Preconcentration and voltammetry of mercury on a functionalized sol-gel thin film modified glassy carbon electrode

Yizhu Guo, Ana R. Guadalupe *

Department of Chemistry, PO Box 23346, University of Puerto Rico, Rio Piedras Campus, San Juan 0931-3346, Puerto Rico

Abstract

A functionalized sol-gel thin film modified glassy carbon electrode has been prepared for the determination of mercury. The tetrasulfide in the sol-gel matrix has a high affinity for mercury species. The chemically integrated functional groups in the sol-gel precursor ensure a high chemical and mechanical stability of the modified electrodes, and therefore a stable and reproducible analytical performance. By medium exchange anodic stripping voltammetry, this modified electrode allows reliable, low cost and interference-free determination of mercury. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Heavy metals are attracting more attention in environmental toxicology and pharmaceutical and biomedical analysis [1–3]. Among those the detection of mercury has been the subject of an increasing number of reports [4]. The toxicity of mercury compounds have caused widespread public concern as a result of several widely publicized disasters in some areas where there had been heavy localized pollution with mercurial compounds [5,6]. There are several techniques employed in metal analysis, for example, atomic absorption spectrometry, atomic emission spectrometry, X-ray fluorescence and neutron activation analysis. These techniques often require laborious sample treatment, enrichment steps and expensive instrumentations.

Electrochemical techniques, in particular anodic stripping voltammetry, have been used extensively for metal ion analysis [7,8], because they possess advantages of little or no sample pretreatment, short analysis time, readily automated, compact, and low cost instrumentation. Many efforts have been made to improve the selectivity and sensitivity of these techniques [9–11]. Chemically

* Corresponding author. Fax: + 787 7567717.

modified electrodes have received much attention for trace metal analysis in recent years [12–15]. As for mercury determination, many modifiers have been employed, which are generally based on two types of interaction: ion-exchange [16,17] and complexation [18–20]. In the former case, cation-exchangers [21] like Nafion, are capable of pre-concentrating cationic metal ions, e.g. Hg^{2+}, and anion-exchangers [22], like oxidized polypyrrole and its derivatives, for anionic species, e.g. $HgCl_4^{2-}$ in water containing a high chloride concentration. However, due to the ubiquitous attractive interaction between opposite-charged species, the selectivity of these materials is relatively low.

On the other hand, analysis based on complexing interaction is more selective, due to the specific interaction between specially-designed ligands and metal ions. Among various chelating resins and complexing agents, the sulfur-containing ones are mostly used as modifiers for mercury determination, due to their high affinity for different species of mercury [23–26]. These modifiers are usually covalently bonded on the electrode surfaces, physically entrapped in a polymer matrix, or mechanically mixed with graphite powder. The chemical binding method is usually time-consuming and requires strict preparation conditions. Physical entrapment or mixing methods usually suffer from leakage of the modifiers from the matrix, and therefore instability, especially under flow operating conditions. Besides, sulfur-containing ligands that normally are mercapto-based resins or agents, with a high affinity of –SH for heavy metals, are readily oxidized [27], during routine analysis procedures, leading to a deteriorating performance of the modified electrodes.

Sol-gel inorganic polymers fabricated from the hydrolysis and condensation of alkoxysilanes have proven to be useful matrices for sensor applications and electrochemical studies because of their mild preparation conditions, physical and chemical stability [28,29]. However, the application of sol-gel materials in electrochemistry is usually hampered by their poor adhesion and easy cracking on various electrode surfaces. Here we report a tetrasulfide modified electrode for the determination of mercury. The functional complexing group is chemically integrated in the skeleton of

the hydrolysis precursor, bis[(3-triethoxysily)-propyl]tetrasulfide (SIS, structure shown in Scheme 1), for the sol-gel films. SIS has been widely used as an excellent coupling agent for various substrates. Distinguished from other sol-gel films, the crackless SIS sol-gel film has high adhesion on various electrode surfaces. All of these unique characteristics ensures a stable and reproducible performance.

2. Experimental

2.1. Reagents

Ultrapure water from the Ultrapure water system (Barnstead) and analytical reagent grade reagents were used throughout. Hg^{2+} stock solution was obtained by dissolving the appropriate amount of its nitrate salt (Aldrich) in 0.01 M HNO_3 solution to a concentration of 10^{-3} M. $HgCl_4^{2-}$ was prepared from its chloride salt in 0.5 M NaCl and 0.01 M HCl solution. A certified Hg^{2+} solution was purchased from Thorn Smith Laboratories. Bis[(3-triethoxysily)-propyl]tetrasulfide (SIS) was from Petrarch Systems. Acetate buffer was obtained by titrating a solution of sodium acetate at the desired concentration with glacial acetic acid to the required pH. All containers and glasswares were treated with 10% HNO_3 before use.

2.2. Apparatus

A spin-coating machine, adapted from a rotating disc electrode, was used to coat the electrode surfaces. Electrochemical experiments were performed with a BAS Electroanalyzer 100W/B interfaced to a 33 MHz Gateway 2000 computer (Bioanalytical Systems, West Lafayette, IN). The
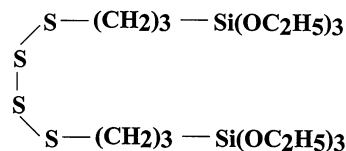
Scheme 1. Structure of SIS.

electrochemical cell consisted of a BAS Ag/AgC1 (3 M NaCl) reference electrode, a platinum auxiliary electrode, and a sol-gel-modified glassy carbon working electrode.

2.3. Sol-gel preparation

The sol-gel solution of SIS was prepared as 5% SIS in ethanol solution, the optimum molar ratio SIS:H_2O was 1:8, using 0.1 M HCl as the catalyst. The solution was prepared overnight before being applied to the electrode surfaces.

2.4. Electrode preparation

The glassy carbon electrodes (BAS, 3 mm diameter) were polished with alumina (0.3 μ)-water slurry and diamond paste, respectively, sonicated and cleaned with distilled water and acetone. Ten microliters of the sol-gel solution were placed on the electrode surface and spun at 3000 rpm for 1 min. All the sol-gel modified electrodes (SIS/GC) were left to dry under room conditions overnight before use.

2.5. Procedure for the determination of Hg^{2+}

Unless otherwise specified, the determination of Hg^{2+} consists of the following four steps: (a) Accumulation step: the electrode was immersed in the stirred (250 rpm) sample solution for a fixed period of time at open circuit; (b) Reduction step: after accumulation, the electrode was rinsed thoroughly with distilled water, and transferred to a 'clean' stripping media, then a reduction potential was applied for a fixed time; (c) Stripping step: after reduction, the anodic stripping of the reduced metal was conducted; (d) Cleaning step: after stripping, the electrode was cleaned by immersing in a stirred (250 rpm) 6 M HCl solution for 2 min. Then the electrode was ready for the next experiment.

3. Result and discussion

3.1. Voltammetric studies

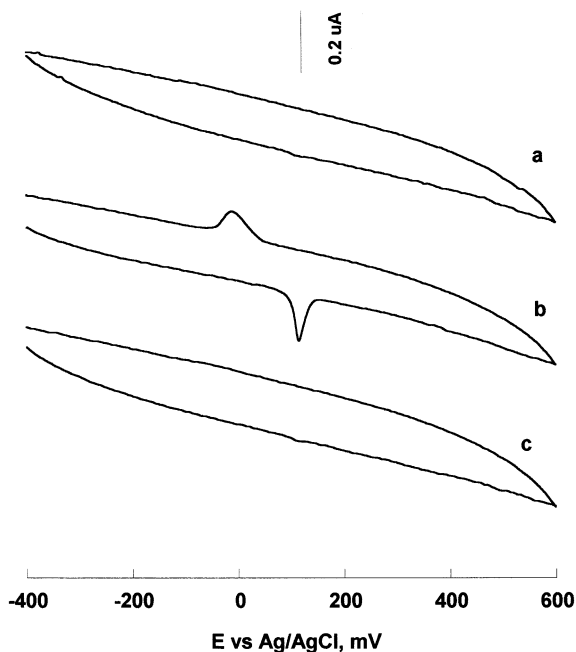The SIS sol-gel modified glassy carbon electrode

Fig. 1. Cyclic voltammograms with the SIS/GC electrode. (a) After accumulation in blank acetate buffer (0.1 M, pH 4.8) for 10 min. (b) After accumulation in acetate buffer containing 5.0×10^{-6} M Hg^{2+}. (c) After (b), then soaked in stirred (250 rpm) 6 M HCl for 2 min. Scan rate: 50 mV s^{-1}; scanning from -0.4 to $+0.6$ V in 0.1 M NaCl + 0.1 M HCl.

showed no electroactivity in the potential range between -1.0 and $+1.0$ V under the experimental conditions used (0.1 M NaCl + 0.1 M HCl), giving a stable signal with a low residual current. Fig. 1(a) shows a cyclic voltammogram at the SIS/GC electrode in 0.1 M NaCl + 0.1 M HCl supporting solution, which had been previously immersed in acetate buffer. In the potential range between -0.4 and $+0.6$ V, no electrochemical process was observed. Meanwhile, when the acetate buffer contained 5.0×10^{-6} M Hg^{2+}, a sharp anodic stripping peak with $E_p = +0.114$ V (at 50 mV s^{-1}) appeared (Fig. 1b). These results indicate the accumulation of Hg^{2+} at the modified electrode surface (whereas no peaks were seen at a bare glassy carbon electrode under the identical conditions), and the peak current was found to increase with increasing concentration of Hg^{2+} in the accumulation media and with accumulating time. This evidence further

supports the complexing interaction and preconcentration of Hg^{2+} at the SIS sol-gel thin film modified electrode surface. There is a cathodic peak at around -0.01 V, however, it is broader than the anodic one. This is consistent with the fact that mercury, like other 3D metals such as copper, cadmium or zinc [30] has poorly-defined reduction waves, however, sharp and intense reoxidation (stripping) waves. That is why anodic stripping techniques are often used for trace metal determination.

Fig. 2(a) shows the linear sweep stripping voltammetry (LSSV) at the SIS/GC electrode after accumulation in 5.0×10^{-6} M Hg^{2+} for 10 min at open circuit. The stripping peak is very sharp, with a width at half height of about 30 mV. It has been observed that mercury electrodeposited at carbon-based electrode is not evenly spread out over the electrode surface but exists as droplets [31]. In our case, the pla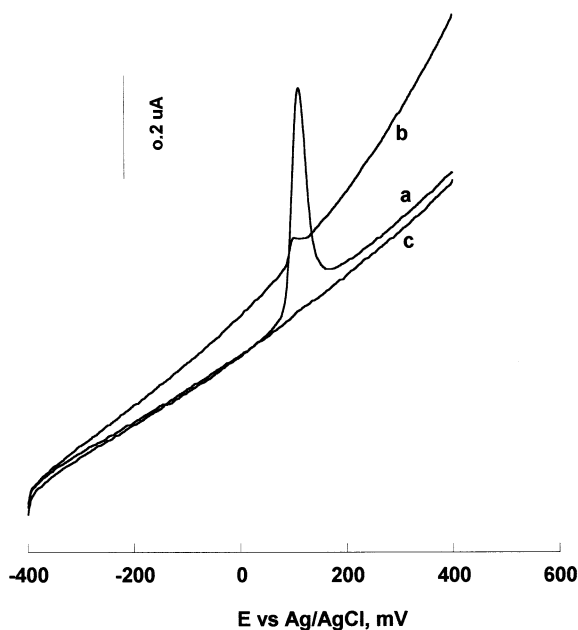cement of the mercury atoms is controlled largely by the complexing sites which are uniformly distributed at the electrode surface, therefore giving a single and sharp stripping peak. Double-peaked anodic stripping curves were observed at a wax impregnated graphite electrode [31] which was attributed to different forms of the metal. The sloped voltammograms are indicative of a relatively high interfacial resistance due to the insulating properties of the film. The thicker the films, the more sloped the voltammograms.

3.2. Electrode cleaning

Two cleaning methods were tried out. The electrochemical method involved an electrolysis process after each measurement, with applied potential at $+0.4$ V for 2 min. The chemical one involved an immersion period in 6 M HCl solution for 2 min.

Fig. 1(c) shows the cyclic voltammogram at the SIS/GC electrode in supporting electrolyte after cleaned in HCl solution. Fig. 2(b, c) are LSSVs at the modified electrode after cleaned electrochemically and chemically, respectively. The second method was found to be more efficient than the first, considering the cleaning efficiency and the background current after cleaning. Therefore the chemical cleaning method was used after each measurement.

3.3. Optimum conditions for stripping

The effects of several experimental parameters on the determination of Hg^{2+} were explored. First of all, different stripping techniques were tested. LSSV was found to give more well-defined stripping peaks and reproducible background currents than Osteryoung square wave stripping voltammetry (OSWSV) and differential pulse stripping voltammeby (DPSV). Therefore, LSSV was chosen for all the measurements, and the following parameters were used: initial potential: -0.4 V, final potential: $+0.4$ V, scan rate: 400 mV s^{-1} and reduction time: 15 s. After accumulation in Hg^{2+} containing acetate buffer at open circuit, the SIS/GC electrode was transferred to a 'clean' supporting electrolyte, then the LSSV was carried out.
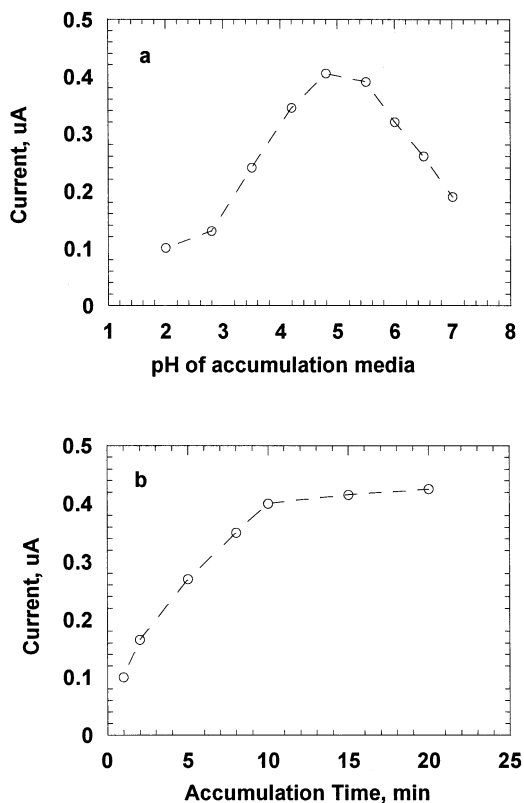

Fig. 2. LSSV with the SIS/GC electrode. (a) After accumulation in acetate buffer containing 5×10^{-6} M Hg^{2+} for 10 min. (b) After the electrode was electrochemically cleaned. (c) After the electrode was chemically cleaned. Scan rate: 400 mV s^{-1}. Reduction time: 15 s.

Fig. 3. Effects of pH of accumulation media (a) and accumulation time, t_a (b) on the stripping peak current. Other conditions same as Fig. 2.

Different buffers such as acetate buffer, phosphate buffer and Britton–Robinson buffer were tested for the complexation and accumulation of Hg^{2+} at the SIS/GC electrode surface. Among those, acetate buffer was found most suitable for the purpose. The pH of the buffer had much effect on the stripping peak current, as shown in Fig. 3(a). In acidic media, a small current was obtained. Two stripping peaks were observed at high pH (pH > 7.0), probably due to hydroxy species of mercury in the base solution. A pH region from 4.0 to 6.0 was optimum, and pH 4.8 buffer was chosen. Accumulation times varying from 30 s to 20 min were tested, and 10 min was chosen, since the stripping peak current trended

to level off after 10 min accumulation, as indicated in Fig. 3(b). Various media were examined as stripping medium to obtain the highest stripping peak current, and it was found that 0.1 M NaCl + 0.1 M HCl gave the best results in terms of peak current and sharpness of the stripping peak.

The variation of peak heights with the potential for reduction (E_r) showed that the peak current increased as the E_r negativity increased until − 0.2 V, where a plateau was reached. The current began to decrease at potentials more negative than − 0.6 V. A potential value for Hg^{2+} reduction of − 0.4 V was chosen for further measurements. Study of the variation of time for reduction from 5 to 60 s revealed that 15 s was enough for the highest stripping peak current and therefore chosen.

3.4. Calibration, reproducibility, detection limit and electrode stability

A calibration plot was conducted under the chosen conditions, i.e. accumulation in pH 4.8 acetate buffer for 10 min at open circuit, reduction at − 0.4 V for 15 s, and stripping in 0.1 M NaCl + 0.1 M HCl solution from − 0.4 to + 0.4 V at 400 mV s^{-1}. Linearity was found from 1.0×10^{-6} to 2.0×10^{-5} M, with a regression equation of i_p (μA) = 0.03 + 0.0729 C (μM) (correlation coefficient 0.999). The reproducibility of the results for ten consecutive measurements at 5.0×10^{-6} M gave a 1.4% relative standard deviation. Furthermore, there was no obvious deterioration in the response during 1 months successive operations with one determination a day. Such performance indicates that the SIS/GC electrode is very stable and reproducible. The high stable response, coupled with easy and low-cost preparation, make this modified electrode an attractive alternative to electrodes commonly used in routine stripping operations. From a signal-to-noise ratio of 3, the estimated detection limit was 5.0×10^{-7} M. However, by further optimizing electrode preparation conditions or use of microelectrode arrays, the detection limit could be further improved.

A certified Hg^{2+} sample from Thorn Smith Laboratories was tested on the SIS/GC electrode. The experimental results for the determination of the sample were obtained from the linear regression equation of the calibration plot. The value (4.94 mg ml^{-1}) was in good agreement with the certified one (5.0 mg ml^{-1}) with RSD% ($n = 5$) of 4.73.

3.5. Anionic and cationic species of mercury

As mentioned in Section 1, the prevailing inorganic mercury species is the anionic complex $HgCl_4^{2-}$ in waters containing a chloride concentration > 0.2 M. Electrodes modified with anion-exchangers (e.g. Tosflex) and cationic polypyrrole derivatives have been reported for the ion-exchange of trace $HgCl_4^{2-}$ followed by electrochemical detection. In the foregoing paragraphs, the SIS/GC electrode was demonstrated feasible for cationic species of mercury, Hg^{2+}. Fig. 4 shows the LSSV at the SIS/GC electrode after accumulation in 5×10^{-6} M $HgCl_4^{2-}$ solution for 10 min.
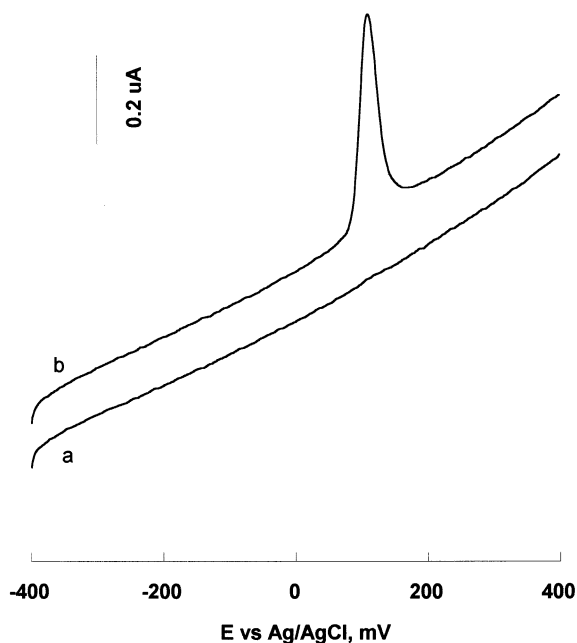
Fig. 4. LSSV at SIS/GC electrode after accumulation in 5.0×10^{-6} M $HgCl_4^{2-}$ for 10 min (b) and after accumulation in blank acetate buffer (a). Other conditions same as in Fig. 2.
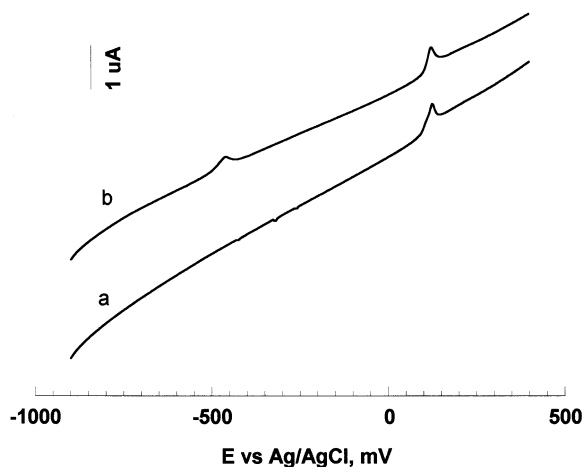
Fig. 5. LSSVs with the SIS/GC electrode. (a) After accumulation in acetate buffer containing 1×10^{-5} M Hg^{2+} for 10 min. (b) After accumulation in acetate buffer containing 1×10^{-5} M Hg^{2+}, 1×10^{-5} M Cd^{2+}, 1×10^{-5} M Pb^{2+} and 1×10^{-5} M Cu^{2+} for 10 min. Scan rate: 400 mV s^{-1}. Reduction time: 15 s.

It was found that a similar magnitude of stripping peak currents was obtained for the cationic and anionic species. That is, the SIS/GC electrode surface is effective for the complexation of different species of mercury, regardless of whether their charge states are positive or negative. This property holds promising applications for the determination of the total amount of mercury in inorganic species. The application of SIS/GC electrode in the determination of various species of mercury, charged, neutral and atomic ones, is being exploited.

3.6. Interferences

Metal ions may cause interference if, under the conditions used, they effectively compete for complexation with the SIS sites. Studies on the effect of foreign ions on the LSSV response at the SIS/GC electrode show that a 500-fold excess of Ca^{2+}, Ba^{2+}, Fe^{3+}, a 50-fold excess of Ni^{2+}, Co^{2+}, Bi^{3+}, and 20-fold excess of Zn^{2+} (relative to Hg^{2+}) did not interfere under the experimental conditions. Besides Hg^{2+}, Cu^{2+}, Pb^{2+} and Cd^{2+} usually compete for the complexation of sulfur-containing chelating reagents. Fig. 5(a, b) are the

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LSSVs of 1×10^{-5} M Hg^{2+} on the SIS/GC electrode in the absence and presence of 1×10^{-5} M Cd^{2+}, 1×10^{-5} M Pb^{2+} and 1×10^{-5} Cu^{2+} in the accumulation solution. It shows that only Pb^{2+} competes for the complexation of SIS sites under the tested conditions, and the peak current for Hg^{2+} in Fig. 5(b) decreased only about 2% compared with that in Fig. 5(a). This indicates that the tetrasulfide complexing sites have a much higher affinity for mercury than for other metals, indicating a good selectivity for mercury determination.

4. Conclusions

The above results show that the application of the SIS/GC electrode in stripping analysis is very promising. The functional group (tetrasulfide) is chemically integrated in the skeleton of the sol-gel film which adheres tightly on various electrode surfaces. The simple one-step preparation procedure allows rugged and low-cost electrode fabrication. This chemically and mechanically stable characteristic ensure a prolonged-life and reproducible performance of the modified electrodes. The detection limit could be improved by further optimizing electrode preparation conditions or use of microelectrode arrays.

Acknowledgements

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