A facile method to prepare noble metal nanoparticles modified Self-Assembly (SAM) electrode

Feng Liu, Long Huang, Xiao Duan, Yun-yan Li, Jin-quan Hu, Bai-hui Li and Jun Lu
Sino-Precious Metals Holding Co., Ltd., Kunming, China

ABSTRACT
Noble metal nanoparticles (NPs) modified electrodes have shown promising applications in the areas of catalysis, (electro)chemical analysis and biosensing due to their unique characters. In this paper, we introduced a so-called ligand exchange method to prepare self-assembly (SAM) electrode modified with noble metal nanoparticles. The noble metal nanoparticles protected by weakly adsorbed tetraoctylammonium bromide (TOAB) were synthesized firstly, then self-assembly (SAM) dithiol-modified Au electrode (Au-SH$_{SAM}$) was immersed into the solutions containing TOAB-protected nanoparticles. Due to the strong interaction between the dithiol groups on the electrode and noble metal nanoparticles, the weakly adsorbed TOAB on the surface of noble metal NPs were replaced by dithiol groups. As a result, the TOAB protected NPs were anchored on the Au-SH$_{SAM}$ template electrode surface by ligand exchange, obtaining noble metal NPs modified electrode with high quality and stability. By adjusting the soaking time, the coverage of nanoparticles on the Au-SH$_{SAM}$ electrode surface could be controlled. The morphology and distribution of noble metal NPs on Au-SH$_{SAM}$ surface was analysis by scanning tunneling microscope (STM), and their electrochemical property was studied by cyclic voltammetry (CV) in H$_2$SO$_4$ solution. The approach is proved as a universal way to prepare noble metal NPs modified SAM electrode.

1. Introductions
Noble metal nanomaterials have some unique properties in the field of electronics, magnetics and optics [1–3]. Meanwhile, noble metal NPs modified electrodes have shown promising applications in the areas of catalysis, (electro)chemical analysis and biosensing due to their unique characters such as good conductivity, strong capacity to promote electronic transmission, high catalytic activity and high sensitivity and/or selectivity in electrochemical analysis [4–7]. For example, Au NPs can promote electrocatalytic reaction by accelerating electron transfer process in redox center. By using Au NPs modified electrode to activate the carbonyl group in CO$_2$ molecule, Deng et al. [8] reported one of the most efficient catalysts to synthesize cyclic carbonate. Fu et al. [9] adopted polydopamine and Pt NPs as bio-coupled electrode probes for immunoassays, the as-prepared probes show...
ultrahigh catalytic activity towards hydrogen peroxide detection and effectively amplify the response signal, as a result, the detection limit can be as low as 0.018 ng/ml. Chen et al. [10] prepared carbon supported PtAu alloy NPs with high activity towards formic acid electrooxidation by pyrolysis of PtAu/C precursor.

The current methods of preparing NPs modified electrode including dip coating method [11], drop coating method [12], electrodeposition [13] et al. In dip coating method, electrode was immersed in sol solution containing target NPs, NPs were adsorbed on the electrode surface to form a thin film. However, the amount of NPs adsorbed on the electrode surface was changed as the nano-sol concentration changes, and the coverage of adsorbed NPs is difficult to control. In drop coating method, a certain volume of target solution was dropped on the electrode surface, a thin film was formed after the solvent was evaporated. Although the amount of adsorbed NPs can be adjusted by controlling the original solution concentration and/or drop volume, the as-formed NPs film are easily peel off from the electrode surface, results in poor stability and reproducibility. In electrodeposition method, metal ions in the solution are reduced into nanoparticles under appropriate electrode potential, forming nano-films on the electrode surface. Although as-prepared NPs modified electrode shows high catalytic stability, the size and dispersion of NPs are difficult to control due to the excessive deposition rate [14]. Kolb et al. modified the Au (111) electrode with Zn, Fe and Cu nanoclusters by electron probe [15,16], however, the method is far from universal since it needs strict control and complicated operation, the area of electrode being modified is greatly limited so the efficiency is low. In recent years, assembling the surface functional NPs onto electrode was commonly used to form modified electrode [17,18]. Generally, in this method, ligands with strong affinity to Au (such as thiol) was adopted to react with weak ligands (such as citrate [19] and phenylphenol [20]) protected Au NPs, forming functional Au NPs, and then the functional NPs were adsorbed onto the electrode surface to form NPs modified electrode. However, the electrochemical sensitivity of as-prepared modified electrode is greatly reduced due to the surface of NPs are tightly wrapped by functionalized organic molecules. The situation might be varied if the order of modification and assembly is changed. In specific, the surface of the electrode is modified with thiol first, and then noble metal NPs protected by weak-adsorbed ligands (such as tetroactylammonium bromide (TOAB)) were anchored on the thiol modified electrode by ligand exchange. In this way, NPs modified electrode with high activity and stability can be achieved. Based on the idea, the authors prepared NPs (such as Au, Pt and Pd NPs) modified SAM electrode and studied their influences on electron transfer in outer-spherical reaction molecules (Ru (NH₃)₆Cl₃) and inner-spherical reaction molecules (mercapto ferrocene). The long range electron transfer property of cytochrome c was also studied using the Au NPs modified electrode [21].

In this paper, we developed a method to prepare NPs modified electrode by anchoring noble metal NPs on the surface of the electrode by ligand exchange. First, the Au-SH_{SAM} template was constructed by self-assembly of C-8 alkyl dithiol on the metal surface. The TOAB-protected metal NPs were assembly onto Au-SH_{SAM} template electrode by strong interaction between metal NPs and mercapto groups. In this way, the electrode was successfully modified with noble metal NPs such as Au, Ag, Pt and Pd NPs. We also investigated the factors that influence the quantity of as-prepared modified electrode.
2. Experimental

2.1. Reagents and apparatus

HAuCl₄·4H₂O (Au % > 47.8 wt%), AgNO₃ (AR), H₂PtCl₆·6H₂O (Pt % > 37.0 wt%), PdCl₂ (Pd % > 59 wt%) and toluene (AR) are purchased from Sinopharm Chemical Reagent Shanghai Co., Ltd., DL-Thioctic acid (TA, 98%), 3-Mercaptopropionic acid (MPA, 98%) and Tetraoctylammonium bromide (TOAB) are purchased from Alfa Aesar. Ultrapure water (18.2 MΩ·cm) provided by a Milli-Q Labo apparatus (Nihon Millipore Ltd.).

Electrochemical test was performed by CHI 760C electrochemical station in normal three electrode electrochemical cell. Saturated calomel electrode (SCE) and Pt foil were used as reference electrode and counter electrode, respectively. Ultrapure N₂ was purged into the solutions for 30 min before electrochemical test to get rid of dissolved O₂, during the electrochemical test, the N₂ was keep purged above the solution to maintain the inert gas atmosphere. cyclic voltammetry (CV) was performed in solution containing 0.5 mol/L H₂SO₄ and 0.05 mol/L Ru(NH₃)₆Cl₃, the scan rate is 50 mV/s. Transmission electron microscope (TEM; Hitachi TEM-2100/UHR) was used to characterize the morphology and structure of NPs, scanning tunneling microscope (STM) was used to characterize the surface morphology of electrode by constant current mode with Pt-Ir tip.

2.2. Preparation of TOAB-stabilized Au, Ag, Pt and Pd nanoparticles

Method of preparing TOAB-stabilized Au, Ag, Pt and Pd NPs were reported elsewhere [22,23], in brief, 15 mL toluene solution containing 5 mmol/L TOAB was added into 50 mL round-bottomed flask, then 5 mL solution containing 0.6 mg/mL metal precursor was added and stirred for 30 min, TOAB acts as phase transfer agent, which makes the metal ion transferred from water phase to organic toluene phase. The color in the upper liquid layer comes from metal ion dissolved in toluene. The metal ion was reduced by adding certain among of ice cold 0.1 mol/L NaBH₄ solution, the amount of NaBH₄ was depends on the metal precursor. After stirring for 2 h, NP sol dispersed in the upper layer of toluene was obtained by filtering through a separatory funnel, the residual NaBH₄ in toluene was removed by repeatedly washed with water. The as-prepared NPs were stored in refrigerator (≈ 4 °C) for further use.

2.3. Preparation of thiol template electrode and process of nanoparticles self-assembly

Preparation of thiol template electrode and subsequently process of NPs self-assembly on thiol template electrode was illustrated in Figure 1. In first, fresh polishing 4 mm Au electrode was immersed in ethanol solution containing 4.26 mmol/L 1,8-octanedithiol for 12 h, densely packed monomolecular layer SHSAM was formed by 1,8-octanedithiol self-assembly, the residual physical adsorbed thiol molecules were removed by washing with large amount of ethanol and water. The compaction degree of the thiol assembly layer was examined by electrochemical cyclic voltammetry using Ru(NH₃)₆Cl₃ as probe molecule. The as-prepared SHSAM electrode was then immersed into NPs sol solutions, the original TOAB coating layer on the NPs was replaced by thiol. As a result, the NPs were
anchored on the SHSAM electrode due to stronger interaction between NPs and thiol molecule than that between NPs and TOAB. After washing the electrode with water, the modified electrode (Au-SH\textsubscript{SAM}-NP) was successfully prepared.

3. Results and discussions

3.1. Preparation and electrochemical characterization of thiol template electrode

To characterize the electrochemical property of adsorbed thiol, the CV curves of the surface adsorbed thiol in H\textsubscript{2}SO\textsubscript{4} solution were recorded, as illustrated in Figure 2. The electrochemical windows were chosen as 0.0 \textasciitilde +1.35 V and \textasciitilde -0.50 \textasciitilde 0.0 V to study the electrooxidation and desorption of thiol on electrode surface, respectively. When the electrochemical window is 0.0 \textasciitilde +1.35 V, in the first cycle of CV curves, a sharp peak at around 1.1 V was observed in the positive-going scan as showed in Figure 2a, the oxidation peak corresponding to the oxidation of mercapto group (-SH), which is consistent with literature [24]; the relatively small peak at 1.3 V corresponding to the surface oxidation of bared Au, since most of the Au surface was cover by thiol, the oxidation peak of Au surface was smaller than that of thiol. On the second cycle of CV curves, the peak at 1.1 V was disappear while the peak at 1.3 V was largely increased, indicated than the adsorbed thiol was totally oxidized in the first cycle. Meanwhile, no desorption peak was observed in the CV curve range from \textasciitilde -0.45 V to 0.0 V after thiol was oxidized, as showed in Figure 2b. When the CV of the fresh absorbed electrode was performed between \textasciitilde -0.45 V and 0.0 V, a reduction peak at around \textasciitilde -0.35 V was observed in the negative-going scan, which corresponding to the desorption of thiol as illustrated in Figure 2c. The peak current is gradually decreased at the sweep cycle number increased due to the reduced coverage of thiol, meanwhile, desorption of thiol became more difficult as the coverage of thiol became low, which evidence by the negatively shifted of reduction desorption peak in the CV curve as the cycle number was increased. After the thiol was totally desorbed from the Au surface, no oxidation peak in the CV curve range from 0.0 V to 1.35 V was observed, as showed in Figure 2d.

Figure 3 illustrates the results of CV and STM characterization before and after the thiol molecules were assembled on the Au surface. Ru(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{3} was selected as probe molecule to characterize whether the modified Au electrode surface was covered by a
monolayer thiol molecule, the results are displayed in Figure 3a. On unmodified electrode, the redox peaks are clearly observed in the CV curve. The redox current density in the CV curves was decreased after the Au electrode was immersed in thiol solution for 1 h, and the reversibility of the reaction is also deteriorated as indicated by the larger potential difference between the oxidation peak and the reduction peak of Au. The redox current is continuous decreasing as the immersion time increasing, after 6 h immersion, the redox peaks of Ru(NH₃)₆Cl₃ was totally disappeared, indicating that the Au surface was totally covered by thiol molecule and a monolayer thiol was absorbed on the Au electrode surface, similar to the behavior of alkyl thiol modified Au electrode [20]. The thiol molecules on the Au electrode surface form a densely non-conductive polymer film, preventing the electrochemical active species penetrating from the membrane into the electrode surface, thus hindering their oxidation and/or reduction on the electrode. In addition, the charging/discharging current in double-layer region was greatly suppressed after the Au electrode was immersed in thiol solution, this might be due to the strong van der Waals forces between the template thiol molecules [25]. After electrochemical polishing and hydrogen flame annealing, the electrode surface was clean, and the surface steps can be clearly seen as showed in Figure 3b. After assembled thiol molecules on Au surface, many small less-regular pin-hole structure was observed as showed in Figure 3c, due to the strong strength of Au-S bond, Au atoms were easily pulled out by thiol molecule in disordered vibrations, forming the pin-hole structure [26]. The dithiol molecules modified on the electrode surface were arranged in a short-range order, which can be observed by zoom in the dotted box in Figure 3c, as display in Figure 3d.

Figure 2. CV curves of the oxidation and desorption of thiol on Au electrode. (a) The oxidation of thiol on electrode; (b) After thiol being oxidized; (c) The desorption of thiol on electrode; (d) After thiol being desorbed.
3.2. Anchoring metal nanoparticles by thiol SAM template

In order to verify the assembly of NPs on the electrode surface, the electrochemical properties of Au NPs, Ag NPs, Pt NPs and Pd NPs in H₂SO₄ solution was characterized by electrochemical cyclic voltammetry, the results are display in Figure 4. The CV curve of Au NPs modified electrode was similar to that of bare Au electrode, the difference is that

![Figure 4. CV and STM images of the Au NPs, Ag NPs, Pt NPs, Pd NPs after modified on Au electrode (150 × 150 nm²).](image-url)
a small shoulder peak was appeared at less positive position of the main peak of bulk Au electrode, which corresponding to the oxidation peak of Au NPs. The oxidation peak potential of Au NPs was less positive than that of bulk Au, because the surface energy of Au NPs was higher compared with that of bulk Au due to the size effect of nanoparticles [27]. On Ag NPs modified electrode, peak at 0.4 V in the positive-going scan and 0.3 V in the negative-going scan were observed, corresponding to the oxidation and reduction of Ag and AgOx, respectively, which are in accordance with literature [28]. On Pt NPs modified electrode, the onset potential of hydrogen evolution reaction (HER) was negatively shifted due to the excellent catalytic activity of Pt NPs [29]. Obvious peak at −0.3 V corresponding to HER was observed, similar to that of Pt electrode in H2SO4 solution. Peaks corresponding to oxidation/reduction of Pd NPs were also seen in the CV curve of Pd NPs modified electrode in H2SO4 solution, similar to the results reported elsewhere [30]. Thus, the electrochemical properties discuss above confirms the successfully anchoring noble metal NPs on the thiol modified electrode. The morphology of assembled noble metal NPs on the electrode surface was characterized by ex situ STM to further study the anchoring of metal NPs by thiol SAM template. As illustrate in Figure 4, after immersing the thiol-modified electrode in different noble metal nano-sol solution for a certain period of time, the electrode surface was fully covered by the target NPs, and the NPs with uniform size were tightly arranged in a dispersed monolayer state, and no agglomeration was observed.

### 3.3. Regulation the coverage of nanoparticle on electrode

In order to modify the electrode with a monolayer of NPs, the influence of soaking time on the coverage of NPs on the modified Au electrode was investigated. Figure 5 illustrates the STM images of Au-SH\textsubscript{SAM} electrode after soaking in Au and Pt nano-sol solution with different time. In the case of Au NPs, when the soaking time is short (less than 0.5 h), the NPs attached to the electrode surface are sparse, only a sub-monolayer of NPs was adsorbed on the Au-SH\textsubscript{SAM} electrode. When the soaking time was increased to 1 h, the amount of NPs on the electrode surface are increasing rapidly, a monolayer of NPs were formed. When the soaking time was further prolonged to 3 h, the thickness of adsorbed NPs on the electrode surface was increased and the NPs on the electrode were significantly accumulated. While for the Pt NPs modified electrode, the situation is quite similar to that of Au NPs modified electrode.

### 4. Conclusion

The Au, Ag, Pt and Pd NPs colloidal solutions with suitable size and good monodispersity were synthesized by using the weakly-adsorbed tetraoctylammonium bromide as protecting agent. The Au-SH\textsubscript{SAM}-NP modified electrode was successfully prepared by anchoring TOAB-protected metal NPs to the thiol-modified electrode surface with ligand exchange method. The Au-SH\textsubscript{SAM}-NP modified electrode was characterized by CV and STM. This preparation method is facile and universal, the coverage of the NPs on the electrode surface can be carefully controlled by adjusting the soaking time in the NPs sol solution. Noble metal NPs modified electrode shows excellent performance in electrochemical process. What’s more, the noble metal NPs modified electrode is a promising material in
bioelectrochemical sensor, which shows great potential in the application of biological detection.

**Acknowledgments**

The authors gratefully acknowledge the financial support given for this work from National Key R&D Program of China under grants number 2016YFB0101309.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**Funding**

This work was supported by National Key R&D Program of China [grant number 2016YFB0101309]

**ORCID**

Long Huang http://orcid.org/0000-0002-8345-0423
References

[1] Ozbay E. Plasmonics: merging photonics and electronics at nanoscale dimensions. Science. 2006;311:189–193.
[2] Burda C, Chen X, Narayanan R, et al. Chemistry and properties of nanocrystals of different shapes. Chem Rev. 2005;105:1025–1102.
[3] Mason MG. Electronic structure of supported small metal clusters. Phys Rev B. 1983;27:748–762.
[4] Meng Q, Ye Q, Liu W, et al. Application of precious metal catalysts in drug synthesis. Precious Metals. 2012;33:78–82.
[5] Hsu M-S, Chen Y-L, Lee C-Y, et al. Gold nanostructures on flexible substrates as electrochemical dopamine sensors. ACS Appl Mater Interfaces. 2012;4:5570–5575.
[6] Abad JM, Mertens SFL, Pita M, et al. Functionalization of thiocystic acid-capped gold nanoparticles for specific immobilization of histidine-tagged proteins. J Am Chem Soc. 2005;127:5689–5694.
[7] Nitzan A, Ratner MA. Electron transport in molecular wire junctions. Science. 2003;300:1384–1389.
[8] Shi F, Zhang Q, Ma Y, et al. From CO oxidation to CO2 activation: an unexpected catalytic activity of polymer-supported nanogold. J Am Chem Soc. 2005;127:4182–4183.
[9] Fu Y, Li P, Wang T, et al. Novel polymeric bionanocomposites with catalytic Pt nanoparticles label immobilized for high performance amperometric immunoassay. Biosens Bioelectron. 2010;25:1699–1704.
[10] Chen G, Li Y, Wang D, et al. Carbon-supported Pt Au alloy nanoparticle catalysts for enhanced electrocatalytic oxidation of formic acid. J Power Sources. 2011;196:8323–8330.
[11] Li C, Wang H, Yamauchi Y. Electrochemical deposition of mesoporous Pt–Au alloy films in aqueous surfactant solutions: towards a highly sensitive amperometric glucose sensor. Chem Eur J. 2013;19:2242–2246.
[12] El-Deab MS, Okajima T, Ohsaka T. Fabrication of Phase-separated multicomponent self-assembled monolayers at gold nanoparticles electrodeposited on glassy carbon electrodes. J Electroanal Chem. 2001;516:119–126.
[13] Kolb DM, Engelmann GE, Ziegler JC. Nanoscale decoration of electrode surfaces with an STM. Solid State Ionics. 2000;131:69–78.
[14] Kolb DM, Ullmann R, Will T. Nanofabrication of small copper clusters on gold(111) electrodes by a scanning tunneling microscope. Science. 1997;275:1097–1099.
[15] Abad JM, Gass M, Bleloch A, et al. Direct electron transfer to a metalloenzyme redox center coordinated to a monolayer-protected cluster. J Am Chem Soc. 2009;131:10229–10236.
[16] Jensen PS, Chi Q, Grumsen FB, et al. Gold nanoparticle assisted assembly of a heme protein for enhancement of long-range interfacial electron transfer. J Phys Chem C. 2007;111:6124–6132.
[17] Yonezawa T, Kunitake T. Practical preparation of anionic mercapto ligand-stabilized gold nanoparticles and their immobilization. Colloids Surfaces A: Physicochem Eng Aspects. 1999;149:193–199.
[18] Shein JB, Lai LMH, Eggers PK, et al. Formation of efficient electron transfer pathways by adsorbing gold nanoparticles to self-assembled monolayer modified electrodes. Langmuir. 2009;25:11121–11128.
[19] Liu F, Khan K, Liang J-H, et al. On the hopping efficiency of nanoparticles in the electron transfer across self-assembled monolayers. Chem Phys Chem. 2013;14:952–957.
[22] Liu F, Gu Y, Hu J, et al. Two phase preparation of small size of precious metal nanoparticles modified with mercapto carboxylic acid. Precious Metals. 2015;35:1–5.

[23] Fink J, Kiely CJ, Bethell D, et al. Self-organization of nanosized gold particles. Chem Mater. 1998;10:922–926.

[24] Hagenström H, Schneeweiss MA, Kolb DM. Modification of a Au(111) electrode with ethanethiol. 1. Adlayer structure and electrochemistry. Langmuir. 1999;15:2435–2443.

[25] Aliganga AKA, Duwez A-S, Mittler S. Binary mixtures of self-assembled monolayers of 1,8-octanedithiol and 1-octanethiol for a controlled growth of gold nanoparticles. Org Electron. 2006;7:337–350.

[26] Kaun C-C, Guo H. Resistance of alkanethiol molecular wires. Nano Lett. 2003;3:1521–1525.

[27] Murata K, Kajiya K, Nukaga M, et al. A simple fabrication method for three-dimensional gold nanoparticle electrodes and their application to the study of the direct electrochemistry of cytochrome c. Electroanalysis. 2010;22:185–190.

[28] Liu H, Favier F, Ng K, et al. Size-selective electrodeposition of meso-scale metal particles: a general method. Electrochim Acta. 2001;47:671–677.

[29] Engelbrekt C, Sørensen KH, Lübcke T, et al. 1.7 nm platinum nanoparticles: synthesis with glucose starch, characterization and catalysis. Chem Phys Chem. 2010;11:2844–2853.

[30] Soreta TR, Strutwolf J, Henry O, et al. Electrochemical surface structuring with palladium nanoparticles for signal enhancement. Langmuir. 2010;26:12293–12299.