Determination of Hg^{2+} using a glassy carbon electrode modified with $[ZnSO_4\{ZnCl_2(u\text{-}S\text{-}CH_2CH_2NH_2\}]n$

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Abstract: An electrochemistry sensor composed of glass carbon electrode modified with $[ZnSO_4\{ZnCl_2(u\text{-}S\text{-}CH_2CH_2NH_2\}]n$ was used for the determination of mercury(II) ions with differential pulse voltammetry(DPV) in 0.1mol/L KCl solutions. The proposed electrochemistry sensor had good operating characteristics towards Hg^{2+}, including a relatively good selectivity, the response to Hg(II) ions in a concentration range of 1.8×10^{-5} to 4.5×10^{-4} mol/L, and the corresponding linear regression aquation was I=-0.2234C-1E-05, the correlation coefficient was 0.9970, the detection limit was 0.1umol/L. Modified electrode was verified through the experiment of standard addition analysis application in water samples with a recovery rate of 95.12%～102.58%. Additionally, some common metal ions (Mg^{2+}、Mn^{2+}、Zn^{2+}) had no obvious effects on the determination of Hg^{2+}.

Introduction

Mercury(II) is likely to be an important public health hazard in our life because of it is a highly toxic as one of heavy mental ions[1-2]. It can be transferred to human body through bio-accumulative on food chain, will directly lead to heart, liver, thyroid disease, and even affects the nervous system and cause the formation of the malignant tumor[3-4]. The determination analysis of mercury(II) in water environment is one of the focuses of the scientific research. Several analytical techniques, such as atomic absorption spectrometry[5], fluorescence spectrometry[6-8], atomic fluorescence spectrometry[9], quantum dots[10], nanosensor[11-13], and biosensors[14] have been applied for the determination of the value of mercury(II) in analytical samples. The above mentioned analytical method are preferred for their sensitivity, reproducibility, and easy surface renewal. However, the toxicity and complicated procedures of handling and storing mercury(II) make it unsuitable for the applications of outside the laboratory. Therefore, it is desirable to develop green method as alternatives to the detect of mercury(II). The modified electrodes have attracted attention and successfully used to determine trace levels of mercury(II) in electro-analytical chemistry[15-17], due to their advantages of inexpensive, easy fabrication, simple operation, sensitivity and fast in response[18-20]. Some studies reported various conducting polymers such aspolythymine-methylene blue[14], graphene[21], and graphene-Au[17] have been used in modified electrodes to detect heavy metal ions with promising results. Furthermore, the materials safe and green which are desirable for electrochemical sensing applications as compared to conventional materials[22]. The main objective of the present paper was to develop a simple, fast, and practically useful technique for sensitive and selective determination of Hg^{2+} ions.

In this work we synthesised the complex of $[ZnSO_4\{ZnCl_2(u\text{-}S\text{-}CH_2CH_2NH_2\}]n$(CS-Zn), and obtained the pure substance by solvent evaporation method. We report herein the glass carbon

electrode was modified with complex of CS-Zn, obtained CS-Zn/GCE electrodes as sensors for determination of Hg^{2+} in solution. Directly modified GCE with complex, changed the two kinds of materials of ligand and metal salt modified electrodes. We explored the electrochemical response of CS-Zn/GCE electrodes to the presence of Hg^{2+} and other interfering heavy metal ions using differential pulse voltammograms(DPVs) were studied.

Experimental

Materials

Acid complex of $[ZnSO_4\{ZnCl_2(u\text{-}S\text{-}CH_2CH_2NH_2\}]n$ was synthesised by chemical synthesis method, and purified by the solvent evaporation method. All the other chemicals were analytical reagent in the experiment.

Apparatus and measurements

Electrochemical measurements were performed on CHI650C eletrochemical workstation(Chenhua Instrument Shanghai Co., Ltd, China, www.chinstr.com). A conventional three-electrode system was used including a bare GCE(3.0mm in diameter) or modified GCE as the working electrode, a platinum foil as the counter electrode, and a saturated calomel electrode(SCE) as reference electrode, respectively. Differential pulse voltammetry was recorded by using the following setting: step potential of 4mV, amplitude of 50mV, pulse width of 0.05s, sample width of 0.0167s, and pulse period of 0.2s. All measurements were performed at 22℃and all potentials in this work were reported with respect to the SCE.

Modified Glassy Carbon Electrode Preparations and Potential Measurements

The glassy carbon electrode was polished with alumina powder(3um, 0.5um, 0.03um) in metallographic sand paper burnish until a mirror shiny surface appeared. Using 2mol/L NaOH, HNO_3(1+1), anhydrous ethanol and secondary water ultrasonic clean the electron sequentially. After processing, dry the electron at room temperature , then put bare glassy carbon electrode in 0.5mol/L H_2SO_4 solution in a potential range of -1.2 to 1.6V scanning until voltammograms stability, activation electrode. The preparation process for CS-Zn modified GCE was described in following work. The electrodeposition process was performed by applying a constant potential range of -1.2 to 1.6V at a scan rate of 50mV/s on a clean GCE for 30 cycles in the 6.0×10^{-3}mol/L CS-Zn solution, then obtained CS-Zn/GCE electrode. Finally, the electrodes were thoroughly washed with water and dried in air.

Results and discussion

Characterization

According to the method of mentioned above, the cyclic voltammogram of electrodeposition is shown in experiment. It can be seen from the experiment, with the increase of scanning circles, the peak current of curves were gradually reduced, polymer film were growing on the electrode surface.

Electrochemical behavior of Hg^{2+} at modified electrode

After performing the electrochemical characterization of modified electrodes, the electrochemical behavior of Hg^{2+} was carefully investigated at the bare GCE and CS-Zn/GCE by cyclic voltammetry in a potential range of -1.2 to 1.6V at a scan rate of 50mV/s. The electrochemical responses obtained on the bare GCE and CS-Zn/GCE in 0.1mol/L KCl solution are given in Fig.1. It was clear that, the oxidation peaks obtained at CS-Zn/GCE is emerged at 0.16V and there is no oxidation peaks obtained at bare GCE, which are well separated from each other. Impressively, the oxidization current is very obvious for Hg^{2+}, indicating its strong sensitivity. Therefore, it is most practical and reasonable for simultaneous determination of Hg^{2+} in the

presence of 0.1mol/L KCl on CS-Zn/GCE.

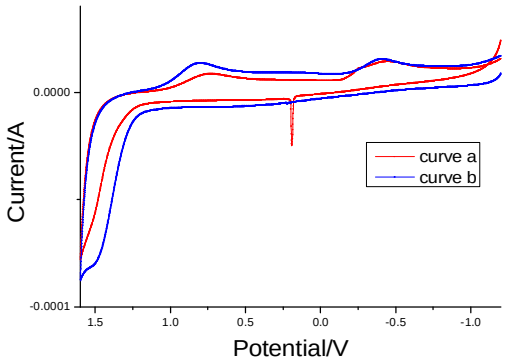

Fig.1 CVs of CS-Zn/GCE(curve a)and bare GCE(curve b) in 0.1mol/L KCl solution containing Hg^{2+}

Electrochemical determination of Hg^{2+}

The determination of Hg^{2+} was performed at the CS-Zn/GCE. Fig.2 illustrates DPV curves of Hg^{2+} with different concentrations in 0.1mol/L KCl solutions. The results shows that the peak current is linear to the concentration of Hg^{2+} in the one concentration intervals, which is 1.8×10^{-5} to 4.5×10^{-4} mol/L. The regression equations is I=-0.2234C-1E-05 with a linear relative coefficient R^2=0.9970. The detection limit is 1×10^{-6} mol/L with a signal-to-noise ratio of 3. The peak current may be explained as follows: with the increasing of Hg^{2+} concentration, the main contributions to the peak currents of Hg^{2+} was adsorbed at the electrode surface, which results in the decreased of the current peaks. The molecules of CS-Zn containing $-NH_3^+$ and -SH which do not involved in coordination with Zn(II) ion, $-NH_3^+$ and -SH can improve Hg^{2+} enriched on the electrode surface by electrostatic attraction.

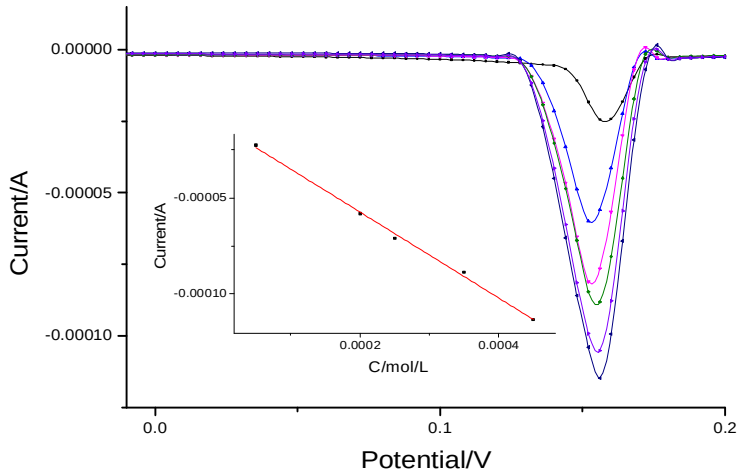

Fig. 2 Differential pulse voltammograms of CS-Zn/GCE in 0.1mol/L KCl containing different concentrations of Hg^{2+}

Analytical Applications

To investigate the practical application of the CS-Zn/GCE for the determination of Hg^{2+}, standard addition experiment in water samples were tested. The recovery experiments were performed by measuring the DPV responses to the samples in which the known concentrations of Hg^{2+} were added. The samples were determined by calibration method and the results were summarized in Table 1. The recovery of Hg^{2+} is in the range from 96.31 to 101.78%, which clearly indicated the applicability and reliability of the method.

Table 1 Determination of Hg^{2+} in water samples using the CS-Zn/GCE

Sample	Original C/(10^{-5}mol/L)	Added C/(10^{-5}mol/L)	Found C/(10^{-5}mol/L)	Recovery R/%	RSD/%
1	2	4.5	6.580	101.78	3.29
2	6	6.5	12.26	96.31	3.11
3	14	25	39.08	100.32	0.55
4	18	15	32.85	99	0.31

Reproducibility, stability and interference of the modified electrode

The reproducibility of the CS-Zn/GCE was examined by DPV in 0.1mol/L KCl solution containing 10% interfering substance and Hg^{2+}. The modified electrode was fabricated based on the simple construction to examine their DPV responses, and the relative standard derivation(RSD) of the anodic peak currents were under 3.3%(Table 1). The repeatability of the electrode was also examined by successive measurements, all data showing that the modified electrode had good reproducibility. Additionally, the stability of the modified electrode was investigated by storing it at room temperature and measuring after two weeks. The peak currents remained 80% of their original values, indicating that CS-Zn/GCE electrode was stable. The influence of some inorganic ions(K+, Zn^{2+}, Na^{+}, $NO3^{-}$, $SO4^{2-}$, Cl^{-}) and organic compounds(ethanol, lysine, methyl alcohol) on the determination of Hg^{2+} was studied. It was found that these substance do not interfere with the determination.

Conclusions

One simple and facile one-step electrodeposition method was developed for preparation of CS-Zn/GCE. The resultant electrodes showed improved sensitivity, reproducibility, anti-interference, and stability for the determination of Hg^{2+}. Moreover, the stable of CS-Zn/GCE toward Hg^{2+} was almost unchanged in the absence and presence interference substance. Meawhile, CS-Zn/GCE displays good linear relation ability for Hg^{2+}.

Acknowledgments

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