STUDY OF AN ELECTROCHEMICAL BEHAVIOUR OF MODIFIED BINARY SELF-ASSEMBLED MONOLAYERS FOR ENHANCING SENSITIVITY OF Hg(II) DETECTION

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Abstract

In the present study, an electrochemical behavior, the charge (Q) estimated from reductive desorption voltammograms, of the binary self-assembled monolayer (SAMs) prepared by immersing the primary 4-pyridineethanethiol (PET-SAM) into the solution of 2-aminoethanethiol (AET) was investigated for enhancing the sensitivity of Hg(II) detection. The optimized conditions was selected to be 20 minutes for immersion in the concentration of 0.1 mM AET solution to reach the maximum peak current (i_{pHg}) obtained by differential pulse voltammetry for detection of Hg(II). Interestingly, the variation of Q by these factors was similar with that of i_{pHg}, indicating the role of the introduction of the second component, AET, in kinetic formation of the binary SAMs for enhancing sensitivity of Hg(II) detection at ultra trace level.

Keywords. Self-assembled monolayer, binary SAMs, 4-pyridineethanethiol, 2-aminoethanethiol.

1. INTRODUCTION

The use of alkanethiol self-assembled monolayers (SAM) to modify different types of electrode for improving sensitivity and selectivity of heavy metal analysis has been attractive to numerous studies. For example, 4-mercapto-n-alkylpyridinium modified gold electrode was employed for detection of Cr(VI) as reported by I. Turyan [1]; or based on binding between the carboxylic terminal group of 3-mercaptopropionic acid modified gold electrode with Cd(II), D. Mandler was successful in detection of Cd(II) [2]; meanwhile 2,5-dimercapto-1,3,4 thiadiazole exhibited a significant sensitivity with Pb(II) as presented by H.Q. Luo [3]. In our previous study, we used SAM of 4-pyridineethanthiol modified gold nanoparticles (Au-NPs) on glassy carbon electrode (GCE) to detect Hg(II) at ultralow concentrations [4]. We showed that N-pyridine terminal group could selectively bind to Hg(II). Thus, preconcentration of Hg(II) onto the modified electrode surface can take place without applied potentials. This result brings advantages in increasing the selectivity in analysis of Hg(II). Since, the obtained results in this field provide a new concept in the use of nanostructured materials prepared by self assembly to modify solid substrates for detection of heavy metal ions.

Recently, we investigated the formation of binary SAMs composed of PET and AET by Fourier Transform Infrared Spectroscopy (FTIR), and discovered that this type of binary SAMs could enhance the sensitivity of Hg(II) analysis due to conformation of PET molecules during introducing AET from solution phase. The obtained results played a crucial role of the second component, AET, in self assembly of PET during formation of the binary PET-AET SAMs. Introduction of such second component, thus, could effectively influence the binding of the N-pyridine terminal groups of SAMS with Hg(II) in solution during preconcentration. Therefore, it is essential to study electrochemical behaviors of the binary PET-AET SAMs to provide more evidences for correlating data obtained from different techniques. This is very useful to bring further knowledge on the formation of the new nanostructured materials used in the field of electrochemical sensors. Hence, in the present study, we investigated effects of the immersion time and the concentration of AET in solution on the amount of PET molecules in the binary SAMs of PET-AET, as well as influences on the sensitivity of Hg(II) detection by differential pulse Voltammetry (DPV).

2. EXPERIMENTAL

2.1. Reagents

4-pyridineethanthiol hydrochloride (PET), 2-aminoethaniol (AET) purchased from Wako Chemicals was used without further purification. Hg(NO$_3$)$_2$ stock solution (5.0×10^{-3} M) purchased from Merck was used for dilution. More diluted solutions were prepared daily from the stock solution. All other reagent grade chemicals were used without further purification.

2.2. Apparatus

Electrochemical measurements were performed with a home-made potentiostat/galvanostat. A three-electrode configuration was used for measurements, which consists of binary SAMs modified Au-NPs/GCE working electrode, calomel (saturated) reference electrode and Pt counter electrode.

2.3. Pretreatment of GCE

The GCE was prepared by cutting available plate-shaped glassy carbon (Tokai GC-20 company, NY) into cylinder-shape and mounting into Teflon tubes holder so that only a circular area of 0.071 cm^2 was exposed to the electrolyte. GCE was polished with emery paper. Upon polishing, GCE was rinsed and ultra sonicated in distilled water for 3 minutes, rinsed and dried in air. GCE was then electrochemically pretreated as reported in elsewhere [5].

2.4. Preparation of Au-NPs, primary PET-SAM and binary PET-AET SAMs

Electrochemical deposition of Au-NPs on the GCE surface was carried out at potential of + 0.5 V in 1.0×10^{-3} M HAuCl$_4$ solution for a desired time under stirring rate of 50 rpm.

The primary PET-SAM was prepared by immersing Au-NPs/GCE into 1.0×10^{-6} M ethanolic solution of PET over night at room temperature.

The binary PET-AET SAMs was prepared by immersing the primary PET-SAM into ethanolic solution of AET with various concentrations for duration from 1 to 60 minutes to study kinetic process.

2.5. Electrochemical behaviors

The electrochemical behavior of the primary and binary SAMs was investigated by cyclic Voltammetry (CV) for reductive desorption. Measurement was performed in 0.5 M KOH solution, from 0.0 V to - 1.1 V at scan rate of 0.1 V. s^{-1}.

Detection of Hg^{2+} was performed with two steps. First, Hg(II) was chemically preconcentrated by immersing PET-SAM/Au-NPs/GCE in a 0.1 M KCl + HCl solution, pH 6.7, containing Hg(II) for a desired time under open circuit potential. During the preconcentration, the solution was efficiently stirred at 60 rpm. Second, the reduction of Hg(II) accumulated onto PET-SAM/Au-NPs/GCE was obtained by differential pulse Voltammetry (DPV). The Voltammogram was recorded in a 0.1 M KCl + HCl solution, pH 3.0; the potential was scanned from + 0.7 V to + 0.3 V with pulse amplitude 0.050 V; pulse time 0.040 s; Voltage step 0.005 V; step time 0.08 s; sweep rate 0.05 V s^{-1}.

All measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

In order to study electrochemical behavior of the binary SAMs, reductive desorption processes in KOH solution was investigated by cyclic Voltammetry. Here, influences of introducing the second component, AET, into the primary PET-SAM to form binary PET-AET SAMs were studied by varying the immersion time in AET solution ($t_{immer.}$) and the concentration of AET (C_{AET}). As seen in both typical cyclic Voltammograms in figure (1a) and (1b), the variation in $t_{immer.}$ and C_{AET} both gives an appearance of two peaks on each voltammogram. Of those, the peak at potential of - 1.05 V (Peak I) corresponds to the reductive desorption of PET-SAM. Meanwhile the peak appeared at -0.85 V (Peak II) is attributed to the reduction of AET-SAM on gold surface [6]. We used the term of charge (Q) estimated from area under the peak, to evaluate the effects of introduction of AET because Q roughly reflects the amount of adsorbed alkanethiolate molecules in SAMs. Interestingly, as shown in inset (1a), an increase of $t_{immer.}$ up to 20 minutes in AET solution at concentration of 0.1 mM leads to significant increase of Q at Peak I but not Q of Peak II. This means that the immersion of PET-SAM in AET solution can facilitate the conformation of PET molecules laying on the Au-NPs surface due to intermolecular interactions, leading to increase of number of PET molecules in domains. This can be interpreted that after diffused from solution, AET molecules adsorb on vacant sites on Au-NPs and change their orientation from laying down to standing up states for stabilization [7, 8]. During

this process taking place, AET molecules are able to cause neighboring PET molecules become more organized assembly due to intermolecular interactions. This makes the increase in number of stabilized PET molecules. However, further introduction of AET into PET-SAM taking place for a longer time can induce a removal of PET molecules in the binary SAMs because the formation of monolayer self assembly is a thermodynamic process [9], adsorbed PET molecules, thus, having weak lateral interactions can diffuse from the Au-NPs surface to the solution phase. This phenomenon in our study can be obtained as seen in inset (1a) when $t_{immer.}$ increases over 20 minutes.

As discussed, the conformation of PET molecules in the primary SAM takes place as introducing AET from solution. The formation of binary PET-AET SAMs, thus, is affected by number of AET molecules adsorbed on vacant sites on the Au-NPs surface. Therefore, AET concentration dependence of Q at $t_{immer.}$ of 20 minutes was also investigated. As seen in inset (1b), Q of Peak I clearly reaches to the maximum value at concentration of 0.1 mM, and followed by a decrease with increasing the concentration.
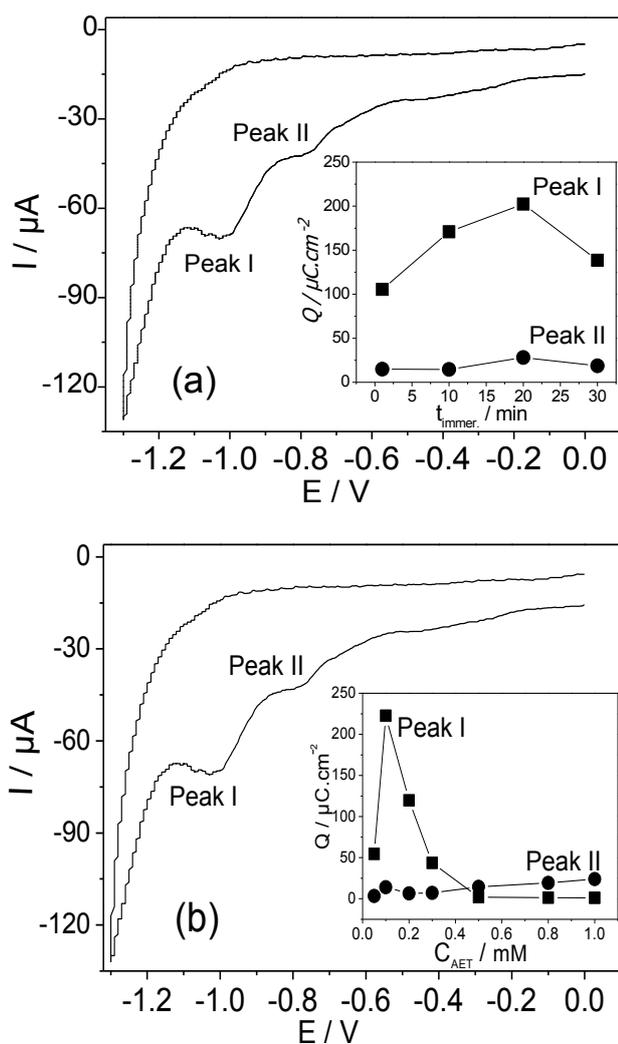

Fig. 1: Typical cyclic voltammograms for reductive desorption of the binary PET-AET SAMs prepared at concentration of 0.1 mM AET solution and 20 minutes immersion. Insets: the dependence of charge on immersion time in AET solution at concentration of 0.1 mM (a); and concentrations of AET at immersion time of 20 minutes (b)
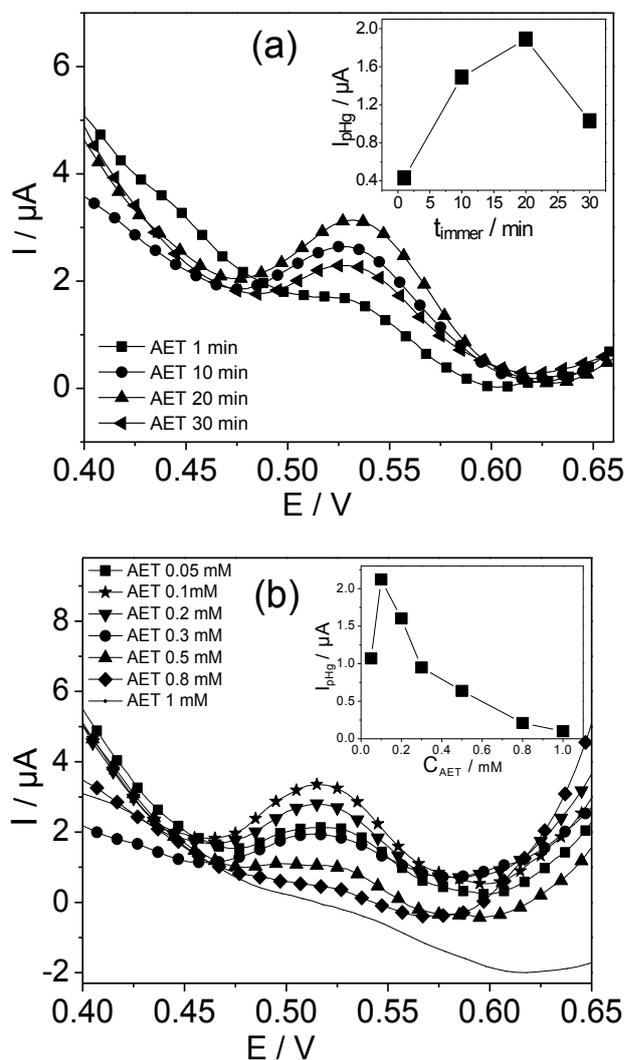

Fig. 2: DPV for detection of Hg(II) at concentration of 1.0 ppb by using binary PET-AET SAMs prepared by immersing PET-SAM in 0.1 mM AET solution for various immersion time (a) and at 20 minutes in AET solution with different concentrations (b). Insets: corresponding variation of the peak current of Hg(II) with immersion time and concentration of AET

Meanwhile, Q of Peak II increases gradually.

Such variation in Q of both Peak I and Peak II suggests the replacement of a number of PET molecules on the primary SAM with AET molecules from solution phase. A similar evidence has also been reported by another authors when a thiol SAM on a metal substrate is exposed to an organic solution containing thiol or alkyl disulfides [10-12]. The details of this replacement reaction have been studied in view of its importance in studying the mechanism of formation of multi-component SAMs [13, 14].

The role of the introduction of AET into the primary PET-SAM to form the binary PET-AET SAMs in detection of Hg(II) is presented in figures 2, in which voltammograms for detection of Hg(II) by using binary PET-AET SAMs prepared in various t_{immer} (figure (2a)) and C_{AET} (figure (2b)) are depicted. As seen in both figures, there is a peak appeared at $E = +0.52$ V, corresponding to reduction of Hg(II) bound to functional groups of the binary PET-AET SAMs [5]. The variation of the height of peak by varying t_{immer} and C_{AET} is presented in inset (1a) and (1b), respectively. Interestingly, it can be seen in both insets that there is a good consistence in the tendency of variation between i_{pHg} and Q as varying C_{AET} and $t_{immer.}$. This strongly indicates that C_{AET} and $t_{immer.}$ are two key factors that can significantly affect to the amount of PET molecules and their self assembly during introduction of AET into the primary PET-SAM, leading to effects on sensitivity of Hg(II) detection. Such variation of Q, is an electrochemical behavior, is completely consistent with results obtained by FTIR technique as reported in our previous study.

4. CONCLUSION

In this study, the electrochemical behavior of binary PET-AET SAMs has been investigated by reductive desorption method for enhancing the sensitivity of Hg(II) detection. The obtained results indicated the role of introduction of AET in kinetic formation of the binary SAMs. The optimum concentration of AET and immersion time has been selected to prepare the binary SAMs. The sensitivity of Hg(II) detection by the use of the binary SAM has improved two-fold compared with use of single PET-SAM. The obtained results are also consistent with those obtained by FTIR technique, providing further knowledge on the formation of the binary SAMs, in which the conformation of PET molecules caused by AET molecules plays the key role. This result can be helpful for studies of multi-component SAMs by similar technique.

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