doi:10.1246/cl.2010.690

Enantioselective ITO Electrode Modified with Chiral Salen Co(II) Complex

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An enantioselective potentiometric sensor was constructed by immobilizing chiral salen Co(II) complex on an indium tin oxide (ITO) electrode modified with self-assembled monolayer of (3-aminopropyl)triethoxysilane (APTES). The proposed sensor displayed an excellent Nernstian slope of $-58.6 \pm 0.6\,\mathrm{mV\,decade^{-1}}$ in a linear range of 1×10^{-5} to $1 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$ toward D-mandelic acid (D-MA) and its enantioselectivity coefficient for the counter isomer (L-MA) was -2.71, indicating that the sensor possesses excellent chiral discrimination ability.

The design of enantioselective potentiometric sensors is an interesting challenge and also a very difficult task, because electrochemical properties do not have any direct relationship with chirality, and considerable stereoselectivity of sensors can only arise from the chiral recognition elements.[1] Chiral metallosalen complexes as highly enantioselective catalysts have been developed by virtue of their ease of preparation, highly hydrophobic and structural diversity, which endow them with various catalytic performance. We have been investigating selective discrimination using chiral salen Mn(III) as chiral selector in poly(vinyl chloride) (PVC) membrane electrodes.[2] The results obtained varied with time due to the reason that the carrier can easily run out from PVC, so the response is not stable. In addition, many factors can directly affect the potential response including plasticizer and addictive. This problem can be overcome by directly immbolized ionophore using silane monolayer as bridge linking onto the electrode to determine analytes.

Much attention has been paid to the surface modification of an indium tin oxide (ITO) electrode by assembling functional small molecules via chemical linkages. It is well known that the organosilane can be used as molecular bridge for linking specific functional groups onto many solid substrates including silicon, aluminum oxide, and indium tin oxide.[3] Thus, the 3-aminopropyltriethoxysilane (APTES) was employed as molecular bridge linking onto the thin ITO film in our experiments, which can decrease the factor of determination, and raise the sensitivity, lifetime, and accuracy of the sensor for the assay of optical active compounds. Considering the mechanism of immobilization and reorganization, only bivalent compounds can be used as active ionophore in this experiment. Therefore, we chose chiral salen Co(II) complex (Figure 1) instead of Mn(III) as chiral sensing element for the enantiorecognition of MA in this report.

The ionophore chiral salen Co(II) complex was synthesized and purified according to the literature.[4] The modification steps for chiral salen Co(II) complex on the ITO electrode surface are illustrated in Figure 1. Previous report[5] had confirmed that $\mathrm{Co^{II}}$(salen) complexes is stable once the complex was produced and cannot be oxidized on the electrode.

Chiral salen Co(II) complex was immobilized onto the surface of ITO electrode through interacting with amino group of APTES via coordinate bond.[6] The potential responses of the salen Co(II)-modified ITO electrode to D-MA and L-MA at various concentrations are shown in Figure 2. It is obvious that the different potential responses are observed between enantiomers D-MA and L-MA. The electrode exhibits excellent stereoselective recognition toward D-MA with a slope of $-58.6 \pm 0.6\,\mathrm{mV\,decade^{-1}}$, a detection limit of 4.0×10^{-6} in a concentration range of 1×10^{-5} to $1 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$, while a non-Nernstian slope of $-11.5 \pm 0.8\,\mathrm{mV\,decade^{-1}}$ toward L-MA. The resulting system has an excellent discrimination behavior to the enantiomers of mandelic acid, this may be explained by the stereorecognition power of the active chiral salen Co(II) compound.

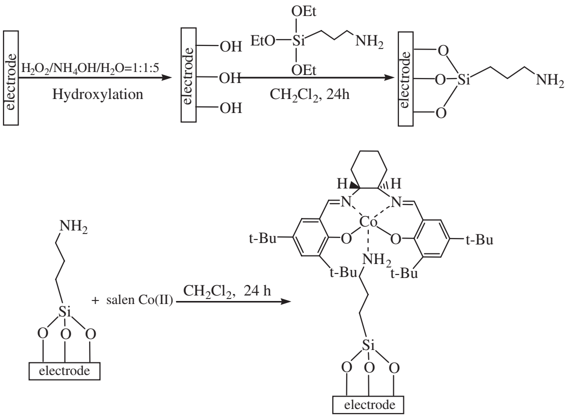

Figure 1. The procedure of immobilizing chiral salen Co(II) complex onto a conductive surface of ITO glass support.

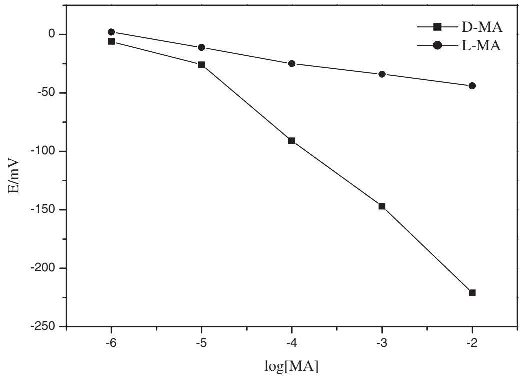

Figure 2. The potential response characteristics of salen Co(II)-modified ITO electrode for D-MA and L-MA at various concentrations.

During the experiments, we found that the ITO electrode was sensitive to pH changes. The effects of functional moieties other than salen Co(II), such as residual –OH, $-NH_2$ on the enantioselective potential response of the modified ITO electrode were examined for comparison. Results (data not shown) depicted that there is no obvious potential recognition of MA by using either of bare ITO and APTES-modified electrodes. In addition, effect of pH on bare ITO electrode and silane monolayer had been analyzed

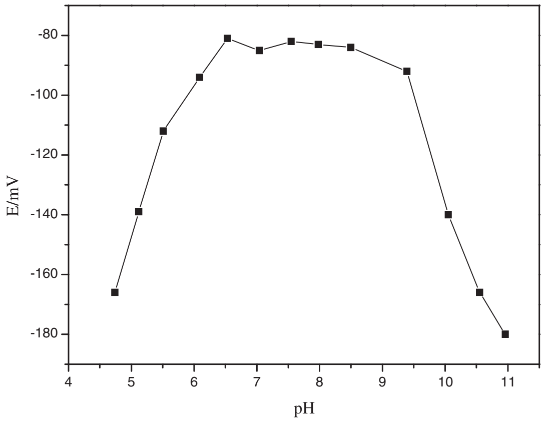

Figure 3. The influence of pH on the potential response of the modified ITO electrode measured at $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ D-MA solution.

after exposed to MA. As the pH increased, the potential response decreased from the positive to around zero.

The influence of sample pH on the potential response of modified ITO electrode was tested with $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ D-MA solution in the pH range of 4.5–11.0. The results are shown in Figure 3. It can be seen that the potential response remains nearly constant in the pH range of 6.90–9.35. Variation of the potential at pH ($\leq$6.90) could be related to the protonation of MA ion, which mainly exists as a neutral molecule in the aqueous phase. At higher pH, such as 9.35, the observed potential drift can be reasonably related to hydroxide-coordinated central metal interference. Therefore, the pH range 6.90–9.35 was taken as the working pH range of the proposed electrode.

Different methods of selectivity determination have been found in the literature. In this work, the enantioselectivity coefficients ($K^{\mathrm{pot}}_{\text{D-MA,j}}$) of sensor have been evaluated using a modified fixed interference at $1.0 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$ concentration of interfering ions as per IUPAC recommendation. In this method, an entire calibration curve is measured for varying concentration of the primary ion ([D-MA]) in a constant concentration of the interfering ion ([j]) background. The value of $K^{\mathrm{pot}}_{\text{D-MA,j}}$ can be calculated from the following equation:[7]

$$K^{\mathrm{pot}}_{\text{D-MA,j}} = \frac{[\text{D-MA}]}{[\text{j}]} \tag{1}$$

The effect of interfering compounds on the response of the electrodes usually is described in terms of selectivity coefficients. The selectivity was investigated in the presence of some hydroxycarboxylic acids and amino acids structurally similar with D-MA. Table 1 shows potentiometric selectivity coefficients of modified electrode for interfering anions relative to D-MA, which indicate that the proposed electrode is highly sensitive and enantioselective toward D-MA over L-MA and other anions.

The potentials of the salen Co(II)-modified electrode changed with the added species in the electrochemical cell and depended on the nature of the charged species.[8] Once the chiral salen Co(II) complex-based electrode was exposed to MA solution, the potential had negative shift. This is suggested to be caused by the enantioselectivity of MA, which is believed to possess a negative charge in the phosphate buffer solution (pH 7.5). While MA bound with salen Co(II), the ionophore was electronegative and reflected on the anodic shift of the potential. The chiral molecular recognition depends on the difference in stability constants of diastereomeric complexes with applied selectors, different migration of enantiomers based on the formation and dissociation of diastereomeric measured complexes, and on a different interaction rate of enantiomers with selector.[9] The enantiorecognition ability of salen Co(II) compound was confirmed by different energy and thermodynamic stabilities of complexes formed by D-MA and L-MA coordinated to salen Co(II). By quantum chemistry simulation, the geometry optimization and energy calculation were performed using Gaussian 03 at the HF/STO-3G method and basis set level.[10] Energy analysis indicates that a minimum energy of salen Co(II)–D-MA complex with a stable structure is $35\,\mathrm{kJ\,mol^{-1}}$ lower than these salen Co(II)–L-MA complexes, which may explain why the electrodes based on salen Co(II) complex enantioselectively exhibit Nernstian response to D-MA.

Table 1. The selectivity coefficients values of various interfering compounds against D-MA

Interferents	$\log K^{\mathrm{pot}}_{\text{D-MA,j}}$
L-MA	−3.21
Salicylic acid	−3.57
Benzoic acid	−3.54
D-Pro	−4.43
L-Pro	−4.42
D-Phe	−4.44
L-Phe	−4.44

In summary, we present a novel chiral sensor for the selective detecting of D-MA, which was carried out using 3-aminopropyltriethoxysilane (APTES) monolayer as a binder for chemical anchoring of chiral salen Co(II) complex on the surface of the conductive ITO electrode. These coated electrodes showed a good selective response to the corresponding configuration decade. In order to achieve enhanced stereocontrol and chiral recognition performance, the structure of metallosalen compounds can be modulated by steric and electronic properties, which can be replaced by varying the substitution pattern at the salicylidene moiety and the chiral diamine part. The investigation on metallosalen of versatile configuration and detail mechanism of the enantioselective potential response are now in progress.

This work was financially supported by Natural Science Foundation of Chongqing City, China (No. CSTC-2008BB4263), and the Fundamental Research Funds for the Central Universities of Chongqing City, China (XDNo. JK2009C091).

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