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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, PR China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, PR 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, PR China*

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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 0.07–70 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.

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.

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

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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 toward 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

2.1. Reagents

Unless stated otherwise, all chemicals used are analytical reagent grade. Deionized water (18.2 MΩ 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 DRCII, 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 $K_3[Fe(CN)_6]$/KCl (0.1 M) solution with the frequency ranging from 10^{-2} Hz 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 nm to 60 nm (Fig. 1b). A thin membrane-like substance