



An electrochemical sensor based on reduced graphene oxide/gold nanoparticles modified electrode for determination of iron in coastal waters



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ABSTRACT

An electrochemical sensor based on reduced graphene oxide (rGO) and gold nanoparticles (AuNPs) modified electrode was utilized for determination of trace iron in coastal waters with the aid of the iron complexing ligand 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP). 5-Br-PADAP reacted with iron in short chelating reaction time (<3 min). rGO as a support provided large specific surface area for AuNPs, which would facilitate the electrochemical reduction of Fe(III)-5-Br-PADAP. Under the optimized conditions, the response of Fe(III) at this resulting sensor was linear in the range of 30 nM to 3 μM with a detection limit of 3.5 nM. This sensor also had excellent reproducibility and repeatability. Additionally, the modified electrode had been successfully applied to the determination of Fe(III) in real coastal waters.

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1. Introduction

Iron is one of the essential micronutrient elements for the organisms in the ecological system [1]. It is imperative in plant metabolism, electron transport of photosynthesis and respiration, chlorophyll synthesis, nitrate reduction, and detoxification of reactive oxygen species [2]. So the accurate quantitative determination of total dissolved iron in coastal waters is extremely important to be developed for the environment monitoring. The concentration of soluble iron in natural water is diverse in coastal water (10^{-6} – 10^{-9} M), and ocean water (10^{-9} – 10^{-12} M) [3]. The coastal water has some properties such as salinization [4] and no permanently oxygenated condition [5]. Because the concentration of iron in coastal water is relatively lower, the accurate determination of iron concentrations in coastal water is one of the challeng-

ing problems in environmental analysis. Many techniques have been developed to determine iron such as spectrophotometry [6,7], atomic absorption spectrometry (AAS) [8,9], inductively coupled plasma-mass spectrometry (ICP-MS) [10] and fluorescence [11], etc. However, most of the methods need for expensive and bulky devices which restrict their use for in situ determination. Moreover, some methods suffer from serious matrix interferences.

Electrochemical method [12–14] has been identified as an extremely sensitive technique for iron determination due to its advantages of low cost, fast analysis speed, quick detection, portable instruments, high sensitivity and selectivity. Nowadays iron was always detected by using mercury electrode as working electrode [15,16]. Several complexing agents had been used to accumulate iron complexes on the electrode surface such as salicylaldehyde [17], 1-(2-pyridylazo)-2-naphthol [18], 1-nitroso-2-naphthol (NN) [19,20], 2-(2-thiazolylazo)-*p*-cresol (TAC) [21] and 2, 3-dihydroxynaphthalene (DHN) [22,23]. However, mercury electrode had some drawbacks including toxicity and difficulties in the handling [24] and the chelating reaction time was relatively longer. Chemically modified electrodes have been gradually developed for iron determination to avoid these disadvantages of mercury electrode.

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Nowadays, Nanomaterials [25–28] play an important role in analytical chemistry. Graphene [29] was found by Geim [30] in 2004. Many researchers pay more attention to it because of its high surface area, excellent conductivity, strong mechanical strength and high chemical stability. Gold nanomaterials [31,32] have the advantages of high catalytic activity, good biocompatibility and fast electron transfer rate [33]. Recently, some researchers showed that the deposited metal nanoparticles can improve the performance of the electrode. Graphene and gold nanocomposites have more excellent performance so they can be widely used in analysis field.

In this study, our working electrode was modified with rGO and AuNPs via one single step, which was similar to the reported literatures [34,35]. GO and HAuCl_4 changed to rGO and AuNPs by electrochemical reduction at -1.0 V for 400s. rGO might provide large specific surface area for AuNPs, which could accelerate the electron transfer. 5-Br-PADAP as the complexing ligand had the advantage of short chelating reaction time and Fe(III)-5-Br-PADAP could be absorbed on the modified electrode [36]. The rGO/AuNPs modified electrode was easily fabricated and had excellent electrochemical properties. Experimental parameters such as the deposition time of rGO/AuNPs, the pH value of the acetate buffer, the accumulation potential and time, the concentration of 5-Br-PADAP and the time of chelating reaction were investigated in detail. The rGO/AuNPs modified electrode had the benefits of excellent selectivity, sensitivity and reproducibility for the determination of Fe(III). Additionally, the rGO/AuNPs modified electrode was also applied to the determination of Fe(III) in real coastal waters with satisfactory results.

2. Experimental

2.1. Reagents

All chemicals were of analytical reagent grade. Iron standard solutions were prepared from iron chloride (Sinopharm Chemical Reagent Co., Ltd., China.) in 0.1 M HCl. GO was supplied by Nanjing Jcnano Technology Co. Ltd. $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ was purchased from Sinopharm Chemical Reagent Co. Ltd. 5-Br-PADAP was purchased from Aladdin industrial corporation. Deionized water (18.2 M Ω cm specific resistance) obtained with a Pall Cascada laboratory water system was used throughout.

2.2. Apparatus

The morphologies of the rGO and AuNPs were characterized by scanning electron microscopy (SEM, Hitachi S-4800 microscope, Japan.). Electrochemical Work Station (CHI 660D, Shanghai CH Instruments, Shanghai, China) was utilized throughout all the electrochemical experiments. The rGO and AuNPs coated glassy carbon electrode (3 mm in diameter) served as a working electrode, an Ag/AgCl (saturated KCl solution) was used as a reference electrode, and a platinum foil counter electrode was employed as an auxiliary electrode. All potentials were measured with respect to the Ag/AgCl reference electrode.

2.3. Preparation of the rGO/AuNPs modified electrode

Prior to use, the GCE was polished using aqueous alumina slurry (0.3 and 0.05 μm), washed with deionized water thoroughly, and then ultrasonicated in deionized water for a while. The GCE electrode was immersed in 0.2 M sodium sulfate solution containing 0.5 mg/mL GO and 1.0 mM chlorauric acid to electrochemically electrodeposit rGO and AuNPs with constant potential at -1.0 V for 400 s according to the literatures [34,35,37,38]. The obtained

rGO/AuNPs modified electrode was washed carefully with deionized water.

2.4. Preparation of real coastal water samples

Coastal river water samples were collected from Yuniao river (a local coastal river, which flows into the Huanghai Sea, Shandong province, China). Coastal sea water samples were collected from the Huanghai Sea (Shandong province, China). All the water samples were stored in acid-cleaned polyethylene bottles after filtration (0.45 μm membrane filters) and kept at 4°C until determination. The samples were digested in quartz tubes using a 500 W UV lamp (Metrohm MVA-UV 705, Switzerland). Voltammetric measurements were performed on diluted water samples to an appropriate concentration with the 0.1 M acetate buffer (pH 6.0) supporting electrolyte.

2.5. Electrochemical analysis procedure

Unless otherwise stated, the experiments were performed in 0.1 M acetate buffer (pH 6.0) supporting electrolyte containing 20 μM 5-Br-PADAP. Firstly, Fe(III)-5-Br-PADAP complex was accumulated onto the surface of the modified electrode under a potential of -0.1 V for 360 s with stirring. Then the stripping voltammetry was carried out from -0.40 to -0.65 V by differential pulse voltammetry (DPV) using the following parameters: initial potential of -0.40 V , final potential of -0.65 V , amplitude of 0.05 V, potential incremental of 0.004 V, pulse width of 0.05 s, pulse period of 0.5 s and quiet time of 2 s.

3. Results and discussion

3.1. Characterization of the rGO/AuNPs modified electrode

The morphologies of the various modified electrodes were characterized by SEM. Fig. 1a shows the surface morphology of GCE/rGO, large flakes of rGO with slightly scrolled edges form was obtained. Fig. 1b–d show the surface morphologies of the rGO/AuNPs modified electrode at different magnifications. The successful attachment of the AuNPs on the rGO was obviously observed and the shape of AuNPs was spherical nanostructure with diameter in 20–40 nm.

3.2. Electrochemical responses of iron on the rGO/AuNPs modified electrode

Fig. 2 shows the DPVs of the glassy carbon electrode, rGO/AuNPs, AuNPs and rGO modified electrode in 0.1 M acetate buffer (pH 6.0) with and without 20 μM 5-Br-PADAP or 300 nM Fe(III). No cathodic signal of Fe(III) was observed at the rGO/AuNPs electrode in 0.1 M acetate buffer supporting electrolyte (curve a). In the absence of Fe(III), a cathodic peak attributed to the reduction of free 5-Br-PADAP was obtained at -0.4 V (curve b). While two peaks at -0.4 and -0.5 V were obtained in the presence of Fe(III) (curve c). The peak at -0.5 V was attributed to the reduction of the Fe(III)-5-Br-PADAP complex. More importantly, the peak current of Fe(III)-5-Br-PADAP at rGO/AuNPs modified electrode is larger than that at AuNPs modified electrode (curve d).

Comparatively, DPVs of the glassy carbon electrode and rGO modified electrode in 0.1 M acetate buffer (pH 6.0) supporting electrolyte containing 20 μM 5-Br-PADAP and 300 nM Fe(III) were shown in Fig. 2b. From the curve f and curve g, the rGO modified electrode can enhance electrochemical signals, the peaks of the Fe(III)-5-Br-PADAP and 5-Br-PADAP were not separated in glassy carbon electrode and rGO modified electrode. But they were separated in rGO/AuNPs modified electrode (curve c), which indicated

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