

Trace Determination of Arsenite With an Ionophore-Coated Selective Micro Sensor

Li Wang[✉], Wenshuai Lu, Gaoshan Jing, *Member, IEEE*, and Tianhong Cui, *Senior Member, IEEE*

Abstract—This paper reports a highly sensitive micro sensor utilizing an ion selective membrane to determine trace arsenite with anodic stripping voltammetry in the presence of interferences. The sensor was fabricated by depositing an arsenite (As (III)) ion selective membrane on a gold electrode surface. Compared with the traditional sensor without an ionophore membrane, the proposed sensor achieved better voltammetric performance due to its superior selectivity to As (III). After applying the ionophore film, the sensor's background current decreased from 1.375 μA to 0.320 μA , and its standard deviation decreased from 0.150 μA to 0.007 μA , leading to lower background noise and higher conformity. Meanwhile, the sensor demonstrated high selectivity with the existence of interference ions, such as Cd^{2+} , Pb^{2+} , and Hg^{2+} . The detection and statistical analysis of As (III) were performed in the linear concentration range of 10–100 ppb ($R^2 = 0.993$) and a low limit of detection (LOD) of 1.10 ppb was obtained for 300s deposition. The sensor was successfully employed for the determination of As (III) in waste water and the results were in good agreement with those from a standard procedure. This highly sensitive and selective portable sensor holds great potential for on-line environmental monitoring.

Index Terms—Anodic stripping voltammetry (ASV), arsenite determination, chemical sensor, ionophore.

I. INTRODUCTION

ARSENIC, commonly exists in polluted natural environment, can cause severe impairment to the health of humans, including dermal changes, respiratory and cardiovascular disorders, genotoxic and carcinogenic effects [1]. Among the compounds of arsenic, inorganic arsenic compounds have been proved to be the most toxic, especially arsenite (As (III)) and arsenate (As (V)) [2]. Researchers have found that arsenite is 50 times more toxic for humans than arsenate [3]. For the safety of human health, world health organization (WHO) has suggested that arsenic concentration in drinking water should be no more than 10 ppb and various techniques have been used to detect trace arsenite [4], [5].

Manuscript received February 17, 2018; accepted March 29, 2018. Date of publication April 10, 2018; date of current version May 9, 2018. This work was supported in part by Dongshan Coal Electricity Group Co. Ltd. The associate editor coordinating the review of this paper and approving it for publication was Dr. Chang-Soo Kim. (*Corresponding author: Tianhong Cui.*)

L. Wang and G. Jing are with the Department of Precision Instrument, Tsinghua University, Beijing 100084, China (e-mail: l-w13@mails.tsinghua.edu.cn; gaoshanjing@mail.tsinghua.edu.cn).

W. Lu is with the China Academy of Electronic and Information Technology, Beijing 100041, China (e-mail: luwenshuai_dky@163.com).

T. Cui is with the Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455 USA (e-mail: tcui@me.umn.edu).

Digital Object Identifier 10.1109/JSEN.2018.2825332

For laboratory analysis, highly sensitive techniques, such as inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS) [6], [7], are usually adopted. ICP-MS and AAS instruments can achieve detection limits at ppt level for As. However, they are cumbersome, time-consuming and expensive to analyze elements [8]. The huge size makes them especially unsuitable for on-line monitoring. For field analysis, most commercially available sensors are based on the reaction between zinc powder and arsenite [9]. Hydrogen gas will be generated and cause color change in the reagent paper. However, researchers have reported that there is a weak correlation between this method and laboratory methods [10]. Based on the difficulty of achieving both portability and sensitivity, low cost and highly sensitive portable instruments for trace arsenite determination are still in great demand.

Two major electrochemical techniques: anodic stripping voltammetry (ASV) and ion selective electrode (ISE), have been used in metal analysis as they are fast, simple and sensitive for trace detection [11]. ASV is especially suitable to determine various ions with extremely low detection limits due to its unique pre-deposition process [12]. Target elements are reduced at a low potential and accumulated on the working electrode. So the concentration of the target element at the surface of the working electrode will increase and the output signal in the following stripping process will be amplified. Many researchers working on ASV sensors are dedicated to improving the efficiency of the pre-deposition step by decorating different materials on the working electrode. Specifically, for As (III) detection, carbon based nanomaterials (for example, carbon nanotubes and graphene) [13] and nanoparticles of noble metals [14], [15] are the most frequently used materials. Carbon nanotubes and graphene can be decorated with functional groups, enhancing electron transfer and improving the sensor's sensitivity to As (III). Nanoparticles of noble metals, on the other hand, have advantages over catalysis, surface area and controllable morphology. However, these ASV sensors can be easily influenced by its environment as some surface active organic compounds could be adsorbed on the electrode and affect the pre-deposition of arsenite. In addition, some interfering ions, such as Hg (II), can form intermetallic compounds with arsenic and inhibit the reduction of As (III) [16]. Though some functional polymers, such as Nafion [17], were deposited on the working electrode's surface to prevent interferences from reaching the electrode [18], these cation-exchanging films help little for

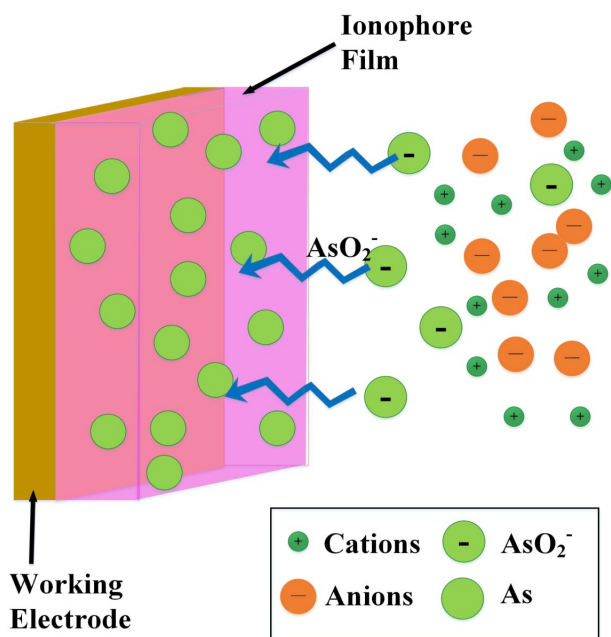


Fig. 1. Illustration of working principle of the ionophore coated working electrode for arsenite determination. With an ionophore film, interference ions can be prevented from reaching the surface of the working electrode.

the detection of As (III) because As (III) exists as an anionic radical.

In contrast, ion selective electrode (ISE) detection is a potentiometric technique widely applied to determining heavy metals by detecting the potential change of a working electrode [19]. The core material for an ISE sensor is the ion selective film of ionophore coated on the working electrode surface [20]. Ionophore, also known as an ion carrier, is a polymer film with a certain ligand which can reversibly bind a specific type of ion [12], [22]. The ionophore film serves as a blocking layer, preventing the rest ions from passing through the film. However, as the whole process is spontaneous, the potential change is very small. ISE sensors can barely achieve low LODs at ppb level for heavy metals because of tiny output signal and perturbation caused by interfering ions [23].

In this paper, we proposed a highly sensitive micro sensor which combined the advantages of ASV and ISE to detect trace amount of As (III). An arsenite-selective ionophore film was coated on a working electrode's surface to determine trace As (III) using anodic stripping voltammetry. Different from nanomaterials, the proposed sensor in this paper worked by selectively depositing arsenic on the working electrode. The arsenite ionophore film acted as a blocking layer for ions (except As (III)), preventing them from diffusing onto the working electrode surface, and hindering the mass transfer process, as shown in Fig. 1 [24]. High selectivity was achieved due to ionophore film and high sensitivity was achieved by the ASV analysis method. Finally, background current of the stripping voltammetry was significantly reduced by the permselectivity of the ionophore film, leading to lower background noise and smaller standard deviation. Consequently, a low limit of detection (LOD) of 1.10 ppb can be obtained for As (III).

Together with the advantages of low cost and small size, this highly sensitive and selective sensor is particularly suitable for family use and mass production.

II. MATERIALS AND METHODS

A. Reagents

All the chemicals were purchased from Sigma-Aldrich unless mentioned specifically. The 1000 mg/L arsenic (III) standard solution and 1000 mg/L Hg (II) standard solution were used as the stock solution to prepare solutions at lower concentrations. Lead nitrate (99.999%) and cadmium nitrate tetrahydrate (99.999%) were dissolved into de-ionized (DI) water to prepare standard stock solutions. $0.1 \text{ mol} \cdot \text{L}^{-1}$ HCl solution was chosen as the supporting electrolyte as low pH can enhance the peak current caused by arsenic [25] and it was prepared by diluting $3 \text{ mol} \cdot \text{L}^{-1}$ HCl standard solutions, purchased from Aladdin Co. (Shanghai, China). Poly (vinyl chloride) (PVC), 5,10,15, 20-tetrakis (4-methoxyphenyl) porphyrinatocobalt(II) (TMOPP-Co), dibutyl butyl phosphonate (DBBP) and Tetrahydrofuran (THF) were used to make arsenite selective membranes. All the arsenite solutions were prepared with DI water ($18.2 \text{ M}\Omega \cdot \text{cm}$) from a Milli-Q system (Millipore, Milford, MA, USA).

B. Apparatus

Four-inch glass wafers with thickness of $500 \mu\text{m}$ were purchased from Shanghai Gous Optics Co., Ltd., China. An Ag/AgCl ($3 \text{ mol} \cdot \text{L}^{-1}$ KCl) (Tianjin Aidahengsheng Technology Co., LTD, China) was used as a reference electrode instead of the gold pseudo reference electrode for more accurate results. Electrochemical measurements were performed by a CHI660e electrochemical workstation (Chenhua Instrumental Corporation, China), which is controlled by a workstation.

C. Ionophore Solutions Preparation

The ionophore solution was prepared according to previous published results [26]. The main ingredients of the membrane were PVC, TMOPP-Co and DBBP. PVC was used as an inert supporting matrix, TMOPP-Co as an arsenite ion exchanger and DBBP as a solvent mediator [23]. The three chemical reagents were prepared at the ratio of 150:5:150 [23]. 8 mg TMOPP-Co, 246 mg PVC and 246 mg DBBP were prepared and dissolved in 10 mL THF to obtain the ionophore solution. The inert supporting membrane were prepared by dissolving the same amount of PVC matrix and DBBP plasticizer in 10 mL THF at the absence of TMOPP-Co. A stirring procedure was required to ensure uniform dispersion in the THF solvent.

D. Device Fabrication

As shown in Fig. 2 (a), the micro sensor is mainly integrated with three layers, including a substrate layer, a conducting layer, and an ionophore layer. The sensor's fabrication process is illustrated in Fig. 3. Mainly, there are two parts in the fabrication process: the formation of the three-electrode system and the working electrode modification with an ionophore film. First, 20 nm chromium and 100 nm gold were patterned

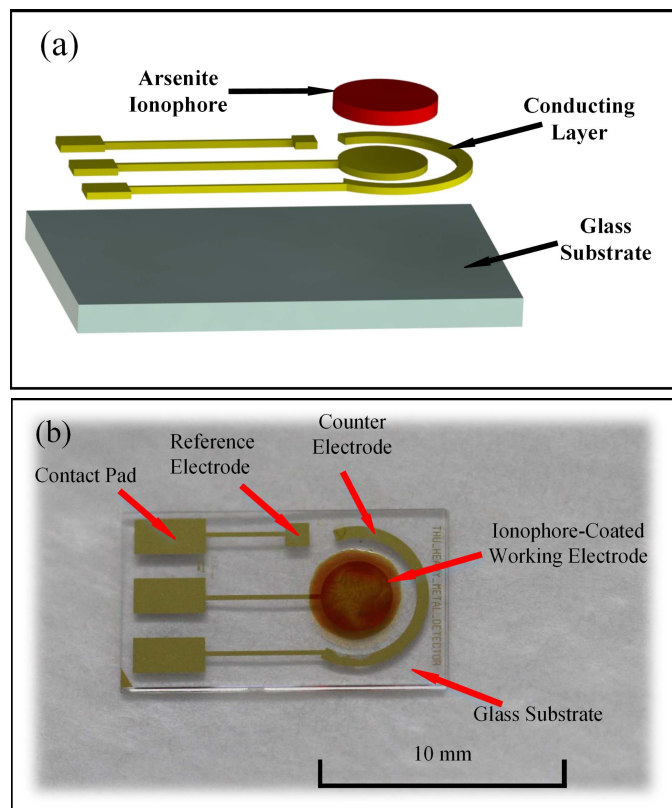


Fig. 2. (a) Schematic diagram of the sensor's layer structures: As (III) ionophore, a conducting layer and the glass substrate, and (b) an optical image of the ionophore-coated selective sensor fabricated on a glass substrate.

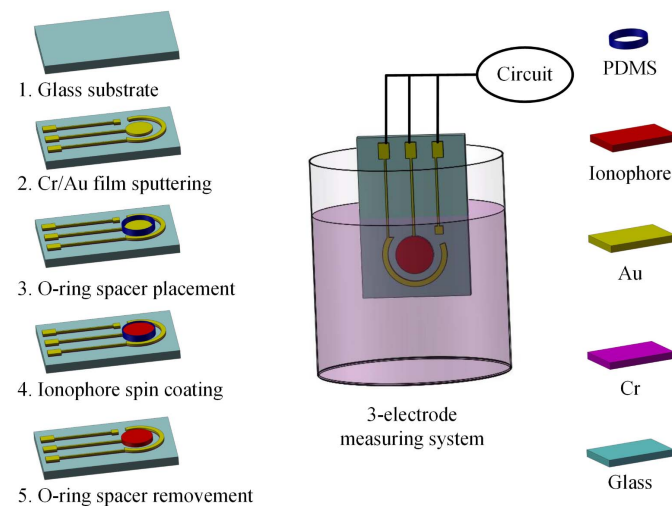


Fig. 3. Illustration of an As (III) selective sensor's fabrication process along with the measuring system.

on the glass substrate by sputtering and lift-off process to form the three-electrode system. Next, a PDMS based O-ring spacer was placed around the working electrode and a drop of ionophore solution was applied on the electrode's surface. The O-ring spacer was utilized to prevent the ionophore solution from reaching the counter electrode and the reference electrode. Finally, the sensor was baked in an oven at 80 °C for 10 minutes to evaporate the solvent. Fig. 2 (b) shows a photograph of the arsenite ionophore coated chemical sensor.

The size of the sensor is 0.8 cm × 1.5 cm. Additionally, plasticizer-coated sensor and bare gold sensor were also prepared to compare with the proposed sensor.

E. Measurement Procedure

A series of As (III) solutions, with concentrations ranging from 10 ~ 100 μg/L, were prepared by diluting stock solutions in 0.1 mol · L⁻¹ HCl supporting solution. The three electrodes were immersed in the As (III) solutions and dissolved oxygen was removed by purging nitrogen. Anodic stripping measurements were performed on an electrochemical workstation and the sensors were analyzed afterwards. Deposition potential of -0.4 V was applied on the working electrode. Following the pre-concentration step for five minutes, a square wave voltammetric scan (frequency: 25 Hz; pulse height: 20 mV; step voltage: 4 mV) was applied to the working electrode from -0.4 V to 0.8 V and the corresponding responses were recorded.

III. RESULTS AND DISCUSSION

For an electrochemical sensor, its detection limit can be derived by the following formula [27]:

$$LOD = 3\sigma/S \quad (1)$$

where σ is the standard deviation of the peak current which is obtained from supporting solutions and S is the sensor's sensitivity. Smaller standard deviation of the peak current and larger sensitivity result in lower LOD. Here, we used an ionophore coated sensor to determine trace As (III) ion using ASV method. Our hypothesis is that this ionophore film will greatly reduce background current and lead to lower LOD. Typically, for a sensor analyzing aqueous solutions, amplitude and standard deviation of the background current is heavily influenced by the supporting electrolyte. Stronger interfering reactions can result in higher background current and increase the sensor's noise. When the ionophore film is used, it can prevent interfering ions in the supporting electrolyte from reaching the working electrode and diminishing these ions' influence on the sensor's response. Thus, the repeatability of the sensor response can be improved, and the standard deviation of the sensor is lowered, leading to a lower LOD [28].

A. Effect of Arsenite Ionophore on Background and Stripping Signals

Arsenite ionophore solution was prepared by mixing arsenite ionophore powder with PVC and DBBP in THF solution. DBBP is the plasticizer and PVC is an inert supporting matrix. These two ingredients form as an inert supporting film, providing sufficient mechanical strength for the membrane, making the ionophore film tough and flexible. As a comparison, ionophore-free plasticizer solution was also prepared by dissolving PVC and DBBP in THF solution.

To characterize the effect of arsenite ionophore on background current and the determination of trace As (III) ion, a bare gold sensor, an ionophore-free PVC supporting film-coated sensor and an ionophore-coated sensor were tested in 0.1 mol · L⁻¹ HCl supporting solutions respectively. Fig. 4 shows the background current, i.e., the response current

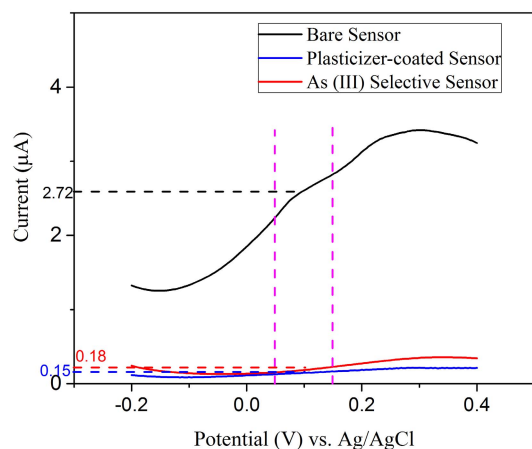


Fig. 4. Anodic stripping voltammograms of $0.1 \text{ mol} \cdot \text{L}^{-1}$ HCl solutions using a bare sensor, an ionophore-free PVC supporting film-based sensor and an ionophore coated selective sensor. Both the supporting film-coated sensor and the ionophore coated selective sensor reduced the background current severely.

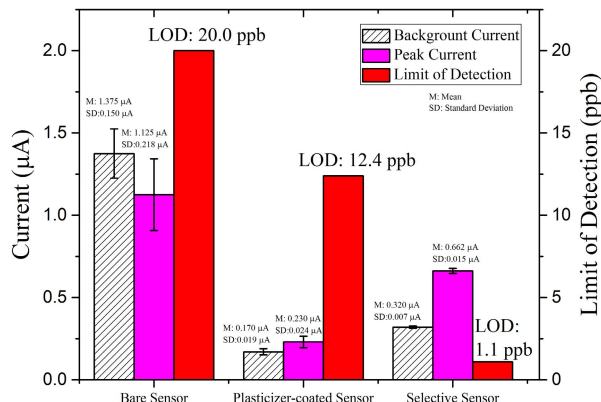


Fig. 5. Histogram of background current and peak current recorded with a bare sensor, ionophore-free PVC supporting film-coated sensor and ionophore coated selective sensor, from $0.1 \text{ mol} \cdot \text{L}^{-1}$ HCl solutions containing 50 ppb As (III), along with calculated limits of detection.

from supporting solutions, of these three sensors. When using a bare sensor, the average value of background current is about $2.72 \mu\text{A}$ at the potential range of $0.10 \text{ V} \sim 0.15 \text{ V}$, where arsenic ions stripping occurs [22]. In contrast, the supporting film-coated sensor and ionophore coated sensor exhibit background currents at the average value of $0.16 \mu\text{A}$ and $0.19 \mu\text{A}$. This clearly shows that plasticizer based film can effectively impede the reaction of the interfering ions. For a bare gold sensor, various ions around the sensor can be attracted on the working electrode's surface in the pre-concentration step, while for a plasticizer coated sensor, these ions are prevented from reaching the working electrode's surface by the film on the working electrode, resulting in decrease of their concentration on the working electrode and lower background current.

To further investigate the effect of ionophore on the determination of As (III), three types of sensors were used to measure solutions with 50 ppb As (III). As shown in Fig. 5, an ionophore-coated sensor exhibited peak currents at the average value of $0.662 \mu\text{A}$ in the stripping step, significantly larger than that of a supporting film-coated sensor ($0.230 \mu\text{A}$) and

smaller than that of a bare gold sensor (averagely, $1.125 \mu\text{A}$). Compared with the PVC supporting film-coated sensor without ionophore, the ionophore coated sensor improved the peak current by nearly three times. This owes to the attraction of TMOPP-Co to the preferred As (III), making the concentration of arsenite around the ionophore-coated working electrode higher than that of an ionophore-free PVC supporting film-coated sensor. One drawback of the ionophore film is that the peak current for arsenite is still not as high as that of a bare sensor, and this may thank to the reduction of ion mass transfer.

Another advantage of the ionophore film is that it greatly improves the uniformity of the ASV sensor. Owing to the arsenite ionophore film, interference caused by surface active compounds and other interfering ions in the solution can be drastically reduced. As Fig. 5 shows, with ionophore films, the background current standard deviation dropped from $0.150 \mu\text{A}$ to $0.007 \mu\text{A}$ and the peak current standard deviation dropped from $0.218 \mu\text{A}$ to $0.015 \mu\text{A}$, compared to a bare gold electrode. The decrease of standard deviations for both background currents and peak currents highlights the advantage of ionophore-coated sensor in uniformity and repeatability. With the standard deviation of background current dropped to 4.7% and the sensitivity dropped to 58.8% of the original values, the limit of detection of ionophore coated sensors can be lowered to 7.9% of the bare sensor's value. This reduction in LOD makes the sensor eligible for trace arsenite determination in drinking water.

B. Effect of Ionophore Film Thickness on the Stripping Response of As (III)

The thickness of the ionophore film is a critical parameter to determine the sensor's performance, because films with different thicknesses will influence the mass transport of the Arsenite ions [29]. For a uniformly distributed ionophore film, the average thickness l_{iop} , can be derived by the following formula:

$$l_{iop} = \frac{m}{\pi R^2 \rho} \quad (2)$$

where m is the mass of the solute attached on the working electrode, ρ is the density of the solute, and R is the radius of the working electrode (1.5 mm). As DBBP and THF can be easily evaporated after heat treatment, the solutes remained on the electrode are arsenite ionophore and PVC at the ratio of 5:150. For every microliter ionophore solution, 50 ng of solution was contained and the density of the resulting membrane was 1.4 g/mL . In this work, films were made by ionophore solutions with the volume of 3.0, 5.0, 7.0 or 9.0 μL . Theoretically, the film thickness can be calculated as 15.17, 25.28, 35.39, 45.50 μm , respectively. To ensure that the film thickness agrees with the theoretical value, films were measured by a surface profilometer (Dektak 150, Veeco, USA) and the thickness of corresponding films was measured as 12.52, 22.27, 32.09, 38.42 μm . Compared with the theoretical values, the measured values were smaller. This may owe to the fact that part of the ionophore solution seeped into the gap between the O-ring spacer and the substrate.

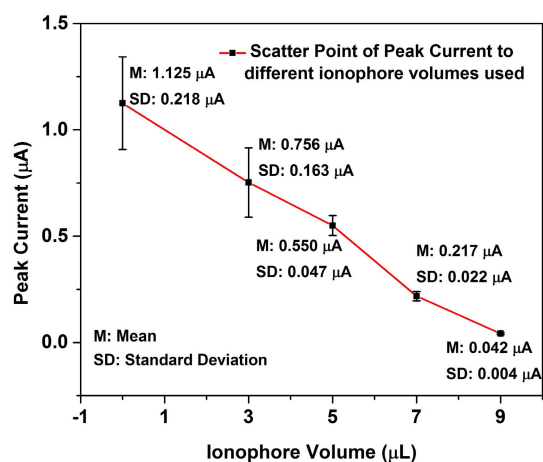


Fig. 6. Peak current vs. ionophore volume from 0 to 9 μL used. The ionophore membrane thickness changes linearly with the ionophore volume used. The sensor achieves the highest signal-to-noise ratio when a drop of 5 μL ionophore solution was applied.

Performance of ionophore films with different thickness was characterized by testing solutions with 50 ppb As (III), respectively. As shown in Fig. 6, the sensor without a coating film exhibited the biggest peak current. As the film thickness increased from 0, 12.52, 22.27, 32.09, to 38.42 μm , the peak current decreased from 1.125 μA , 0.756 μA , 0.550 μA , 0.217 μA to 0.042 μA . The standard deviation of the peaking current decreased from 0.218 μA , 0.163 μA , 0.047 μA , 0.022 μA to 0.004 μA .

According to previous work, the PVC made by PVC powder can form a microporous membrane and the micro pores may hinder mass transfer process [30]. Arsenite ionophore, accounting for about four percent of the membrane mass, is evenly dispersed in the membrane. The dispersed ionophore component will allow arsenite to pass through the membrane. Meanwhile, the microporous membrane will reduce all the ions passing through by non-specific bonding. Larger ionophore film thickness will lead to higher selectivity, while also decreasing the amount of arsenite ions accumulated on the electrode surface.

Higher selectivity will lead to smaller standard deviation of peak current, while more arsenite ions accumulated on the electrode surface may get larger sensor sensitivity. To obtain a low LOD for such a sensor, these two critical parameters have to be balanced. For this experiment, the ionophore film made by 5.0 μL ionophore solution achieved the highest average-peak-current to standard-deviation ratio (11.7) and decent amplitude of peak current (0.550 μA). Eventually, we chose 5.0 μL as the optimized ionophore volume for the sensor.

C. The Selectivity of the Ionophore Film

Existence of other types of heavy metal ions, such as mercury and cadmium, may interfere with the reaction of arsenite ions during the electrochemical detection process. For instance, researchers have found that arsenic in the soil can influence the concentration of mercury in the roots of rice, indicating that complex interaction happened between arsenic and mercury [31]. Thus, the selectivity of the sensor need to be studied to ensure its independence from interference ions.

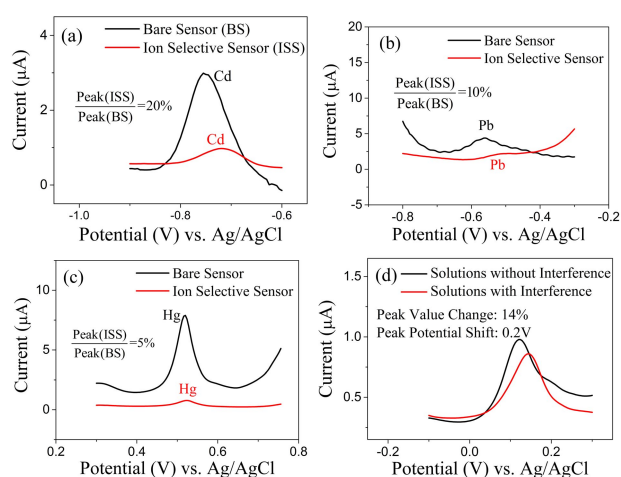


Fig. 7. Anodic stripping voltammograms of (a) 50 ppb cadmium, (b) 50 ppb lead, and (c) 50 ppb mercury using bare sensor (black line) and ion selective sensor (red line); and (d) analysis of 50 ppb arsenite in solutions with (red line) and without (black line) heavy metal interferences using ion selective sensor.

In this work, the permeability of lead, cadmium and mercury was investigated to evaluate the selectivity of the ionophore-coated sensor. Solutions with 50 ppb Cd^{2+} , Pb^{2+} or Hg^{2+} were analyzed by both bare sensors and the proposed sensors. As the peak potentials of Pb and Cd are both below the deposition potential of As, the permeability analysis of lead and cadmium was done by accumulating at -1.2 V (vs. Ag/AgCl) for five minutes and stripping from -1.2 V to -0.2 V. Analysis for mercury was done with the same parameters for arsenite. The anodic stripping voltammograms obtained from bare sensors and the proposed sensors were shown in Fig. 7 (a), 7 (b) and 7 (c). For Cd, Pb and Hg, after coated with the ionophore film, the peak current decreased drastically to 20%, 10% and 5% the value of a bare electrode separately. This means that over 80% interference reactions caused by these elements were eliminated by the ionophore film and the sensor's capacity of resisting disturbance was improved.

As part of the heavy metal ions (other than arsenite) can still penetrate through arsenite ionophore film, which may interact with arsenite and bring in deformation or distortion to the response curves, solutions with and without heavy metal interferences were analyzed respectively with the proposed sensors. As shown in Fig. 7 (d), when analyzing the As (III) solution without interferences, the ion selective sensor exhibited a well-defined curve with the peak value of 0.643 μA . After adding interfering ions (Cd^{2+} , Pb^{2+} and Hg^{2+} , each at the concentration of 50 ppb), the peak current decreased to 0.563 μA and the peak potential shifted 0.02 V. That was because the interfering ions penetrated through the ionophore film interacted with arsenite and prevented it from being reduced and oxidized. Since the stripping potential is within the potential range where arsenic ions stripping occurs [23], the shift will not alter the result of designating the element as arsenic.

D. ASV Determination of As (III)

In order to evaluate the feasibility of using the selective sensor for quantitative determination of trace As (III), a series

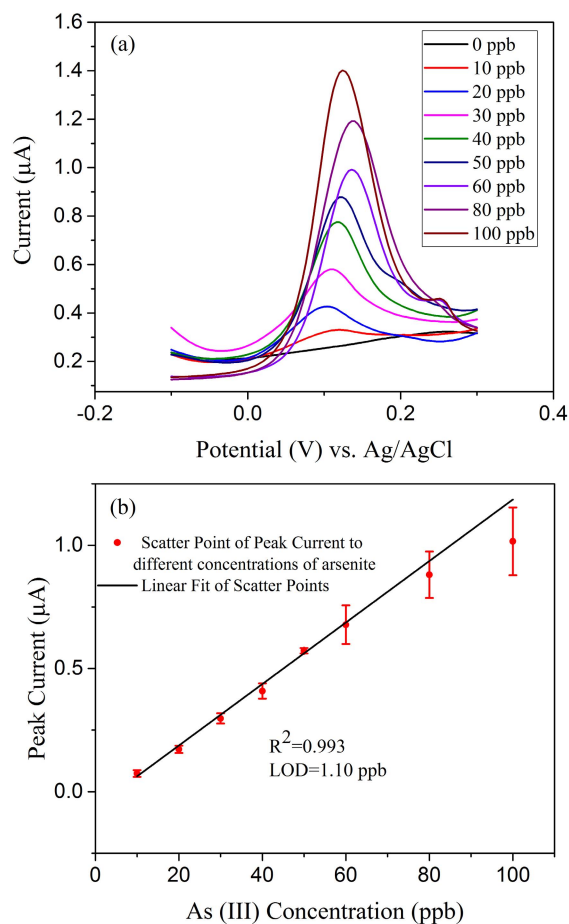


Fig. 8. (a) Anodic stripping voltammograms of As (III) measured by the selective sensor with peak potentials at +0.12 V. (b) Linear fitted calibration curve of As (III) from 10 to 100 ppb, with the limit of detection (LOD) derived as 1.10 ppb.

of concentrations of As (III) in $0.1 \text{ mol} \cdot \text{L}^{-1}$ HCl supporting solutions were prepared and analyzed using the proposed sensor. Square wave anodic stripping voltammetry was chosen because this technique can greatly reduce the background noise coming from the charging current during the stripping scan. Stirring was avoided to eliminate the interferences caused by convection and dissolved oxygen. Deposition time was chosen to be five minutes to balance detection time and detection limit.

Stripping voltammograms were obtained from solutions with As (III) concentrations varied from 0 to 100 ppb, as shown in Fig. 8 (a). Well-defined sharp current peaks were observed at the peak potentials between 0.115 V and 0.135V versus Ag/AgCl reference electrode ($3 \text{ mol} \cdot \text{L}^{-1}$ KCl). Oxidation peak current of As (III) increased linearly with the concentration of As (III). Corresponding calibration is shown in Fig. 8 (b), with five repeated measurements at each concentration. Fine linearity was achieved over the concentration range of 10-100 ppb ($R^2 = 0.993$) due to the ionophore film selectivity, highly uniform microfabrication method, the static conditions, and low standard deviations at each measurement. Limit of detection (LOD) achieved is 1.10 ppb ($S/N = 3$) with a deposition time of 300 s.

TABLE I
A COMPARISON OF SENSORS WITH DIFFERENT DECORATIONS

Electrodes	Linear range (ppb)	LOD (ppb)	Reference
Bare Au	148-1480	13.5	32
PtNPs-Fe(III)/MWCNT/GCE	0.75-22.5	0.75	13
AuNPs-GCE	0.05-15	0.025	14
AgNPs/CT-GCE	10-100	1.2	15
PtNPs-BDD	0-100	0.5	33
The proposed sensor	10-100	1.10	

PtNPs, Platinum nanoparticles; MWCNT, Multiwalled carbon nanotube; GCE, Glassy carbon electrode; AuNPs, Gold nanoparticles; AgNP/CT, Silver nanoparticle chitosan; BDD, Boron-doped diamond electrode.

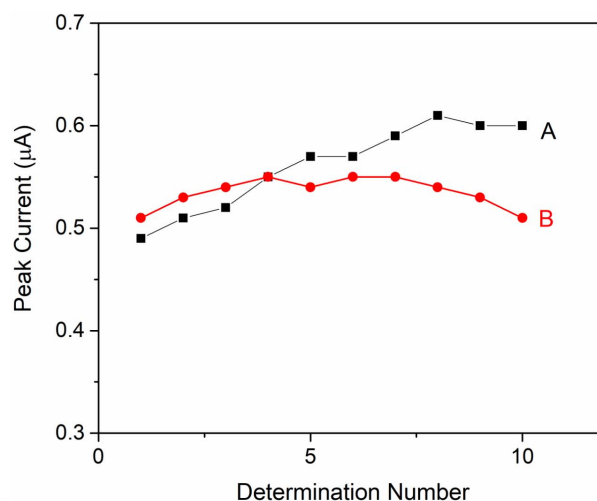


Fig. 9. Current peak values as a function of time for determinations of 50 ppb As (III) solution. Data was obtained by carrying out 10 consecutive determinations (A) and 10 determinations with electrochemical cleaning between two adjacent determinations (B).

The performance of this proposed sensor was compared with other works in TABLE I. Without decorations, the bare gold electrode can only achieve detection limit of 13.5 ppb, which cannot meet the requirement for drinking water determination. After decorating with nanoparticles, the detection limit was significantly decreased to 1 ppb or lower. As the expense to make noble metal nanoparticles is very high, the proposed sensor stood out for its low-cost property and comparable detection limit. Together with the advantage over fighting against interferences, the ionophore-coated sensor owned more potential in industrialization.

E. Reusability of the Sensor

The proposed sensor can be reused and the reusability is guaranteed by the electrochemical cleaning between two determinations. After each ASV determination, part of As (III) in the ionophore film was not fully dissolved in the solutions and could be accumulated on the working electrode again if a second determination is applied directly. So high potential should be applied to the working electrode between two determinations to further remove the arsenic residue in

TABLE II
AS (III) IN STANDARD SOLUTIONS AND WASTE WATER

Samples	ICP-MS method (ppb)	Proposed sensor (ppb)	T score
10ppb As (III) solution	10.4	10.8 ± 0.6	1.49
50ppb As (III) solution	48.0	48.6 ± 1.1	1.22
100ppb As (III) solution	95.2	91.6 ± 7.1	1.13
Waste water	16.0	15.4 ± 0.7	1.92

the ionophore. To confirm the importance of electrochemical cleaning on the repeatability of the sensor, two independent studies were performed. On the one hand, 50 ppb As (III) solution was determined with the ionophore sensor for 10 consecutive times. No extra cleaning process was performed between two determinations. As shown in Fig. 9 (curve A), peak current kept increasing as the determination went on, resulting in a 20% increase from the first determination to the tenth one. On the other hand, another experiment was carried out by determining As (III) solution with the same concentration using the ionophore sensor. The potential with the value of +0.5 V was applied to the working electrode for 5 minutes before each determination, ensuring that As (III) residue in the ionophore was effectively removed. Ten determinations were obtained (Fig. 9, curve B) and no upward or downward trend was observed. The relative standard deviation (ratio of the standard deviation to the mean, mean peak current value: 0.535 μ A, standard deviation: 0.015 μ A) for 10 determinations was 2.8%. Hence, we can conclude that the proposed sensor is reusable on the premise that electrochemical cleaning is applied between two determinations.

F. Waste Water Determination

For the propose of testing the feasibility of using the proposed sensor for real water determination, As (III) standard solutions and waste water solutions were prepared and analyzed by the proposed sensor as well as a standard process. Fresh waste water sample was taken from the St. Paul Metro Plant (St. Paul, MN, USA). Filtration and centrifugation were operated to remove big particles in waste water before analysis. The standard ICP-MS analysis was operated at Research Analytical Laboratory at University of Minnesota. TABLE II showed the As (III) content analyzed by these two methods. For As (III) standard solutions, both ICP-MS and the proposed sensor got results close to the real concentration of the samples. Compared to the standard method, the relative error from the proposed sensor were 3.85%, 1.25% and 3.78% respectively, which were all below normal value (10%) for sensors. This validated the accuracy and reliability of the proposed sensor for As (III) determination in samples without interferences. For waste water sample, the results obtained from the proposed sensor were in good agreement with that from the standard method (relative error: 3.75%). This is another proof for the ionophore sensor's selectivity against interferences and it demonstrates that this sensor is applicable

for As (III) determination of environmental samples such as waste water. Besides, Student's t-test was applied to the four samples to evaluate the consistency of the results between the proposed sensor and the standard method. As shown in TABLE II, the corresponding T score value for the four samples were 1.49, 1.22, 1.13 and 1.92, respectively. The T score values were all below the Student's T critical value (2.776), meaning that the results from the proposed sensor and ICP-MS had no significant difference. Accordingly, we can conclude that the proposed ionophore sensor is well qualified for the environmental monitoring of real water.

IV. CONCLUSION

This paper reports a novel selective micro sensor to determine trace arsenite using anodic stripping voltammetry. The selective sensor's performance was greatly improved due to the permselectivity of the ionophore film. Ions other than As (III) were prevented from reaching the working electrode surface and interferences from active compounds were reduced, leading to higher signal-to-noise ratio. The mechanism of the membrane was analyzed and the thickness was optimized. The sensor was successfully applied to detecting trace As (III) and the LOD was achieved at 1.10 ppb, much lower than the guideline value (10 ppb) from WHO. High selectivity of the sensor was demonstrated by detecting arsenite with lead, cadmium and mercury ions. Finally, the results of real water detection from the proposed sensor were consistent with those from a standard process, validating the sensor's potential as a sensitive, rapid, simple and inexpensive sensor for online monitoring of trace elements.

ACKNOWLEDGMENT

The authors would like to thank Prof. R. Ruan, Prof. P. Chen and Dr. M. Addy for the assistance in testing of arsenic samples.

REFERENCES

- [1] M. F. Hughes, "Arsenic toxicity and potential mechanisms of action," *Toxicol. Lett.*, vol. 133, no. 1, pp. 1–16, 2002.
- [2] M. Vahter, "Species differences in the metabolism of arsenic compounds," *Appl. Organomet. Chem.*, vol. 8, no. 3, pp. 175–182, 1994.
- [3] B. K. Mandal and K. T. Suzuki, "Arsenic round the world: A review," *Talanta*, vol. 58, no. 1, pp. 201–235, 2002.
- [4] *Guidelines for Drinking-Water Quality*, 4th ed., World Health Organization, Geneva, Switzerland, 2011.
- [5] A. Salimi, H. Mamkhezri, R. Hallaj, and S. Soltanian, "Electrochemical detection of trace amount of arsenic(III) at glassy carbon electrode modified with cobalt oxide nanoparticles," *Sens. Actuator B, Chem.*, vol. 129, no. 1, pp. 246–254, 2008.
- [6] K. L. Ackley, C. B'Hymer, K. L. Sutton, and J. A. Caruso, "Speciation of arsenic in fish tissue using microwave-assisted extraction followed by HPLC-ICP-MS," *J. Anal. Atomic Spectrometry*, vol. 14, no. 5, pp. 845–850, 1999.
- [7] F. Shemirani, M. Baghdadi, and M. Ramezani, "Preconcentration and determination of ultra trace amounts of arsenic(III) and arsenic(V) in tap water and total arsenic in biological samples by cloud point extraction and electrothermal atomic absorption spectrometry," *Talanta*, vol. 65, no. 4, pp. 882–887, 2005.
- [8] D. Q. Hung, O. Nekrassova, and R. G. Compton, "Analytical methods for inorganic arsenic in water: A review," *Talanta*, vol. 64, no. 2, pp. 269–277, 2004.
- [9] I. Jaunakais and D. Wood, "Testing to ensure proper disinfection," *Water Technol.*, vol. 26, no. 11, pp. 38–39, 2003.

- [10] M. M. Rahman *et al.*, "Effectiveness and reliability of arsenic field testing kits: Are the million dollar screen projects effective or not?" *Environ. Sci. Technol.*, vol. 36, no. 24, pp. 5385–5394, 2002.
- [11] L. Rassaei, M. Sillanpää, R. W. French, R. G. Compton, and F. Markenc, "Arsenite determination in phosphate media at electroaggregated gold nanoparticle deposits," *Electroanalysis*, vol. 20, no. 12, pp. 1286–1292, 2008.
- [12] J. Barón-Jaimez, M. R. Joya, and J. Barba-Ortega, "Anodic stripping voltammetry—ASV for determination of heavy metals," *J. Phys. Conf. Ser.*, vol. 466, pp. 120–123, Nov. 2013.
- [13] S.-H. Shin and H.-G. Hong, "Anodic stripping voltammetric detection of arsenic(III) at platinum-iron(III) nanoparticle modified carbon nanotube on glassy carbon electrode," *Bull. Korean Chem. Soc.*, vol. 31, no. 11, pp. 3077–3083, Nov. 2010.
- [14] Y. Lan, H. Luo, X. Ren, Y. Wang, and L. Wang, "Glassy carbon electrode modified with citrate stabilized gold nanoparticles for sensitive arsenic (III) detection," *Anal. Lett.*, vol. 45, no. 10, pp. 1184–1196, 2012.
- [15] S. Prakash, T. Chakrabarty, A. K. Singh, and V. K. Shahi, "Silver nanoparticles built-in chitosan modified glassy carbon electrode for anodic stripping analysis of As(III) and its removal from water," *Electrochim. Acta*, vol. 72, pp. 157–164, Jun. 2012.
- [16] F. R. Bento, M. T. Grassi, A. Sales, and L. H. Mascaró, "Determination of Cu and As by stripping voltammetry in utility poles treated with chromated copper arsenate (CCA)," *Int. J. Electrochem. Sci.*, vol. 3, no. 12, pp. 1523–1533, 2008.
- [17] G. Kefala, A. Economou, and A. Voulgaropoulos, "A study of Nafion-coated bismuth-film electrodes for the determination of trace metals by anodic stripping voltammetry," *Analyst*, vol. 129, no. 11, pp. 1082–1090, 2004.
- [18] C. M. A. Brett, A. Alves, and D. A. Fungaro, "Nafion-coated mercury thin film and glassy carbon electrodes for electroanalysis?: Characterization by electrochemical impedance," *Electroanalysis*, vol. 13, no. 3, pp. 212–218, 2001.
- [19] A. A. Ensaifi, S. Meghdadi, and A. R. Allafchian, "Highly selective potentiometric membrane sensor for Hg(II) based on bis(benzoyl acetone) diethylene triamine," *IEEE Sens. J.*, vol. 8, no. 3, pp. 248–254, Mar. 2008.
- [20] P. Bühlmann, E. Pretsch, and E. Bakker, "Carrier-based ion-selective electrodes and bulk optodes. 2. Ionophores for potentiometric and optical sensors," *Chem. Rev.*, vol. 98, no. 4, pp. 1593–1688, 1998.
- [21] A. Mahdaviifar, M. Navaei, P. J. Hesketh, M. Findlay, J. R. Stetter, and G. W. Hunter, "Transient thermal response of micro-thermal conductivity detector (μ TCD) for the identification of gas mixtures: An ultra-fast and low power method," *Microsyst. Nanoeng.*, vol. 1, p. 15025, Oct. 2015.
- [22] L. Wang, G. Jing, W. Lu, and T. Cui, "Highly selective sensor for trace arsenite determination using anodic stripping voltammetry," in *Proc. IEEE 29th Int. Conf. Micro Electro Mech. Syst. (MEMS)*, Jan. 2016, pp. 901–904.
- [23] V. K. Gupta and S. Agarwal, "PVC based 5,10,15,20-tetrakis (4-methoxyphenyl) porphyrinatocobalt(II) membrane potentiometric sensor for arsenite," *Talanta*, vol. 65, no. 3, pp. 730–734, 2005.
- [24] X. He *et al.*, "Square wave anodic stripping voltammetric determination of lead(II) using a glassy carbon electrode modified with a lead ionophore and multiwalled carbon nanotubes," *Microchim. Acta*, vol. 176, nos. 1–2, pp. 81–89, 2011.
- [25] G. Forsberg, J. W. O'Laughlin, R. G. Megargle, and S. R. Koortyihann, "Determination of arsenic by anodic stripping voltammetry and differential pulse anodic stripping voltammetry," *Anal. Chem.*, vol. 47, no. 9, pp. 1586–1592, 1975.
- [26] A. Craggs, G. Moody, and J. Thomas, "PVC matrix membrane ion-selective electrodes," *J. Chem. Edu.*, vol. 51, no. 8, pp. 541–544, 1974.
- [27] H. P. Longrich, S. E. Jackson, and D. Gunther, "Inter-laboratory note. Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation," *J. Anal. Atomic Spectrometry*, vol. 11, no. 9, pp. 899–904, 1996.
- [28] H. C. S. H. L. Walg, "Base-line noise and detection limits in signal-integrating analytical methods. Application to chromatography," *Chromatographia*, vol. 8, no. 7, pp. 311–323, 1975.
- [29] B. Hoyer, T. M. Florence, and G. E. Batley, "Application of polymer-coated glassy carbon electrodes in anodic stripping voltammetry," *Anal. Chem.*, vol. 59, no. 13, pp. 1608–1614, 1987.
- [30] Y. Mizutani, "Structure of ion exchange," *J. Membrane Sci.*, vol. 49, no. 2, pp. 121–144, 1990.
- [31] X. Du, Y. G. Zhu, W. J. Liu, and X. S. Zhao, "Uptake of mercury (Hg) by seedlings of Rice (*Oryza sativa* L.) grown in solution culture and interactions with arsenate uptake," *Environ. Experim. Botany*, vol. 54, no. 1, pp. 1–7, 2005.
- [32] A. Simm, C. Banks, and R. Compton, "Sono-electroanalytical detection of ultra-trace arsenic," *Electroanalysis*, vol. 17, no. 4, pp. 335–342, Mar. 2005.
- [33] S. Hrapovic, Y. Liu, and J. H. T. Luong, "Reusable platinum nanoparticle modified boron doped diamond microelectrodes for oxidative determination of arsenite," *Anal. Chem.*, vol. 79, no. 2, pp. 500–507, 2007.

Li Wang received the B.S. degree from the School of Mechanical Science and Engineering, Huazhong University of Science and Technology, Wuhan, China, in 2013. She is currently pursuing the Ph.D. degree with the Department of Precision Instrument, Tsinghua University, Beijing, China. Her research interests include MEMS chemical sensors, ion-selective membrane, and trace heavy metal determination.

Wenshuai Lu received the B.S. and the M.S. degrees from the School of Electrical Engineering and Automation, Harbin Institute of Technology, Harbin, China, in 2009 and 2011, respectively, and the Ph.D. degree from the Department of Precision Instrument, Tsinghua University, Beijing, China. His research interests include MEMS chemical sensors, embedded computing and controlling systems, and the Internet of Things (IoT).

Gaoshan Jing received the B.S. degree in biomedical engineering from Zhejiang University, Hangzhou, China, in 1998, the M.S. degree in biophysics from Tsinghua University, Beijing, China, in 2001, the M.S. degree in electrical engineering from the University of Cincinnati, Cincinnati, OH, USA, in 2004, and the Ph.D. in electrical engineering from Lehigh University, Bethlehem, PA, USA, in 2009. He is currently an Associate Professor with the Department of Precision Instruments, Tsinghua University. His research interests include MEMS/nano sensors for various chemical and biological applications.

Tianhong Cui is currently the Distinguished McKnight University Professor at the University of Minnesota. He is a Professor with the Department of Mechanical Engineering and an Affiliate Senior Member of the graduate faculty in the Department of Electrical Engineering and Department of Biomedical Engineering. He joined the faculty of the University of Minnesota in 2003. From 1995 to 2003, he held research or faculty positions at Tsinghua University, the University of Minnesota, the National Laboratory of Metrology, Japan, and Louisiana Tech University, respectively. He was a Humboldt Fellow at the University of Freiburg, Germany, in 2006, and he holds a Visiting Professorship at the University of Paris East and Tsinghua University. Recently, he was awarded the Braise Pascal Chair for Excellence from ENS Foundation, France. His current research interests include MEMS/ NEMS and nanotechnology for medical applications. He is a Fellow of the American Society of Mechanical Engineering (ASME). He is the founding Executive Editor-in-Chief for two Nature journals, *Light: Science & Applications* and *Microsystems & Nanoengineering*.