An all-solid-state Ion-Selective Electrode with Ag₃AsO₄ as the Sensitive Membrane for Detecting Arsenate in Aqueous Environments

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In this work, an all-solid-state ion-selective electrode, using Ag wire as a substrate, Ag particles as a mid-layer and Ag_3AsO_4 as a sensitive membrane was prepared for detecting arsenate in aqueous environments. The Ag particles were electrodeposited using a function generator and Schottky diode in $AgNO_3$ solution. Electrochemical polymerisation of the Ag_3AsO_4 sensitive membrane was achieved via chronoamperometry on an electrochemical workstation. The membrane successfully polymerised on the surface of the electrode, which was demonstrated from scanning electron microscopy images. The energy-dispersive X-ray spectroscopy results prove that the sensitive membrane is Ag_3AsO_4, based on the main elements of the sensitive membrane being determined as, As, O and Ag. The detection limit of the electrode was measured as 1.8165×10^{-6} M with a linear range of 5×10^{-6}–1×10^{-1} M, which indicates that the Ag_3AsO_4 electrode has a wide response range and low detection limit, exhibiting a response time of around 1–2 s with good stability and repeatability. The average potential fluctuation of the electrode in 1 h was 1.48 mV. The electrode shows good anti-interference properties in that it is far more sensitive to arsenate than interfering ions, including sulfate, carbonate, acetate and nitrate. The lifespan of the Ag_3AsO_4 electrode was confirmed as being more than 80 days, showing great recovery in water sample testing, which shows that the electrode is accurate and can be used for aqueous environmental testing.

1. INTRODUCTION

Arsenic is one of the most toxic elements and is regarded as a serious pollutant [1, 2]. Arsenic pollution can be contributed to by both anthropogenic and natural factors [3]. Mining, burning and smelting of arsenic-containing metal ores can cause arsenic-containing dust, waste water, waste gas, etc. [4]. The use of arsenic-containing pesticides also leads to arsenate pollution of water sources, soil,

fruit and vegetables [5, 6]. Because of its toxicity, wide distribution and being difficult to treat, arsenic pollutants are a key issue in environmental pollution control [7, 8]. Arsenic in its inorganic form, as arsenate and arsenite, is common and the stable form of arsenic that exists in water. Arsenic is not only harmful to aquatic species, but also highly toxic to human organs.

Arsenic detection in the aquatic environment is therefore of great significance for water quality monitoring. Traditional analytical techniques used to detect arsenic, such as atomic absorption spectroscopy, inductively coupled plasma mass spectrometry (ICP-MS), and neutron activation analysis, are highly accurate with a low detection limit, but are limited by expensive instrumentation, time-consuming testing, etc. Ion-selective electrodes (ISEs) based on charged carriers (ionophores) can effectively remedy the above shortcomings as they have the advantages of simple manufacturing, quick response, and it is possible to use them for *in situ* monitoring [9-11]. All-solid-state ISEs, which have small volume and high intensity, can be used in extreme water environments such as deep sea [12, 13].

Several research studies have focussed on the fabrication and materials of arsenate detection electrodes. Khan et al. used polyacrylonitrile/silica gel as an anion-exchange membrane [14], Somer et al. used solid salts of Cu_2S, Ag_3AsO_4 and Ag_2S as arsenate electrode compositions [15], a polypyrrole conducting polymer doped with arsenate ions has been applied for the determination of As(V) by Ansari et al. [16], and a bis(dichloroorganostannyl)methane derivative $[Cl_2(4\text{-}n\text{-}C_8H_{17}\text{-}C_6H_4)Sn]_2CH_2$ has been reported by Chaniotakis as an arsenate-selective sensor [17].

In this study, an all-solid-state ion-selective electrode was developed using Ag wire as the base material, Ag_3AsO_4 as a sensitive membrane for detecting arsenate, and Ag particles as an interlayer. The fabrication process is simple in terms of execution and low in cost and the electrode has a linear range of 5×10^{-6}–1×10^{-1} M, a detection limit of 1.885×10^{-6} M, a response time of 1–2 s, and lifetime of more than 80 days, making it suitable for the quick detection of As(V).

2. EXPERIMENTAL

2.1 Reagents and apparatus

Sodium arsenate was obtained from Shanghai Jinjinle Industrial Co., Ltd. Sodium carbonate, sodium nitrate, sodium sulfate and sodium acetate trihydrate were obtained from Sinopharm Chemical Reagent Co., Ltd. All reagents were of analytical grade. A 0.1 M silver nitrate standard solution and 0.1 M hydrochloric acid were obtained from Shenzhen Bolinda Technology Co., Ltd. Ag wire (99.9%, 0.4 mm in diameter) was purchased from the Precious Material Company of Changzhou, China.

Ag particles were electrodeposited by a SG1020A function generator using a Schottky diode (S4 IN5819). Electrochemical polymerisation and electrochemical performance tests on the electrode were accomplished using a CHI760D electrochemical workstation using an Ag/AgCl reference electrode (3.8 mm) obtained from Shanghai Jinghong Electronic Technology Development Co., Ltd, and a platinum electrode obtained from Gaoss Union Electronic Technology Co., Ltd. A Zeiss Sigma

500 field emission scanning electron microscope (SEM, Carl Zeiss, Germany) was used in the SEM and energy-dispersive X-ray spectroscopy (EDS) measurements.

2.2 Pretreatment and fabrication of the electrode

An Ag wire of 4 cm in length and 0.4 mm in diameter was polished using abrasive paper and then ultrasonically cleaned in 0.1 M dilute hydrochloric acid for 10 min to remove oxide film on the Ag wire surface. The Ag wire was then washed with deionised water and dried prior to use.

For the Ag particle electrode, a SG1020A function generator was used with sine wave parameters of an amplitude of 1.2 V and frequency of 50 Hz. The anode was connected to a Schottky diode and contributing Ag wire in turn and the cathode was connected to the Ag wire via a pretreatment process. Two Ag wires were placed in a 0.1 M $AgNO_3$ solution. After 60 s of electrification, the cathode Ag wire was coated with Ag particles.

To carry out the measurements, a three-electrode system was employed using a CHI760D electrochemical workstation with Ag wire and Ag particles serving as the working electrode, Ag/AgCl serving as the reference electrode, and a Pt electrode serving as the auxiliary electrode. A 0.1 M sodium arsenate solution was prepared using deionised water. Electrochemical polymerisation of the Ag_3AsO_4 sensitive membrane was achieved by chronoamperometry in 50 s at a potential of 0.8 V and sensitivity of 10^{-2}. The electrode fabrication process can be seen in Figure 1.
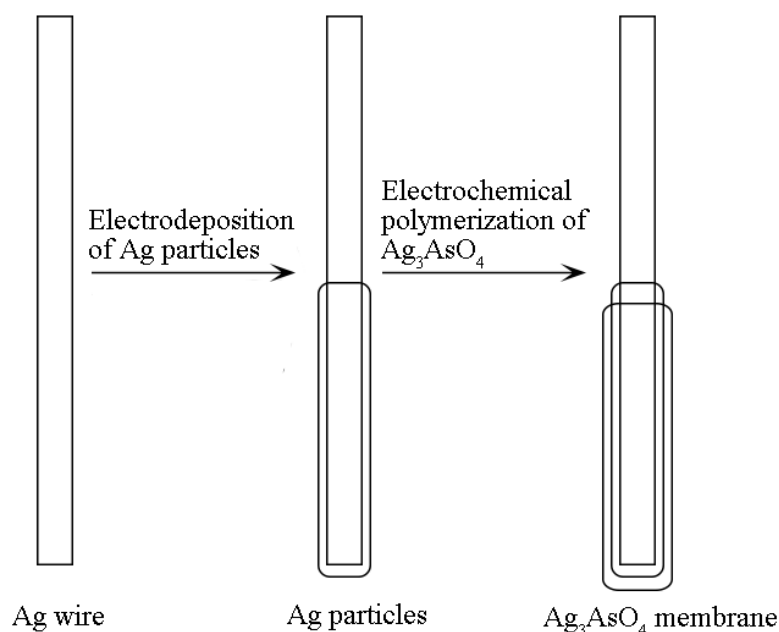

Figure 1. Electrode fabrication process.

2.3 Performance of the electrode

SEM and EDS measurements were carried out to observe the electrode membrane and determine its elemental distribution.

The performance of the electrode was evaluated on a CHI760D electrochemical workstation using a two-electrode system open circuit technique for all of the potential measurements. The potential was recorded when the value became stable. A series of Na_3AsO_4 solutions, which were prepared via serial dilution, were used as calibration solutions.

2.4 Application

Alpas natural spring water (Alpas Drinks Co., Ltd) samples with standard addition of arsenate ions were prepared. Three samples with different added amounts of arsenate ions were measured using the Ag_3AsO_4 electrode to test the electrode accuracy. Each sample was tested three times and the measured values were compared with real arsenate contaminated water samples and the recovery rates were calculated.

3. RESULTS AND DISCUSSION

3.1 Electrochemical polymerisation of the Ag_3AsO_4 sensitive membrane

Chronoamperometry at a potential of 0.8V was used for the electrochemical polymerisation of the Ag_3AsO_4 sensitive membrane at an initial current of 8.40×10^{-3} A (Figure 2). During the first 5 s, the current reduced substantially as Ag_3AsO_4 polymerised rapidly on the surface of the Ag wire. Then, the current decreased slowly until it stabilised at 2.17×10^{-3} A. In this period of time, Ag_3AsO_4 polymerised slowly and the surface of the electrode turned brown as the Ag_3AsO_4 sensitive membrane successfully polymerised on it.
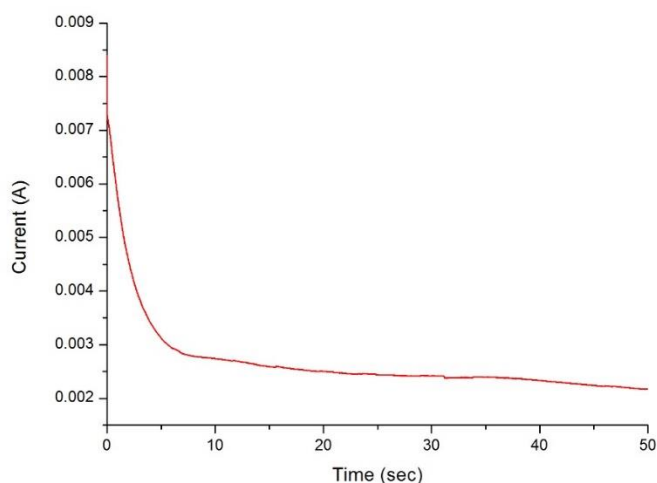
3.2 SEM and EDS studies

**Figure 2.** Current–time curve of Ag_3AsO_4 membrane polymerisation based on chronoamperometry at a potential of 0.8 V.

Figure 3 (a), (b) and (c) show a 500× magnified SEM image of the Ag particle layer formed on the surface of the Ag wire, a 500× magnified SEM image of the Ag_3AsO_4 membrane formed on the surface of the Ag particle layer, and a 15,000× magnified SEM image of the Ag_3AsO_4 membrane, respectively.
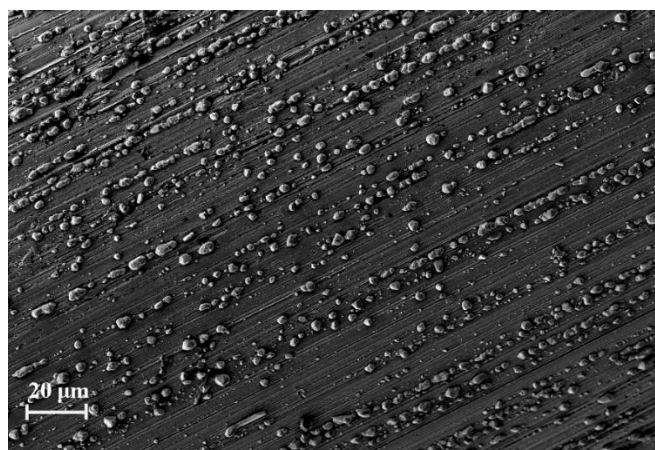
(a)
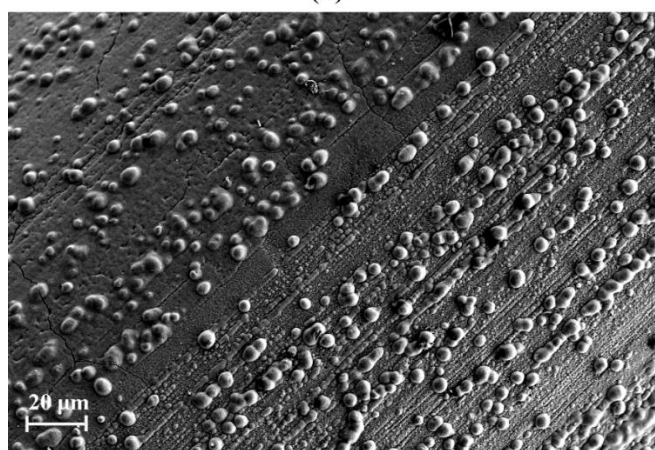
(b)
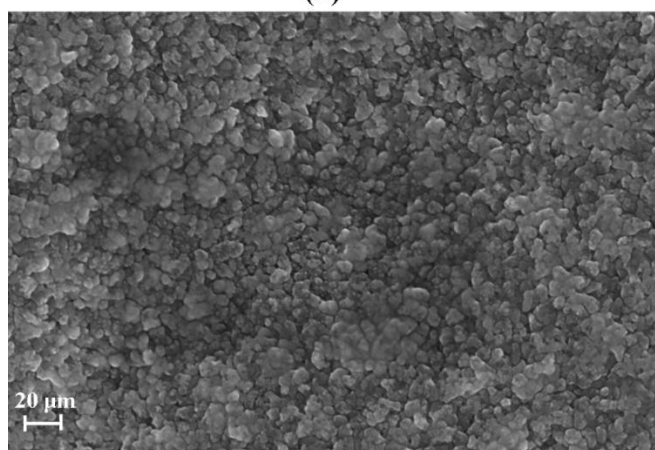
(c)

Figure 3. SEM images of the Ag_3AsO_4 electrode. (a) The Ag particle layer viewed at a magnification of 500×, (b) the Ag_3AsO_4 membrane viewed at a magnification of 500× and (c) the Ag_3AsO_4 membrane viewed at a magnification of 15,000×.

It can be seen from Figure 3 that the Ag particles are evenly coated on the surface of the Ag wire after electrification, which effectively increases the specific surface area of the Ag wire and made the combination of the substrate and sensitive membrane more secure. From Figure 3 (b), it can be seen that after electrochemical polymerisation of sodium arsenate, the surface of the Ag particle layer is evenly covered with the Ag_3AsO_4 sensitive membrane. At 15,000× magnification, it can be seen from Figure 3 (c) that the Ag_3AsO_4 adheres to the electrode surface in the form of densely packed block-like particles.

Table 1. Elemental analysis of the Ag_3AsO_4 sensitive membrane by EDS

Element	Atom%	Weight%
Ag	44.05	76.07
As	10.18	12.21
O	45.77	11.72

As seen from the EDS results shown in It can be seen from Figure 3 that the Ag particles are evenly coated on the surface of the Ag wire after electrification, which effectively increases the specific surface area of the Ag wire and made the combination of the substrate and sensitive membrane more secure. From Figure 3 (b), it can be seen that after electrochemical polymerisation of sodium arsenate, the surface of the Ag particle layer is evenly covered with the Ag3AsO4 sensitive membrane. At 15,000× magnification, it can be seen from Figure 3 (c) that the Ag3AsO4 adheres to the electrode surface in the form of densely packed block-like particles.

Table 1 and Figure 4, the elemental analysis of Ag_3AsO_4 indicates that Ag, as the substrate, makes up the greatest proportion of the elemental composition. The atomic ratio of arsenic to oxygen is close to 1:4, due to arsenic being connected to four oxygen atoms in the atomic structure of arsenate. The successful synthesis of the sensitive membrane was thus proved from EDS measurements.
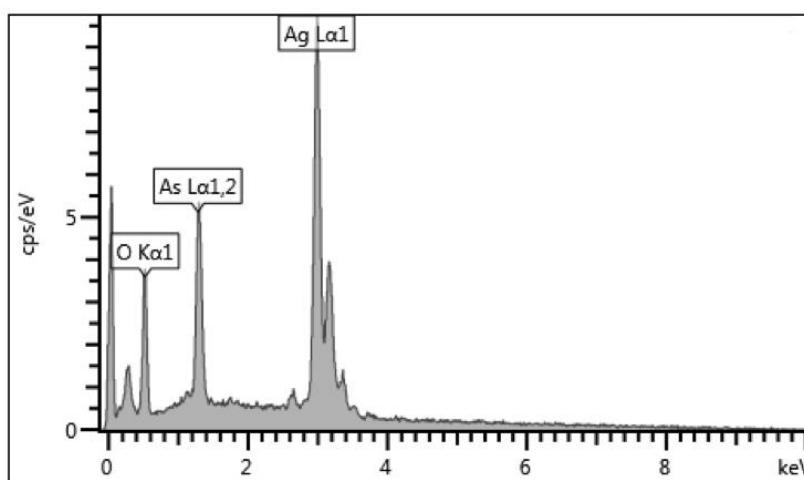

Figure 4. EDS results of the Ag_3AsO_4 sensitive membrane.

3.3 Detection limit, linear range and calibration curve of the Ag₃AsO₄ electrode

To measure the detection limit and linear range of the Ag_3AsO_4 electrode, a series of sodium arsenate solutions with concentrations of 1×10^{-7} M (logC = −7), 5×10^{-7} M (logC = −6.301), 1×10^{-6} M (logC = −6), 5×10^{-6} M (logC = −5.301), …, 1×10^{-2} M (logC = −2), 5×10^{-2} M (logC = −1.301) and 1×10^{-1} M (logC = −1) were prepared for electrode calibration. The potential of each solution was recorded and plotted, as seen in Figure 5. By definition, the detection limit is the point of intersection between the straight and the tangent part of the calibration curve [18]. The linear range of the Ag_3AsO_4 electrode was determined as 5×10^{-6}–1×10^{-1} M, with a fitting line of y = −34.417x + 139.82 with an R^2 value of 0.99361, as shown in Figure 5. The detection limit was determined as 1.8165×10^{-6} M, indicating that the Ag_3AsO_4 electrode has a wide response range and low detection limit.

Compared to previous related research in the literature, the electrode has a wider linear range with high correlation. Furthermore, the electrode has a lower detection limit than those of many reported electrodes, the detection limits of which are generally in the range of 10^{-5} M [15, 16].
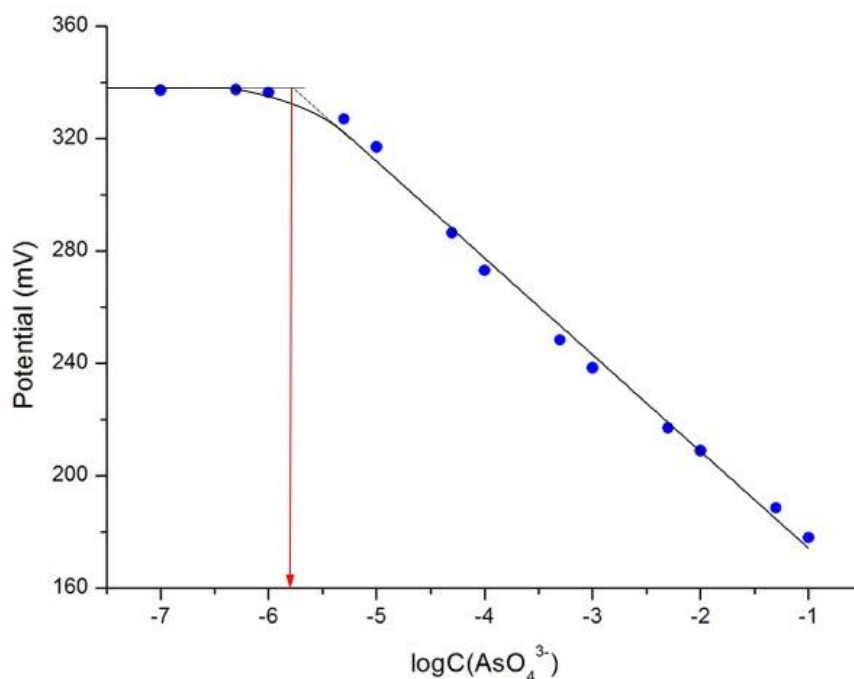

Figure 5. Electrode performance in 10^{-7}–10^{-1}M Na₃AsO₄ solutions.

3.4 Response curve

The response potential of the Ag_3AsO_4 electrode in sodium arsenate solution was recorded. Figure 6 shows the real-time calibration curve of the Ag_3AsO_4 electrode in sodium arsenate solution at five concentrations of 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} M, measured from low to high in turn with each solution calibrated for 200 s.

The response time is the time that it takes for the potential value of the electrode to reach stability and is an important characteristic that affects the accuracy of real-time monitoring and throughput of the sensor [19]. Figure 6 shows that the Ag_3AsO_4 electrode is sensitive as it responds quickly with a response time of around 1–2 s, due to the closeness of the sensitive membrane and base material and also the high conductivity of the membrane. The potential was relatively stable in each solution, with an observed potential drift of <2 mV in 200 s.

For other all-solid-state electrodes, the response time is normally more than half a minute or even several minutes [20-22]. Even for other electrodes that detect As(V), the response time is more than 10 s [14-16], so, in contrast, the Ag_3AsO_4 electrode shows a much faster response.
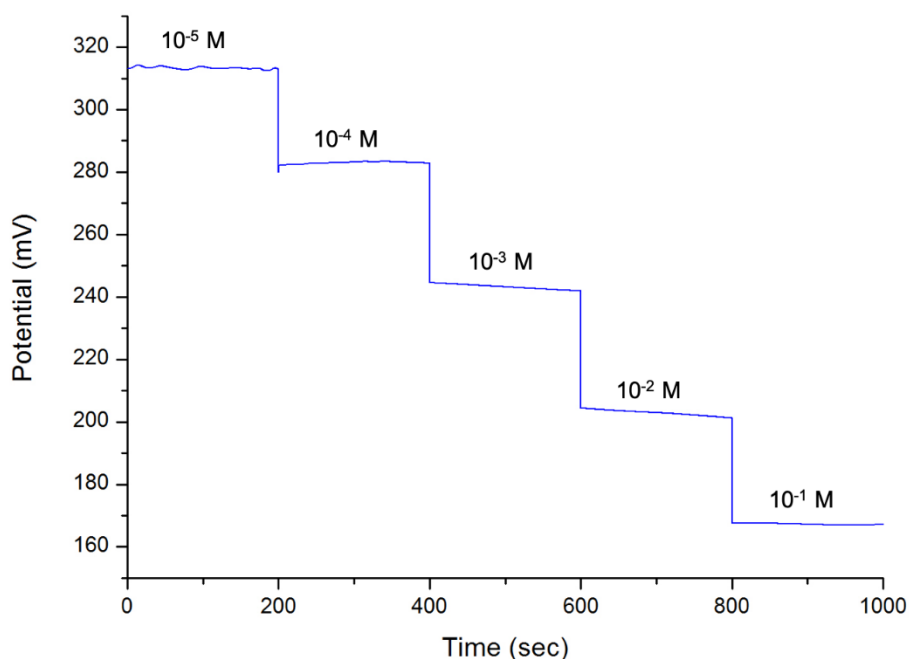

Figure 6. Potential–time curve of the Ag_3AsO_4 electrode in $10^{-5}-10^{-1}$ M sodium arsenate solutions using an open circuit technique.

3.5 Stability and repeatability of the electrode

To verify its long-term stability, the Ag_3AsO_4 electrode was tested in each of the different concentrations of the sodium arsenate solution for 1 h. Figure 7 clearly illustrates that the potential is relatively stable with little fluctuation observed during the tests. The highest potentials measured in the concentrations of 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} M were 316, 279.5, 237.4, 205.7 and 175.1 mV respectively, while the lowest potentials were 313.3, 278.7, 236.5, 203.8 and 174 mV. In general, the average difference of the potential fluctuation was 1.48 mV. In low concentrations, the fluctuation was relatively bigger, which may be due to the instability of the solution and also the low concentration approaching the detection limit of the electrode.
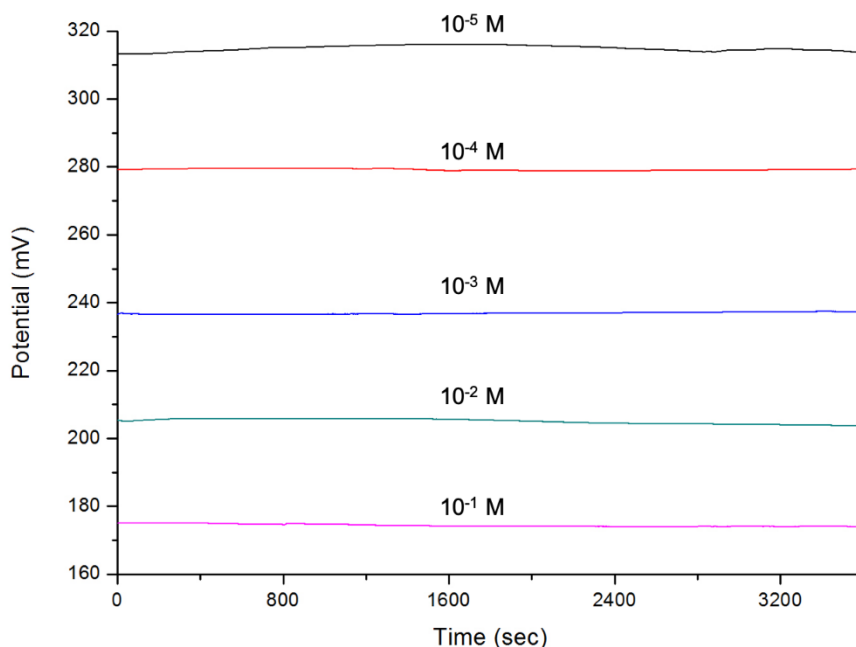
Figure 7. 1 h potential measurements of the Ag_3AsO_4 electrode in sodium arsenate solution with concentrations from 10^{-5}–10^{-1} M.
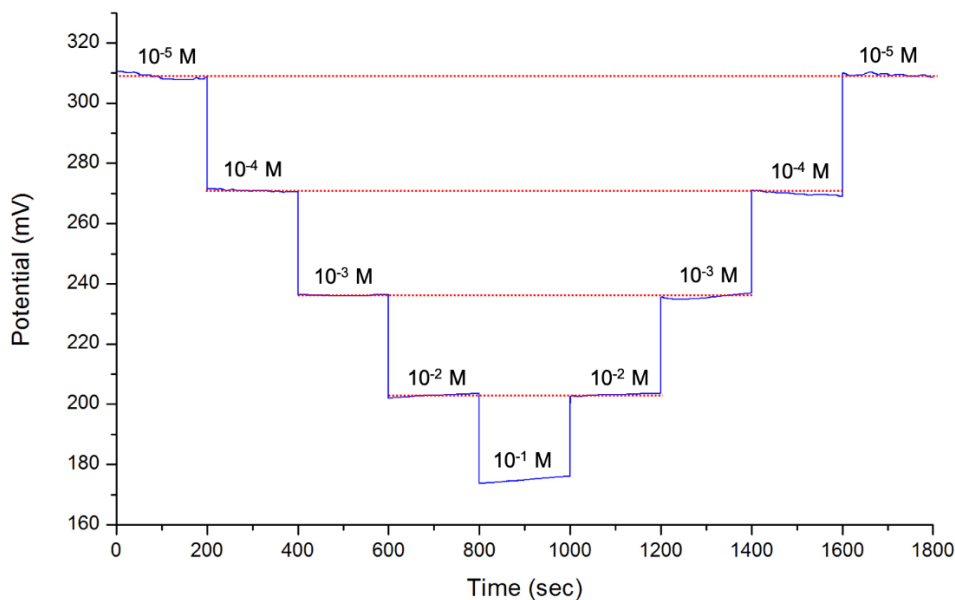

Figure 8. Repeatability tests of the Ag_3AsO_4 electrode with potential measurements in 10^{-5}–10^{-1} M sodium arsenate solutions.

To test the repeatability of the electrode, which is an important property, its potential was measured from low to high concentration (10^{-5}–10^{-1} M) and then immediately from high to low

concentration (10^{-1}–10^{-5} M), as seen in Figure 8. After 200 s of measuring each stage, the Ag_3AsO_4 and reference electrodes were washed with deionised water and immediately immersed into the next solution.

The final potential values of each stage were 308.7, 270.6, 236.4, 203.5, 176.1, 203.7, 236.9, 269.1 and 308.6 mV respectively, which illustrated that after changing the solution, the potential was stable near to the same value when in the same concentration. Thus, the good repeatability of the electrode indicates that it is reliable for quick detection.

3.6 Interference study

Interference studies can clearly illustrate the sensitivity of the electrode to the target ion over those of interfering ions [23]. To test the specificity of the Ag_3AsO_4 electrode, a series of sodium arsenate solutions with different added amounts of interference anions were prepared. The interference ions used were sulfate, carbonate, acetate, and nitrate, which are common anions found in aqueous environments. Four experimental groups of 10^{-5}–10^{-1} M Na_3AsO_4 solutions containing interference anions with a fixed concentration of 10^{-2} M were compared with a control group of 10^{-5}–10^{-1} M Na_3AsO_4 solutions without the interference anions. As can be seen in Figure 9 the slopes of the fitting line of the experimental groups are from -35.84 to -35.25, values that are all very close to that of the control group (-35.56), with an R^2 value of >0.99. With the addition of the interference anions, the response curves did not show any significant changes, which indicates that the electrode is far more sensitive to arsenate than the interference anions.
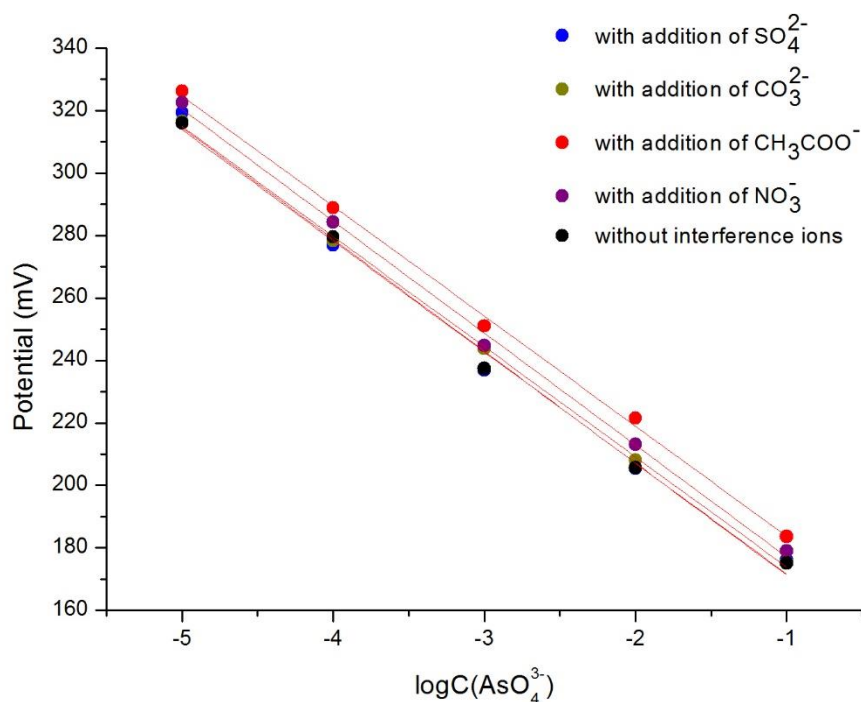

Figure 9. Anti-interference performance of the Ag_3AsO_4 electrode in 10^{-5}~10^{-1} M sodium arsenate solutions with 10^{-2} M of sulfate, carbonate, acetate and nitrate interference anions.

3.7 Lifespan of the electrode

Lifespan is an important factor that can directly affect the long-term serviceability of the electrode. To test the lifespan, an Ag_3AsO_4 electrode was stored in deionised water for 80 days and tested in standard sodium arsenate solution regularly to calculate the slope of the fitting line and the R^2 value. As can be seen in Table 2, the slopes over 80 days were stable between values of −35.56 to −37.74 with R^2 values of >0.99, which indicates that the Ag_3AsO_4 electrode has guaranteed accuracy for more than 80 days of continuous use in aqueous environments.

The lifespan of electrodes for detecting As(V) is normally about 2 months [16]. Compared with other research studies, the Ag_3AsO_4 electrode in this work shows a longer lifespan, which indicates its potential to be used for long-term monitoring.

Table 2. Performance of the Ag_3AsO_4 electrode (mV) in 10^{-5}–10^{-1} M sodium arsenate over 80 days

Days	10^{-5} M	10^{-4} M	10^{-3} M	10^{-2} M	10^{-1} M	Slope	R^2
1	313.1	281.5	240.8	201.9	167.4	-37.10	>0.99
3	318.8	278.5	240.8	208.2	172.3	-36.33	>0.99
6	317.6	280.2	245.9	204.2	169.3	-37.26	>0.99
14	316.3	273.1	231.4	200.0	169.8	-36.61	>0.99
30	316.0	277.4	238.0	199.8	166.1	-37.74	>0.99
58	315.5	276.2	239.1	202.0	170.3	-36.46	>0.99
80	311.6	272.1	235.5	203.7	168.0	-35.56	>0.99

3.8 Application of the electrode

Alpas natural spring water (Alpas Drinks Co., Ltd) is a popular drinking water that contains H_2SiO_3 (25.0–50.0 mg/L), total dissolved solids (50–150 mg/L), K^+ (1.0–2.0 mg/L), Na^+ (3.0–5.0 mg/L), Mg^{2+} (0.7–1.5 mg/L) and Ca^{2+} (5.0–8.0 mg/L). To determine the application capabilities of the Ag_3AsO_4 electrode, four water samples of Alpas natural spring water with different added amounts of arsenate ranging from 8.11×10^{-6}–3.8×10^{-2} M were prepared using a standard addition method. Each sample was tested by the Ag_3AsO_4 electrode three times and the average amount of arsenate tested was calculated, as can be seen in

Table 3. Recovery rates of 91.26–99.23% were observed, indicating good recovery and demonstrates that the electrode has good accuracy and applicability for drinking water or aqueous environmental testing.

Table 3. Water sample testing of arsenate ions by the Ag_3AsO_4 electrode

Sample	Arsenate ions (M)		Recovery (%)
	Added	Found	
No. 1	8.11×10^{-6}	7.41×10^{-6}	91.2
No. 2	6.89×10^{-4}	6.40×10^{-4}	92.8
No. 3	5.14×10^{-3}	4.90×10^{-3}	95.5
No. 4	3.81×10^{-2}	3.79×10^{-2}	99.2

3.9 Comparison of the As₃AsO₄ electrode with previously reported electrodes

A summary of the comparison between the properties of the As_3AsO_4 electrode and other previously reported electrodes is presented in Table 4. The As_3AsO_4 electrode reported in this work shows superior properties, exhibiting a much shorter response time and detection limit. The fast response enhances the accuracy of the real-time monitoring and throughput of the sensor. Furthermore, the electrode also performs well in terms of its other properties, showing that it has the potential to be used for long-term *in situ* monitoring.

Table 4. Comparison of the performance of the As_3AsO_4 electrode and other electrodes previously reported in the literature

Materials of membrane	Linear concentration range /M	Detection Limit /M	Response time /s	Lifespan
Ag_3AsO_4(this work)	$5\times10^{-6}\sim1\times10^{-1}$	1.8165×10^{-6}	1~2	More than 80 days
polyacrylonitrile/silica gel [14]	$1\times10^{-6}\sim1\times10^{-1}$	--	15	Less than 3 months
solid salts of Cu_2S, Ag_3AsO_4 and Ag_2S [15]	$1\times10^{-5}\sim1\times10^{-1}$	1×10^{-5}	30~60	-
Polypyrrole conducting polymer doped with arsenate ion [16]	$5\times10^{-5}\sim1\times10^{-1}$	2.8×10^{-5}	10	60 days
Bis(dichloroorganostannyl)methane derivative [Cl_2(4-*n*-C_8H_{17}-C_6H_4)Sn]$_2CH_2$ [17]	$1\times10^{-5}\sim1\times10^{-2}$	2×10^{-6}	--	--

4. CONCLUSIONS

An all-solid-state ion-selective electrode was developed in this work using Ag wire as a substrate, Ag particle as an interlayer, and Ag_3AsO_4 as a sensitive membrane. Ag particles were electrodeposited on the Ag wire using a function generator and Schottky diode. Electrochemical polymerisation of the Ag_3AsO_4 sensitive membrane was achieved via chronoamperometry on an electrochemical workstation.

SEM images of the membrane indicate that the membrane successfully polymerised on the surface of the electrode and the EDS results indicate that the main elements of the sensitive membrane are As, O and Ag, proving that the composition of the sensitive membrane is Ag_3AsO_4.

The detection limit of the electrode is 1.8165×10^{-6} M with a linear range of 5×10^{-6}–1×10^{-1} M and fitting line of the linear range of y = −34.417x + 139.82 with an R^2 value of 0.99361, which indicates that the Ag_3AsO_4 electrode has a wide response range and low detection limit. Furthermore, the Ag_3AsO_4 electrode is sensitive as it responds quickly with a response time of around 1–2 s. Furthermore, the electrode shows good stability and repeatability, with an average potential fluctuation of only 1.48 mV in 1 h.

The electrode was found to be far more sensitive to arsenate than interference ions, including sulfate, carbonate, acetate and nitrate, indicating the good specificity of the electrode and has a lifespan of more than 80 days.

The Ag_3AsO_4 electrode shows good recovery in water sample tests, which shows that it exhibits good accuracy and can be used in drinking water and aqueous environment testing.

Compared with previously reported electrodes in the literature, the Ag_3AsO_4 electrode in this work shows a low detection limit, fast response and long lifespan, indicating that it has the potential to be applied in field work.

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