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Electrochemical detection of arsenic(III) using porous gold via square wave voltammetry

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Abstract−Electrochemical detection of trace arsenic(III) in aqueous phase was studied with a porous gold (PAu) electrode, which was prepared by paper-based templating method. Square wave voltammetry was performed in As(III) solutions. The limit of detection of 0.1 ppb was obtained with a linear detection range of 0.1-14 ppb, which complies with the regulations for As(III) content in drinking water. The analysis of roughness factor and diffusion coefficient showed that the porous structure of the PAu electrode might have a stronger contribution to improving the sensitivity and selectivity of the target ion, compared to bulk gold electrode.

Keywords: Arsenic, Porous Gold, Square Wave Voltammetry, Electrochemical Detection

INTRODUCTION

The contamination of arsenic in groundwater and drinking water is a serious worldwide threat to human health, and has become a challenge for environmental scientists [1]. The chronic toxicity of arsenic in drinking water is known to cause various types of cancers and skin hardening [2]. The World Health Organization (WHO) has recommended that the maximum contaminant level for arsenic in drinking water be reduced to 2-10 ppb [3]. Thus, an efficient and inexpensive method to detect arsenic in drinking water with sufficient sensitivity is required.

The electrochemical methods are potentially the most promising techniques available for use in the field, due to their cost-effectiveness and rapid analysis compared to lab-based instruments, such as inductively coupled plasma spectroscopy, atomic absorption spectroscopy, and ion chromatography [4,5]. Among the electrochemical methods available, stripping voltammetry analysis is the most popular due to its excellent sensitivity and unique ability to detect trace levels of elements in distinct oxidation states [1,5]. The anodic stripping voltammetry (ASV) process involves electrochemical deposition of arsenic ions on an electrode for several minutes (i.e., $As^{3+}+3e^{-}\rightarrow As^{0}$) followed by oxidation of the metal back into the solution by a reverse potential scan (i.e., $As^{0}\rightarrow As^{3+}+3e^{-}$) [6]. With the introduction of new pulse voltammetric techniques such as square wave voltammetry (SWV), signal-to-noise enhancement through reduction in a capacitance background provides considerably better detection limits than expensive spectroscopic techniques. Various materials (Pt, Au, and Ag) have been employed as working electrodes for the square wave anodic stripping voltammetry (SWASV) of arsenic [1-7], and Au-electrodes have been extensively used for As^{3+} detection because Au is non-toxic and interacts with As^{0} and As^{3+} during the processes of deposition and stripping.

In previous work, a simple and facile method for the synthesis of paper-based porous gold (PAu) with large surface area was suggested [8]. Compared with gold nanoparticle (AuNP)-based electrodes, PAu electrodes not only allow rapid mass transport of ions through the electrolyte/electrode interface, but also rapid active electrochemical reactivity [9]. Therefore, electrochemical detection of As^{3+} in aqueous phase was tested with PAu electrode in the presence of HCl through the SWASV method.

EXPERIMENTAL

A paper-based PAu electrode was prepared by a previously reported method [8,9]. In brief, 20 nm AuNPs were prepared by wet-chemistry method and filtered several times by a syringe using a cellulose filter with 200 nm pore size. The reddish-filter paper was then dried at 60 °C, followed by heat-treatment at 450 °C to remove the cellulose of the filter paper and to further sinter between the neighboring AuNPs. The surface morphology of PAu and Au foil was analyzed by scanning electron microscopy (SEM, S-4700, Hitachi).

SWV was obtained using a three-electrode configuration with an electrochemical analyzer (VSP, BioLogic). A Pt wire and an Ag/AgCl electrode were used as auxiliary and reference electrodes, respectively. PAu was used as the working electrode, and bulk Au foil was used to compare the electrochemical sensitivity for As^{3+}. 1 M HCl as the acid media was used due to the enhanced As^{0} formation caused by Cl^{-} serving as an ionic bridge between the electrodes as the As^{3+} species [5]. All the SWV measurements were performed with amplitude of 10 mV at 80 Hz (pulse width of 25 ms and step height of 4 mV). The deposition of As^{0} by reduction of As^{3+} was at a potential of −0.4 V for 60 s, and anodic stripping was performed from −0.3 to 0.3 V.

RESULTS AND DISCUSSION

To synthesize the PAu electrode, AuNPs were used as a precur-

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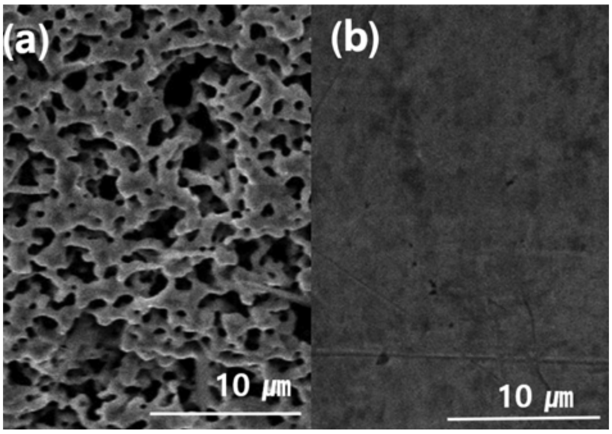

Fig. 1. SEM images of (a) free-standing PAu and (b) Au foil.

sor material for the electrode backbone. After injection of AuNPs into the cellulose filter-paper, the color of the filter changed from white to dark red, indicating that AuNPs were physically loaded into the cellulose substrate. After thermal treatment of the resulting filter with the incorporated AuNPs, the cellulose template was removed and AuNPs were sintered to form a gold network as the free-standing backbone structure of the electrode. As shown in Fig. 1(a), the surface morphology of PAu was a coral-like structure that showed a window pore of 200-400 nm. Conversely, Au foil showed a very smooth surface in the SEM image (Fig. 1(b)). The roughness factor (RF) of the electrode can be calculated by using the ratio of the real surface area to the geometric surface area. As described in previous work [11], the RF of PAu and the Au foil electrode was 147 and 14, respectively. The large surface area and high RF of PAu with a porous structure compared to planar gold was helpful in enhancing the electrochemical activity in sensors and the mineralization of target materials [10,11].

SWASV measurement of the trace level of arsenic was performed using the PAu and the bulk Au foil. The deposition potential of As^{3+} in SWASV was varied from 0 to −1 V [5], and a typical cyclic voltammogram of As^{3+} shows a well-defined reduction of an As^{3+} wave at −0.3 V and a corresponding oxidation wave at ~0.2 V (As^0 to As^{3+}) [4]. Herein, As^{3+} was deposited at −0.4 V, and anodic stripping was performed at a range of from −0.3 to 0.3 V. The concentration of As^{3+} was increased from 0.1 to 15 ppb. As shown in Fig. 2, the stripping peak was at 0.15-0.2 V and the response current of the peak was increased with increasing concentration of As^{3+}. The current density of the oxidation peak from As^0 to As^{3+} in the presence of 15 ppb As^{3+} was calculated as 1.63 mA/cm^2 for PAu, which was similar to that of the Au-embedded carbon film electrode [12]. While the PAu electrode showed gradual increment of the response current from As^{3+} concentration of 0.1 ppb (Fig. 2(a)), the peak current for the Au foil electrode changed from As^{3+} of 1 ppb (Fig. 2(b)). The linearity of PAu and Au foil was calculated as y=0.348x+40.613 (R^2=0.979) and y=0.401x+36.794 (R^2=0.874), respectively. Since the open-porous microstructure of PAu facilitates ease of transport of analytes to the inner large surface of the electrode during reduction and stripping processes, the electrochemical activity of PAu for detecting As^{3+} was enhanced and showed distinct current change in a very low concentration of As^{3+}. This structural effect on the electrochemical activity for As^{3+} was also found in other reports. Kato et al. demonstrated that the AuNP-embedded nanostructure plays a key role in achieving higher electrocatalytic activity for As^{3+} pre-concentration than the bulk Au electrode [12]. To quantify the structural effect on the transport of As^{3+} ion to the target electrodes, the apparent diffusion coefficient (D) was calculated using the classical Cottrell's equation [13]. The D values of the PAu and Au foil were estimated at 7.7×10^{-4} and 5.4×10^{-5} cm^2/s, respectively. The diffusion of analyte through the surface of PAu was 1.5 times larger than that of Au foil; thus, the porous structure of the electrode plays an important role in enhancing the electrochemical sensitivity of target ions in ultra-low concentration.

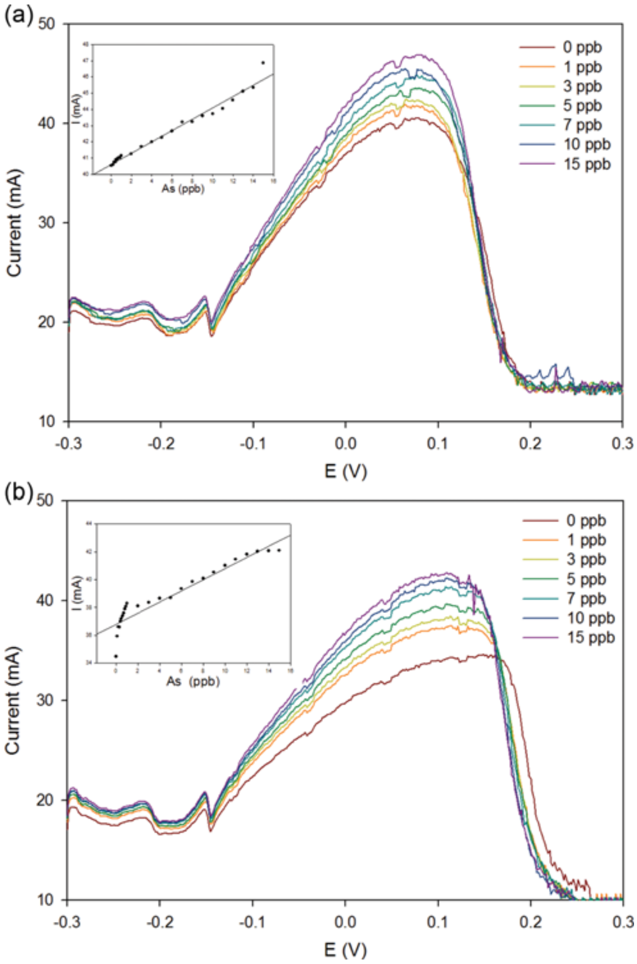

Fig. 2. SWASV curves for various As^{3+} concentrations with (a) PAu and (b) Au foil.

A linear relation occurs between the response current and the As^{3+} concentration (inset in Fig. 2). While the linear least squares calibration curve of PAu was in the range of from 0 to 14 ppb, the linear detection range (LDR) of Au foil was narrow (from 1 to 12 ppb). Although the sensitivity of Au foil has a somewhat large value (0.401 vs. 0.348 mA/ppb), the PAu electrode has some advantages such as good limit of detection (LOD) (0.1 ppb), high sensitivity in low concentration, broad LDR, and good linearity between

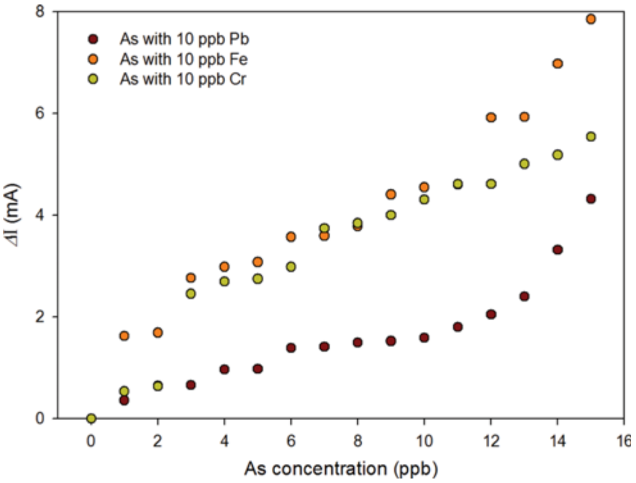

Fig. 3. Selectivity test of As^{3+} in the presence of other ions.

As^{3+} concentration and response current. The sensitivity and LOD of As^{3+} using the PAu electrode was comparable to those of other methods reported in the literature [1,3,5-7,12]. While the detection of As^{3+} through electrochemical impedance spectroscopy (EIS) is also possible [14], SWASV provides a more rapid analysis with a short potential cycle, and is thus suitable to detect the trace metal ions in drinking water.

The major problem associated with the available Au or Au-based electrodes is the interference from some commonly coexisting ions present in the real water sample [15]. Therefore, artificial wastewater contained with some other common heavy metal ions (Cr, Fe, and Pb) was used to evaluate the selectivity of PAu electrode for As^{3+}. Other metal ions were fixed at 10 ppb and the As^{3+} ion was changed from 0.1 to 15 ppb. As shown in Fig. 3, in the presence of other ions, the sensitivity and linearity for detecting As^{3+} using PAu were maintained. Although Pb^{2+} ion was interfered with As^{3+} ion below 10 ppb, they are generally a linear correlation in the test range.

CONCLUSIONS

This study demonstrates a fast and efficient method for the preparation of PAu electrodes with large surface area and porous structure, and demonstrates its application in the detection of arsenic via SWASV. With PAu electrodes synthesized using AuNPs and syringe-filter paper, we obtained good analytical performance for As^{3+} detection including an LOD of 0.1 ppb, an LDR of 0.1-14 ppb, and a sensitivity of 0.348 mA/ppb. The PAu electrodes therefore comply with the WHO regulations. In addition, it is shown that the diffusion coefficient of PAu was larger than that of Au foil. Therefore, the porous structure of the electrode contributed to improving the electrochemical sensitivity and selectivity of target ions.

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REFERENCES

1. C. Gao, X. Y. Yu, S. Q. Xiong, J. H. Liu and X. J. Huang, *Anal. Chem.*, **85**, 2673 (2013).
2. Y. Kim, C. Kim, I. Choi, S. Rengaraj and J. Yi, *Environ. Sci. Technol.*, **38**, 924 (2004).
3. B. K. Jena and C. R. Raj, *Anal. Chem.*, **80**, 4836 (2008).
4. J. H. T. Luong, E. Lam and K. B. Male, *Anal. Methods*, **6**, 6157 (2014).
5. D. E. Mays and A. Hussam, *Anal. Chim. Acta*, **646**, 6 (2009).
6. A. O. Simm, C. E. Banks and R. G. Compton, *Electroanalysis*, **17**, 1727 (2005).
7. L. Xiao, G. C. Wildgoose and R. G. Compton, *Anal. Chim. Acta*, **620**, 44 (2008).
8. S. Y. Oh, J. Kim and Y. Kim, *Mater. Lett.*, **154**, 60 (2015).
9. S. Y. Oh, R. Selvaraj and Y. Kim, *J. Ind. Eng. Chem.*, **26**, 95 (2015).
10. Y. Du, J. J. Xu and H. Y. Chen, *Electrochem. Commun.*, **11**, 1717 (2009).
11. J. Kim, C. Yeom and Y. Kim, *Korean J. Chem. Eng.*, **33**, 1855 (2016).
12. D. Kato, T. Kamata, D. Kato, H. Yanagisawa and O. Niwa, *Anal. Chem.*, **88**, 2944 (2016).
13. T. A. Silva, G. F. Pereira, O. Fatibello-Filho, K. I. B. Eguiluz and G. R. Salaza-Banda, *J. Electroanal. Chem.*, **769**, 28 (2016).
14. X. Liu, P. A. Duckworth and D. K. Y. Wong, *Biosens. Bioelectron.*, **25**, 1467 (2010).
15. M. Yang, X. Chen, J.-H. Liu and X.-J. Huang, *Sensors Actu. B*, **234**, 404 (2016).