Voltammetric determination of total dissolved iron in coastal waters using a glassy carbon electrode modified with reduced graphene oxide, Methylene Blue and gold nanoparticles

5 **AUTHORS**, INCLUDING:

Mingyue Lin
Chinese Academy of Sciences
11 PUBLICATIONS **26** CITATIONS

SEE PROFILE

Dawei Pan
Chinese Academy of Sciences
26 PUBLICATIONS **178** CITATIONS

SEE PROFILE

Haiyun Zhang
9 PUBLICATIONS **19** CITATIONS

SEE PROFILE

Voltammetric determination of total dissolved iron in coastal waters using a glassy carbon electrode modified with reduced graphene oxide, Methylene Blue and gold nanoparticles

Mingyue Lin · Haitao Han · Dawei Pan · Haiyun Zhang · Zhencui Su

Abstract A nanocomposite, prepared from reduced graphene oxide (rGO), Methylene Blue (MB) and gold nanoparticles (AuNPs), was used to modify a glassy carbon electrode for the determination of total dissolved iron by differential pulse voltammetry. The use of rGO warrants a larger electrode surface and the presence of more active sites, while electron transfer is accelerated by incorporating AuNPs. MB acts as an electron mediator, as an anchor for the AuNPs (which were grown in situ), and also prevents the aggregation of rGO. The modified electrode displayed a remarkably improved sensitivity and selectivity for Fe(III). The kinetics of the electrode reaction is adsorption-controlled, and the reversible process involves one proton and one electron. The response to Fe(III) is linear in the 0.3 to 100 μM concentration range, and the detection limit is 15 nM. Possible interferences by other ions were studied. The electrode was successfully applied to the determination of total dissolved iron in real coastal waters.

M. Lin · H. Han · D. Pan (✉) · H. Zhang
Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences; Shandong Provincial Key Laboratory of Coastal Environmental Processes, Yantai, Shandong 264003, People's Republic of China
e-mail: dwpan@yic.ac.cn

M. Lin · H. Zhang
University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

H. Han · Z. Su
School of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, People's Republic of China

Introduction

Iron is one of the most common elements in the earth's crust with a natural abundance of 5.6 % [1]. It is essential for chlorophyll synthesis, nitrate reduction, and detoxification of reactive oxygen species [2]. Besides, it is responsible for hemoglobin synthesis, oxygen transport, and mitochondrial electron transfer because of its presence in the active site of the molecules [3]. The concentration of soluble iron in natural water is significantly different than those in river water (1 μM), coastal water (1 nM), and ocean water (10 pM) [4]. Moreover, iron plays an important role in aquatic biogeochemistry and can limit phytoplankton productivity like other nutrients such as phosphate, silicate, and nitrate in some certain ocean areas [5], which may have a close connection to the global carbon cycle [6]. Therefore, accurate determination of iron in natural water is of significant interest because of its abundance and variable oxidation states in the environment. Many analytical methods such as spectrophotometry and flow injection analysis [7], Fluorescence [8], electrothermal atomic absorption spectrometry [9], inductively coupled plasma optical emission spectrometry [10], inductively coupled plasma–mass spectrometry [11], chemiluminescence [12], and electrochemical methods [13, 14] have been developed for the determination of iron. Although the spectrophotometric methods have been widely used, the size and weight of the instruments limit their use for in situ experiments. Moreover, the ultra trace determination of iron is very expensive and may be affected by other interferences.

The concentration of total dissolved iron in water is difficult to determine without preconcentration. The most common electrochemical method was based on the mercury electrode using adsorptive cathodic stripping voltammetry to measure reduction current of the adsorbed complex to obtain

iron's concentration, and the complexation had to be performed prior to the concentration determination. Besides, the reduction potential of iron complexes changes with different chelating agents such as salicylaldoxime (SA) [15], 1-nitroso-2-naphthol (NN) [16, 17], 2-(2-thiazolylazo)-p-cresol (TAC) [18], and 2,3-dihydroxynaphthalene (DHN) [19]. The complicated, expensive, time-demanding procedure, and mercury toxicity [20] have restricted its widespread use irrespective of its quite low detection limit for the determination of iron in water samples. In recent years, mercury-free and modified electrodes such as bismuth film electrode [21], chemically modified carbon electrode [13], and gold microelectrode ensemble [22] have been developed for iron determination owing to their lower mercury toxicity and considerably sensitive voltammetric detection. Carbon is an ideal replacement material for mercury and has been widely used due to its low price and disposability. Nanocomposite has always been a hot research topic in the past few years; in particular, the materials derived from reduced graphene oxide and gold nanoparticles have been broadly used as the electrode modifier because of their excellent electrochemical properties.

In this study, chemically reduced graphene oxide/Methylene Blue/gold nanoparticles (rGO/MB/AuNPs) composite was used to modify the glassy carbon electrode to achieve the sensitive determination of the total dissolved iron in coastal water samples. The activation of the electrode surface with graphene resulted in the modification with functional groups such as carboxyl and carbonyl, which accelerated the reduction of Fe(III) [22]. Besides, the AuNPs can accelerate the electron transfer, thus increasing the sensitivity. Methylene Blue is an electron mediator full of π electrons and can avoid the aggregation of reduced graphene oxide (rGO) and increase the dispersity [23], rendering a positive role in AuNPs in situ growth on the surface and cavity of rGO [24]. A number of factors have been optimized to obtain the best analytical signal for Fe(III) and the linear response is in the concentration range of 0.3–100 μM with a detection limit of 15 nM. The aim of this study is to establish an effective method for electrochemical determination of total dissolved iron in coastal waters using a long lived and sensitive rGO/MB/AuNPs composite modified electrode.

Experimental

Materials

All chemicals and reagents were of analytical grade. Graphene was supplied by Nanjing Jcnano Technology Company (Nanjing, China. http://www.jcnano.com/). Methylene Blue and HAuCl₄ were purchased from Sinopharm Chemical Reagent (Shanghai, China. http://www.sinoreagent.com.cn/). Iron standard solution was purchased from Acros Organics

(USA. http://www.acros.com/). Standard (10 mM) solutions of Zn^{2+}, Cu^{2+}, Ag^+, As^{3+}, Sn^{4+}, and Fe^{2+} were provided by Sinopharm Chemical Reagent (Shanghai, China. http://www.sinoreagent.com.cn/) and lower concentration of the solutions were prepared by diluting with deionized water. HNO_3, HCl, H_2SO_4, and $HClO_4$ were also supplied by Sinopharm Chemical Reagent (Shanghai, China. http://www.sinoreagent.com.cn/). HNO_3 and HCl were guaranteed Reagents and were sub-boiling distilled using a quartz condenser. All experiments were conducted at room temperature (25 °C) without the removal of oxygen from the solutions and all solutions were prepared using deionized water (18.2 MΩ cm^{-1} specific resistance) from Pall Cascada laboratory water system (USA. http://www.pall.com/main/home.page).

Apparatus

The morphology of the modified electrodes was characterized by scanning electron microscopy (SEM, Hitachi S-4800 microscope, Japan. http://www.hitachi.com/) and transmission electron microscopy (TEM, JEOL JEM-1400 STEM, Japan. http://www.jeol.co.jp/en/). Inductively coupled plasma-mass spectrometry (ICP-MS, ELAN DRC, Perkin Elmer Instruments, USA. http://www.perkinelmer.com/) was used for comparative testing. pH measurements were performed using an E-201-C Model pH meter (Shanghai Leici Instrument Factory, China. http://www.lei-ci.com/). Salinities of the real water samples were measured by a multi-parameter controller (YSI 556MPS, http://www.ysi-china.com/main.aspx). Electrochemical Work Station (CHI 660D, Chenhua Instruments, Shanghai, China. http://chi.instrument.com.cn/) was used throughout all electrochemical experiments. A conventional three electrode system consisting of a modified glassy carbon working electrode (GCE, 3 mm in diameter, Chenhua Instruments, Shanghai, China. http://chi.instrument.com.cn/), a platinum foil auxiliary electrode, and a silver chloride reference electrode (Ag/AgCl, 3 M) was employed. All potentials were measured with respect to the Ag/AgCl reference electrode.

Preparation of the rGO/MB/AuNPs composite modified electrode

rGO/MB/AuNPs composite was synthesized according to the previous report in our lab [24]. rGO/MB/AuNPs composite powders were dispersed in ethanol under ultrasonication for 10 min to get a suspension (0.5 mg mL^{-1}). 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 for 1 min. The rGO/MB/AuNPs suspensions (10 μL) were added on the surface of GCE and dried using an infrared lamp to get the rGO/MB/AuNPs composite modified electrode.

Electrochemical analysis procedure

All the experiments were performed in the 0.1 M HCl electrolyte. The rGO/MB/AuNPs composites were electrochemically characterized by cyclic voltammetry (CV). The parameters used in CV are as follows: initial potential of −0.2 V, final potential of 0.8 V and a scan rate of 100 mV s^{-1}. The reduction responses of Fe(III) to Fe(II) on the bare and modified electrode were investigated by differential pulse voltammetry (DPV), using the following parameters: initial potential of 0.8 V, final potential of 0.1 V, an amplitude of 0.05 V, pulse width of 0.2 s, pulse period of 0.5 s, and an equilibrium time of 2 s.

Water analysis for the total dissolved iron determination

All bottles and containers used for standards and samples were soaked in 5 % nitric acid at least for 24 h and thoroughly cleaned with deionized water prior to use. Water samples were collected from Jiehe river (a local coastal river, which flows into the Bohai Sea, Shandong province, China) and coastal water of Bohai Sea. All the water samples were collected in acid-cleaned polyethylene bottles after filtration (0.45 μm membrane filters) and kept at 4 °C until determination. A certain amount of HCl (30 %) and H_2O_2 (30 %) were added to adjust the pH of water samples less than 2.0, then digested samples in quartz tubes for 30 min using a 500 W UV lamp (Metrohm MVA-UV 705, Switzerland. http://www.metrohm.com/).

Results and discussion

Choice of materials

Nanomaterials have been widely used for construction of electrochemical sensors because they have various shapes, sizes, and compositions which can increase the analytical selectivity and sensitivity [25]. Amongst them, rGO and AuNPs are increasingly applied to fabricate the novel electrodes which have shown great sensitivity due to their unique electronic conductivity and large specific surface area [26, 27]. rGO is a two-dimensional carbon-based monolayer, it has attracted considerable attention and shown great application potentials due to its outstanding properties, such as high mechanical strength, high electrical conductivity, and versatile surface modification [28, 29]. Besides, electrochemical sensors based on AuNPs have been widely used since it possesses brilliant electrical properties, large surface-to-volume ratio, high surface reaction activity, and great adsorption ability [24]. More importantly, AuNPs have shown electrochemical signals to Fe(III) in HCl electrolyte [22]. The functional groups in rGO's basal and edge planes, such as carboxyl and carbonyl, will not only facilitate surface modification but also accelerate the reduction of Fe(III).

In our preliminary experiments, the responses of Fe(III) on various nanomaterials such as the multi-walled carbon nanotube, rGO, AuNPs and TiC nanoparticles were investigated. No signal responses were observed at multi-walled carbon nanotube and rGO modified electrodes, while the largest current response could be obtained at AuNPs modified electrode. rGO modified electrodes could provide larger electrode surface and more active sites. MB is a typical electron mediator which has been frequently used in chemical and biochemical sensors [30]. MB is used here to help AuNPs in situ growth uniformly on the surface of rGO. A novel glassy carbon electrode modified with rGO/MB/AuNPs composite was fabricated based on their synergistic effects for Fe(III) determination.

Characterization of the rGO/MB/AuNPs composite

The surface morphologies of the synthesized rGO/MB/AuNPs composite were characterized by SEM and TEM. Figure 1 shows the SEM images of rGO (Fig. 1a), rGO/MB (Fig. 1b), and rGO/MB/AuNPs (Fig. 1c), and the TEM image of the rGO/MB/AuNPs composite (Fig. 1d). Figure 1a shows that rGO was slightly scrolled because of its partial aggregation. However, the surface of rGO/MB (Fig. 1b) was much rougher than that of rGO and a thin membrane-like substance probably formed on the surface of rGO because of the adsorption of MB. Figure 1c shows that AuNPs were distributed uniformly on the surface of the rGO/MB. Furthermore, the TEM image of the rGO/MB/AuNPs (Fig. 1d) indicated the successful attachment of the AuNPs on the rGO/MB composite.

The electrochemical behaviors of the bare GCE and rGO/MB/AuNPs composite modified GCE were studied in 0.1 M HCl by CV in the potential range from −0.2 to +0.8 V. As shown in Fig. 2, no obvious redox peaks were observed in the CV of bare GCE (curve a) within the scan range, indicating the absence of electroactive substances on bare GCE. Besides, CV of the rGO/MB/AuNPs composite modified GCE (curve b) showed two apparent pairs of redox peaks in the potential ranges of 0.3–0.4 V and 0.1–0.2 V for the oxygen-containing functional groups and the redox of electroactive MB on the electrode surface, respectively. Moreover, the background current of the rGO/MB/AuNPs composite modified GCE was relatively larger than bare GCE due to the fast electron transfer of the AuNPs or the increase of the electrode surface.

The redox behaviors of Fe(III) at the as-prepared electrodes were studied by DPV. Figure 3 shows the DPV responses of 10 μM Fe(III) at three different electrodes in 0.1 M HCl. There are not any reduction peak at bare GCE without and with Fe(III) (curve a and b). To better understand the role of MB in Fe(III) determination, the redox behaviors of Fe(III) were also investigated at the rGO/AuNPs (curve c and d) and rGO/MB/AuNPs (curve e and f) composite modified electrode, which
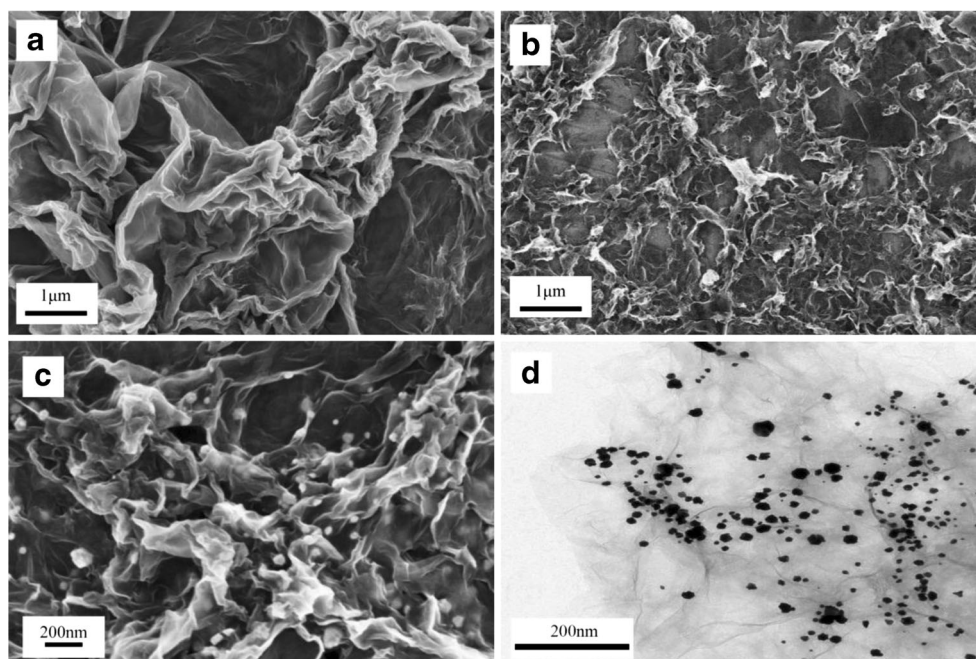
were synthesized in the same way without and with adding MB. However, both sharp reduction peaks at almost 0.5 V at the rGO/AuNPs and rGO/MB/AuNPs composite modified electrode were observed (curve d and f). Considering no background signal responses were observed for rGO/MB/AuNPs composite modified electrode (curve c and e), the reduction peak was attributed to the reduction of Fe(III). Obviously, the reduction peak of Fe(III) at the rGO/MB/AuNPs modified GCE (curve f) has a better shape and is about 10 times greater than that at the rGO/AuNPs modified GCE (curve d). rGO provided larger electrode surface and more active sites while AuNPs were helpful for the reduction of Fe(III) [22]. Meanwhile, MB as electron mediator accelerated the electron transfer and acted as a bridge to connect the

AuNPs and rGO, which could result in the increase of the reduction current of Fe(III). The perfect electrochemical properties of the rGO/MB/AuNPs composite modified electrode exhibit a promising prospect for the detection of iron.

Optimization for the determination of iron on the rGO/MB/AuNPs composite modified electrode

The effect of the film thickness of the rGO/MB/AuNPs composite

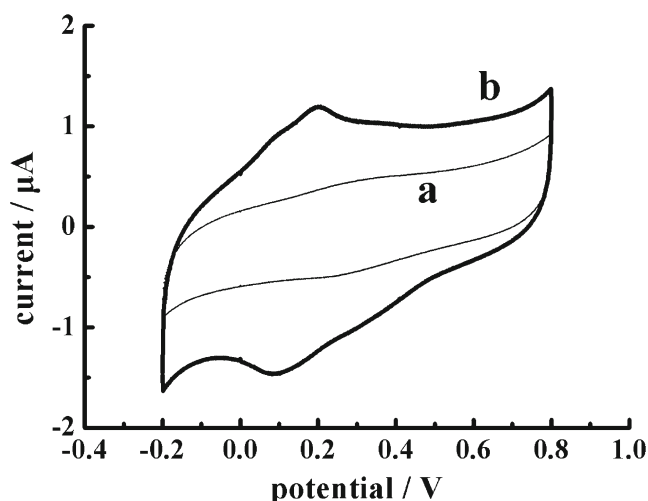The film thickness of the rGO/MB/AuNPs composite at the electrode surface was investigated at the volumes ranging

Fig. 2 Cyclic voltammograms of bare GCE (*a*) and the rGO/MB/AuNPs composite modified GCE (*b*) in 0.1 M HCl at a scan rate of 100 mV s^{-1}
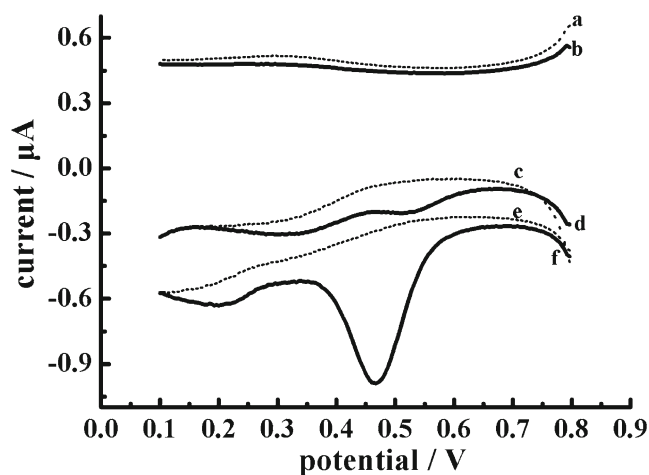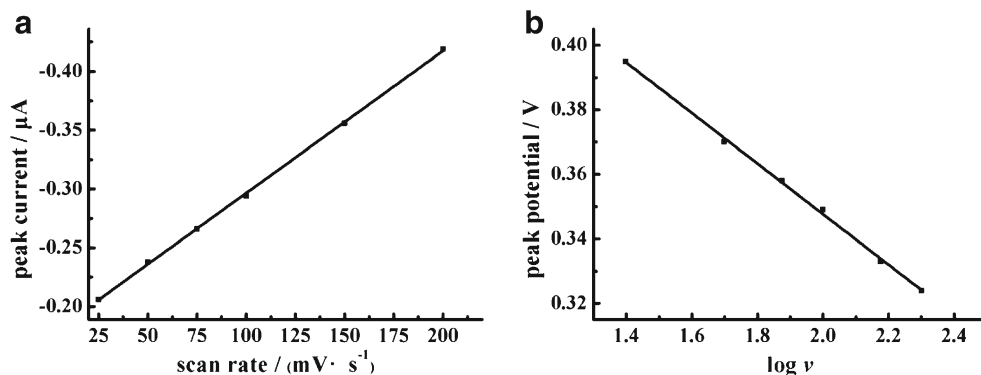

Fig. 3 DPVs of bare GCE (*curve a and b*), the rGO/AuNPs composite modified GCE (*curve c and d*) and the rGO/MB/AuNPs composite modified GCE (*curve e and f*) in 0.1 M HCl without (*curve a, c and e*) and with (*curve b, d and f*) 10 μM Fe(III)

Fig. 4 The variation of the peak current with scan rate (**a**) and the peak potentials with log v (**b**)

from 4.0 to 20.0 μL. The cathodic peak current gradually increased from 4.0 to 10.0 μL volume of the composite. The maximum current was observed at a volume of 10 μL. However, the cathodic peak current decreased with increasing volume from 10.0 to 20.0 μL because the redundant rGO/MB/AuNPs may hinder the electron transfer between Fe(III) and the electrode. The composite could not cover the electrode surface, and the modifier was uneven at volumes less than 10.0 μL. Thus, 10.0 μL volume of the composite was considered as the optimal film thickness.

The effect of electrolytes and pH values

Fe(III) salts are known to hydrolyze easily in slightly acidic and alkaline environment. Therefore, 0.1 M solutions of H_2SO_4, $HClO_4$, HNO_3, and HCl were chosen as the possible electrolytes. Among them, HCl was the best choice for Fe(III) detection because Cl^- can be adsorbed on the AuNPs in the potentials more positive than 0.0 V, which may increase the electron transfer by bridging mechanism [31]. Because the pH value of HCl is an important factor affecting the signal response of Fe(III), the effect of the pH value of the solution on

Fig. 5 Calibration curve of Fe(III) on the rGO/MB/AuNPs composite modified GCE. Inset is the current response of Fe(III) concentrations in linear range

the electrochemical response of 10 μM Fe(III) at the rGO/MB/AuNPs composite modified GCE was examined in various HCl solution at pH of 2.97, 1.99, and 0.98, respectively. The peak potential shifted in negative direction and was linear with increasing solution pH from 0.98 to 2.97. Moreover, the linear regression equation was $E_p=-0.062pH+0.50$ ($R^2=0.999$) according to Nernst Equation $E=E_0-2.303RTmpH/\alpha nF$, where m and n are proton and electron transfer numbers, respectively [32]. The slope of 62 mV pH^{-1} was close to the expected Nernstian theoretical value of 59.1 mV pH^{-1} at 25 °C, indicating that equal numbers of protons and electrons (one electron and one proton) were involved in the electrode reaction [33].

The effect of scan rate

To obtain the kinetic parameters of Fe(III) at the rGO/MB/AuNPs composite modified GCE, the effect of scan rate with the analytical signal of Fe(III) was studied by linear sweep voltammetry. Figure 4a shows that the cathodic peak current increased gradually and was linear with the increasing scan rate from 25 to 200 mV s^{-1}, indicating that the electro-reduction reactions of iron at the rGO/MB/AuNPs composite modified GCE were typical adsorption-controlled processes. A scan rate of 25 mV s^{-1} was chosen for the best signal to noise ratio. The relationship between the reduction peak potential and the logarithm of scan rate (log v) is shown in Fig. 4b, and the regression equation is expressed as $E_p=-0.0783\log v+0.504$ ($R^2=0.998$). According to the Laviron theory $K_s=-2.303RT/(\alpha nF)$ [34], where n is the electron transfer numbers, the value of α was calculated as 0.76. Compared with a totally irreversible electrode reaction process ($\alpha=0.5$), an adsorption-controlled and reversible electrode process can be obtained at the rGO/MB/AuNPs composite modified GCE.

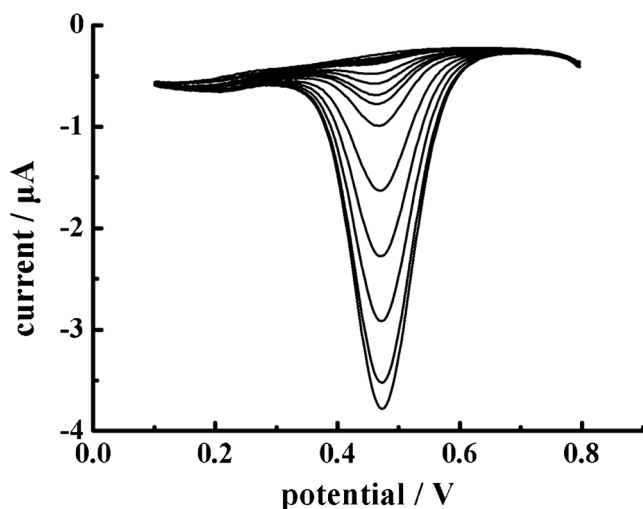Calibration curve

The calibration curve of the Fe(III) was derived from the DPVs obtained at the rGO/MB/AuNPs composite modified

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

Methods	Electrode/agents	Linear range (nM)	LOD (nM)	Testing environment	Applicable waters	Possible interferences	Reference	Notes
Spectrophotometry and flow injection analysis	Diphenylamine-4-sulfonic acid sodium salt (DPA-4-SA)	89.3–357	17.8	Acetate buffer of pH 5.5	Seawater and river water	100-fold Fe^{2+}	[7]	1. Using a chelating agent 2. Complicated procedure
Fluorescence	Salicylic acid	1,000–10,000	50.0–357	Ammonium solution of pH 8.4	Tap water and natural water	7-fold Fe^{2+}; 10-fold Co^{2+}; Sm^{3+}, Y^{3+}, La^{3+}, 20-fold Pb^{2+}, Cr^{3+}	[8]	1. Using a chelating agent 2. Relatively higher linear range and LOD 3. Expensive instrument
Chemiluminescence	8-hydroxyquinoline (8-HQ) chelating resin column	0.04–10	0.04	Acetate buffer of pH 5.5	Seawater	1-fold Co^{2+}	[12]	1. Using a 8-HQ resin to preconcentrate iron from its sea-salt matrix 2. Indirect determination by transforming Fe(III) to Fe(II) 3. An aerobic environment
Inductively coupled plasma–mass spectrometry	Nitrilotriacetic acid (NTA) chelating resin	0.020–0.069	0.02–0.07	HNO_3 of pH 1.9	Seawater	Not mentioned	[11]	1. Using a NTA superflow resin to preconcentrate iron and matrix speciation 2. Using a isotope dilution method 3. Complicated pretreatment 4. Quite expensive agents and instrument for testing
Electrochemical Method	Mercury electrode, 2-(2-Thiazolylazo)-p-cresol	Not mentioned	0.1	N-(2-hydroxyethyl)piperazine-N'-2-propanesulfonic acid (EPPS) of pH 8.0	Coastal seawater	Not mentioned	[18]	1. Mercury toxicity 2. Using a chelating agent 3. Long-time and complicated procedure
Electrochemical Method	Chitosan modified glassy carbon electrode, oxalates	357–5,357	178	HCl of pH 3	Tap water and mineral water	50-fold Se^{4+}; 30-fold Cd^{2+}; 15-fold Cr^{3+}; 14-fold Ni^{2+}; 10-fold Al^{3+},Co^{2+}	[13]	1. Long-time deposition 2. Relatively higher LOD
Electrochemical Method	Reduced graphene oxide/methylene blue/gold nanoparticles composite modified glassy carbon electrode	300–100,000	15	HCl of pH 0.98	Coastal seawater and river water	50-fold Zn^{2+}; 10-fold Cu^{2+}, As^{3+}, Sn^{4+}; Fe^{2+};	This paper	1. Cheap instrument 2. Simple and one-step measurement 3. Do not need preconcentration and chelating agents

GCE in 0.1 M HCl under the optimal conditions (Fig. 5). The peak current increased linearly in the Fe(III) concentration ranging from 0.3 to 100 μM. The equation for linear regression was $i_p = -0.0340C - 0.0599$ with a correlation coefficient of 0.995. The sensitivity and detection limit of the rGO/MB/AuNPs composite modified GCE for Fe(III) determination were 34 nA μM^{-1} and 15 nM (s/n = 3), respectively. Additionally, comparisons about iron determination by electrochemical and other analytical methods were presented in Table 1. The electrochemical methods showed relatively superior performances, such as simple procedure, cheap instrument, low testing cost and relatively lower detection limit. Considering the toxicity of mercury and higher detection limit of chitosan modified electrode, the rGO/MB/AuNPs composite modified GCE is easy to construct and has a good linear range without using chelating agents. Above all, the rGO/MB/AuNPs composite modified GCE may be a good choice for iron determination in coastal seawater and river water because of its satisfactory results.

Reproducibility, repeatability and selectivity

The inter-electrode reproducibility of the rGO/MB/AuNPs composite modified GCE was evaluated in 10 μM Fe(III) by ten independently modified electrodes prepared with the same method and the corresponding relative standard deviation (RSD) was 5.5 %, which indicated that there was no significant difference among the analytical signals at various electrodes. The repeatability of the modified electrode was studied by detecting 10 μM Fe(III) using the same electrode for 10 measurements and the RSD was 3.2 %. Therefore, rGO/MB/AuNPs composite modified GCE exhibited good reproducibility and repeatability.

The oxygen present in the solution was better for detection because it can relatively accelerate the redox of Fe(III)/Fe(II). Moreover, to investigate the effects of possible interfering species for iron determination, various potentially interfering ions were added into 0.1 M HCl containing 10 μM Fe(III). The 500-fold K^+, 50-fold Zn^{2+}, 10-fold Cu^{2+}, As^{3+}, and Sn^{4+} addition did not affect the determination of Fe(III) (<5 % of current change). The addition of sodium chloride at a concentration greater than 0.03 M would influence the signal of iron due to the background signal splits and shifts in the negative direction which was the same to the previous report [22], making it difficult to correctly measure the signal for iron. Considering that our method was carried out in 0.1 M HCl (pH=0.98) and the seawater samples must be diluted 10-fold to determine, the effect of salinity was under control. Besides, adding equivalent of Ag^+ resulted in a sharp decrease in the signal probably because of silver chloride precipitation could be absorbed to the AuNPs which will hinder the electron transfer between electrode and Fe(III) [35]. The addition of Fe(II) resulted in a large increase in the cathodic signal of
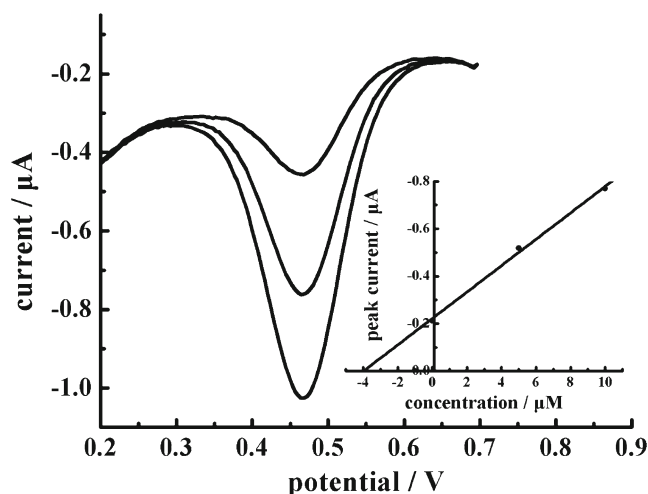

Fig. 6 Typical voltammograms for the determination of total dissolved iron in coastal seawater sample 1 by the standard addition method. The inset shows a series of DPVs after addition of 0, 5 and 10 μM Fe(III) (from *top* to *bottom*)

Fe(III), further proving that the mechanism of the detection was based on the redox of Fe(III)/Fe(II).

On the other hand, organic species may be absorbed on the surface of the electrode or be reduced in DPV, which will cause the obvious changes of current response. Humic substances are the most common natural reducible organic matter presented in aquatic environments which consist predominantly of polyphenols and benzoic/carboxylic acids. Catechol is a typical reducible organic species which is often used as the competing chelator to iron. The effects of humic substances and catechol have been investigated. The results showed that the signals were not interfered after adding 30-fold humic substances, but adding 10-fold catechol would change the peak shape. Because the determination of real water samples was carried out after UV digestion treatment, the organic substances have been all destroyed. The sample with 30-fold humic substances and 10-fold catechol was digested for 30 min under the UV lamp, the signals were similar to the original values. So, our method was not interfered by the organic species after UV digestion. These results indicated good selectivity of the composite modified electrode.

Table 2 Comparison of this method and ICP-MS for determination of total dissolved iron in real coastal waters ($n=3$)

Samples	Detected by rGO/MB/AuNPs composite modified electrode (μM)	Detected by ICP-MS (μM)
Coastal river water 1	123±2.11	119
Coastal river water 2	23.8±1.16	23.6
Coastal sea water 1[a]	44.7±4.76	45.0

[a] The salinity is 14.8‰

Practical application of rGO/MB/AuNPs composite modified GCE

To evaluate the practical application of the established electrode, the rGO/MB/AuNPs composite modified GCE was used for the total dissolved iron determination in real coastal water samples. The coastal seawater sample 1 was diluted 10 times when it was added into 0.1 M HCl and standard additions of Fe(III) of 0, 5 and 10 μM were applied during the measurement. The DPVs obtained at the optimal conditions are shown in Fig. 6. The peak currents are linear with the concentrations (the inset in Fig. 6) and the equation was $i_p=-0.558C-2.22$ with a correlation coefficient of 0.997. The calculated result (39.8 μM) was in agreement with the value detected by ICP-MS (45.0 μM). The comparison results of our method and ICP-MS method on the local river samples and coastal sea water are shown in Table 2. Obviously, the results were consistent with ICP-MS detection, indicating that the fabricated electrode may function as a new and functional electrochemical sensor for the total dissolved iron determination in river water samples and is also suitable for water samples from coastal zone area.

Conclusions

In summary, a novel and effective rGO/MB/AuNPs composite modified GCE was fabricated for sensitive determination of Fe(III). Compared to the bare GCE, the obtained rGO/MB/AuNPs composite modified GCE significantly enhanced the reduction signal of Fe(III) with a detection limit of 15 nM. Moreover, the modified GCE showed excellent reproducibility, repeatability and selectivity for determination of total dissolved iron in real water samples. The fabricated electrode may function as a novel electrochemical sensor for determination of iron and is a promising platform for accurate electroanalysis of trace iron.

References

1. Taylor S (1964) Abundance of chemical elements in the continental crust: a new table. Geochim Cosmochim Acta 28:1273–1285
2. Sunda WG, Huntsman SA (1995) Iron uptake and growth limitation in oceanic and coastal phytoplankton. Mar Chem 50:189–206
3. Dallman PR, Yip R, Oski F (1993) Iron deficiency and related nutritional anemias. Hematology of infancy and childhood 4:413
4. Lu M, Rees NV, Kabakaev AS, Compton RG (2012) Determination of iron: electrochemical methods. Electroanalysis 24:1693–1702
5. Martin JH, Fitzwater S (1988) Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic. Nature 331:947–975
6. Sunda WG (2001) Bioavailability and bioaccumulation of iron in the sea. IUPAC Ser Anal Phys Chem Environ Syst 7:41–84
7. Asan A, Andac M, Isildak I, Tinkilic N (2008) Flow injection spectrophotometric determination of iron (III) using diphenylamine-4-sulfonic acid sodium salt. Chem Pap 62:345–349
8. Cha KW, Park KW (1998) Determination of iron (III) with salicylic acid by the fluorescence quenching method. Talanta 46:1567–1571
9. Freschi GPG, Freschi CD, Neto JAG (2008) Evaluation of different rhodium modifiers and coatings on the simultaneous determination of As, Bi, Pb, Sb, Se and of Co, Cr, Cu, Fe, Mn in milk by electrothermal atomic absorption spectrometry. Microchim Acta 161:129–135
10. Cui Y, Hu ZJ, Yang JX, Gao HW (2012) Novel phenyl-iminodiacetic acid grafted multiwalled carbon nanotubes for solid phase extraction of iron, copper and lead ions from aqueous medium. Microchim Acta 176:359–366
11. de Jong J, Schoemann V, Lannuzel D, Tison JL, Mattielli N (2008) High-accuracy determination of iron in seawater by isotope dilution multiple collector inductively coupled plasma mass spectrometry (ID-MC-ICP-MS) using nitrilotriacetic acid chelating resin for preconcentration and matrix separation. Anal Chim Acta 623:126–139
12. Bowie AR, Achterberg EP, Mantoura RFC, Paul JW (1998) Determination of sub-nanomolar levels of iron in seawater using flow injection with chemiluminescence detection. Anal Chim Acta 361:189–200
13. Lu GH, Yao X, Wu XG, Zhan T (2001) Determination of the total iron by chitosan-modified glassy carbon electrode. Microchem J 69:81–87
14. Shervedani RK, Hatefi-Mehrjardi A, Asadi-Farsani A (2007) Sensitive determination of iron(III) by gold electrode modified with 2-mercaptosuccinic acid self-assembled monolayer. Anal Chim Acta 601:164–171
15. Rue EL, Bruland KW (1995) Complexation of iron (III) by natural organic ligands in the Central North Pacific as determined by a new competitive ligand equilibration/adsorptive cathodic stripping voltammetric method. Mar Chem 50:117–138
16. Den Van Berg C, Nimmo M, Abollino O, Mentasti E (1991) The determination of trace levels of iron in seawater, using adsorptive cathodic stripping voltammetry. Electroanalysis 3:477–484
17. Gledhill M, van den Berg CM (1994) Determination of complexation of iron (III) with natural organic complexing ligands in seawater using cathodic stripping voltammetry. Mar Chem 47:41–54
18. Croot P, Johansson M (2000) Determination of iron speciation by cathodic stripping voltammetry in seawater using the competing ligand 2-(2-Thiazolylazo)-p-cresol (TAC). Electroanalysis 12:565–576
19. van den Berg CMG (2006) Chemical speciation of iron in seawater by cathodic stripping voltammetry with dihydroxynaphthalene. Anal Chem 78:156–163
20. Palmer RF, Blanchard S, Stein Z, Mandell D, Miller C (2006) Environmental mercury release, special education rates, and autism disorder: an ecological study of Texas. Health Place 12:203–209
21. Segura R, Toral MI, Arancibia V (2008) Determination of iron in water samples by adsorptive stripping voltammetry with a bismuth film electrode in the presence of 1-(2-piridylazo)-2-naphthol. Talanta 75:973–977
22. Zakharova E, Elesova E, Noskova G, Lu M, Compton R (2012) Direct voltammetric determination of total iron with a gold microelectrode ensemble. Electroanalysis 24:2061–2069
23. Liu H, Gao J, Xue M, Zhu N, Zhang M, Cao T (2009) Processing of graphene for electrochemical application: noncovalently functionalize graphene sheets with water-soluble electroactive methylene green. Langmuir 25:12006–12010

24. Han H, Pan D, Wu X, Zhang Q, Zhang H (2014) Synthesis of graphene/methylene blue/gold nanoparticles composites based on simultaneous green reduction, in situ growth and self-catalysis. J Mater Sci 49:4796–4806

25. Baca AJ, Zhou FM, Wang J, Hu JB, Li JH, Wang JX, Chikneyan ZS (2004) Attachment of ferrocene-capped gold nanoparticle-streptavidin conjugates onto electrode surfaces covered with biotinylated biomolecules for enhanced voltammetric analysis. Electroanalysis 16:73–80

26. Zhou M, Zhai Y, Dong S (2009) Electrochemical sensing and biosensing platform based on chemically reduced graphene oxide. Anal Chem 81:5603–5613

27. Ge SG, Yan M, Lu JJ, Zhang M, Yu F, Yu JH, Song XR, Yu SL (2012) Electrochemical biosensor based on graphene oxide–Au nanoclusters composites for L-cysteine analysis. Biosens Bioelectron 31:49–54

28. Fu XL, Chen LX, Li JH (2012) Ultrasensitive colorimetric detection of heparin based on self-assembly of gold nanoparticles on graphene oxide. Analyst 137:3653–3658

29. Liu YX, Dong XC, Chen P (2012) Biological and chemical sensors based on graphene materials. Chem Soc Rev 41:2283–2307

30. Zhang Y, Liu L, Xi F, Wu TX, Lin XF (2010) A simple layer-by-layer assembly strategy for a reagentless biosensor based on a nanocomposite of methylene blue-multiwalled carbon nanotubes. Electroanalysis 22:277–285

31. Burke LD (2004) Scope for new applications for gold arising from the electrocatalytic behaviour of its metastable surface states. Gold Bull 37:125–135

32. Huang KJ, Xu CX, Xie WZ, Wang W (2009) Electrochemical behavior and voltammetric determination of tryptophan based on 4-aminobenzoic acid polymer film modified glassy carbon electrode. Colloids Surf B: Biointerfaces 74:167–171

33. Nicholson RS (1965) Theory and application of cyclic voltammetry for measurement of electrode reaction kinetics. Anal Chem 37:1351–1355

34. Laviron E (1974) Adsorption, autoinhibition and autocatalysis in polarography and in linear potential sweep voltammetry. J Electroanal Chem Interfacial Electrochem 52:355–393

35. Chu X, Fu X, Chen K, Shen GL, Yu RQ (2005) An electrochemical stripping metalloimmunoassay based on silver-enhanced gold nanoparticle label. Biosens Bioelectron 20:1805–1812