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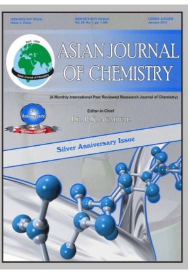

Voltammetric Behaviour of Two Stacking Layers of Copper-Bound 3-Mercaptopropionic Self-Assembled Monolayers on Gold Electrode and Application in Enhancement of Detection of Cu(II)

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Formation of two stacking layers composed of copper-bound self-assembled monolayer (SAM) of 3-mercaptopropionic acid (MPA) for modifying the gold electrode has been studied by electrochemical method. Stack of self-assembled monolayers of 3-mercaptopropionic acid *via* a Cu(II) layer was elucidated by peak potentials and charge values obtained from cyclic voltammetry for reductive desorption of self-assembled monolayer in 0.5 M KOH solution. The attachment of Cu(II) layers to self-assembled monolayers was detected by differential pulse voltammetry with the appearance of a reduction peak at 0.18 V. This modified electrode has been successfully used for enhancing the sensitivity in determination of Cu^{2+} ions at picomolar concentration. The linear range obtained from 1.56×10^{-12}-1.56×10^{-9} M with a correlation coefficient of 0.9962. The detection limit approached to 9.10×10^{-13} M. The electrochemical behaviour of the modified electrode was also obtained for speculating further formation and structure features.

Key Words: Self-assembled monolayer, Two stacking layers, Copper-bound 3-mercaptopropionic acid.

INTRODUCTION

Over the past two decades, the design of electrodes with controllable surface properties has been effectively achieved by employing self-assembled monolayers (SAMs) for widening applications. Of those, self-assembly of multilayer thin films are well known for their potential applications in nonlinear optical uses[1,2], molecular electronics[3] and molecular ruler lithography[4-6]. Among the different approaches leading to well-define multilayer assembly[7,8], methods based on the selective ionic interaction between ω-mercaptoalkanoic acid and copper salt have resulted in particularly stable and easy to prepare systems[9,10]. The advantage of this process is that it does not utilize alkyltrichlorosilane derivatives, which are difficult to purify, mercaptoalkanoic acids are not also moisture sensitive and can be stored for long periods of time[10]. In this multilayer system, a potential problem with multilayer formation has been considered. That is the competition between an acid-copper-acid or/and acid-copper-thiol interactions. Various studies employed long alkyl chain mercaptoalkanoic acid focus on nature of the interfacial layers and the formation of multilayer by using spectrometric methods, such as grazing-angle Fourier transform infrared reflection spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and single-wavelength ellispsometry[3,9,11]. Obtained results indicated that the ω-mercaptoalkanoic acid is attached to the copper-carboxylate surface through the thiol end, forming $-CO_2-Cu-S$ connection[9]. But a small fraction of molecules in the adlayer inverts to bind their $-CO_2H$ group to the surface with Cu^{2+} ions *via* formation of an ionic $-CO_2-Cu-CO_2-$[11]. The oxidation state of copper in the multilayer of copper-bound carboxyl thiolates has been controversial. Ulman *et al.*[12] reported that Cu is present in the +1, whereas Bard *et al.*[3] suggested that copper ion adsorbed to the surface of carboxylate as Cu(II) but is subsequently reduced to Cu(I) upon binding to the thiol.

Due to characteristics of spectrometric methods that multilayer systems composed of long alkyl chain(n) mercaptoalkanoic acid have been used for investigating the structure. However, use of short alkyl chains can be useful for improving the electron transfer that is potentially applicable in the field of electrochemical/bio sensors. Therefore, in this work, we used electrochemical method to attempt elucidate the formation of a system composed of two stacking layers composed of copper-bound SAMs of MPA, n = 2. We expect that the dependence of the reductive desorption peak potential of alkanethiolate SAMs on the Gibbs energy[13] can be helpful in elucidating the presence of the adlayer of SAM in the multilayer system. Furthermore, the presence of Cu(II) layers in the multilayer systems provide electrochemical behaviour of Cu(II) that can also be employed for elucidating the formation as well as the structure of the system based on the oxidation state of copper. In the present paper, we also report an applicability of the system of two stacking layers of copper-bound SAM of MPA, that is effective use for enhancing the sensitivity in determination of Cu^{2+} ions at trace concentration without electrochemical pre-concentration. The use of the modified electrode can bring advantages such as avoiding the deposition of unknown electrochemically active species, enhancing the sensitivity while the area of electrode can be limited. Determination of copper at untralow concentration is well known to be meaningful because it is an essential micronutrient in at least 30 enzymes[14] and plays fundamental in many metabolic processes, in the formation of red blood cells and the maintenance of normal brain function[15].

EXPERIMENTAL

3-Mercaptopropionic acid (MPA) (Wako Chemicals) and 10-carboxy-1-decanethiol (MUA) (Aldrich) were used without further purification. The stock solution of Cu^{2+} (1000 mg L^{-1}) purchased from Merck was prepared in 0.1 M nitric acid. More diluted solutions were prepared daily from the stock solution. All other reagent grade chemicals were used without purification.

All voltammetric measurements were performed with a home-made potentio-galvanostat instrument (PGS-HH5) analyzer. A conventional three-electrode cell consisted of saturated calomel reference (SCE) electrode and a platinum wire auxiliary electrode and studied working electrodes. Cyclic voltammetry was used for studying the reductive desorption of SAMs built up on the electrodes in 0.5 M KOH solution. Measurements were recorded from 0.0 V to -1.1 V at scan rate of 0.1 V s^{-1}. The attachment of Cu(II) to SAMs was studied by differential pulse voltammetry (DPV). All measurements were performed at room temperature.

Modification of the gold electrode with two stacking layers of copper-bound MPA for accumulation of Cu(II) ions under open circuit: The working electrode with geometrical area of 0.0314 cm^2 was made from the polycrystalline gold plate by Metrohm (6.1204.140, Switzerland). The modification of the gold surface by two stacking layers composed of copper-bound SAMs of MPA is depicted in Fig. 1. The electrode was first polished on 3 μm silicon carbide disk followed by a 0.3 μm aluminum oxide disk. After removal of the trace alumina from the surface by rinsing with distilled water and dry in the air, the electrode was cleaned electrochemically in 0.05 M H_2SO_4 aqueous solution by cycling between -0.2 and 1.7 V at 100 mV s^{-1} until reproducible scans were recorded. The gold electrode was then dried in the air again before immersing into an ethanolic solution of 1 mM MPA for 3 h to form SAM of MPA (step 1). Followed by immersing the SAM of MPA-modified electrode into phosphate buffer solution containing Cu^{2+} ions at pH = 5.7 for a desirable time under stirring at 60 rpm to obtain the first layer of copper-bound MPA layer (MPA/Cu) (step 2). The second layer of copper-bound MPA was then building up again with step 1 to obtain MPA/Cu/MPA (step 3) and followed by step 2 to get MPA/Cu/MPA/Cu (step 4) (Fig. 1).

Determination of Cu^{2+} ions: After accumulation under the open circuit at desirable immersion time in solution containing Cu^{2+} in various concentrations, the modified electrodes were introduced into 0.05 M phosphate solution, pH = 5.7 as reported in elsewhere[16,17] for recording differential pulse voltammograms with negative scan from + 0.5 V to - 0.2 V; pulse amplitude 0.0050 V; pulse time 0.040 s and voltage step 0.050 V and sweep rate 0.008 V s^{-1}.

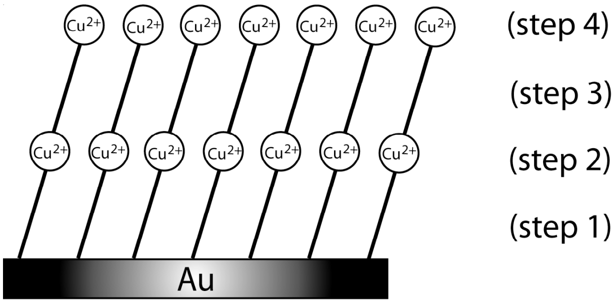

Fig. 1. Schematic illustration of the gold electrode modified with two stacking layers composed of copper-bound SAMs of MPA

RESULTS AND DISCUSSION

Stack of two SAMs of MPA *via* the layer of Cu(II) forming MPA/Cu/MPA: For the purpose of study, the reductive desorption behaviour of SAMs-modified the gold electrode in 0.5 M KOH solution was investigated as shown in Fig. 2. Curve (a) shows the cyclic voltammogram (CV) for reductive desorption of SAM of MPA. Two peaks appeared at - 0.81 and - 0.98 V having the charge estimated from area under the peak (Q) is 1.61 and 2.84 μC cm^{-2}, respectively, can be clearly observed. The appearance of two cathodic peaks is due to polycrystalline gold surfaces are mainly composed of three low-index crystallographic orientations, *i.e.*, the Au(111), Au(100) and Au(110) domains[18,19]. Hence, the different crystal faces exhibit different binding strengths to the chemisorbed MPA molecules. Such obtained feature is almost identical to that obtained by adsorption of cysteine on polycrystalline gold[20-22]. The reduction peaks corresponding with crystal faces have also been reported[20]. Since, it is attributed that the obtained peaks correspond to the reductive desorption of SAM of MPA on Au(111) and Au(100) facets, respectively[20-22].

Modification of the surface of MPA SAM with a layer of copper ions in step 2 occurs by binding between Cu(II) and carboxyl groups[11] to form MPA/Cu. The presence of Cu(II) on the carboxylate surface was detected as shown in Fig. 3. This result will be discussed further in the following part to elucidate the formation of MPA/Cu. Here, we continuously focus on the stack of the adlayer SAM of MPA on the first MPA/Cu to build up MPA/Cu/MPA in step 3 by studying CV for reductive desorption of SAMs. As seen, curve (b) in Fig. 2 shows the potentials of reductive desorption peaks (E_p) and peak areas that are similar with those obtained in curve (a). Hence, these results reflect two possibilities for the formation of the adlayer SAM of MPA in step 3. The first, the adlayer was formed on the surface of Cu(II) layer but not on the gold surface. This is plausible because if MPA molecules continuously adsorbed on the gold surface, it would cause an increase in Q because the reductive desorption process of alkanethiolates in KOH solution takes place at Au-S bond[23]. The second corresponds to none adsorption of the adlayer SAM

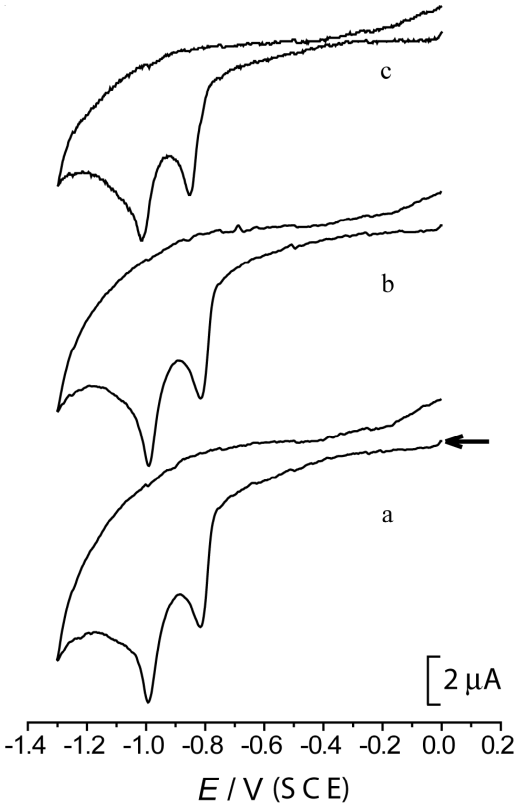

Fig. 2. Cyclic voltammograms for reductive desorption of SAMs-modified the gold electrode: (a) MPA SAM; (b) MPA/Cu/MPA; and (c) MPA/Cu/MUA in 0.5 M KOH solution, v = 0.1 V/s. Arrow denotes the scan direction for curves (a to c)

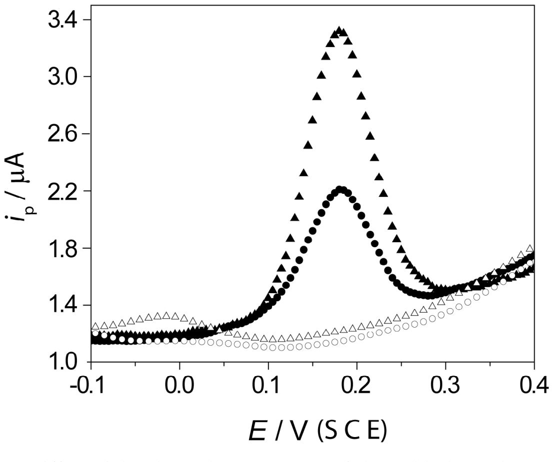

Fig. 3. Differential pulse voltammograms of the gold electrode modified with MPA/Cu/MPA/Cu(▲); MPA/Cu(●) built up in the presence/absence of 1.56 × 10^{-8} M Cu^{2+}; and their backgrounds (△), (○), respectively, built up in phosphate buffer solution at pH = 5.7, immersion time of 20 min. DPV were recorded at pulse amplitude 0.0050 V; pulse time 0.040 s; voltage step 0.050 V and sweep rate 0.008 V s^{-1} in phosphate buffer solution, pH = 5.7

on the surface of Cu(II) layer. In order to prove this possibility is false, we substituted MUA for MPA in step 3 with expectation of increasing n up to 10 which is sufficiently long to increase the Gibbs energy due to the increase in val der Waals interactions between lateral adsorbed alkanethiolate molecules[24,25]. Since, the increase in n can shift E_p to the noble potential[26] for evaluation. It can be clearly seen in curve (c) recorded for reductive desorption of SAMs on MPA/Cu/MUA modified the gold electrode, two peaks at -0.81 and -0.98 V are shifted to the negative direction by 40 and 18 mV, respectively. Meanwhile the values of Q estimated from these peaks are 1.66 and 2.96 μC cm^{-2}, that are similar with values obtained for SAM of MPA. Therefore, the shift of E_p is an clear evidence for the presence of the adlayer MUA on the surface of Cu(II). Besides the shift of E_p, values of Q estimated for the adlayers MUA and MPA are same, suggesting that the adsorption of the adlayer MPA occurs in step 3 to form MPA/Cu/MPA.

Other evidences for the presence of the adlayer MPA SAM as well as for the formation of MPA/Cu/MPA/Cu can be observed by DPV technique as presented in the following.

Detection of Cu^{2+} in multilayer systems-the role of MPA/Cu/MPA/Cu in enhancing the sensitivity of Cu^{2+} determination: Here, the presence of Cu(II) in the first and second layers of copper-bound SAM of MPA is presented. As shown in Fig. 3, the differential pulse voltammogams were recorded for the gold electrodes modified with SAM systems built up in steps 2 and 4. It can be clearly seen that there is only a peak at 0.18 V appeared in the presence of Cu^{2+} ions in both steps, indicating the presence of Cu(II) binding with carboxylate groups of adsorbed MPA molecules[11]. The peak thus corresponds to reduction of Cu(II) to form Cu(I)[3]. Interestingly, the height of this reduction peak significantly rises with the use of the SAM system built up in step 4, indicating an increase in the amount of Cu(II) attached to the SAM system. One plausible explanation for this evidence is that there is an attachment of Cu(II) on the surface of carboxylate groups of the adlayer SAM to form MPA/Cu/MPA/Cu. In this aspect, it is noted that the contribution of Cu^{2+} ions diffused through the SAMs to adsorb on the gold surface in raising the voltammetric wave can be negligible. Because Cu^{2+} ions solvated by counter ions if physically adsorbed on the gold surface they can then be removed by washing the electrode with distilled water before each measurement.

From the peak currents (Ip), the amount of Cu(II) accumulated (Γ_{Cu}) in MPA/Cu/MPA/Cu and MPA/Cu estimated by the equation reported in elsewhere[27] is 5.8 × 10^{-10} and 3.6 × 10^{-10} mol cm^{-2}, respectively. Although the total immersion time in the solution of Cu^{2+} ions for MPA/Cu/MPA/Cu was 20 min (10 min for each step 2 and 4), which is same to MPA/Cu. But the significant increase in Γ_{Cu} indicates the advantage of the gold electrode modified with MPA/Cu/MPA/Cu over the one modified with MPA/Cu in determination of Cu^{2+} ions.

Particularly, the formation of MPA/Cu/MPA/Cu depends on the immersion time ($t_{immer.}$) in ethanolic solution of MPA as well as in the solution containing Cu^{2+} ions. Thus, $t_{immer.}$ in step 1 was varied from 1-12 h and studied by CV for reductive desorption in 0.5 M KOH solution. Obtained results indicated that $t_{immer.}$ of 3 h is sufficient for the formation of SAM of MPA (data not shown). Fig. 4 shows the dependence of I_p on the total $t_{immer.}$ in solutions of Cu^{2+} at concentrations of 1.56 × 10^{-10} and 1.56 × 10^{-11} M Cu^{2+} for MPA/Cu/MPA/Cu and on $t_{immer.}$ at concentration of 7.81 × 10^{-8} M Cu^{2+} for MPA/Cu. It is clearly seen that the higher the concentration of Cu^{2+} ions the earlier the I_p approaches to the plateau. The results indicate that 20 min is sufficient for attachment Cu^{2+} to SAMs of MPA. Furthermore, this result also shows that though the concentration

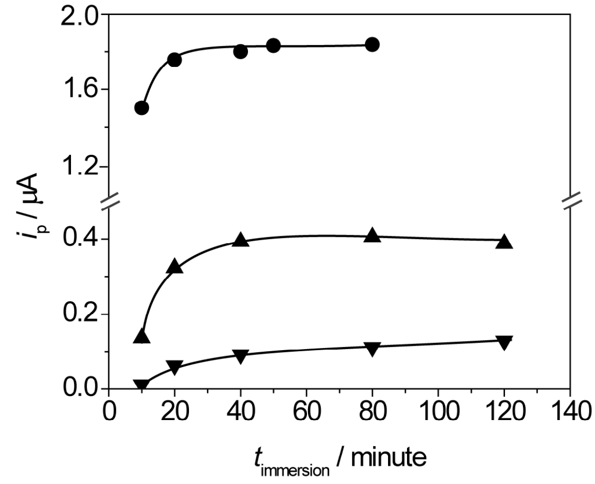

Fig. 4. Immersion time dependence of the reduction peak current at E_p = 0.18 V for the gold electrode modified with MPA/Cu/MPA/Cu built up from phosphate solution containing Cu^{2+} at concentrations of 1.56×10^{-10} M(▲), 1.56×10^{-11} M (▼) and with MPA/Cu prepared from the solution containing Cu^{2+} at concentrations of 7.81×10^{-8} M (●)

of Cu^{2+} is *ca.* 500-fold lower but I_p approached to plateau for MPA/Cu/MPA/Cu is just about four-fold lower than that modified with MPA/Cu. This clearly indicates the enhancement of sensitivity in detection of Cu^{2+} for MPA/Cu/MPA/Cu. Fig. 5 shows voltammograms recorded for determination of Cu^{2+} in various trace concentrations. It can be seen that the height of peak increases with increasing the concentration of Cu^{2+}. The dependence was found to be linear within the concentration of Cu^{2+} ions from 1.56×10^{-12}-1.56×10^{-9} M. The relative standard deviations slope was 0.9266 μA/nM, the y-intercept was 0.061 μA and correlation coefficient of 0.9962. The detection limit for Cu^{2+} estimated from the signals equals 3 (standard deviation) of the background noise was 9.10×10^{-13} M, according to the IUPAC recommendation.

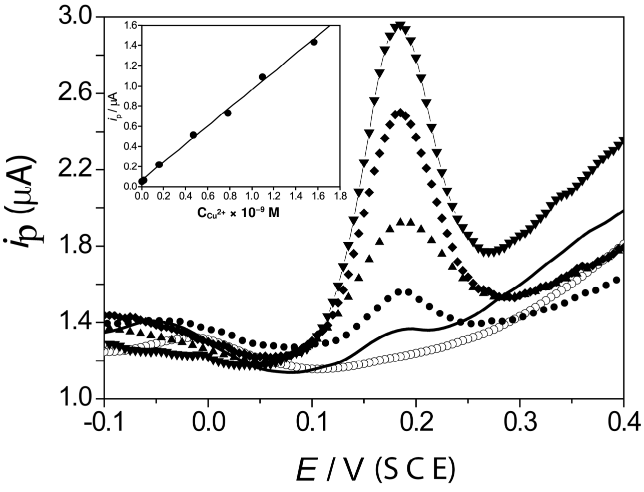

Fig. 5. Differential pulse voltammograms of the gold electrode modified with MPA/Cu/MPA/Cu built up from solution containing different concentrations of Cu^{2+}: 0 (○); 1.56×10^{-11} (thin line); 1.56×10^{-10} (●); 4.68×10^{-10} (▲); 1.09×10^{-9} (◆); 1.56×10^{-9} M Cu^{2+} (▼) recorded with the same conditions in Fig. 3. The inset: calibration curve for determining Cu^{2+} of the gold electrode modified with MPA/Cu/MPA/Cu

Electrochemical behaviour-structure of two stacking layers composed of Cu-MPA: As seen in Fig. 6, curves (b to d) recorded for the gold electrodes modified with different multilayer systems built up in steps 2-4 show a pair of well-defined redox peaks, whereas curve (a) recorded for MPA SAM in step 1 is flat. Such behaviours are different from those obtained in the multilayer thin film composed a copper layer buried in between two SAMs of MPA and *n*-pentanthiol studied by Bard *et al.*[3]. Authors reported that the electrochemical behaviour of this multilayer system is complicated and is characterized by ill-defined and poorly reproducible feature. In present voltammograms, the peaks in forward scans correspond to the reduction of Cu(II) attached to SAM layers and the oxidation peaks in backward scans indicate the formation of oxidation products, Cu(II). A feature of these systems consisting of Cu(II) layer can be observed that is the redox peak separation (ΔE_p) is *ca.* 50 mV, which is different from ideal reversible CV for adsorption, as the anodic and cathodic peaks are mirror images across the potential exist[28]. It is reported that the change in structure of the monolayer with the oxidation state of the redox center can arise peak splitting[28]. The obtained feature thus reflects the change in structure of SAMs in forward scan. We speculate that after reduction process occurred to form Cu(I)[3], one of two carboxylate groups binding with Cu(II)[11] will be free and it is possibly protonated to form hydrogen binding with lateral ones for stabilizing MPA SAM. This process leading to Cu(I) coordinates with the remain carboxylate group become looser and can be removed by diffusion to the bulk solution. Such removal of the reduction product was addressed by repeating the circling measurements as shown in Fig. 7. In the voltammogram, the height of both anodic and cathodic peaks decreases with increasing the cycling numbers, suggesting the lost of Cu(I) after reduction process.

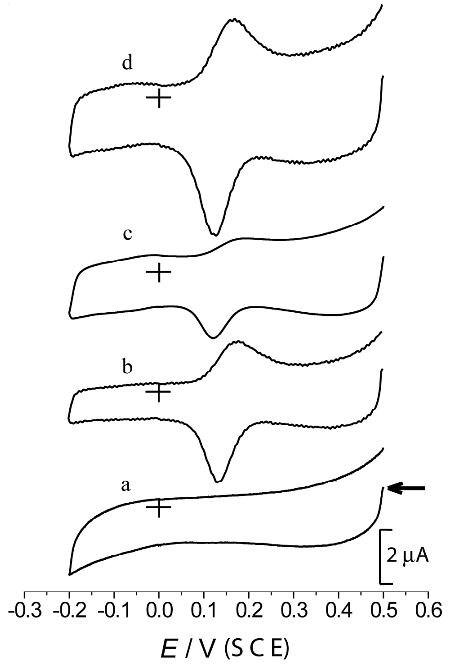

Fig. 6. Cyclic voltammograms of the gold electrode modified with MPA SAM (a); MPA/Cu (b); MPA/Cu/MPA (c) and MPA/Cu/MPA/Cu (d) built up from solution containing 3.1×10^{-7} M Cu(II), recorded in phosphate buffer solution at pH = 5.7, v = 0.1 V/s. Arrow denotes the scan direction for curves (a to d)

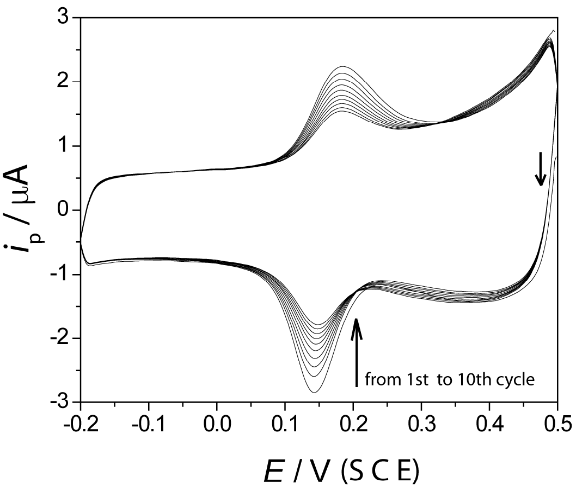

Fig. 7. Cyclic voltammogram consisting of 10 cycles of the gold electrode modified with MPA/Cu built up from solution containing 7.80 × 10^{-10} M Cu^{2+}, recorded in phosphate buffer solution at pH = 5.7, v = 0.1 V/s. Short arrow denotes the scan direction

Another feature can be seen for the system of MPA/Cu/MPA that is the significant decrease in the height of the reduction and oxidation peaks in curve (c) of Fig. 6, corresponding with considerable lowering the amount of Cu(II) reduced in the forward scan. We attribute that the main reason is the loss of Cu(II) as immersing the modified electrode in the solution of MPA in step 3. To figure out this feature, we will evaluate the Γ_{Cu} in steps. Theoretic estimation of Γ_{Cu} in monolayer of copper ions built up in step 2 and 4 was carried out with assumptions as following. First, the binding ratios of Cu:S (formed in step 3) is 1:1, Cu:COOH (formed in step 4) is 1:2 as reported by Bard *et al.*[3]. Second, there is no loss in step 3. This results in the ratio of Γ_{Cu} in MPA/Cu/MPA/Cu and Γ_{Cu} in MPA/Cu = 2. But in fact, this ratio is equals to 1.5 as presented. Thus, such item less than theory must be caused by the loss of Γ_{Cu} in step 3. This is in agreement with the value of Γ_{Cu} estimated from reduction peak in curve (c) that equals to half of the value estimated in curve (b). However, the loss of attached copper ions will be compensated in step 4. We suggest that the attachment of Cu(II) in this step can be taken place in different sites: (i) to the carboxylate in the adlayer MPA to form MPA/Cu/MPA/Cu, (ii) to the free-carboxylate in the first layer due to Cu(II) is reduced to Cu(I) upon binding to the thiol in step 3 and (iii) to the carboxylate in the first layer exposed by the loss in step 3.These processes result in an increase of Cu, as seen the remarkable increase in the height of both oxidation and reduction peaks in curve (d).

Conclusion

The formation of two stacking layers of copper-bound SAM of MPA having short alkyl chain on the gold electrode has been studied by CV and DPV techniques. Obtained results are good evidences for the formation of MPA/Cu/MPA/Cu. The effective formation of MPA/Cu/MPA/Cu has been utilized as a trap for accumulating Cu^{2+} from solution on the gold electrode. Since, the modified gold electrode has been successfully employed for enhancing the sensitivity for determination of Cu^{2+} in the concentration of parts per trillion in comparison with modifying with MPA/Cu. The electrochemical behaviour of gold electrode modified with MPA/Cu/MPA/Cu has been obtained that can interpret the loss of copper ions after reduction process as well as during immersing in thiol solution for building up the subsequent SAM of MPA. Results obtained by electrochemical method reflects that the oxidation state of copper ions presence in two stacking layers composed of copper-bound SAMs of MPA is in agreement with that reported by Bard *et al*[3].

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REFERENCES

1. P.N. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Molecules & Polymer, Wiley Interscience: New York (1991).
2. W. Lin, G.K. Wong and T.J. Marks, *J. Am. Chem. Soc.*, **118**, 8034 (1996).
3. M. Brust, P.M. Blass and A.J. Bard, *Langmuir*, **13**, 5602 (1997).
4. A. Hatzor and P.S. Weiss, *Science*, **291**, 1019 (2001).
5. M.E. Anderson, C. Srinivasan, R. Jayaraman, P.S. Weiss and M.W. Horn, *Microelectron. Eng.*, **248**, 78 (2005).
6. G.S. McCarty, *Nano Lett.*, **4**, 1391 (2004).
7. L. Netzer and J. Sagiv, *J. Am. Chem. Soc.*, **105**, 674 (1983).
8. H. Lee, L.J. Kepley, H.G. Hong and T.E. Mallouk, *J. Am. Chem. Soc.*, **110**, 618 (1998).
9. S.D. Evans, A. Ulman, K.E. Goppert-Berarducci and L.J. Gerenser, *J. Am. Chem. Soc.*, **113**, 5866 (1991).
10. T.L. Freeman, S.D. Evans and A. Ulman, *Langmuir*, **11**, 4411 (1995).
11. T.A. Daniel, S. Uppli, G. McCarty and D.L. Allara, *Langmuir*, **23**, 638 (2007).
12. T.L. Freeman, S.D. Evans and A. Ulman, *Thin Solid Films*, **244**, 784 (1994).
13. D.W. Hatchett, R.H. Uibel, K.J. Stevenson, J.M. Harris and H.S. White, *J. Am. Chem. Soc.*, **120**, 1062 (1998).
14. K.C. Honeychurch, D.M. Hawkins, J.P. Hart and D.C. Cowell, *Talanta*, **57**, 565 (2002).
15. D.G. Barceloux, *J. Toxicol. Clin. Toxic*, **37**, 761 (1999).
16. Y.N. Jiang, H.Q. Luo and N.B. Li, **22**, 1079 (2006).
17. P.D. Ding, L.M. Niu, H.Q. Luo and N.B. Li, *Croatica Chem. Acta*, **80**, 61 (2007).
18. M.S. El-Deab, K. Arihara and T. Ohsaha, *J. Electrochem. Soc.*, **151**, E213 (2004).
19. C.J. Zhong and M.D. Porter, *J. Electroanal. Chem.*, **425**, 147 (1997).
20. K. Arihara, T. Ariga, N. Takashima, K. Arihara, T. Okajima, F. Kitamura, K. Tokuda and T. Ohsaka, *Phys. Chem. Chem. Phys.*, **5**, 3758 (2003).
21. M.S. El-Deab and T. Ohsaka, *Electrochem. Commun.*, **5**, 214 (2003).
22. M.S. El-Deab, T. Sotomura and T. Ohsaka, *J. Electrochem. Soc.*, **152**, C1 (2005).
23. C.B. Gorman, H.A. Biebuyck and G.M. Whitesides, *Langmuir*, **11**, 2242 (1995).
24. R. Zhang and A.J. Gellman, *J. Phys. Chem.*, **95**, 7433 (1991).
25. R.G. Nuzzo, L.H. Dubois and D.L. Allara, *J. Am. Chem. Soc.*, **112**, 558 (1990).
26. S. Imabayaki, M. Iida, D. Hobara, Z.Q. Feng, K. Niki and T. Kakiuchi, *J. Electroanal. Chem.*, **428**, 33 (1997).
27. A.J. Bard and L.R. Faulkner, Electrochemical Methods: Fundamentals and Application, Wiley & Sons, Inc. New York, edn. 2, Ch. 14, p. 591 (2001).
28. H.O. Finklea, Electrochemistry of Oganized Monolayers of Thiols and Related Molecules on Electrodes, Marcel Dekker, Inc. New York, Vol. 19, Ch. 5, p. 243 (1999).