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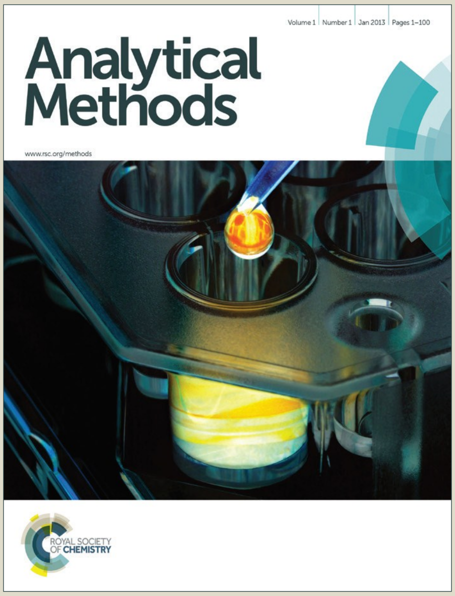

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Studies on fabrication and application of arsenic electrochemical sensors based on titanium dioxide nanoparticle modified gold strip electrodes

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Abstract

A sensitive electrochemical sensor for the determination of arsenic (III) based on a titanium dioxide (TiO_2) nanoparticle modified gold strip electrode (GSE) was developed. The gold strip electrode was prepared by a seeded growth method using polyethylene terephthalate (PET) films as the template. This GSE can be provided with an excellent electrochemical performance comparable to commercial gold disk electrodes, and possessed better flexibility and size controllability, as well as larger effective surface area. A disposable thin-film electrochemical sensor was fabricated by chemically modification method based on the gold strip electrode coating with TiO_2 nanoparticles. The resulting sensor showed a sensitive electrochemical response toward the oxidation of As (III) in hydrochloric acid (HCl) medium. Under optimized working conditions, the oxidation peak current of As (III) by linear sweep voltammetry (LSV) linearly increased with its concentration in the range of 10~80 μg/L. The arsenic sensor also showed good stability and reproducibility, and was successfully applied to the detection of As (III) in blood samples.

Keywords: titanium dioxide, gold strip electrode, arsenic ions, linear sweep voltammetry, blood samples.

1. Introduction

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As is well known, arsenic is one of the most toxic heavy metal elements. Humans are exposed to arsenic via a number of environmental and dietary sources, such as soil, drug, drinking water and industrial wastes. It has been confirmed by international agency for research on cancer (IARC) that long time exposure to even a small concentration of arsenic will lead to the increase of the cancer risk [1]. However, arsenic played a more and more significant role in medicine recently. Especially, the use of arsenic trioxide (As_2O_3) in the treatment of acute promyelocytic leukemia (APL) has achieved a notable accomplishment [2]. As arsenic is a protoplasm toxic element, the accumulations of arsenic for a long time will seriously harm our organs. Thus, it is of great importance to monitor the concentration of arsenic in blood in order to prevent arsenic poisoning.

There are already many matured developed techniques for arsenic determination, including graphite furnace atomic absorption spectrometry (GFAAS) [3], flame atomic absorption spectrometry hydride (FASS) [4], generation atomic absorption spectroscopy (HG-AAS) [5], inductively coupled plasma/mass spectrometry (ICP-MS) [6-7] and inductively coupled plasma/atomic emission spectroscopy (ICP-AES) [8]. However, expensive and sophisticated instrumentation as well as trained staff are required by all the measurements above. Compared with those technologies, great attention has been paid to electrochemical techniques due to their low cost, high integration and good sensitivity. Linear Sweep Voltammetry (LSV) is an applicable electrochemical method for the determination of trace metal elements due to its simple and quick operation as well as accurate and reliable results. Anodic stripping voltammetry (ASV) [9-13] and chemically modified electrode [14] have been considered as a leading technique in the determination of trace amounts of arsenic and other metal ions .

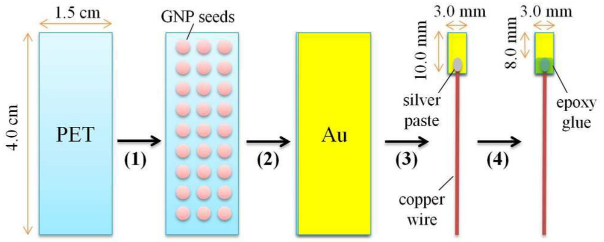
In this work, a disposable electrochemical sensor based on gold strip electrodes for the sensitive determination of As (III) was reported. The sensor was fabricated by firstly depositing highly conductive gold layers on common PET films through electroless plating and then coating the gold electrodes with TiO_2 nanoparticles by drop casting. The resulting sensor, looking like a piece of golden plastic strip and possessing excellent electrochemical quality, showed a sensitive electrochemical response for the oxidation of As (III), which was successfully applied to the detection of As (III) in blood samples. The unique properties of the gold strip electrode, including easy fabrication, good size/shape controllability, excellent electrochemical performance and low cost, also foresaw its promising applications for developing high-quality and cost-effective electrochemical sensors.

2. Materials and methods

2.1. Chemicals and apparatus

Arsenic trioxide AR.(Chemical experiment center of Wuhan University).Titanium oxide nanoparticles, chloroauric acid ($HAuCl_4 \cdot 4H_2O$), hydroxylammonium chloride ($NH_2OH \cdot HCl$), trisodium citrate dehydrate, sulfuric acid, hydrochloric acid, nitric acid, potassium chloride, sodium dihydrogen phosphate, zinc chloride, copper chloride, citric acid, ascorbic acid, ethylenediaminetetraacetic acid (EDTA) and sodium borohydride ($NaBH_4$) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Projection PET films were obtained from Dongting screen factory (Wuxi, China). All chemicals were of analytical grade and used as received without further purification. The water used was doubly distilled. Silver paste BQ6880E was the product of UNINWELL Internation CO., LTD (UAS). Epoxy glue was from Magpow (Changsha, China).

All electrochemical measurements were performed on a CHI 830 analyzer (CH Instruments, Shanghai, China). The analyzer was equipped with a conventional three-electrode cell, including a platinum wire counter electrode, a saturated calomel reference electrode (SCE) and a modified gold strip working electrode. SEM images were obtained on FEI Quanta 200, Holland.



Scheme 1 Procedures for preparing the gold strip electrode.

2.2. Preparation of the gold strip electrode

The gold strip electrode was prepared by a two-step seeded growth method using a PET film as the templates according to previous works i.e., the gold nanoparticle (GNP) seeds were firstly grafted onto the PET film by spontaneous adsorption, and then the adsorbed high-density GNP seeds were further grown into conducting gold layers by the self-catalytic growth of the GNP seeds in a growing solution of $HAuCl_4$ and NH_2OH. The detailed procedures for preparing the gold strip electrode were presented as Scheme 1. The thickness of sensitive layer is 0.5 µm which is discussed in our previous paper [15]. Briefly, a PET film was cut into strips of 1.5 cm ×4 cm, then cleaned by sonicating in 1.0 mol/L HNO_3 and rinsing with ethanol for at least three times, and finally dried under an infrared lamp. The cleaned strips were immersed in 0.01 mol/L cetyltrimethylammonium bromide (CTAB) solution at 45 ºC for 30 min, and then washed with water for several times to remove unbound CTAB molecules. The CTAB modified PET strips were incubated in a plastic vial containing 4 mL gold nanoparticle seed solution , kept shaking at room temperature for 1 h adsorption, and rinsed with water for at least three times to remove unbound GNP seeds (step 1). The GNP seed decorated PET strips were transferred to a plastic vial containing the growth solution (i.e., a mixture solution of 4 ml water, 50 µL 0.2 mol/L $NH_2OH{\cdot}HCl$ and 100 µL 1.0 wt % $HAuCl_4$ solution), allowed for 20 min growth and thoroughly rinsed with water. This growth process was repeated for several typically six cycles until the resistance is less than 100 Ω teseed by a BM8300L multimeter (ShenzhenbingJiang Co., Shenzhen, China). The produced gold strip films were cut into smaller strips of 3.0 mm×10.0mm, of which one side was electrically connected to a copper wire with the aid of silver paste (step 3). The junction area was further sealed with epoxy glue to produce a gold strip electrode with an effective area of 3.0mm ×8.0 mm (step 4).

2.3. Fabrication of the TiO_2 nanoparticle modified gold strip electrode

The TiO_2 nanoparticle modified gold strip electrode (TiO_2/GSE) was prepared by a simple drop casting method. Briefly, 100 mg TiO_2 nanoparticles were added into a 10 mL aqueous solution and sonicated for 0.5 h to form a homogeneous dispersion. Then, 25 µL of the TiO_2 dispersion solution was dropped onto the sensing area of a gold strip electrode. The modified electrode was dried at room temperature for 24 h to produce the TiO_2 nanoparticle modified gold strip electrode.

2.4. Detection of As (III) standard by the TiO_2 nanoparticle modified gold strip electrode

The electrochemical detection of As (III) on TiO_2/GSE was performed by linear sweep voltammetry (LSV). In a typical procedure, a certain volume of 10 mg/L As (III) standard solution was added into 10 mL 3.0 M HCl solution, and potential sweep was carried out from -0.3 to 0.6 V after the pre-accumulation of As (III) at -0.3 V for 240 s.

2.5. Detection of As (III) in blood samples by the TiO_2 nanoparticle modified gold strip electrode

The blood samples for the detection of As (III) by TiO_2/GSE were prepared as follows: (1) a volume of 3 mL unfrozen blood sample was added to a 5 mL centrifugal tube, and then a certain volume of 250 mg/mL As (III) solution and 1 mL 1.0 mol/L HNO_3 were added subsequently drop by drop; (2) the above mixture was stirred for several minutes and kept standing for 2 h, which was then centrifuged at 10000 rpm for 5 min; (3) the supernatant fluid was carefully collected and transferred to another 5 mL centrifugal tube, and the pH of the solution was adjusted to pH 7.0 by 1.0 mol/L NaOH. The procedures for the detection of As (III) in the blood samples were similar to the detection of As (III) standard.

3. Results and discussion

3.1. Characterizations of the TiO_2 nanoparticle modified gold strip electrode

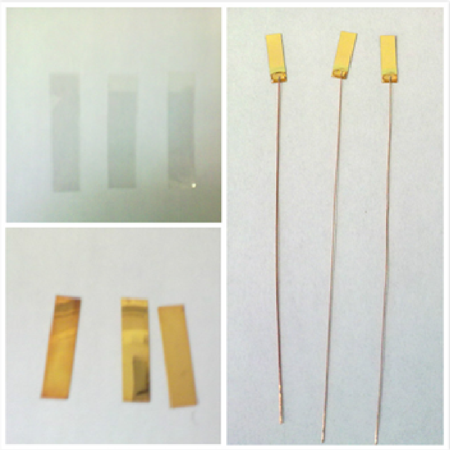


Fig 1 Preparation of gold membrane electrode

The morphology of virgin gold strip electrode and TiO_2 modified gold strip electrode were compared and shown in Fig. 2. From Fig. 2a, a dense coverage of Au nanoparticles (AuNPs) was achieved on the surface of PET strip with the diameter at the range of 200-230 nm. Fig. 2b shows the surface of modified electrode with TiO_2 nanoparticles depositing on the surface of the electrode,TiO_2 nanoparticles are uniformly distributed on the surface of the gold strip electrode. TiO_2 is strip without any agglomeration, indicating that TiO_2 nanoparticles are distributed uniformly on the surface of gold strip electrode. This highly ordered nanostructure TiO_2 array can provide larger specific surface area and specific surface-area-to-volume ratio for active substance loading.

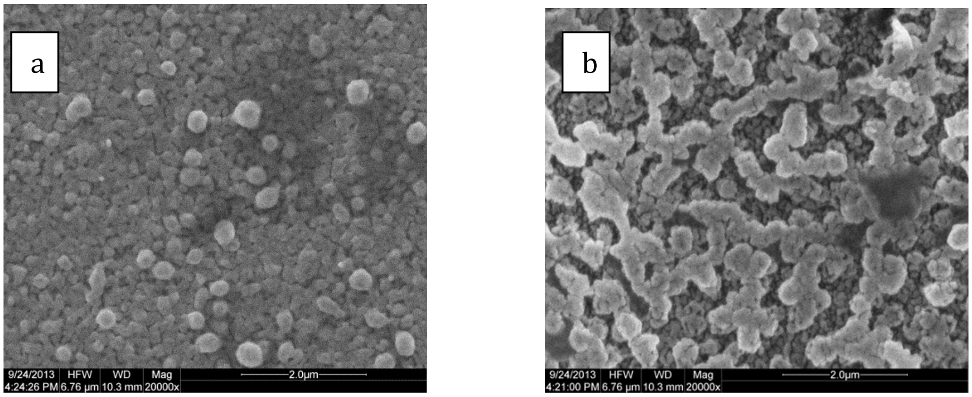


Fig. 2 SEM images of bare (a) and TiO_2 modified (b) gold strip electrodes.

The preparation of a sensing film of TiO_2/GSE is importance for the development of an electrochemical sensor for the determination of As (III) in blood. GSE is an excellent conductor with low cost, and has a good adhesion with TiO_2. And nanometer TiO_2 particles as a new type of electrochemical catalytic materials have drawn much attention in recent years, which has large surface area, long-term stability, catalytic effect and other characteristics [16]. In this paper, nanometer TiO_2 coating electrode, namely TiO_2/GSE electrode, therefore showed a sensitive electrochemical response for the oxidation of As (III).

3. 2. Electrochemistry characterization of nano-TiO_2 modified gold strip electrode

Fig. 3 shows the typical cyclic voltammetry responses of a gold strip eletrode (GSE) (curve a) and TiO_2 modified gold strip (TMGS) electrode (curve b) in 5.0 mmol/L $K_3Fe(CN)_6$/$K_4Fe(CN)_6$ and 1.0 mol/L KCl mixed solution. A couple of stable and well-defined redox peaks could be observed on both curve (a) and curve (b). TMGS showed a comparative higher oxidation and reduction peak current and a smaller interval between oxidation peak and reduction peak than that of GSE. The increase of current can be related to the nanostructure TiO_2 on the surface of the TMGS. The results indicated that the nanostructure TiO_2 favor the transport of the electron from the electrolyte to the surface of the electrode, which leads to the larger arsenic response of electrode surface.

The electrodes without and with modification of TiO_2 nanoparticles were characterized by Electrochemical Impedance Spectroscopy (EIS) techniques, which was performed in a solution of 1.0 m mol/L $[Fe(CN)_6]^{3-/4-}$ with 0.1 mol/L KCl. The value of the charge transfer resistance (semicircle diameter) (R_{CT}) depends on the dielectric and insulating features of the electrode/electrolyte interface. From Fig. 4, it can be concluded that both GSE and TMGS electrodes possess the little resistance. It is interesting that TMGS has a small semicircle than GSE. The results indicate that the TiO_2 particles improve the resistance of GSE electrode. The structure of TiO_2 nanoparticles modified electrode such as its high porosity and specific surface area coupled with its good electrical conductivity allows achieving large peak currents by using linear sweep voltammetric method, suggesting that TiO_2 particles coating helps to the reduction of As (III) and the preconcentration of As (0) at the surface of the electrode. Moreover, the accumulation and reduction of ions on the electrode surface is a diffusion-controlled process. The result of smaller semicircle diameter of TiO_2 modified electrode is consistent with the increase of the electron transfer rate on the surface of the TiO_2 modified electrode.

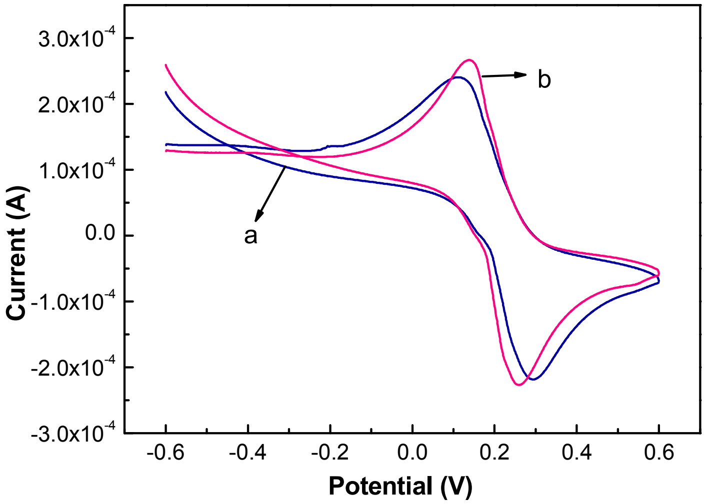


Fig. 3 Cyclic voltammogramms of GSE (a) and TMGS (b) in 5.0 mmol/L $K_3Fe(CN)_6$/$K_4Fe\ (CN)_6$

with 1.0 mol/L KCl, from -0.6 V to +0.6 V. Scan rate: 100 mV/s.

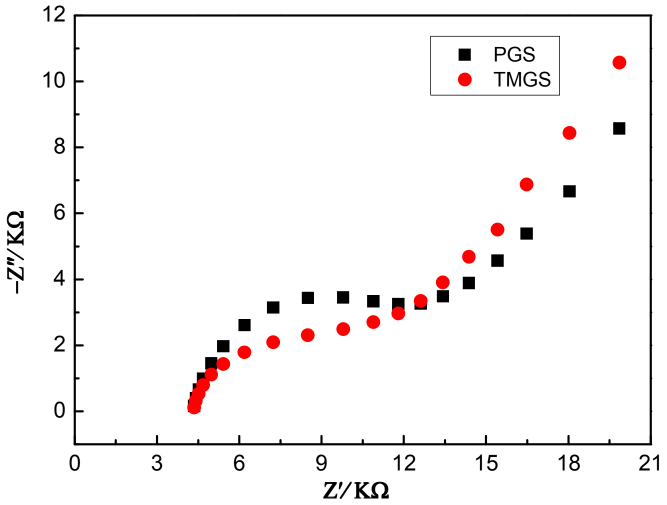


Fig. 4 Nyquist diagram (Z" vs. Z') for the EIS measurements of GSE and TMGS in the 5.0 mmol/L $K_3Fe(CN)_6$-$K_4Fe(CN)_6$ / 0.1 mol/L KCl mixed solution.

3.3. LSV analysis

3.3.1. Response of As (III) on different electrodes

The effect of the nano-TiO_2 modified electrode on the As stripping peak current is investigated by LSV. Fig. 5 illustrates the typical LSV responses of As (III) at gold strip electrode and nano-TiO_2 modified gold strip electrode. Compared with GSE (curve a), the peak current was increased when gold strip electrode was modified by nano-TiO_2 (curve b). The mechanism for the determination of As (III) can be described as following:

Accumalation: $As^{3+} + 3e \rightarrow As(0)$ (1)

LSV scanning: $As(0) - 3e \rightarrow As^{3+}$ (2)

The oxidation peak appeared in LSV scanning. The accumulation of As on the electrode surface was enhanced by the active adsorption sites increasing due to the large surface area of nano-TiO_2. This indicates that TiO_2 nanoparticles on the surface of the electrode could enhance the accumulation of As (III) by the adsorption. Increased sorption capacity and kinetics are expected because of the electrochemical reactivity as well as the high porosity of nano-TiO_2, resulting in easily and rapidly accessible sorption sites. TiO_2 is a potential sorbent candidate as previous reports have observed excellent sorption performance toward As(III) [17]. As a result, the electric current was increased in LSV scanning, which leaded to the sensitivity of As (III) increasing.

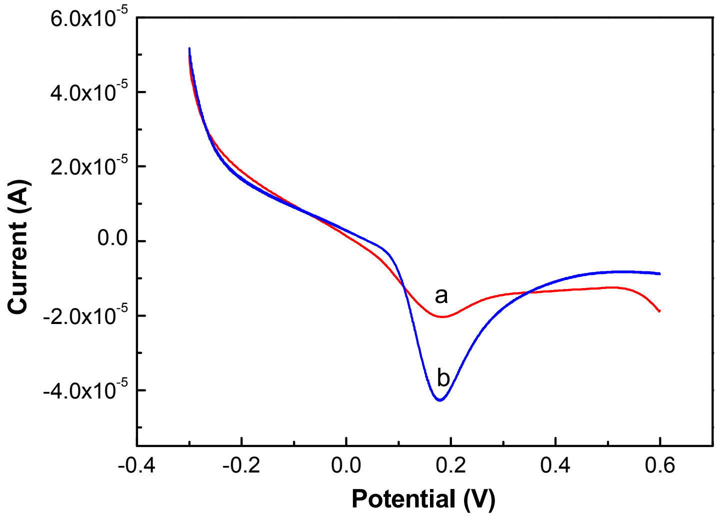


Fig. 5 LSV of GSE (a) and TMGS (b) in 3 mol/L HCl with 50 μg/L As (III). Scan range: from -0.4 V to +0.6 V, scan rate: 100 mV/s, deposition time: 180 s.

3.3.2. Effect of different supporting electrolytes

Several supporting electrolytes were introduced in respect of the response toward As (III) on nano-TiO_2 modified electrodes using LSV. The electrolytes include H_2SO_4, HCl, HNO_3, KCl, NaH_2PO_4, CH_3COOH, CH_3COONa and two type buffer solutions. Buffer pH = 4.00 is made by dissolving potassium hydrogen phthalate alone in dist. Buffer pH = 6.86 is made by dissolving disodium hydrogen phosophate (Na_2HPO_4) and sodium dihydrogen phosphate (NaH_2PO_4). with pH = 4.00 and pH = 6.86. The concentration of the electrolyte solution is 0.1 mol/L except the buffer solution. As shown in Fig. 6, arsenic oxidation peaks were obtained at acidic condition but not in other electrolyte. Well-shaped peaks were observed in present of HCl, HNO_3 and H_2SO_4. The absolute values of current decreased in the order HCl > HNO_3 > H_2SO_4. HCl was considered as the best supporting electrolyte due to the low background response and high sensitivity. A nice shape of arsenic oxidation peak was obtained when HNO_3 was used as the supporting electrolyte. However, concentrated nitric acid has strong oxidizing. Thus, 1.0 mol/L HCl was chosen as the supporting electrolyte in the following experiments.

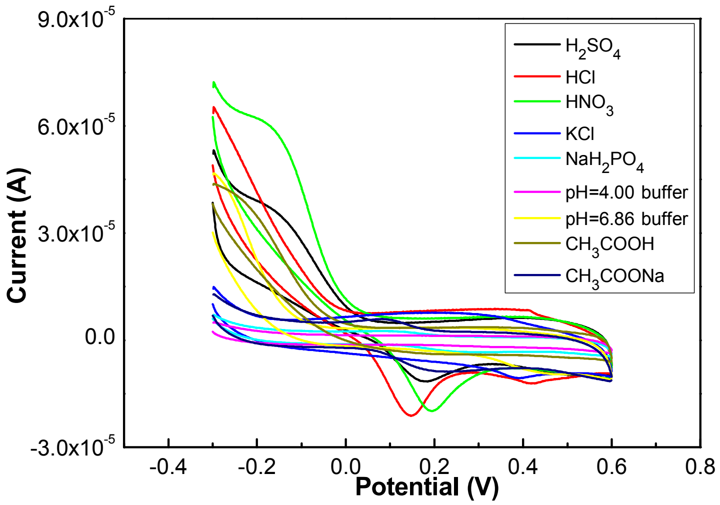


Fig. 6 Individualyl LSV for TMGS in 1 mol/L H_2SO_4, HCl, HNO_3, KCl, NaH_2PO_4, CH_3COOH, CH_3COONa, pH = 4.00 and pH = (6.86) buffer solution with 50 µg/L As (III) from -0.4 V to +0.6 V. Scan rate: 100 mV/s. Deposition time: 180 s.

3.3.3. Concentration of HCl

The concentration of the supporting electrolyte which also means different pH is another important factor to determination sensitivity. As shown in Fig. 7, several concentrations of HCl were compared in respect of the response toward As (III) on modified electrodes using LSV. As shown in Fig. 7, the current increases when the HCl concentration increased from 0.01 to 4.0 mol/L. However, the current decreases when HCl concentration further increased from 4.0 to 5.0 mol/L. The highest oxidation peak current was observed at HCl concentration of 4.0 mol/L. When the concentration of HCl solution was kept at 3.0 mol/L, the current is almost equal to that at 4.0 mol/L. The electrode could be corroded in strong acid condition. Thus, 3.0 mol/L HCl was chosen as the best concentration in the following electrochemical experiments.

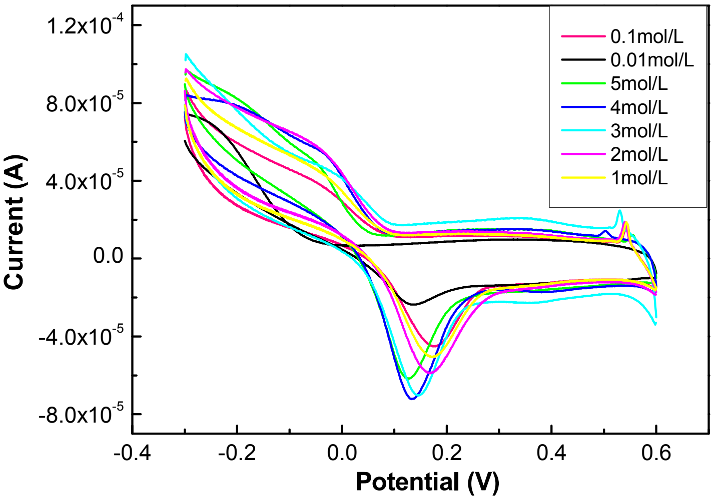


Fig. 7 The effect of the concentration of HCl on the response current of As (III).

3.3.3. Effect of loading of nano-TiO_2

Different concentration loading of nano-TiO_2 on electrode surface was examined by using LSV in sample solution. Different volume of TiO_2 nanoparticles solution (5, 10, 15, 20, 25 μL solution with the concentration of 10 g/L) were dropped on gold strip electrode surface. With the surface modification amount increased from 5 μL to 15 μL, the peak current increased. When the modification amount was further increased to 25 μL, the peak current decreased (Fig. 8). This may be due to the porous structure of nano-TiO_2, which leads to the increase of the active sites and favors the oxidation of As (III) in the solution. But the large thickness of TiO_2 layer can also block the electron transfer between the electrode surface and As (III), which is attributed to the peak current decrease when the modification amount is more than 15 μL. In order to keep the balance of enough active sites and efficient electron transfer rate, 15 μL TiO_2 was chosen to be the optimized amount.

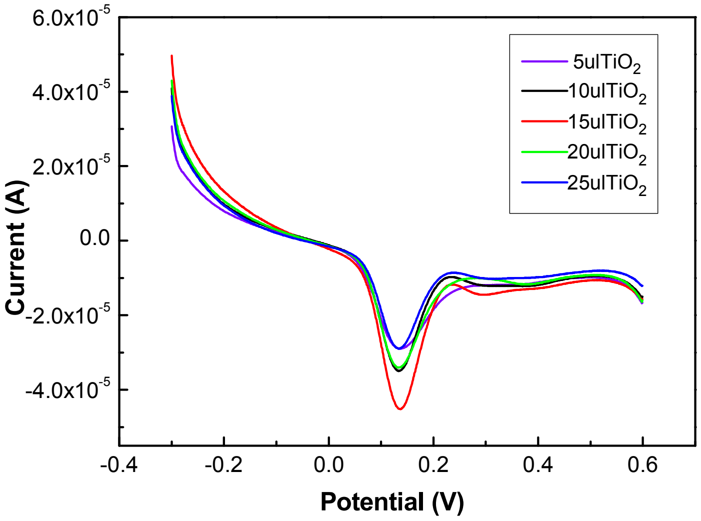


Fig. 8 The effect of TiO_2 concentration on the response current of As (III) in 3 mol/L HCl.

3.4. Optimization of experiment condition

3.4.1. Scan range

To evaluate the proper potential range of LSV, the measurements started from -0.3 V and stopped at different potential. The results indicated that the peak current increased obviously with the potential increasing from 0.4 to 0.6 V. When the potential was further increased, the peak current decreased. When potential started from various values and stopped at 0.6 V, results showed that the highest response value was observed at the potential range of -0.3~0.6 V. So the potential range in this experiments was chosen to be -0.3 ~0.6 V.

3.4.2. Deposition time

ASV is a voltammetry method for quantitative determination of specific ionic species, which includes a deposition step and a stripping step. Deposition is a crucial procedure which could affect the further determination of the ionic species. In our work, different deposition times of 30, 60, 120, 180, 240 and 300 s were examined using ASV with standard additions of As (III) (Fig. 9). With the deposition time increasing, the peak heights increased rapidly from 30 s to 240 s. Than 240 s, the current value increased slowly when the deposition time further increased (as inset in Fig. 9). The determination was directly related to the deposition of the arsenic ion on the surface of the working electrode. By increasing the pre-deposition time, the response peak current can be enhanced and the sensitivity can be also improved. When the deposition amount gets saturation after a period of time, deposition amount is not increased significantly with deposition time further increasing. Based on an overall consideration of the sensitivity and determination time, we choose 240 s as the proper deposition time for the arsenic determination.

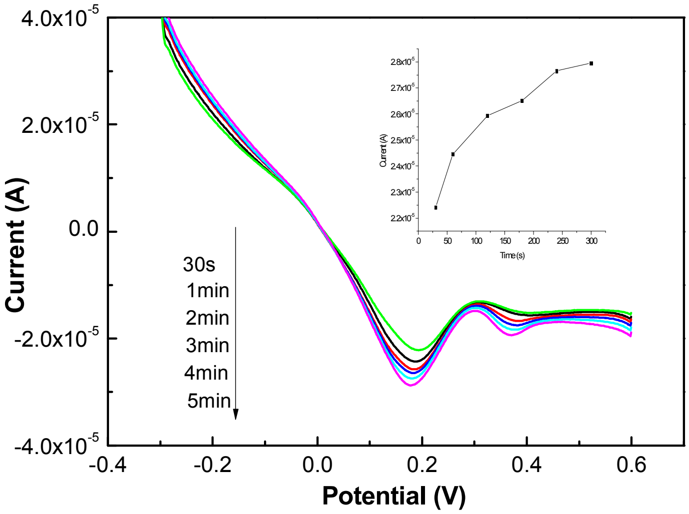


Fig. 9 The effect of the deposition time on the response current of As (III) in 3 mol/L HCl solution

3.4.3. *Effect of scan rate*

The effect of scan rate on the oxidation of As (III) on nano-TiO_2 modified electrode in 3 mol/L HCl was investigated. The anodic LSV were recorded between -0.3 V and 0.6 V at different scan rate (10~200 mV) and presented in Fig. 10. The current values for the As (III) oxidation increase linearly in the range of 10~200 mV/s. It confirms that the oxidation of As (III) is a surface control process. For the next measurement, we choose the 100 mV/s as the proper scan rate due to the low stability at the scan rate of 200 mV/s.

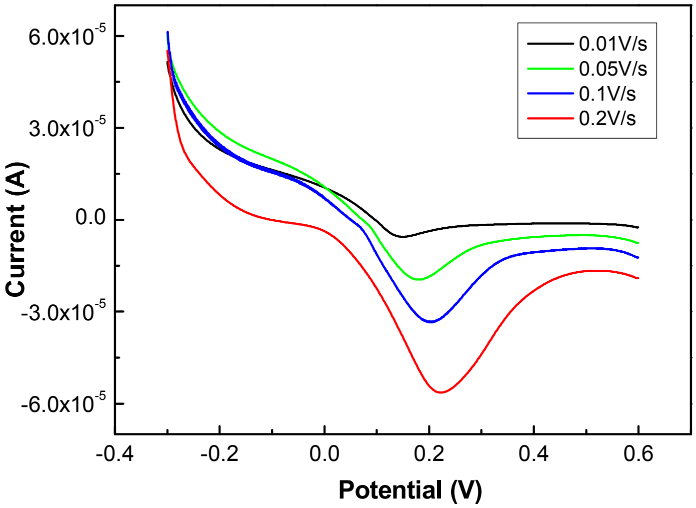


Fig. 10 The effect of the scanning speed on the response current of As (III) in 3 mol/L HCl.

3. 5. Ion interference

The interference of other ions on the detection of arsenic was studied. The interference ions include Zn^{2+}, Fe^{2+} and Cu^{2+}. The effect of citrate, ascorbic acid and EDTA was also investigated. Gradient volume of disruptors (1.0 mol/L) was added into the 100 μg/L arsenic solution. The results showed that the interference of disruptors above could be neglected. It indicated that the nano-TiO_2 modified gold strip electrodes have high selectivity for the determination of arsenic ion.

3.6. Calibration

Calibration plots was made using nano-TiO_2 modified gold strip electrodes with the optimal deposition conditions in 3.0 M HCl. When the detection was performed at the optimized conditions, the oxidation peak current was linearly incresed with the concentration of arsenic (III) from 10 μg/L to 80 μg/L and the detection limit is 10 μg/L (S/N = 3). The arsenic sensor showed the good reproducibility (R^2=0.9941).

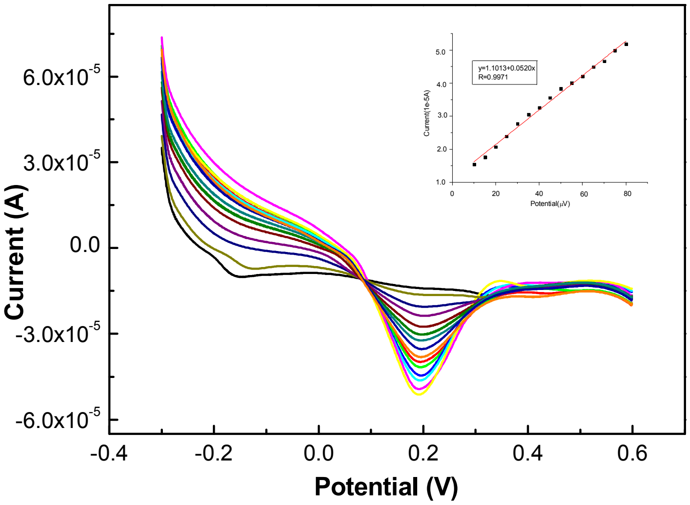


Fig. 11 LSV responses of different concentrations of As (III) on TMGS in 3 mol/L HCl sample solution.

3.7. Stability and reproducibility

The prepared nano-TiO_2 modified gold strip electrodes showed the good reproducibility. The relative standard deviation (RSD) of the current response was 1.20% for 7 successive measurements by using one electrode (Table 1). The RSD for 7 different modified electrodes to test the same sample was 3.3% (Table 2). The stability of the nano-TiO_2 modified gold strip electrodes was also investigated. The response current remained 96% of its initial response after 15 days. From the results we can conclude that the nano-TiO_2 modified gold strip electrode performs a good stability and reproducibility.

Table 1 The result of seven times determination of a single electrode

No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**SD**	**RSD**
Ip(10^{-5}A)	4.517	4.534	4.546	4.544	4.517	4.523	4.527	0.028	1.20%

Table 2 The result of seven times determination of a single of seven different electrodes.

No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**SD**	**RSD**
Ip(10^{-5}A)	4.576	4.555	4.517	4.522	4.5	4.534	4.535	0.079	3.30%

The performances of the sensor proposed were compared with those of sensors previously reported.[18-20] From Table 3, it is clear that previous electrode was developed for determination of As in water samples. In this study, the electrode we prepared was used to detect the concentration of As in blood sample. Compared to the determination of As in water, it is more difficult to detect As in blood. The sensor prepared here shows a larger sensitivity, which can be attributed to the high adsorption ability of nano-TiO_2 nanoparticles and the excellent electrocatalytic ability of gold nanoparticles.

Table 3 Comparison of the proposed sensor for detection of As(III) with other sensors

Sensor	Method	Sample	Sensitivity (μA/μM)	Ref.
Magnetic Fe_3O_4 nanoparticles and gold nanoparticles modified electrode	SWV	Drinking water and surface water	1015	18
IrO_2 nanotube modified electrode	LSV	As aqueous solution	0.0038	19
Ibu-AuPNFs/Ibu-AuNSs electrode	LSV	Water	0.36	20
The proposed method	LSV	Blood	82.6	This work

3.8. Detection of As (III) in real blood sample

The nano-TiO_2 modified gold strip electrode was used for the spiked detection of real blood samples by ASV technology. 30, 50, 60, 70, 80 μL well treated blood samples were dropped into 5 mL 3 mol/L HCl solution. The sample analysis was carried out at optimal condition. As shown in table 4, high correlations were found between the experiment results from ASV analysis and the actual value and a high recovery was obtained. The results from the current data set indicate acceptable accuracy and precision when our electrode was used to detect As (III) in real blood sample.

Table 4 The recovery of arsenic in blood standard addition

Number	**1**	**2**	**3**	**4**	**5**
Added(μg/L)	30	50	60	70	80
Detected (μg/L)	31.46	46.3	58.63	67.9	76.1
Recovery	105%	93%	97%	97%	95%

4. Conclusions

In summary, a fast, easy and cheap disposable nano-TiO_2 modified gold strip electrode was fabricated and used to detect As (III) successfully. A high sensitivity, low LOD, wide linear range and good stability and reproducibility was obtained by using LSV. The TMGS electrode was used to detect As (III) in real blood sample with an acceptable accuracy and precision. The current data set indicate the possibility in the application of the TMGS electrode for the detection of arsenic in real blood samples. Further studies will focus on the application of this method for the disposable biosensor for detecting arsenic in real blood sample.

Acknowledgements

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