Robust single-piece all-solid-state potassium-selective electrode with monolayer-protected Au clusters

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High stability of the signal and simplicity in fabrication of the device are the two important requirements in development of potentiometric sensors. A robust single-piece all-solid-state potassium-selective electrode (K-SPE) was developed by incorporating monolayer-protected Au clusters (MPCs) as advanced ion-to-electron transducers into a conventional ion-selective membrane (ISM). The extraordinary properties of MPCs such as high solubility, profound hydrophobicity and large capacitance make them quite suitable to be used in fabrication of single-piece electrodes (SPEs) with advanced performance. The developed K-SPEs containing small amount of MPCs in the membrane showed a significant increase in the potential stability (12.9 \mu V/h), lower detection limit (10^{-6} M) and prolonged life time (high performance still after 3 weeks). The multi-valence MPCs in the membrane facilitated the ion-to-electron transduction and fast establishment of the potential equilibrium resulting in fast response time in potential measurements. The inserted MPCs did not cause any interference either in the potential formation process or in the selectivity of the ion-selective membrane.

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1. Introduction

To simplify the construction of ion-selective electrodes (ISEs) Cattrall and Freiser introduced the concept of coated-wire electrode (CWE) where the ion-selective membrane (ISM) is applied directly on Pt substrate [1]. In this construction the inner reference electrode and reference solution are not needed simplifying the construction of the device. The problem with CWEs, however, is the stability of the electrode potential formation of which requires fast and reversible ion-to-electron transduction at the ISM/substrate interface without any contribution from parasitic side reactions [2]. The poor potential stability of CWEs is due to the blocked interface formed between the purely electronic conductor-metal substrate, and the purely ionic conductor-ISM [3]. This interface is capacitive and susceptible to interferences. Ivaska et al. introduced the concept of solid-contact ISE, where a layer of conducting polymer (CP) is introduced between the substrate and the ISM [4]. The advantage of this construction is that the conducting polymer has mixed ionic and electronic conductivity and therefore functions as ion-to-electron transducer with a well-defined equilibria at the ISM/CP and CP/substrate interfaces. The concept of solid-contact has been used in many applications and with several type of materials: conducting polymers [5–9], redox-active self-assembled monolayers [10] and carbon-based materials [11–15]. These materials acted either as ion-to-electron transducers or improved the hydrophobicity between the substrate and the ISM. Replacement of the inner reference solution of ISEs by a solid contact has a variety of advantages such as the possibilities of miniaturization, and maintenance-free etc. [16,17]. Uptake of water by the ISM from aqueous samples and accumulation of water at the CP/ISM interface also introduces instability in the ISE. These phenomena have been discussed by Pretsch et al. [18]. Lindfors et al. have thoroughly studied transport of water in the polyvinyl chloride (PVC) and silicon rubber based ISM [19,20].

The next step in development of solid-state ISEs was to combine the ion-to-electron transducing material with the ISM to make single-piece all-solid-state ion-selective electrode (SPE) by dissolving the conjugated polymer in a conventional ISM cocktail. This concept was initially put forward by Bobacka et al. [21,22]. Both polypyrrole and polyaniline were used in these constructions. Recently, carbon-based materials as well as several conducting polymers were introduced as components of ISM to mediate the charge transfer at the substrate/membrane interface [23,24]. Use of these materials in the construction of solid-state ISE
improved the reproducibility and stability of the potential response when compared to the corresponding CWEs. Unfortunately, the sensitivity of most conducting polymers to CO₂, pH, light and the poor compatibility of carbon based materials in polymer materials are still the major problems in constructing stable ISE and their use in many applications.

The extraordinary size-dependent, chemical, electronic, and physical properties of monolayer-protected gold clusters (MPCs) have attracted great interests in exploring a wide range of phenomena including self-assembly [25], biolabeling [26], catalysis [27], electron-transfer theories [28], DNA melting and assays [29]. Quite recently, we have used the MPCs as an effective solid contact in ISE to develop high quality solid-contact ISE based on their profoundly good chemical stability, hydrophobicity and redox activity [30]. The equimolar mixed-valent MPC₀/₁⁺ doped with tetrakis(4-chlorophenyl)bora was found to facilitate reversible charge transfer at the substrate/solid-contact ISE interface. The sever drawbacks with the developed solid-contact ISE with MPCs are the synthesis, purification of monodisperse MPCs and the electrode fabrication making the concept complicated for many practical applications and to be used in mass-production.

The alkanethiolate-protected MPCs have good solubility in organic solvents and are also compatible with the PVC matrix of the ISM. Their stability and chemical inertness to light, CO₂, and redox species meets the basic need for usage in SPEs. The high hydrophobicity of the alkanethiolate-protected MPCs in the ISM decreases leaching of the ion-exchangers from the ISM as well inhibits the uptake of water. These improvements increase the long-term use of the developed sensors. Therefore the alkanethiolate-protected MPCs are attractive candidates in fabrication of advanced SPEs.

In this work, hexanethiolate monolayer protected gold clusters (C₆SH-MPCs) are used as advanced ion-to-electron transducers into a conventional ISM. A robust C₆SH-MPCs based single-piece all-solid-state potassium-selective electrode (MPC-SPE) was developed and get advanced performance.

2. Experimental section

2.1. Reagents

Tetrachloroauric(III) acid (HAuCl₄·3H₂O), hexanethiol(C₆SH), sodium borohydride (NaBH₄), and tetraoctylammonium bromide were obtained from AlfaAesar. Valinomycin (90%), bis(2-ethylhexyl)sebacate, potassium tetrakis(4-chlorophenyl)borate, and high molecular weight PVC were obtained from Fluka. Tetrahydrofuran (THF), acetone, and methanol were purchased from Shanghai Chemicals, China. All aqueous solutions were prepared with ultrapure water obtained from a Milli-Q Plus system (Millipore).

2.2. Fabrication of MPC-SPE

As can be seen in the Fig. 1 (c), the ISM cocktail used in this work has the following composition (w/w%): 1.0% valinomycin, 0.5% tetrakis(4-chlorophenyl)bora, 65.2% bis(2-ethylhexyl)sebacate, and 33.3% PVC. The components are dissolved in THF at a concentration of ~15% (w/w). Monodisperse hexanethiolate-protected MPCs were prepared with the method presented by Qian et al. [31]. (Synthesis of the as-prepared MPCs is described in the Supporting Information). The MPC-SPE were prepared by depositing 30 μL of the THF solution containing the ISM cocktail with amounts of MPCs (2.0 wt.%) on a well-polished GC substrate (diameter 3 mm), and the membranes were then dried in air at room temperature overnight. For comparison, an electrode modified by ISM containing 2.0 wt.% polyaniline was prepared, which was named PANI-SPE. Potassium-selective CWE were also prepared by coating the ion selective membrane on the GC electrode. The prepared

![Fig. 1](image-url)
electrodes were conditioned in 0.01 M KCl solution for 24 h prior to use and also between the experiments.

2.3. Electromotive force measurements

The potentiometric measurements were carried out by using a CHI660A electrochemical workstation (CHI, USA). The working electrode was the MPC-SPE or (CWE and PANI-SPE). The reference electrode was a Ag|AgCl electrode (3 M KCl) connected to the test solution through an electrolyte bridge filled with 1 M LiAcO (lithium acetate). The EMF readings were taken in un unstirred solutions at room temperature (22 ± 2 °C). The values were corrected for liquid-junction potentials according to the Henderson equation and the activity coefficients were calculated by using the Debye-Huckel approximation.

2.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy was performed by using a Solartron 1255B Frequency Response Analyzer (Solartron Inc., UK) with a one-compartment, three-electrode cell. The electrode under study (MPC-SPE or CWE) was connected as the working electrode. The reference electrode was a Ag|AgCl electrode (3 M KCl), and the auxiliary electrode was a platinum wire. Impedance spectra were recorded in the frequency range 100 KHz-10 mHz at the open circuit potential. The amplitude used was 200 mV in order to enhance the signal/noise ratio. The measurements were done in 0.1 M KCl at room temperature.

2.5. Chronopotentiometric measurements

These measurements were record by using a CHI660A workstation with a one-compartment, there-electrode cell. A constant current of 1 nA was applied to the working electrode for 100 s followed by a reversed current of the same magnitude for the same time span. The measurements were done in 0.1 M KCl at room temperature.

3. Results and discussion

A schematic picture of C$_2$SH-MPCs is represented in Fig. 1 (a). The strong chemical interaction between gold and thiolates creates ubiquitous Au-S interfaces in thiolate-stabilized gold clusters. The as-prepared MPCs were characterized by high resolution transmission electron microscopy (HRTEM) in Fig. 1 (b). The image shows a monodisperse characteristic of MPCs with an average sized of about 2 nm. A schematic picture of an ISM containing MPCs is shown in Fig. 1 (c). The ISM thickness was characterized by scanning electron microscope (SEM) in Fig. 1 (d). The image shows the thickness is about 54.2 μm.

3.1. Electrical characterizations of MPC-SPE

Impedance spectra of the CWE and the MPC-SPE containing 2.0% MPCs are shown in Fig. 2 (a). The high-frequency semicircles of the MPC-SPE and the CWE are similar and can be related to the bulk impedance process of the membrane. This indicates that MPCs have no effect on the bulk conductivity of the membranes [32]. The time constant ($\tau_b$) of the bulk process is calculated by using the frequency ($f_{\text{max}}$) at the top of the high-frequency semicircle: [21]

$$\tau_b = \frac{1}{2\pi f_{\text{max}}}.\left(1\right)$$

CWE showed a time constant of 0.08 ms while the MPC-SPE showed a slightly smaller time constant of 0.05 ms. It suggests that the bulk process of the electrodes becomes faster with incorporated MPCs. Beginning of a second semicircle can be observed at low frequency in the spectra of both CWE and MPC-SPE. This semicircle is related to charge transfer process at the GC|ISM interface. As can be seen in Fig. 2 (a) this low-frequency semicircle become significantly smaller with increasing amount of MPC in the membrane indicating that the charge transfer impedance is largely decreased by incorporating MPCs into the membrane.

If an undesirable water layer is formed between the ISM and substrate, a potential drift would be observed when the electrode is exposed to a solution of interfering ions. This was introduced by Pretsch et al as an indirect indicator to study the influence of the water layer at the substrate/ISM interface [18]. In this study, the CWE, PANI-SPE and MPC-SPE were first stabilized in 0.1 M KCl solution and then move to a solution of 0.1 M NaCl. A clear potential drift was observed with two electrodes. After 4 h the electrodes were changed back to the 0.1 M KCl solution. Fig. 2(b) unambiguously shows a difference between the behavior of the K-CWE and the K-SPE with amount of MPCs.

As can be seen in Fig. 2(b), the potential drift of CWE and PANI-SPE are positive when the 0.1 M KCl solution was switched to a 0.1 M NaCl solution and then negative when the solution was switched back to 0.1 M KCl. When the MPC-SPE were exposed to 0.1 M NaCl solution after 0.1 M KCl solution some potential drift was also observed. But when the electrodes were then changed back to 0.1 M KCl a stable potential was practically immediately obtained with the MPC-SPE. The MPC-SPE electrode obtained the original potential but the CWE electrode showed a continuous drift and the PANI-SPE also showed a little negative drift. The result presents that the hydrophobic MPCs are favorable in preventing the present undesirable water layer at the substrate/ISM interface. The intermediate-term stability of the MPC-SPE calculated after 20 h in the third step (from 0.1 M NaCl to 0.1 M KCl) is 12.9 μV/h, which is comparable with most of solid-contact ISE (see the Supporting Information, Table S1).

Reversal chronopotentiometry with $\Delta I = ±1$ nA was used to estimate the capacitance and potential stability of the membrane with 2.0% MPCs in ISM [33]. As shown in Fig. 2 (c), a potential jump that is
related to the resistance of the ISM is followed by a slow potential polarization. The resistance values estimated for the CWE and MPC-SPE are 4.60 MΩ and 4.24 MΩ, respectively, which are in accordance with the results from the impedance measurement. The potential stability, increases with the addition of MPCs in the ISM. The potential drift of the CWE was \( \frac{dE}{dt} = 1.0 \times 10^{-5} \) V/s and decreased to \( \frac{dE}{dt} = 3.1 \times 10^{-5} \) V/s by addition MPCs in the membrane. From the fundamental capacitor equation, \( I = C \frac{dE}{dt} \), the electrical capacity of MPC-SPE can be estimated to 32.6 μF which is comparable with some solid-contact ISE with an ion-to-electron transducing layer between the ISM and the substrate. Therefore, incorporating even a small amount of MPCs has a great effect on the capacitance of the SPEs which is essential to the long-term potential stability.

### 3.2. Potentiometric characteristics

The stability of the electrode was studied by recording the potential drift in a cycle. Fig. 3 (a) shows that the calibration curve of a MPC-SPE remains almost unchanged for two weeks indicating that accurate and reproducible potential values can be measured without recalibration of the electrode. After three weeks, the low detection limit was slightly increased to \( 10^{-5.7} \) M and the slope of the calibration curve was also slightly changed. The parallel shift of the calibration curve from two to three weeks indicates that the standard potential was changed slightly over this time period as would have been expected according to the long-term potential stability. The good potential stability of MPC-SPE is useful in actual applications where fast and stable potential readings are required [17].

The stability of CWE and MPC-SPE in 0.1 M KCl over a period of 3 weeks is shown in Fig. 3 (b). The potential of the CWE constantly drift during the test period, which may be attributed to the influence of the water layer formation at substrate/ISM interface [34]. Reproducibility of the standard potential is, however, significantly improved with addition of MPCs in the ISM. The standard potential of the MPC-SPE was found to maintain a stable value of about 350 mV for over 2 weeks after three days’ conditioning. The reasons why MPCs have such a great stabilizing influence on the standard potential of the electrodes may be as the following. The as-prepared MPCs\(^{n/n+1}\) act as multivalent redox centers and provide a sufficient well-defined ion exchange properties. Therefore, a stable electron exchange equilibrium potential appears at the GC|ISM interface. The exact cause for the increased rate of the equilibrium process in not clear but the increased hydrophobicity of membrane preventing the water layer formation is no doubt. The MPCs are also advantageous for the ionic processes at the ISM/solution interface. Their large capacitance, profoundly good hydrophobicity and chemical inertness all promote to the long-term potential stability of MPC-SPE. In addition no interferences from light or redox couples were found (in the Supporting Information, Fig. S1).

The calibration curves of the CWE and the PANI-SPE and the MPC-SPE are shown in Fig. 4 (a). The MPC-SPE has a near-Nernstian slope with the sensitivity of 57.4 mV/decade (standard deviation of the slope with three different electrodes is ±0.6 mV/decade), which was rather stable and did not deteriorate as the sensitivity of the CWE. It is worth to note that the linear range of the MPC-SPE is from \( 10^{-5} \) to \( 10^{-1} \) M and the detection limit is 10⁻⁶ M. These results are superior to that of the CWE (10⁻⁵ M) and the PANI-SPE (10⁻⁵.4 M) in the same conditioning. The lower detection limit of MPC-SPE may be due to the improved hydrophobicity of the membrane preventing leaching of ionophores from the ISM [35]. The lower detection limit of the MPC-SPE electrode may also be due to lower co-extraction of the electrolyte to these ISM [36]. The MPC-SPE also has a fast response time as shown in Fig. 4 (b). It can response in 10s when the activity of \( K^+ \) was increased from \( 10^{-6} \) M to \( 10^{-5} \) M. The potential of MPC-SPE was stabilized with in few seconds after each increase in the concentration of \( K^+ \). The signal to noise ratio is greater than three at \( 10^{-6} \) M \( K^+ \), which is in accordance with above result.

Introduction of MPCs in the ISM did not have any influence on the selectivity coefficients (\( \lg K_{pot} \)) of the electrodes \((n = 3)\) calculated with the separated solution method:\( ^{17} \lg K_{pot} = -4.2 \pm 0.3 \), \( \lg K_{pot} = -4.3 \pm 0.2 \), \( \lg K_{pot} = -2.1 \pm 0.3 \), \( \lg K_{pot} = -4.2 \pm 0.2 \), \( \lg K_{pot} = -4.5 \pm 0.3 \), which are similar as observed with the CWE.

### 3.3. The response mechanism

The proposed response mechanism of the MPC-SPEs studied in this work is schematically shown in Fig. 5. As illustrated in the scheme, the process of ion recognition and signal transduction can ideally be divided into several steps: 1) ions transfer and complex formation at the interface SIM/aqueous phase. 2) transport of the complex ion in ISM including coupled ion and electron transfer. 3) electron transport at the GC|ISM interface. In the second step, when open the coupling of ion and electron transfer is expected to be facilitated through the MPCs as multivalent redox centers. For their high electron conduction, the MPCs exchange e⁻ with the GC and facilitate electron transfer across the GC|ISM interface in step 3. In our work, the reaction at that interface

![Fig. 3.](image1) (a) The calibration curves of the MPC-SPE over three weeks, conditioned in 0.01 M KCl and stored in the same solution between uses. (b) Long-term potential stability of the CWE, and MPC-SPE recorded in 0.1 M KCl solution.
can be written as follows

\[ \text{MPC}^n + \text{K}^+ \text{TCIPB}^- \leftrightarrow \text{MPC}^{n+1} \text{TCIPB}^- + \text{K}^+ + e^- \]  

(2)

where \( \text{K}^+ \) is the complexes of \( \text{K}^+ \) and valinomycin. At equilibrium, the overall reaction at the GC|ISM interface can be described by the Nernst equation.

\[ E = E^0 + \frac{RT}{F} \ln \frac{C_{\text{ISM}[\text{MPC}^{n+1}]} \cdot C_{\text{ISM,K}^+}}{C_{\text{ISM,\text{V}^-}} \cdot C_{\text{water},K^+}} \]  

(3)

\( E^0 \) is the standard potential of the MPC-SPE. \([\text{MPC}^n]\) and \([\text{MPC}^{n+1}]\) are the concentrations of the MPC in the membrane. The efficient ion-to-electron transition and large redox capacitance of MPCs, together with the improved hydrophobicity of the ISM result in a better potential stability and reproducibility of the MPC-SPE.

### 4. Conclusions

Small amount of soluble hexanethiolate-protected MPCs was introduced to the conventional ISM to construct MPC-SPE with improved analytical performance. The MPCs based MPC-SPE show well-defined phase-boundary potential at the GC|ISM interphase. Its large redox capacitance and good chemical stability ensure good potential stability and reproducibility. The high hydrophobicity of MPCs helps to prevent formation of an undesirable water layer at the substrate/ISM interface, which plays a key role in its long working lifetime. In the meantime, decreasing leakage of the membrane components is also essential for good performance of MPC-SPE. The ion-to-electron transduction efficiency in the ISM was improved by MPCs. Construction of the SPE is rather simple: making the ISM cocktail and simple one-step drop casting of the cocktail on the electrode substrate. Hence, we propose MPCs to be used as additives in conventional ion-selective membranes to construct all-solid-state ISE.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.jelechem.2016.10.053.

### References


