



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



Yun Zhu^{a,b}, Dawei Pan^{a,b,c,*}, Xueping Hu^{a,b}, Haitao Han^a, Mingyue Lin^{a,b}, Chenchen Wang^a

^a Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), Shandong Provincial Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai, Shandong 264003, PR China

^b University of Chinese Academy of Sciences, Beijing 100049, PR China

^c Department of Earth, Ocean and Ecological Sciences, School of Environmental Science, University of Liverpool, Liverpool L69 3GP, UK

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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.

* Corresponding author at: Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), Shandong Provincial Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai, Shandong 264003, PR China.

E-mail address: dwpan@yic.ac.cn (D. Pan).

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

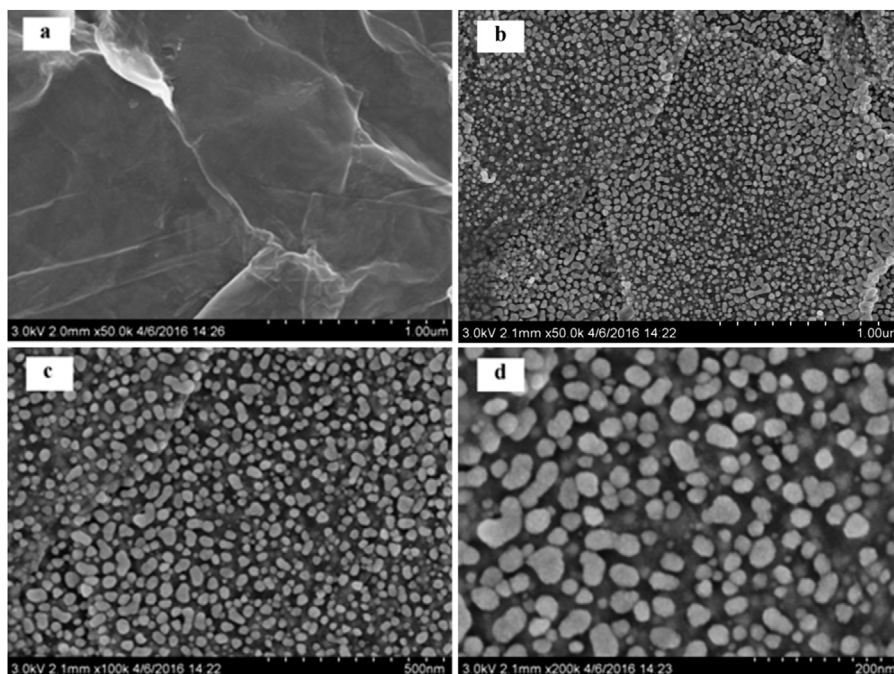


Fig. 1. SEM micrographs of the GCE/rGO (a), GCE/rGO/AuNPs (b, c and d).

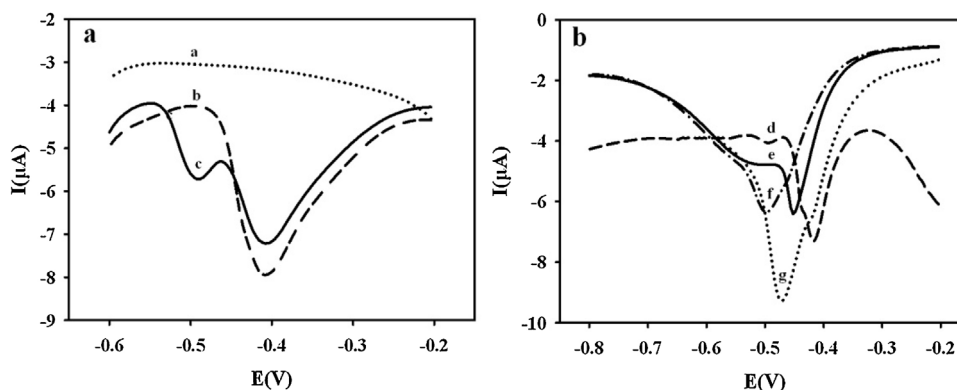


Fig. 2. DPVs of the rGO/AuNPs (curve a, b and c) modified electrode (a) and glassy carbon (curve e and f), AuNPs (curve d) and rGO (curve g) modified electrodes (b) in 0.1 M acetate buffer (pH 6.0) (curve a), containing 20 μM 5-Br-PADAP (curve b and e) and 300 nM Fe(III) (curve c, d, f and g).

the rGO/AuNPs modified electrode could be used to detect the Fe(III) with the help of 5-Br-PADAP.

3.3. Optimization for iron measurement on the rGO/AuNPs modified electrode

3.3.1. Effect of the deposition time of the rGO/AuNPs at the GCE surface

The deposition time of the rGO/AuNPs at the GCE surface was investigated with the time ranging from 60 to 500 s. As shown in Fig. 3a, the peak current gradually decreased from 60 to 300 s and then increased from 300 to 400 s as well as decreased again. The maximum peak current of the complex was observed at the deposition time of 400 s. Although the little amount of AuNPs was obtained at short time, the rare rGO was formed. After almost 300 s deposition, the rGO/AuNPs nanocomposite was obtained. Considering that the amount and size of AuNPs became larger and larger and the specific surface area might decrease with the increase of the deposition time. Deposition time of 400 s was considered as the optimum.

3.3.2. Effect of pH value of the acetate buffer

Considering that the formation and stability of the Fe(III)-5-Br-PADAP complex are strongly dependent on the pH value of solution. The effect of pH value of the acetate buffer was investigated at the pH value ranging from 4.0 to 7.0. As shown in Fig. 3b, the maximum peak current of the complex was observed at pH 6.0. The peak current was smaller at a lower pH value, which is probably due to the high background current caused by the hydrogen dissolving. Moreover, the peak current decreased with the pH value above 6.0, which was probably due to the decomposition of the Fe(III)-5-Br-PADAP complex. The optimum pH value of the acetate buffer was chosen to be 6.0.

3.3.3. Effect of the accumulation potential

The accumulation potential of Fe(III)-5-Br-PADAP at the modified electrode was investigated at the potential ranging from -0.4 to 0.1 V. As shown in Fig. 3c, the maximum peak current of the complex was observed at the accumulation potential of -0.1 V. The peak current of the complex gradually increased from -0.4 to -0.1 V, which probably due to the positive charged complex being strongly adsorbed on the negative charged surface of the rGO/AuNPs mod-

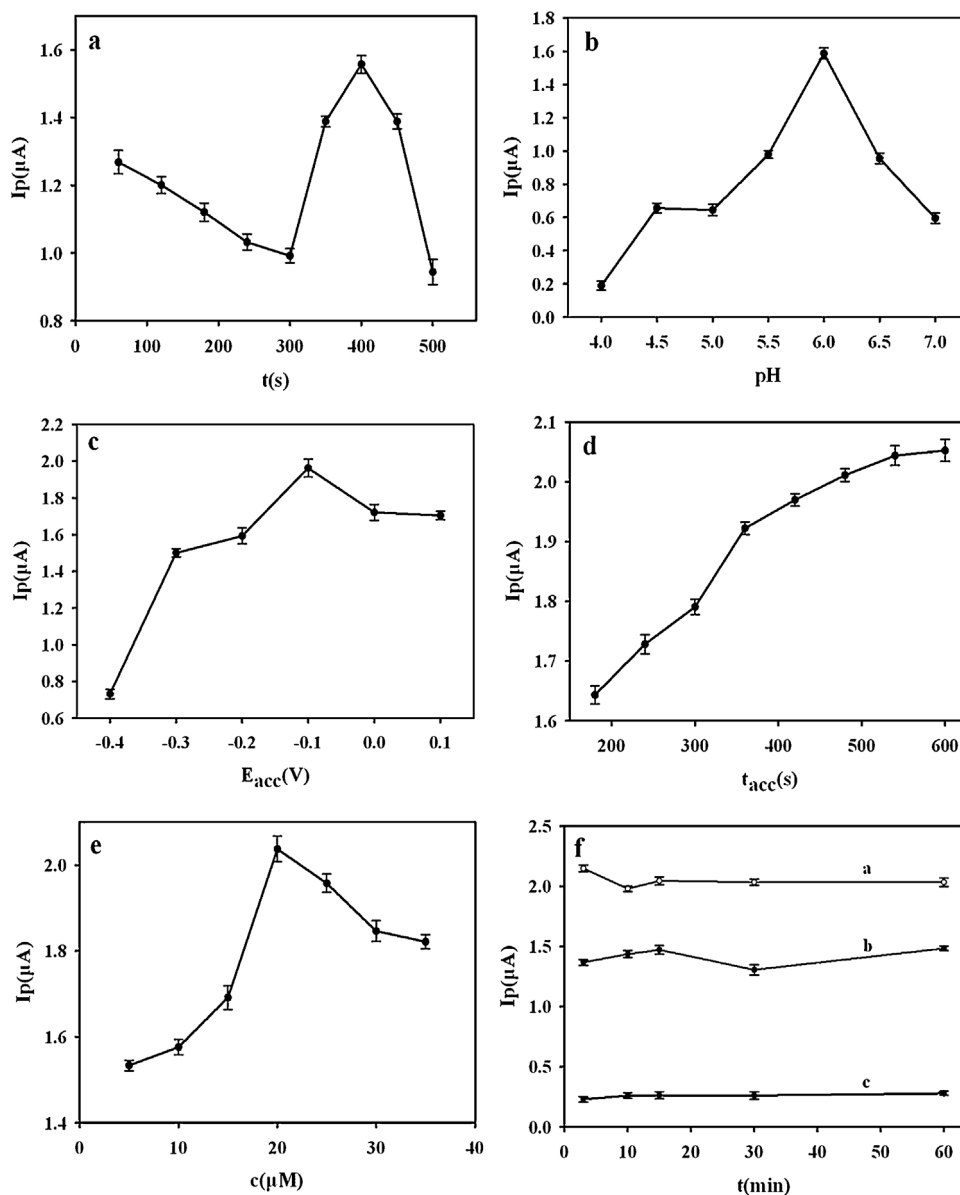


Fig. 3. Effect of the deposition time (a), pH value of the acetate buffer (b), the accumulation potential (c) and the accumulation time (d) of rGO/AuNPs at the GCE surface on the reduction current response of Fe(III)-5-Br-PADAP. Conditions: a supporting electrolyte of 0.1 M acetate buffer (pH 6.0) containing 500 nM Fe(III), 20 μM 5-Br-PADAP. Effect of the concentration of 5-Br-PADAP on the reduction current response of 500 nM Fe(III) in 0.1 M acetate buffer (pH 6.0) (e). Effect of the time of chelating reaction of Fe(III)-5-Br-PADAP. Conditions: a supporting electrolyte of 0.1 M acetate buffer (pH 6.0) containing 500 nM Fe(III), 20, 10, 1 μM 5-Br-PADAP (curve a, b and c) (f).

ified electrode. The maximum current was observed at a potential of -0.1 V. However, the peak current decreased with increasing potential from -0.1 to 0.1 V because enough Fe(III)-5-Br-PADAP complex were not adsorbed at the modified electrode. Thus, -0.1 V was considered as the optimal accumulation potential.

3.3.4. Effect of accumulation time

The effect of accumulation time on the peak current was studied ranging from 180 to 600 s, As shown in Fig. 3d, the peak current of the Fe(III)-5-Br-PADAP complex increased rapidly as the accumulation time increased from 180 s to 360 s, and then tended to increase slowly. Considering the time of analysis and energy consumption problem, 360 s was considered as the optimal accumulation time.

3.3.5. Effect of the concentration of 5-Br-PADAP

The effect of the concentration of 5-Br-PADAP was investigated at the concentration ranging from 5 to 35 μM in 0.1 M acetate

buffer (pH 6.0) containing 500 nM Fe(III). As shown in Fig. 3e, the maximum peak current of the complex was observed at the concentration of 20 μM , the peak current was smaller at a lower concentration value, which is probably due to the lower concentration were too dilute to have enough deposition points. However, the peak current decreased with increasing concentration from 20 to 35 μM because the higher concentration of 5-Br-PADAP can be competitive with Fe(III)-5-Br-PADAP. Thus, the optimum 5-Br-PADAP concentration was chosen as 20 μM .

3.3.6. Effect of the time of chelating reaction

The chelating reaction between Fe(III) and 5-Br-PADAP was very quick. As shown in Fig. 3f, the effect of the time of chelating reaction was investigated with the time ranging from 3 to 60 min in 0.1 M acetate buffer (pH 6.0) containing 500 nM Fe(III) and 20, 10 and 1 μM 5-Br-PADAP (curve a, b and c), respectively. The peak current of the Fe(III)-5-Br-PADAP complex was almost no matter

Table 1
Comparison of the electrochemical methods with other analytical methods for iron determination.

Methods	Electrode	Agents	Linear range (nM)	LOD (nM)	Reference
DLLME ^a / UV-vis	No	5-Br-PADAP ^b	90–7000	27	[6]
ICP-MS	No	Nitrilotriacetic acid chelating resin	0.02–0.07	0.02	[10]
Fluorescence	No	RHA ^c	500–5000	300	[11]
CSV ^d	HMDE ^e	NN ^f	Not mentioned	0.08	[20]
CSV	HMDE	DHN ^g	Not mentioned	0.005	[22]
CSV	Mercury coated, gold, micro-wire electrode	DHN	Not mentioned	0.1	[23]
CSV	HMDE	5-Br-PADAP	0.25–100	Not mentioned	[36]
SWV	IL-rGO/AuNDs/Nafion	No	300–100000	35	[13]
DPV	rGO/AuNPs	5-Br-PADAP	30–3000	3.5	This work

^a Dispersive liquid–liquid microextraction.

^b 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol.

^c Rhodamine amide.

^d Cathodic stripping voltammetry.

^e Hanging mercury drop electrode.

^f 1-nitroso-2-naphthol.

^g 2,3-dihydroxynaphthalene.

Table 2
Comparison of this method and AAS for determination of Fe(III) in real water samples.

Real samples	Fe(III) added (nM)	Detected by this method (nM)	Detected by AAS (nM)	Recovery (%)
Coastal river water 1	–	179 ± 4.2	178	–
Coastal river water 2	–	60.7 ± 3.2	62.5	–
Coastal sea water	0	–	–	–
	50	49.1 ± 2.7	–	98.2
	100	97.3 ± 3.9	–	97.3

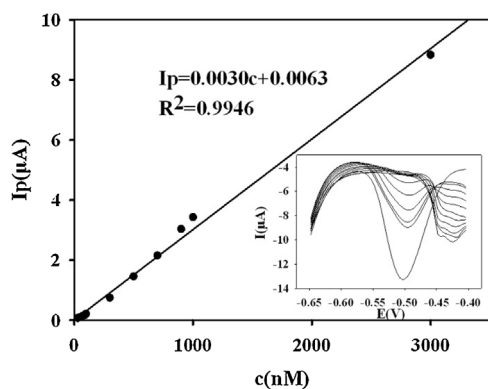


Fig. 4. Calibration curve of Fe(III) at the rGO/AuNPs modified electrode, where the concentrations of Fe(III) are from 30 nM to 3 μM in 0.1 M acetate buffer (pH 6.0) containing 20 μM 5-Br-PADAP. Inset is the voltammetric responses of Fe(III).

the chelating reaction time was 3 or 60 min. These imply that 5-Br-PADAP reacted quickly with iron and got matured in short reaction time (< 3 min). So, using 5-Br-PADAP might effectively shorten the testing time.

3.4. Calibration curve

The calibration curve of the Fe(III) determination was derived from the DPVs obtained at the rGO/AuNPs modified electrode under the optimum conditions mentioned above (Fig. 4). The peak current was linear with the concentration of Fe(III) ranging from 30 nM to 3 μM. The equation for linear regression was $I_p = 0.0030c + 0.0063$ ($R^2 = 0.9946$). The sensitivity and detection limit of the rGO/AuNPs modified electrode for Fe(III) determination were 3 nA nM⁻¹ and 3.5 nM (s/n = 3), respectively. Additionally, comparisons about iron determination by electrochemical methods and other analytical methods were shown in Table 1. Compared with other electrodes, the rGO/AuNPs modified electrode may be a good choice for iron

determination with higher sensitivity, lower detection limit and wider linear range.

3.5. Reproducibility, repeatability and selectivity

The reproducibility of the rGO/AuNPs modified electrode was investigated in 300, 500, 700 nM Fe(III) by six independently modified electrodes prepared with the same method and the relative standard deviation (RSD) was 5.7%, 5.4%, 4.7%, respectively. The repeatability of the developed method was also evaluated by detecting 300, 500, 700 nM Fe(III) at the same electrode for six measurements and the RSD was 3.6%, 3.9%, 3.5%, respectively. Hence, the rGO/AuNPs modified electrode showed good reproducibility and repeatability. If the modified electrode was stored in air condition and tested by two determinations for both 300 and 500 nM Fe(III) in each day, the response current had no obvious decrease during six days. But it would retain only 70% of its initial response from the seventh day.

To investigate the effects of possible interfering species for the iron determination, various foreign species were added into 0.1 M acetate buffer (pH 6.0) containing 500 nM Fe(III). 200-fold Ca²⁺, 50-fold Mg²⁺, Mn²⁺ and Al³⁺, 30-fold Cd²⁺ and Cr³⁺, 10-fold Zn²⁺, Pb²⁺ and Cu²⁺ did not affect the determination of Fe(III) (<5% of response current change). We also investigated the effects of organic species, such as humic substances and catechol. The results showed that 10-fold humic substances did not affect the determination of Fe(III), but 5-fold catechol would decrease the peak current, because catechol was one of the common chelators of iron. However, after the UV digestion, the peak currents returned to be normal, because UV digestion can destroy the organic substances.

3.6. Practical application

To evaluate the practical application of the rGO/AuNPs modified electrode, the modified electrode was used for the total dissolved iron determination in coastal water samples. Coastal river water 1 was diluted 10 times then added to 0.1 M acetate buffer (pH 6.0) for

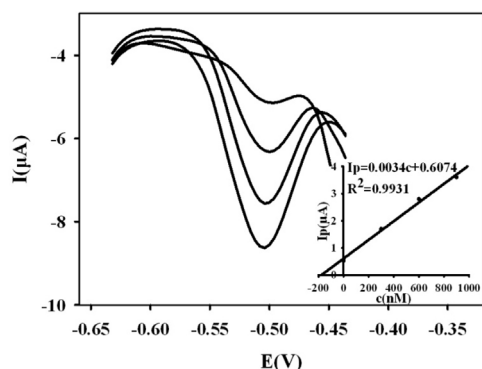


Fig. 5. Voltammetric responses of Fe(III) in coastal river water 1 by the standard addition method. The concentrations of the addition of Fe(III) are 0, 300, 600, 900 nM (from top to bottom). Inset is the fitted curve for Fe(III) determination.

detection by using the standard addition method under the optimal conditions. The adsorptive cathodic stripping curves of the coastal river water 1 were shown in Fig. 5 and the linear regression was shown in the inset of Fig. 5. The concentration of Fe(III) was calculated to be 179 nM which was in agreement with the value detected by AAS (178 nM). Besides, the concentrations of Fe(III) in other samples were determined by our proposed method and AAS and the corresponding results were displayed in Table 2. The results indicated that our proposed sensor was reliable and suitable for the determination of Fe(III) in waters from the coastal zone area.

4. Conclusions

In summary, a novel and effective rGO/AuNPs coated GCE was fabricated with 5-Br-PADAP as complexing agents for sensitive determination of Fe(III) in real coastal water samples. Compared to other complexing agents, 5-Br-PADAP has the advantage of short chelating reaction time. Moreover, the modified electrode has several advantages such as easy fabrication, excellent reproducibility, repeatability and selectivity. The fabricated electrode will be of great benefit to determine iron in waters from the coastal zone area.

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Biographies

Yun Zhu earned the BS degree of applied chemistry in 2014 at Yantai University. She is currently a master's degree student at Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences. Her scientific interest includes electrochemical sensors and environmental analysis.

Dawei Pan is currently a professor at Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences. He received the Ph.D. degree in 2007 at Hunan University. His research interests focus on electrochemical sensor system's research and integration, electroanalysis of coastal environment's pollutants and nutrients, and interface electrochemistry.

Xueping Hu earned the BS degree in 2013 at Linyi University. She is currently a Ph.D. student at Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences. Now she is engaged in synthesis of novel bismuth nanomaterials and environmental analysis.

Haitao Han is currently a research assistant at Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences. He earned his master degree in 2014 at Yantai University. His research interests are in the area of synthesis of novel nanocomposites, electrochemical sensors and environmental analysis.

Mingyue Lin earned the BS degree in 2012 at Nanjing University of Information Science & Technology. She is currently a Ph.D. student at Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences. Her scientific interest includes electrochemical sensors, analysis of environmental pollutants and nutrients.

Chenchen Wang is currently a research assistant at Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences. She earned her master degree in 2015 at Southeast University. Her research interests focus on the determination of heavy metals in intertidal sediments and coastal waters.