

Electropolymerization of 4-Aminothiophenol Self-Assembled Monolayer on Au Electrode

Qing Ji XIE¹*, Xiao Lan GU¹, You Yu ZHANG², Man Cai XU¹, Ming MA¹

¹Chemistry Department, Hunan Normal University, Changsha 410081

²Center of Analysis & Test, Hunan Normal University, Changsha 410081

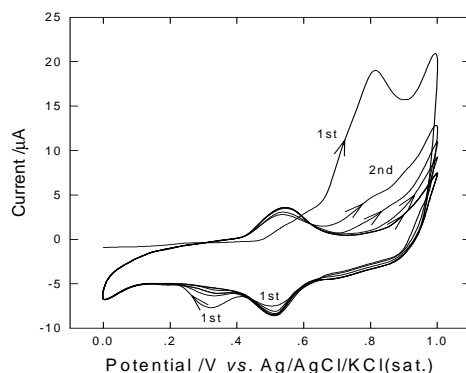
Abstract: In this letter, we report that oxidation of 4-aminothiophenol self-assembled monolayer on Au electrode produces a couple of redox current peaks with close peak potentials in 0.5 mol/L HClO₄ aqueous solution, and the peaks are ascribed to an electroactive monolayer. Electrochemical properties of the monolayer polymer were investigated with use of electrochemical quartz crystal microbalance and cyclic voltammetry.

Keywords: Molecular self-assembly, monolayer polymer, 4-aminothiophenol, EQCM.

It is well known that electrochemical oxidation of aniline dissolved in electrolyte solutions is a very useful method for preparing polyaniline films on electrodes¹. However, it is very difficult for this method to prepare a uniform monolayer polymer since local nucleation and growth of polymer in the nucleation sites are involved in the initial polymerization stage. There have been many reports on preparing uniform monolayer polymers on substrates from Langmuir-Blodgett (LB) monolayers², however, only very few researchers reported on polymerization of self-assembled monolayers^{3,4}. We have prepared a stable electroactive monolayer poly(aminothiophenol) by oxidation of 2-/3-aminothiophenol self-assembled monolayer in acidic aqueous solutions⁴. In this letter, we report that electrochemical oxidation of a 4-aminothiophenol self-assembled monolayer can produce a couple of redox current peaks with close peak potentials which may be ascribed to the corresponding monolayer polymer, and electrochemical properties of the monolayer poly(4-aminothiophenol) on Au in HClO₄ aqueous solutions were studied by cyclic voltammetry and electrochemical quartz crystal microbalance (EQCM) technique.

Modification of a 4-aminothiophenol self-assembled monolayer on Au was achieved by immersing EQCM Au electrodes in a 4-aminothiophenol ethanol solution overnight. The Au electrode was then used as the working electrode after rinsing thoroughly by doubly distilled water and by ethanol successively. A three-electrode electrolytic cell was used, a glassy carbon plate served as the counter electrode and the reference electrode was Ag/AgCl/KCl (sat.). Piezoelectric quartz crystals were At-cut 9M Hz crystals having crystal diameters of *ca.* 12.5 mm and gold electrode diameters of *ca.* 6.0 mm. The gold electrodes were vacuum-evaporated by using an Eiko IB-3 ion coater and a highly pure

Figure 1. Cyclic voltammogram of 4-aminothiophenol self-assembled monolayer on Au electrode in 0.5 mol/L HClO₄ aqueous solution. dE/dt=50 mV/s.



gold foil purchased from Hitachi Inc.. The mass sensitivity of the EQCM, 0.178 Hz cm² g⁻¹, which was measured during silver deposition, coincides well with that calculated from Sauerbrey's equation⁵.

Cyclic voltammetry of the 4-aminothiophenol self-assembled monolayer was conducted in 0.5 mol/L HClO₄ aqueous solution and the result is shown in **Figure 1**. A large anodic current peak was observed at *ca.* 0.80 V in the first scan, this peak decreased sharply in the second anodic scan and completely disappeared after the 5th cyclic potential scan, in the meantime, a couple of redox current peaks centered at 0.54 V ($E_{pa}=0.55$ V, $E_{pc}=0.53$ V) appeared after the first anodic scan and the two currents increased gradually and reached their steady values after the 7th cyclic potential scan. It is interesting that a cathodic current peak was observed at *ca.* 0.30 V in the first cathodic scan and it also decreased sharply in the second scan and completely disappeared after the 5th scan, but there seems no anodic peak corresponding to such a cathodic current peak at *ca.* 0.30 V. The redox current peaks centered at 0.54 V were stable within *ca.* 40 potential scans but decreased by *ca.* 15% after 100 potential scans in the region of 0 to 1 V, moreover, peak potentials were independent of scan rates from 0.01 to 0.1 V/s while peak currents were proportional to scan rates, and redox current peaks of identical heights and peak potentials were still observed after the solution was replaced with a freshly-prepared 0.5 mol/L HClO₄ aqueous solution, which suggested that the electrochemical behavior was caused by surface-confined species. Since no such current peaks were found with bare Au electrode, we believe that the redox current peaks centered at 0.54 V should result from the electroactive monolayer poly (4-aminothiophenol) on Au, as illustrated in **Scheme 1**. In addition, surface coverages with aniline units have been estimated to be $7.0 \pm 0.2 \times 10^{-10}$ mol cm⁻² by integrating the current under anodic and cathodic current peaks, which seems to be reasonable for monolayer formation on an Au electrode⁶.

We have also investigated the acidity effect on monolayer poly (4-aminothiophenol) in 0.5 mol/L LiClO₄/HClO₄ by cyclic voltammetry. It was found that the peak currents and peak potentials were largely dependent on pH values of the solution. Peak currents

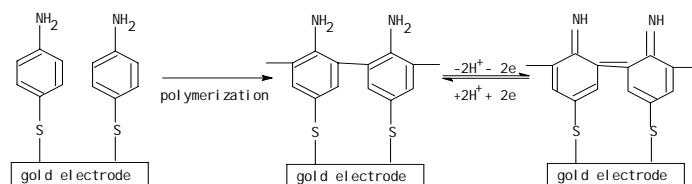
almost decreased to zero if pH of the solution was larger than *ca.* pH 6. Cathodic (E_{pc}) and anodic (E_{pa}) peak potentials were shifted negatively as pH was increased. Linear relationships between peak potentials and pH were obtained ($E_{pa} = -0.062\text{pH} + 0.575$, $r = -0.9872$; $E_{pc} = -0.061\text{pH} + 0.551$, $r = -0.9898$), suggesting that transfer of one electron corresponds to one proton as judged from the approximate Nernstian slopes of E_p vs. pH relationships. To further understand the electrochemical behaviors of monolayer poly (4-aminothiophenol), we also performed cyclic voltammetric experiments of the aminothiophenol monolayer modified on Au in 0.3 mol/L LiClO₄/ACN. We found a higher anodic current peak at *ca.* 0.67 V vs. Ag/Ag⁺ in the first anodic scan and much lower cathodic peaks at *ca.* 0.46 V vs. Ag/Ag⁺ and at *ca.* 0.25 V vs. Ag/Ag⁺ in the first cathodic scan. These current peaks decreased sharply and were not seen after the 3rd cyclic potential scan, suggesting that monolayer poly (4-aminothiophenol) is electroinactive in the non-aqueous solution. However, the same monolayer poly (4-aminothiophenol) recovered its electroactivity after the non-aqueous solution was replaced with HClO₄ aqueous solution. These findings indicate that electrochemical activity of monolayer poly (4-aminothiophenol) is determined by the presence of H⁺ in solution.

In situ frequency response of monolayer poly (4-aminothiophenol) on Au in 0.5 mol/L HClO₄ aqueous solution to potential cyclic switching is illustrated in **Figure 2**. 5 Hz of frequency decrease was found on oxidation of the monolayer polymer and the frequency returns to its initial value when the oxidized state was completely reduced, suggesting a higher protonation degree of the oxidized state of the monolayer polymer than the reduced state in aqueous solution.

Figure 2. Cyclic voltammogram (1) and simultaneously recorded frequency shift (2) of monolayer poly (4-aminothiophenol) on Au electrode in 0.5 mol/L HClO₄ aqueous solution. $dE/dt = 50$ mV/s.

A mechanism may therefore be suggested as shown in **Scheme 1** for monolayer poly (4-aminothiophenol) in acidic aqueous solution. Here polymerization through coupling of nitrogen atoms at para position as in the case of poly (2/3-aminothiophenol)⁴ is impossible, hence m-m (or o-o, not shown here) coupling is assumed.

Scheme 1. Polymerization of 4-aminothiophenol self-assembled monolayer and electrochemical process of monolayer poly (4-aminothiophenol) in acidic aqueous solution.



Acknowledgment

Financial supports from the National Natural Science Foundation of China and Education Commission Foundations of China and of Hunan Province are gratefully acknowledged. We are also highly indebted to the kind assistance from Prof. H. Yoneyama and Dr. S. Kuwabata in Osaka University, Japan.

References

1. D. Orata and D. A. Buttry, *J. Am. Chem. Soc.*, **1987**, *109*, 3574.
2. D. M. Collard and M. R. Fox, *J. Am. Chem. Soc.*, **1991**, *113*, 9414
3. R. J. Willcut and R. L. McCarely, *J. Am. Chem. Soc.*, **1994**, *116*, 10823.
4. Q. J. Xie and M. Ma, *Chinese Chem. Lett.*, **1997**, *8*, 533.
5. G. Sauerbrey, *Z. Phys.*, **1959**, *155*, 206.
6. E. Katz, D. D. Sclereth and H.L. Schmidt, *J. Electroanal. Chem.*, **1994**, *367*, 59.

Received 4 September 1998