Simple and Efficient Synthesis of Gold Nanoclusters and Their Performance as Solid Contact of Ion Selective Electrode

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**A B S T R A C T**

Gold nanoclusters are ideal materials as solid transducer in all-solid-state ion-selective electrodes (ISEs) due to their high hydrophobicity, excellent ion-to-electron transduction, high specific capacitance and outstanding chemical stability. In this paper, monolayer-protected gold nanoclusters (MPCs) were synthesized by a simple one-phase method requiring a relatively short reaction time with high yield (60%). Transmittance electronic microscopy (TEM) and atomic-force microscopy (AFM) were used to characterize the morphology of MPCs. The composition of MPCs was studied by UV–vis spectrometry, Matrix-assisted laser desorption ionization (MALDI) mass spectrometry, X-ray diffraction (XRD) measurement and X-ray photoelectron spectroscopy (XPS) measurements. The performance of MPCs based ISEs was thoroughly characterized by electrochemical impedance, electromotive force and chronopotentiometry measurement. Comparison with the performance of ISE with other signal transducing materials such as conductive polymer, carbon nanotube, graphene and fullerene, the MPCs based ISEs have higher potential st ability and reproducibility, lower detection limit, longer operating life (one year) and higher anti-interference ability.

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1. Introduction

Due to their unique advantages (such as maintenance-free, easy microminiaturization, long-term stability and low cost), all-solid-state ion-selective electrodes (ISEs) have been attracting broad interest of scientists. One bottleneck of all-solid-state ISEs development is the lack of a clear definition of solid transducer. The other is the presence of a water layer at the interface between the electrode substrate and the ion-selective membrane (ISM), which leads to poor stability and reproducibility of all-solid-state ISEs. Different materials have been used as solid transducer such as Ag|AgCl, redox-active self-assembled monolayer [1], Prussian blue [2], carbon-based materials [3–8] and conducting polymers (CPs) [9–11]. Since Nobel Prize in Chemistry was honored to the research with CPs, they have received a lot of attention [2,9–12]. However, most CPs are photosensitive and partially hydrophilic making them not ideal transducer materials. Other materials also have their own shortcomings, such as low redox capacitance of electroactive monolayers, and hydrophility of carbon-based materials [13].

Due to the excellent physical, chemical and electronic properties, monolayer-protected gold nanoclusters (MPCs) have been widely used in many fields, e.g. self-assembly [14], biological label [15], catalysis [16], electron transfer theory [17], DNA immune analysis [18]. MPCs as solid contact transducer material can provide a clearly-thermo-defined, electrochemical-reversible, non-polarizable interface. In addition, MPCs are more hydrophobic than other materials, which can effectively eliminate formation of water layer. Our group prepared an all-solid-state ISEs using MPCs (Au144) in 2012 [19]. In that work, the tetrakis(4-chlorophenyl) borate (TB\textsuperscript{−}) anion doped MPCs was synthesized by a two-phase method at 0°C by low stirring rate. The synthesis time was long with a low yield (20–30%).

Akola et al. obtained the structure of Au25(SR)\textsubscript{18} cluster by theoretical calculations [20], confirmed by Heaven et al. by single
crystal X–ray crystallography [21]. \( \text{Au}_{25}(\text{SR})_{18} \) clusters with different charge states (0, +1 and −1) have high stability and can reversibly be transferred between ionic and electronic conductions. In this work, \( \text{Au}_{25} \) nanoclusters (Au NCs) with different charge states (0, +1 and −1) were prepared by an efficient one-phase method. Comparison with the traditional two-phase method, the revised approach needs shorter reaction time, simpler operation and gives a higher yield (60%). ISEs based on \( \text{Au}_{25}(\text{SR})_{18} \) (\( \text{K}^+\text{-MPCs-ISE} \)) have shown good analytical properties.

2. Experimental

2.1. Chemical reagents

All of the chemicals used are commercially available and used without any further purification. Hydrogen tetrachloroaurate tetrahydrate (HAuCl\(_4\)•4H\(_2\)O, Shanghai Chemical Reagent Co. Ltd), Tetra-n-octyl ammonium bromide (TOAB, 98%), 1-dodecanethiol (98%), cerium (IV) sulfate tetrahydrate (Ce(SO\(_4\))\(_2\)•4H\(_2\)O, AR) and tetrabutylammonium perchlorate (Bu\(_4\)NClO\(_4\), 98%) were purchased from Alfa. Sodium tetrachloroaurate (NaAuCl\(_4\), 98%, powder, Shanghai Chemical Reagent Co. Ltd). Sodium perchlorate (NaClO\(_4\), 98.0%), methanol (AR), acetone (AR), dichloromethane (AR), and tetrahydrofuran (THF, AR) were purchased from Beijing Chemical Works. Di[2-ethylhexyl]sebacate (DOS), valinomycin, potassium tetrakis[4-chlorophenyl] borate (KTB) and polyvinyl chloride (PVC) were purchased from Fluka. Nanopure water with a resistivity of >18 M\(\Omega\) cm was used in this study.

2.2. Synthesis of anionic \( \text{Au}_{25} \) nanoclusters (\( \text{Au}_{25}^- \), \( \text{Au}_{25}^{00} \) and \( \text{Au}_{25}^+ \))

\( \text{Au}_{25}^- \) was firstly synthesized by a modified one-phase procedure. All the experiments were conducted at room temperature. As shown in Fig. 1, HAuCl\(_4\)•4H\(_2\)O and TOAB (1:1.2, w/w) were first mixed in THF solution under stirring. Then, \( \text{C}_{12}\text{H}_{25}\text{SH} \)(5 eq. to HAUCl\(_4\)•4H\(_2\)O) was slowly added to the flask at room temperature and keeping the same stirring rate. The color of the solution gradually changed from red to yellow and then to colorless within ~30 min. After that, an aqueous solution of NaBH\(_4\) (with concentration of 0.5 M and temp. 0°C) was rapidly poured into the flask. The reaction generated some bubbles and the solution turned immediately black, indicating the formation of Au nanoclusters. The reaction was allowed to proceed under constant stirring for ca. 3 h. After removal of the water layer, the precipitates were collected and thoroughly washed with water and methanol, then dried under reduced pressure at room temperature. The resulting \( \text{Au}_{25}^- \) nanoclusters were dispersed in acetone and extracted by a vacuum rotary evaporator at room temperature. The resulting solid material was dissolved under \( \text{N}_2 \) atmosphere in \( \text{CH}_2\text{Cl}_2 \) for further use. In order to convert \( \text{Au}_{25}^- \) to \( \text{Au}_{25}^{00} \) nanoclusters, the solution was bubbled with \( \text{O}_2 \) for about 20 min. The \( \text{Au}_{25}^{00} \) nanoclusters were then obtained by oxidation with Ce (IV). (More experimental details are shown in the supporting information)

2.3. Preparation of potassium ISE, \( \text{K}^+\text{-MPCs-ISE} \)

Glassy carbon disc electrode (GC, 3 mm diameter) was polished with 0.3 and 0.05 µm aluminium oxide powder, washed by water and dried with \( \text{N}_2 \). 7 µL of a solution containing both \( \text{Au}_{25}^- \) and \( \text{Au}_{25}^{00} \) in 1/1 concentration ratio was dropped onto the surface of GC electrode for 7–8 times and the solvent was allowed to evaporate after each addition. Then, 50 µL of the ISM cocktail in THF (15 wt. %) was dropped on the MPCs modified substrate. The composition of the ISM cocktail (w/w %) was: 1.0% valinomycin, 0.5% KTB, 65.2% DOS and 33.3% PVC. The as prepared \( \text{K}^+\text{-MPCs-ISE} \) was kept in 0.01 M KCl solution for storage. Coated wire electrode with the same ISM (\( \text{K}^+\text{-CWEs} \)) was prepared by the same method and used as the reference.

2.4. Material characterization

Transmittance electronic microscopy (TEM) and high resolution transmittance electron microscopy (HRTEM) measurements were performed by a Tecnai G2 T20 system (FEI Company) operating at 200 kV. All atomic-force microscopy (AFM) images were recorded in the tapping mode using a 5500 AFM system (Agilent Technologies, Chandler, USA). X-ray diffraction (XRD) measurement was performed by using a D8 ADVANCE of BRUKER company in Germany with Cu-K\(\alpha \) as X-Ray source. UV–Vis spectra were recorded by a VARIAN CARY 50 UV/Vis spectrophotometer at room temperature. Matrix-assisted laser desorption ionization (MALDI) mass spectra were obtained on a linear-mode time-of-flight (TOF) mass spectrometer (AutoflexIII, Bruker, Germany) and Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was used as the matrix. The laser intensity was kept low enough (just above the threshold intensity) and the cluster-to-matrix ration was optimized to 1:1000. X-ray photoelectron spectroscopy (XPS) measurements were performed by using a VG Thermo ESCALAB 250 spectrometer (VG Scientific) operated at
120 W. The binding energy was calibrated against the carbon 1s line.

2.5. Electrochemical characterization

**Electrochemical Impedance measurement:** EIS was performed by using a Solartron 1255 B Frequency Response Analyzer (Solartron Inc., UK) with traditional three-electrode system: KCl-MPCs-ISE or KCl-CWEs as the working electrode, Ag/AgCl/3 M KCl (1 M LiAc solution in salt bridge) as the reference electrode and a platinum wire as the counter electrode). The measurements were performed in 0.1 M KCl at the open-circuit potential within the frequency range from 100 kHz to 10 mHz. Disturbance amplitude was 10 mV.

**Electromotive force measurements:** The potentiometric measurements were carried out by using a CHI660A electrochemical workstation (CHI, USA). The EMF readings were taken in unstirred solutions at room temperature (20 ± 2 °C). The indicator and the reference electrode were the same as those used in the impedance measurement. All of tests were measured in KCl solution with different concentration.

**Chronopotentiometry:** 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 for 100 s. The measurements were done in 0.1 M KCl at room temperature.

3. Results and discussion

TEM and HRTEM image of the as-synthesized Au NCs shows that the sizes of Au NCs were within a narrow range of <2 nm (Fig. 2A and B). Fig. 2C shows a high-resolution image obtained in the area marked in Fig. 2B. The observed lattice spacing of 0.235 nm can be corresponded to (111) crystal plane of cubic Au. AFM topographic image reveals that the as-synthesized Au NCs are spherical and quasi-spherical particles (Fig. 2D). From the cross-sectional height profiles, it can also demonstrate the small size of the as-synthesized Au NCs.

XRD analysis for the as-synthesized Au NCs is shown in Fig. 3A. Four distinct diffraction peaks at 38.2°, 44.4°, 64.6°, 77.5° are corresponding to (111), (200), (220), and (311) of the Au face-centered cubic (fcc) crystal structure, respectively [22]. The composition of as-synthesized Au NCs was analyzed through MALDI-TOF MS under a very low laser pulse intensity (just above the threshold intensity). As shown in Fig. 3B, an obvious peak at ~8549.3 Da was obtained in the MALDI spectrum, which is attributed to the Au_{25}(SC_{12}H_{25})_{18}^{18} ion (theoretical value: 8549.32 Da). Another clean peak at ~6958.6 Da [23] was attributed to Au_{25}(SC_{12}H_{25})_{14}^{14} (theoretical value: 6955.86 Da), which was due to laser-induced fragmentation of Au_{25}(SC_{12}H_{25})_{18}. Fig. 3C shows the characteristic UV–vis fingerprints of the thiol-capping Au_{25} nanoclusters [24,25]. Three distinct absorption bands centered at 677, 443 and 392 nm were observed. Moreover, there are additional spectrum features, including a broad shoulder centered

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Fig. 2. (A) TEM and (B) HRTEM image of the as-synthesized Au NCs. (C) A high-resolution image obtained in the area marked in (B). (D) An AFM image of the as-synthesized Au NCs and cross-sectional height profiles (inset) obtained along the green line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Fig. 3. (A) XRD patterns of the as-synthesized Au NCs. (B) MALDI-TOF mass spectrum of Au$_{25}$ nanoclusters in N$_2$-saturated CH$_2$Cl$_2$ solution. Inset figure shows the zoomed-in spectrum in the range of mass number 8.50–8.60 kDa. The red patterns are from the theoretical simulation. (C) UV-vis absorbance spectra of Au$_{25}$ nanoclusters with different charge states in CH$_2$Cl$_2$ solution, Au$_{25}$$^{00}$ (blue curve); Au$_{25}$$^{0+}$ (red curve); and Au$_{25}$$^{+1}$ (black curve). (D) XPS spectra of Au$_{25}$ nanoclusters with different charge states, Au$_{25}$$^{0+}$ (blue curve); Au$_{25}$$^{00}$ (red curve); and Au$_{25}$$^{+1}$ (black curve).

at 800 nm and another small shoulder at 550 nm. It can be seen that the spectroscopic fingerprints of Au$_{25}$$^{00}$ and Au$_{25}$$^{+1}$ are different from the original Au$_{25}$$^{-3}$ clusters. In addition, XPS spectra can also be used to distinguish between Au$_{25}$ nanoclusters with different charge states. As shown in Fig. 3D, the Au 4f$_{7/2}$ binding energy of gold clusters shows a positive shift with the charge state changing from $-1$ (83.75 eV), to 0 (83.85 eV) and to +1 (84 eV), suggesting the successful synthesis of Au$_{25}$ nanoclusters with different charge states.

Impedance measurements, chronopotentiometry, water-layer tests and interferences tests were done in order to demonstrate the performance of the as-synthesized MPCs transducers in the solid-contact K$^+$-ISEs. The impedance responses of K$^+$-MPCs-ISEs and K$^+$-CWE are shown in Fig. 4A. There are big semicircles in the high frequency region of both K$^+$-MPCs-ISEs and K$^+$-CWE, which are related to the bulk resistance of the membranes. The diameter of the semicircle decreased from 1 to 0.5 MΩ with the addition of MPCs, i.e. from K$^+$-CWE to K$^+$-MPCs-ISEs. The presence of MPCs film effectively reduces the contact resistance and improve the charge transfer at solid contact interface [26]. At low frequency region, a large semicircle is observed with the K$^+$-CWE but none with the K$^+$-MPCs-ISEs. The reason is that K$^+$-CWE has a small contacting capacitance and a large charge transfer resistance at the interface between the ISM and the GC substrate. The MPCs film tremendously increases the interface contact capacitance and greatly promotes the ion-electron transfer.

Fig. 4. (A) Impedance plot of K$^+$-MPCs-ISE (red) and K$^+$-CWE (black) in 0.1 M KCl solution. (B) Chronopotentiometry for K$^+$-MPCs-ISE (red) and K$^+$-CWE (black) in 0.1 M KCl solution. (C) Water layer tests for K$^+$-MPCs-ISE (red) and K$^+$-CWE (black) switched from 0.1 M KCl to 0.1 M NaCl and finally to 0.3 M KCl solution.
Chronopotentiometry has been proposed to evaluate the electric capacity of the low frequency capacitance of MPCs transducer layer, which is connected with potential stability of the electrode [27]. The chronopotentiometric curves of K⁺-MPCs-ISEs and K⁺-CWE are shown in Fig. 4B. The slope of the potential and time (ΔE/Δt) curve was used to calculate the electric capacity of MPCs transducer layer. The obtained ΔE/Δt of K⁺-MPCs-ISEs was 4.32 μV/s. By using the formula ΔE/Δt = i/Cm, the electric capacity of K⁺-MPCs-ISEs was calculated to 231.5 μF. The high electric capacity of the K⁺-MPCs-ISEs plays an important role in resisting the external current polarizing [28].

Water-layer tests is also an important indicator for ISEs. The existence of a water-layer causes large potential drift in the response of the ISEs [29]. Potentiometric measurements with K⁺-MPCs-ISEs and K⁺-CWE were done by switching them from 0.1 M KCl to 0.1 M NaCl solution and then finally back to 0.1 M KCl (Fig. 4C). When the electrodes were changed back to 0.1 M KCl, a stable potential was immediately obtained with the K⁺-MPCs-ISEs. But the potential of the K⁺-CWE continuously changed in the test. The hydrophobic MPCs are favorable in preventing the present of water layer at the substrate/ISM interface. Gas, light and redox interferences were also conducted with the K⁺-MPCs-ISEs and K⁺-CWE. As shown in Fig. S1, all the results indicated that the K⁺-MPCs-ISEs had a good resistance to these negative influences. The good stability of the K⁺-MPCs-ISEs may be attributed to the following reasons: (1) the as-prepared MPCs N°°°° as multivalent redox centers can provide a stable ion exchange equilibrium-based potential at the GC/ISM interface. (2) The large redox capacitances of MPC films play an important role in the potential stability [19]. (3) The high hydrophobicity of MPC films is also essential to the long-term stability of K⁺-MPCs-ISEs.

The electromotive force measurements with the K⁺-MPCs-ISEs were recorded at different concentrations of K⁺. As shown in Fig. 5, the sensitivity of the electrode, i.e. the slope of the calibration curve is 55.1(±1.22) mV/decade. A linear response is obtained between 10⁻⁶ and 10⁻¹ M. The detection limit is 1.55 × 10⁻⁷ M. All data are better than those obtained with the K⁺-CWE. As shown in Fig. 6, the lifetime of the K⁺-MPCs-ISEs was about one year when it was left in 0.01 M KCl solution. The details were shown in the supporting information. After two weeks, the detection limit slightly increased to 10⁻⁶.3 M and the slope of the calibration curve changed from 55.1(±1.83) mV/decade to 55.8(±0.82) mV/decade, as shown in Fig. S2. After one month, the slope decreased to 53.6 (±0.49) mV/decade (Fig. S3 in the supporting information) and the detection limit decreased to 10⁻⁶ M. As shown in Fig. S4, two months later, the values changed to 51.22 (±1.37) mV/decade and 10⁻⁶.22 M, respectively.

After storage for one year, the performance of the K⁺-MPCs-ISEs were also studied. The sensitivity value changed to 51.0 (±1.03) mV/decade and the detection limit was 10⁻⁴.72 (Fig. S5), indicating the acceptable stability and reproducibility of the produced K⁺-MPCs-ISEs [30]. The decrease of detection limit was attributed to the leakage of the membrane components and the partial dissolution of Au NCs in the membrane. It was also due to the increase of bulk resistance of the membrane leading to the difficult charge transfer at solid contact interface. The increase of bulk resistance of the membrane was verified in Fig. S6, the diameter of the semicircle increased from 1 to 2 MΩ. According to a previous work, the decrease of detection limit can be reduced by storing ISE in distilled water or at dry station [31]. An immobilization method of the membrane components will be studied in the near future.

4. Conclusion

Au₂₅ nanoclusters were synthesized in a simple one phase method with a high yield. The method is very useful for bulk production of MPCs based ISEs. ISE with MPCs films as redox SC layers has good performance, such as great chemical stability, high hydrophobicity, low electrical resistance and high resistance to gas, light and redox interferences. Moreover, the hydrophobicity and
excellent adhesive strength of the MPC layer with the ISM are essential to improving the detection limit, prohibiting the water layer formation, preventing the leaking of the membrane components, and prolonging the service life time. Even the partial dissolution of the Au clusters in the ISM improves the performance of K+-MCPs-ISEs. Electrochemical studies have clearly demonstrated that the developed MCPs solid-contact layer improves the stability of ISEs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2016.11.069.

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