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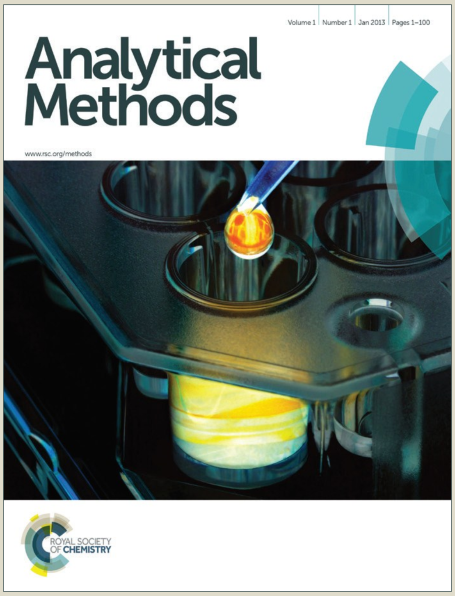

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Covalent Anchoring of Multifunctionized Gold Nanoparticles on Electrodes towards an Electrochemical Sensor for Detection of Cadmium Ions

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Abstract

This paper studied an electrochemical sensor based on covalent anchoring aryldiazonium salt modified AuNPs to gold electrodes for sensitive detection of cadmium ions (Cd^{2+}). AuNPs modified with 4-nitrophenyl and 4-carboxylphenyl were firstly prepared, which were then in situ immobilized on gold electrodes to achieve Au-Ph-AuNP modified interfaces. Glutathione (GSH) were finally modified to Au-Ph-AuNP by amide bonding to achieve the Au-Ph-AuNP-GSH sensing interface, which was used to detect Cd^{2+} in the concentration range of 0.1 nM to 100 nM with the detection limit of 0.1 nM. This electrochemical sensor demonstrates high stability and sensitivity to Cd^{2+}. It is potential to use the in situ anchoring AuNP strategy to fabricate portable devices for onsite monitoring of trace amount of heavy metals.

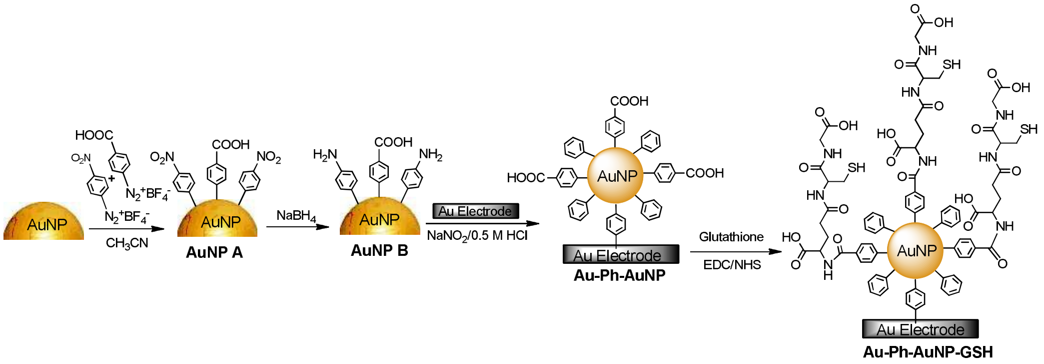
Keywords：Aryl diazonium salts；Gold nanoparticles; C-Au bond; Electrochemical sensor; Cadmium ion

1. Introduction

Monitoring levels of cadmium (II) in aquatic ecosystems is an increasingly important issue due to the environmental and biological importance of this ion.[1] The content of cadmium in most fresh water is less than 1 μg L^{-1}. The ability to monitor low levels of cadmium using a cheap, fast and reliable method is desirable. Various methods involving the use of classical elemental analysis techniques such as atomic absorption spectroscopy have been developed for the detection and measurement of cadmium ions.[2, 3] These classical methods are relatively rapid and highly accurate but are expensive, require trained personnel, and are not compatible with in-field sampling and analysis. On the contrary, the electrochemical methods as an alternative of these spectroscopic techniques, have been accepted as the efficient methods to detect heavy metal ions due to their excellent sensitivity, short analysis time, portability, and low cost. As a consequence there is a growing interest in the development of electrochemical sensors to determine levels of heavy metal ions.[4-7] Among all the electroanalytical methods, anodic stripping voltammetry, as a highly sensitive technique for detecting diverse trace heavy metal ions, has been used by chemists for several decades.[8] This method relies on the physisorption of metal recognition molecules on electrode surfaces. Electrode material selection is still one of the key technical issues for stripping voltammetry although mercury-based electrodes have been replaced by the environmental friendly materials, such as bismuth-film electrodes[9] and antimony-film electrodes.[10] As alternatives, electrochemical sensors based on chemically modified electrodes based on self-assembled monolayers of thiols on gold have obtained attractive attention due to their low cost, simplicity, and reliability for metal detection.[11] A gold electrode modified with glutathione (GSH) was used for voltammetric determination of cadmium ions with the detection limit of 5 nM.[5] The detection limit (0.9 nM) compared with a GSH modified electrode for the detection of Cd^{2+} has been significantly improved by replacing GSH with cadmium-selective hexapeptide His-Ser-Gln-Lys-Val-Phe.[12] In addition, electrochemical sensors based on aryldiazonium salts modified gold surfaces have been applied to metal ion sensing, which demonstrated far more stable than alkanethiol based monolayers on gold electrodes.[13] However, the rational design of electrochemical sensor interface with high sensitivity, selectivity, stability, and potential for on-site detection still remains as an active topic for the determination of metal ions in low content.

The modification of sensing interface with nanomaterials such as carbon nanotubes and nanoparticles to achieve enhanced properties such as increasing the sensitivity has received considerable attention in electroanalytical chemistry.[14] Lots of efforts have been invested to fabricate the nanostructured sensing interface for metal detection.[6, 15] Compared to carbon based nanomaterials, metal nanoparticles, especially gold colloidal nanoparticles (AuNP), as a more homogeneous nanomaterial have been extensively studied because of their attractive physicochemical characteristics, such as high surface-to-volume ratio, good biocompatibility, and being able to facilitate electron transfer between biomolecules and electrode.[16] Taking advantages of AuNP, many AuNP based electrochemical sensors for metal detection have been reported.[17] However, these reported sensing interfaces are still based on the affinity between AuNP and NH_2 or the affinity between AuNP and SH, which have been claimed to be instable. Besides forming S-Au bond or NH-Au bond, AuNP also can be covalently modified on the electrodes by Au-C bonding through diazonium salt chemistry.[18-20] AuNP tethered on interfaces by forming Au-C bonding is very stable, which presents an interesting issue for sensing applications.[21]

Here we aim to develop a stable sensing interface based on covalent anchoring AuNP on gold substrates by Au-C bonds followed by the covalent attachment of glutathione as shown in Scheme 1. Firstly, AuNPs modified with the mixture of 4-nitrophenyl and 4-carboxylphenyl was prepared based on aryl diazonium salt chemistry. Then the terminal nitro groups can be converted to diazonium groups by incubating in HCl solution containing $NaNO_2$ to form $Au\text{-}Ph\text{-}N_2^+Cl^-$. Subsequently, the prepared AuNPs are in situ immobilized on the interface by forming Au-C bonds to achieve an Au-Ph-AuNP modified interface. Finally, Glutathione (GSH) can be covalently modified to the AuNP modified surfaces by amide bonding to achieve the Au-Ph-AuNP-GSH sensing interface, which can be used for the detection of cadmium ions. The analytical performance of the electrochemical sensor for detection of cadmium ions is evaluated along with the influence of a variety of experimental parameters. To our knowledge, it is the first time to report an electrochemical sensor based on in situ covalent anchoring of aryldiazonium salts modified gold nanoparticles on electrodes for detection of metal ions.



Scheme 1. Schematic of the preparation of Au-Ph-AuNP-GSH sensing interface for detection of cadmium ions.

2. Experimental Section

2.1. Materials

Acetonitrile (CH_3CN, HPLC grade), tetrabutylammonium tetrafluoroborate (NBu_4BF_4), 4-carboxyphenyl diazonium tetrafluoroborate, 4-nitrophenyl diazonium tetrafluoroborate, $K_3Fe(CN)_6$, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), *N*-hydroxysuccinimide (NHS), 2-(*N*-morpholino) ethanesulfonic acid (MES), glutathione (GSH), hydrochloric acid, were obtained from Sigma-Aldrich (Shanghai, China). Reagent grade dipotassium orthophosphate, potassium dihydrogen orthophosphate, potassium chloride, sodium hydroxide, sodium chloride, sodium nitrite, ammonium acetate, perchloric acid, sulfuric acid, and hydrochloric acid, were purchased from Sanyi Chemicals (Wuhan). All reagents were used as received, and aqueous solutions were prepared with Milli-Q water (18 MΩ cm, Millipore). Buffer solutions used in this work were 50 mM ammonium acetate (pH

7.0) and 0.1 M MES (pH 6.8). The pH was adjusted with NaOH or HNO_3 solution. The stock cadmium (II) solution (0.1 M) was prepared in Milli-Q water and diluted cadmium (II) solutions in ammonium acetate buffer. All glasswares were rinsed with 6 M HNO_3, then thoroughly with Milli-Q water to remove contamination by metal ions.

2.2. Preparation of multifunctionalized AuNP

All glassware was cleaned with piranha (H_2SO_4/H_2O_2 3:1 v/v) followed by aqua regia (HCl/HNO_3 3:1 v/v), then rinsed with copious amounts of distilled water before nanoparticle synthesis and functionalization. The 15 nm AuNPs were synthesized using the method reported previously[19]. To 980 μL synthesized AuNPs solution, 10 μL 5 mM 4-carboxyphenyl diazonium tetrafluoroborate and 10 μL 5 mM 4-nitrophenyl diazonium tetrafluoroborate in acetonitrile were added, and incubated for overnight. Then the modified AuNPs were separated from solution via cenfugation at 8000 rpm for 15 min in a sigma 3-16PK centrifuger. Next, the AuNP pellet was redispersed in 1 mL MilliQ water and centrifugated again to wash the particles further to get AuNP A, which were then suspended in 1 mM of a basic solution (phosphate buffer, pH=10) and treated with 10 mM $NaBH_4$ as reducing agent. Finally, they were centrifuged and rinsed with MilliQ water to get AuNP B (Scheme 1).

2.3. Preparation of Au-Ph-AuNP-GSH sensing interface

Gold electrodes with the diameter of 3 mm was polished with 1.0 mm alumina, followed by 0.3 and 0.05 mm alumina slurry on microcloth pads (Buehler, Lake Bluff, IL, USA).After removal of trace alumina from the surface, by rinsing with Milli-Q water and brief cleaning in an ultrasonic bath, the electrodes were further cleaned by cycling between -0.3 V and +1.5 V in 0.05 M H_2SO_4 at a scan rate of 100 mV/s until a reproducible scan was obtained. The electrode surfaces were modified with AuNP B by constant potential electrolysis at -0.4 V for 4 min in 0.5 mol L^{-1} HCl containing AuNP B and 10 mM $NaNO_2$. Following rinsing with acetonitrile and MilliQ water, respectively, the carboxyl terminus was activated by immersing the AuNP modified gold electrode (Au-Ph-AuNP) in a stirred solution of 20 mM EDC and 4 mM NHS in 100 mM MES (pH 6.8) for 1 h. After thorough rinsing with 25 mM MES buffer, the modified electrode was reacted overnight with glutathione (50 mg mL^{-1}) in MES buffer at 4 ^{o}C to form the Au-Ph-AuNP-GSH sensing interface (Scheme 1). The modified electrode was rinsed thoroughly with 25 mM MES buffer (pH 6.8) prior to use.

2.4. Cadmium (II) Measurement

Cadmium ions were accumulated on the Au-Ph-AuNP-GSH sensing interface at open circuit potential by immersing the electrode into 10 mL of a stirred solution of cadmium (II) nitrite in 50 mM ammonium acetate buffer (pH 7.0) for 10 min. The electrode was removed, rinsed with ammonium acetate buffer (pH 7.0) and transferred to a cell with electrolyte of 50 mM ammonium acetate buffer (pH 7.0) and 50 mM NaCl for electrochemical measurements by cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV). After the measurement, bound cadmium was eliminated from the electrode at +0.5 V for 15 s in 0.1 M $HClO_4$.

All metal ion concentrations were independently determined using an ELAN 6100

ICP-MS (from Perkin-Elmer, Shanghai). These concentrations are quoted in the paper. All concentrations of added interferents are calculated from masses of pure solids dissolved in known volumes of solutions.

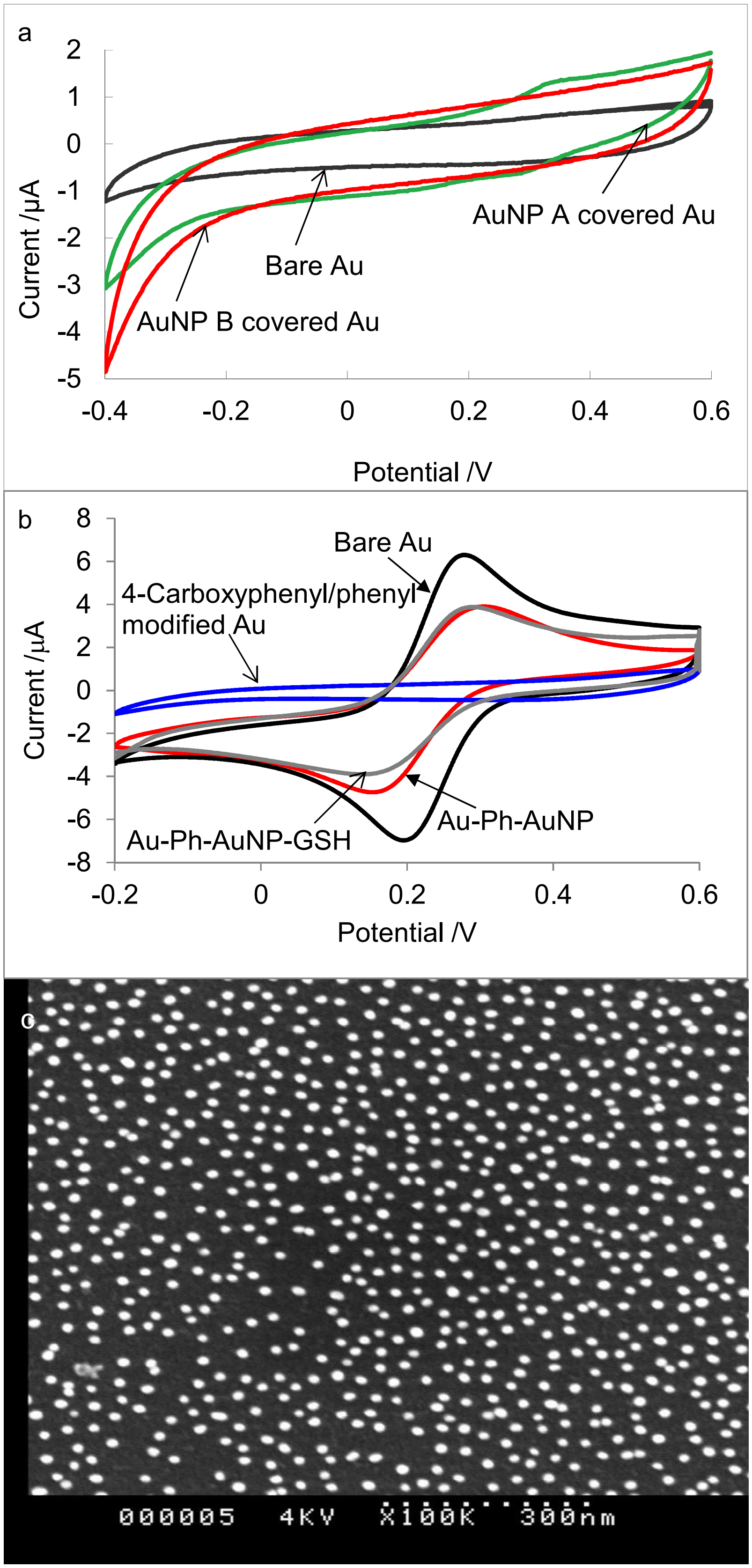
2.5. Electrochemical Measurement

All electrochemical measurements were performed with a GaossUnion EC510 potentiostat (GaossUnion, China) with a conventional three-electrode system, comprising a bare or modified working electrode, a platinum flag auxiliary electrode and a Ag/AgCl/3.0 M NaCl reference electrode. All potentials are reported against this reference at 25 °C unless otherwise stated. The solution was degassed with argon for at least 15 min prior to data acquisition and was blanketed with an argon atmosphere during the entire experimental period. Cyclic voltammetry was conducted at a sweep rate of 0.1 V s^{-1} between -0.4 V and +0.4 V. In OSWV the pulse amplitude was 25 mV with a step of 4 mV and frequency of 25 Hz. OSW voltammograms were measured between -0.4 V and +0.4 V.

3. Results and discussion

3.1. Characterization of AuNP modified gold electrodes

As shown in Scheme1, the conversion of original AuNP to AuNP A was easily indentified by the color change from red to blue. The conversion of AuNP A to AuNP B was firstly characterized by electrochemistry. Fig.1 a shows the electrochemistry of different gold surfaces in 0.5 M HCl solution. There was no electrochemistry for bare gold electrode in 0.5 M HCl. A pair of redox peaks centred at about 0.3 V was observed after dropping down AuNP A on gold electrode, which is responsible for the redox peaks of –NO_2 groups[22]. However, there was no redox process after dropping down AuNP B on gold electrodes, indicating the successful conversion of NO_2 groups to NH_2 groups on AuNP surfaces. Fig.1 b shows the electrochemistry in 1 mM potassium ferricynide redox solution for gold surfaces after modification of AuNP. The well-defined peaks characteristic of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ were observed on the bare gold electrode. The electrochemistry of Au-Ph-AuNP is similar to that of bare gold electrodes. For control the electrochemistry in ferricynide redox solution for gold surfaces after modification of the binary layers of 4-carboxyphenyl/phenyl was also recorded, and no Faradaic peaks for $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ were observed between -0.2 V to +0.6 V. This control indicates that the presence of AuNP can significantly increase the electronic coupling to the underlying electrode. Meanwhile, there is no significant difference between the electrochemistry of Au-Ph-AuNP-GSH and Au-Ph-AuNP in ferricynide redox solution, suggesting the further attachment of GSH did not affect the electronic coupling of Au-Ph-AuNP. The SEM image of AuNP modified gold surfaces confirms the successful modification of AuNP on gold electrode by in situ covalent coupling strategy.


a
Current /µA
2
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-4
-5
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Potential /V
AuNP A covered Au
Bare Au
AuNP B covered Au
b
Current /µA
8
6
4
2
0
-2
-4
-6
-8
-0.2
0
0.2
0.4
0.6
Potential /V
Bare Au
4-Carboxyphenyl/phenyl modified Au
Au-Ph-AuNP
Au-Ph-AuNP-GSH
c
000005 4KV X100K 300nm

Fig. 1 (a) Cyclic voltammograms in 0.5 M HCl for Au electrodes after dropping down AuNP A and AuNP B on the electrode surfaces. (b) Cyclic voltammograms in 0.1 M phosphate buffer solution containing 0.05 M KCl and 1 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ with the scan rate of 100 mV s^{-1} for bare, 4-carboxyphenyl/phenyl modified, and AuNP modified gold electrodes. (c) SEM image of Au-Ph-AuNP-GSH interfaces.

3.2. Electrochemical behavior of Cd^{2+} at Au-Ph-AuNP-GSH interfaces

The cyclic voltammogram of a freshly prepared Au-Ph-AuNP-GSH electrodes prior to cadmium accumulation is illustrated in Fig. 2 a. The voltammogram displays no electrochemistry between +0.1 V and -0.5 V. After accumulating cadmium ions at the electrode in a stirred solution of 10 nM Cd^{2+} for 10 min, distinct peaks of the redox chemistry of Cd^{2+}/Cd^0 were observed with $E^{o`}$= -260 mV. In addition, there was no loss in the cadmium current after 5 repetitive cycling or sonication in water for 30 s, suggesting that the fabricated sensing interface for cadmium is very stable. It is worth to highlight that this observed formal potential is more positive than the standard formal potential of Cd^{2+}/Cd^{o} redox couple (-620 mV), which was previously reported on gold surfaces modified with GSH and argued with the underpotential deposition of cadmium onto gold surfaces. However, it was more likely for the underpotential deposition of cadmium to happen on AuNPs in this study. The underpotential deposition of metals on AuNPs has been reported previously.[5, 23, 24] In order to confirm that the covalent attachment of AuNPs and GSH in Scheme 1 is essential for the obtained electrochemistry, three controls were investigated. Firstly, no sodium nitrite was added to the multifunctionized AuNPs solution during the step of modifying AuNPs onto gold electrodes (The absence of $NaNO_2$ suggests no AuNPs was attached to gold surfaces), and then the processed gold electrode was incubated with GSH solution with the presence of EDC/NHS followed by the accumulation of Cd^{2+}. No detectable cadmium electrochemistry was observed, which indicates that underpotential deposition of cadmium did not happen without the presence of AuNP although the adsorption of GSH is possible to happen on gold electrodes. Secondly, the performance of sensing interface to cadmium by incubation of Au-Ph-AuNP in GSH solution without the presence of EDC/NHS was studied. The electrochemistry of Cd^{2+}/Cd^0 was observed but it diminished obviously with repeated cycling and disappeared completely after sonication the interface in water for 30 s. This control suggests that it is possible for GSH adsorbing on AuNPs through Au-SH bonding to form Au-Ph-AuNP/GSH sensing interface but it was unstable as reported previously.[19] Another control was carried out by modification of gold electrode with 4-carboxyphenyl followed by the activation of carboxylic acid group in EDC/NHS solution. Then the activated interface was incubated in GSH solution to obtain the Au-Ph-GSH interfaces. The redox process of Cd^{2+}/Cd^0 was also observed after incubation of GSH modified gold electrode in a 10 nM Cd^{2+} solution for 10 min. However, compared with the Cd^{2+}/Cd^0 electrochemistry obtained on Au-Ph-AuNP-GSH interfaces, the Cd^{2+}/Cd^0 electrochemistry obtained on Au-Ph-GSH interfaces was much smaller (1.4 μA cm^{-2} at 10 nM Cd^{2+}) than that obtained on Au-Ph-AuNP-GSH interfaces (3.5 μA cm^{-2} at 10 nM Cd^{2+}). These controls have demonstrated that the obtained stable cadmium electrochemistry at Fig. 2 is not due to the adsorption of GSH on gold electrodes and AuNPs but the covalent modification of GSH onto AuNPs to complex cadmium. Meanwhile, the presence of AuNP is vital to increase the sensitivity of the sensing system, and can facilitate the electron transfer between the complexed cadmium ions and the electrode. Thus the herein fabricated Au-Ph-AuNP-GSH interface is stable and sensitive, and can be used for the detection of cadmium ions. For quantification purposes, Osteryoung square wave voltammograms were measured in cadmium-free solution of 50 mM ammonium acetate (pH=7.0) and 50 mM NaCl for Au-Ph-AuNP-GSH interfaces before and after enrichment of cadmium ion (Fig. 2 a). Similar to that observed in cyclic voltammogram, prior to enrichment of cadmium ion, the sensing interface has no redox reaction between -0.5 V and +0.1 V. Enriching in cadmium ion solution (10 nM) for 10 min, an obvious oxidation and reduction peak were observed.

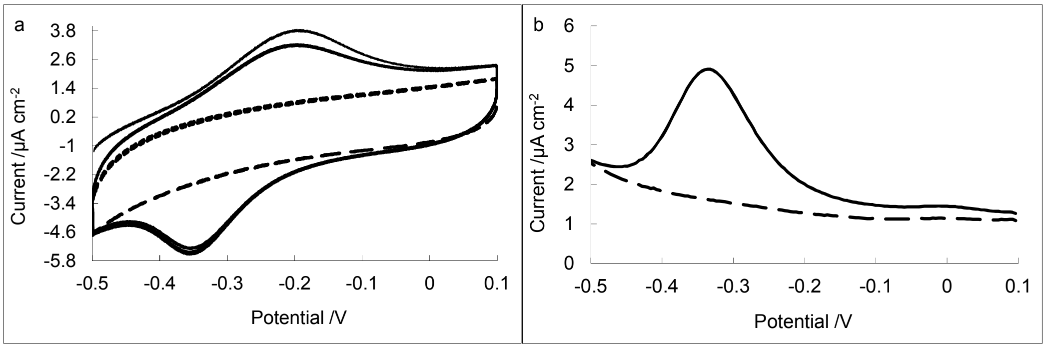

Fig. 2 (a) Cyclic voltammograms and (b) Osteryoung square wave voltammograms of Au-Ph-AuNP-GSH electrodes for the detection of Cd^{2+} ions measured in 50 mM ammonium acetate (pH 7.0) and 50 mM NaCl before (straight line) and after (dotted line) accumulation in 10 nM Cd^{2+} for 10 min at the scan rate of 100 mV s^{-1}.

3.3. Optimization of analytical conditions

Optimization of analytical conditions such as temperature, pH, salt concentration and accumulation time affecting the performance of Au-Ph-AuNP-GSH interfaces for detection of Cd^{2+} was carried out. The effect of incubation temperature was studied in the range from 20-45 ^{o}C (Fig. 3 a). When the temperature of the solution increased gradually from 20-30 ^{o}C, the peak currents increased because higher temperature during the accumulation process could result in faster diffusion of Cd^{2+} species and faster kinetics of complexation, hence an acceleration of the kinetic complexation reaction with GSH ligands. Then the current decrease above 30 ^{o}C, which might be due to the instability of the complex formed between metal ions and the ligands on the modified electrode at these temperatures. Thus, the incubation temperature of 30 ^{o}C was selected in all experiments. Fig. 3 b demonstrated pH effect on the peak current at the range of pH4.0-9.0. The peak current gradually increased from pH 4.0 to pH 7.0 and the maximum current was obtained at pH 7.0. The current decreased above pH7.0. When the pH is raised to a certain level, hydroxo complexes will form removing metal ions from the system resulting in the attenuation of the obtained cathodic currents. The optimum pH here was chosen as pH7.0. The accumulation time in 10 nM Cd^{2+} solution for Au-Ph-AuNP-GSH electrodes was studies between 1 and 30 min (Fig. 3 c). The peak current increased linearly when the incubation time increased from 1 to 10 min, suggesting a longer accumulation time allows for a greater amount of Cd^{2+} to access the exposed binding sites. There was no significant increase in peak currents when the incubation time was longer than 10 min. For a sensor to be practical for in-field analysis, however, the accumulation time should be relatively short, hence 10 min was selected as the optimized accumulation time as a compromise. Fig. 3 d demonstrated salt concentration effect on the peak current at the range of 10 mM-100 mM. It was observed that maximum peak current was obtained when the salt concentration was 50 mM. The peak current decreased when the salt concentration increased from 50 mM to 100 mM, which was attributed to the presence of high concentration of sodium chloride ions which could slow down the access of Cd^{2+} to GSH ligand. Thus, 50 mM was chosen as the optimized salt concentration.

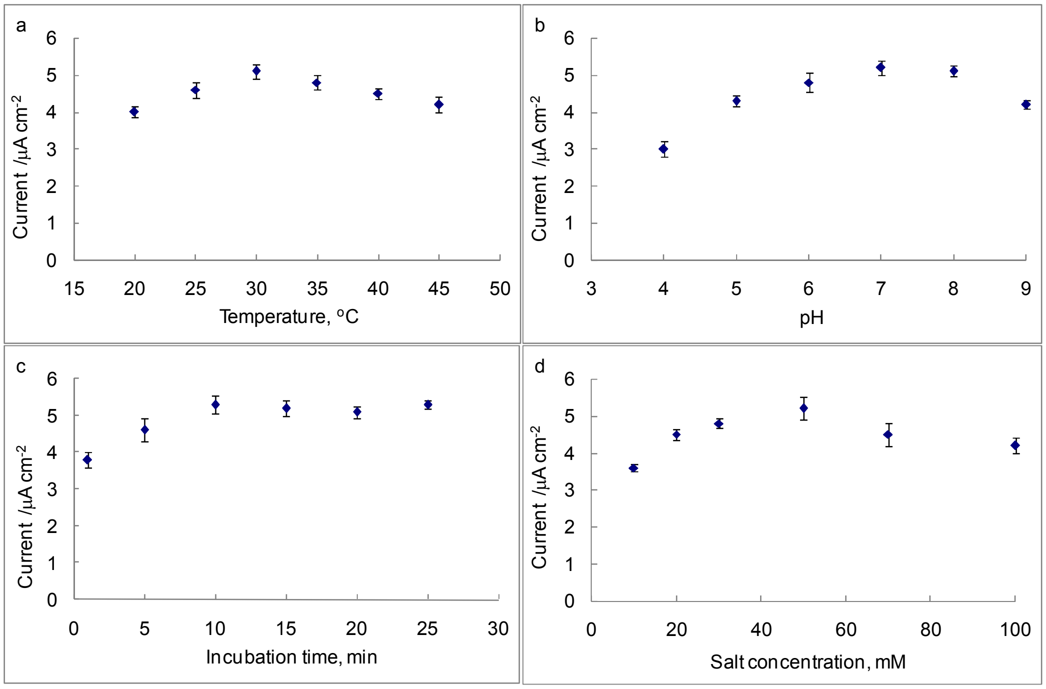

Fig. 3 Effect of (a) temperature, (b) pH, (c) accumulation time, and (d) salt concentration on OSWV peak currents of 10 nM Cd^{2+} in the ammounium acetate buffer solution.

3.4. Interference studies

The selectivity of the AuNP/GSH based sensor system for Cd^{2+} was investigated in the presence of the common metal ion interferents, such as Fe^{3+}, Hg^{2+}, Cr^{3+}, Ni^{2+}, Pb^{2+}, Cu^{2+}, Mg^{2+}, Ca^{2+}, and Zn^{2+}. Fig. 4 shows the effect of these metal ions with low (1 nM) or high (100 nM) concentration on the current density of 10 nM cadmium ions. There is no significant effect on Cd^{2+} current density from Cr^{3+}, Mg^{2+}, Ca^{2+}, and Fe^{3+}, which are hard acids and have different binding preference from soft acids such as Cd^{2+} with both high and low concentrations, indicating these metal ions have no detectable interference on Cd^{2+} detection. The effects from Cu^{2+}, Ni^{2+} and Zn^{2+} were observed, which was ascribed to these ions are borderline acids and have no preference for hard/soft electron donor atoms and hence competes with Cd^{2+} for binding sites, which is different from the observation in a previous study.[8] Meanwhile, negative effect from soft acid Hg^{2+} was also observed. A positive effect from Pb^{2+} was observed, which is due to a similar redox potential of lead to that of cadmium enhancing the signal from cadmium.[8, 25] Thus the fabricated Au-Ph-AuNP-GSH sensing interface has no particular selectivity to Cd^{2+} in the studied potential window.

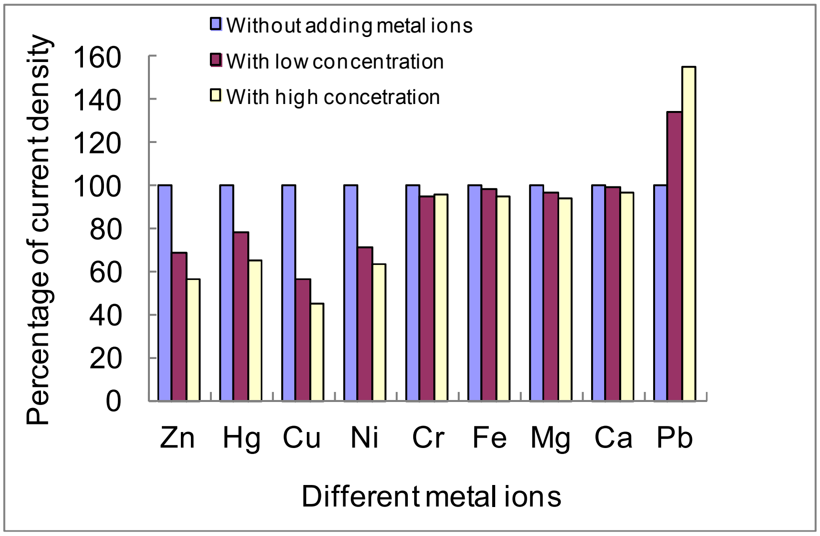

Fig. 4 Effect of different metal ions with low (1 nM) or high concentration (100 nM)

on the current density of 10 nM cadmium ions.

3.5. Stability and regeneration of AuNP/GSH modified gold electrodes

The stability of Au-Ph-AuNP-GSH interface after regeneration in 0.1 M $HClO_4$ was examined. The cathodic OSWV peak current was measured daily for 30 days or continuously 30 times in a day in a series of accumulation-regeneration experiments. The electrodes were stored in 50 mM ammonium acetate buffer (pH 7.0) at room temperature when not in use. Daily and continuous use stability of Au-Ph-AuNP-GSH sensing interface is shown in Fig. 5. For continuous regenerations, there is a decrease in the cadmium current of 0.13% per regeneration/accumulation cycle. For once a day regenerations, there is a decrease in the cadmium current of 0.17 per regeneration/accumulation cycle. The storage life of Au-Ph-AuNP-GSH sensing interface was also investigated by testing the cadmium signal 30 days later after electrode preparation. The electrode was stored in ammonium acetate buffer at 4 ^{o}C when not in use. It was observed that the current remains the same before and after 30 days storage period. These results indicate that the prepared Au-Ph-AuNP-GSH sensing interface is very stable and regenerable.

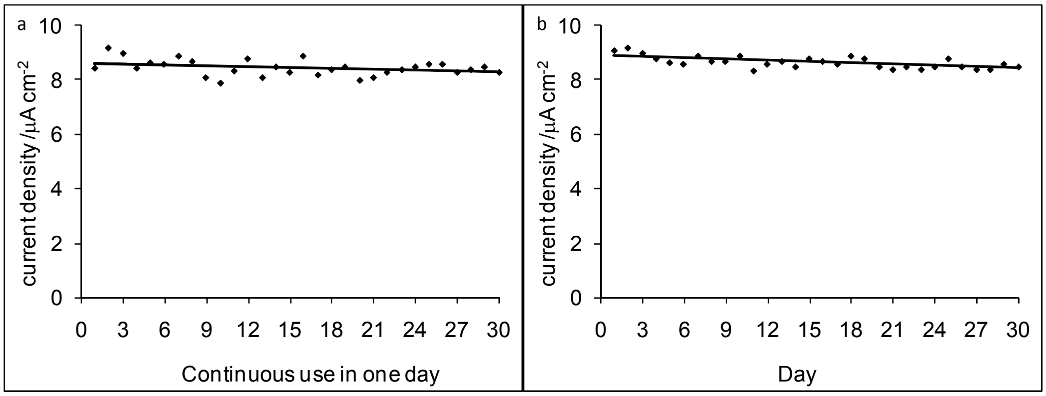

Figure 5. (a) Daily and (b) continuous use stability studies of Au-Ph-AuNP-GSH

sensing interfaces. After each measurement, the Cd^{2+} was removed by holding the potential at +0.5 V in $HClO_4$ for 30 s. Re-accumulation was conducted at ammonium acetate buffer (pH 7.0) containing 10 nM Cd^{2+} with 10 min accumulation time. The electrodes were stored in ammonium acetate buffer (pH 7.0) at room temperature when the electrodes were not in use.

3.6. Calibration curve for the determination of cadmium ions

Under optimized conditions Cd^{2+} was accumulated at the modified electrode in ammonium acetate buffer at room temperature for 10 min before OSWV measurements, the OSWV current density increased with the concentration of cadmium ions (Fig. 6). The current density at the AuNP/GSH modified gold electrode was calibrated as a function of the concentration of cadmium ions. The relation between current density and cadmium ion concentration is clearly nonlinear but does conform to a Langmuir-like relation. In general, the Au-Ph-AuNP-GSH interface displayed a good linear relationship between current density and cadmium ion concentration in the range of 0.1 nM to 100 nM. The lowest measurable cadmium concentration was 0.1 nM, which is one order lower than the detection limit of a sensor based on GSH/alkanthiol modified gold electrode (1 nM)[5] although it is one order higher than graphene oxide modified glassy carbon electrode.[26] Table 1 compares with the performance of the electrochemical sensors for detection of cadmium ions. Recently a luminescent sensor for cadmium has been reported to have the detection limit of 0.11 nM claiming to be best detection limit for any luminescent nanosensor.[27]

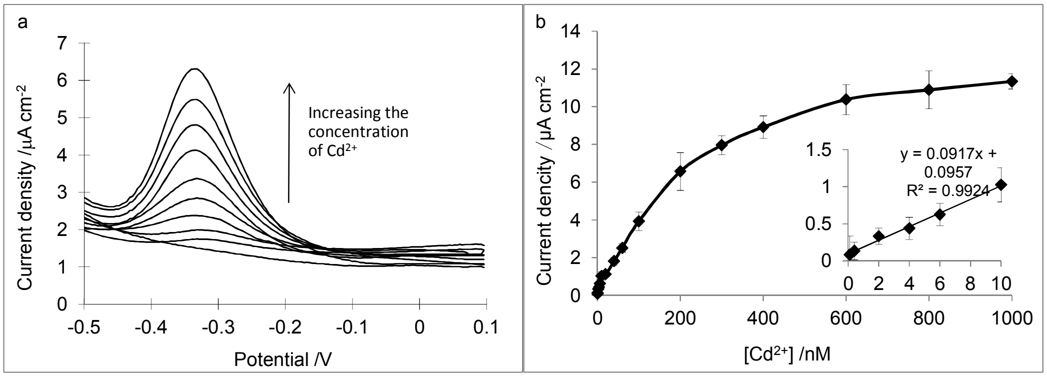

Fig. 6 (a) OSWV of the Au-Ph-AuNP-GSH interface after incubation with Cd^{2+} in different concentration from 0 nM, 0.1 nM, 1 nM, 2 nM, 4 nM, 6 nM, 10 nM, 20 nM, 40 nM, and 100 nM. (b) Calibration curve of OSWV peak current density of Cd^{2+} at the Au-Ph-AuNP-GSH interfaces as a function of Cd^{2+} concentration. Error bars are ± 1 standard deviation of the current densities of three different electrodes.

Table 1 Comparison of the performance of electrochemical sensors for cadmium ions.

	Performance of the sensors		
Sensors	Linear range	Detection limit	Stability
Sensor in this work	0.1-100 nM	0.1 nM	30 days
Sensor[5]	5-100 nM	5 nM	2 weeks
Sensor[8]	3-80 nM	3 nM	8 cycles
Sensor[28]	0.5-10 nM	0.13 nM	-
Sensor[26]	0.01-0.5 nM	0.01 nM	60 days
Sensor[29]	0.5 nM-50 mM	9 pM	-
Sensor[12]	0.9-100 nM	0.9 nM	2 weeks

3.7. Measurement of field samples

Aiming at verifying the practicability of the proposed cadmium sensor, the Au-Ph-AuNP-GSH sensing interface was used to detect Cd^{2+} in environmental water samples. Measurements of tap water, marine water and river water samples were performed by 10 times dilution so that the cadmium ion concentration of the solution tested was within the range of the herein fabricated sensors. The results were compared with those obtained using ICP-MS, which is the gold standard in metal quantification (Table 2). The measured cadmium concentrations by Au-Ph-AuNP-GSH interfaces are agreed well with that measured by ICP-MS although the results by ICP-MS are higher for all three samples. This difference is acceptable thinking about the different Cd detection theory between herein sensor and ICP-MS. The herein sensor measures the free Cd^{2+}, but the ICP-MS measures the total concentration of cadmium in a sample. The precision of the herein sensor is also comparable to that of ICP-MS. The lower concentration was obtained from Marine water, which might be due to the high salt concentration.

Table 2 Analyses of Cd^{2+} in local tap water, marine water and river water samples using ICP-MS and herein Au-Ph-AuNP-GSH sensing interface.

	Concentration of Cd^{2+} (μM)[a]		
	Tap water	Marine water	River water
ICP-MS	6.18±0.10	4.92±0.07	7.90±0.12
Sensor in this work	5.69±0.12	4.03±0.10	7.15±0.15

[a] Values correspond to the average of three separate measurements±standard deviation

4. Conclusions

In summary, we have demonstrated for the first time that AuNPs modified with mixed aryl diazonium salts of 4-nitrophenyl and 4-carboxylphenyl can be covalently anchored to the electrode interface by Au-C bonds through one-step fabrication strategy. The carboxylizated AuNPs (Au-Ph-AuNP) allow to covalently bind large amounts of GSH which can complex cadmium ions, in which AuNPs have been successfully used as electronic bridges and signal amplifiers for an electrochemical sensor towards the ultra-sensitive detection of Cd^{2+}. It demonstrated that one-step covalent anchoring of multiple aryldiazonium salt functionalized AuNPs on the electrode surface has greatly increased the coupling efficiency and subsequently increased the sensitivity. The Au-Ph-AuNP-GSH sensing interface can be used for the detection of Cd^{2+} in ammonium acetate buffer at the concentration range of 0.1 nM to 100 nM with the detectable limit of 0.1 nM. The analytical performance of the electrochemical sensor for detection of Cd^{2+} is evaluated along with the influence of a variety of experimental parameters. Meanwhile, the sensing interface is very stable with the storage life of 30 days and can be used to detect of cadmium ions in environmental water sample with comparable accuracy with ICP-MS. So we have developed a simple, robust, and sensitive electrochemical sensor for detection of Cd^{2+} in both buffers and field water samples. It is potential to use the in situ anchoring AuNP strategy to fabricate portable devices for onsite monitoring of trace amount of heavy metals if the molecule showing high selectivity to specific metal ions can be modified to the sensing interfaces.

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