

Determination of As³⁺ Based on Nanoporous Gold by Square Wave Anodic Stripping Voltammetry

Suiping Wang^{1,2,*}, Xu Wang¹, Jinfeng Zhong¹, Shaolan Zhai¹, Yafei Li¹, Lizhong Lin³, Yejiu Liu³, Xiaodi Mei³, Yanjun Ding^{4,*}

¹ Hunan College Key Laboratory of Heavy Metal Pollution Control, College of Chemical Engineering, Xiangtan University, Xiangtan 411105, China

² Collaborative Innovation Center for Efficient and Health Production of Fisheries in Hunan Province, College of Life and Environmental Sciences, Hunan University of Arts and Science, Changde 415000, China

³ Hunan Jinjian Cereals Industry CO., Ltd., Changde 415000

⁴ Department of Forensic Science, School of Basic Medical Sciences, Central South University, Changsha 410013

*E-mail: suiping66@126.com

Received: 11 May 2017 / Accepted: 9 July 2017 / Published: 13 August 2017

In this paper, the preparation of nanoporous gold (NPG) was established by the dynamic bubble template electrodeposition. Taking advantages of the large specific surface area and good catalytic activity of the NPG, a method of determining trace As³⁺ by the NPG modified electrode was developed. The deposition time, enrichment time, supporting electrolyte and pH was optimized. Under the optimized experimental conditions, a good linearity was obtained in the concentration range of 0.001 to 4 µg/mL and the detection limit is 0.001 µg/mL. The linear equation is $y=14.6753x-0.0132$ ($r=0.9992$). The reproducibility was investigated with a RSD of 3.11% ($n=6$). The repeatability was investigated with a RSD of 2.41% for six measurements. The developed As³⁺ sensor based on NPG has advantages such as simple fabrication, fast response, low detection limit and good reproducibility.

Keywords: nanoporous gold; As³⁺; electrochemical sensor

1. INTRODUCTION

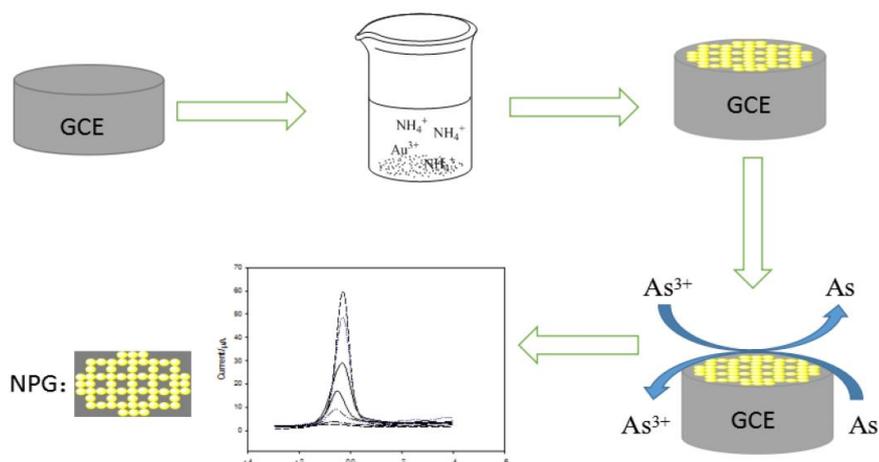
Arsenic as a kind of heavy metal ions is highly toxic and harmful to human beings. The enrichment of arsenic in the human body may cause many health effects, such as skin lesion and respiratory, cardiovascular, gastrointestinal, nervous, mutagenic, and carcinogenic effects [1]. Substantial evidence have shown that there is a connection between liver, lung and kidney disease as

well as adverse dermal effects such as hyperkeratosis and depigmentation and arsenic intake [2, 3]. Therefore, exploiting simple, reliable and high-sensitive techniques to detect trace arsenic is very necessary.

Recently, several methods have been developed to estimate the trace arsenic, such as atomic absorption spectrometry [4], atomic fluorescence spectroscopy [5], surface plasmon resonance [6], and inductively coupled plasma spectrometry [7]. But these methods tend to require sophisticated instruments, tedious sample preparation procedures, and professional personnel. What's more, they are difficult to be used for on-site detection because of the non portable device. Compared with those techniques, electrochemical techniques, especially square wave anodic stripping voltammetry (SWASV), are quite compelling due to its unique ability for high sensitivity, rapid analysis, cost effective and routine in-field monitoring for a large number of samples.

It is generally known that the electrode material is an important factor affecting the sensitivity of electrochemical sensors. Nanoporous metals, recently, have raised great research interests due to their three-dimensional morphology, and some unique structural properties such as mechanical rigidity, electrical conductivity, and high corrosion resistance [8]. Many electrodes are decorated with precious metal, particularly Au, which have received much more attention due to its good ability of electron transfer and catalytic activity [9, 10]. Nanoporous gold (NPG) as a kind of nanostructured gold, with high surface-to-volume ratio and great porosity was demonstrated in catalyst, sensors, and electrochemistry [11-13]. Due to its unique properties substantially, the nanoporous gold is expected to use for the detection of As^{3+} .

Here, a facile and fast approach was used to synthesize NPG at a glassy carbon electrode. A rapid and highly sensitive NPG-based electrochemical sensor for As^{3+} detection combined with square wave anodic stripping voltammetry was constructed. The quantitative range of the proposed NPG sensor for the analysis of As^{3+} was studied; the SWASV parameters and the electrolyte composition were optimized. A schematic representation of the fabrication of the NPG/GCE and the analytical process for As^{3+} is shown in scheme 1.



Scheme 1. Schematic illustration of the modification of the NPG/GCE sensor and the analytical process for As^{3+} .

2. EXPERIMENTAL

2.1. Materials and apparatus

Ammonium chloride (AR), chloroauric acid tetrahydrate (AR), sodium sulfate (AR), sodium chloride (AR), potassium chloride (AR), phosphoric acid (AR), boric acid (AR), acetic acid (AR), sodium hydroxide (AR) and sodium nitrate (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Ethanol (AR), sulfuric acid (98%, AR) and hydrochloric acid (37%, AR) were purchased from Zhuzhou star glass Co. Ltd. The stock standard solutions of 1 mg/ml of arsenic(III), copper(II), cadmium(II) and lead(II) were provided by National Analysis and Testing Center for Nonferrous Metals and Electronic Materials. Analytical-grade HCl (0.1 M) were used to adjust the pH value of the 0.1 M Na₂SO₄, NaNO₃, NaCl and KCl. Britton-Robinson solution (BR) with pH=3 was prepared by mixing 100 ml mixed acid containing 0.04 M phosphoric acid, 0.04 M boric acid, and 0.04 M acetic acid with 18 ml sodium hydroxide (0.2 M). The deionized water (18.2 MΩ cm) was used to prepare all solutions.

Electrochemical measurements were carried out on CHI 660D electrochemical workstation (Shanghai CH Instruments Co., China). Scanning electron microscopy analysis was performed using a JSM-6610LV microscope (JEOL, Ltd., Japan).

2.2. Fabrication of the NPG/GCE

Bare GCE was first polished with 0.05 μm of alumina power, followed by ultrasonic treatment in ultrapure water, alcohol and ultrapure water successively. Then the GCE was electrochemically cleaned by scanning in 0.5 M H₂SO₄ from -0.2 V to 1.2 V until the curve of CV became stable [14, 15]. Then the bare GCE was immersed in a solution containing 0.01 M HAuCl₄ and 2.5 M NH₄Cl. The NPG was structured by electrodeposited with a fixed potential of -3.0 V under the condition of magnetic stirring for 60 s [16].

2.3. Electrochemical measurements

All electrochemical measurements were performed with a CHI660D electrochemical workstation which purchased from Chenhua Instruments Co. (Shanghai, China). A traditional three-electrode electrochemical system with a mirror polished glassy carbon electrode (GCE) as working electrode, saturated calomel electrode (SCE) as reference electrode, platinum wire as the auxiliary electrode was used in the analysis. Cyclic voltammetry (CV) was performed in 0.1 M KCl (pH = 3.0), the potential step from -0.2 V to 1.4 V with a scan rate of 100 mV/s. The accumulation process was performed under the potential of -0.6 V with a preconcentration time of 120 s. SWASV was performed in 0.1 M KCl (pH = 3.0), the voltage range was from -0.30 V to 0.50 V at the following conditions: frequency, 15 Hz; amplitude, 25 mV; increment potential, 4 mV.

2.4. Real sample analysis

To investigate the practicability of the proposed strategy in real water samples, tap water and water of Huamei Lake was adopted and recovery tests were performed using the standard addition technique. Fresh tap water and water of Huamei Lake was allowed to stand for half an hour, the supernatant was measured. The samples were spiked with $1 \mu\text{g/mL As}^{3+}$, and then detected by our method. The results of recoveries are computed based on the experiment.

3. RESULTS AND DISCUSSION

3.1. SEM images

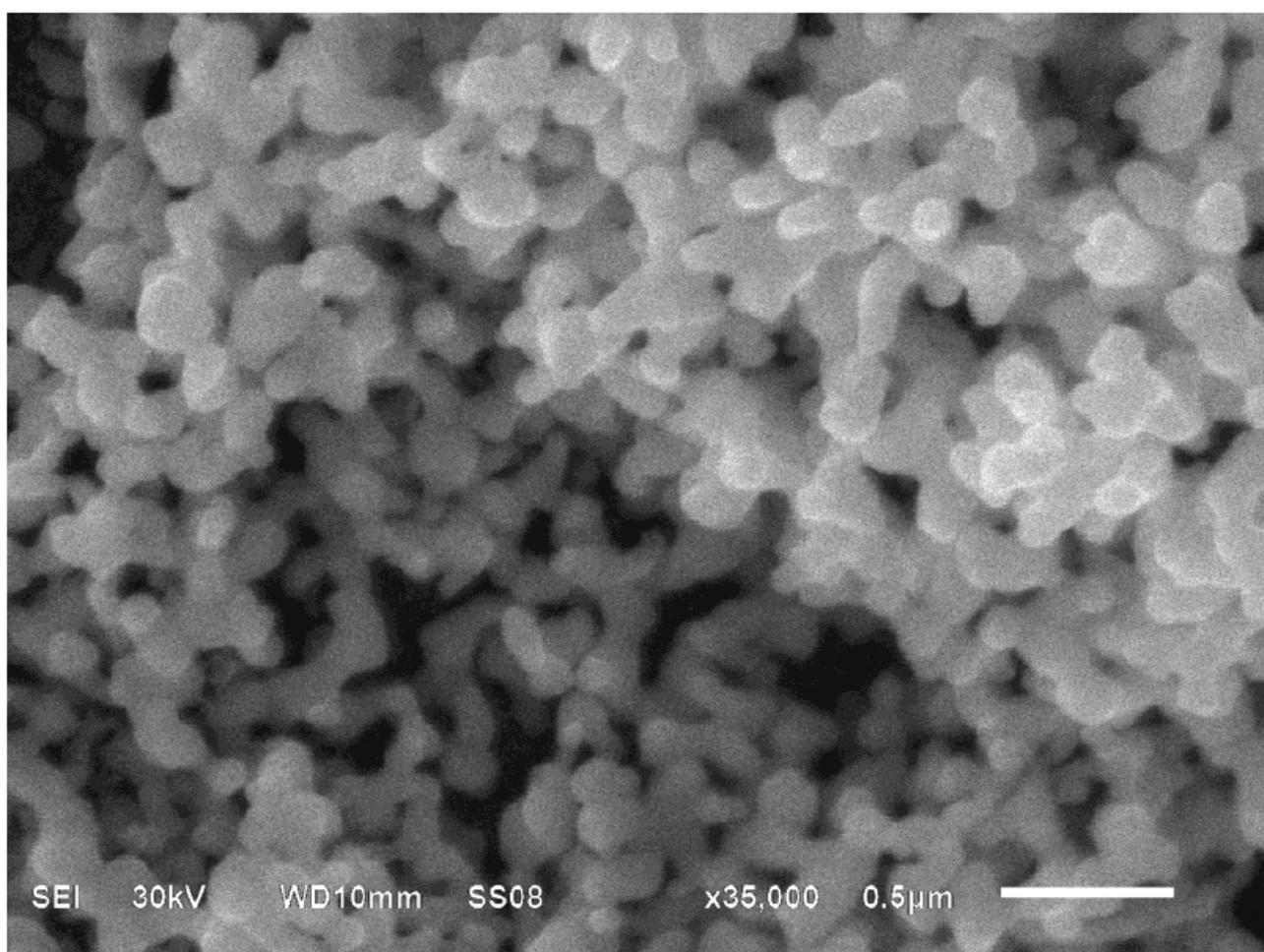


Figure 1. SEM image of the NPG.

The morphology and structure of the NPG were characterized by SEM. As shown in figure 1, a very clear coral microstructure is constructed with holes in the nanoscale. This architecture exhibits a high specific surface area because of the porous film formed by coral-like structure. The hydrogen

evolution plays a significant role in a dynamic bubble template electrodeposition, so a high concentration of NH_4^+ (2.5M) is necessary to increase the rate of evolution of hydrogen [17]. The gold was organized on the GCE at a high overpotential of -3.0 V. During the electrodeposition, continuous bubbles are released on the electrode surface; the gold is deposited in the bubbles gap leaving a porous film formed on the surface [18, 19]. Finally, only pure material is obtained without any template left due to the same time removing of the bubble template during deposition. The porous structure could provide more sites for the deposition of metal ions on the surface of the electrode compared with bulk gold. The high surface areas of NPG could enhance the loading capacity of metal ions. Therefore this structure was further used for the detection of As^{3+} .

3.2. Electrochemical characterization of NPG

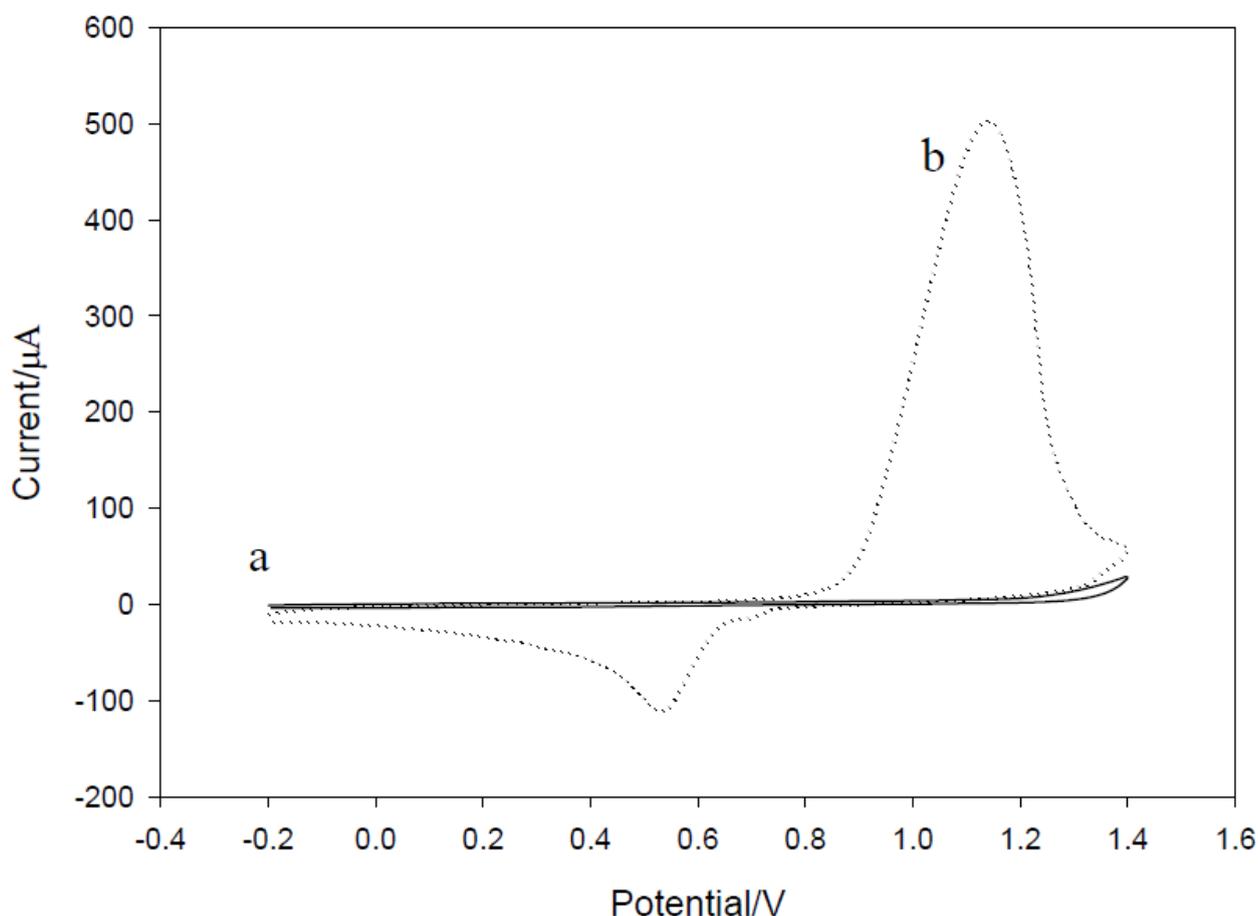


Figure 2. CV responses of bare GCE (a), and NPG/GCE (b). The cyclic voltammetry was performed in 0.1 M KCl (pH = 3.0) from -0.2 V to 1.4 V with a scan rate of 100 mV/s.

In figure 2, CVs of the NPG modified electrode and bare GCE in a 0.1 M KCl (pH=3) solution at 100 mV/ s are shown. As can be seen, the bare glassy carbon electrode (a) appears no redox peaks, while a pair of distinct redox peaks were obtained from the NPG modified GCE (curve b), due to the oxidation and reduction of Au, indicating the successful modification of NPG on the surface of GCE.

3.3. Amplification performance of the NPG

In order to investigate whether the employment of the nanocoral NPG can significantly enhance the electrochemical response of As, the typical SWASV analysis of different electrodes were recorded in 0.1 M KCl (pH = 3) containing 1 $\mu\text{g/mL}$ As^{3+} . As shown in fig. 3, the bare glassy carbon electrode (a) appears no stripping peak; the Au electrode (b) appears an obvious dissolution peak of arsenic.

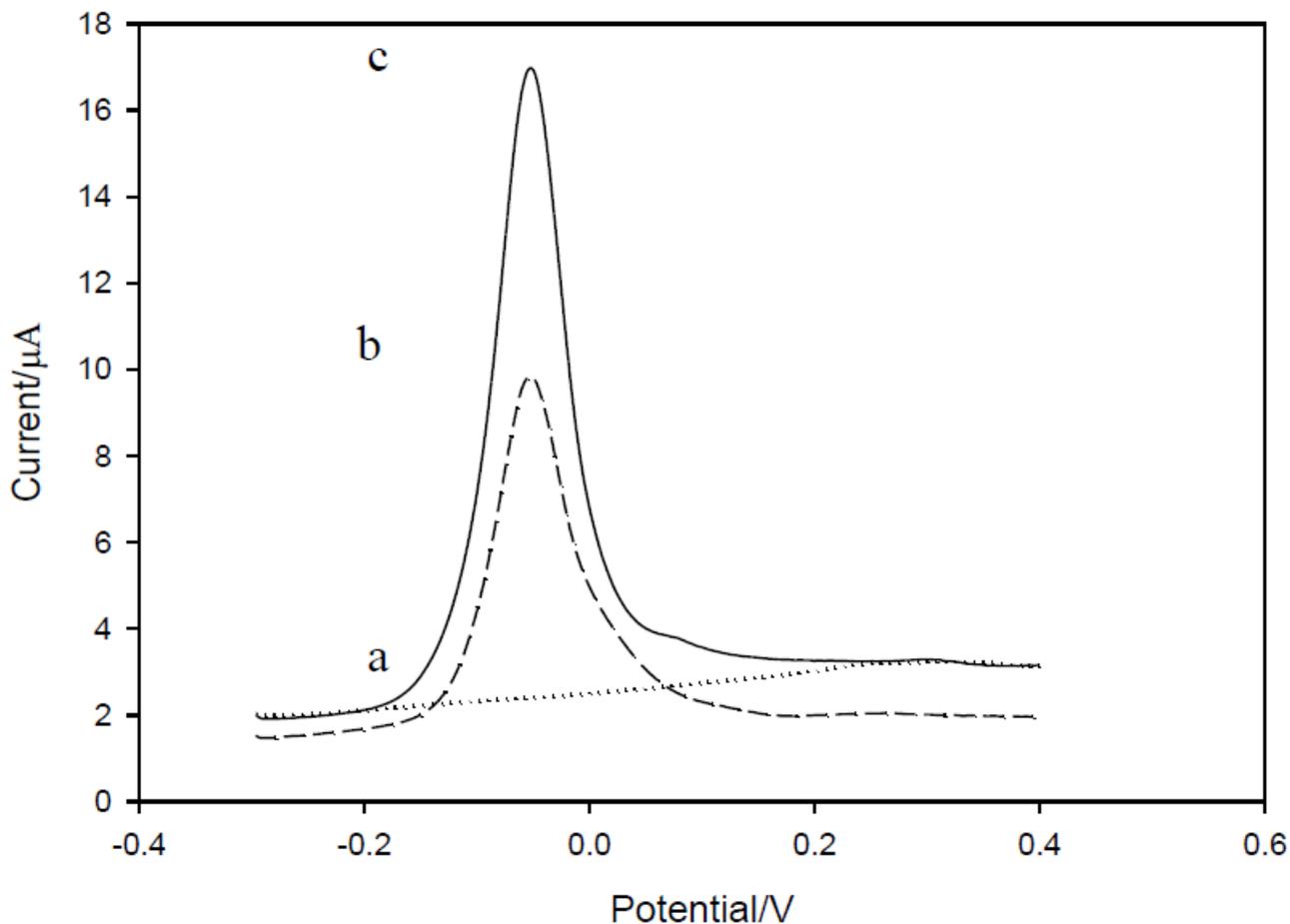


Figure 3. SWASV responses of bare GCE (a), gold electrode (b), and NPG/GCE (c) in 0.1 M KCl (pH=3.0) containing 1 $\mu\text{g/mL}$ As^{3+} . The accumulation process was performed under the potential of -0.6 V with a preconcentration time of 120 s. SWASV was performed in 0.1 M KCl (pH = 3.0) at the following conditions: voltage range, -0.30 V—0.50 V; frequency, 15 Hz; amplitude, 25 mV; increment potential, 4 mV.

Compared with the bare GCE and Au electrode, the NPG/GCE (c) has the largest stripping peak current. And the peak current of NPG is about 2 fold than that of the Au electrode. This comparison clearly indicates that the NPG improves greatly the sensitivity of the sensor towards As. The increase in peak current on the NPG modified GCE is attributed to the NPG, which increases the active sites of the electrode surface, and promotes the electron transfer.

3.4 Optimization of the electrochemical measurements

In order to increase the sensitivity of the sensor, experimental conditions such as the deposition time of the gold, accumulation time of the arsenic ion, pH value and electrolyte which are the critical parameters were optimized using SWASV analysis in the presence of As^{3+} .

As can be seen in figure 4, the peak current increased remarkably till the deposition time of NPG increased to 60 s. Then, the stripping peak current of As reached a steady plateau when the deposition time increased from 60 s to 80 s. It seems that, after deposition of 60 s, a very stable and complete structure is formed. Thus, the deposition time of 60 s was considered to be the optimal deposition time for the determination of As^{3+} .

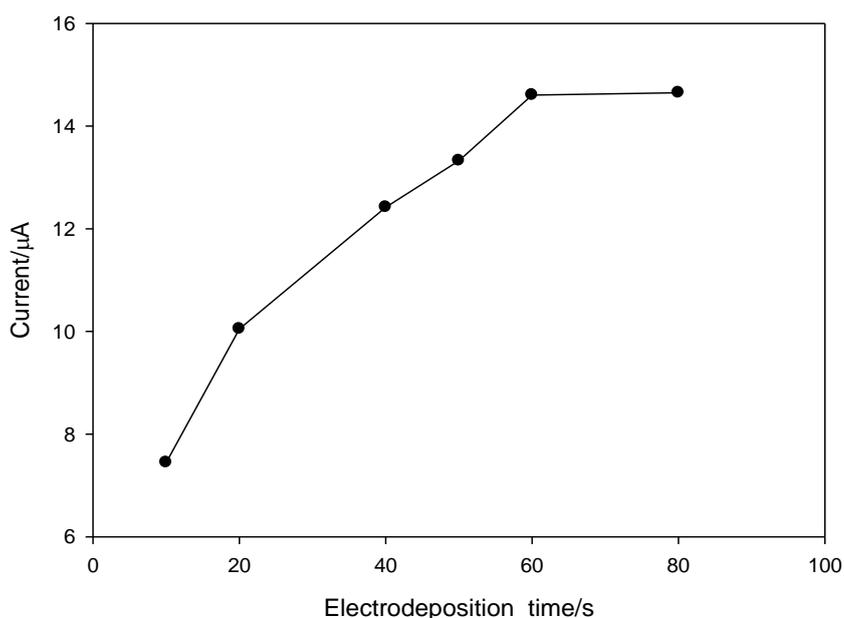


Figure 4. Effect of the deposition time of the NPG on the stripping peak current response of arsenic. The concentration of As^{3+} is $1 \mu\text{g/mL}$.

Fig 5 shows the connection between stripping peak current and accumulation time. It is observed that the stripping peak current of arsenic increases rapidly with accumulation time up to 300 s and then increases relatively slow over 300 s. To shorten the analysis time, 300 s was selected as the optimal accumulation time for further detection.

The effect of the pH value of the measuring solution was also studied (figure 6). The pH value of the electrolyte solution ranged from 1.0 to 7.0 was investigated in 0.1 M KCl. It was observed that the maximum current was obtained at pH 3. Thus, pH 3 was employed throughout the detection process.

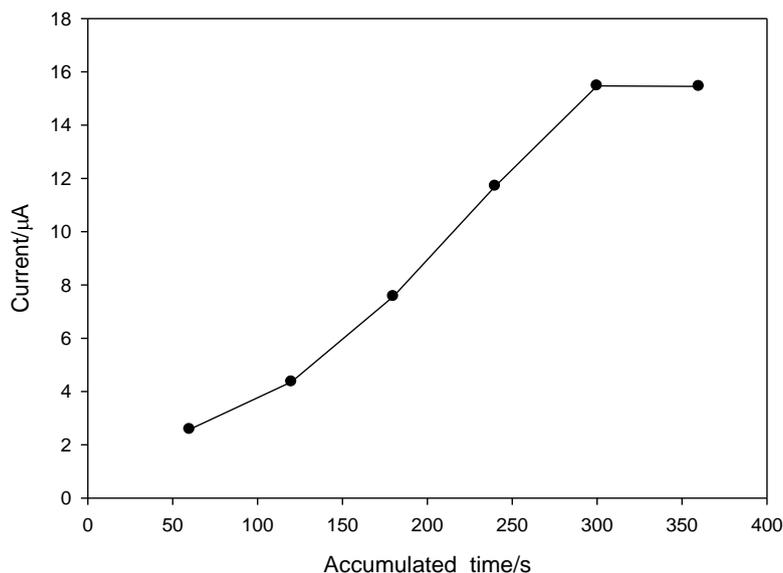


Figure 5. Effect of accumulation time of the arsenic ion on the stripping peak current response of arsenic. The concentration of As^{3+} is $1 \mu\text{g/mL}$.

The composition of electrolyte solution was also studied. The different stripping peak current observed in different supporting electrolytes is likely due to that these supporting electrolytes form different structures with heavy metal ions [20]. It can be seen in figure 7 a maximum stripping peak was obtained when 0.1 M KCl (pH=3) was used in this system. Therefore, 0.1 M KCl was adopted in the detection procedure.

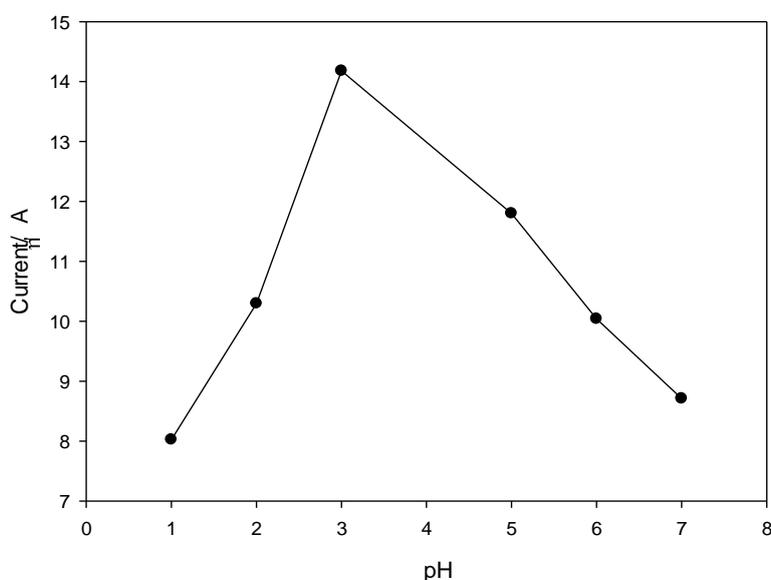


Figure 6. Effect of the pH value on the stripping peak current response of arsenic. The concentration of As^{3+} is $1 \mu\text{g/mL}$.

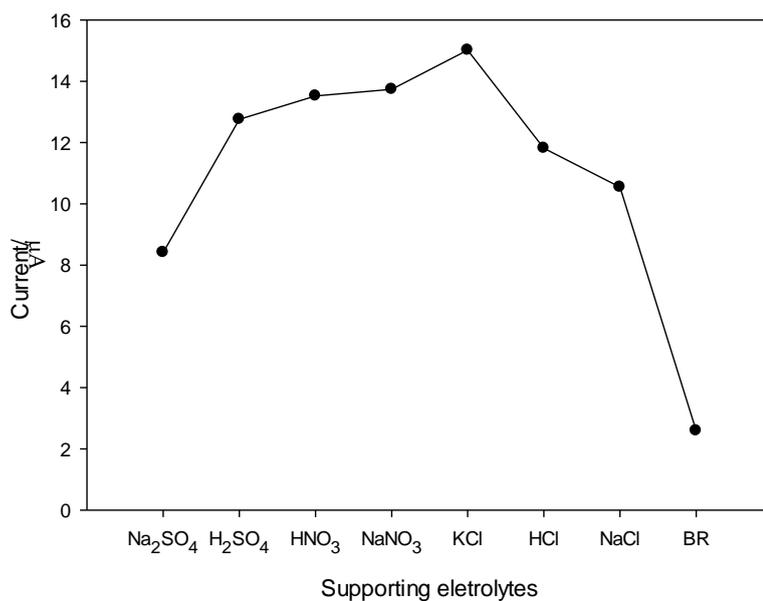


Figure 7. Effect of supporting electrolytes on the stripping peak current response of arsenic. The concentration of As³⁺ is 1 μg/mL.

3.5. Analytical performance of the NPG modified electrode

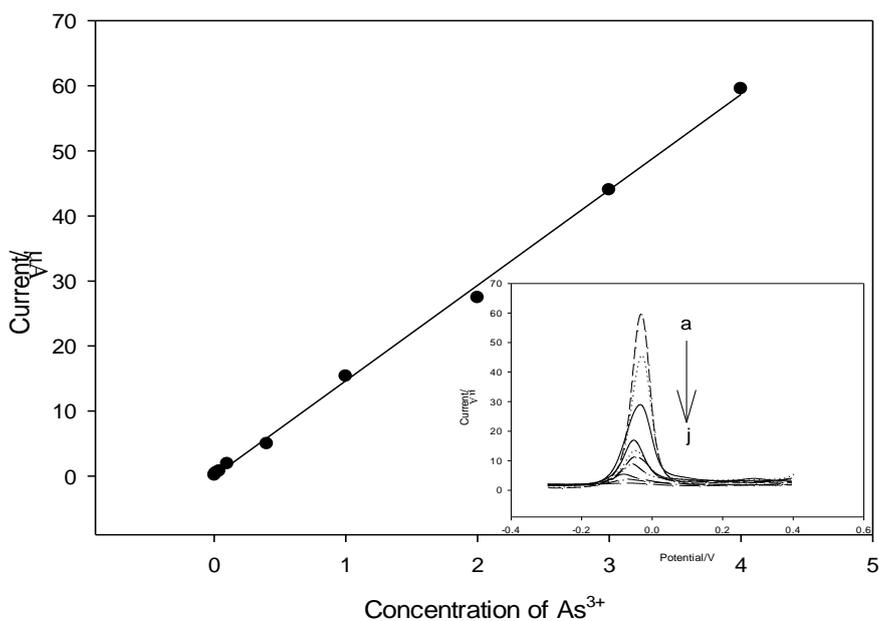


Figure 8. The calibration curve of stripping peak current versus the concentration of As³⁺. The inset shows the SWASV responses of NPG/GCE in the presence of different concentration of As³⁺ under the optimized experiment conditions (from a to j: 4, 3, 2, 1, 0.5, 0.4, 0.3, 0.2, 0.1, 0.04 μg/mL).

The quantitative range of the proposed NPG sensor for the analysis of As^{3+} was studied with the optimized parameters above. As presented in figure 8, the stripping peak current was increased with the increasing concentration of As^{3+} , and a good linearity was obtained in the concentration range from 0.001 to 4 $\mu\text{g/mL}$. A detection limit (LOD) of 0.001 $\mu\text{g/mL}$ was obtained ($\text{S/N}=3$). The linear equations is $y=14.4797x+0.3081$. The linear correlation coefficient is 0.9992.

The influence of any other heavy metal ions such as Cd^{2+} , Pb^{2+} and Cu^{2+} on the detection of As^{3+} was studied. SWASV responses of 1 $\mu\text{g/mL}$ As^{3+} in the presence of 1 $\mu\text{g/mL}$ Cd^{2+} , Pb^{2+} and Cu^{2+} were investigated on the NPG/GCE in 0.1 M KCl ($\text{pH} = 3$) after preconcentration at -1.0 V for 300 s. The results show that Cd^{2+} , Pb^{2+} and Cu^{2+} will produce interference for the detection of As^{3+} .

To monitor the reproducibility of the sensor, six NPG modified GCE were used to measure 1 $\mu\text{g/mL}$ As^{3+} , the relative standard deviation (RSD) was 3.11% ($n = 6$), indicating that the sensor have a good reproducibility.

In order to investigate the repeatability of the sensor, the same NPG modified GCE was used to measure 1 $\mu\text{g/mL}$ As^{3+} for six times in a row. The relative standard deviation (RSD) was 2.41% ($n = 6$), showing a satisfactory repeatability.

3.6. Analysis of real sample

To further assess the practicality of our strategy in real samples. Water samples were collected from Huamei Lake and tap water. These two kinds of water samples were mixed with known amount As^{3+} , and then detected with the proposed method. The results are presented in table 1. As shown in table 1, the recovery obtained varied from 98% to 102%, revealing the favorable potential of the NPG/GCE sensor to be applied in practical application.

Table 1. The recovery experiments of the spiked samples

| Real Sample | Found($\mu\text{g/mL}$) | Added($\mu\text{g/mL}$) | Total($\mu\text{g/mL}$) | Recovery(%) |
|----------------------|---------------------------|---------------------------|---------------------------|-------------|
| Tap water | 0 | 1 | 1.03 | 102 |
| Water of Huamei Lake | 0 | 1 | 0.98 | 98.0 |

In our study, a dynamic bubble template electrodeposition process was used to synthesis nanoporous gold onto glassy carbon electrode. Compared with other synthesis methods of gold nanoparticles, the bubble template one-step electrodeposition process offers several advantages, including green, efficient, inexpensive, and rapid. Furthermore, an evident coral structure could be formed with nano-sized pore. The porous structure makes the material has a larger specific surface area which could enhance the ability of electron transfer and catalytic activity. All of these advantages could make the sensor more sensitive.

Compared with several typical As^{3+} sensors reported previously (table 2), the present NPG modified GCE owns a superior comprehensive performance than that of the other modified electrodes

[2, 20-23]. The wide linear range and relatively low detection limit for As^{3+} may be attributed to the high specific surface area, strong adsorption ability and catalytic of the NPG.

Table 2. Comparison of the different modified electrodes for the determination of As^{3+}

| Electrode | Technique used | LOD(ppb) | Linear range ($\mu\text{g/L}$) | Refs. |
|-------------------------------|----------------|----------|----------------------------------|-----------|
| AgNPs/CT | DPV | 1.2 | 10-100 | [26] |
| AgNP | LSV | 10 | 10-500 | [27] |
| (PDDA-AuNPs) ₅ /Au | DPV | 4.4 | - | [28] |
| FePt NPs on Si | SWV | 0.8 | 1-5 | [24] |
| EG-Bi | SWV | 5 | 20-100 | [2] |
| NPG/Au | SWV | 1 | 1-4000 | This work |

NP-Nanoparticle, CT-Chitosan, PDDA-Poly(Diallyldimethylammonium Chloride), EG-Exfoliated Graphite, DPV-Differential Pulse Voltammetry, LSV-Linear Sweep Voltammetry, SWV-Square Wave Voltammetry

4. CONCLUSIONS

Nanoporous gold has been synthesized onto GCE by using a dynamic bubble template electrodeposition process, which is fast, cheap, green, and easy preparation. The nanoporous gold exhibits excellent electron transfer ability, huge specific surface area and good catalytic performance, which can remarkably improve the electrochemical performance of the sensor for the As^{3+} detection. The proposed sensor exhibits a high sensitivity with the detection limit of $0.001 \mu\text{g/mL}$ for As^{3+} . A good stability and reusability can also be obtained with the sensor. The modified electrode will offer potential applications for monitoring total As, if As(V) can be reduced to As(III) [25].

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (31401577), Hunan Provincial Natural Science Foundation of China (13JJ9004, 2017JJ3511), Hunan 2011 Collaborative Innovation Center of Chemical Engineering & Technology with Environmental Benignity and Effective Resource Utilization.

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