the pre-deposition time increases. The sensitivity for As detection on the NPG electrodes is three times higher than that on flat Au electrodes with 150 s of pre-deposition time. When the pre-deposition time increases to 400 s, the NPG electrode exhibits 11 times higher sensitivity than the flat Au electrodes. A pre-deposition time of 150 s is enough for As detection on flat Au electrodes, whereas significantly improved electroanalytical efficiency for As detection could be achieved on the NPG electrodes with a pre-deposition time of 400 s.

Cu(II) is one of the main interfering substances during electrochemical As(III) detection, wherein Cu forms intermetallic compounds such as Cu_2As_3 .^{4,10} Therefore, we investigated the effect of Cu(II) interference on the electrochemical detection of As(III) on the NPG electrodes. Fig. 6(a) shows the SWV behavior of NPG (50 s) electrodes upon the addition of As(III) in the presence of Cu(II). Stripping peaks for As(III) and Cu(II) appear at 0.06 V and 0.42 V, respectively. The stripping peak potentials of As(III) in the presence of Cu(II) are similar to those observed in the absence of Cu(II) as shown in Fig. 5(a). The stripping peaks for Cu(II) are well separated from the As(III) stripping peaks on the NPG electrodes. In contrast, the stripping peaks for Cu(II) overlap considerably with those of As(III) on flat Au electrodes (Fig. S5), indicating that Cu(II) interference is significant for As(III) detection on flat Au electrodes.

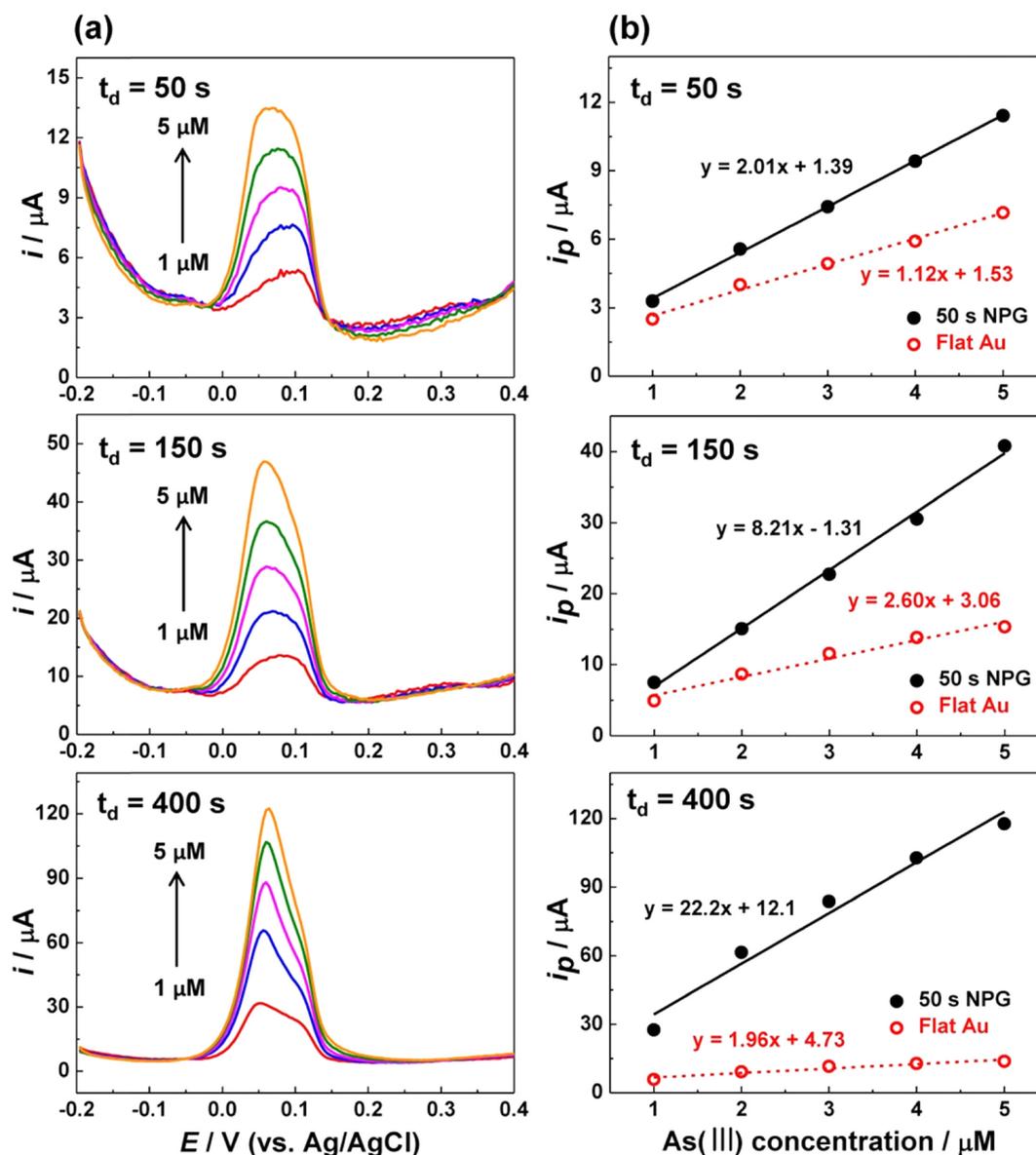


Figure 5. (a) SWVs obtained on NPG (50 s) electrodes in 1 M HCl containing various concentrations of As(III) at different pre-deposition times. (b) Calibration curves obtained on flat Au and NPG (50 s) electrodes at different pre-deposition times.

Fig. 6(b) compares the calibration curves for As(III) detection on the NPG electrodes in the presence and absence of Cu(II). The sensitivity of the NPG electrodes for As(III) detection in the presence of Cu ($8.15 \mu\text{A}/\mu\text{M}$) is almost the same as that obtained in the absence of Cu ($8.21 \mu\text{A}/\mu\text{M}$). On flat Au electrodes, the sensitivity decreases from $2.60 \mu\text{A}/\mu\text{M}$ to $1.57 \mu\text{A}/\mu\text{M}$ when Cu(II) is added as an interfering substance (Fig. S5(b)). These results clearly demonstrate that the NPG electrodes exhibit an improved interference effect compared to flat Au electrodes. We presume that the large surface area of NPG provides abundant active sites for As(III)

deposition even in the presence of Cu(II), which results in this anti-interference effect during the electrochemical detection of As.

Moreover, we examined the variation of stripping peak currents for As detection as the concentration of Cu(II) increased (Fig. S6). On both the NPG and flat Au electrodes, the stripping peak currents gradually decreased as the Cu(II) concentration increased because of co-deposition of As(III) and Cu(II) on the Au surface.¹⁷ On flat Au electrodes, the As stripping peak current obtained in the absence of Cu(II) decreased by 46% when Cu(II) was suc-

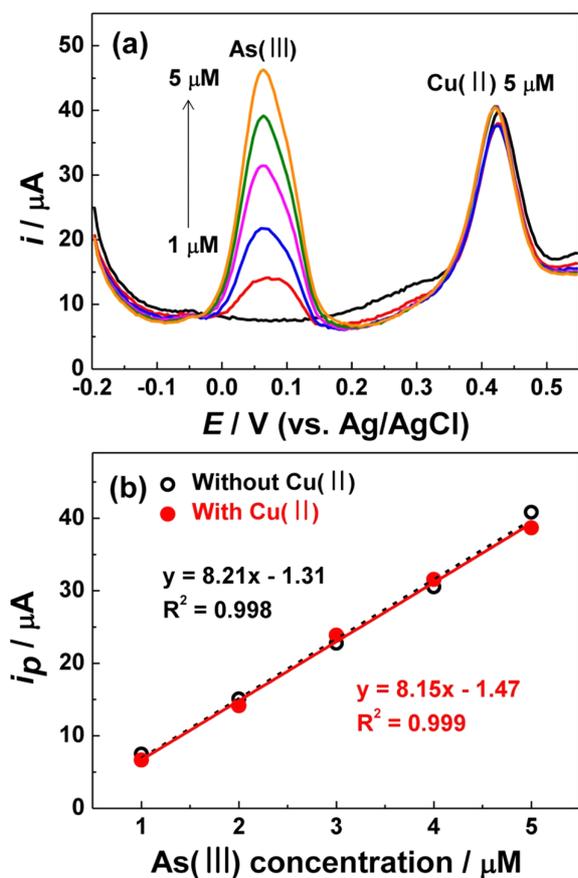


Figure 6. (a) SWVs obtained on NPG (50 s) electrodes in 1 M HCl containing various concentrations of As(III) in the presence of 5 μM Cu(II). Deposition potential = -0.2 V and pre-deposition time = 150 s. (b) Calibration curves of As detection in the presence and absence of Cu(II).

cessively added up to 5 μM . In contrast, the stripping current decreased by only 28% on the NPG electrodes when Cu(II) was added. These results demonstrate again the superior selectivity of the NPG electrodes over flat Au electrodes for the electrochemical detection of As.

CONCLUSIONS

In this study, we investigated the anodic stripping determination of As(III) on the NPG electrodes with different surface areas controlled by the reaction times during the anodization of Au for NPG preparation. Because the stripping current is proportional to the electrochemical surface area, the efficiency of As detection was expected to improve by using the NPG electrodes with a high surface area. The electrochemical behavior of the NPG electrodes for As detection with different surface areas revealed that the

detection efficiency was improved as the reaction time of the NPG electrodes increased up to 50 s (roughness factor of ~ 100). However, a further increase in the surface area of the NPG electrodes resulted in a decrease of detection efficiency because of high background current levels. For the NPG electrodes, a longer pre-deposition time can improve the As detection efficiency compared to flat Au electrodes. The NPG electrodes exhibited a better selectivity for As(III) detection against Cu(II) interference than flat Au electrodes. These results provide new insights into the fabrication of electrochemical As sensors.

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Supporting Information. Additional electrochemical results for As detection on the NPG electrodes.

REFERENCES

- Mandal, B. K.; Suzuki, K. T. *Talanta*. **2002**, *58*, 201.
- Zhang, W.; Cai, Y.; Tu, C.; Ma, L. Q. *Sci. Total Environ.* **2002**, *300*, 167.
- Muñoz, E.; Palmero, S. *Talanta*. **2005**, *65*, 613.
- Yang, M.; Chen, X.; Liu, J.-H.; Huang, X.-J. *Sens. Actuators, B*. **2016**, *234*, 404.
- Jiang, J.; Holm, N.; O'Brien, K. *ECS J. Solid State Sci. Technol.* **2015**, *4*, S3024.
- Rahman, M. R.; Okajima, T.; Ohsaka, T. *Anal. Chem.* **2010**, *82*, 9169.
- Dai, X.; Compton, R. G. *Analyst*. **2006**, *131*, 516.
- Simm, A. O.; Banks, C. E.; Compton, R. G. *Electroanalysis*. **2005**, *17*, 1727.
- Dai, X.; Nekrassova, O.; Hyde, M. E.; Compton, R. G. *Anal. Chem.* **2004**, *76*, 5924.
- Jaramillo, D. X. O.; Sukeri, A.; Saravia, L. P. H.; Espinoza-Montero, P. J.; Bertotti, M. *Electroanalysis*. **2017**, *29*, 2316.
- Jena, B. K.; Raj, C. R. *Anal. Chem.* **2008**, *80*, 4836.
- Kim, M.; Kim, J. *Langmuir*. **2014**, *30*, 4844.
- Wang, S.; Wang, X.; Zhong, J.; Zhai, S.; Li, Y.; Lin, L.; Liu, Y.; Mei, X.; Ding, Y. *Int. J. Electrochem. Sci.* **2017**, *12*, 8345.
- Lee, E.; Sung, M.; Wang, Y.; Kim, J. *Electroanalysis*. **2018**, *30*, 2028.
- Hossain, M. M.; Islam, M. M.; Ferdousi, S.; Okajima, T.; Ohsaka, T. *Electroanalysis*. **2008**, *20*, 2435.
- Giacomino, A.; Abollino, O.; Lazzara, M.; Malandrino, M.; Mentasti, E. *Talanta*. **2011**, *83*, 1428.
- Feeney, R.; Kounaves, S. P. *Anal. Chem.* **2000**, *72*, 2222.