Dual-nanomaterial based electrode for voltammetric stripping of trace Fe(II) in coastal waters

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ABSTRACT

In this work, a dual-nanomaterial based electrode was established for selective and sensitive detection of trace Fe(II) in the presence of complexing agent (2,2′-bipyridyl). Titanium carbide nanoparticles (TiCNPs) were used as the growth-template for the formation of three-dimensional platinum nanoflowers (PtNFs) due to their unique cubic structures. Nafion was employed as the conducting matrix to help TiCNPs better attached onto the surface of the electrode and slow down the crystal rate of PtNFs during electrodeposition, which resulted in flower structure and more active surface of PtNFs. Taking advantage of synergistic effects of TiCNPs and Nafion as well as the catalytic amplifying effect of PtNFs, the excellent anodic signal responses for the voltammetric stripping determination of Fe(II) were obtained. The linear range of Fe(II) on this dual-nanomaterial based electrode was from 1 nmol L^{-1} to 6 μmol L^{-1} with the lowest detectable concentration of 0.1 nmol L^{-1} and a detection limit of 0.03 nmol L^{-1}. Additionally, the effect of several experimental parameters, such as concentration and pH value of buffer solution, concentration of modifier and ligand, deposition potential and time of electrochemical determination, and scan rate were studied for analytical applications. The fabricated sensor had been successfully applied for the sensitive determination of trace Fe(II) in coastal waters.

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1. Introduction

Iron exits widely in natural environment, and is an essential micro-nutrient for almost all organisms [1]. However, iron has been considered to be a key factor of phytoplankton growth limitation in several oceans because of its quite low concentration in surface water which was owing to the limited solubility of its oxyhydroxide and particulate forms [2]. As we all known, there are several species of iron exist in seawater. Compared to Fe(III), Fe(II) is the more soluble form, and has been found in anoxic and sub-oxic waters, such as deep lake waters and isolated water basins in marine systems, etc [3,4]. Fe(II) is readily oxidized to the insoluble Fe(III) in oxic waters due to its fast oxidation [5]. Because Fe(II) is more soluble and more easily to be adsorbed by microorganisms, the redox chemistry of iron is thus to be an important factor in understanding iron's biochemistry in seawaters [6]. In order to better understand the bioavailability of redox iron species to microorganisms, it is necessary to improve our knowledge of iron redox speciation and its behavior in the marine system. Therefore, many sensitive methods have been developed to determine Fe(III) in seawater with good limits of detection [7–9], there is an urgent need to develop an applicable method to determine Fe(II) in seawaters.

Several spectrophotometric methods have been established for Fe(II) determination in natural waters. Samples need to be concentrated on chelating resins at different pH in order to reach low detection limits, which may cause the change of redox speciation [10]. Among all the analytical methods under development, electrochemical method has been considered as one of the most sensitive methods for trace iron analysis. Until now, only few papers have reported the determination of Fe(II) by using electrochemical methods. C.M.G. van den Berg, et al. reported a sensitive and indirect method of Fe(II) analysis by masking Fe(II) with bipyridyl in 1995 and 1998 [4,5]. The direct determination of Fe(II) was reported by Mikkelsen and Schroder [11] using a dental amalgam electrode in the solution containing ammonium oxalate to a nanomolar level. Recently, M.B. Gholivand, et al. reported a method for Fe(II) determination based on a carbon paste electrode modified with dithiodianiline and gold nanoparticles and the detection limit of 0.05 nmol L^{-1} could be calculated after 40 s accumulation [12].

In order to obtain the better data to understand the redox chemistry of iron in biogeochemistry, there is an urgent task to develop a sensitive and applicable method for Fe(II) analysis. Although P. Zuman had reported that mercury electrode had no ill effects for lab use for centuries if it was used in an appropriate way [13], glassy carbon electrode (GCE) was even mostly chosen from the safety aspect as the working electrode to avoid mercury toxicity and its difficulties in operation. Considering that the concentration of Fe(II) in seawater is very low, some chemical modification of GCE is necessary to improve the method's sensitivity and selectivity. Recently, some studies showed that using the deposited metal nanoparticles as alloy with another metal [14] or supported by some "active supporting materials", such as nitrogen containing carbon nanotube [15], carbon-silica composite [16], would improve the electrochemical catalytic effects due to the strong metal-support interaction [17]. Nanosized titanium carbide is a kind of cubic phase nanoparticle possessed many advantages, such as larger specific surface area, high electron transfer rate, and electrocatalytic behaviors [18], which has been widely used in analytical chemistry [19]. Our recent research works reported the increase of the current response of Cr(VI) and Fe(III) [20,21] by using titanium carbide nanoparticles (TiCNPs) as the electrode modification material. Besides, TiCNPs had been successfully used as support of Pt catalysts for methanol electrooxidation [17].

The aim of this paper is to combine the unique properties of TiCNPs and the preconcentration ability of Nafion (a kind of ion-exchange polymer) with the aid of the catalytic amplifying effect of PtNFs to establish an electrochemical sensing platform for Fe(II) determination. Such a designed TiCNPs-Nafion/PtNFs modified electrode can offer dramatically improved sensitivity and selectivity in the presence of 2,2′-bipyridyl (Bp) for voltammetric measurement of Fe(II). Experimental conditions and analytical performances were systematically investigated. This novel sensor was also applied for the determination of Fe(II) in real coastal waters with satisfactory results.

2. Experimental

2.1. Chemicals

All the chemicals used in the experiments were analytical reagent grade. Deionized water (18.2 MΩ cm specific resistance) obtained from Pall Cascada laboratory water system was used throughout the experiment. Iron standard solutions were prepared from iron(II) sulfate heptahydrate (Sinopharm Chemical Reagent Co., Ltd., China.) in 0.01 mol L^{-1} HCl. Stock solutions of 2 mmol L^{-1} 2,2′-bipyridyl (Bp) was also prepared in 0.01 mol L^{-1} HCl. The 0.05% w/v Nafion solution was prepared by 1:100 dilution with methanol of 5% w/v Nafion solution (Sigma-Aldrich Co. LLC). The suspension of 0.5 mg mL^{-1} TiC nanoparticles (particle size: 20–60 nm, Nanjing Emperor Nano Material Co., Ltd., China) was dispersed and ultrasonicated in 0.05% w/v Nafion. 1.9 mmol L^{-1} H_2PtCl_6 was prepared in 0.5 mol L^{-1} H_2SO_4 for electrodeposition. Reduced graphene oxide nanoparticles (rGO) and multi-walled carbon nanotubes (MWCNT) were supplied by Nanjing Jcnano Technology Company. All bottles and containers used for standards and samples were soaked in 5% HNO_3 at least for 24 h and then washed with deionized water before use. All experiments were conducted at room temperature (25 °C) and all solutions used had been pre-purged with nitrogen.

2.2. Instruments

An electrochemical work station (CHI 660D, Shanghai CH Instruments, Shanghai, China) was used throughout the electrochemical experiments with a conventional three-electrode system. The working electrode was a glassy carbon electrode (3 mm in diameter), the reference electrode was an Ag/AgCl (saturated with 3 mol L^{-1} KCl) electrode, and the auxiliary electrode was a platinum foil counter electrode. The morphologies were characterized by scanning electron microscopy (SEM, Hitachi S-4800, Japan). Polarograph (VA 797 Metrohm) was used for comparative testing.

2.3. Preparation of the modified GCEs

Prior to use, the GCE was thoroughly polished with aqueous alumina slurry (0.3 and 0.05 μm, respectively), and washed and ultrasonicated with deionized water and ethanol. 2 μL TiCNPs-Nafion (0.5 mg mL^{-1}) was dropped on the surface of GCE and dried under an infrared lamp to get the TiCNPs-Nafion modified GCE (TiCNPs-Nafion/GCE). Then TiCNPs-Nafion/GCE was immersed in 0.5 mol L^{-1} H_2SO_4 containing 1.9 mmol L^{-1} H_2PtCl_6 to electrodeposit Pt nanoflowers with constant potential of −0.25 V for 100 s with an extremely slow stirring rate. For comparison, other modified GCEs were prepared in the same manner. It took about 4 min to completely prepare the platinum nanoflowers modified electrode from polish to deposition. The modified electrode can be stable after 3 days if stored in a sealed environment, and one electrode can be used repeatedly for about 50 times with response current change less than 5%.

2.4. Electrochemical analysis procedure

All experiments were performed in 0.2 mol L^{-1} acetate buffer (pH 4.5). 50 μmol L^{-1} Bp was firstly added to buffer before adding Fe(II) standard solutions or real water samples. The square wave voltammetry (SWV) was chosen as the detecting technique rather than differential pulse voltammetry (DPV), because the testing time of SWV was much shorter and the oxidation signal of Fe(II)-Bp obtained by SWV was three times higher than that obtained by DPV under the same conditions. Therefore, the anodic stripping currents of Fe(II)-Bp on the bare and modified GCEs were investigated by SWV, using the following parameters: deposition potential of −0.1 V, deposition time of 60 s, initial potential of 0.4 V, final potential of 1.4 V, an amplitude of 0.025 V, increment potential of 0.004 V, frequency of 15 Hz, and a quiet time of 2 s.

2.5. Preparation of real coastal seawater samples

Coastal seawater samples were obtained from Chinese Bohai sea. Water samples were collected and stored in clean FEP bottles covered with foil to avoid the sunlight. Then, water samples were immediately transferred to lab and purged with nitrogen for 5 min to remove oxygen before filtration (0.45 μm). After that, the water samples were diluted to an appropriate concentration and added to 0.2 mol L^{-1} acetate buffer (pH=4.5) for subsequent analysis. Standard addition method was used for quantitative analysis.

3. Results and discussion

3.1. Characterization of the modified electrode

The SEM micrographs of bare GCE (Fig. 1a), TiCNPs-Nafion (Fig. 1b), TiCNPs-Nafion/PtNFs (Fig. 1c and d), PtNFs (Fig. 1e), and Nafion/PtNFs (Fig. 1f) modified GCE were shown. Compared with the smooth surface of the bare GCE (Fig. 1a), TiCNPs-Nafion suspension was uniformly distributed on the surface of GCE with sizes ranging from 20–60 nm (Fig. 1b). Nafion was served as the conductive matrix to help TiCNPs tightly attached to the GCE and most
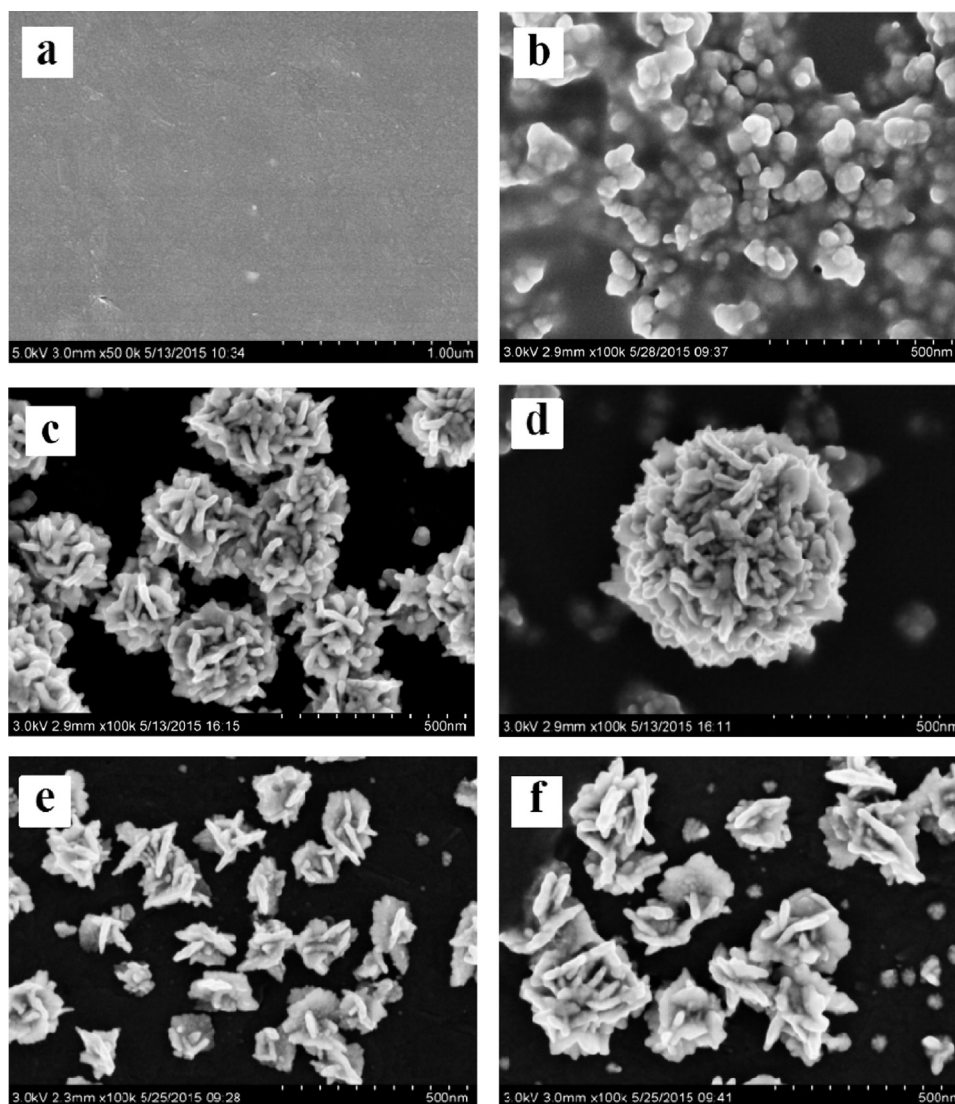
Fig. 1. SEM images of (a) bare GCE, (b) TiCNPs-Nafion, (c,d) TiCNPs-Nafion/PtNFs, (e) PtNFs and (f) Nafion/PtNFs modified GCE.

of the TiCNPs were incorporated into the Nafion film. Besides, the existence of Nafion can slow down the rate of crystal procedure which will help to obtain more uniform PtNFs during electrodeposition. As shown in Fig. 1c and d, platinum nanoparticles with flower structure was composed of ultrafine Pt petals with thickness of average 400 nm after electrodeposition. Moreover, the PtNFs were more uniformly grown on the surface of TiCNPs-Nafion modified GCE, and its active surface areas were much larger compared with those on GCE (Fig. 1e) and Nafion modified GCE (Fig. 1f). These results indicated the successful achievement of dual-nanomaterial with unique and exciting three-dimensional structure.

3.2. Mechanism of Fe(II) oxidation on the modified electrode

The sensing strategy is clearly illustrated in Scheme 1. In this fabricated sensor, TiCNPs were employed as an active support material to support PtNFs' growth due to its cubic structure and catalytic effect on electrochemical oxidation. Nafion was used here to help TiCNPs better attached on the surface of bare GCE and slow down the rate of crystal procedure during PtNFs electrodeposition. In order to increase the selectivity and sensitivity of this method, the mostly used 2,2′-bipyridyl (Bp) was chosen as the complexing ligand to Fe(II), which can form a very strong bond to Fe(II) and the
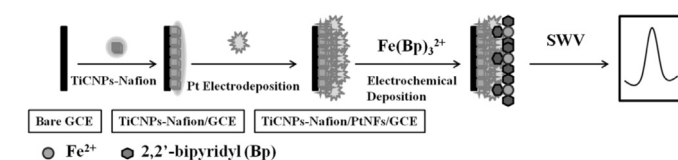
Scheme 1. Schematic illustration of the enhanced electrochemical detection strategy for Fe(II) on TiCNPs-Nafion/PtNFs modified GCE by anodic stripping voltammetry.

complex is very stable [22]. During electrochemical deposition, Fe(II)-Bp can be adsorbed onto the surface of TiCNPs-Nafion/PtNFs modified GCE, then a positive scanning potential was applied to get the anodic stripping voltammetry of Fe(II)-Bp. Since reduced graphene oxide nanoparticles and multi-walled carbon nanotubes have same nanomaterials' properties as titanium carbide nanoparticles, the electrochemical oxidation of Fe(II)-Bp has also been studied on these two kinds of nanomaterials with the same modified method as TiCNPs-Nafion/PtNFs modified GCE under the same experimental conditions. Although there are also the response current on other nanomaterials modified electrode, the peak current of Fe(II)-Bp on TiCNPs-Nafion/PtNFs modified GCE was about 1.5 times larger than that on the reduced graphene oxide nanoparticles or multi-walled carbon nanotubes modified
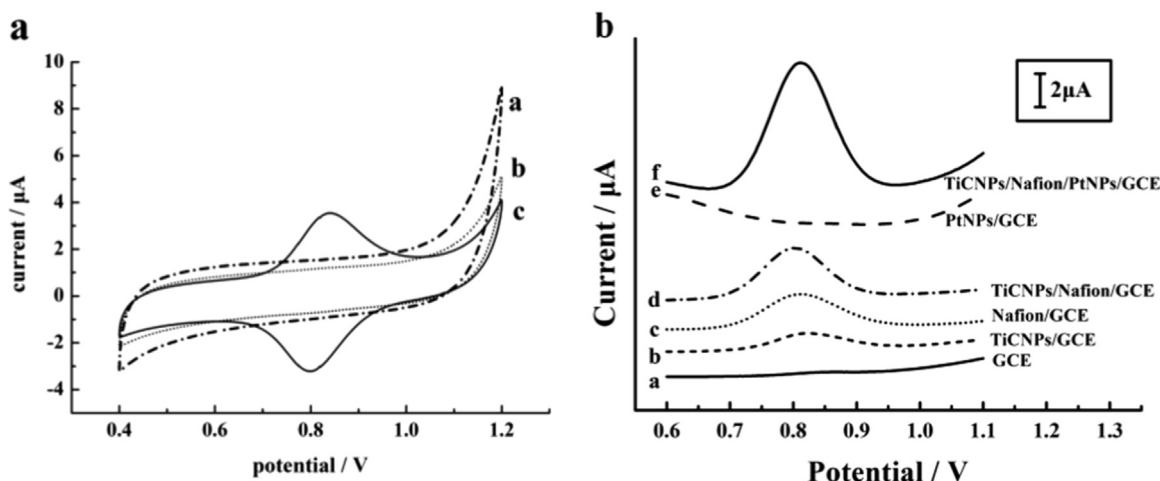
Fig. 2. (a) The cyclic voltammograms of Fe(II)-Bp on the modified electrode. The solution contained (curve a) only 0.2 mol L^{-1} acetate buffer; (curve b) 0.2 mol L^{-1} acetate buffer and 50 µmol L^{-1} Bp; (curve c) 0.2 mol L^{-1} acetate buffer (pH 4.5), 50 µmol L^{-1} Bp, and 2 µmol L^{-1} Fe(II). (b) The anodic stripping current response of different modified GCEs to Fe(II)-Bp in 0.2 mol L^{-1} acetate buffer (pH 4.5) containing 50 µmol L^{-1} Bp and 2 µmol L^{-1} Fe(II) by square wave voltammetry.

electrode (Fig. S1), which indicated that TiCNPs was a better choice of nanoparticle in this system compared with other carbon na-nomaterials due to the catalytic property of TiCNPs and its low background current.

To verify the effect of fabricated sensor on Fe(II) detection, cyclic voltammetry (CV) was measured. As shown in Fig. 2a, there was no redox peaks showed on the modified GCE in the solution that only contained 0.2 mol L^{-1} acetate buffer or 50 µmol L^{-1} Bp. After adding 2 µmol L^{-1} Fe(II) into the solution that contained Bp, an obvious redox peak was observed at the potential about 0.8 V with a peak separation (ΔEp) of 43 mV which indicated the electron transfer rate was very fast. From the CV of Fe(II)-Bp in Fig. 2a, there was a reversible reaction with only one electron transfer according to equation of ΔEp = 0.059 V/n (for a reversible reaction, n is the electron transfer number) [23]. As shown in Fig. 2b, the electrochemical behaviors of Fe(II)-Bp at the modified electrodes were studied by square wave voltammetry (SWV). No anodic signal of Fe(II)-Bp was seen on the bare GCE (curve a). The peak current of Fe(II)-Bp at the TiCNPs-Nafion modified GCE (curve d) was larger than the sum of that at TiCNPs modified GCE (curve b) and Nafion modified GCE (curve c), indicating that TiCNPs and

Nafion would synergistically improve the anodic current response of Fe(II)-Bp. Interestingly, there was no obvious response to Fe(II)-Bp on PtNFs modified GCE (curve e), but the anodic current of Fe (II)-Bp on TiCNPs-Nafion/PtNFs modified GCE (curve f) was three times higher than its on TiCNPs-Nafion modified GCE (curve d), suggesting TiCNPs and Nafion were acting as the sensing elements and PtNFs was acting as the catalytic element in this fabricated sensor. These results indicated that the response current of Fe(II) could be apparently improved by synergistic and catalytic effects.

3.3. Optimization for Fe(II) measurement on TiCNPs-Nafion/PtNFs modified GCE

3.3.1. Effect of the amount of the modifiers and the concentration of 2,2′-bipyridyl

To get the maximum current response, the amount of modified materials, such as the concentration of the TiCNPs, the deposition time and potential of PtNFs were investigated. As shown in Fig. S2a, the anodic peak current increased gradually with the amount of TiCNPs increasing from 0.1 to 0.5 mg mL^{-1} and the maximum current was observed at a volume of 0.5 mg mL^{-1}. Then, it was decreased with increasing volume from 0.5 to 1.0 mg mL^{-1} due to the redundant TiCNPs might hinder the electron transfer between Fe(II)-Bp and the electrode. Thus, 0.5 mg mL^{-1} of TiCNPs was considered as the optimal concentration.

The investigation of PtNFs electrodeposition was shown in Fig. S2b and S2c. From Fig. S2b, the optimal deposition potential was observed at −0.25 V which might owing to the PtNFs' morphol-ogies were not that good at the too negative or positive potentials (compared with −0.25 V). Besides, the maximum current was observed at the deposition time of 100 s with stirring (Fig. S2c). The anodic peak current decreased with the increasing deposition time from 100 to 140 s due to the size of PtNFs became bigger and the specific surface area decreased. Thus, the deposition potential of −0.25 V and deposition time of 100 s were considered as the optimal PtNFs electrodeposition conditions.

As shown in Fig. S2d, the anodic peak current was affected by the amount of 2,2′-bipyridyl (Bp) greatly. The peak current in-creased gradually with the concentration of Bp increased to 50 µmol L^{-1}, and then decreased from the concentration of Bp varied from 50 µmol L^{-1} to 70 µmol L^{-1}. This might because too much free Bp would compete with Fe(II)-Bp to adsorb on the modified GCE. Thus, a Bp concentration of 50 µmol L^{-1} was cho-sen as the optimal condition.
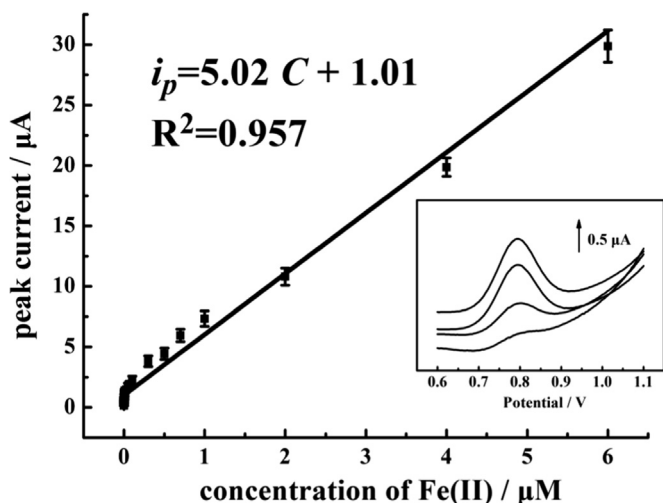

Fig. 3. Calibration curve of Fe(II)-Bp on the modified GCE with the linear range of 1 nmol L^{-1} to 6 µmol L^{-1}. Inset is the voltammetric responses in lower con-centrations (0.1, 0.5, 0.7, 0.9 nmol L^{-1}, respectively, from bottom to up) which were not in the linearity.

$$i_p = 5.02\ C + 1.01$$
$$R^2 = 0.957$$

Table 1
Comparison of the established method with other electrochemical methods for Fe(II) determination. **Method**: DPASV, differential pulse anodic stripping voltammetry; SWV, square wave voltammetry. **Electrode**: GCE, glassy carbon electrode; CPE, carbon paste electrode; DAE, dental amalgam electrode; ADE, Ag-alloy disk electrode. **Modifier/complexing agent**: DTDA, dithiodianiline; AuNPs, gold nanoparticles.

| Technique	Electrode	Modifier/complexing agent (if any)	Testing environment	Linear Range (mol L^{-1})	Detection Limit (mol L^{-1})	Reference
DPASV	GCE	pyrophosphates	Pyrophosphate buffer (pH 9.0)	10^{-6}–10^{-4}	2.7×10^{-8}	[25]
DPASV	DAE	Ammonium oxalate	citrate solution (0.02 M)	3.9×10^{-8}–8.9×10^{-7}	9.0×10^{-9}	[11]
DPASV	Rotating ADE	N/A	Seawater (pH 8.0)	5.0×10^{-9}–5.0×10^{-8}	3.0×10^{-10}	[26]
DPASV	CPE	DTDA and AuNPs	acetate buffer (pH 3.0)	10^{-9}–10^{-7}	5.0×10^{-11}	[12]
SWV	GCE	TiCNPs-Nafion/PtNFs, Bp	acetate buffer (0.2 M, pH 4.5)	10^{-9}–6.0×10^{-6}	3.0×10^{-11}	This work
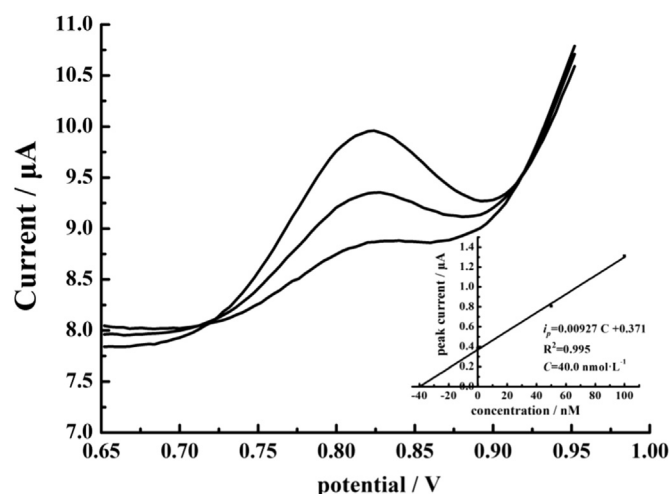
Fig. 4. Square wave voltammogram of detecting Fe(II) concentration in coastal water sample 1 on the modified GCE (adding Fe(II) concentration of 0, 50, 100 nmol L^{-1} from bottom to up). Inset is the calibration curve of standard addition.

3.3.2. Effect of different buffer solutions and pH values

The effect of pH values was studied in the range from 1.8 to 7.0 in different buffer solutions. Because Fe(II) can be readily oxidized and hydrolyzed in slightly acidic and alkaline conditions, the pH was chosen less than 7.0. Firstly, Britton-Robinson buffer (BRB) was chosen to study the effect of pH on Fe(II)-Bp complex oxidation. From Fig. S3, the best signal was obtained at pH 4.1 in BRB solution. Then, 0.1 mol L^{-1} acetate buffer was chosen to study the pH range from 3.5 to 5.5, and 0.1 mol L^{-1} phosphate buffer was chosen to study the pH of 6.0 and 7.0. From Fig. S3, the maximum peak current of the complex was obtained at pH 4.5 in acetate buffer which might due to the small background current. Therefore, the 0.1 mol L^{-1} acetate buffer of pH 4.5 was chosen as the best buffer solution for Fe(II)-Bp oxidation because there was no oxidation peak of Fe(II)-Bp in strong acidic (pH $\leq$ 2.1) and neutral (pH 7.0) solutions. In order to obtain the best signal response, the different concentrations of acetate buffer (pH 4.5) ranging from 0.05 to 0.4 mol L^{-1} were studied. As shown in Fig. S4, the result showed that 0.2 mol L^{-1} acetate buffer presented the highest anodic peak current, because the complex formation and stability can be affected by the ionic strength. Thus, 0.2 mol L^{-1} acetate buffer of pH 4.5 was chosen as the optimal electrolyte.

3.3.3. Effect of accumulation potential and time of Fe(II)-Bp

To get the best stripping response, the accumulation time and potential were studied. Because the modified electrode was negatively charged and the Fe(II)-Bp complex was positively charged, electrostatic interaction would help Fe(II)-Bp complex strongly adsorb on the surface of the TiCNPs-Nafion/PtNFs modified GCE.

Table 2
Validation of the proposed method compared with catalytic CSV method for trace Fe(II) determination in coastal waters.

Samples	Concentrations (nmol L^{-1})		t-test value	F-test value
	This method	Catalytic CSV		
Coastal water sample 1	40.0	38.7	1.17	4.00
	41.5	42.1		
	42.3	40.1		
Mean[a] (nmol L^{-1}) $\pm$ RSD	41.3 $\pm$ 1.2	40.4 $\pm$ 2.4		
Coastal water sample 2	56.4	54.0	2.67	2.11
	58.5	58.1		
	54.1	51.9		
Mean[a] (nmol L^{-1}) $\pm$ RSD	56.3 $\pm$ 2.2	54.7 $\pm$ 3.2		

[a] Each value is calculated from three experiments.

As shown in Fig. S5a, the peak current was low when the accumulation potential was set to 0 V, indicating the Fe(II)-Bp complex can be adsorbed on the surface without the attract of negatively charged electrode which may owing to Nafion film would adsorb positively charged cation ions-ligand complex in acidic solution [24]. The peak current was increased when the potential varied from 0 to −0.1 V and then decreased in the potential range of −0.1 to −0.4 V due to the complex might be too strongly adsorbed on the negatively charged surface. The best accumulation potential was −0.1 V. The effect of accumulation time ranging from 10 s to 200 s was investigated. As shown in Fig. S5b, the peak current increased rapidly as the accumulation time increased from 10 s to 140 s, and then tended to increase slowly. Considering the time of analysis, 60 s was chosen as the accumulation time because it was enough for real coastal water sample determination in this system. Thus, the optimal accumulation potential was −0.1 V and accumulation time was 60 s.

3.4. Calibration curve

The calibration curve of the Fe(II) was derived from the SWVs obtained at the TiCNPs-Nafion/PtNFs modified GCE under the optimal conditions (Fig. 3). The linear calibration curve of 1 nmol L^{-1} to 6 μmol L^{-1} Fe(II) was established which can be expressed by the regression equation $i_p = 5.02C + 1.01$ (R^2=0.957) where i_p represents the peak current in μA and C is Fe(II) concentration in μmol $\cdot L^{-1}$. The sensitivity was 5.0 μA L μmol^{-1}. The relative standard deviation (RSD) of slope and intercept were 0.03 and 0.03 (n=3), respectively. The detection limit and its RSD (n=3) were 0.03 nmol L^{-1} and 0.25%, which were calculated as the blank response plus three times the blank standard deviation divided by the slope of calibration curve. From inset of Fig. 3, the lowest detectable concentration of Fe(II) on the TiCNPs-Nafion/PtNFs modified GCE

was 0.1 nmol L^{-1}. Additionally, the comparison of Fe(II) determination by our developed method and other electrochemical methods were presented in Table 1. Our new fabricated sensor shows lower detection limit, wider linear range and easier experimental processes for Fe(II) determination compared with other modified electrodes. Besides, compared with Gholivand's work [12], the procedure of our fabricated electrode is much easier and the analysis time is quite similar although the carbon paste electrode is little cheaper than modified glassy carbon electrode. But the electrode material used in carbon paste electrode was only applicable for about one month and each electrode showed a little bit different behavior in Gholivand's work [12]. For our fabricated electrode, the electrodes have good repeatability and reproducibility (the difference between different glassy carbon electrodes and difference in independently modified electrodes are very small). Above all, TiCNPs-Nafion/PtNFs modified GCE in this work may be a good choice for Fe(II) determination.

3.5. Reproducibility, repeatability and selectivity

The reproducibility of TiCNPs-Nafion/PtNFs modified GCE was investigated in the solutions that contained 2 μmol L^{-1} Fe(II) and 50 μmol L^{-1} Bp by ten independently modified electrodes prepared in the same way. The relative standard deviation (RSD) of the reproducibility was calculated to be 4.7%, and the RSD of repeatability was measured as 4.0% by using the same electrode for 10 measurements. Therefore, the TiCNPs-Nafion/PtNFs modified GCE presented good reproducibility and repeatability. Besides, the modified electrode showed a very good selectivity. Possible interference by other metal ions with the anodic stripping voltammetry of Fe(II) was investigated by the addition of the interfering ions to a solution containing 2 μmol L^{-1} Fe(II) and 50 μmol L^{-1} Bp under the optimized conditions with 60 s deposition time. The 50-fold Cr(III), Zn(II), Ag(I), 40-fold Co(III), Pb(II), Mg(II), 30-fold Cd(II), Hg(II), and 20-fold Cu(II), *Bi*(III) did not affect the determination of Fe(II) (< 5% of response current change) because these metal ions can not form stable complex with Bp in such pH conditions or the complex do not oxidize in the given potential range. These results showed that our proposed TiCNPs-Nafion/PtNFs modified GCE has a very good selectivity.

3.6. Practical application

To evaluate the practical application of the established electrode, the TiCNPs-Nafion/PtNFs modified GCE was used for Fe(II) determination in two coastal seawater samples. The concentration of Fe(II) was estimated by standard addition method. As shown in Fig. 4, Fe(II) concentration in coastal water sample 1 was calculated as 40 nmol L^{-1}. The results obtained were compared favorably with those obtained by the methods of catalytic cathodic stripping voltammetry (CSV) used VA 797 Metrohm based on hanging mercury electrode reported by C.M.G. van den Berg's group [4] (Table 2). The accuracy was verified by the Student's *t*-test and Fisher *F*-test with the calculated values [27]. It was seen that experimental *t*-test and *F*-test value for Fe(II) were less than the theoretical values (*t*-test=3.182, n=3; *F*-test=39.0, n=2) at a confidence level of 95% (*P* value of 0.05). Reasonable agreement was found in the results obtained by our proposed method and catalytic cathodic stripping voltammetry, indicating our fabricated electrode may function as a new and functional electrochemical sensor for Fe(II) determination in coastal waters.

4. Conclusions

In summary, a novel and effective TiCNPs-Nafion/PtNFs modified GCE was fabricated for sensitive determination of Fe(II).

Compared to other electrochemical sensors, our proposed modified electrode has a wider linear range and lower detection limit and shows good reproducibility, repeatability and selectivity for real coastal seawater samples. The cost of one analysis is very cheap owing to the amount of modifier is very few and the modified electrode still has a good performance after continuous scanning for 50 times. Besides, this modified electrode only needs about 4 min to fabricate and less than 2 min to get the voltammograms. This fabricated electrode may function as an applicable sensor for accurate electroanalysis of trace Fe(II) in coastal waters.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2016.03.060.

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