Highly sensitive [Ru(bpy)$_3$]$^{2+}$/Nafion® modified indium tin oxide-based sensor for heavy metal detection

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ABSTRACT

Indium tin oxide-coated glass substrates were modified with tris (2,2′-bipyridyl) ruthenium (II) dichloride hexahydrate [Ru(bpy)$_3$]$^{2+}$/Nafion® solution via dip-coating. The Nafion®—[Ru(bpy)$_3$]$^{2+}$ ratio was varied to optimize the sensitivity of the modified electrodes in detecting lead (Pb^{2+}) and cadmium (Cd^{2+}). The surface morphology of the deposited thin film was characterized by scanning electron microscopy (SEM). The lowest concentration detected was 0.007 μM (0.001 μg/mL) and 4.91 μM (0.552 μg/mL) for lead and cadmium, respectively. The optimum Nafion® volume concentration in the film was 0.4% which gave an average film thickness of 217.90 nm.

1. Introduction

Heavy metals are essential to growth and survival of plants and animals. However, these metals at relatively high concentrations are hazardous and often lethal [1–7]. The Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO) established the Joint Expert Committee on Food Additives (JECFA) to determine the maximum tolerable intake of heavy metals [2]. Among the heavy metals, cadmium and lead have a great impact on biota [3]. Cadmium can affect the kidney and can trigger lung cancer [4,5] when the amount of exposure to the said metal exceeds 26 μg/kg body mass on a monthly basis [6]. Lead can greatly affect the nervous system and the hormones; and it can trigger some cancers [3] at > 0.02 μg/kg for adults and 0.03 μg/kg for children on a daily basis [7].

The rapid development of technology also accompanies too much exposure to heavy metals. With this, early detection has been the area in focus to at least minimize the frequency of exposure [8,9]. Various techniques in detecting heavy metals can be utilized like atomic absorption spectroscopy (AAS) [10], inductively coupled plasma-atomic emission spectroscopy (ICP-AES) [11], X-ray fluorescence [12], energy dispersive X-ray (EDX) [13], electron microprobe analysis [14], polarography [15], and anodic stripping voltammetry (ASV) [16]. Among these techniques, only polarography and ASV are considered low-cost and can compete with the capability of other techniques in terms of low concentration detection of up to parts per billion (ppb) [17]. Anodic stripping voltammetry has the advantages of selectivity in its wide-range detection, simplicity, and portability. The working electrode usually uses mercury-based material which has adverse effects to human health. An alternative to mercury is the use of modified electrodes such as mediator/polymer coated substrates [18]. The use of Nafion® polymer protects the electrode from chemical attacks which can possibly interfere with the study [19–24]. Incorporation of tris (2,2′-bipyridyl) ruthenium (II) ([Ru(bpy)$_3$]$^{2+}$) to Nafion® augments the transport of electrons [18,25].

In this study, dip coating technique was employed to deposit a thin film of Nafion®-doped with [Ru(bpy)$_3$]$^{2+}$ on ITO-coated glass substrates. These modified electrodes were characterized using SEM. The modified electrodes were used as the working electrode in anodic stripping voltammetry to detect heavy metals. The concentrations of Nafion® and [Ru(bpy)$_3$]$^{2+}$ were varied to obtain the most sensitive electrode that can detect trace amounts (ppb) of heavy metals. The obtained optimum ratio of Nafion® and [Ru(bpy)$_3$]$^{2+}$ is utilized to attain a linear calibration curve.

2. Experiment

2.1. Chemicals and reagents

Indium tin oxide (ITO)-coated glass slides (7.5 cm × 2.5 cm; sheet resistance 8–12 Ω/sq.) was from Sigma Aldrich. Tris (2,2′-bipyridyl) ruthenium (II) dichloride hexahydrate was also purchased from Sigma Aldrich. Nafion® (10 wt%) was from Fuel Cell Earth.

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Laboratory grade lead II chloride was purchased from Techno Pharmachem, India and cadmium chloride was from Sigma Aldrich as well.

2.2. Apparatus

BST8-stat Potentiostat/Galvanostat (ALV Technologies) along with voltammetric cell and the three electrode system (Pine Research Instrument) was interfaced to a computer with installed BST8-stat software to perform the electrochemical measurements. The three electrode system consisted of a platinum wire as counter electrode, saturated calomel electrode (SCE) as reference electrode, and the modified electrode as the working electrode. During the cleaning and deposition stages of the anodic stripping voltammetry, a high purity nitrogen gas was used for sparging while a ceramic magnetic stirrer was used for stirring. The surface morphology of the modified electrode was investigated using the JEOL Model 5310 Scanning Electron Microscope (SEM).
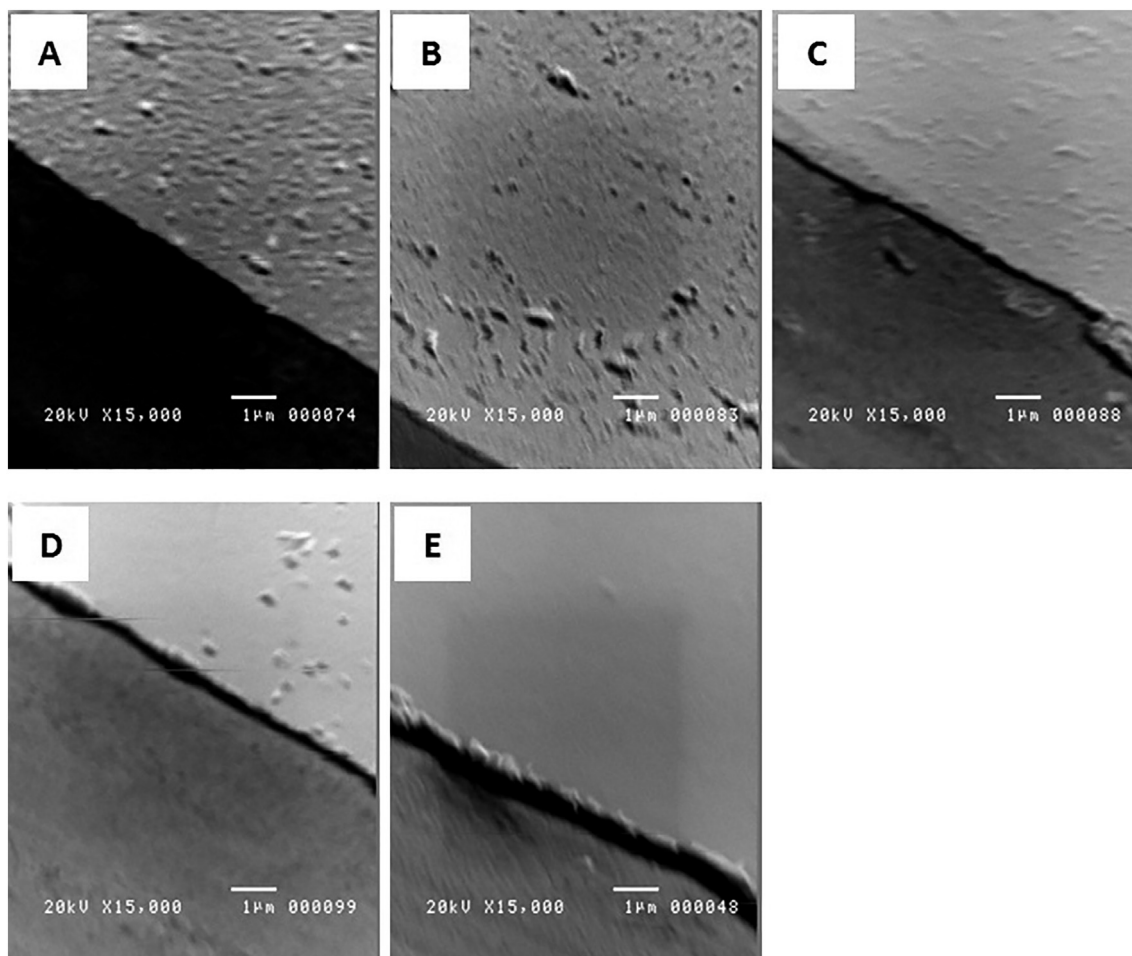

Fig. 1. Modified electrodes with varying Nafion® concentrations at (A) 0.1%, (B) 0.2%, (C) 0.3%, (D) 0.4%, and (E) 0.5% volume concentration. SEM micrographs at 15000 × magnification.
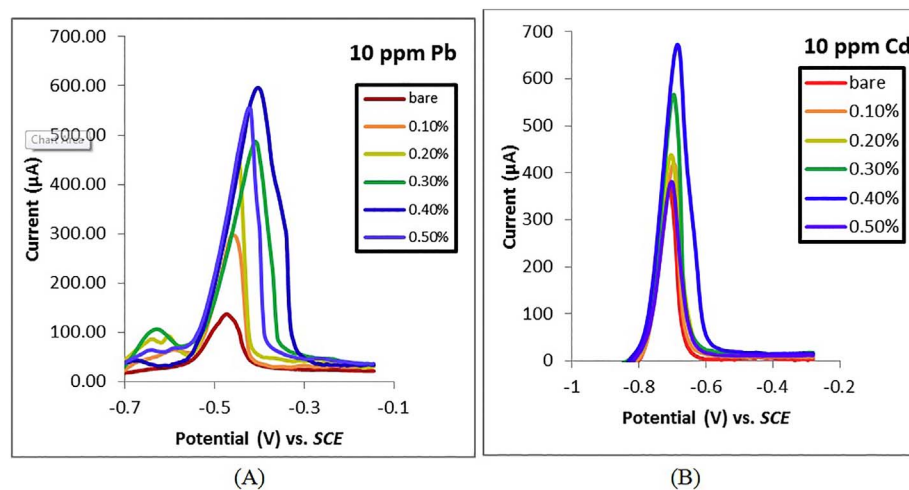

(A)

(B)

Fig. 2. Anodic stripping voltammograms of (A) 10 μg/mL lead chloride concentration and (B) 10 μg/mL cadmium chloride concentration using working electrodes with varying Nafion® volume concentration.

Table 1
Dip coated modified electrodes thickness.

Nafion® volume concentration	Measured thickness		
	Upper, nm	Lower, nm	Average, nm
0.10%	74.60	121.20	97.90
0.20%	102.80	140.20	121.50
0.30%	117.20	195.00	156.10
0.40%	135.00	300.80	217.90
0.50%	155.20	323.60	239.40

2.3. Procedure

2.3.1. First optimization: varying Nafion® volume concentration

Tris(2,2′-bipyridyl) ruthenium (II) dichloride hexahydrate powder (4 mg) [8] was dissolved in a 20 mL total volume concentration of methanol and Nafion® (10 wt%). The volume concentration of Nafion® was varied to obtain different thicknesses of the thin film using 0.1%, 0.2%, 0.3%, 0.4% and 0.5% volume percentage. The ITO-coated glass substrates were cut into 2.5 cm × 1.0 cm strips and cleaned with ethanol in an ultrasonicator. The cut substrates were dipped into the coating solution for 30 s, air dried for ≥ 2 h at 26 ± 1 °C, and baked for 30 min at 90-100 °C.

Each coated substrate was tested in anodic stripping voltammetry with 10 μg/mL concentrations of lead and cadmium. The two heavy metals were sequentially detected with the following parameters: + 1.0 V at 1 min (cleaning step), − 1.0 V at 1 min (deposition step),
− 1.0 V at 5 s (equilibration step), and 50 mV/s scan rate with 5 mV step size which has initial − 1.0 V potential (stripping step). The concentration that recorded the highest anodic current value was used for the second optimization.

2.3.2. Second optimization: varying $[Ru(bpy)_3]^{2+}$ concentrations

The Nafion® volume concentration that obtained the highest anodic current for the first optimization was held constant in this optimization. The mass of the mediator per unit volume of Nafion® in the coating solution was varied at 1 mg/mL, 5 mg/mL, 10 mg/mL [8], 20 mg/mL, and 40 mg/mL. The same dip coating and ASV parameters from the first optimization were applied.
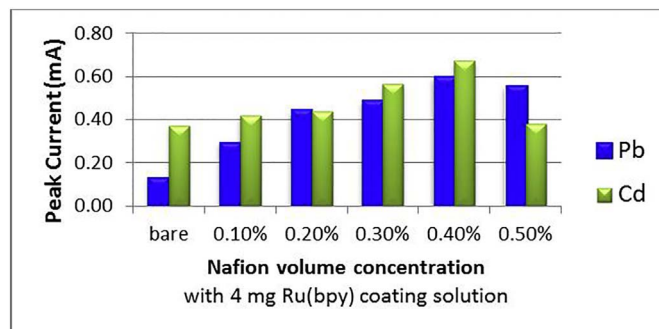

Fig. 3. Peak current obtained from the voltammograms versus the Nafion® volume concentration graph.
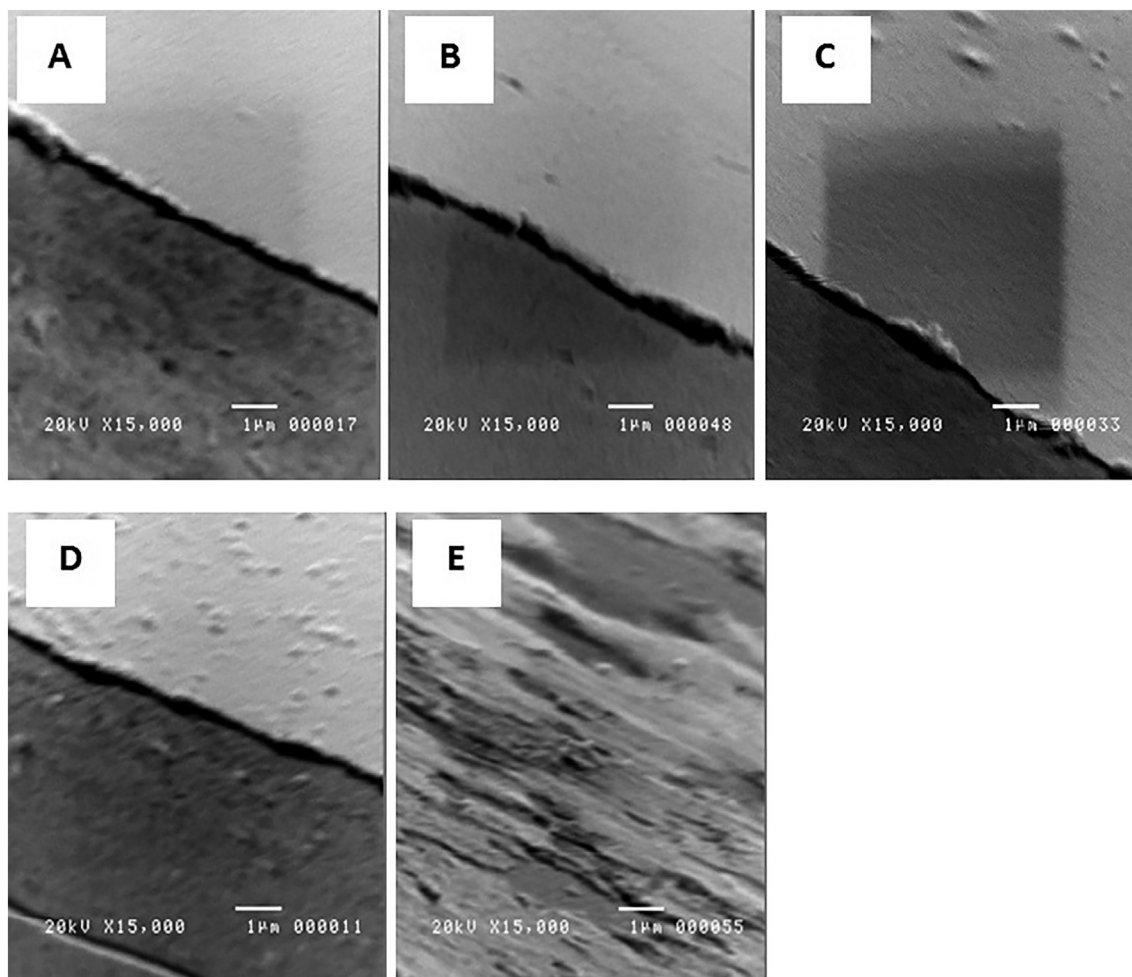

Fig. 4. Modified electrodes with varying Nafion® concentrations at (A) 1 mg/mL (B) 5 mg/mL, (C) 10 mg/mL, (D) 20 mg/mL, (D) 20 mg/mL, and (E) 40 mg/mL $[Ru(bpy)_3]^{2+}$ mediator concentration. SEM micrographs at 15000 × magnification.
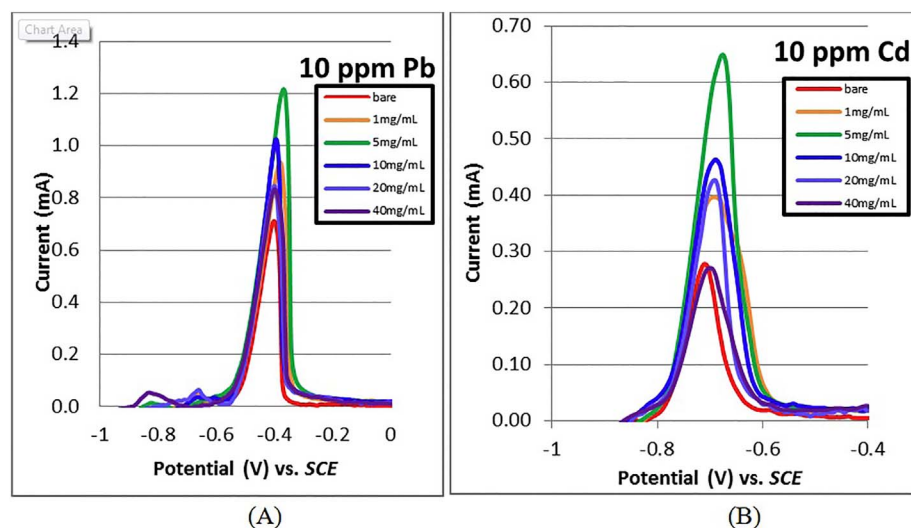
Fig. 5. Anodic stripping voltammograms of (A) 10 μg/mL lead concentration and (B) 10 μg/mL cadmium chloride concentration using working electrodes with varying [Ru (bpy)$_3$]$^{2+}$ mediator concentration.

2.3.3. Calibration curve

The optimized modified electrode was used to determine increasing concentrations of lead and cadmium in an electrolyte solution. The same parameters from the first and second optimizations were applied in the ASV tests. The minimum detection concentration was identified by getting a series of voltammograms until a flat line (zero current) or noise was registered. The highest anodic current was plotted against the heavy metal concentration. The Pearson coefficient (R^2) and the slope were then determined.

3. Results and discussion

3.1. First optimization

Fig. 1 showed different micrographs of the deposited thin film on ITO surface. The smoothness of the surface became more evident as the Nafion® volume concentration was increased. The thicknesses of the film deposited from the upper (near the clip) and lower (other end) regions of a 2.5 cm × 1.0 cm dip coated substrate were measured by scraping the center of the sample, then the SEM stage was lowered maintaining a working distance of 14 mm and tilted to an angle 75°.

Table 1 showed the direct relationship of the Nafion® volume concentration to the thickness of the deposited film. The difference in the upper and lower regions was attributed to gravity since the substrate was dip coated into the solution and allowed the remaining solution to drip off the substrate. As expected, the upper regions have thinner film than the lower regions.

As the fabricated electrodes were used in ASV, a noticeable increase in the peak current as the Nafion® volume concentration was increased. The Nafion® concentration that maximized the effectivity of the modified electrode was 0.4%. This means the resulting film was not too thick enabling the incorporated redox mediators to facilitate electron transfer relatively faster compared to other concentrations [25,27–29]. At greater concentrations, the polymeric thickness was thicker than the diffusion layer thus preventing the effective detection of the heavy metals (cf. Figs. 2 and 3).

3.2. Second optimization

Nafion® volume concentration of 0.40% was used as the constant parameter for the second optimization since it gave the highest peak current among the other concentrations. The mediator concentration was varied in the second optimization. The SEM micrographs showed increasing roughness to the surface as the amount of [Ru(bpy)$_3$]$^{2+}$ was increased (cf. Fig. 4).

The plots of the reduction current versus the mediator concentration (Figs. 5 and 6) show that the reduction current increased as the mediator concentration was increased from 1 mg/mL to 5 mg/mL and decreased when the mediator concentration was increased from 10 mg/mL to 40 mg/mL. The optimum concentration was therefore 5 mg of [Ru(bpy)$_3$]$^{2+}$ for every 1 mL of 10% Nafion®.

3.3. Calibration curve

The optimized dip coated modified electrode was used as the working electrode in ASV to detect different concentrations of lead and cadmium. The voltammograms obtained in the ASV tests were overlaid (Fig. 7-A and Fig. 8-A) and the peak current was plotted against the heavy metal concentration (Fig. 7-B and Fig. 8-B).

From the figures shown, the peak current increases as the heavy metal concentration was increased, both for lead chloride and cadmium chloride. The concentrations of the heavy metal ions were calculated (cf. Table 2) since the chlorine component of the compound dissociated during the ASV tests. The lowest concentrations of lead and cadmium that the optimized electrode has detected are 0.007 μM (0.001 μg/mL) and 4.91 μM (0.552 μg/mL), respectively. Triplicate ASV runs were performed to determine the detection limit of the electrode.
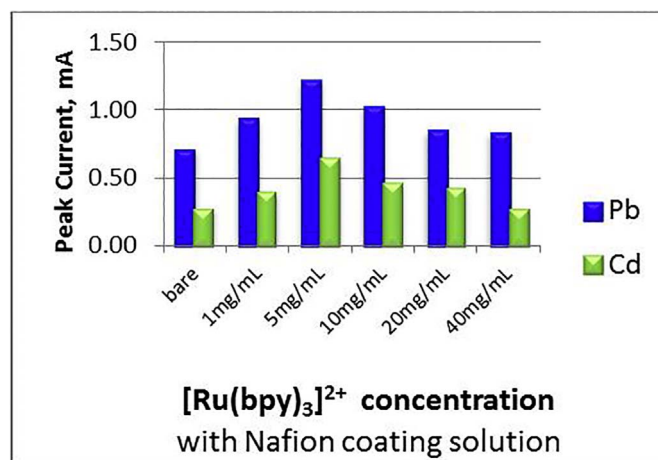

Fig. 6. Peak current obtained from the voltammograms versus the [Ru(bpy)$_3$]$^{2+}$ concentration graph.
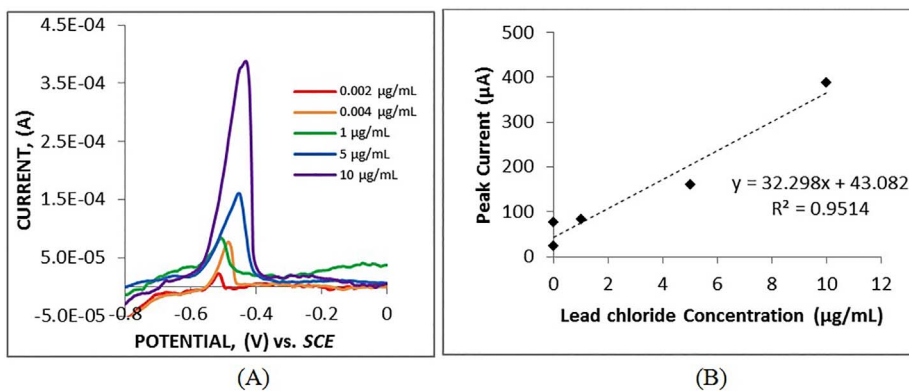
Fig. 7. (A) Voltammograms of different lead chloride concentrations present in a 0.1 M NaCl electrolyte; and (B) calibration curve obtained by plotting highest peak current and lead chloride concentrations.
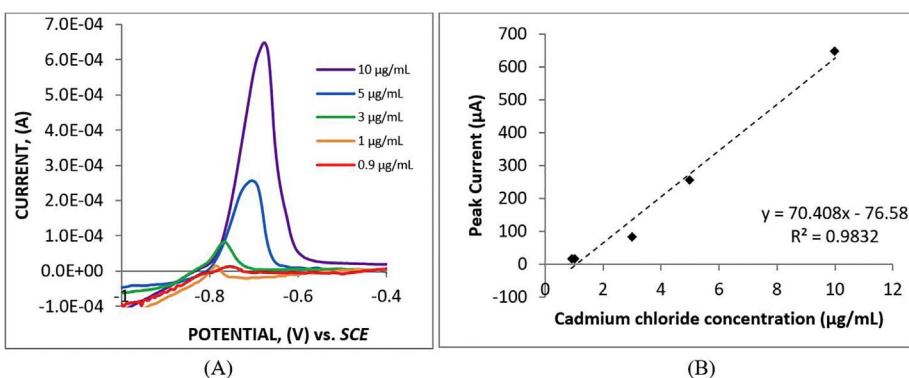

Fig. 8. (A) Voltammograms of different cadmium chloride concentrations present in a 0.1 M NaCl electrolyte; and (B) calibration curve obtained by plotting highest peak current and cadmium chloride concentrations.

Table 2
Stoichiometric calculation of heavy metal ion concentration detected.

Compound concentration, µg/mL	Heavy metal concentration, mg/L	Concentration, µM
Lead		
0.002	0.001	0.007
0.004	0.003	0.014
1	0.745	3.596
5	3.725	17.979
10	7.450	35.958
Cadmium		
0.9	0.552	4.910
1	0.613	5.455
3	1.840	16.365
5	3.066	27.275
10	6.132	54.550

3.4. Cyclic voltammetry

To determine the transport property of the modified electrode, cyclic voltammetry measurements were performed on the optimized electrode using 100 mL of 0.1 M NaCl as supporting electrolyte and saturated calomel electrode as reference electrode. Fig. 9 shows defined anodic and cathodic peaks which represent the redox reaction during the run. The occurrence of the anodic and cathodic peaks at a specific potential is attributed to the presence of $[Ru(bpy)_3]^{2+}$ mediator which facilitated the electron transfer to the surface during the oxidation and reduction processes [23,25,30]. The reversibility and stability of the electrode for separate runs and for continuous cycles are also evident in Fig. 9-A and B. With an average anodic current of 82.73 µA and cathodic peak of −58.29 µA, the repeatability of the result has an average of 99.5%, therefore the modified electrode can be reused with consistent results. This stability can be attributed to the presence of Nafion® since it can resist chemical attacks during the measurements [26]. Consistent results were found as compared to the spin-coated Nafion®-$[Ru(bpy)_3]^{2+}$ modified electrode of Tuason et al. [23,25] for the peak potential with saturated calomel electrode as reference. The electrodes were found to have 94.94% stability for anodic peak current and 99.65% percent stability for cathodic peak current from the first scan to the last scan (Fig. 10).
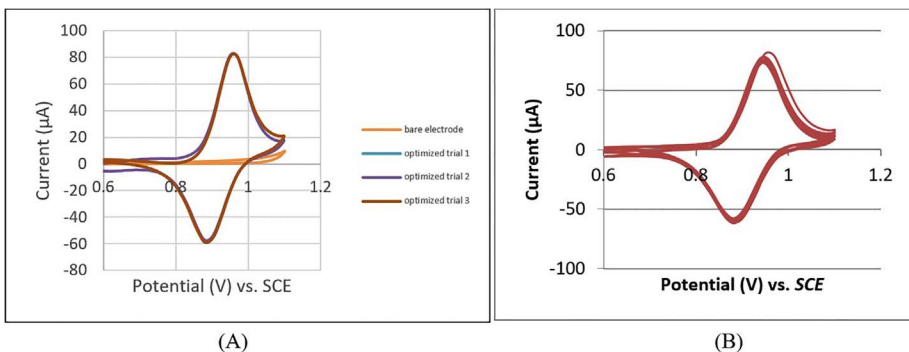

Fig. 9. Cyclic voltammograms of optimized modified electrode (A) for three trials and (B) for 10 continuous cycles.
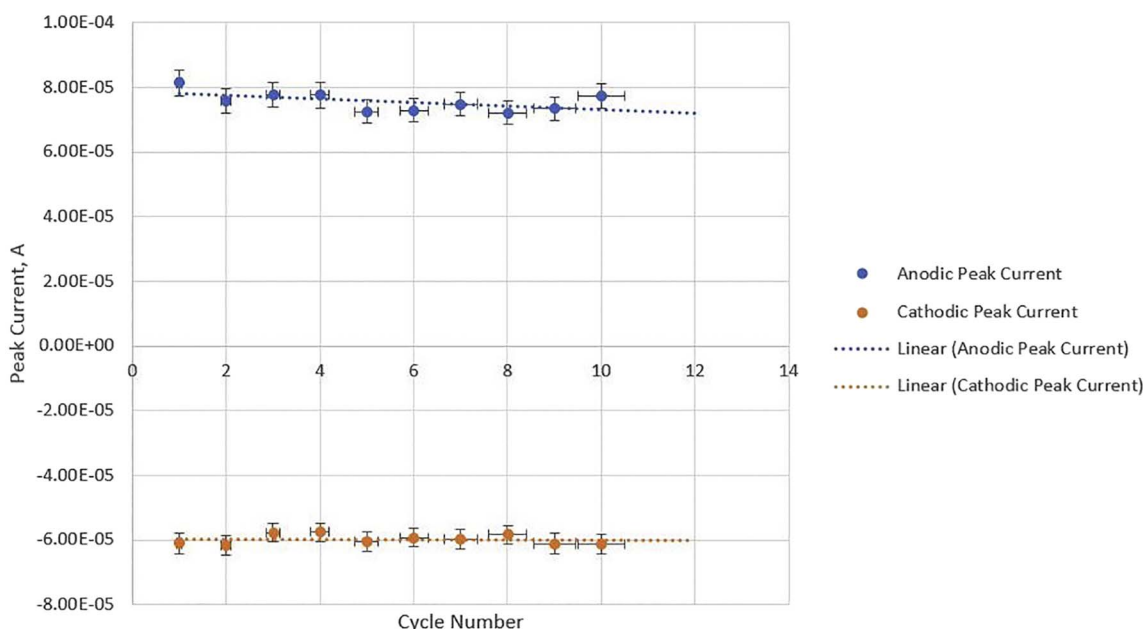
Fig. 10. Peak Current vs. Cycle Number graph showing relatively constant peak current values as the number of cycle is increased.

4. Conclusion

The study successfully fabricated ultra-sensitive Nafion®/[Ru (bpy)$_3$]$^{2+}$/ITO modified electrodes via the dip coating deposition technique. The presence of Nafion® polymer adds to the stability of the electrode to eliminate chemical attacks to the surface. Moreover, [Ru (bpy)$_3$]$^{2+}$ mediator enhances electron transfer to the surface as compared to a bare ITO-based substrate. Finally, the optimized electrode was successfully applied as a sensor for the detection of heavy metal ions in an electrolytic solution. With the experimental determination of the limit of detection, the optimized electrodes were able to detect up to 0.007 μM (0.001 μg/mL) of lead and 4.91 μM (0.552 μg/mL) of cadmium. These modified electrodes therefore are excellent for the determination of lead and cadmium at trace levels because their selectivity, sensitivity and cost-effectiveness.

Conflicts of interest

The authors don't have any conflict of interest.

Acknowledgement

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