

Trace Determination of Lead and Cadmium using Graphene/[Ru(NH₃)₆]³⁺/Nafion Modified Glassy Carbon Electrodes

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Abstract: Graphene/[Ru(NH₃)₆]³⁺/nafion modified glassy carbon electrodes were fabricated using the drop coating technique. The fabricated electrodes were characterized using scanning electron microscopy (SEM) and cyclic voltammetry (CV). Simultaneous detection of lead (Pb²⁺) and cadmium (Cd²⁺) was done via anodic stripping voltammetry (ASV). The effects of varying the amounts of graphene and [Ru(NH₃)₆]³⁺ on the transport and sensing properties of the modified electrodes were determined. SEM results showed that the deposited films were smooth and uniform. CV results showed that the peak currents increase monotonically with the amounts of graphene and [Ru(NH₃)₆]³⁺. ASV results showed that modification of the GCE with graphene, [Ru(NH₃)₆]³⁺ and Nafion greatly enhanced the electrode's sensitivity in detecting Pb²⁺ and Cd²⁺. This can be attributed to the high surface area-to-volume ratio of graphene, the mediation of electron transfer by [Ru(NH₃)₆]³⁺ and the antifouling and cationic exchange capabilities of Nafion. The highest peak current for both Pb²⁺ and Cd²⁺ were obtained from the electrode modified with 1.5 mg [Ru(NH₃)₆]³⁺ and 3.0 mg graphene. A linear relationship between the peak current and metal concentration was obtained in the range of 1.4 ppb to 20 ppb for both Pb²⁺ and Cd²⁺ with a detection limit of 1.4 ppb. The modified electrodes were successful in detecting Cd²⁺ in real water samples. ASV results were verified using atomic absorption spectroscopy.

Keywords: Graphene, Nafion, glassy carbon, modified electrode, anodic stripping voltammetry, lead, cadmium

1. INTRODUCTION

Toxic metals such as cadmium (Cd) and lead (Pb) are metals that are harmful to human health. Exposure to these metals even in minute quantities can be life threatening. Cadmium is primarily toxic to the kidney, can cause bone demineralization, may impair lung function and increase the risk of lung cancer. Lead can cause a rise in blood pressure, kidney damage, brain damage, miscarriages and subtle abortions, disruption of the nervous system, declined fertility of men through sperm damage, diminished learning abilities of children, and behavioural disruptions of children, such as aggression, impulsive behaviour and hyperactivity. Human exposure to these toxic metals mainly occurs through contaminated food, water, and soil, smoking and industrial activities.

Due to the adverse effects of Pb and Cd on human health, accurate and precise monitoring of these harmful metals in the environment is essential. Thus, several techniques of detecting toxic met-

als have been developed. Among these are spectroscopic and electrochemical techniques. Electrochemical techniques such as anodic stripping voltammetry (ASV) are more popular due to their low cost, high sensitivity and portability. On the other hand, spectroscopic techniques such as atomic absorption spectroscopy, atomic emission spectroscopy, mass spectroscopy, x-ray fluorescence spectroscopy and electrochemical techniques are expensive, their availability is limited, they are not well suited for *in situ* measurements, and require complicated instrumentation [1].

In anodic stripping voltammetry, three electrodes are used: a working electrode, a counter electrode and a reference electrode. For many years, mercury was used as a working electrode material because of its high reproducibility and sensitivity to anodic stripping voltammetry. However, mercury is toxic and has limited anodic potential. Thus, chemically modified electrodes have been developed and utilized as an alternative to mercury electrodes. One of the common approaches of modifying electrodes is coating the surface with a thin film of an appropriate polymer such as Nafion.

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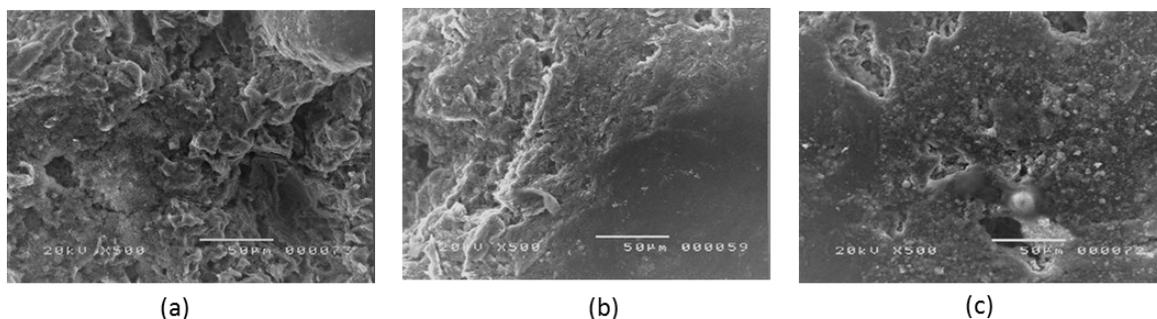


Figure 1. SEM micrographs of the surface of (a) bare GCE, (b) graphene/Nafion/GCE and (c) graphene/Ru[(NH₃)₆]³⁺/Nafion/GCE at x500 magnification.

Nafion modified electrodes are currently being utilized in sensors such as heavy metal sensors [2-15] and biosensors [16-25]. The working electrode of these sensors is modified by coating it with Nafion doped with a redox mediator (e.g. Ru[(NH₃)₆]³⁺ and Ru(bpy)₃²⁺) or a nanomaterial (e.g. graphene and carbon nanotubes) which enhances their sensitivity by accelerating the transfer of electrons [26-28]. The Nafion coating also makes the electrode more damage resistant, and more lasting.

In this study, Nafion doped with graphene and Ru[(NH₃)₆]³⁺ was used to modify glassy carbon electrodes (GCE). The fabricated electrodes were characterized by scanning electron microscopy (SEM) and cyclic voltammetry (CV). The electrodes were also used in ASV to detect Pb²⁺ and Cd²⁺.

2. METHODOLOGY

2.1. Reagents and solutions

Graphene nanopowder was purchased from Graphene Supermarket (Calverton, NY, USA) and Hexaammineruthenium(III) chloride from Sigma, Aldrich (Sigma-Aldrich Pte Ltd, Singapore). Nafion solution (5 wt%) was purchased from Fuel Cell Earth (Wakefield, MA, USA). Laboratory grade heavy metals, CdCl₂ and ZnCl₂, were also purchased from Sigma, Aldrich while PbCl₂ was purchased from Pharmchem (Bahadurgarh, Haryana, India). Stock solutions of heavy metals were prepared with high purity deionized water.

2.2. Instruments

A BOSCH SAE200 electronic balance (BOSCH-Wägesysteme GmbH, Jungingen, Germany) was used to measure 1.0 mg, 2.0 mg, and 3 mg of graphene, 1.5mg, 3.0mg and 4.5mg of [Ru(NH₃)₆]³⁺ and 0.584 g of NaCl. A transferpette®S micropipette (Sigma-Aldrich Pte Ltd, Singapore) was used in drop coating the coating solutions onto the tip of glassy carbon rods with a diameter of 3mm. All glasswares were put into a BANDELIN SONOREX ultrasonic bath (BANDELIN electronic GmbH & Co. KG, Berlin, Germany) for cleaning. The glassy carbon rods were polished using 0.05μm and 0.3μm alumina slurry. A BST8-stat potentiation/galvanostat (MTI Corporation, Richmond, CA, USA) was used for the CV and ASV experiments.

2.3. Experimental Procedure

2.3.1. Fabrication of graphene/Ru[(NH₃)₆]³⁺/Nafion modified GCE

Graphene/Nafion solution was prepared by mixing graphene nanopowder (1.0 mg, 2.0 mg, and 3.0 mg) with 5 mL of 1wt% Nafion solution. Each resulting graphene-Nafion solution was mixed with Ru[(NH₃)₆]³⁺ (1.5mg, 3.0mg and 4.5mg). The mixture then underwent ultrasonication for one hour and 30 minutes at ambient temperature to obtain a uniformly dispersed graphene-Ru[(NH₃)₆]³⁺-Nafion solution. The suspension was then deposited onto the prepared glassy carbon electrodes using a micropipette. The electrodes were air dried at constant ambient temperature (26°C).

2.4. Characterization

The surface morphology of the deposited films was characterized by scanning electron microscopy (JEOL 5310). The samples were placed inside a coater (JEOL JFC-1200) where each was coated with gold. The samples were then attached to the sample holder and placed inside the SEM (JEOL 5310) chamber. The spot size was set to 8 nm and the magnification to x500.

The fabricated modified electrodes were also characterized using cyclic voltammetry. The fabricated modified glassy carbon electrode was used as the working electrode, a platinum coil was used as the counter electrode, and a saturated calomel was used as the reference electrode. A 100 mL solution of 0.1 M NaCl was prepared as the supporting electrolyte. The scan rate was 100 mV/s and the step size 10 mV.

2.4.1. Detection of Pb²⁺ and Cd²⁺

The fabricated electrodes were used as the working electrode in ASV to simultaneously detect trace amounts of Pb²⁺ and Cd²⁺. The voltammetry cell was filled with 100 ml of 0.1 M NaCl. Pb and Cd were added to the electrolyte solution which was stirred by a ceramic magnetic stirring bar and sparged by nitrogen gas. The concentrations of Pb and Cd were varied from 1ppb to 100ppm. During the voltammetry tests, a potential of 0.95V was applied for five minutes and thirty seconds while the solution was stirred at 400rpm. ASV scan was performed between -95V and 0.5V. Cleaning was done by applying a potential of 1.0 V for one minute.

3. RESULTS AND DISCUSSION

3.1. SEM Characterization

Figure 1 shows the SEM micrographs of the surface of (a) bare GCE, (b) graphene/Nafion/GCE and (c) graphene/Ru[(NH₃)₆]³⁺/Na-

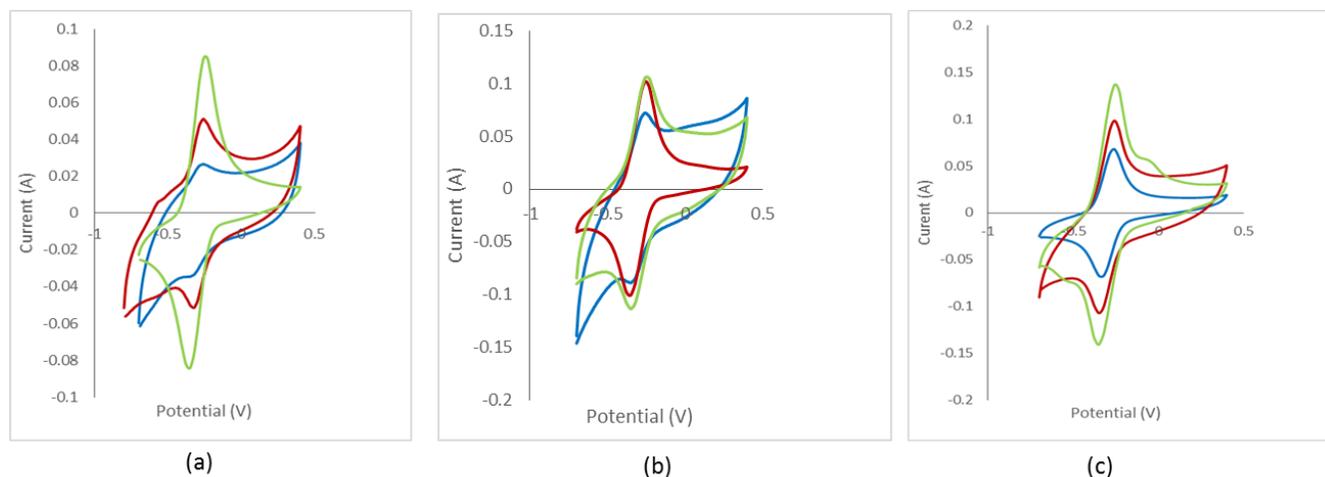


Figure 2. Cyclic voltammograms of the electrodes modified with (a) 1mg graphene, (b) 2mg graphene, (c) 3 mg graphene, (red) 1.5 mg [Ru(NH₃)₆]³⁺, (blue) 3 mg [Ru(NH₃)₆]³⁺, and (green) 4.5 mg [Ru(NH₃)₆]³⁺.

tion/GCE. It can be observed from the figure that the surface of the modified electrode improved with the addition of graphene. The surface further smoothens with the addition of [Ru(NH₃)₆]³⁺. The recrystallization level also increased with the incorporation of graphene as the grain boundaries become more pronounced and the presence of minute hillocks on the surface totally vanished.

3.2. CV Characterization

The cyclic voltammograms of the modified GCE showed a monotonically increasing peak current as the amount of [Ru(NH₃)₆]³⁺ increased keeping the concentration of graphene constant (Fig. 2). The line correlation between peak current and graphene concentration with the concentration of [Ru(NH₃)₆]³⁺ constant is also linear. Reversibility tests showed that seven of the nine modified electrodes have excellent reversibility. Stability tests of CV scans showed that the voltammograms of the electrode with 3 mg graphene are more precise compared to lower graphene concentrations. Overall, the electrodes with 3mg graphene and 1.5 mg [Ru(NH₃)₆]³⁺, 3mg graphene and 4.5mg [Ru(NH₃)₆]³⁺, and 1mg graphene and 4.5mg [Ru(NH₃)₆]³⁺ gave the best results in terms of linear correlation in the peak current vs scan rate results and also being the three best electrodes in terms of stability and reversibility.

3.3. Anodic Stripping Voltammetry

Figure 3 shows the anodic stripping voltammograms obtained using a bare GCE, [Ru(NH₃)₆]³⁺/Nafion modified GCE, graphene/Nafion modified GCE and graphene/[Ru(NH₃)₆]³⁺/Nafion modified GCE. It can be observed from the figure that modification of the GCE with graphene, [Ru(NH₃)₆]³⁺ and Nafion enhanced the detection of Pb²⁺ and Cd²⁺. The highest peak current was obtained from the graphene/[Ru(NH₃)₆]³⁺/Nafion modified GCE. This can be attributed to the combined benefits of graphene, [Ru(NH₃)₆]³⁺ and Nafion. The high surface area-to-volume ratio which is a unique property of graphene [29] increased the number of active sites within the electrode resulting to an increase in the amount of metal

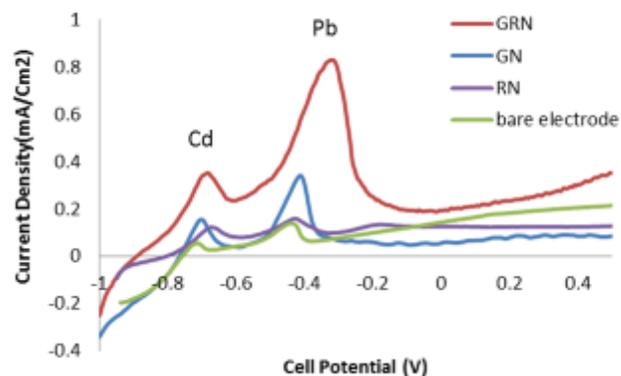


Figure 3. Anodic stripping voltammograms obtained using bare GCE, [Ru(NH₃)₆]³⁺/Nafion modified GCE (RN), graphene/Nafion modified GCE (GN) and graphene/[Ru(NH₃)₆]³⁺/Nafion GCE (GRN).

ions deposited on the electrode's surface [9, 24, 25]. The redox mediator [Ru(NH₃)₆]³⁺ enhanced the conductivity of the electrode [15] by accelerating the electron transfer while the antifouling and cationic exchange capabilities of Nafion improved the stability of the electrode.

Figure 4 shows the voltammograms for five concentrations of Cd²⁺ and Pb²⁺ obtained using the modified GCE. It can be observed from the figure that the reduction current increases linearly with the concentration of the heavy metals. This is due to the increase in the amount of heavy metals which is deposited onto the surface of the working electrode during the deposition stage thereby increasing the amount of heavy metals detected during the stripping stage.

The calibration curve for each heavy metal was obtained by plotting the reduction current vs. the heavy metal concentration. The Pearson correlation coefficient (R²) of each plot was determined. The calibration curves for lead and cadmium had R² values close to

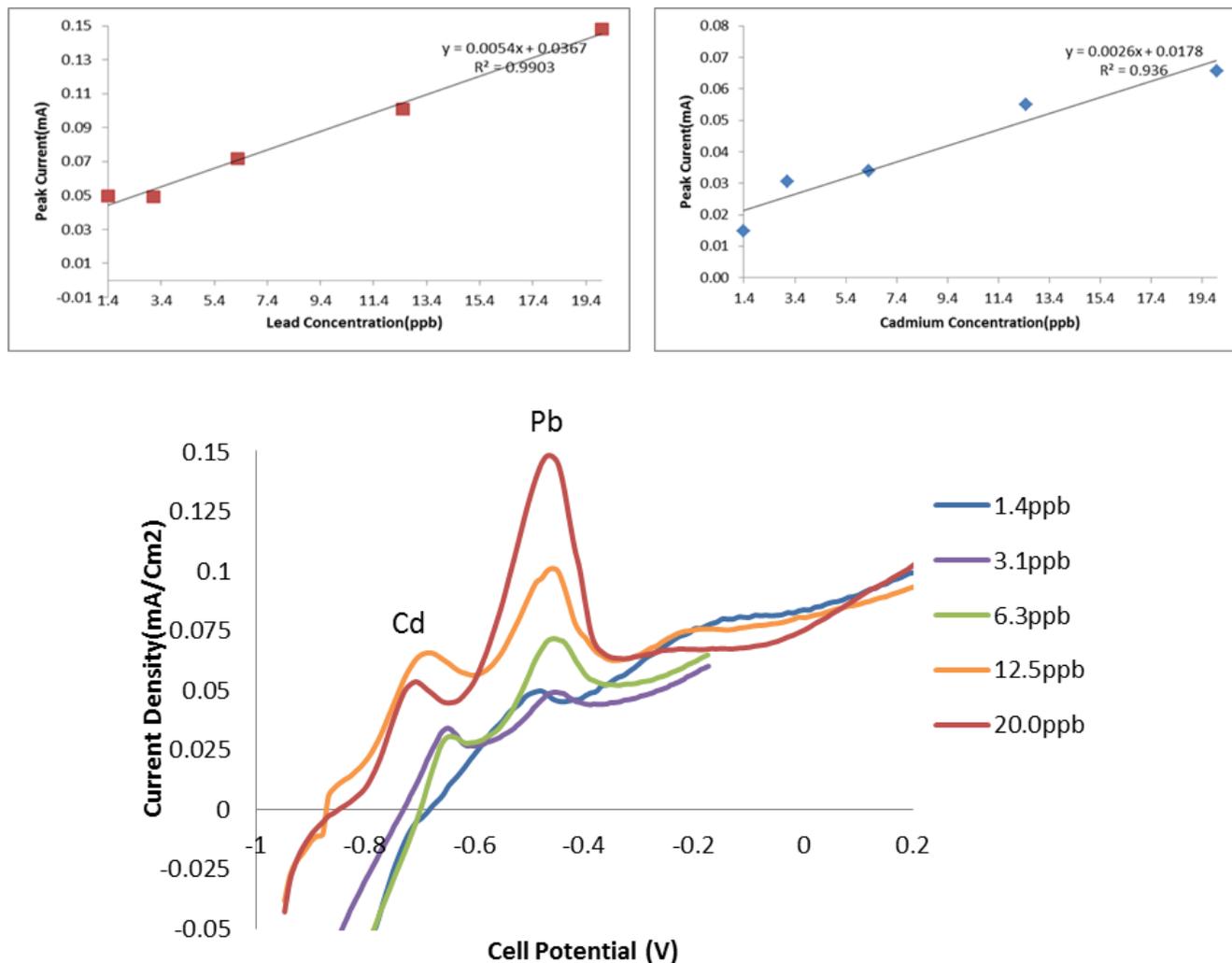


Figure 4. ASV voltammograms of Cd^{2+} and Pb^{2+} in 5 concentrations detected using the electrode with 3mg graphene and 1.5 mg $[\text{Ru}(\text{NH}_3)_6]^{3+}$. The inset shows the calibration curves for the determination of Cd^{2+} and Pb^{2+} .

1, indicating that there is a strong positive linear relationship between the reduction current and heavy metal concentration. The detection limit of the modified electrode is 1.4 ppb.

3.4. Variation of Graphene and $[\text{Ru}(\text{NH}_3)_6]^{3+}$

Figures 5 shows the anodic stripping voltammograms obtained for the modified electrodes with constant graphene (3mg) and varying amounts of $[\text{Ru}(\text{NH}_3)_6]^{3+}$. It can be observed from the figure that the reduction peak current for both Pb^{2+} and Cd^{2+} decreased linearly with the amount of $[\text{Ru}(\text{NH}_3)_6]^{3+}$.

Figures 6 shows the anodic stripping voltammograms obtained using the modified electrodes with constant $[\text{Ru}(\text{NH}_3)_6]^{3+}$ (1.5 mg) and varying amounts of graphene. It is evident from the figure that the reduction peak current for both Pb^{2+} and Cd^{2+} increased linearly with graphene concentration.

3.5. Real Sample Analysis

To demonstrate the utility of the fabricated electrodes for sensing

applications, the electrodes were used to detect heavy metals in water samples. The electrodes were able to detect ca. 1.57 ppb of Cd in tap and drinking water samples. The results were confirmed using atomic absorption spectroscopy (AAS).

4. CONCLUSIONS

Graphene/ $[\text{Ru}(\text{NH}_3)_6]^{3+}$ /nafion thin films were deposited using the drop coating technique on the polished surface of glassy carbon electrodes to fabricate a modified GCE. SEM results show that the deposited films were smooth and uniform. CV results show that the peak current increases monotonically with the concentration of graphene. It is directly proportional, as well as, to the concentration of $[\text{Ru}(\text{NH}_3)_6]^{3+}$.

The fabricated electrodes were able to simultaneously detect trace amounts of Cd and Pb. ASV results showed that as the amount of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ was increased, the reduction peak current for both Cd and Pb decreased while it increased as the amount of graphene was increased. A linear relationship between the peak

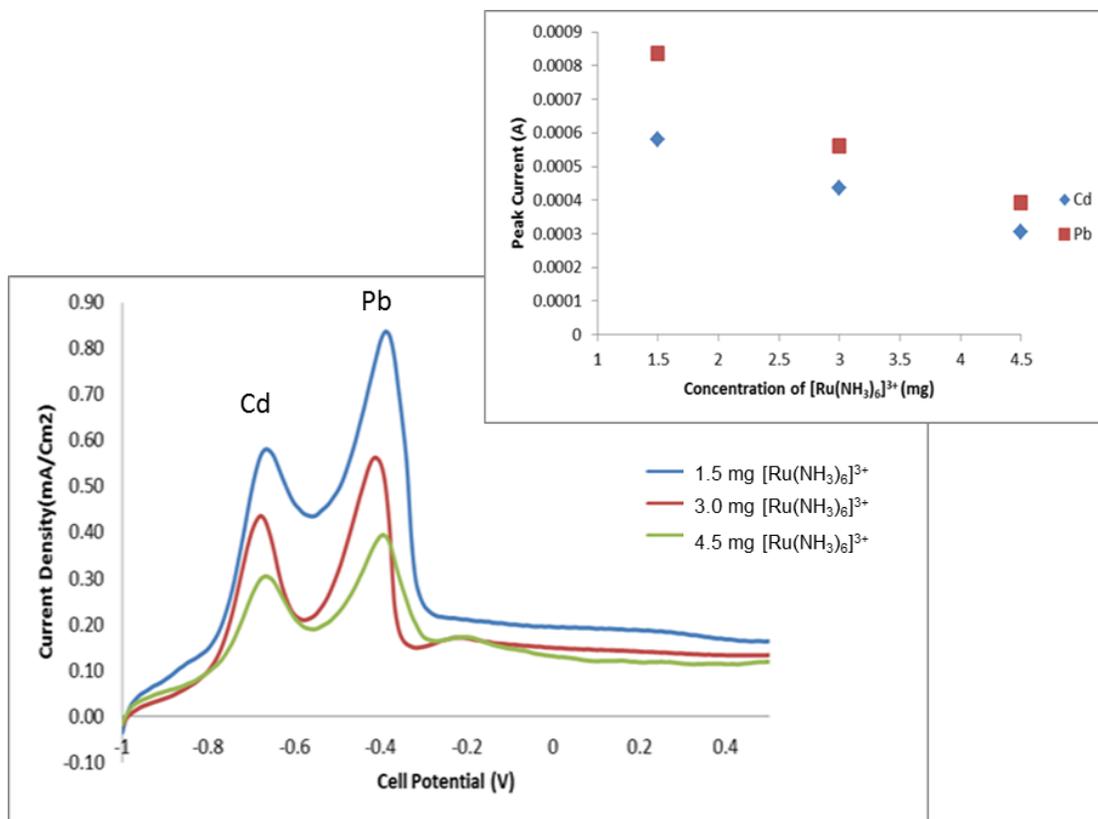


Figure 5. Anodic stripping voltammograms of Cd²⁺ and Pb²⁺ (10 ppm each) using electrodes with 3mg graphene and varying amounts of [Ru(NH₃)₆]³⁺. The inset shows the graph of Peak current vs. concentration of [Ru(NH₃)₆]³⁺ for Cd²⁺ and Pb²⁺.

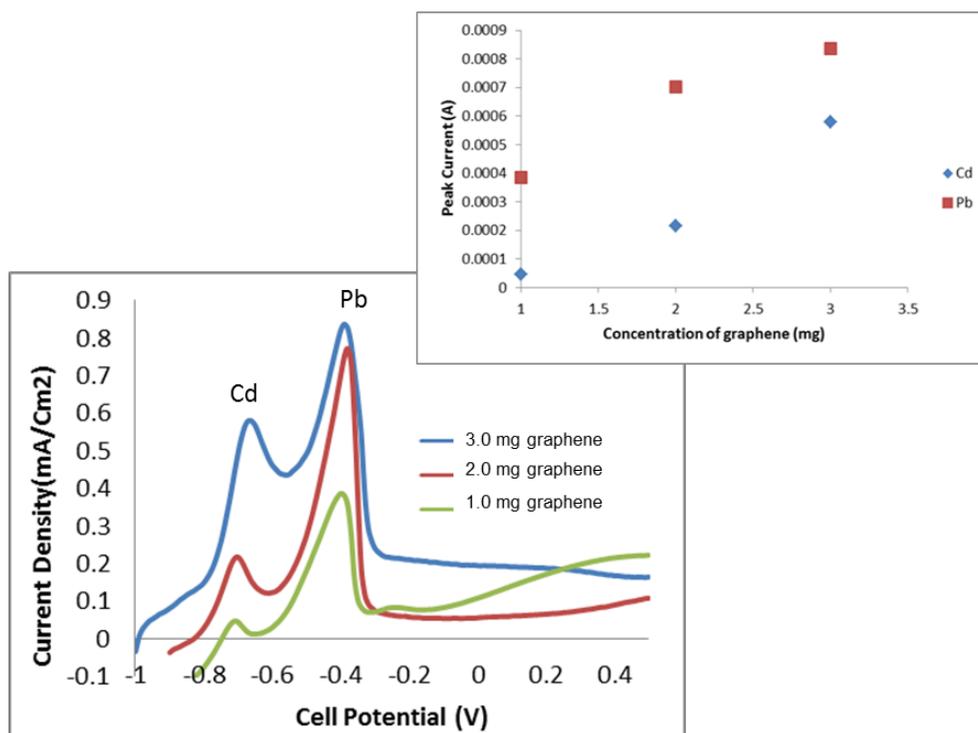


Figure 6. Anodic stripping voltammograms of Cd²⁺ and Pb²⁺ (10 ppm each) using electrodes with 1.5 mg [Ru(NH₃)₆]³⁺ and varying amounts of graphene. The inset shows the graph of Peak current vs. concentration of graphene for Cd²⁺ and Pb²⁺.

current and the metal concentration was obtained in the range of 1.4 ppb to 20 ppb for both Pb^{2+} and Cd^{2+} . The detection limit of the electrode is 1.4ppb. The modified electrodes were successful in detecting Cd^{2+} in real water samples. The results were verified using AAS analyses.

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