

Accepted Manuscript

Title: Titanium carbide nanoparticles/ion-exchange polymer-based sensor for catalytic stripping determination of trace iron in coastal waters

Author: Mingyue Lin Dawei Pan Xueping Hu Haitao Han Fei Li



PII: S0925-4005(15)00640-1
DOI: <http://dx.doi.org/doi:10.1016/j.snb.2015.05.034>
Reference: SNB 18475

To appear in: *Sensors and Actuators B*

Received date: 18-3-2015
Revised date: 4-5-2015
Accepted date: 14-5-2015

Please cite this article as: M. Lin, D. Pan, X. Hu, H. Han, F. Li, Titanium carbide nanoparticles/ion-exchange polymer-based sensor for catalytic stripping determination of trace iron in coastal waters, *Sensors and Actuators B: Chemical* (2015), <http://dx.doi.org/10.1016/j.snb.2015.05.034>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Titanium carbide nanoparticles/ion-exchange polymer-based sensor for catalytic stripping determination of trace iron in coastal waters

Mingyue Lin,^{a,b} Dawei Pan,^{*,a} Xueping Hu,^{a,b} Haitao Han,^a Fei Li^c

^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, P. R. China. Tel.: +86 535 2109155. E-mail: dwpan@yic.ac.cn

^b University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

^c The Key Lab in Molecular and Nano-materials Probes of the Ministry of Education of China, College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan Shandong 250014, P. R. China

Abstract: We establish a novel nanoparticle/ion-exchange polymer-based sensor for selective and sensitive detection of trace iron (Fe^{3+}) in coastal waters. Titanium carbide nanoparticles (nano-TiC) are used as a typical nanomaterial with promising physical and chemical properties to accelerate the electron transfer. Nafion is chosen as the widely used cation-exchange polymer to facilitate the preconcentration of Fe^{3+} . Taking advantage of synergistic effects of nano-TiC and Nafion as well as the catalytic amplifying effect of hydrogen peroxide (H_2O_2), the excellent cathodic signal responses for the stripping determination of Fe^{3+} which is linear in the range of 0.07 to 70 μM with a detection limit of 7.2 nM can be obtained. This analytical method can be used to effectively and simply detect Fe^{3+} without using any complexing agents. The fabricated sensor has been successfully applied for the sensitive determination of Fe^{3+} in real coastal waters.

Keywords: iron; TiC nanoparticles; Nafion; catalytic stripping voltammetry; coastal waters

*Corresponding author: Tel.: +86 535 2109155; Fax.: +86 535 2109155.
E-mail address: dwpan@yic.ac.cn (D. Pan).

1. Introduction

Iron is one of the most common elements in the earth's crust. As one of the essential micronutrients, iron is involved in the plant metabolism where it is pivotal for photosynthetic and respiratory electron transport, nitrate reduction, and chlorophyll synthesis [1]. According to iron limitation hypothesis [2], its existence in the environment is of major interest due to its important role in oceanic biogeochemical processes [3]. In addition, it has been shown that iron also plays an important role in nutrient cycling processes such as nitrogen fixation and can limit growth in non-HNLC (high-nutrient, low chlorophyll) regions [4] and coastal upwelling areas [5-7], and may have a connection with red tide [8]. It has been reported that the concentration of dissolved iron in coastal water is greater than that in seawater and the iron cycle in coastal zones is more complex due to the proximity to terrestrial, continental shelf sources and human activity [9]. Therefore, the accurate and simple methods for the detection of iron in coastal waters are very eager to be developed.

Among a variety of new analytical tools under development, electrochemical method has been recognized as one the most sensitive methods for trace iron analysis and it possesses the advantages of low cost, simple and convenient operation, fast experimental process, high sensitivity and selectivity, as well as potential application for *in situ* experiments or on-site monitoring [10]. Traditionally, the most sensitive electrochemical methods for iron determination were based on hanging drop mercury electrodes by stripping voltammetry with the aid of complexing agents to lower the detection limit which required complicated procedures such as pre-complexation, pH adjustment, and so forth [11,12]. Considering the drawbacks of mercury electrode, such as toxicity, difficulties in handling, storage and disposal as well as the complicated procedures in pretreatment, it may severely restrict its application [13]. In order to solve these problems, great efforts have been taken to develop mercury-free solid electrodes. For example, solid-state gold-amalgamation [14], ion-selective membranes [15], ionomer-coatings [16-19], carbon paste [20], glassy carbon [21] electrodes and gold microelectrode ensembles [22] as new solid electrodes have been developed for iron determination. However, the continuous improvements of functional electrodes are still urgently required for achieving simple, rapid and sensitive detection of trace iron, especially in coastal waters.

In order to increase the selectivity and sensitivity of the electrode, current works mainly focus on the chemical modification of electrode surface [23]. Polymers which can form a thin film on a solid electrode surface are usually utilized for the preconcentration of target and play an important role in trace environmental analyses [24,25]. Nafion as one of the most widely used cation-exchange polymer possesses the ideal electrochemical properties as well as the high chemical and mechanical stability. In previous reports, Nafion has shown benefits in facilitating the preconcentration of Fe^{3+} , Fe^{2+} and iron complexes [16-19]. Except for the selectivity, the acceleration of electron transfer rate is also an important aspect to be considered. The application of nanotechnology has become one of the most active areas in analytic chemistry. Nanomaterials of various shapes, sizes, and compositions have been widely used for the construction and modification of electrochemical sensors, because they possess unique electronic conductivity, and large specific surface areas [26,27]. Nanomaterials, such as gold

nanoparticles [28], multiwall carbon nanotubes [29], nanocomposite of reduced graphene oxide, methylene blue, and gold nanoparticles [30] have been successfully used for iron determinations. Nowadays, nanosized transition metal carbides, particularly titanium carbide nanoparticles (nano-TiC) have attracted significant interest for a number of applications in analytical chemistry due to its intrinsic material properties such as high electrical conductivity, low density, high surface area and catalytic activity [31-33]. Moreover, nano-TiC shows greater advantages and novel characteristics than regular sized particles, such as larger specific surface area and high electron transfer rate [34]. Besides, its cubic phase exhibits interesting photocatalytic and electrocatalytic behaviors [35-37], which has been used as the electrode material for catalytic determination of H_2O_2 [34].

The aim of this paper is to combine the unique properties of nanomaterials with the specific preconcentration ability of ion-exchange polymer to fabricate an electrochemical sensing platform towards Fe^{3+} determination. Based on the synergistic effects of nano-TiC and Nafion, as well as the help of the catalytic amplifying effect of H_2O_2 , such a designed nano-TiC/Nafion modified electrode can offer remarkably improved sensitivity and selectivity for voltammetric measurement of Fe^{3+} . Experimental conditions and analytical performances were systematically investigated. The developed sensor was also successfully applied for the detection of total dissolved iron in real coastal waters with satisfactory results.

2. Experimental section

2.1. Reagents

Unless stated otherwise, all chemicals used are analytical reagent grade. Deionized water (18.2 M Ω cm specific resistance) from Pall Cascada laboratory water system was used throughout to prepare the solutions. HNO_3 and HCl were Guaranteed Reagents and were sub-boiling distilled using a quartz condenser. Iron standard solutions were prepared from chloride of Fe^{3+} (Sinopharm Chemical Reagent Co., Ltd., China.) in 0.1 M HCl . HNO_3 , HCl , H_2SO_4 , HClO_4 and other affiliated chemicals were all obtained from Sinopharm Chemical Reagent. The 0.5% w/v Nafion solution was prepared by 1:10 dilution with methanol of 5% w/v Nafion solution (Sigma-Aldrich Co. LLC). The suspension of 0.5 mg mL^{-1} TiC nanoparticles (20 nm, Nanjing Emperor Nano Material Co., Ltd., China) were obtained by dispersing the powders with deionized water, and then ultrasonicated for 10 min. All bottles and containers used for standards and samples were soaked in 5% HNO_3 at least for 24 h prior to use. Then they were thoroughly rinsed with deionized water and samples. All experiments were conducted at room temperature (25 °C) without the removal of oxygen from the solutions.

2.2. Apparatus

The morphologies of the modified glassy carbon electrode (GCE) were characterized by scanning electron microscopy (SEM, Hitachi S-4800, Japan) and transmission electron microscopy (TEM, Hitachi HT7700, Japan). Inductively coupled plasma-mass spectrometry (ICP-MS, ELAN DRC \square , Perkin Elmer Instruments, USA) was used for comparative testing. Electrochemical Work Station (CHI

660D, Shanghai CH Instruments, Shanghai, China) was used throughout all the electrochemical experiments. A nano-TiC/Nafion 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 modified GCEs

The nano-TiC/Nafion coated GCE was prepared by adding 10 μL nano-TiC (0.5 mg mL^{-1}) on the surface of GCE and dried using an infrared lamp. Then 10 μL Nafion (0.5 % w/v) was added on the surface of nano-TiC coated GCE and dried under the infrared lamp. Prior to use, the GCE was polished using aqueous alumina slurry (0.3 and 0.05 μm), washed with deionized water and acetone thoroughly, and then ultrasonicated in deionized water for 1 min. For comparison, Nafion or nano-TiC coated GCE was prepared in the same manner, respectively.

2.4. Preparation of real coastal water samples

Water Samples were collected from Jiehe river and Xiaoqinghe river (two local coastal rivers, which flow into the Bohai Sea, Shandong province, China), and coastal water of the Bohai Sea. Samples were immediately filtered by 0.45 μm membrane filters and collected in FEP bottles, then kept at 4°C until determination. In order to remove the organic complexes, the samples were digested for 30 min at pH less than 2.0 in acid-cleaned quartz tubes using a 500 W UV lamp (Metrohm MVA-UV 705, Switzerland). Then the samples were diluted to an appropriate concentration and measured by the standard addition method.

2.5. Electrochemical analysis procedure

All experiments were performed in 0.1 M HCl electrolyte. The modified GCEs were electrochemically characterized by electrochemical impedance spectroscopy (EIS). EIS of modified electrodes was measured in 10 mM $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{KCl}$ (0.1 M) solution with the frequency ranging from 10^{-2} to 10^5 Hz. The cathodic responses of Fe^{3+} on the bare and modified GCEs were investigated by square wave voltammetry (SWV), using the following parameters: initial potential of 0.7 V, final potential of 0.2 V, an amplitude of 0.025 V, increment potential of 0.001 V, frequency of 15 Hz, and a quiet time of 2 s.

3. Results and discussion

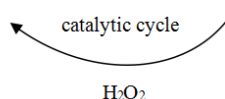
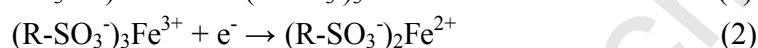
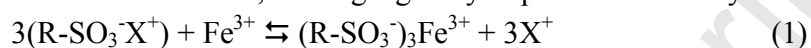
3.1. Characterization of the nano-TiC/Nafion modified electrode

The surface morphologies of the various modified electrodes were characterized by SEM and TEM (Fig. 1). Compared with the smooth surface of the bare GCE (Fig. 1a), nano-TiC particles were compactly coated on the GCE surface with size distribution ranging from 20 to 60 nm (Fig. 1b). A thin membrane-like substance was formed after Nafion coating of the nano-TiC coated GCE: some nano-TiC particles were incorporated into the Nafion film and others remained outside (Fig. 1c). TEM imaging

showed that the nano-TiC is cubic in structure (Fig. 1d).

3.2. Mechanism of Fe^{3+} reduction on fabricated sensor

The sensing strategy is clearly illustrated in Scheme 1. Particles of nano-TiC which functioned as the electron transfer wires were well coated on the surface of a GCE to accelerate electron transfer rate and increase the current response since the reactions are limited by the rate of electron transfer. Then the “wire” surface was coated with Nafion to capture more Fe^{3+} by reaction (1), where X is the supporting electrolyte cation [26]. The detection process can be described by equation (2). During the voltammetric scan, Fe^{3+} is reduced to Fe^{2+} , which is then re-oxidized chemically to Fe^{3+} by H_2O_2 . The re-oxidized Fe^{3+} contributes again to the reduction current, causing a greatly improved sensitivity.



To verify the effect of nano-TiC and Nafion on Fe^{3+} detection, electrochemical impedance spectroscopy (EIS) was measured. Fig. 2 shows the Nyquist plots of the modified electrodes using $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple as electrochemical probe. The squeezed semicircle at high frequency indicates an electron-transfer-limited process on an electroactive surface. This is followed by diffusion-controlled electron transfer, indicated by the linear plot region at low frequency. The Nyquist plot of nano-TiC coated GCE (Fig. 2b) showed a linear region only at low frequency, indicating that nano-TiC lowers the electron transfer resistance. The electron transfer resistance (R_p) of the electroactive surface was measured by the semicircle diameter at high frequency. It was clearly observed that the R_p of nano-TiC/Nafion coated GCE (Fig. 2c) was significantly larger than that of bare GCE (Fig. 2a). Because Nafion is negatively charged, it will hinder electron transfer between $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$. The results demonstrate that nano-TiC provides a larger electrode surface and more active sites as well as accelerating electron transfer, while Nafion facilitates a cation-exchange reaction for the preconcentration of Fe^{3+} . To further understand the sensing mechanism, the effect of scan rate with the analytical signal of Fe^{3+} was studied by linear sweep voltammetry. The cathodic peak currents of Fe^{3+} increased linearly with scan rates from 25 to 250 mV s^{-1} . The regression equation is expressed as $i_p = -0.122\nu - 5.79$ ($R^2=0.989$). The results revealed that the electron transfer of Fe^{3+} with the nano-TiC/Nafion coated GCE was a typical surface-controlled electrochemical process [38]. Besides, to estimate the charge transfer coefficient (α), Laviron's model was used [39]. The plot of the cathodic peak potentials versus the logarithm of the scan rates yielded a straight line, the regression equation can be expressed as $E_p = -0.099 \log \nu + 0.483$ ($R^2=0.989$). From the slopes, α was estimated as 0.6, indicating it was a quasi-reversible electron transfer process.

As shown in Fig. 3, the redox behaviors of Fe^{3+} at the fabricated sensor were studied by square wave voltammetry (SWV). No cathodic signal of Fe^{3+} was seen on the bare GCE (Fig. 3 a and b). The SWV response for nano-TiC/Nafion coated GCE (Fig. 3h) was greatly larger than the responses for

nano-TiC (Fig. 3d) and Nafion coated GCE (Fig. 3f). More importantly, the response current at the nano-TiC/Nafion modified electrode was larger than the sum of the currents at the nano-TiC and Nafion singly modified electrodes, indicating that nano-TiC combined with Nafion synergistically improve the cathodic current response of Fe^{3+} . Since carbon nanomaterials can also provide the large surface area and considerable active sites, the responses of Fe^{3+} on multi-walled carbon nanotubes and graphene-modified GCE under the same experimental conditions were investigated. The results showed no obvious signal responses might be observed because there were large background currents at the potential range of 0.4-0.5 V caused by the oxygen-containing functional groups on the multi-walled carbon nanotubes and graphene's surfaces. But the background current was very low and smooth at nano-TiC modified electrode, which implies nano-TiC has significant advantages for Fe^{3+} detection than other carbon nanomaterials. Moreover, it has been demonstrated that the addition of H_2O_2 causes rapid oxidation of Fe^{2+} due to the generated radical species $\text{HO}\cdot$, resulting in a large increase in the analytical signal. As shown in Fig. 4, the reduction peak for Fe^{3+} in the presence of H_2O_2 at the nano-TiC/Nafion coated GCE (Fig. 4c) has a straighter shape, and is about 3 times greater than the signal in the absence of H_2O_2 (Fig. 4b). These results indicate that the response current of Fe^{3+} can be obviously increased by synergistic and catalytic effect.

3.3. Choice of supporting electrolyte

The effect of supporting electrolyte to the response of Fe^{3+} was investigated because Fe^{3+} is easily hydrolyzed in slightly acidic and alkaline environments. Meanwhile, the supporting electrolyte can play a double role in the preconcentration of Fe^{3+} due to the complexation reactions by anions from the supporting electrolyte, and competition for the cation-exchange sites between the analyte and supporting electrolyte cation [20]. Therefore, 0.1 M solutions of H_2SO_4 , HClO_4 , HNO_3 , and HCl were chosen as possible electrolytes, the results showed that HCl solution was the best electrolyte for Fe^{3+} detection. The peak currents of Fe^{3+} in the different acidic media were increased in the order of $\text{HClO}_4 < \text{H}_2\text{SO}_4 < \text{HNO}_3 < \text{HCl}$, which was same as the previous report [22]. The peak current of Fe^{3+} in HCl was about ten times higher than other electrolytes. This can be attribute to the increasing acid anion adsorption on the surface of modified electrode and the reduction of Fe^{3+} to Fe^{2+} occurs fastest in HCl by judging the value of ΔE_p [22]. Besides, considering the reference electrode salt bridge and real coastal water samples with high salinity, choosing HCl as the electrolyte was more suitable.

3.4. Calibration Curve

For accurate quantitative analysis, a linear calibration curve between cathodic current and Fe^{3+} concentration is necessary. As shown in Fig. 5, the current was linearly related to the concentration of Fe^{3+} under the concentration range of 0.07-70 μM . The linear regression equation was $i_p = -0.934C + 1.04$ ($R^2=0.997$). The sensitivity and detection limit of the nano-TiC/Nafion coated GCE for Fe^{3+} determination were 0.93 $\mu\text{A } \mu\text{M}^{-1}$ and 7.2 nM ($s/n=3$), respectively. These results indicate that the proposed modified GCE can qualitatively and quantitatively detect Fe^{3+} in experimental system. Additionally, comparisons about iron determination by this sensor and other Nafion modified electrodes

were presented in Table 1. Our new fabricated sensor shows better sensitivity, lower detection limit for Fe^{3+} , and easier experimental processes compared with other Nafion modified electrodes.

3.5. Reproducibility, repeatability and selectivity

The inter-sensor reproducibility of the nano-TiC/Nafion modified electrode was evaluated in $10\ \mu\text{M}$ Fe^{3+} by six independently sensors prepared in the same way and the corresponding relative standard deviation (RSD) was 4.7%. The repeatability of the modified sensor was studied by detecting $10\ \mu\text{M}$ Fe^{3+} using the same sensor for six measurements and the RSD was 2.8%, which indicated there were no significant differences among the analytical signals. To verify whether there were cathodic responses to other cations, various foreign species were added into 0.1 M HCl containing $10\ \mu\text{M}$ Fe^{3+} . Additions of 30-fold Cu^{2+} , Cr^{3+} , and 10-fold Zn^{2+} and As^{3+} did not affect the determination of Fe^{3+} (5% current change). The addition of less than 0.03 M sodium chloride also did not influence the signal of Fe^{3+} . However, adding equivalent Ag^{+} resulted in a sharp decrease in signal because of silver chloride precipitation on the electrode surface, which hinders electron transfer between the electrode and Fe^{3+} [41]. The influence of common reducible organic species such as humic substances and catechol were also investigated. The results showed that the addition of 20-fold humic substances did not interfere with the signals, but adding 5-fold catechol would decrease the peak current and change the peak shape due to catechol was one of the common chelators of iron. However, after the UV-digestion, the peak currents returned to the original values because all organic substances in solution have been destroyed during UV digestion. So, this method was not obviously interfered with the organic species after UV digestion.

3.6. Practical application

After having demonstrated the selectivity and sensitivity of the nano-TiC/Nafion coated GCE for Fe^{3+} in optimal experimental conditions, it has been applied to determine the total dissolved iron in real coastal waters. All water samples were filtered with $0.45\ \mu\text{m}$ membrane filters and then UV-digested after adjusting the pH to less than 2.0 to make sure all ligands bound to iron were released, and all iron species were oxidized to Fe^{3+} . SWVs were obtained under optimal conditions for water samples from the Jiehe river (Fig. 6). The water sample was diluted 10 times, then added to 0.1 M HCl for detection. A series of SWVs were obtained after the successive addition of 0, 4, and $8\ \mu\text{M}$ Fe^{3+} , and the linear regression is shown in the inset of Fig. 6. The concentration of total dissolved iron in the Jiehe river was determined to be $2.3\ \mu\text{M}$, consistent with the ICP-MS result ($2.4\ \mu\text{M}$). A comparison of results on the total dissolved iron in coastal waters from our proposed method and ICP-MS are shown in Table 2. The results show that the proposed method is suitable for the total dissolved iron determination for real coastal water samples.

4. Conclusions

In summary, we have developed a novel nano-TiC/Nafion coated GCE that exhibits high selectivity and sensitivity for Fe^{3+} determination in real coastal water samples without using complexing agents.

Our new modified GCE shows better sensitivity, lower detection limit for Fe^{3+} detection. This catalytic stripping method has easier experimental processes and is suitable for total dissolved iron determination in coastal water samples. The nano-TiC/Nafion coated GCE will be of great benefit to investigate the effects of iron in coastal aquatic biogeochemistry.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (41276093), the Youth Innovation Promotion Association (2011170), and the Outstanding Young Scientists Program of CAS.

References

- [1] W.G. Sunda, S.A. Huntsman, Iron uptake and growth limitation in oceanic and coastal phytoplankton, *Mar. Chem.* 50 (1995) 189-206.
- [2] J.H. Martin, R.M. Gordon, S. Fitzwater, W.W. Broenkow, VERTEX: phytoplankton/iron studies in the gulf of Alaska, *Deep-Sea Res. A* 36 (1989) 649-680.
- [3] P.J. Statham, Y. Jacobson, C.M.G. van den Berg, The measurement of organically complexed Fe(II) in natural waters using competitive ligand reverse titration, *Anal. Chim. Acta* 743 (2012) 111-116.
- [4] C. Schlosser, J.K. Klar, B.D. Wake, J.T. Snow, D.J. Honey, E.M.S. Woodward, M.C. Lohan, E.P. Achterberg, C.M. Moore, Seasonal ITCZ migration dynamically controls the location of the (sub) tropical Atlantic biogeochemical divide, *Proc. Natl. Acad. Sci. U. S. A.* 111 (2014) 1438-1442.
- [5] K.W. Bruland, E.L. Rue, The biogeochemistry of iron in seawater IUPAC series on analytical and physical chemistry of environmental systems. John Wiley, New York 2001, pp. 255-290.
- [6] D.G. Capone, D.A. Hutchins, Microbial biogeochemistry of coastal upwelling regimes in a changing ocean, *Nat. Geosci.* 6 (2013) 711-717.
- [7] Z. Chase, K.S. Johnson, V.A. Elrod, J.N. Plant, S.E. Fitzwater, L. Pickell, C.M. Sakamoto, Manganese and iron distributions off central California influenced by upwelling and shelf width, *Mar. Chem.* 95 (2005) 235-254.
- [8] S.M. Zhou, C.X. Zhang, The main characteristic parameters and chemical environment of the red tides, *Journal of Oceanography of Huanghai & Bohai Seas* 10 (1992) 73-76. (in Chinese)
- [9] E.P. Achterberg, T.W. Holland, A.R. Bowie, R.F.C. Mantoura, P.J. Worsfold, Determination of iron in seawater, *Anal. Chim. Acta* 442 (2001) 1-14.
- [10] D. Pan, Y. Wang, Z. Chen, T. Lou, W. Qin, Nanomaterial/ionophore-based electrode for anodic stripping voltammetric determination of lead: an electrochemical sensing platform toward heavy metals, *Anal. Chem.* 81 (2009) 5088-5094.
- [11] L.M. Laglera, J. Santos-Echeandía, S. Caprara, D. Monticelli, Quantification of iron in seawater at the low picomolar range based on optimization of bromate/ammonia/dihydroxynaphthalene system by catalytic adsorptive cathodic stripping voltammetry, *Anal. Chem.* 85 (2013) 2486-2492.
- [12] C.M.G. van den Berg, Chemical speciation of iron in seawater by cathodic stripping voltammetry with dihydroxynaphthalene, *Anal. Chem.* 78 (2006) 56-163.
- [13] J. Wang, Stripping analysis at bismuth electrodes: a review, *Electroanalysis* 17 (2005) 1341-1346.
- [14] M.E. Dollhopf, K.H. Nealson, D.M. Simon, G.W. Luther, Kinetics of Fe (III) and Mn (IV) reduction by the Black Sea strain of *Shewanella putrefaciens* using in situ solid state voltammetric Au/Hg electrodes, *Mar. Chem.* 70 (2000) 171-180.

- [15] M.H. Mashhadizadeh, I.S. Shoaie, N. Monadi, A novel ion selective membrane potentiometric sensor for direct determination of Fe (III) in the presence of Fe (II), *Talanta* 64 (2004) 1048-1052.
- [16] P. Ugo, L.M. Moretto, D. Rudello, E. Birriel, J. Chevalet, Trace iron determination by cyclic and multiple square-wave voltammetry at Nafion coated electrodes. Application to Pore-Water Analysis, *Electroanalysis* 13 (2001) 661-668.
- [17] P. Ugo, L.M. Moretto, A. De Boni, P. Scopece, G.A. Mazzocchin, Iron (II) and iron (III) determination by potentiometry and ion-exchange voltammetry at ionomer-coated electrodes, *Anal. Chim. Acta* 474 (2002) 147-160.
- [18] S.X. Yang, L.H. Du, B.X. Ye, Cathodic stripping voltammetry determination of trace iron with a chemically modified electrode, *Microchem. J.* 52 (1995) 216-222.
- [19] Z.Q. Gao, P. Li, G. Wang, Z. Zhao, Preconcentration and differential-pulse voltammetric determination of iron(II) with Nafion-1,10-phenanthroline-modified carbon paste electrodes, *Anal. Chim. Acta* 241 (1990) 137-146.
- [20] E.M. Ghoneim, Simultaneous determination of Mn (II), Cu (II) and Fe (III) as 2-(5'-bromo-2'-pyridylazo)-5-diethylaminophenol complexes by adsorptive cathodic stripping voltammetry at a carbon paste electrode, *Talanta* 82 (2010) 646-652.
- [21] R. Segura, M.I. Toral, V. Arancibia, Determination of iron in water samples by adsorptive stripping voltammetry with a bismuth film electrode in the presence of 1-(2-pyridylazo)-2-naphthol, *Talanta* 75 (2008) 973-977.
- [22] E. Zakharova, E. Elesova, G. Noskova, M. Lu, R. Compton, Direct voltammetric determination of total iron with a gold microelectrode ensemble, *Electroanalysis* 24 (2012) 2061-2069.
- [23] R.K. Shervedani, A. Hatefi-Mehrjardi, A. Asadi-Farsani, Sensitive determination of iron (III) by gold electrode modified with 2-mercaptopropionic acid self-assembled monolayer, *Anal. Chim. Acta* 601 (2007) 164-171.
- [24] M.W. Espenscheid, A.R. Ghatak-Roy, R.B. Moore, R.M. Penner, M.N. Szentirmay, C.R. Martin, Sensors from polymer modified electrodes, *J. Chem. Soc. Faraday Trans. I* 82 (1986) 1051-1070.
- [25] P. Ugo, L.M. Moretto, Ion-exchange voltammetry at polymer-coated electrodes: principles and analytical prospects, *Electroanalysis* 7 (1995) 1105-1113.
- [26] N. Zhou, H. Chen, J. Li, L. Chen, Highly sensitive and selective voltammetric detection of mercury (II) using an ITO electrode modified with 5-methyl-2-thiouracil, graphene oxide and gold nanoparticles, *Microchim. Acta* 180 (2013) 493-499.
- [27] C.S. Shan, H.F. Yang, J.F. Song, D.X. Han, A. Ivaska, L. Niu, Direct electrochemistry of glucose oxidase and biosensing for glucose based on graphene, *Anal. Chem.* 81 (2009) 2378-2382.
- [28] M.B. Gholivand, B. Geravandi, M.H. Parvin, Anodic stripping voltammetric determination of iron (II) at a carbon paste electrode modified with dithiodianiline (DTDA) and gold nanoparticles (GNP), *Electroanalysis* 23 (2011) 1345-1351.
- [29] D.I. Anguiano, M.G. Garcia, C. Ruiz, J. Torres, I. Alonso-Lemus, L. Alvarez-Contreras, Y. Verde-Gomez, E. Bustos, Electrochemical detection of iron in a leachant solution of polluted soil using a modified glassy carbon electrode, *Int. J. Electrochem.* 739408 (2012) 6.
- [30] M. Lin, H. Han, D. Pan, H. Zhang, Z. Su, Voltammetric determination of total dissolved iron in coastal waters using a glassy carbon electrode modified with reduced graphene oxide, Methylene Blue and gold nanoparticles, *Microchim. Acta* 182 (2015) 805-813.
- [31] T. Yu, Y.H. Deng, L. Wang, R.L. Liu, L.J. Zhang, B. Tu, D.Y. Zhao, Ordered mesoporous nanocrystalline titanium-carbide/carbon composites from in situ carbothermal reduction, *Adv. Mater.* 19 (2007) 2301-2306.
- [32] D.W. Flaherty, R.A. May, S.P. Berglund, K.J. Stevenson, C.B. Mullins, Low temperature synthesis and characterization of nanocrystalline titanium carbide with tunable porous architectures, *Chem. Mater.* 22 (2010) 319-329.

- [33] J.A. Rodríguez, L. Feria, T. Jirsak, Y. Takahashi, K. Nakamura, F. Illas, Role of Au-C interactions on the catalytic activity of Au nanoparticles supported on TiC(001) toward molecular oxygen dissociation, *J. Am. Chem. Soc.* 132 (2010) 3177-3186.
- [34] M. Wang, Q. Sheng, D. Zhang, Y. He, J. Zheng, TiC nanoparticles-chitosan composite film for the direct electron transfer of myoglobin and its application in biosensing, *Bioelectrochemistry* 86 (2012) 46-53.
- [35] Y.H. Chang, C.W. Chiu, Y.C. Chen, C.C. Wu, C.P. Tsai, J.L. Wang, H.T. Chiu, Syntheses of nano-sized cubic phase early transition metal carbides from metal chlorides and n-butyllithium, *J. Mater. Chem.* 12 (2002) 2189-2191.
- [36] Y. Bi, H. Hu, S. Ouyang, G. Lu, J. Cao, J. Ye, Photocatalytic and photoelectric properties of cubic Ag₃PO₄ sub-microcrystals with sharp corners and edges, *Chem. Commun.* 48 (2012) 3748-3750.
- [37] M. Jin, H. Zhang, Z. Xie, Y. Xia, Palladium nanocrystals enclosed by {100} and {111} facets in controlled proportions and their catalytic activities for formic acid oxidation, *Energ. Environ. Sci.* 5 (2012) 6352-6357.
- [38] S.F. Wang, T. Chen, Z.L. Zhang, X.C. Shen, Z.X. Lu, D.W. Pang, K. Wong, Direct electrochemistry and electrocatalysis of heme proteins entrapped in agarose hydrogel films in room-temperature ionic liquids, *Langmuir* 21 (2005) 9260-9266.
- [39] E. Laviron, General expression of the linear potential sweep voltammogram in the case of diffusionless electrochemical systems, *J. Electroanal. Chem.* 101 (1979) 19-28.
- [40] Z. Gao, P. Li, Z. Zhao, Determination of iron (II) with chemically-modified carbon-paste electrodes, *Talanta* 38 (1991) 1177-1184.
- [41] X. Chu, X. Fu, K. Chen, G.L. Shen, R.Q. Yu, An electrochemical stripping metalloimmunoassay based on silver-enhanced gold nanoparticle label, *Biosens. Bioelectron.* 20 (2005) 1805-1812.

Figure captions

Scheme 1. Schematic illustration of the enhanced electrochemical detection strategy for Fe^{3+} on nano-TiC/Nafion modified electrode by catalytic stripping voltammetry.

Figure 1. SEM images of (a) bare GCE, (b) nano-TiC coated GCE, (c) nano-TiC/Nafion coated GCE, and (d) TEM image of nano-TiC.

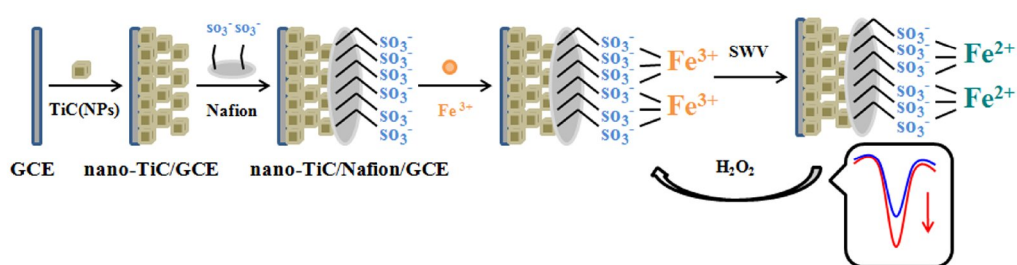
Figure 2. Nyquist plots of bare GCE (curve a), nano-TiC coated GCE (curve b), and nano-TiC/Nafion coated GCE (curve c) in 10 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.1 M KCl solutions. Inset is enlarged drawing of the Nyquist plots of bare GCE (curve a), nano-TiC coated GCE (curve b) at higher frequency.

Figure 3. SWVs of bare GCE (curve a and b), nano-TiC coated GCE (curve c and d), Nafion coated GCE (curve e and f), and nano-TiC/Nafion coated GCE (curve g and h) in 0.1 M HCl without (curve a, c, e, g) and with (curve b, d, f, h) 10 μM Fe^{3+} .

Figure 4. Comparison of the SWV current signals at the nano-TiC/Nafion coated GCE in 0.1 M HCl containing 0 μM Fe^{3+} (curve a), 10 μM Fe^{3+} (curve b), 10 μM Fe^{3+} and 20 mM H_2O_2 (curve c).

Figure 5. Calibration curve of Fe^{3+} on the nano-TiC/Nafion coated GCE in 0.1 M HCl in the presence of 20 mM H_2O_2 . Inset is the current response of Fe^{3+} concentrations in the linear range from 0.07 μM to 70 μM .

Figure 6. Typical voltammograms for the determination of Fe^{3+} in water samples from the Jiehe River by the standard addition method. The concentrations of Fe^{3+} are 0, 4 and 8 μM Fe^{3+} (from top to bottom). The inset shows the corresponding curve ($n=3$).



Scheme 1.

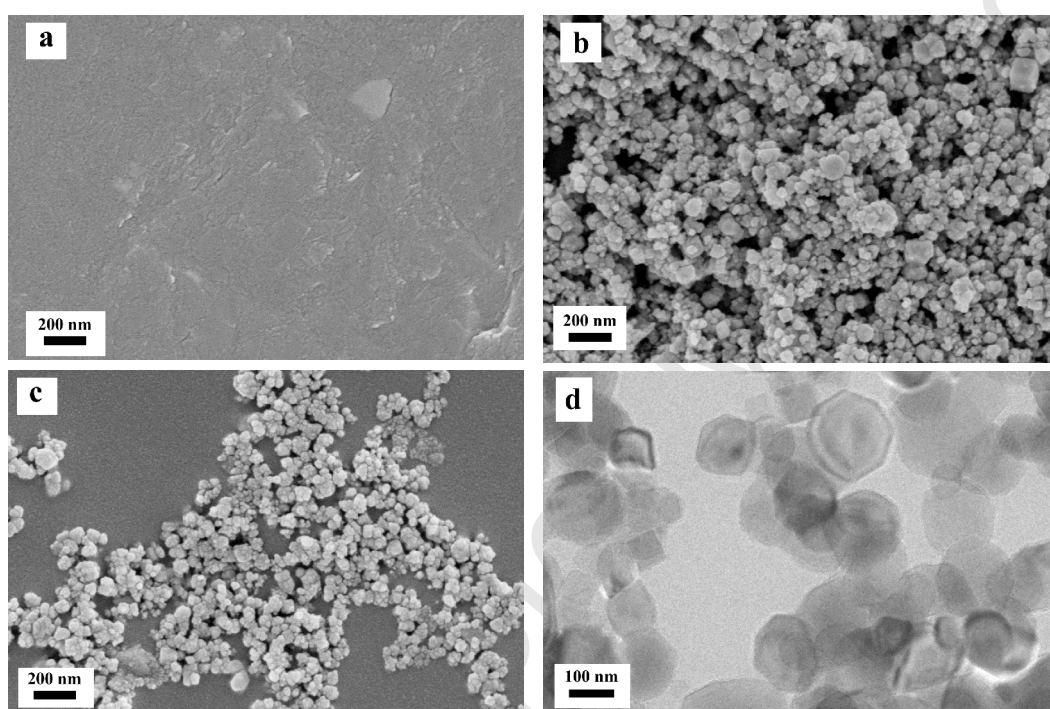


Fig. 1

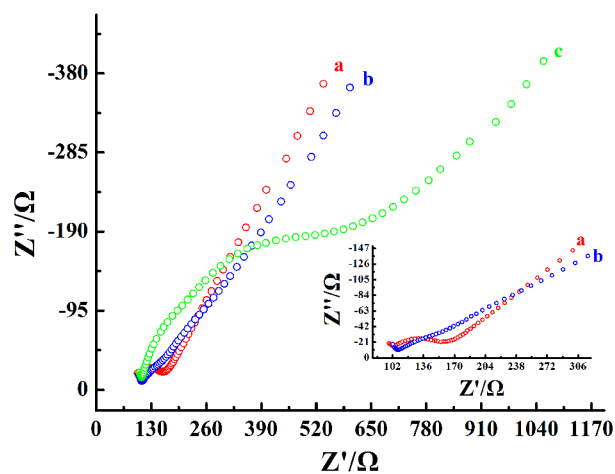


Fig. 2

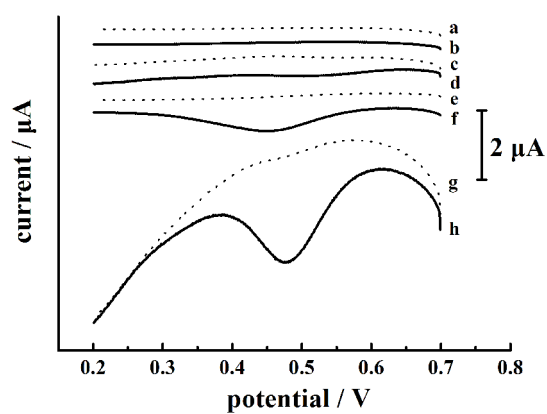


Fig. 3

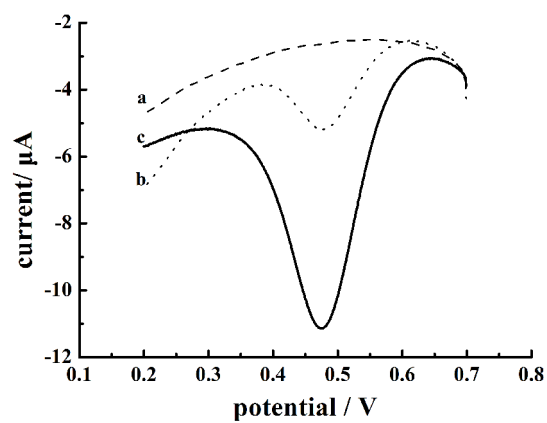


Fig. 4

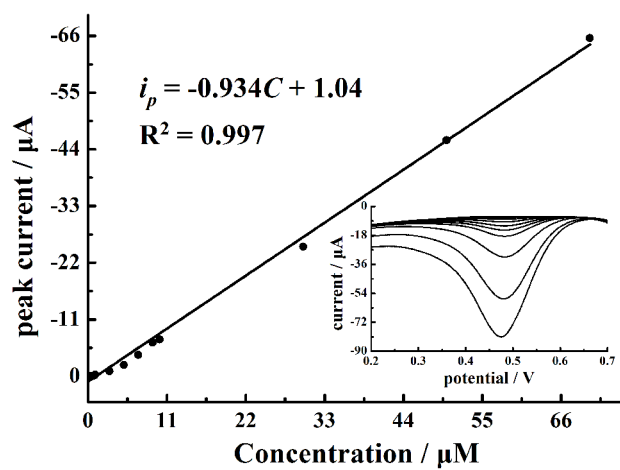


Fig. 5

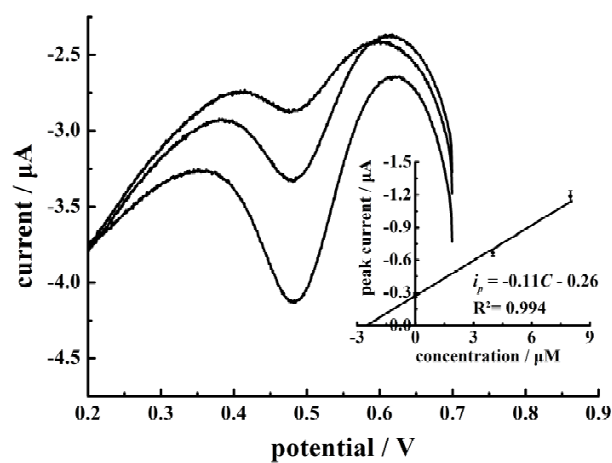


Fig. 6

Table 1. Comparison with other Nafion modified electrodes. Technique: SWV, Square Wave Voltammetry; IEV, Ion-Exchange Voltammetry; MSWV-DD, Double Differential Multiple Square Wave Voltammetry; CSV, Cathodic Stripping Voltammetry; DPASV, Differential Pulse Anodic Stripping Voltammetry. Electrode: GCE, Glassy Carbon Electrode; CPE, Carbon Paste Electrode.

Technique	Electrode	Modifier/Complexing agent (if any)	Speciation	LOD (M)	Year	Reference
IEV	GCE	Nafion, Tosflex	$\text{Fe}^{3+} + \text{Fe}^{2+}$	1.0×10^{-7}	2002	[17]
MSWV-DD	GCE	Nafion	$\text{Fe}^{3+} + \text{Fe}^{2+}$	1.5×10^{-6}	2001	[16]
CSV	GCE	Nafion, $\alpha\alpha$ -bipyridine	Fe^{3+}	8.9×10^{-10}	1995	[18]
DPASV	CPE	2,2-bipyridyl, Nafion	Fe^{2+}	1.0×10^{-8}	1991	[40]
DPASV	CPE	Nafion, 1,10-phenanthroline	Fe^{2+}	3.0×10^{-8}	1990	[19]
SWV	GCE	nano-TiC and Nafion	Fe^{3+}	7.2×10^{-9}	2015	This work

Table 2. Comparison of nano-TiC/Nafion coated GCE and ICP-MS for determination of total dissolved iron in coastal waters

Samples	Detected by this method (μM)	Detected by ICP-MS (μM)
Coastal Jiehe river water 1	2.3 ± 0.2	2.4
Coastal Jiehe river water 2	12.0 ± 0.2	11.9
Coastal Xiaoqinghe river water 3	4.3 ± 0.2	4.3
Coastal sea water	4.4 ± 0.2	4.5

Biographies

Mingyue Lin earned the BS degree of environmental engineering 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.

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 master's degree student at Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences. Now she is engaged in on-spot detection of pollution by screen-printed electrode.

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.

Fei Li earned her BS degree in 2013 at Shandong Normal University. She is currently a master's degree student at college of Chemical Engineering and Materials Science, Shandong Normal University. Her scientific interests focus on electrochemical sensors and microelectrode.