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A Novel All-Solid-State Ion-Selective Electrode with Selenite-doped Polyaniline

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A novel all-solid-state selenite electrode with Ag and nano-Ag as a substrate and selenite-doped polyaniline as a sensitive membrane was fabricated by using electrochemical methods. Nano-Ag particles were electrodeposited on the surface of a cathode Ag wire in 0.1 M $AgNO_3$ standard solution with a 1.2 V amplitude, 50 Hz frequency and 30 s action time. The polyaniline layer was coated by chronoamperometry and doped with selenite in selenite solution by the same technique. Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) analysis proved the successful doping of selenite. The selenite electrode, which had excellent stability and repeatability, had an excellent Nernst linear response (slope -30.08 mV per decade, $R^2>0.99$) with a linear range of $5\times10^{-6}\sim 1\times10^{-1}$ M and detection limit of 1.627×10^{-6} M. The response time was less than 2 s, and the lifespan was more than 178 days. The electrode showed a high selectivity to selenite ions during the interference study. The recovery rates in the sample test were from 95~99%, indicating that the electrode can be applied in real sample measurements. Compared to previous work, this electrode is superior in terms of multiple properties.

Keywords: Ion-selective electrode; Selenite; selenite doped polyaniline; all-solid-state

1. INTRODUCTION

Selenium is commonly identified as an essential trace element for the human body. Selenium exists in the natural world in organic and inorganic form[1]. Organic selenium, which is more frequently found in biological systems, has high bioavailability[2]. Inorganic selenium exists in the form of selenite and selenate, which are both toxic and are not easily absorbed by the body. As high levels of selenium in the environment result in severe health and ecosystem threats[3], selenium is an important indicator of water safety, and the detection of selenium in water environments has attracted increasing interest in recent years[4]. Se(IV) is much more toxic than Se(VI)[5]. Selenite (SeO_3^{2-}) is a common and stable form present in soil and water bodies. Therefore, a reliable determination system for the selenite content in water is crucial.

The conventional methods for the detection of selenite include atomic absorption spectrophotometry (AAS)[6, 7], atomic fluorescence spectrophotometry (AFS)[5, 8], gas chromatography (GC)[9], high-performance liquid chromatography (HPLC)[10], and inductively coupled plasma-mass spectrometry (ICP-MS)[11-13]. Although these methods are accurate and have high selectivity, the instruments are expensive, and operation is complicated, with long testing times. Furthermore, these methods cannot achieve in situ monitoring.

Ion-selective electrodes (ISEs) are based on the potentiometric signal and give Nernst response to certain ions. ISEs have good performance in terms of response time, selectivity, linear range and lifespan[14] and have attracted researchers' attention[15]. The traditional ion-selective electrodes are glass-housed electrodes with a solution interface. This structure has limitations in terms of miniaturization and cannot endure high pressures or high/low temperatures. Correspondingly, all-solid-state electrodes, as another type of ISE, are preferred and have shown great improvements[15, 16]. The elimination of internal solution effectively reduces the impedance and volume of electrodes[17]. This makes it possible for different all-solid-state electrodes to be mounted together in a multiple-parameter chemical sensor for in situ monitoring.

There is some research based on selenite ion-selective electrodes. Cai and colleagues used 4,6-dibromopiaselenole as an active material, PVC as a membrane matrix and dibutyl phthalate as a plasticizer[18]. Zareh and others used $HgSeO_3$ or a mixture of $HgSeO_3$ and Hg_2Cl_2 as a sensitive membrane[19]. Solid salts of Ag_2Se and Cu_2S have also been developed for selenite ion-selective electrodes[20]. The 1,2-phenylenediamine selen complex PIS (piaselenol) has been applied as an active material with PVC or SR (silicon rubber) as a membrane matrix and DBF (dibutylphthalate) as a plasticizer[21]. Polymeric membrane electrodes (PMEs), modified carbon paste electrodes (MCPEs), and coated wire electrodes (CWEs), selenite ion-selective electrodes based on 5,10,15,20-tetrakis-(4-methoxyphenyl)-21H,23H-porphyrin-Co(II) (CoTMeOPP), have been reported by Ibrahim and others[4].

Polyaniline (PANI) is commonly used as a conductive polymer in solid-state ion-selective electrodes. In recent years, this compound has attracted considerable interest in the study of conducting polymer materials[22]. PANI features flexible mechanical properties, good conductivity, simple synthesis methods and anti-biofouling properties and shows good prospects in the field of electrochemical sensors [23, 24]. Two groups have used PANI as a conductive layer in ammonium and sulfate ion-selective electrodes[25, 26].

In this study, an all-solid-state electrode in the form of a Ag wire with nano-Ag particles and coated with H_2SeO_3-doped PANI has high selectivity for selenite. The linear range of this electrode is 5×10^{-6}~ 1×10^{-1} M with a detection limit of 1.627×10^{-6} M. The response time is less than 2 s, and the lifespan is more than 178 days. From the above, this electrode is also suitable to be applied in the long-term in situ monitoring of selenite ions in a freshwater environment.

2. EXPERIMENTAL

2.1 Reagents and apparatus

Selenious acid, sodium selenite, and sodium selenate were obtained from Xiya Reagent Company, Shandong, China. The 0.1 M $AgNO_3$ standard solution and 0.1 M HCl standard solution were obtained from Shenzhen Bolinda Technology Co., Ltd, China. Aniline hydrochloride was purchased from Aladdin. Sodium sulfate, sodium carbonate, sodium acetate trihydrate, sodium sulfite, sodium nitrate, trisodium phosphate anhydrous, and sodium silicate were obtained from Sinopharm Chemical Reagent Company, China. All reagents were analytical grade. Ag wire (99.9%, 0.6 mm in diameter) was obtained from Precious Materials Company of Changzhou, China.

The fabrication and calibration of electrodes were performed by using a CHI660E workstation (Chenhua, Shanghai, China). Electrochemical impedance spectroscopy (EIS) measurements of the electrode were collected by using a Parstat 4000 from AMETEK Company. The electrodeposition of nano-Ag particles was conducted by using a SG1020A function generator (Ruite Company, China) with a MBR1045 Schottky diode. A commercial Ag/AgCl electrode (CHI111, Chenhua, Shanghai, China) was used as the reference electrode. A platinum electrode (Leici Instrument Company, China) was utilized as the auxiliary electrode. Experiments were performed at ambient temperature.

2.2 Fabrication of the Selenite Electrode

For pre-treatment of the substrate, the Ag wire (40 mm long) was polished by chamois leather with 0.05 mm alumina powder. The wire was then ultrasonically cleaned sequentially by diluted hydrochloric acid and deionized water for 10 min.

The fabrication of the selenite electrode had three steps. First, the Ag wire was electrodeposited with nano-Ag particles by using a SG1020A function generator (Ruite Company, China) with a MBR1045 Schottky diode. A 0.1 M $AgNO_3$ standard solution was used as the electrolyte. The parameters included a 1.2 V amplitude, 50 Hz frequency, and 30 s action time.

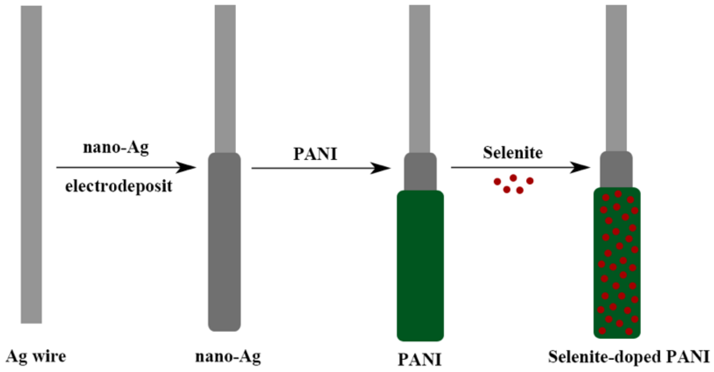

Figure 1. Schematic diagram of electrode fabrication steps

The nano-Ag particles were deposited on the surface of the cathode Ag wire. Then, the substrate was coated with a PANI layer (in 1.0 M aniline hydrochloride solution) with a three-electrode system (Ag/AgCl reference electrode, platinum-auxiliary electrode and working electrode) of CHI660E workstation using chronoamperometry. The potential was 0.6 V, and the time was 80 s. Finally, the substrate was electrodeposited with selenious acid (in 0.5 M selenious acid solution), forming a selenite-doped PANI layer using chronoamperometry with a 0.8 V potential for 400 s. Figure 1 shows the schematic diagram of the electrode fabrication steps.

2.3 SEM and EDS analysis of electrode

The PANI and selenite-doped PANI layer were analysed by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) for micromorphology observation and element composition analysis.

2.4 Potential measurements for calibration

The potential measurements of the selenite electrode were carried out by the open-circuit technique of the CHI660E workstation with a two-electrode system. The Ag/AgCl electrode served as a reference electrode, and the selenite electrode served as a work electrode. The sample interval was set at 0.1 s.

The calibration solution was a series of sodium selenite solutions from 1×10^{-7} to 1×10^{-1} M. The Na_2SeO_3 solution consisted of 1.7294 g Na_2SeO_3 dissolved to 100 mL with deionized water to obtain a 1×10^{-1} M Na_2SeO_3 solution. Na_2SeO_3 solutions of 1×10^{-2} M to 1×10^{-7} M were stepwise diluted from 1×10^{-1} M standard Na_2SeO_3 solution with deionized water. Na_2SeO_3 solutions of 5×10^{-2} M, 5×10^{-3} M, … 5×10^{-7} M were diluted from 1×10^{-1} M, 1×10^{-2} M, … 1×10^{-6} M Na_2SeO_3 solutions, respectively.

2.5 Interference study

Selectivity coefficients were estimated to analyse the interference of the electrode. The fixed interference method (FIM) was used to calculate selectivity coefficients.

$$k_{SeO_3^{2-},j}=\frac{a_x}{a_j^{2/z_j}}$$

where a_x is the detection limit of SeO_3^{2-} under fixed interference mixed with sodium selenite; and a_j and z_j are the concentration and charge, respectively, of the interfering ion j.

The interfering ions, SO_4^{2-}, CO_3^{2-}, CH_3COO^-, SO_3^{2-}, NO_3^-, SeO_4^{2-}, PO_4^{3-}, and SiO_3^{2-}, at concentrations of 10^{-2} mol/L were mixed into selenite ion solutions from 1×10^{-7} to 1×10^{-1} M to determine the response of the electrode.

2.6 Sample test

To test the accuracy and reliability of the selenite electrode, four samples of Nongfu spring water (Nongfu Springs Co., Ltd.) with the addition of selenite ions were prepared. The selenite electrode was used to measure the selenite concentrations of samples. A standard titration method[27] was used for comparison.

3. RESULTS AND DISCUSSION

3.1 SEM and EDS observation

Field emission scanning electron microscopy (SEM) was used to observe the PANI layer and the selenite-doped PANI layer, as shown in

Figure 2.

Figure 2(a)(b) shows the PANI layer with 2000 and 5000 times magnification. Under the scanning electron microscope, it can be seen that the PANI microparticles cross the surface of the silver wire in a plate-like structure. After doping with selenite (

Figure 2(c)(d)), the morphology changed greatly to yield smaller interspaces, forming a dense structure. This indicates the successful doping of selenite. The interspacing was reduced in the doping process, which enhanced the conductivity and sensitivity of the electrode[28]. This enabled the electrodes to have more stable performance and a faster response time.

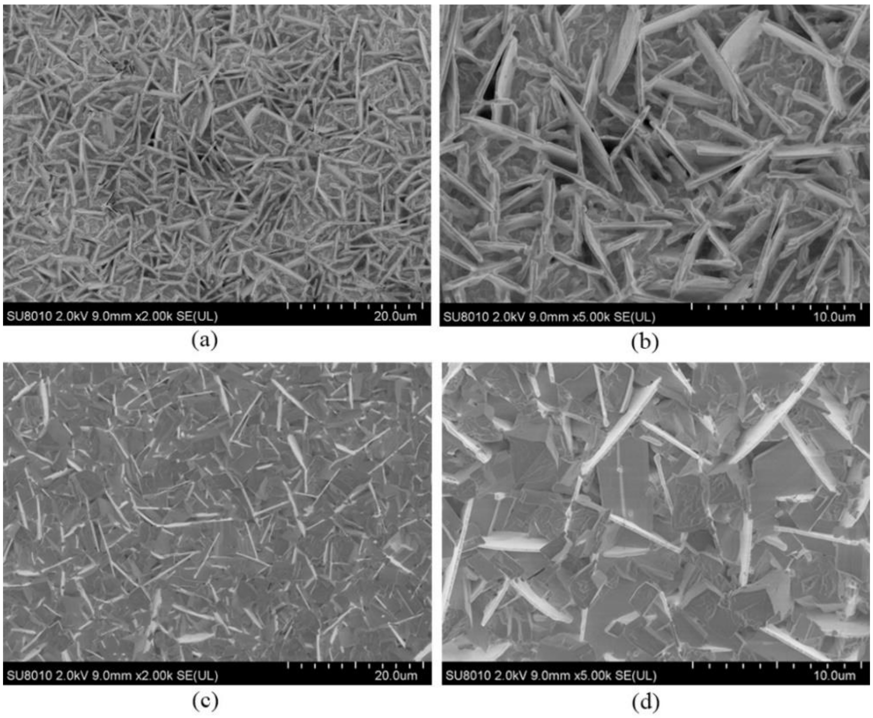

Figure 2. SEM images of the selenite electrode (a) PANI layer with magnification 2000 times; (b) PANI layer with magnification 5000 times; (c) selenite-doped PANI layer with magnification 2000 times; and (d) selenite-doped PANI film with magnification 5000 times

The elemental composition of the PANI and selenite-doped PANI layers were determined by energy-dispersive spectroscopy (EDS), and the results are shown in Table 1. The elements of the PANI coating were carbon, nitrogen, oxygen, chlorine and silver. Silver was the substrate with the highest content in the silver wire on the electrode. Carbon, nitrogen and oxygen were the main elements of PANI. As aniline hydrochloride also contains chlorine, when the substrate was coated with the PANI layer, a substantial amount of chloride ion was grafted onto the main chain of PANI (Figure 3(a)). After doping with selenite, the chloride ions were replaced by selenite ions. As can be seen, the chlorine content was reduced greatly with a large addition of elemental selenium and oxygen (Figure 3(b)). This also proves the successful doping of selenite.

Table 1. The elemental composition (weight%) of PANI and selenite-doped PANI layers by EDS

Element	Layer	
	PANI	Selenite-doped PANI
C	5.31	5.27
N	0.44	0.56
O	0.72	12.33
Cl	22.24	4.82
Ag	71.29	62.22
Se		14.79
Total:	100.00	100.00

3.2 Sensitive-membrane structure and response mechanism

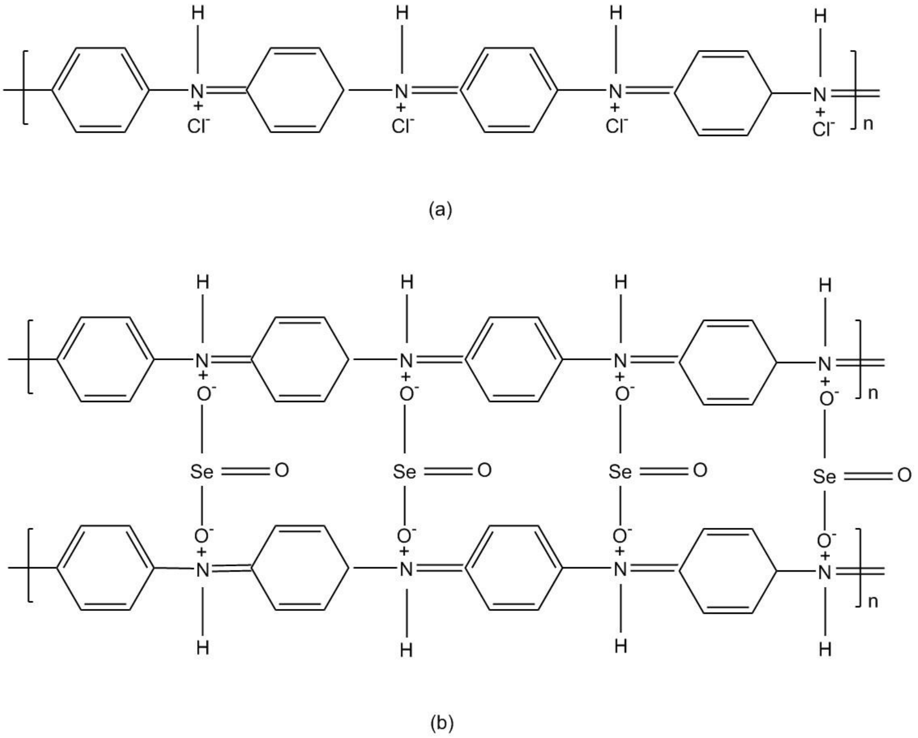

Figure 3. Molecular structure of chloride-doped PANI (a) and selenite-doped PANI (b)

Benzene and quinone are two coexisting structural units in the PANI structural chain[29]. As aniline hydrochloride contains hydrochloric acid, when the substrate was coated with a PANI layer in 1.0 M aniline hydrochloride solution, a large amount of chloride ion was grafted onto the main chain of PANI (Figure 3(a)). When the electrode was electroplated in selenite acid solution, the chloride ions were replaced by selenite ions. Selenite ion acts as a crosslinking agent in the PANI chain so that the PANI molecules were linked together to form a conductive channel (Figure 3(b)).

On the other hand, as there is no stable chemical bond formed between selenite ion and the main chain when the electrode contacts the solution containing selenite ion, the anion on the main chain will dissociate and bind with the main chain repeatedly, thus forming an electric potential signal. The intensity of this potential signal reflects the concentration of target ions. According to the membrane structure and response mechanism, the electrode has a selective response to selenite ions.

3.3 Electrochemical Impedance Spectroscopy (EIS) Studies

A large impedance of an electrode can cause potential measurement errors. The smaller the electrode impedance is, the more accurate the measurement. A small impedance of an electrode can reduce the interference of the noise signal, improve the accuracy of the sensor hardware circuit measurement and enhance the practical performance of the electrode[30]. The impedance of all-solid-state electrodes is determined by membrane composition.

To analyse the impedance of the selenite-doped PANI all-solid-state electrode, the electrochemical impedance spectra of the electrode were measured in 0.1 M sodium selenite solution with a Parstat 4000.

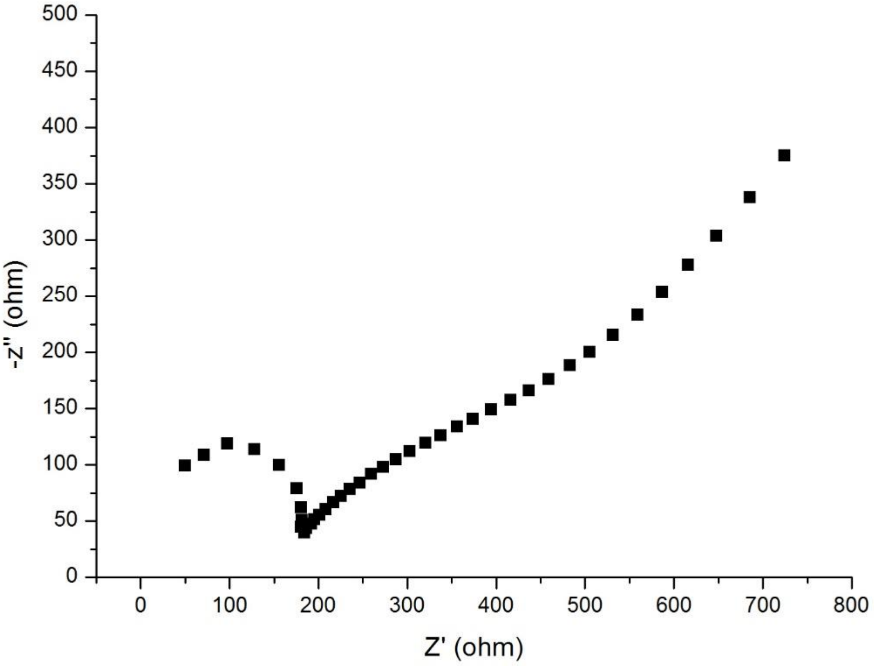

Figure 4. EIS of a Ag/nano-Ag/selenite-doped PANI electrode in 0.1 M sodium selenite solution with frequencies from 100-1000000 Hz and an amplitude of 10 mV.

The frequency range was set as 100 - 1000000 Hz, and the amplitude was set as 10 mV. Figure 4 consists of a semicircle curve and Warburg diffusion. From the EIS of the electrode (Figure 4), the projection of the semicircle part to the x-axis shows that the impedance of the electrode is only 184 Ω, which is far smaller than the impedance of glass electrodes with a liquid internal reference solution (approximately 10^{12} Ω[31]). The impedance of other all-solid-state electrodes is normally approximately 10^4 Ω[32], which is one hundred times that of this electrode. A low impedance, as an advantage of the selenite electrode in the present work, means better conductivity and a higher electrode measurement accuracy. As PANI is synthesized in situ on the surface of the substrate, there is no significant conduction barrier on the substrate. On the other hand, it can be seen that the plate-like structure of selenite is evenly distributed on the surface of the silver wire according to SEM (Figure 2). After being doped with selenite, interspacing was reduced, and the surface formed a dense structure. This is an important factor in reducing electrode impedance.

3.4 Detection limit and linear range

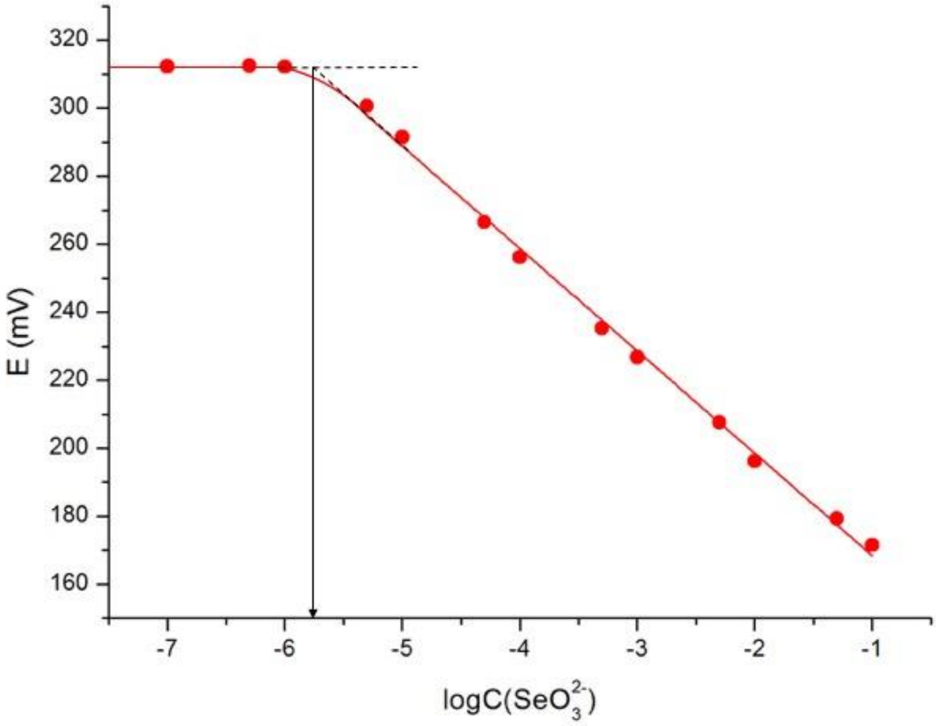

Figure 5. Detection limit and linear range of the selenite electrode tested in 1×10^{-7} M to 1×10^{-1} M Na_2SeO_3 solutions

The detection limit of the selenite electrode is the intersection between the extrapolation of the straight part and the tangent line of curve part[33]. The selenite electrode was calibrated in 1×10^{-7} M, 5×10^{-6} M, 1×10^{-6} M, 5×10^{-5} M, … 5×10^{-2} M, and 1×10^{-1} M Na_2SeO_3 solutions. The calibration graph of the selenite electrode is shown in Figure 5. The linear range of the selenite electrode was 5×10^{-}

^{6}~1×10^{-1} M with a fitting line *y*=-30.088*x*+138.33 and a correlation coefficient R^2=0.99692. The average slope of -30.08 was very close to the theoretical Nernst value (-29.5 mV per decade). The detection limit of the electrode was 1.627×10^{-6} M as seen in Figure 5. The selenite-doped PANI electrode shows better performance in terms of the detection limit and linear range compared with selenite electrodes in other works [19-21], whose linear concentration ranges were mainly approximately 1×10^{-5}~1×10^{-1} M and even smaller.

3.5 Response curve, repeatability and stability

The response curve demonstrates the response time, potential gradient change and response stability information of electrodes, which reflect the electrode properties. Figure 6 shows the response curve of two selenite-doped PANI electrodes in 10^{-5}~10^{-1} M sodium selenite solutions.

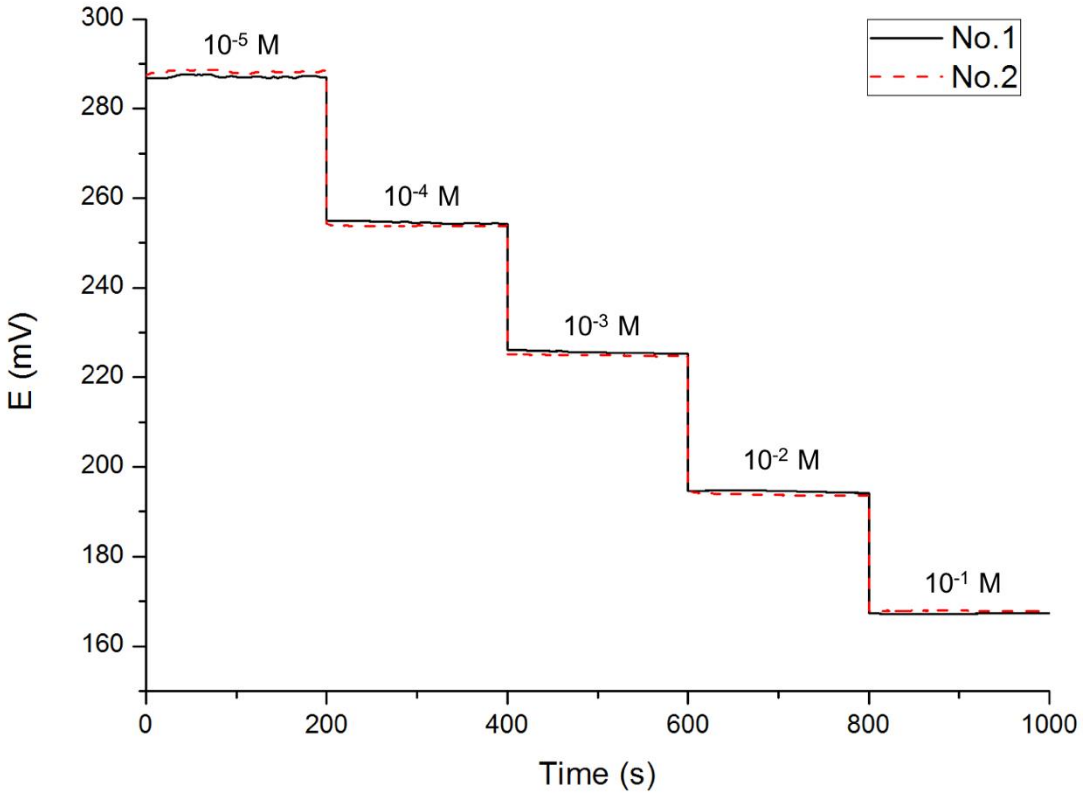

Figure 6. The response curve of two selenite-doped PANI electrodes in 10^{-5}~10^{-1} M sodium selenite solutions

The response was stable in the same concentration solution and changed steadily when the concentration changed. The electrode response time to achieve a stable signal was approximately 2 s. This value is much smaller than those reported for other all-solid-state electrodes[34-36], which normally have response times of more than 15 s or even several minutes. Previous research about selenite electrodes has also reported long response times, as seen in Table 5. The short response time of this electrode is attributed to the good conductivity of the membrane and the dense membrane structure. This performance will be especially useful for water monitoring, as the electrode can feed back correct values in a short time.

The absolute potential drift was 0.1~1.5 mV in 200 s in each solution. Two electrodes performed similarly, which indicates the repeatability and reproducibility of the electrodes.

To test the stability of the selenite electrode, it was monitored in 10^{-3} M sodium selenite solution continuously for 8 hours with a time interval of 0.8 s. The monitoring results can be seen in Figure 7. The highest and lowest potentials for the whole period were 228.7 mV and 227.3 mV, respectively. The potential fluctuation of the electrode was less than 1.4 mV in 8 hours, which fully demonstrates the stability of the electrode.

The repeatability of the selenite electrode was determined by alternately measuring the potential of the same electrode in 10^{-1} M and 10^{-4} M sodium selenite solutions four times. The results can be seen in Figure 8. The potential values in 10^{-4} M sodium selenite solution were 262.0 mV, 263.4 mV, 263.8 mV, and 264.3 mV, and the values were 164.1 mV, 164.8 mV, 165.1 mV, and 164.2 mV in 10^{-1} M sodium selenite solution. This illustrates that the selenite electrode performed well in terms of repeatability.

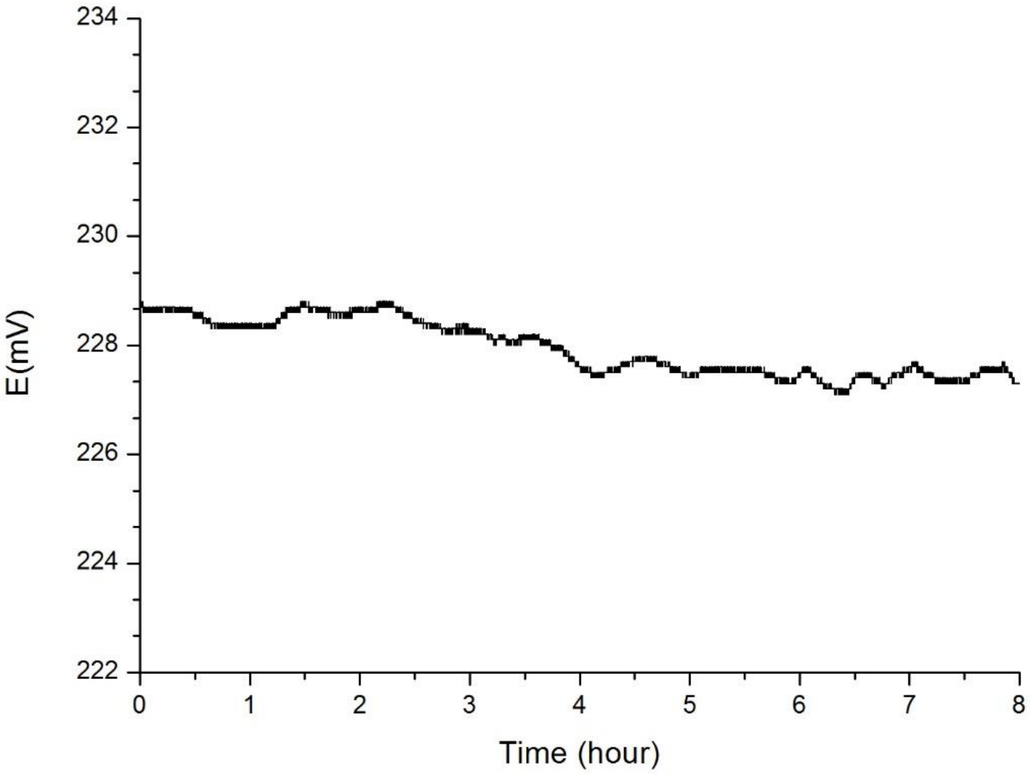

Figure 7. Continuous monitoring in 10^{-3} M sodium selenite solution

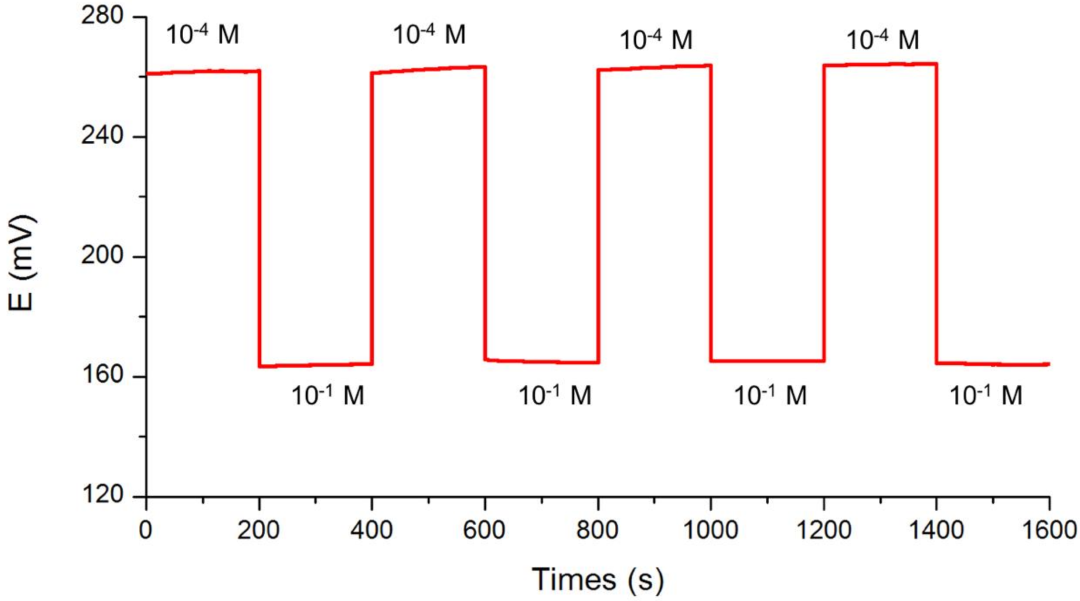

Figure 8. Repeatability performance of selenite electrode in 10^{-4} M and 10^{-1} M sodium selenite solution

3.6 Selectivity

The selectivity coefficients of selenite-doped PANI electrodes based on the fixed interference method (FIM) were compared with the results of previous research (Table 2). The interfering ions included SO_4^{2-}, CO_3^{2-}, CH_3COO^-, SO_3^{2-}, NO_3^-, SeO_4^{2-}, PO_4^{3-}, and SiO_3^{2-}. Table 2 indicates that the selenite-doped PANI electrodes had good anti-interference ability for the interfering ions. The interference coefficient was between 1.86×10^{-4} and 4.61×10^{-2}, which means that the response of the electrode to selenite is 20-5000 times more sensitive than that to interfering ions. Compared to other works, the selenite-doped PANI electrode showed close selectivity coefficient values for SO_4^{2-}, CH_3COO^-, SO_3^{2-} and NO_3^- and higher selectivity for CO_3^{2}, SeO_4^{2-} and PO_4^{3-}.

Table 2. Comparison of the selectivity coefficients of the selenite-doped PANI electrode and other selenite electrodes.

Interfering ion *i*	Selectivity coefficients k_{ij}				
	This work	[19]	[4]	[21]	[18]
SO_4^{2-}	4.19×10^{-4}	5.5×10^{-3}	2.0×10^{-4}	-2.7×10^{-5}	4.6×10^{-3}
CO_3^{2-}	1.0×10^{-3}	4.6×10^{-3}	-	-	-
CH_3COO^-	4.61×10^{-2}	5.6×10^{-3}	-	-	6.1×10^{-3}
SO_3^{2-}	5.63×10^{-3}	3.6×10^{-3}	2.5×10^{-4}	-2.5×10^{-4}	-
NO_3^-	2.79×10^{-2}	1.1	3.2×10^{-3}	-	5.6×10^{-3}
SeO_4^{2-}	1.88×10^{-3}	-	1×10^{-2}	-	-
PO_4^{3-}	1.86×10^{-4}	2.1×10^{-3}	-	1.5×10^{-2}	5.1×10^{-3}

3.7 Lifespan

Electrode lifespan refers to the long-term working ability of ion-selective electrode satisfying the Nernst equation at room temperature. In this study, two selenite-doped electrodes were stored in 1% Na_2SeO_3 solution for 178 days and calibrated regularly in standard sodium selenite solution.

Table 3 shows the slopes and the correlation coefficients R^2 of the electrodes. The slope was stable between 28-31 with $R^2>0.99$, which indicates that the lifespan of selenite electrodes can reach 178 days.

In other research on selenite electrodes as seen in Table 5, the lifespan is normally approximately 1 week, which indicates limited detecting times and testing intervals. The selenite-doped PANI electrode in this work clearly overcame this limitation. Other all-solid-state ion-selective electrodes that detect ions of SO_4^{2-} and CO_3^{2-} and pH have different lifespans, from 10 days to several months[26, 37, 38]. This electrode can be used for approximately 6 months, which is a long lifespan among ion-selective electrodes.

Table 3. Calibration result of two selenite electrodes in 178 days

Days	No. 1		No. 2	
	Slope	correlation coefficient (R^2)	Slope	correlation coefficient (R^2)
1	-30.13	0.99792	-29.9	0.99875
3	-29.46	0.99652	-30.41	0.99697
8	-29.36	0.99929	-30.17	0.99863
21	-30.02	0.99711	-28.6	0.99801
36	-29.62	0.99854	-29.79	0.99711
50	-29.76	0.999	-28.94	0.9995
68	-29.54	0.99858	-31.22	0.99601
83	-28.56	0.99193	-29.75	0.99933
101	-29.41	0.99697	-30.69	0.99654
118	-28.01	0.99849	-30.23	0.99747
135	-30.06	0.99799	-31.29	0.99878
157	-30.08	0.9994	-29.82	0.99777
178	-29.61	0.9981	-29.3	0.99898

3.8 Sample test

Table 4. Sample test results by electrode and titration method

Sample number	Titration (M)	Selenite-doped PANI electrode (M)		Average recovery (%)
		No. 1	No. 2	
1	4.03×10^{-2}	3.98×10^{-2}	3.97×10^{-2}	98.68
2	2.70×10^{-3}	2.59×10^{-3}	2.61×10^{-3}	96.26
3	8.68×10^{-4}	8.30×10^{-4}	8.38×10^{-4}	96.14
4	7.58×10^{-5}	7.19×10^{-5}	7.23×10^{-5}	95.16

The selenite concentrations of four samples were measured by two selenite-doped PANI electrodes. The results were compared with the results of the standard titration method[27], as seen in

Table 4. The average recovery rates were from 95~99%, indicating that the electrode can be applied in real sample measurements.

3.9 Summary of electrode properties compared with related research

The properties of this electrode are compared with those obtained in previous research in Table 5. The electrode is superior to those in previous research in terms of detection limit, response time and lifespan. This enables the electrode to have a wider detection range, a faster response, and a longer detection period in applications.

Table 5. Comparison of electrode properties between the selenite-doped PANI electrode and previous research

Sensitive Membrane Material	Slope	Linear concentration range	Detection Limit	Response time	Lifespan
4,6-dibromopiaselenole[18]	23.6	3.2×10^{-6}~ 1×10^{-1} M	1.0×10^{-6}	<120 s	7 days
$HgSeO_3$ or a mixture of $HgSeO_3$ and Hg_2Cl_2[19]	29.5	6×10^{-5}~ 1×10^{-1} M	---	---	8 days
Ag_2Se and Cu_2S[20]	28	1×10^{-5}~ 1×10^{-2} M	---	>1 min	---
1,2-phenylenediamine selen complex PIS[21]	21	1×10^{-5}~ 1×10^{-1} M	---	>3 min	2 months
5,10,15,20-tetrakis-(4-methoxyphenyl)-21H,23H-porphyrin-Co(II) (CoTMeOPP)[4]	57	5.5×10^{-5}~ 1.1×10^{-1} M	3.4×10^{-5}	5-15 s	6 days
H_2SeO_3-doped PANI (this work)	30.08	5×10^{-6}~ 1×10^{-1} M	1.627×10^{-6}	<2 s	178 days

4. CONCLUSION

A new ion-selective selenite electrode with selenite-doped PANI as a sensitive membrane used Ag wire as a substrate. Nano-Ag particles were electrodeposited on the surface of Ag wire in 0.1 M $AgNO_3$ standard solution Then, the substrate was coated with a PANI layer using chronoamperometry with a potential of 0.6 V and time of 80 s. Finally, selenite was doped using chronoamperometry with a 0.8 V potential for 400 s. According to analysis by SEM, EDS and EIS, selenite was successfully doped and distinctly reduced the interspacing of PANI layers. The membrane had a dense structure with high conductivity.

The linear range of the selenite electrode was 5×10^{-6}~1×10^{-1} M with a fitting line $y=-30.088x+138.33$ ($R^2=0.99692$). The slope, -30.08, was very close to theoretical Nernst value (-29.5), and the detection limit of the electrode as 1.627×10^{-6} M. From the response curve, the response time of the electrodes was approximately 2 s to achieve a stable signal with an absolute potential drift of 0.1~1.5 mV in 200 s in each solution. In the stability testing, the potential fluctuation in the electrode was less than 1.4 mV in 8 hours. Meanwhile, the repeatability of the selenite electrode was determined by alternately measuring the potential of the same electrode in 10^{-1} M and 10^{-4} M sodium selenite solutions. The potential values were similar at the same concentration.

The electrode had good anti-interference ability against interfering ions and a long lifespan (more than 178 days). The recovery rates of the sample test were from 95~99%, indicating that the electrode can be applied in real sample measurements.

Compared with previous research, this electrode is superior in detection limit, response time and lifespan, which enables the electrode to have a wider detection range, a faster response, and a longer detection period in applications.

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