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A Study on Ion Selectivity by Sulfur Compound Self-assembled Monolayer

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3-[4-(benzyloxy)phenoxy]propane isothiourea and 3-[4-(benzyloxy)phenoxy]propanethiol were successfully synthesized by a straightforward reaction. The self-assembled monolayers (SAMs) of 3-[4-(benzyloxy)phenoxy]propane isothiourea and 3-[4-(benzyloxy)phenoxy]propanethiol on the gold electrode as ion-selective electrode showed special capacity in recognition for Ag^+.

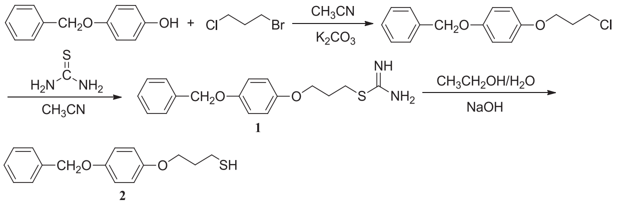
Molecular electronics is a promising area of research that focuses on a bottom-up strategy to fabricate nanoscopic electronic devices based on self-assembled monolayers (SAMs) of organic molecules on the Au surfaces.[1] Self-assembling is a convenient technique for the formation of homogeneous organic monolayers through the interaction between the head group of molecule and substrate.[2] Because of its simple preparation, good film effect, high stability, and small defects, it has been widely used in electrochemistry, molecular devices, and other fields.[3] Recent research has reported that the compound contained nitrogen atom has a high coordination selectivity toward metal ions, organic or inorganic anions; therefore, it is widely used in separation and extraction of metal ions and ion-selective electrodes.[4]

The SAMs of thiols on gold electrodes possess high stability and remarkable ordering and have attracted extraordinary interest for fundamental studies as well as for potential applications. Some efforts have been made to achieve the utilization of UV irradiation for graphene–metal oxide composites. Some recent efforts have been made to fabricate the SAMs of thiols or thioacetate-terminated molecules as ion-selective electrode. However, so far, relatively little attention has been paid to isothiourea-terminate-based SAMs.

Herein, we have successfully synthesized 3-[4-(benzyloxy)-phenoxy]propane isothiourea (**1**) and 3-[4-(benzyloxy)phenoxy]-propanethiol (**2**) (Scheme 1).

The SAM-modified gold electrodes were obtained by modifying with target compound **1** and **2**. The SAMs showed special capacity in recognition for Ag^+.

Immediately before use, the gold disk electrode (CHI, 2 mm in diameter) must be pretreated by polishing with alumina powder (0.3 µm) on a microcloth. Then the electrode was ultrasonicated in millipore water to remove alumina particles. Then it was cleaned in "piranha" solution, which consists of 30% H_2O_2 and concentrated H_2SO_4 at 1:3 ratio. Finally, the polished gold disc electrode was thoroughly cleaned and rinsed in millipore water before the SAM formation.



Scheme 1.

The monolayers were prepared by putting the pretreated gold disk electrodes in 10 mM toluene solution of **1** and **2** for about 24 h at 25 °C. After the adsorption of **1** and **2**, the SAMs-modified gold electrodes (**1**/Au and **2**/Au) were rinsed with distilled water and immediately used for the analysis.

Electrochemical measurements were performed in a conventional three-electrode electrochemical cell using a CHI-920C electrochemical analyzer (CHI, Shanghai Chenghua Co.). A Pt sheet auxiliary electrode and a saturated calomel reference electrode (SCE) were used. The bare Au electrode, the **1**/Au electrode, and the **2**/Au electrode were used as the working electrodes.

Cyclic voltammetry is an important technique to assess the ionic selection SAMs-modified gold electrodes and their blocking ability toward the electron-transfer reactions across the SAM-modified electrode–electrolyte interface.

All the chemical reagents used in this study were analytical grade (AR) reagents.

Figure 1 shows the cyclic voltammograms of the bare Au electrode, **1**/Au, and **2**/Au electrodes in a 0.1 M KCl solution. It could be seen that there were no redox peaks in −0.2 to 0.5 V potential window for the three electrodes. However, for the **1**/Au and **2**/Au electrodes, positive and negative sweep current difference value Δ*I* was much less than that of the bare gold electrode. It was explained as being due to the fact that the SAMs can be formed by the strong interaction of –S– with gold surface, which reduced the electron-transfer rate between the electrode surface and buffer solution, giving rise to the

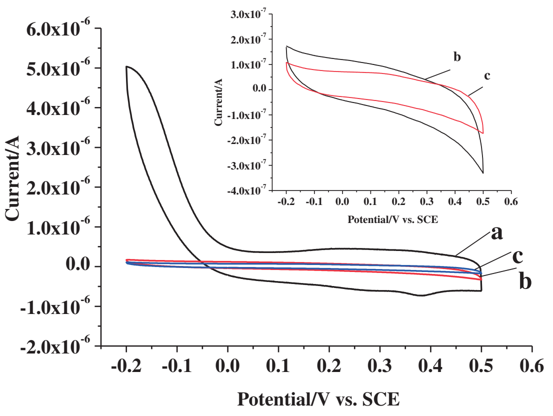


Figure 1. Au (a), **1**/Au (b), and **2**/Au (c) electrode in 0.1 M KCl.

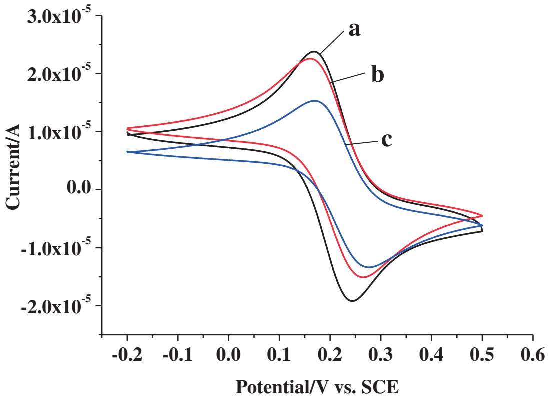


Figure 2. Au (a), **1**/Au (b), **2**/Au electrode (c) in 5.0 mM $K_3Fe(CN)_6$/0.1 M KCl.

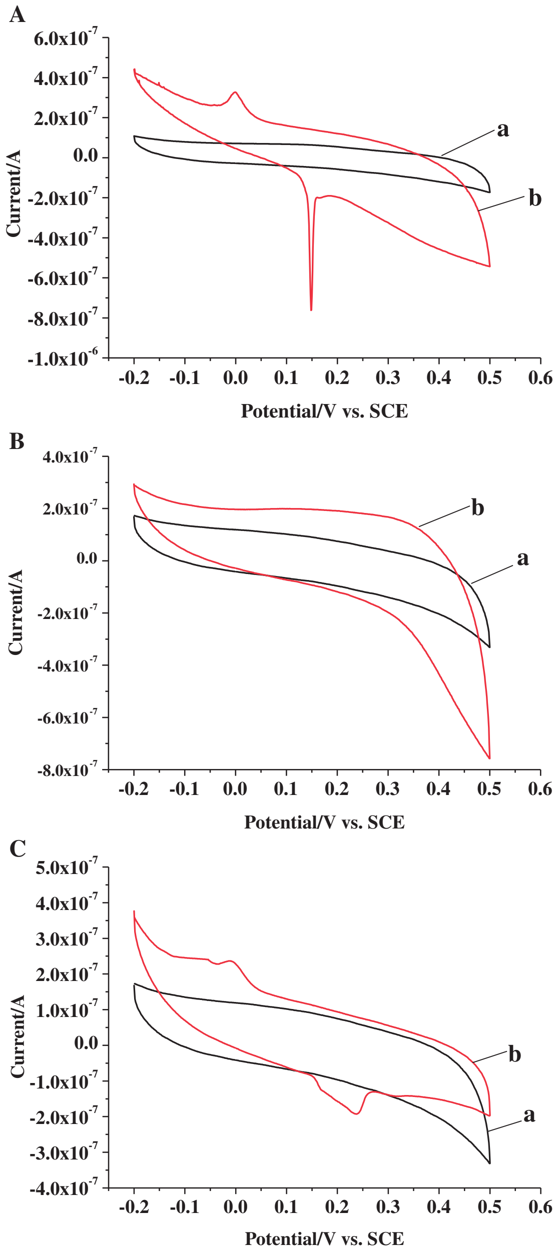


Figure 3. (A) **1**/Au electrode and 5.0 mM Ag^+ in 0.1 M KCl; (B) **1**/Au electrode and 5.0 mM Cu^{2+} in 0.1 M KCl; (C) **1**/Au electrode and 5.0 mM Fe^{3+} in 0.1 M KCl.

membrane electrode background current decrease. According to electrode–solution interface capacitance $C = \Delta I/2Av$ (A is the electrode area, v is the scan rate), the decrease of the interface capacitance actually meant that compounds **1** and **2** were adsorbed on the electrode surface.

The $[Fe(CN)_6]^{3-}$ as redox probe further confirmed the formation of compounds **1** and **2** SAMs on the Au electrode, and the results were shown in Figure 2. For the bare gold electrode (a), a couple of well-defined waves of $[Fe(CN)_6]^{3-/4-}$ appear, and the peak-to-peak separation was 50 mV. However, the reduction peak and oxidation peak spacing increased significantly when the compounds **1** and **2** were soaked in the $[Fe(CN)_6]^{3-/4-}$ solution for 24 h, indicating that electrode reaction reversibility had been significantly decreased after the adsorption of compounds **1** and **2**. The heights of the oxidation peak and reduction peak were lower than that of the bare gold electrode, indicating that the SAMs inhibited electron transfer.

1/Au and **2**/Au electrodes were separately immersed in 5.0 mM $FeCl_3$, $CuCl_2$, and $AgNO_3$ solution for 10 h, then removed, washed with deionized water, and put into 0.1 M KCl solution for the CV test.

Figure 3Ab, we could see that **1**/Au electrode adsorbing chemically silver ions showed a reversible redox peaks, indicating that Ag^+ was adsorbed to the self-assembled monolayer surface; the oxidation peak potential and the reduction peak potential of **1**/Au electrode were 0.15 and −0.08 V, respectively. Under the same conditions, there were no obvious redox peaks of **1**/Au electrode enriched of Cu^{2+} in Figure 3B, which indicated that Cu^{2+} was not adsorbed to the self-assembled monolayer surface. In Figure 3Cb,we got a conclusion that enrichment of Fe^{3+} on **1**/Au electrode had shown a reversible redox peaks, indicating that Fe^{3+} was adsorbed to the self-assembled monolayer surface; the oxidation peak potential and the reduction peak potential were 0.2347 and −0.0015 V, respectively.

Figure 4Ab shows that enrichment of Ag^+ on **2**/Au electrodes produced a reversible redox peaks, indicating that Ag^+ was adsorbed to the self-assembled monolayer surface; the oxidation peak potential and the reduction peak potential were 0.15 and −0.08 V. In Figures 4B and 4C, b showed that under the same condition, enrichment of Fe^{3+} and Cu^{2+} on **2**/Au electrodes produced no obvious redox peaks, which indicated that Fe^{3+} and Cu^{2+} were not adsorbed to the surface of self-assembled monolayer.

SECM is one of the most sensitive and informative techniques to characterize the self-assembled monolayer.[5] When the SECM probe is placed close to the substrate, it can cause current change. The two bare gold electrodes were separately immersed in 1.0×10^{-2} M toluene solution of compound **1** and **2** for 24 h and analyzed through SECM. As shown in Figure 5, for the **1**/Au and **2**/Au electrodes, the average current was respectively about -9.60×10^{-13} and -4.40×10^{-14} A, which was significantly lower than that of the bare gold electrode (-1.40×10^{-9} A), indicating that the bare gold

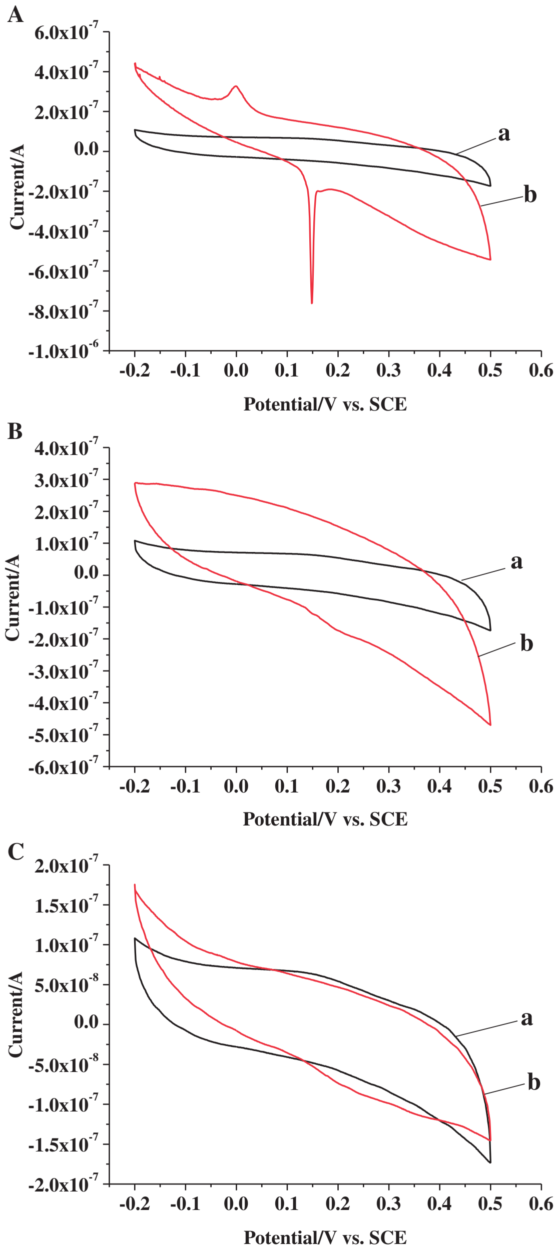


Figure 4. (A) **2**/Au electrode and 5.0 mM Ag^+ in 0.1 M KCl; (B) **2**/Au electrode and 5.0 mM Cu^{2+} in 0.1 M KCl; (C) **2**/Au electrode and 5.0 mM Fe^{3+} in 0.1 M KCl.

electrode played a restraining role on the formation of SAMs of ion spread to the gold electrode surface after adsorbed of compound **1** and **2**.

In conclusion, by cyclic voltammetry and scanning electrochemical microscopy experiments, we have found that compound **1** and compound **2** were easily adsorbed on the gold surface and formed SAMs which inhibited the electron transfer in redox solution phase. The self-assembled monolayers (SAMs) of 3-[4-(benzyloxy)phenoxy]propane isothiourea and 3-[4-(benzyloxy)phenoxy]propanethiol on the gold electrode as ion-selective electrode showed special capacity in recognition for Ag^+. Under the use of oxidation–reduction reaction to design the ligand and the use of cyclic voltammetry to detect metal ions, it has provided the corresponding theory and experimental basis for designing the molecular devices and biological sensors in the future.

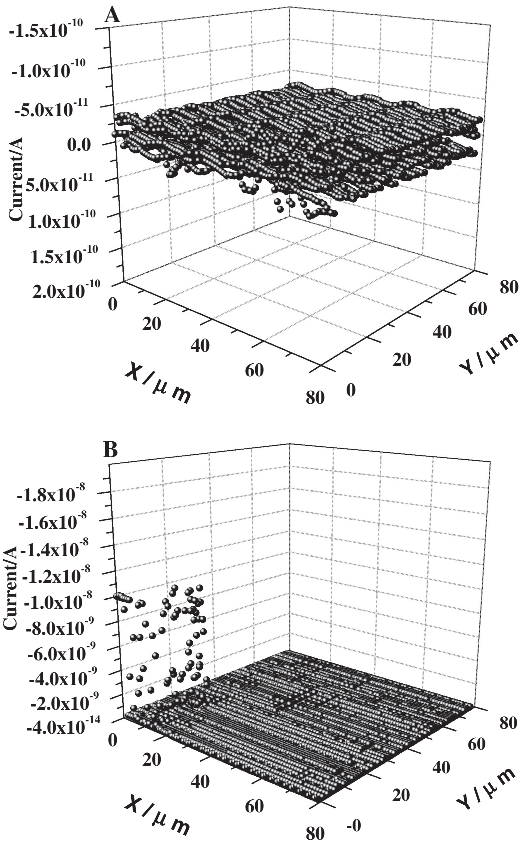


Figure 5. The SECM of **1**/Au (A) and **2**/Au (B) in 0.1 M KCl.

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