

Gold Nanoparticles/Ionophore-Modified Screen-Printed Electrode for Detection of Pb(II) in River Water Using Linear Sweep Anodic Stripping Voltammetry

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In this study, a screen-printed electrode (SPE) was modified with gold nanoparticles (AuNPs) and an ionophore (AuNPs/ionophore/SPE) to provide an electrochemical sensor for the sensitive and selective determination of lead ions using linear sweep anodic stripping voltammetry (LSASV). The effect of electrochemical parameters, including supporting electrolyte, pH, deposition potential, deposition time, and scan rate, on the sensitivity of the sensor for the detection of Pb²⁺ was investigated. Under optimized conditions [deposition time 240 s, deposition potential -1.2 V, Tris-HCl (0.1 mol L^{-1} , pH 2), and scan rate of 0.1 Vs^{-1}], the linear sweep voltammogram at -0.5 V was related to the concentration of Pb²⁺ in the range of 0.4 to $20 \text{ } \mu\text{g mL}^{-1}$ Pb²⁺ with a limit of detection (LOD) of $0.082 \text{ } \mu\text{g mL}^{-1}$. The method was used to determine Pb²⁺ ions in river and tap water with satisfactory results. The modified electrode displayed benefits such as high sensitivity and selectivity, long time stability, easy preparation, and wide linear range.

1. Introduction

Heavy metals are very toxic in nature. They tend to bioaccumulate and bioconcentrate in the food chain and result in many health-related issues such as cardiac problems, digestive difficulties, and neurological and mental problems.^(1–3) They are also carcinogenic, as they interact with DNA and result in malignant tumors.^(4,5) Among all the heavy metals studied, lead ion (Pb²⁺) is of particular concern, as its compounds can be highly toxic. Metallic lead is widely used in solders, cable sheaths, storage batteries, and as a petrol additive.^(6,7) It moves in the environmental biogeochemical cycle and is deposited on surfaces and in ground waters.⁽⁶⁾

Several different techniques are employed for the detection of Pb²⁺, including spectral^(8–11) and electrochemical techniques.^(12–16) However, the conventionally used spectral techniques require a long time and are cumbersome and are also not well suited for the *in situ* measurements of metals owing to the use of complex and unwieldy instruments. In contrast, electrochemical techniques are very attractive, as the required equipment is cost-effective, portable, and easy to operate. Anodic stripping voltammetry (ASV) is considered one of the most sensitive electroanalytical techniques for the determination of trace quantities of heavy metals.⁽¹⁷⁾ To enhance the sensitivity and selectivity of the electrochemical measurement of lead ions, chemically modified electrodes

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such as bismuth,^(18,19) gold nanoparticles,^(20,21) titanium dioxide/zirconium dioxide,⁽²²⁾ SiO₂–Al₂O₃ mixed oxide,⁽²³⁾ and silica⁽²⁴⁾ have received increasing attention in the past decades. Table 1 summarizes some electrochemical methods that have been developed for Pb²⁺ determination. As has been shown, most previous sensors have high sensitivity but suffer from low selectivity for the determination of the Pb²⁺ ion in complex matrixes. In none of the previous modified electrodes has the use of combined gold nanoparticles with a lead ionophore as modifier on screen-printed electrodes (SPEs) for the detection of Pb²⁺ ions been described.

SPE has gained popularity as it has the potential to act as an attractive alternative to the traditionally used electrodes for developing analytical methods that can enable instant ‘in situ’ analysis. SPE is also favoured due to cost-effectiveness, ease of handling, easy sample preparation, no need for surface cleaning, small memory effects, and reliability of measurements without compromising selectivity and sensitivity of detection.⁽²⁵⁾ Nanomaterials are an attractive choice for the development of the SPEs, as they can improve the sensitivity of electrodes for a particular species and also enhance sensor performance. The size, chirality, and composition of the nanomaterials are responsible for their use in many applications. Hence, incorporating nanomaterials with high surface area and conductivity on SPEs to improve electrochemical signals is highly interesting for the sensitive detection of pollutants in the environment. It should also be noted that modifying the SPE with a surface plasmon resonance material such as gold nanoparticles improves detection limits.⁽²⁶⁾

Ionophores, or ion carriers, can be described as macrocyclic molecules containing well-defined cavities. They can extract specific ions present in aqueous solution into an immiscible hydrophobic phase in which the ions would usually not be soluble.^(27,28) Ionophores are very popular for use in the formation of ion-selective polymeric membrane sensors that demonstrate a near-Nernstian response to metal ions. These sensors achieve their potentiometric selectivity by the complexation specificity of their carrier molecules along with the relationship between the ion sizes and the dimension of the ligand sites.⁽²⁹⁾ Although the ionophores show better selectivity towards particular metal ions, their use in voltammetric analysis as compared with potentiometric analysis is limited, probably due to the nonconductive properties of the ionophores.^(30–32)

The aim of this study was to combine the unique properties of AuNPs (i.e., enlarged active surface area and strong adsorptive capability) with the specific complexing ability of an ionophore and SPE to fabricate a selective and sensitive electrochemical sensor for the determination of trace

Table 1
Comparison of various modified electrodes for the detection of Pb²⁺.

Electrode	Method	Linear range ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	Ref.
Nafion/Bi/NMC/GCE	DPASV	0.5–100	0.05	(13)
Nafion/CNTs/ionophore/GCE	SWASV	0.21–6.2	0.21	(37)
Bi/GR/IL-SPE	SWASV	1.0–80.0	0.10	(14)
NPs/SPGE	CV, SWASV	20–200	2.2	(38)
MWNT/Nafion/GCE	DPASV	2.84–213	0.17	(39)
BiO/SPE	SWASV	20–100	2.3	(16)
L-Aspartic acid/L-cysteine/AuNPs microelectrode	SWV	5–2000	1.0	(15)
AuNPs/ionophore/SPE	LSV	$4 \times 10^2 - 2 \times 10^4$	82	This work

NMC: nitrogen-doped microporous carbon

IL-SPE: ionic liquid-doped screen-printed electrode

SPGE: gold screen-printed electrode

quantities of Pb^{2+} ions in natural water. To maintain the neutral environment for cation extraction and provide for the stability of the modifying layer, Nafion, a sulfonated cation-exchange polymer, was used as the conductive membrane matrix in which AuNPs and ionophores can be strongly bonded to the working electrode surface.

2. Materials and Methods

2.1 Chemicals

All chemicals used were of analytical reagent grade. Tert-butylcalix[4]arene-tetrakis(*N,N*-dimethylthioacetamide) was donated by the Chemical Faculty, Gdansk University of Technology in Poland as lead ionophore (IV).⁽³³⁾ Nafion (5% w/w solution in a mixture of water and aliphatic alcohols), *N,N*-dimethylformamide, sodium citrate di-hydrate, and chloroauric acid (HAuCl_4) were purchased from Sigma (Switzerland). The stock solutions of Pb^{2+} were prepared by diluting $\text{Pb}(\text{NO}_3)_2$ standard certified from Fluka (Switzerland), tris hydroxymethylamino methane hydrochloride (Tris-HCl) was from Fisher Scientific (UK) and was used as the supporting electrolyte for Pb^{2+} measurements, NaOH was from Merck (Germany), and HCl was from R&M Chemicals. NaOH and HCl were used to alter the pH of Tris-HCl. Deionized water was used throughout the experiments.

2.2 Instrumentation

Linear sweep voltammetry was carried out using an automated handheld power-driven PalmSens electrochemical analyser (PalmSens BV, The Netherlands). This portable analyser was attached to a computer. The entire diagnostic process, which includes the use of a hot plate magnetic stirrer for the mixing of the samples, was managed by the PalmSens PC software. The SPE for this study comes with a carbon working electrode strip, a carbon auxiliary electrode strip, and a silver reference electrode strip embossed on a plastic substrate. Field emission scanning electron microscopy (FESEM) together with energy dispersive spectroscopy (EDS), Jeol JSM 7600F, was used to ascertain the morphology of the electrode's surface, while a Hitachi H-7100 transmission electron microscope (TEM) was used to record the TEM image. An FT-IR (Perkin Elmer 100 series spectrophotometer) was used to characterize the modified SPE. The validation of the proposed sensor for Pb^{2+} was carried out by inductively coupled plasma mass spectrometry (ICP-MS).

2.3 Preparation of modified electrode

The modified surface of the electrochemical sensor (AuNPs/ionophore/SPE) was fabricated as follows. A AuNP solution was prepared by the chemical reduction of HAuCl_4 using sodium citrate. Briefly, 40 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was dissolved in 100 mL of deionized water, the resultant light yellow solution was heated to boiling with vigorous stirring, and then 10 ml of 38.8 mM sodium citrate was added. The colour of the solution changed from yellow to dark red. The solution was preserved under these conditions for 15 min. Then the heater was turned off and vigorous stirring was continued for an additional 15 min. Then 0.5 mL of the original 5% (w/w) nafion solution was mixed with 0.5% w/w *N,N*-dimethylformamide (DMF). Then 1.05 mg of lead ionophore was

added into 5 mL of this solution followed by 10 mL of the AuNP solution. The AuNPs/ionophore solution was sonicated for 20–30 min. Finally, 5 μL of the AuNPs/ionophore solution was drop-cast onto the working electrode surface and permitted to dry at room temperature.

2.4 Voltammetry for the determination of Pb^{2+}

The determination of Pb^{2+} by linear sweep voltammetry was carried out in a 10 mL solution containing Pb^{2+} and Tris-HCl as the supporting electrolyte (0.1 mol L^{-1}). The analysis of the solution during the mixing process was performed by applying a deposition potential of -1.20 V to the AuNPs/ionophore-modified electrode while stirring for 240 s. Following an equilibration period of 5 s, the linear sweep voltammogram was recorded from -1.5 to 1.0 V at a scan rate of 0.1 Vs^{-1} . The current was gauged within the potential range of -0.50 to -0.70 V and registered as the analytical signal for the detection of Pb^{2+} .

3. Results and Discussion

3.1 Characterization of modified electrode

Before and after modification with AuNPs, the surface morphology and elemental make-up of the SPE were comprehensively examined using FESEM to verify the bonding of AuNPs on the surface of the working electrode. The FESEM images of unmodified SPE and modified AuNPs/SPE are shown in Figs. 1(a) and 1(b), respectively. These images clearly reveal the realization of nanoparticle bonding on the surface of the working SPE. The obvious presence of white deposition

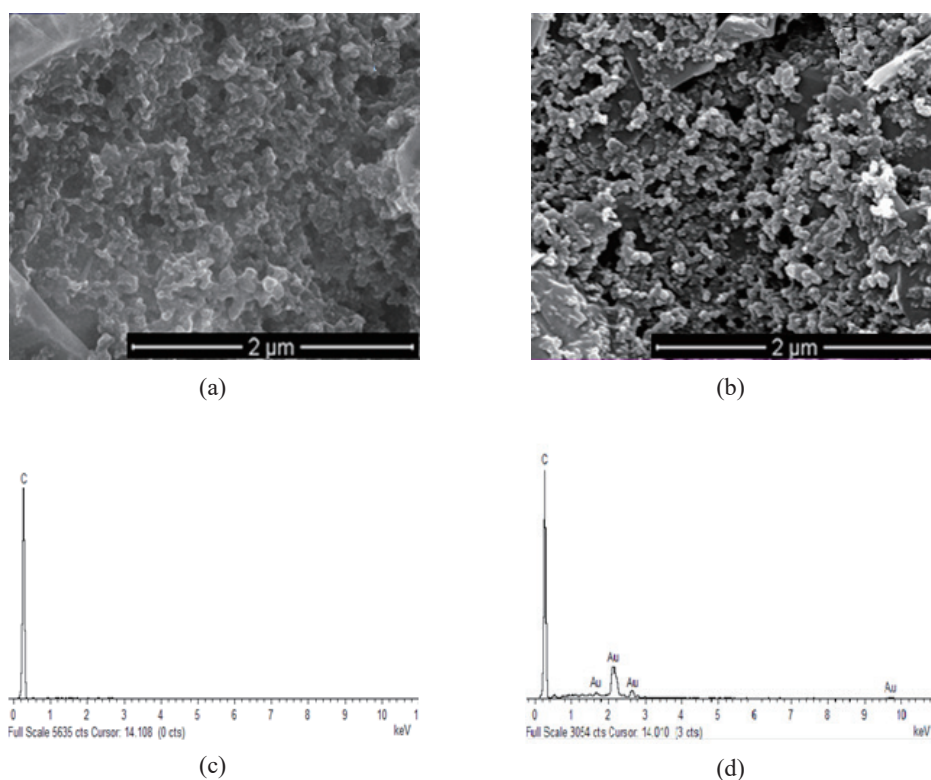


Fig. 1. (a) FESEM image of unmodified SPE, (b) FESEM image of AuNPs/ionophore-modified SPE, (c) EDX image of unmodified SPE, and (d) EDX image of AuNPs/ionophore-modified SPE.

on the modified carbon-based SPE surface indicates the accumulation of AuNPs. The distribution of these AuNPs, which are believed to have nanoscale dimensions, was extensive. Figure 1 also shows the EDX spectral images of unmodified SPE [Fig. 1(c)] and AuNPs/SPE [Fig. 1(d)]. As can be seen, a carbon peak (c) is present on unmodified SPE, while C and Au peaks are present on AuNPs-modified SPE, indicating the successful deposition of AuNPs on SPE.

TEM was employed to study the particle size and shape of AuNPs [Fig. 2(a)]. The distribution plot [Fig. 2(b)] shows that the particles are almost spherical in shape with a size distribution from 9.5 to 17.50 nm as has also been reported by previous researchers.^(34,35)

The SPE modified with the AuNPs/ionophore was also characterized by Fourier transform infrared spectroscopy (FTIR). As shown in Fig. 2(c), FTIR spectra showed medium or strong bands at 3579, 3741, 1530, and 924.18 cm^{-1} , corresponding to the N–H bonding from the thioamide group, and bands at 2711 and 3579 cm^{-1} , which are attributed to the O–H group. The peak at wavenumber 1303 cm^{-1} is assigned to the stretching vibrations of C–O, whereas the two peaks at 1698 and 1793 cm^{-1} are attributed to C=O. The bands at 568 and 406 cm^{-1} are attributed to C–C aromatic and C–N–C bending vibrations, respectively, whereas the band at 1102 cm^{-1} is due to C=S stretching vibrations from the thioamide group.

3.2 Initial investigation on the electrochemical determination of Pb^{2+}

The linear sweep voltammograms (LSVs) for the unmodified SPE, SPE modified with AuNPs, and SPE modified with both AuNPs and ionophore are displayed in Fig. 3. As can be seen, while the LSV of a solution containing Pb^{2+} exhibited a sharp oxidation peak at the unmodified SPE,

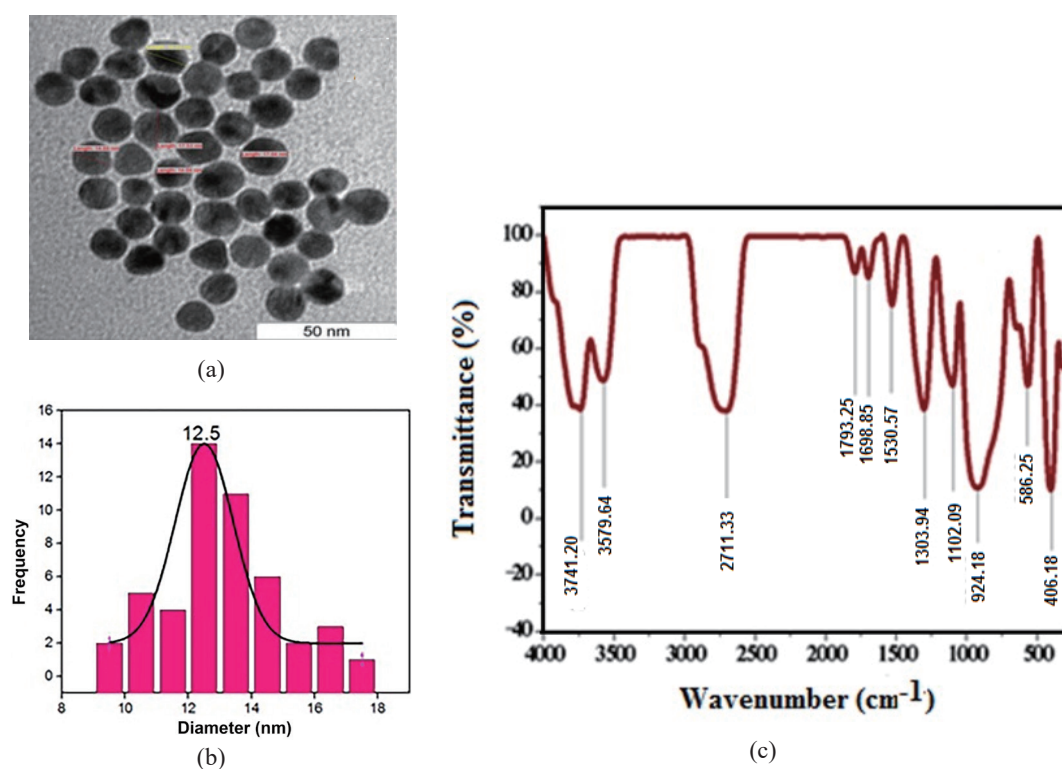


Fig. 2. (Color online) (a) TEM image of the surface of SPE/AuNPs, (b) distribution curve for 48 nanoparticles, and (c) FTIR spectrum of AuNPs/ionophore/SPE.

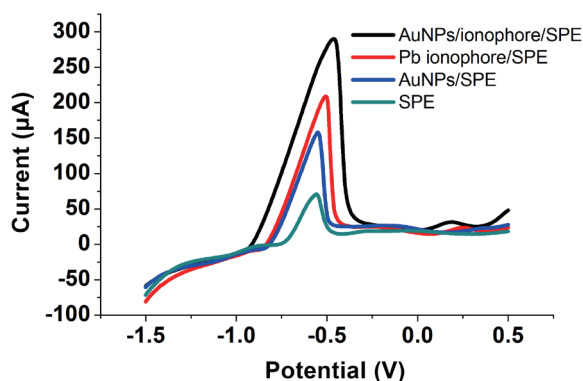


Fig. 3. (Color online) LSVs for $10 \mu\text{g mL}^{-1} \text{Pb}^{2+}$ on the surface of SPE, SPE/AuNPs, and AuNPs/ionophore/SPE at 0.1 M Tris-HCl concentration; deposition potential, -1.2 V ; deposition time, 240 s, and potential scanning in the positive direction from -1.5 to 1.0 V vs Ag/AgCl at a scan rate 0.1 Vs^{-1} .

the LSV at the SPE modified with AuNPs demonstrated a more pronounced peak current. The capacity of the lead ionophore and AuNPs for forming a stable complex with Pb^{2+} ions paved the way towards the development of a sizeable stripping peak at the SPE modified with AuNPs/ionophore. Additionally, the presence of AuNPs in the ionophore raises the accumulation capacity of Pb^{2+} on the surface of the electrode. This is attributed to the fact that AuNPs offer a greater surface area with additional active locations for Pb^{2+} build up on the AuNPs modified electrode. In other words, the elevated build-up of Pb^{2+} ions from the bulk solution to the surface of the electrode leads to an enhancement of the Pb^{2+} detection capability.

3.3 Optimization of parameters

To ascertain the best supporting electrolyte for realizing a superior Pb^{2+} sensitivity level, three dissimilar supporting electrolytes (Tris-HCl, HCl, and KCl) at 0.1 mol L^{-1} were examined. Among the three, the Tris-HCl solution was identified as the one with a superior peak current and the most distinct peak outline. As such, this solution was deemed the best for use in all the following investigations in this area.^(20,36)

To obtain optimal electrochemical sensitivity for Pb^{2+} ions, the effect of the pH of the 0.1 M Tris-HCl supporting electrolyte was studied using AuNPs/ionophore/SPE in the pH range of 2.0 to 8.0. Figure 4(a) shows that the highest peak current occurred at an acidic pH while the sensitivity decreased in alkali media, which may be caused by the formation of metal hydroxides and the precipitation of Pb^{2+} . Consequently, a pH of 2.0 of Tris-HCl (0.1 mol L^{-1}) was chosen as the optimum working pH.

The effect of deposition potential on the reduction of Pb^{2+} ions was studied in the range of -0.9 to -1.5 V , and the result is illustrated in Fig. 4(b). The peak current was raised significantly in the range of -0.9 to -1.2 V owing to the complete reduction of Pb^{2+} during the deposition step. Conversely, at deposition potentials more negative than -1.2 V , the peak current decreased gradually due to the evolution gas of hydrogen. Therefore, a deposition potential of -1.2 V was chosen as the optimum potential for the deposition step.

Deposition time is a vital parameter as it can significantly affect the level of sensitivity during

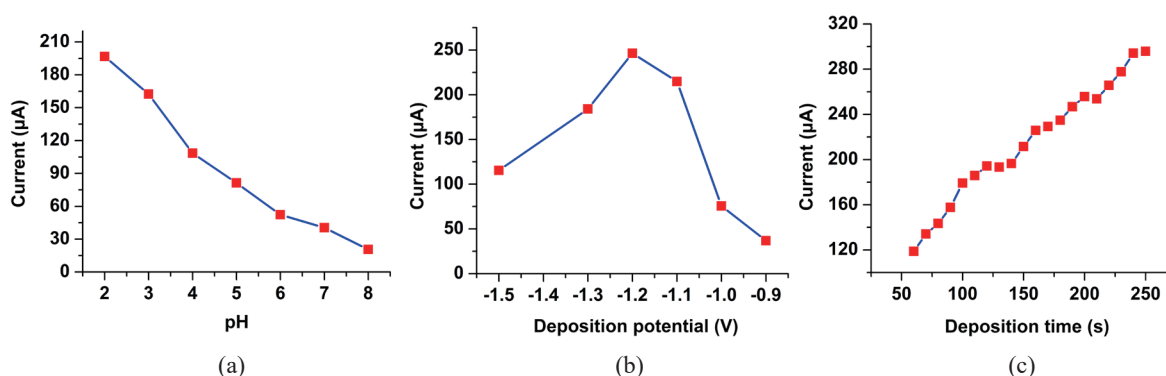
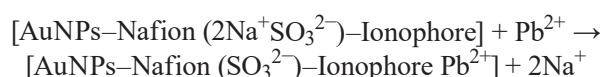


Fig. 4. (Color online) Effect of (a) pH of Tris-HCl, (b) deposition potential, and (c) deposition time on the peak currents of $10 \mu\text{g mL}^{-1} \text{Pb}^{2+}$ at the AuNPs/ionophore/SPE in 0.1 M Tris-HCl buffer.

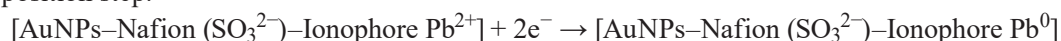
stripping analysis owing to the stirring of the solution during the deposition phase and mass transfer escalations. Any increase in the deposition time causes a rise in the build-up of the analyte on the electrode surface. This circumstance results in an elevation of the peak current. Accordingly, deposition was carried out over the range of 60 to 250 s. The peak current was increased steadily with increases in the deposition time up to 240 s. However, when the deposition time was more than 240 s, the peak current leveled off due to saturation at the electrode surface.⁽¹²⁾ This is shown in Fig. 4(c). Therefore, a deposition time of 240 s was used as the optimal parameter for the deposition of Pb^{2+} ions.

The chemically modified electrode used here operates by accumulating Pb^{2+} from a dilute solution on the modified electrode to give a higher concentration of lead ions at the electrode surface. The chemical reaction of the modified electrode may be written schematically as follows. Figure 5 shows a schematic diagram of the electrochemical sensor.

Accumulation step:



Deposition step:



3.4 Performance of the electrochemical sensor for determination of Pb(II)

The Pb^{2+} peak current was observed to be linear in the concentration range from 0.4 to $20 \mu\text{g mL}^{-1}$ under the most favourable circumstances. The optimum conditions include a deposition potential of -1.2 V , a deposition time of 240 s, and a scan rate of 0.1 Vs^{-1} in 0.1 M with Tris-HCl as the supporting electrolyte. Figure 6 shows a calibration curve using the equation $Y = 25.997C_{\text{Pb}^{2+}} + 42.960$ ($R^2 = 0.99$). The limit of detection (LOD) was calculated as $82 \mu\text{g L}^{-1}$. As shown in Table 1, the proposed sensor (AuNPs/ionophore/SPE) has a wide linear calibration range that is comparable to that of sensors in previous reports in terms of its simplicity, selectivity, stability, and analysis time.

The repeatability and reproducibility of the AuNPs/ionophore/SPE electrode was studied at $10 \text{ mg mL}^{-1} \text{Pb}^{2+}$ with relative standard deviations of 8.54% ($n = 7$) and 9.45% ($n = 6$ new electrodes). The results revealed that the AuNPs/ionophore/SPE modified electrode has reasonable repeatability

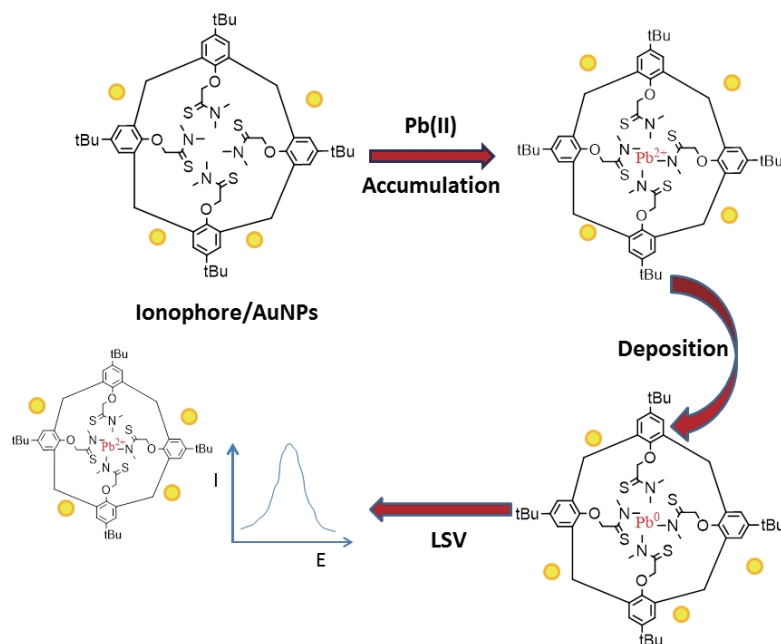


Fig. 5. (Color online) Schematic diagram of the electrochemical sensor sensitive to Pb²⁺.

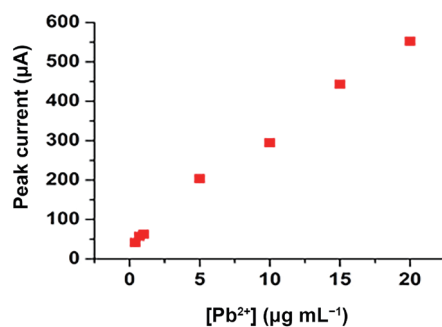


Fig. 6. (Color online) Current vs concentration of Pb²⁺ in range of 0.4–20 µg mL⁻¹ under optimum conditions (0.1 mol L⁻¹; pH 2 Tris-HCl buffer; deposition potential, -1.2 V; deposition time 240 s).

and reproducibility. The current response at the modified electrode showed no significant change for up to 9 days, indicating that the detection system has high stability.

3.5 Interference study

An attractive feature of an analytical procedure is its relative freedom from interferences. The selectivity of the proposed sensor for the analysis of Pb²⁺ was determined by studying under optimum conditions the effect of some ions (Fe³⁺, Mg²⁺, Cu²⁺, SO₃²⁻, and SO₄²⁻) that often accompany Pb²⁺ in natural water using LSV.

In the study of the selectivity of a fabricated sensor towards Pb(II) detection, the tolerance limit was defined as the concentration of interfering ions in the presence of Pb(II), which provide a ±10% deviation on the Pb(II) signal. From the results displayed in Table 2, we suggest that the impact of these ions on the detection of Pb²⁺ was negligible.

Linear sweep scans were conducted for 1 mg L^{-1} of Pb^{2+} in the presence of 1 mg mL^{-1} Hg^{2+} and Cd^{2+} ions for the purpose of ensuring the efficiency of this sensor (AuNPs/ionophore/SPE). These scans also served to facilitate the investigation of the selective function performed by the lead ionophore as far as the detection of Pb^{2+} is concerned. As can be seen in Fig. 7(a), testing with an unmodified SPE resulted in the appearance of two peaks: one for Pb^{2+} and the other for Hg^{2+} . On the other hand, analysis with AuNPs/ionophore/SPE led to the appearance of a single peak for Pb^{2+} . In a similar fashion in Fig. 7(b), the voltammogram for Pb^{2+} in the presence of Cd^{2+} shows two peaks for Cd^{2+} and Pb^{2+} with the unmodified SPE, while AuNPs/ionophore/SPE displays only one peak for Pb^{2+} . This indicates that the presence of the lead ionophore can successfully increase the selectivity of the modified electrode due to the selective transportation of Pb^{2+} ions from the solution to the altered layer by specific complexation with the lead ionophore.

Hence, it can be stated that the AuNPs/ionophore/SPE sensor is exceedingly selective and sensitive towards Pb^{2+} detection. This is supported by the fact that it generated solely the peak current for Pb^{2+} in the presence of interfering ions. This is indicative of the elevated degree of sensitivity and the selectivity of the ionophore towards the Pb^{2+} ion.

Table 2

Study of the selectivity of proposed sensor for Pb^{2+} detection (1 mg mL^{-1}) in the presence of various competitive ions.

Foreign ions	Conc. (mg mL^{-1})	Signal change (%)
SO_3^{2-}	100	+9.33
SO_4^{2-}	100	+8.61
Fe^{3+}	50	+4.51
Mg^{2+}	50	+8.5
Cu^{2+}	10	+3.33

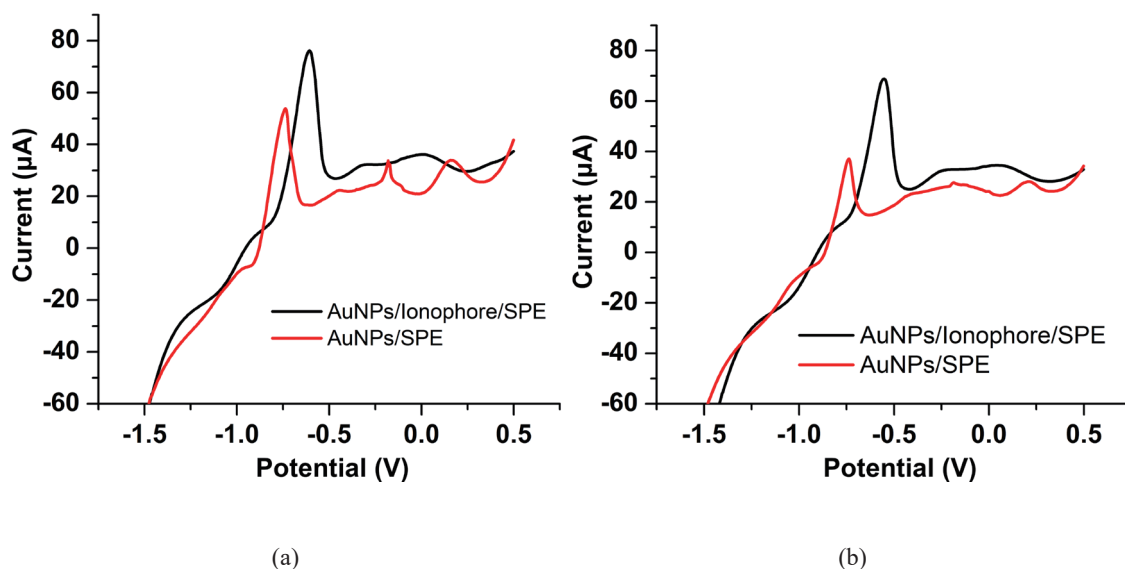


Fig. 7. (Color online) Voltammograms for a mixture of (a) 1 µg mL^{-1} Pb^{2+} and 1 µg mL^{-1} Hg^{2+} and (b) 1 µg mL^{-1} Pb^{2+} and 1 µg mL^{-1} Cd^{2+} in 0.1 M Tris-HCl using AuNPs/SPE and AuNPs/ionophore/SPE.

Table 3

Determination of Pb^{2+} in some real samples using the method based on AuNPs/ionophore/SPE under optimized conditions. The results are shown as $\bar{X} \pm \text{S.D.}$ (standard deviation, $n = 3$).

Sample	Added/ $\mu\text{g mL}^{-1}$	Found/ $\mu\text{g mL}^{-1}$	ICP-MS	Recovery (Developed method) (%)
River	—	<LOD	<LOD	—
	4	3.943 ± 0.1	3.891 ± 0.001	98.5
Tap water	—	0.399 ± 0.1	0.310 ± 0.004	—
	1	1.350 ± 0.4	1.223 ± 0.002	95.1

3.6 Analytical application of the developed electrode

The suitability of the enhanced process was tested by investigating Pb^{2+} in both tap and river water. The level of precision was evaluated by spiking a sample with a typical Pb^{2+} solution. According to the results, the samples spiked with Pb^{2+} exhibited excellent recovery. This confirms that the process is selective and appropriate for determining Pb^{2+} in real samples. As illustrated in Table 3, these favourable results were substantiated through an ICP-MS analysis.

4. Conclusions

An innovative chemically modified screen-printed electrode was developed for the stripping analysis of Pb^{2+} . This electrode was derived by merging the distinctive features of gold nanoparticles (which come with an extensive active surface space and a robust adsorptive capacity) and the unique complexing ability of the ionophore. The effectiveness of the electrode was demonstrated by its ability to detect Pb^{2+} ions in water samples (including SO_3^{2-} , SO_4^{2-} , Fe^{3+} , Mg^{2+} , Cu^{2+} , Hg^{2+} , and Cd^{2+}) despite the competition posed by other ions. This sensor was shown to be exceedingly sensitive as well as selective for the detection of Pb^{2+} ions.

Acknowledgments

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