

Self-Assembled Water-Soluble Cobalt Porphyrin Monolayers at Gold Electrodes with High Electrocatalysis of 2-Mercaptoethanol Oxidation

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We reported the study on the preparation and the electrocatalytic properties of self-assembled monolayers of a water-soluble cobalt(III) *meso*-tetrakis(*N*-methyl-4-pyridyl) porphyrin (CoTMPyP) on gold disk. Cyclic voltammetry showed that the modified electrode is stable, lowers the overpotentials and improves the electrochemical oxidation of 2-mercaptoethanol in 0.1 M NaOH solutions, as compared to the bare Au. Absorption spectral results showed that Co^{III/II} center of CoTMPyP involved in the oxidation reactions. The electrocatalytic reaction mechanisms were proposed.

Keywords: Electrocatalytic oxidation, 2-mercaptoethanol, water-soluble cobalt porphyrins, self-assembled monolayers, cyclic voltammetry.

1. INTRODUCTION

Detection of thiols has been an important research subject in the biological and industrial world [1-3]. Thiols can be present as contaminants in fuels and industrial waste products. They are often used as markers of food deterioration and light oil sweetening. Thiol-containing amino acids are essential substrates for protein synthesis and tissues growth and act as physiological indicators in biological fluids.

Thiols such as 2-mercaptoethanol, cysteine and glutathione have been detected electrochemically [1-8]. Generally, the responses to thiol oxidation at unmodified solid electrodes suffered from large overpotentials or sluggish electrochemical responses. Electrocatalytic detection of cysteine was successfully achieved at edge plane pyrolytic graphite and boron-doped diamond

electrodes [5]. In the presence of proper mediators in solutions, detection of cysteine can be achieved at bare glassy carbon electrodes where electrochemically initiated derivatization reactions occurred [6,7].

The immobilization of electrocatalysts on metal surfaces continues to attract research interest in electrocatalysis. Electrodes modified with metal macrocycles (such as metalloporphyrins (MP) [8,9] and metallophthalocyanines (MPc) [1-3]), providing sites for the molecules to interact, have shown a substantial electrocatalytic activity for the oxidation of a variety of biochemically important molecules in aqueous solutions. Electrode surface modification can be achieved in various ways, such as adsorption by direct deposition [1,8,10], mixing of electrocatalysts with carbon nanotubes [11], layer-by-layer method [9], and electropolymerization [1,8,10,12,13]. However, some modified electrodes suffered from instability, irreproducibility, short lifetime and low electroactivity [10,12].

Self-assembled monolayers (SAM) have advantages of offering dense, stable and highly ordered films of regular and packed orientation on the electrode [2,14,15]. The accessibility for the analytes to the redox centers on the monolayers is feasible and direct, whereas there is limitation at the polymeric film modified electrode [12]. Immobilization of MP SAM on gold electrode can be achieved, using sulfur-substituted MP in peripheral side chain [14,15] and coupling reaction between the properly substituted MP and pre-formed self-assembled monolayers [2].

Water-soluble MP and MPc species are well recognized for their high activity in homogeneous electrocatalysis [16]. However, they are easily washed away when immobilized onto electrode surfaces using the traditional techniques such as carbon paste, drop-dry and electrodeposition, which have limited their use in heterogeneous electrocatalysis in aqueous environment. In this study, we prepared a water-soluble CoTMPyP SAM onto gold electrode via axial coordination, preventing tedious synthesis procedures and only requiring a pre-formed SAM with a terminal pyridyl group [17]. Rubistein's group was the first to report this technique for water insoluble cobalt porphyrins [18], followed by Ozoemena and Nyokong who reported the detailed electrochemistry and electrocatalysis of such SAMs [19-20].

To the best of our knowledge, no examples have been reported to immobilize a water-soluble cobalt porphyrin appended with electron-deficient substituents onto gold electrodes and apply them to the activation of 2-mercaptoethanol. It is expected that the electron-withdrawing nature of *N*-methyl-4-pyridyl substituents will be beneficial for the reaction. The results showed that the obtained CoTMPyP SAM is highly stable and showed high electrocatalytic activity towards 2-mercaptoethanol oxidation.

2. EXPERIMENTAL

2.1. Reagents

2-Mercaptoethanol, 4-mercaptopyridine (4MP) and 2-hydroxyethyl disulphide were obtained from Acros. They were of the highest grade available and used without further purification. Cobalt(III) *meso*-tetrakis(*N*-methyl-4-pyridyl) porphyrin (CoTMPyP) was synthesized as perchlorate salt [16]. The cobalt porphyrin is diamagnetic and the central cobalt ion is in its 3+ oxidation state. All other

chemicals were of analytical reagent grade from Acros. All solutions were prepared using deionized water from a Milli-Q ultrapure water system with a resistivity of 18 M Ω cm.

2.2. Instruments

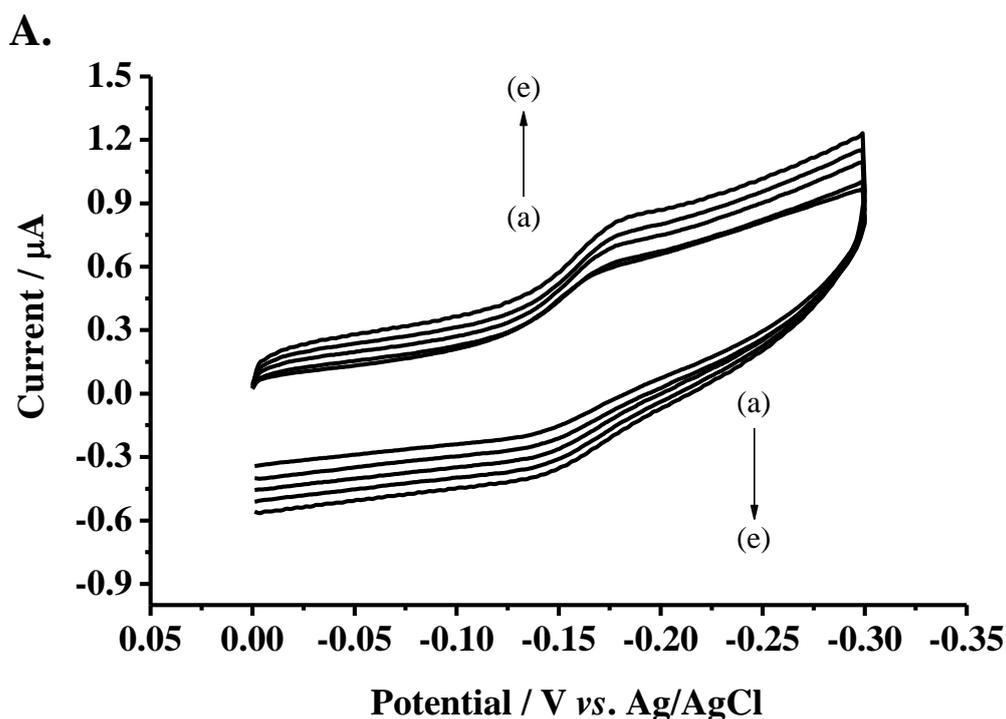
Cyclic voltammetry was performed using a voltammetric analyzer (CH Instruments, model CHI-421A). A gold electrode (CHI101, 2 mm dia.) was used as a working electrode and was polished with 0.05 μ m alumina on a Buehler felt pad. A platinum wire was used as the counter electrode. A home-made Ag|AgCl|KCl(sat.) electrode was used as a reference electrode. All potentials were reported with respect to this reference electrode. UV-vis spectra were recorded on a HP 8453 spectrophotometer.

2.3. Fabrication of self-assembled modified electrode

Au/4MP SAM was obtained by immersing a polished Au electrode in a nitrogen-purged 10 mM 4MP solution in ethanol for 2 h. Au/4MP/CoTMPyP SAM was formed by immersing the Au/4MP SAM in a nitrogen-purged 1 mM CoTMPyP aqueous solution for 5 min. The obtained modified electrodes were thoroughly rinsed with deionized water and kept in 0.1 M KCl solution prior use.

3. RESULTS AND DISCUSSION

3.1. Electrochemical characterization of Au/4MP/CoTMPyP SAM



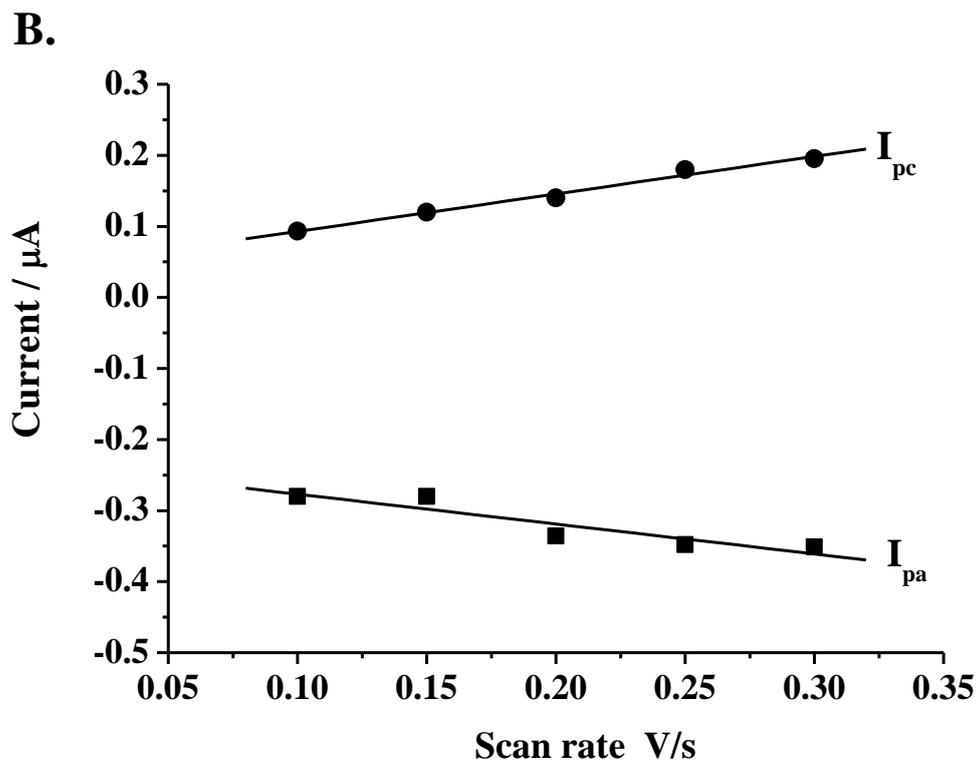
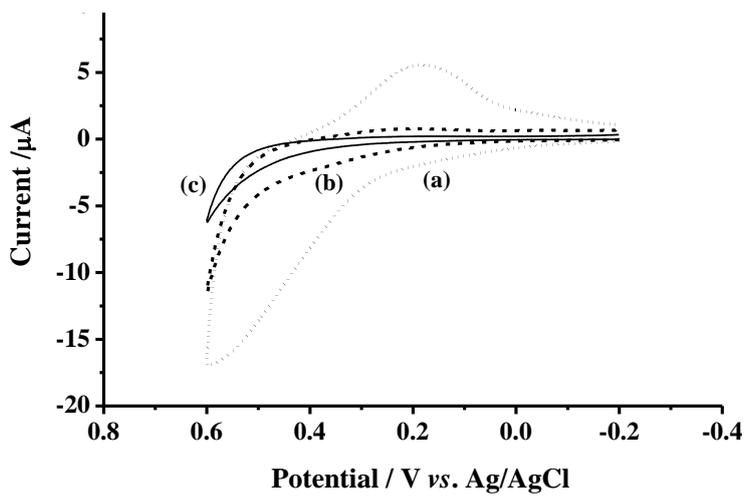


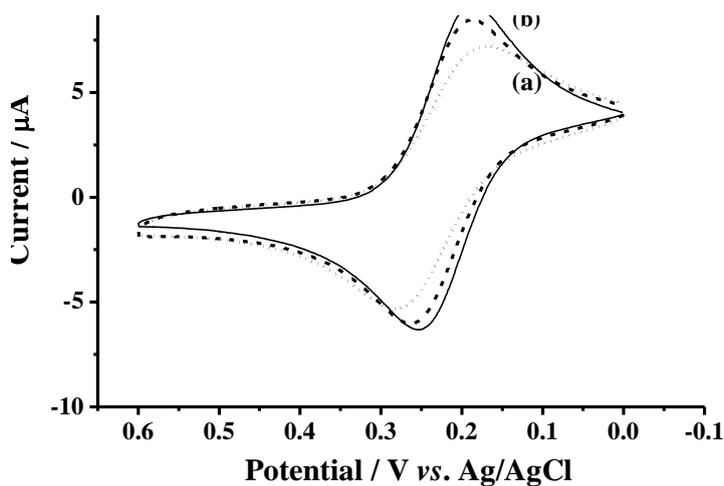
Figure 1. (A) Cyclic voltammograms of Au/4MP/CoTMPyP SAM at 0.5 M KOH buffer solution. (B) peak currents vs. scan rate. Scan rate = (a) 0.1 (b) 0.15 (c) 0.2 (d) 0.25 (e) 0.3 V/s.

In this study, the sulfur head (-SH) of 4MP chemisorbed onto gold surface, exposing the pyridinyl group at the surface of the Au/4MP SAM [17]. This was followed by axial ligation with CoTMPyP, affording the Au/4MP/CoTMPyP SAM. This approach has been used to prepare iron phthalocyanine SAM and applied for electrocatalysis of thiocyanate [17]. The obtained Au/4MP SAM and Au/4MP/CoTMPyP SAM showed reduction of the capacitive charging current compared to bare Au in aqueous solution, confirming the formation of an ultrathin film on electrode surfaces [14,17]. In 0.1 M NaOH deaerated solution containing 1.0 mM CoTMPyP at bare gold electrode, quasi-reversible peaks relating to $Co^{III/II}$ and $Co^{II/I}$ redox process were observed at approximately -0.15 and -0.60 V, respectively. Although the redox behavior of metalloporphyrin immobilized as monolayers usually gave unclear peaks [21], noticeable redox peak of Au/4MP/CoTMPyP SAM was observed in 0.1 M NaOH solution as shown in Fig. 1A. Both the oxidation and reduction peak current increase linearly with the scan rate over the range studied (Fig. 1B), indicating that the electron transfer is an adsorption-controlled process.

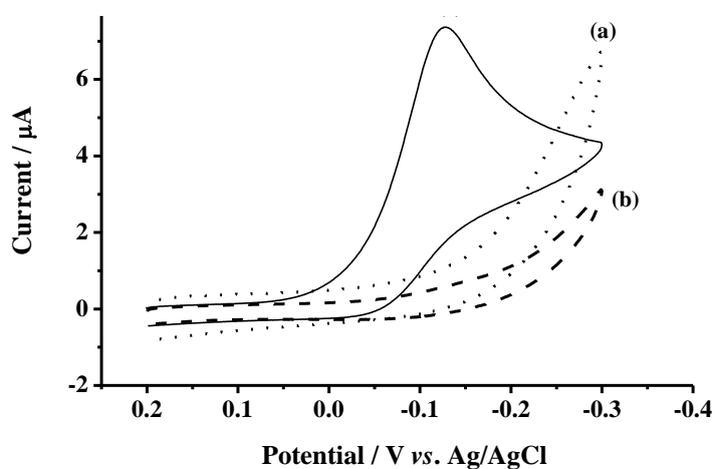
The passivation ability of the obtained SAM film was studied in 0.01 M KOH solution shown in Fig. 2A. Broad gold oxidation wave and the corresponding sharp stripping peak of gold oxide appeared at 0.5 and 0.2 V, respectively. At the Au/4MP SAM and Au/4MP/CoTMPyP SAM, gold oxidation reactions were strongly suppressed. The calculated ion barrier factor is approximately unity, suggesting that the SAM is compact and almost free of pinholes and defects [14,17].



A



B



C

Figure 2. Cyclic voltammograms of (a)bare Au (b)Au/4MP SAM (c)Au/4MP/CoTMPyP SAM electrode in (A) deoxygenated 0.01 M KOH solution (B)deoxygenated 1.0 mM $K_3Fe(CN)_6$ in 0.1 M KCl (C)air-saturated 0.1 M KCl solution. Scan rate: 100 mV/s.

The property of the SAM film was further examined in 0.1 M KCl solution containing 1.0 mM $\text{K}_3\text{Fe}(\text{CN})_6$ as shown in Fig. 2B. The peak currents of the redox couple of $\text{Fe}^{\text{III/II}}(\text{CN})_6^{3-/4-}$ were higher at Au/4MP SAM and Au/4MP/CoTMPyP SAM than those at bare Au electrode. It would result from the electrostatic attraction force between the negatively charged $\text{Fe}(\text{CN})_6^{3-}$ in solution and the positively charged protonated pyridinyl group and porphyrin ring at the SAM film.

The attachment of CoTMPyP SAM was evidenced from the efficient activity for dioxygen reduction [9,21]. A huge reduction peak occurred at Au/4MP/CoTMPyP SAM at -0.12 V in an air-saturated 0.1 M KCl solution, which were not observed at bare Au and Au/4MP SAM (Fig. 2C). The peak disappeared when nitrogen gas was purged into the solution.

3.2. Electrocatalytic oxidation of 2-mercaptoethanol at Au/4MP/CoTMPyP SAM

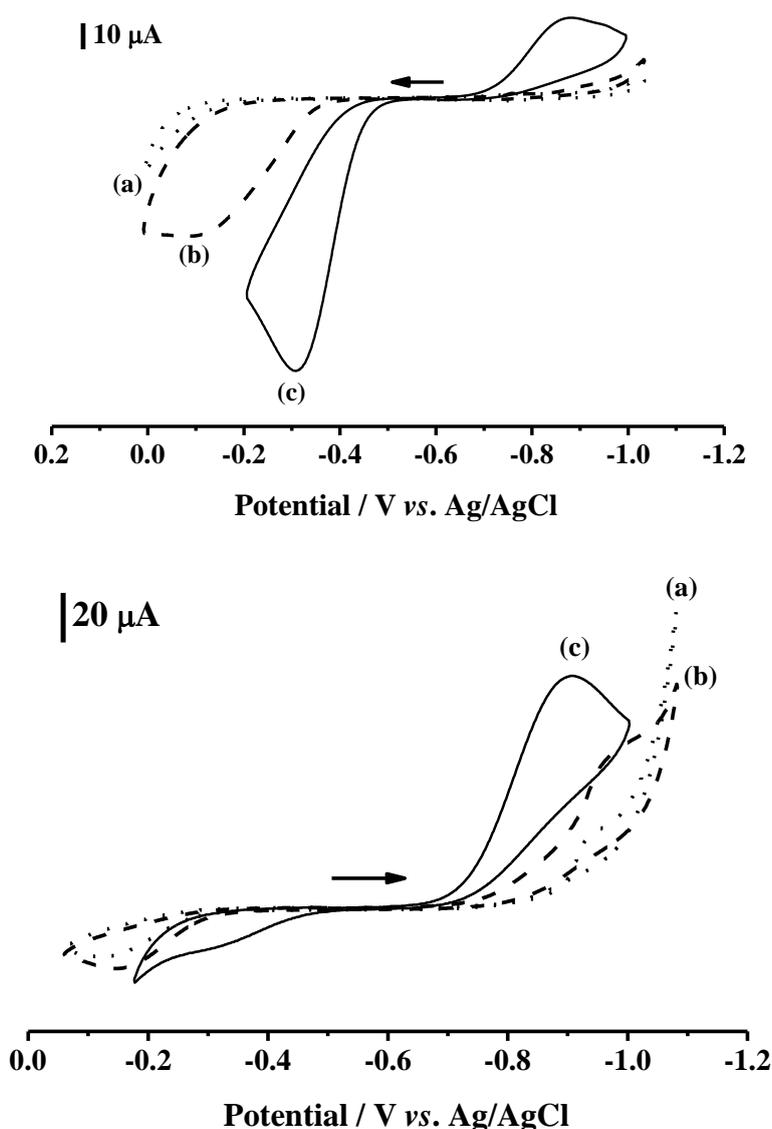


Figure 3. Cyclic voltammograms of (A) 10 mM 2-mercaptoethanol (B) 10 mM 2-hydroxyethyl disulfide in 0.1M NaOH solution at (a) bare Au (b) Au/4MP SAM (c) Au/4MP/CoTMPyP SAM electrode. Scan rate = 0.1V/s.

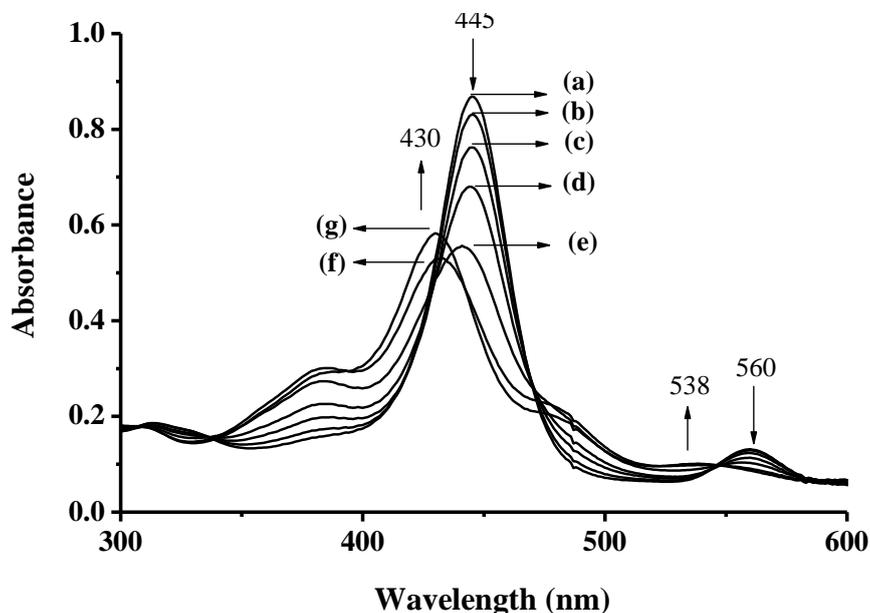
Fig. 3A showed cyclic voltammograms for deaerated 10 mM 2-mercaptoethanol solutions in 0.1 M NaOH solution. At bare gold electrode, a small oxidation wave was noticed at +0.0 V. An irreversible and broad oxidation peak was observed at -0.08 V. The oxidation peak shifted to less positive potentials at Au/4MP/CoTMPyP SAM (-0.28 V) with a higher slope at inclining part of the peak. The oxidation potential of 2-mercaptoethanol at Au/4MP/CoTMPyP SAM was close to that obtained at cobalt porphyrin-based and cobalt phthalocyanine-based electrodes [1,8,12,13].

The formation of 2-hydroxyethyl disulphide during 2-mercaptoethanol oxidation was proved as shown in Fig. 3B. The reduction potential of 2-hydroxyethyl disulphide occurred at -1.15, -0.95 and -0.85 V at bare Au, Au/4MP SAM and Au/4MP/CoTMPyP SAM, respectively. Similar reduction waves were also observed in Fig. 3A, indicating that Au/4MP/CoTMPyP SAM is not only active for oxidizing 2-mercaptoethanol but also acts as an electrocatalyst for reducing the corresponding disulphide formed during anodic process [1,12-14].

The stability of the Au/4MP/CoTMPyP SAM was further investigated in 0.1 M NaOH solution containing 10 mM 2-mercaptoethanol. The oxidation peak current remained the same after multiple scans (stirred and stopped between scans), suggesting the modified electrode possessed activity, without SAM desorbing from the electrode surfaces or poisoning of the modified electrode by the physically adsorbed oxidation product.

3.3. Mechanism studies

The involvement of the central cobalt ion in the catalytic reactions was investigated in aqueous solutions. Fig. 4A shows the UV-vis spectra of Co^{III}TMPyP in 0.1 M NaOH solution, exhibiting a typical B band (445 nm) and Q band (560 nm) (trace a). It is characteristics for the coordination of hydroxide anions as the 5th and 6th ligands to the Co^{III} center.



A

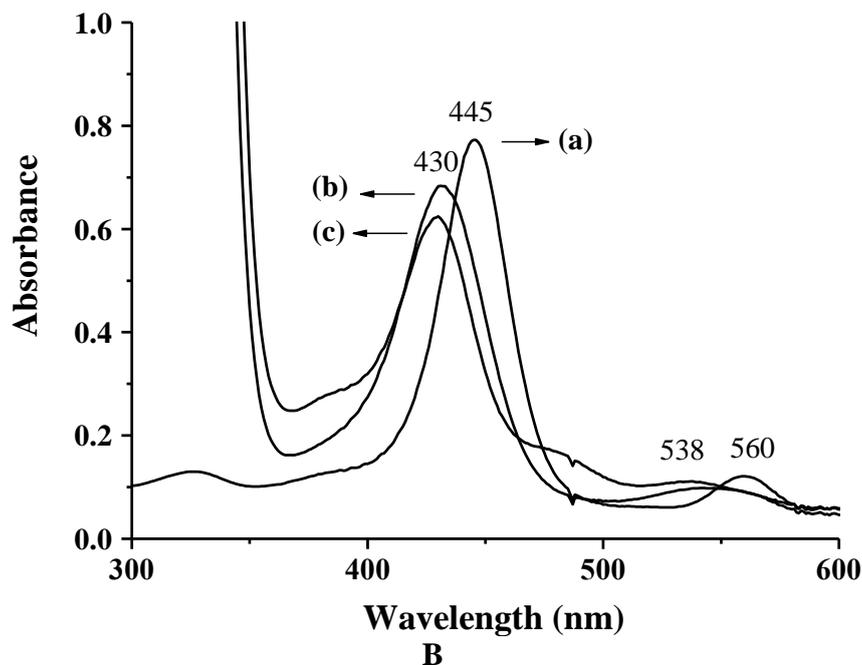
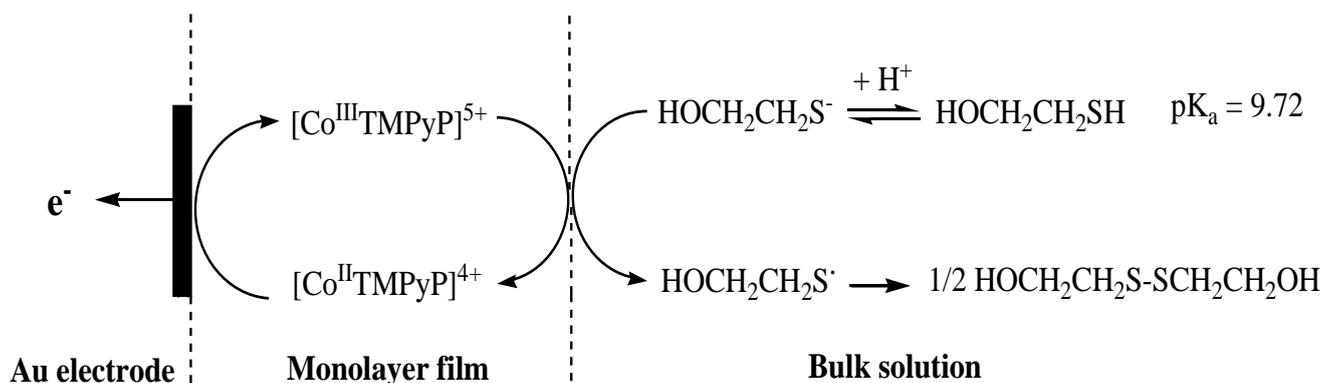


Figure 4. (A) Time-resolved UV/Vis spectral change of $\text{Co}^{\text{III}}\text{TMPyP}$ and 2-mercaptoethanol in degassed 0.1M NaOH solution. Time = (a) 0 (b) 40 (c) 80 (d) 120 (e) 160 (f) 240 (g) 360 s. (B) UV/Vis spectra of (a) $\text{Co}^{\text{III}}\text{TMPyP}$ in degassed 0.1M NaOH solution (b) addition of ascorbic acid to (a) solution (c) addition of 2-mercaptoethanol to (b) solution. $[\text{Co}^{\text{III}}\text{TMPyP}] = 5 \times 10^{-5}$ M. $[\text{2-mercaptoethanol}] = 1.3$ mM. Path length = 1.0 cm

No difference in spectral pattern was noticed at the beginning of addition of 1.3 mM 2-mercaptoethanol, however, the gradual spectral changes with time reflected a chemical reaction occurring between $\text{Co}^{\text{III}}\text{TMPyP}$ and 2-mercaptoethanol in the solution. The final spectrum located at 430 nm with a broad Q band at 538 nm (Fig. 4A, trace g), similar to the spectral pattern of $\text{Co}^{\text{II}}\text{TMPyP}$ obtained by direct chemical reduction of $\text{Co}^{\text{III}}\text{TMPyP}$ with ascorbic acid in the absence (Fig. 4B, trace b) and presence (Fig. 4B, trace c) of 2-mercaptoethanol. The similarity in spectral pattern between traces b and c in Fig. 4B suggests no significant reactions between $\text{Co}^{\text{II}}\text{TMPyP}$ and 2-mercaptoethanol.



Scheme 1. Electrocatalytic oxidation of 2-mercaptoethanol at Au/4MP/CoTMPyP SAM electrode.

The electrocatalytic reaction mechanisms for the electrochemical oxidation of 2-mercaptoethanol at Au/4MP/CoTMPyP SAM are thus explained in Scheme 1. The acid dissociation constant (pKa) is 9.72 for 2-mercaptoethanol [14], therefore, thiolate ions are predominant in alkaline solution and would undergo chemical reactions with the immobilized Co^{III} TMPyP. The active Co^{III} center was reduced to Co^{II} and then electrochemically oxidized to reform Co^{III} at the proper applied potential. The lowered oxidation potential and the enhanced oxidation current as observed in trace c of Fig. 3A indicates the electrocatalytic reactions.

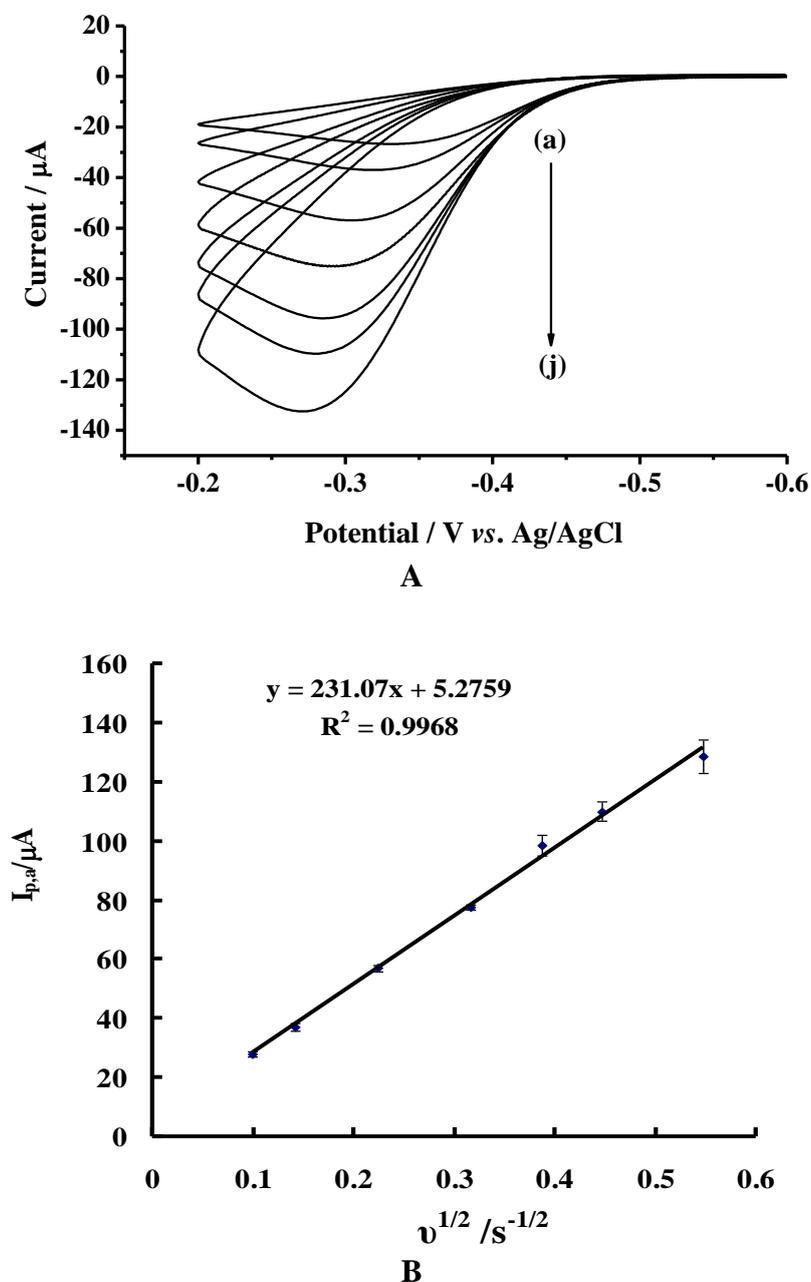
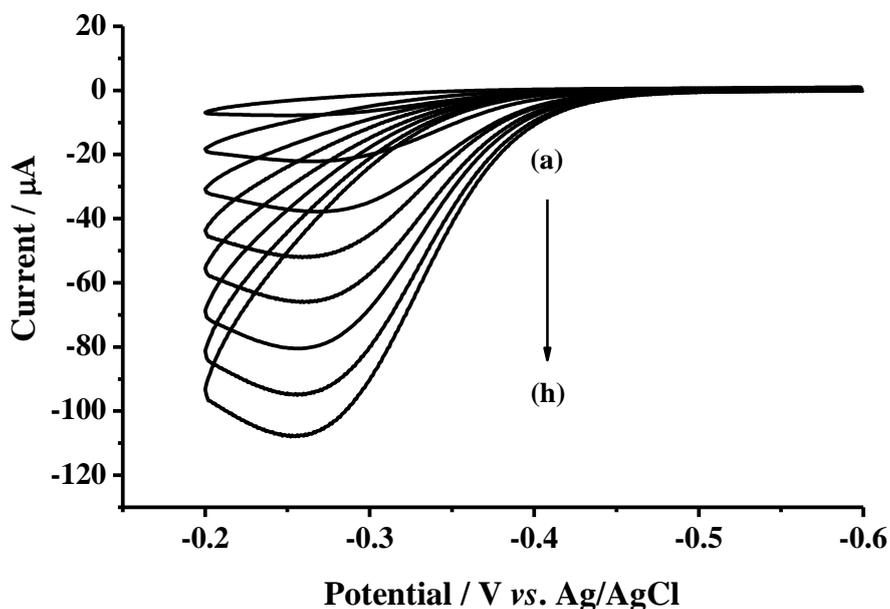
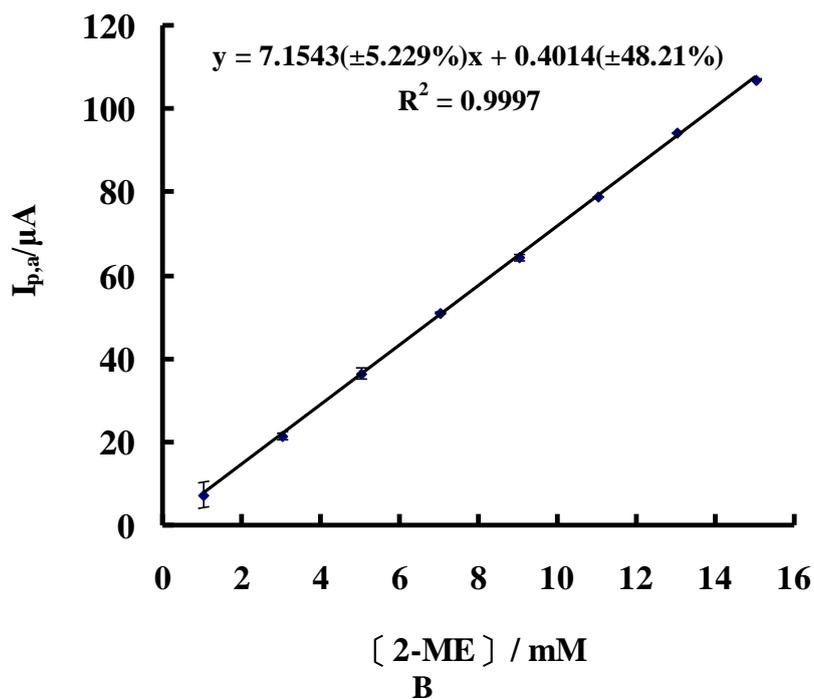


Figure 5. (A) Cyclic voltammograms of Au/4MP/CoTMPyP electrode in 0.1 M NaOH solution containing 10 mM 2-ME. Scan rate = (a) 0.01 (b) 0.02 (c) 0.05 (d) 0.1 (e) 0.15 (f) 0.2 (g) 0.3 V/s. (B) The plot of $I_{p,a}$ vs. (scan rate) $^{1/2}$.

Meanwhile, thiolate was oxidized, releasing the radical intermediate and giving disulfide as the oxidation product. In contrast to what has been observed previously for the oxidation of thiols by $\text{Co}^{\text{II/I}}$ center of organic-soluble porphyrins and phthalocyanines [8,10,13], our results showed that $\text{Co}^{\text{III/II}}$ center of water-soluble CoTMPyP involved.



A



B

Figure 6. (A) Cyclic voltammograms of Au/4-MP/Co(TMPyP) SAM electrode in 0.1 M NaOH buffer solution containing (a) 1 (b) 3 (c) 5 (d) 7 (e) 9 (f) 11 (g) 13 (h) 15 mM 2-ME. Scan rate = 0.1 V/s. (B) The plot of $I_{p,a}$ vs. [2ME].

It is expected that the positive charges on the *N*-methyl-4-pyridyl substituents attract the anionic thiolate close to the reaction sites. The nature of electron-deficient porphyrin ring and thus the high oxidizing power of the cobalt center contribute to the electrocatalytic activity.

In order to obtain information on the kinetics of the electrocatalytic oxidation reactions, the effects of the scan rate and 2-mercaptoethanol concentration on the oxidation waves at Au/4MP/CoTMPyP SAM in 0.1 M NaOH solution were further investigated. The peak potentials shifted positively and the peak current increased when the scan rates increased (Fig. 5). The peak currents were linearly proportional to the square root of the scan rate ($v = 0.01$ - 0.30 V/s), suggesting the current is operated under semiinfinite linear diffusion-control of 2-mercaptoethanol in the electrode/solution interface [4]. The plot of E_p versus $\log v$ showed linearity with a Tafel slope of 0.0926 V/decade, indicating a rate-limiting electron transfer involved in the reaction (assuming $n_a = 1$ and transfer coefficient $\alpha = 0.36$) [4,8,10-14].

The analytical characteristics of Au/4MP/CoTMPyP SAM toward 2-mercaptoethanol oxidation was further investigated by cyclic voltammetry and the results were shown in Fig. 6A. The oxidation peak current increases linearly with 2-mercaptoethanol concentration in the range of 1.0 - 15.0 mM (Fig. 6B). The linear regression equation is expressed as $I_{pa} (\mu A) = 7.15 C (\text{mM}) + 0.401$ ($R^2 = 0.9997$). Similar trend was observed for the concentration ranging from 0.1 - 1.0 mM (data not shown). The detection limit was 0.02 mM based on the signal noise ratio of 3.

4. CONCLUSION

We report here the first study to modify gold electrode easily with a water-soluble cobalt porphyrin by self-assembly techniques. The Au/4MP/CoTMPyP SAM showed good catalytic activity towards 2-mercaptoethanol oxidation in alkaline solutions. The electro-oxidation was mediated by $\text{Co}^{\text{III/II}}$ center of CoTMPyP. The mode of transport of 2-mercaptoethanol to interfacial zone was found to be diffusion. The calculated Tafel slope confirmed one-electron transfer in the rate-determining step. The Au/4MP/CoTMPyP SAM electrodes are highly stable and would be applied to determine biological thiols in aqueous solution.

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1. S. Griveau, M. Gulppi, J. Pavez, J. H. Zagal, F. Bedioui, *Electroanalysis* 15 (2003) 779.
2. P. N. Mashazi, P. Westbroek, K. I. Ozoemena, T. Nyokong, *Electrochim. Acta* 53 (2007) 1858.
3. J. C. Obirai, T. Nyokong, *J. Electroanal. Chem.* 600 (2007) 251.
4. W.-Y. Su, S.-H. Cheng, *Electrochem. Commun.* 10 (2008) 899.
5. J. Kruusma, A. M. Benham, J. A. G. Williams, R. Katakya, *Analyst* 131 (2006) 459.
6. P. C. White, N. S. Lawrence, J. Davis, R. G. Compton, *Electroanalysis* 14 (2002) 89.
7. P. C. White, N. S. Lawrence, J. Davis, R. G. Compton, *Anal. Chim. Acta* 447 (2001) 1.

8. S. Griveau, M. Gulppi, F. Bedioui, J. H. Zagal, *Solid State Ionics* 169 (2004) 59.
9. J. Qu, Y. Shen, X. Qu, S. Dong, *Electroanalysis* 16 (2004) 1444.
10. N. Sehlotho, T. Nyokong, J. H. Zagal, F. Bedioui, *Electrochim. Acta* 51 (2006) 5125.
11. J. F. Silva, S. Griveau, C. Richard, J. H. Zagal, F. Bedioui, *Electrochem. Commun.* 9 (2007) 1629.
12. S. Griveau, V. Albin, T. Pauporte, J. H. Zagal, F. Bedioui, *J. Mater. Chem.* 12 (2002) 225.
13. S. Griveau, F. Bedioui, *Electroanalysis* 13 (2001) 253.
14. N. Sehlotho, T. Nyokong, *Electrochim. Acta* 51 (2006) 4463.
15. T. A. Postlethwaite, J. E. Hutchison, K. W. Hathcock, R. W. Murray, *Langmuir*, 11 (1995) 4109.
16. S.-H. Cheng, Y. O. Su. *Inorg. Chem.* 33 (1994) 5847.
17. K. I. Ozoemena, T. Nyokong, *J. Electroanal. Chem.* 579 (2005) 283.
18. G. Kalyuzhny, A. Vaskevich, G. Ashkenasy, A. Shanzer, I. Rubinstein, *J. Phys. Chem. B* 104 (2000) 8238.
19. K. I. Ozoemena, T. Nyokong, *Talanta* 67 (2005) 162.
20. K. I. Ozoemena, T. Nyokong, *Electrochim. Acta* 51 (2006) 2669.
21. N. Nishimura, M. Ooi, K. Shimazu, H. Fujii, K. Uosaki, *J. Electroanal. Chem.* 473 (1999) 75.