Self-assembled monolayers of 2-mercaptobenzimidazole on gold: stripping voltammetric determination of Hg(II)

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Abstract

Monomolecular level modification of electrode surfaces through a self-assembly approach is, of late, gaining importance in view of its many functional applications in areas such as molecular electronics, molecular recognition, electron transfer studies and electroanalysis. Self-assembled monolayer (SAM) modification of a gold electrode with 2-mercaptobenzimidazole (MBI) has been achieved. On this modified electrode, anodic stripping voltammetric determination of mercury at ppm/sub-ppm level concentrations has been successfully attempted. Pre-concentration, prior to stripping, has been effected through a non-electrolytic process involving chemical interactions between MBI and Hg(II). The results are described and discussed with a plausible scheme.   ©2000 Elsevier Science S.A. All rights reserved.

Keywords: 2-Mercaptobenzimidazole; Self-assembled monolayer; Mercury(II); Anodic stripping voltammetry

1. Introduction

In recent years, the interest in *chemically modified electrodes* has increased, particularly because of their ability to enhance the sensitivity and selectivity of electroanalytical techniques. Modification of an electrode surface [1,2] can be achieved by different methods such as chemisorption, covalent binding, polymerization, etc. An especially attractive approach that has been increasingly employed in the last decade involves the formation of a nano-thin film of the desired material on the electrode surface through the method of *self-assembly* [3]. These films are monomolecular layers and are called *self-assembled monolayers* (SAMs). SAMs exhibit a high degree of organization and are spontaneously formed as a consequence of immersing a solid surface into a solution consisting of amphifunctional molecules. The ability to predesign the monolayer on a molecular rationale, introducing specific interactions between the monolayer and the analyte, should enable tailoring of surfaces and acquiring them with specific properties and functions. The utility of SAMs for different applications like sensors and molecular electronics has been described well in [3,4]. The usefulness of SAM-modified electrodes for catalysis [5], molecular gating [6], molecular recognition [7] and electron transfer studies [8] has been reported from our laboratories.

SAMs offer substantial advantages in analytical electrochemistry. The molecular dimensions of the layer would facilitate rapid diffusion of the electroactive species towards the electrode surface as compared with the polymer films and, at the same time, reduce undesired and often adverse accumulation of species close to the electrode surface. Additionally, the presence of a SAM on the electrode surface would impart selectivity and high sensitivity through the specific interactions between the molecules of the monolayer and the analyte species. The application of a SAM of 2-mercaptobenzimidazole (MBI) for the estimation of Hg(II) has been attempted in the present investigations.

MBI is a well-known analytical reagent for mercury. It has been widely used as a precipitating agent for gravimetric determinations and also as a spectrophotometric reagent [9]. Thus, MBI modification should provide electrodes suitable for voltammetric estimation of Hg(II) and only a very few attempts have been reported. A carbon paste modified electrode containing MBI immobilized onto a silica gel has been described [10]. Again, MBI has been covalently linked to a glassy carbon electrode surface and the modification procedure is tedious and complicated involving electro-oxidation of the glassy carbon surface followed by silanization, etc. [11]. In yet another attempt MBI has been immobilized on the glassy carbon electrode by electropolymerization [12]. On the other hand, the self-assembly approach which offers an elegant methodology involving a very simple modification

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procedure has been adopted here. Moreover, the pre-concentration step preceding the stripping is achieved through a non-electrolytic process, which could enable selective accumulation of analyte species through purely chemical interactions between the analyte and the modifier species. The methodology employed in this study is described in Scheme 1, based on which a gold electrode has been modified with a SAM of MBI and its application to the stripping voltammetric determination of Hg(II) at low levels is described here for the first time.

2. Experimental

Voltammetric experiments were performed with a Wenking potentioscan (POS 73) and *X–Y* recorder (Rikadenki, model RW-201T). A conventional three-electrode cell consisting of a gold working electrode, a platinum auxiliary electrode and a mercury | mercurous sulfate reference electrode were used. All the potential values mentioned in this study are against the above reference electrode. A buffer solution consisting of 0.1 M sodium thiocyanate and 0.1 M sodium nitrate was used as the supporting electrolyte in the voltammetric experiments. The pH of the buffer solution was varied from 2.0 to 7.0 by the addition of dilute nitric acid.

All chemicals used were of analytical grade and triply distilled water was used for the preparation of solutions. Stock solutions of Hg(II) were prepared by dissolving AR grade mercury in the minimum required amount of nitric acid and were then appropriately diluted prior to experiments.

The gold disc (1 mm diameter) working electrode was polished to a mirror-finish using fine emery papers (2/0 to 5/0) followed by an alumina slurry (0.05 μm). The electrodes were then cleaned by sonication in water for 2 min. The cleanliness of the electrode surface was ascertained by recording the cyclic voltammograms (CVs) for the gold oxide formation and its reduction. Whenever necessary, the electrodes were further cleaned by keeping in Piranha solution for 10 min, washing thoroughly with water and then cycling in 0.5 M H_2SO_4 between -0.2 and 1.2 V at a scan rate of 20 mV s^{-1} for about 10 min.

A SAM of MBI was formed on the gold electrode by immersing the electrode overnight in an ethanol solution of MBI (10 mM). The electrode was taken out, rinsed thoroughly with ethanol followed by water and then air-dried. The modified electrode is hereafter referred to as Au | MBI.

2.1. Analysis of Hg(II) using chemical pre-concentration

Hg(II) was chemically pre-concentrated by immersing the Au | MBI electrode in the buffer solution (pH 5.0) containing Hg(II) for 5 min. The concentration of Hg(II) in the buffer solution was varied from 0.5 to 3 ppm. The electrode was taken out, thoroughly washed with water and then kept in the cell containing only the buffer solution (pH 5.0) at a potential of -0.7 V for 10 min to enable the reduction of the Hg(II).
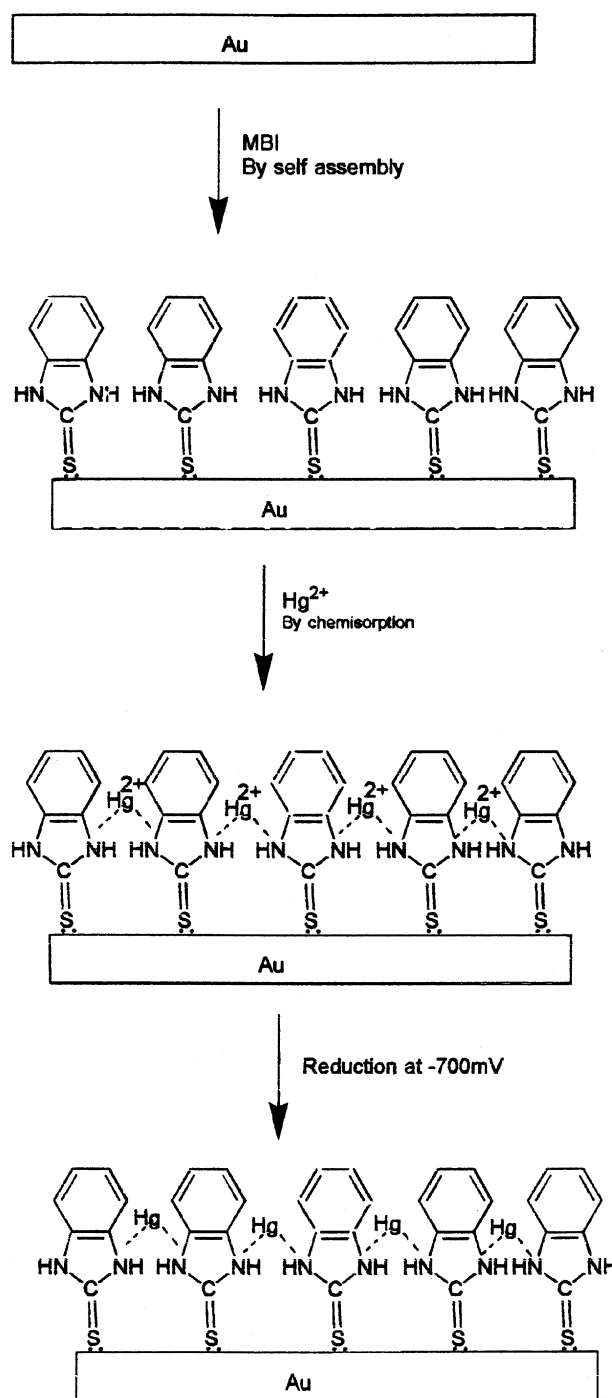
Scheme 1. Formation of the self-assembled monolayer of 2-mercaptobenzimidazole on Au and non-electrolytic pre-concentration of Hg at Au | MBI electrode.

Subsequently, the electrode potential was swept to -0.1 V at a scan rate of 50 mV s^{-1} and the stripping voltammograms recorded.

3. Results and discussion

MBI is a heterocyclic thiol containing an aromatic ring. It is well known that the strong chemical affinity between the

mercaptan group and the Au surface easily enables the formation of SAMs of alkane thiols on Au [13,14]. Hence, MBI containing the thiol group will self-assemble to form a stable monolayer on Au, analogous to the formation of a SAM on Au by mercaptobenzothiazole which is structurally similar to MBI [8,15].

3.1. Stripping voltammetry of Hg(II)

The stripping voltammetric estimation of Hg(II) was studied on Au|MBI after a chemical pre-concentration step. The pre-concentration, as mentioned earlier, was effected by immersing the electrode in the buffer solutions containing different concentrations of Hg(II). Fig. 1 presents the stripping voltammograms obtained on the Au|MBI electrode for different Hg(II) concentrations. The stripping current increases proportionally with increase in concentration. Fig. 2 describes the plot of 'stripping current versus concentration' for the Hg(II) estimation on the Au|MBI electrode. It is found to be linear in the concentration range of 0.5 to 3 ppm with good sensitivity in the sub-ppm range.

To understand the role of the MBI monolayer in the chemical pre-concentration of Hg(II), blank experiments were performed on the unmodified electrode surface. The chemical pre-concentration procedure, as described in Section 2.1, was carried out on a bare Au electrode and the stripping voltammogram was obtained by scanning the potential from -0.7 to -0.1 V (Fig. 3(a)). Moreover, the cyclic voltammogram recorded on bare Au from the thiocyanate buffer (pH 5.0) alone (Fig. 3(b)) is featureless. Thus, it can be seen from

Fig. 2. Calibration graph for the ASV estimation of Hg(II) at Au|MBI electrode.

Fig. 3. (a) Anodic stripping voltammogram recorded at bare Au electrode. Experimental conditions are the same as in Fig. 1; Hg(II) concentration during pre-concentration was 5 ppm. (b) Cyclic voltammogram on bare Au electrode from the thiocyanate buffer (pH 5.0) at a scan rate of 50 mV s^{-1}.

Fig. 3 that the stripping signal for Hg(II) is totally absent under the experimental conditions. This shows that the chemical pre-concentration of Hg(II) does not take place on a bare Au surface.

The accumulation of Hg(II) ions at the modified electrode through chemical pre-concentration and its subsequent stripping voltammetric estimation can be understood as follows. As described in Scheme 1, the MBI SAM on Au is formed through the Au–thiolate linkage and the complexation of Hg(II) with MBI molecules takes place at its nitrogen centres. MBI is known to exist in two different structural forms. The chemisorption of MBI on Au and Ag surfaces has been well studied and it is known that, on a gold substrate, MBI is adsorbed in the thione form leaving the nitrogen centres free
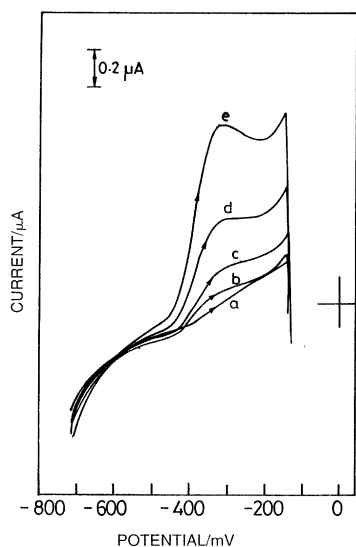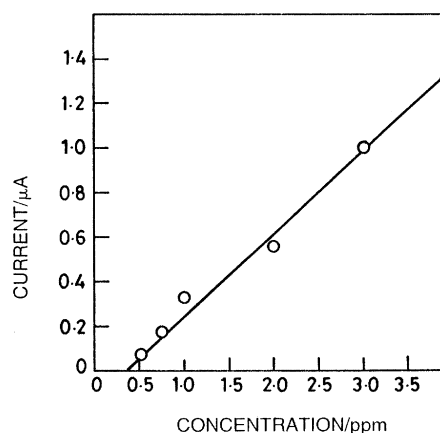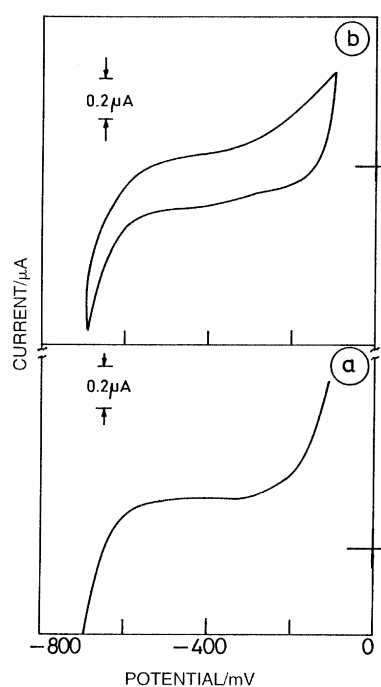

Fig. 1. Anodic stripping voltammograms of Hg(II) at Au|MBI electrode. Prior to stripping, Hg(II) was chemically pre-concentrated on the electrode by immersion in Hg(II) solution for 5 min followed by reduction to Hg at -0.7 V for 10 min. The Hg was then immediately stripped by scanning the electrode potential from -0.7 to -0.1 V at a scan rate of 50 mV s^{-1}. A solution containing 0.1 M NaSCN and 0.1 M NaNO$_3$ (pH 5) was used as the electrolytic medium for both cathodic reduction and anodic stripping. The Hg(II) concentration during pre-concentration was (a) 0.5, (b) 0.75, (c) 1, (d) 2 and (e) 3 ppm.

for complexation [16]. This is supported by our earlier studies [17] which showed that mercaptobenzothiazole, a compound structurally similar to MBI, is also adsorbed on Au only in the thione form. After the chemical pre-concentration, the application of a cathodic potential (namely, -700 mV) enables the reduction of Hg(II) ions at the surface. This is followed by the oxidative stripping of Hg when the potential is swept to -100 mV, and a characteristic stripping voltammogram is obtained. The possibility of the complexed Hg(II) undergoing a chemical reduction to Hg is ruled out since the Au|MBI electrode, after chemical pre-concentration but without electrochemical reduction at -700 mV, did not yield any stripping current.

The values of charge computed for the stripping of Hg from the anodic stripping voltammograms obtained at different Hg(II) concentrations are in the range of 10 ± 2 to 50 ± 5 μC cm^{-2} which correspond to a sub-monolayer coverage of Hg. (Normally, a full monolayer coverage of a divalent metal corresponds to a stripping charge of about 400 μC cm^{-2} [18].) A sub-monolayer coverage arising from the direct adsorption of Hg(II) on the MBI-free Au surface is ruled out since non-electrolytic pre-concentration of Hg(II) on a bare Au electrode yielded no stripping current under identical experimental conditions (cf. Fig. 3(a)). This strongly supports the fact that Hg(II) is only adsorbed on the modified electrode through complexation with MBI molecules.

The above receives further corroborative support from studies on the influence of pH on the chemical accumulation process. The pH of the buffer solution used for the chemical pre-concentration was varied in the pH range 2.0 to 7.0 by the addition of very small amounts of diluted nitric acid. At low pH, no stripping peak was observed indicating thereby the absence of Hg(II) on the electrode surface. This shows chelation is not favoured at low pH. As the pH gradually increased, the stripping peaks could be observed and the maximum peak height was achieved when the pH was maintained at 5.0. At low pH values, the complexation reaction between Hg(II) ions and MBI is inhibited because the nitrogen centres of MBI undergo protonation. At high pH values, the hydrolysis of mercury interferes with the accumulation and the modifier species are likely to be removed from the electrode surface through alkaline cleavages.

Considering the exploratory nature of the present work, a detailed study of the interferents was not made. Addition of an equimolar concentration of Cu(II) influenced the determination of Hg(II). In voltammetric determinations of trace metals at chemically modified electrodes, the nature of interference can be of two types. In one case, the interferent species, either electro-active or not, could compete with the analyte species for complexation at the binding sites during pre-concentration. In the second type, an electro-active interferent could interfere during the anodic stripping process if its stripping potential overlaps with that of the analyte. Detailed investigations in this direction are to be pursued. Nevertheless, it can be seen from the present results that detection limits in the sub-ppm range could be achieved with SAM-modified electrodes and chemical pre-concentration. There is further scope to push down the detection limit by one or two more orders of magnitude by employing the differential pulse mode for the stripping process. Moreover, in solutions of high analyte concentrations, the analysis could be carried out by decreasing the accumulation time to give a good stripping voltammogram. Thus, no upper concentration limit is observed for this method.

4. Conclusions

The results of this preliminary investigation demonstrate the formation of a SAM of MBI on a gold electrode. The modified electrode in combination with non-electrolytic pre-concentration could be used for the anodic stripping voltammetric determination of Hg(II) in ppm and sub-ppm concentration levels.

Acknowledgements

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