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Short Communication

Selective Determination of Iron(III) in Sea Water by Gold Nanoparticles Self-assembled with N-carboxyl- L-cysteine

Benzhi Liu* and Min Wang

School of Environmental Science and Engineering, Yancheng Institute of Technology, Yancheng, Jiangsu Province, 224051 China

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Abstract: *Application of gold nanoparticles self-assembled with N-carboxyl- L-cysteine for the determination of iron(III) was investigated. Differential pulse adsorptive stripping voltammetry was used to detect iron(III). Various operational parameters were investigated and discussed in terms of their effects on the measurement signals. A linear range from 0.1 nM to 1.8 nM with a detection limit of 0.03 nM was obtained under optimized conditions. The applicability of the method was successfully tested by determination of iron(III) in sea water samples.*

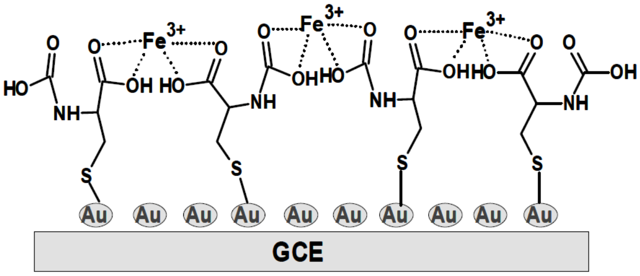
Keywords: gold nanoparticles; self-assemble; differential pulse adsorptive stripping voltammetry; iron(III)

1. INTRODUCTION

Iron (Fe) is an essential element for the biochemical and physiological functioning of terrestrial and oceanic organisms, including phytoplankton, which are responsible for the primary productivity in the world's oceans [1]. Phytoplankton require iron to sustain numerous metabolic processes including photosynthesis, chlorophyll production, nitrate reduction, nitrogen fixation, and other oxidation reactions. The analysis of iron in seawater is difficult due to both the low concentrations and the sea water matrix. Therefore, several analytical methods including inductively coupled plasma mass spectrometry [2], electrothermal atomization atomic absorption spectrometry [3], cathodic stripping voltammetry [4,5], luminescence [6], and spectrophotometry [7], have been developed to measure iron in sea water samples to make better detection limit and sensitivity and minimize interferences from real sample matrix. However, most of the sensitive and selective methods available are expensive to be used in routine analysis. Electroanalytical techniques have important advantages including high sensitivity, accuracy and precision, as well as the low cost of instrumentation. Traditionally, the most sensitive working electrodes, for iron determination by stripping voltammetry, have been hanging drop mercury electrode [8]. Due to the intrinsic drawbacks of mercury electrodes, such as toxicity and instability, great efforts have been taken to develop mercury-free solid electrodes [9-11].

Chemical modification of the electrode surface is a major area of the current research in electrochemistry including corrosion studies, improvement of the electronic properties, increases the electrocatalytic activity, analytical selectivity and sensitivity of the electrode [12]. In this work, glassy carbon(GC) electrode was modified by gold nanoparticles self-assembled with N-carboxyl-L-cysteine (NCLC). Scheme 1 showed a short chain self-assembled monolayer formed on the electrode surface. Benefitting from the carboxyl acid functional groups for selective accumulation of iron(III), voltammetric determination of iron(III) was carried out. Applicability of the method was successfully tested by determination of iron(III) in sea water samples using differential pulse adsorptive stripping voltammetry(DPASV).

Scheme 1. Schematic representation for interaction of Fe3+ ions with NCLC/Au/GCE.



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*To whom correspondence should be addressed: Email: benzhiliu@163.com
Phone: +86 0515-88298806; Fax: +86 0515-88298805

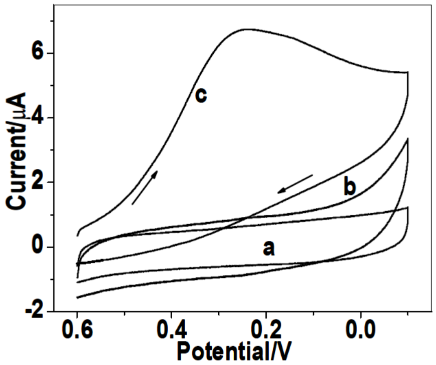

Figure 1. Cyclic voltammograms obtained in 0.15 M KNO_3 solution on Au/GC (a), and NCLC/Au/GC before (b) and after (c) immersion in 5 μM iron(III) for 8 min. pH=4.0, scan rate: 100 mVs^{-1}.

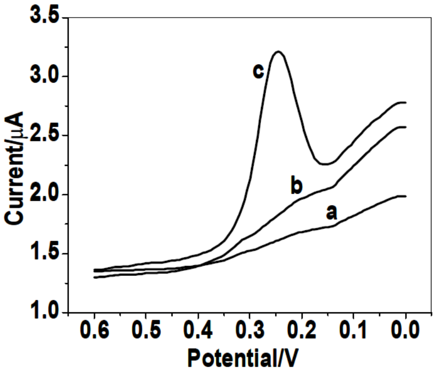

Figure 2. DPASV obtained in 0.15 M KNO_3 solution on Au/GC (a), and NCLC/Au/GC before (b) and after (c) immersion in 1.3 nM iron(III). pH=4.0, step increment of 5mV, amplitude of 50mV, pulse period of 0.1 s.

2. EXPERIMENTAL

2.1. Apparatus

Cyclic voltammetry and differential pulse adsorptive stripping voltammetry experiments were conducted on Electrochemical Workstation LK2005 (LANLIK Instruments company,Tainjin, China). The modified glassy carbon electrode (diameter of 3mm) were used as working electrode with a Ag/AgCl electrode (Saturated KCl) reference electrode, and a platinum wire auxiliary electrode. All pH measurements were made with a Model pHS-23 acidity meter (Shanghai Second Analytical Instruments, China).

2.2. Reagents

N-carboxyl- L-cysteine(NCLC), potassium tetrachloroaurate(III) ($KAuCl_4$) and all other compounds were purchased from Sinopharm Group Chemical Reagents Co., Ltd. All chemicals were of analytical reagent grade and used without any further purification. A solution of 50 μM $KAuCl_4$ in 0.1 M H_2SO_4 was prepared to deposit gold at the GC surface. The iron stock solution (1 mg mL^{-1}) was obtained by dissolution of 1.0 g of extra-pure iron in 100 mL of nitric acid with the aid of heat, and then diluted to 1 L with water. Dilute solutions of iron(III) were prepared immediately before use from a stock solution. Double distilled water was used throughout.

2.3. Preparation of the modified electrode

The glassy carbon electrode(GC) was polished with a water slurry of 0.5 mm Al_2O_3, then rinsed with ethanol and water and placed in an ul-trasonic bath to remove any residual polishing material. The GC was immersed into $KAuCl_4$ solution and deposition was conducted at the potential of -0.4 V (vs. Ag/AgCl) for 600 s to prepare Au/GC. The Au/GC was washed with distilled water to remove physically adsorbed $KAuCl_4$, and then was immersed in a 20 mM NCLC aqueous solution for 20 h to form NCLC/Au/GC. The modified electrode was washed with distilled water to remove physically adsorbed NCLC and used as working electrode for electrochemical measurements.

2.4. Measurement procedure

The supporting electrolyte solution (10 mL of 0.15 M KNO_3) was pipetted into a voltammetric cell and purged with nitrogen for 5 min. After the background voltagram had been obtained, aliquots of the iron standard solution were introduced into the cell while maintaining a nitrogen atmosphere over the solution. After 8 min accumulation, the voltammogram was recorded by applying a negative-going differential pulse stripping voltammetric potential scan from +0.6 V to 0 V with a step increment of 5mV, amplitude of 50mV, pulse period of 0.1 s.

3. RESULTS AND DISCUSSION

3.1. Analytical characteristics of iron(III) on NCLC/Au/GC

The cyclic voltammetry was performed to investigate response of iron(III) on NCLC/Au /GC. Fig. 1 showed the cyclic voltagrams obtained in 0.15 M KNO_3 solution on Au/GC (a) and NCLC/Au/GC before (b) and after (c) immersion in 5 μM iron(III) for 8 min. In the scan range from +0.6 V to -0.1 V, no redox current peak was found in curve (a) implying that iron(III) ions were not adsorbed onto the Au /GC. Curve (b) also did not show any redox peak since no iron(III) in solution. But Curve (c) showed a obvious cathodic irreversible peak around +0.25 V, indicating that iron(III) ions had been accumulated onto the modified surface following the electrochemical reduction to the iron(II). The irreversible behavior of cyclic voltagram confirmed that iron(II), formed from electrochemical reduction of iron(III), has left the surface of NCLC/Au/GC immediately after formation, so that it has not been accessible for oxidation in reverse potential scan. Thus, it is benefit for detecting iron(III) in the presence of large amount of iron(II).

In order to increase sensitivity, we carried out differential pulse adsorptive stripping voltammetry(DPASV) to detect trace iron(III) ions. Fig. 2 showed the DPASV obtained in 0.15 M KNO_3 solution on Au/GC (a) and NCLC/Au/GC before (b) and after (c) immersion in 1.3 nM iron(III). Also, no current peak was found in curve (a) and curve (b), but an obvious cathodic peak was observed in curve (c) around +0.24 V. The results were in good agreement with those observed by CV measurements.

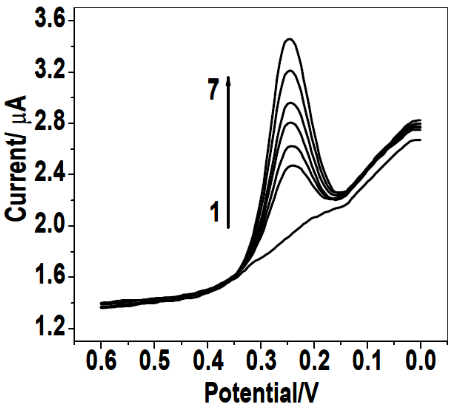

Figure 3. DPASV on NCLC/Au/GC in 0.15 M KNO_3 solution with different iron(III) concentrations. From 1 to 7: 0; 0.1; 0.4; 0.7; 1.0; 1.3; 1.8 nM, respectively.

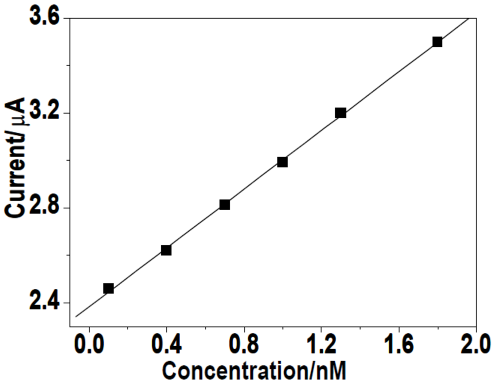

Figure 4. Plot of peak currents vs. the iron(III) concentrations.

3.2. Effect of solution acidity

The pH effect of the supporting electrolyte solutions on the current response of NCLC/Au /GC was investigated in the range of 2~9. The stripping peak current increased with increasing the pH of the supporting electrolyte solution and reached maximum at around pH 4.0. At higher pH values, the peak current response decreased. This behavior may be attributed to the competition of the OH^- with Fe^{3+} ions at higher pH and H^+ with Fe^{3+} for carboxyl groups of NCLC at lower pH. In the stripping step, for pH values higher than 4.0, the interaction between Fe^{3+} and the functionalized monolayer becomes stronger, hindering the charge-transfer between Fe^{3+} and the electrode base, and at lower pH, a part of the Fe^{3+} ions leave the surface before starting the stripping step. Thus, pH 4.0 was chosen for further experiment.

3.3. Calibration graph

Calibration curve for the determination of iron(III) on the NCLC/Au/GC was achieved by DPASV under optimal conditions. The DPASV for different concentrations of iron(III) were illustrated in Fig. 3. The resulting calibration plot, as shown in Fig. 4, is linear over the range from 0.1 nM to 1.8 nM , and the limit of detection was 0.03 nM. These results showed that the NCLC/Au /GC could be an appropriate sensor for detection of iron(III) at low concentrations.

3.4. Interferences study

Possible interferences in the determination of 0.8 nM iron(III) were examined under the optimized experimental conditions. It was found that 100-fold of iron(II), 80-fold of Zn^{2+}, Cr^{3+}, Sn^{2+}, Cd^{2+}, Mn^{2+}, Mg^{2+}, Pb^{2+}, Ag^+, and Cu^{2+} for DPASV measurements have no effect on the determination of iron(III). Furthermore, surface-active substances, such as Triton X-100, Tween-80, sodium dodecylsulfate(SDS) and cetyltrimethylammonium bromide (CTAB) were investigate. Results show that amounts of less than 20-fold of them have little effect on the determination of iron(III). Therefore, this proposed method has high sensitivity and selectivity for the determination of iron(III).

3.5. Reproducibility and stability of NCLC/Au/GC

The fabrication reproducibility was estimated by the measurements of 1.0 nM iron(III) with four different modified electrodes made at the same procedure. The R.S.D. of the measurement was 6.1%, showing a good reproducibility. The long-term stability of the electrode was also investigated. When NCLC/Au/GC was not in use, it was stored in KNO_3 solution and measured intermittently, the current response to 1.0 nM iron(III) decreased less than 10% over two weeks.

3.6. Analysis of sea water samples

The proposed method was used for the direct determination of iron(III) in sea water. A standard addition method was used for Fe(III) determination. The concentrations of iron(III) in Qingdao sea water and Dalian sea water were found to be 0.93 nM and 0.72 nM, respectively. The recovery results summarized in Table 1 demonstrated the validity of the proposed method and the applicability of the fabricated sensor for the determination of iron(III) in real samples.

4. CONCLUSION

In this work, gold nanoparticles self-assembled with N-carboxyl-L-cysteine was used to fabricate a electrochemical sensor for the determination of iron(III). Selective accumulation of iron(III) to the carboxyl acid functional groups of N-carboxyl- L-cysteine could avoid interfering of other electroactive materials. Applicability of the sensor for analysis of real samples was successfully tested by determination of iron(III) in sea water with less interference of the sample matrix.

Table 1. determination and recovery tests of iron(III) in sea water samples.

Samples	Initial found (nM)	Added (nM)	Total found (nM)	Recovery (%)	RSD (%) (n=5)
Qingdao sea water	0.93	0.5	1.39	92.0	4.3
Dalian sea water	0.72	0.5	1.19	94.0	3.9

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