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Electrochemical determination of iron in coastal waters based on ionic liquid-reduced graphene oxide supported gold nanodendrites

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ABSTRACT

An effective and sensitive method for electrochemical determination of iron was reported, based on the ionic liquid-reduced graphene oxide (IL-rGO) supported gold nanodendrites (AuNDs). IL-rGO as a soft support could provide large specific surface area for AuNDs and make them smaller sizes and unique forms, which would benefit to the electrochemical reduction of iron. Nafion is employed as a cation exchange polymer in which IL-rGO and AuNDs can be tightly attached to the electrode surface. The proposed sandwich structured IL-rGO/AuNDs/Nafion modified electrode shows excellent electrochemical properties. The IL-rGO/AuNDs/Nafion modified electrode combined individual advantages as a whole and showed good responses for iron ions. Under the optimized conditions, the reduction peak currents of iron have a good linear relation with its concentrations ranging from 0.30 to 100 μmol L^{-1} with the detection limit of 35 nmol L^{-1}. More importantly, this sandwich structured modified electrode had a good anti-interference ability and successfully applied in the determination of the total dissolved iron in coastal waters.

1. Introduction

Iron is widely distributed in nature and it is an essential nutrient and is abundant in many mineral oxides that exchange iron with surface and ground waters through dissolution and precipitation. Its most common oxidation states are Fe(II) and Fe (III); Fe(II) is a relatively soluble species in water, which is rapidly oxidized in oxygen rich environments. Conversely, Fe(III) forms strong complexes and is thermodynamically stable in water albeit of low solubility [1]. The concentration of soluble iron in natural water is significantly different than those in river water (1 μmol L^{-1}), coastal water (1 nmol L^{-1}), and ocean water (10 pmol L^{-1}) [2]. However, iron concentration can be higher in sediment pore waters. Iron can be determined by several methods such as inductively coupled plasma mass spectrometry (ICP-MS) [3], atomic absorption spectrometry (AAS) [4], cathodic stripping voltammetry (CSV) [5–7], luminescence [8], and spectrophotometry [9,10], preceded sometimes by column preconcentration. However, most of the sensitive and selective methods available are expensive to be used in routine analysis (ICP-MS and AAS). In fact, chemical modification of the electrode surface not only can lead to an increased electrocatalytic activity, but also better analytical selectivity and sensitivity is often achieved.

Nanomaterials play interesting roles in various fields of analytical chemistry [11–14]. In recent years, graphene has received considerable attention due to its high surface area (2600 m^2 g^{-1}), high chemical stability, excellent conductivity and strong mechanical strength. However, graphene sheets, unless well separated from each other, tend to form irreversible agglomerates or even restack to form graphite through *van der Waals* interactions. Graphene-nanoparticle composites have become a hot research topic in material science because the composite process can be an effective strategy to enhance their electronic, chemical, and electrochemical properties [15–17]. However, the lack of an efficient approach to produce polydisperse and long-term stable graphene sheets in different solvents has been a major obstacle to their exploitation in most of the proposed applications. Therefore, great efforts have been made to increase its solubility through the functionalization of graphene such as sulfonated graphene [18–20], using polymers or other molecules as functionalization reagents [21–24]. Among these functionalization

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reagents, ionic liquids (ILs) have attracted much attention because of their tunable structures and unique physicochemical properties such as wide electrochemical windows, high ionic conductivity, superior thermal stability, good solubility, and biocompatibility [25,26]. Furthermore, the introduction of IL moieties into functional graphene composites could not only increase their solubility, but also improve their performance.

Gold nanomaterials have the unique properties such as facilitating electron transfer between the species and electrode [27–29]. Gold nanostructures are more diverse, such as flowers [30] and rods [31]. Among them, there is an increasing interest for the fabrication of gold dendrites (AuNDs) [32]. Gold nanoparticals (AuNPs) is two-dimensional (2D) layer on the electrode surface. Compared to 2D AuNPs structure, AuNDs, which has a hyper-branched three-dimensional (3D) architecture, substantially enlarges the surface area of the electrode available for electrochemical detections.

In present work, ionic liquid-reduced graphene oxide (IL-rGO) was used as a support for electrochemical deposition of AuNDs. The resulting IL-rGO/AuNDs/Nafion modified electrode showed excellent electrochemical activities for iron ions. IL-rGO could provide large specific surface area for AuNDs and make it form smaller particles of the 3D structure, while AuNDs might facilitate electron transfer between the iron ions and electrode. Nafion was utilized as membrane matrix to improve the stability of electrode and accelerate the ion-exchange. The IL-rGO/AuNDs/Nafion modified electrode exhibited excellent selectivity, reproducibility and long-term stability for the determination of Fe(III) with lower detection limit and wider linear range. This novel sandwich structured IL-rGO/AuNDs/Nafion modified electrode was also applied for the determination of total dissolved iron in real coastal waters.

2. Experimental

2.1. Reagents

Iron standard solution was purchased from Acros Organics. 1-(3-aminopropyl)-3-methylimidazolium chloride (IL-NH_2) was supplied by Shanghai Cheng Jie Chemical Co. Ltd. Graphene was supplied by Nanjing Jcnano Technology Co. Ltd. $HAuCl_4{\cdot}4H_2O$ were purchased from Sinopharm Chemical Reagent Co. Ltd. Nafion (5%) was purchased from Sigma Co. Ltd. All other chemicals were of analytical reagents and used without further purification. All experiments were conducted at room temperature, and the solutions were used in the process without nitrogen atmosphere. Deionized water (18.2 MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system was used throughout.

2.2. Apparatus

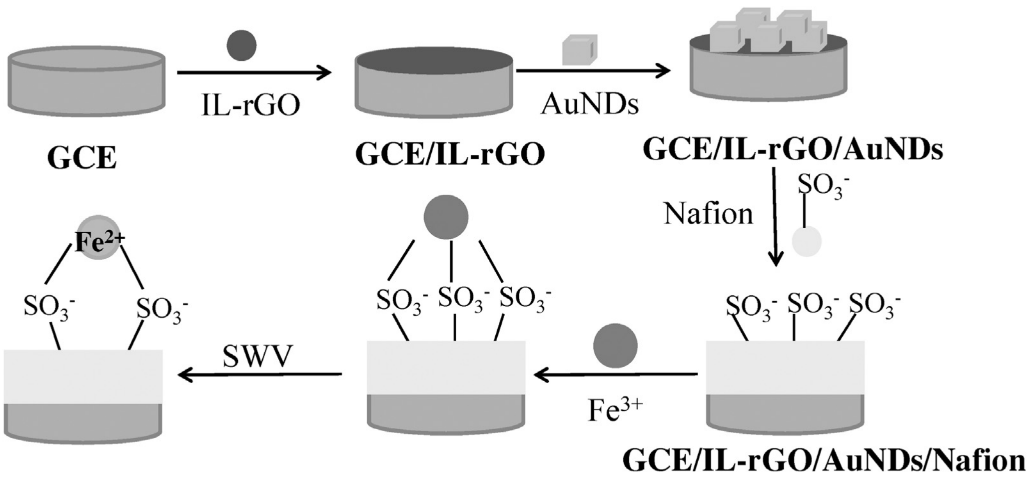
The morphology of the modified electrodes was characterized by using scanning electron microscopy (SEM Hitachi S-4800 microscope, Japan). All electrochemical experiments were carried out in a conventional three-electrode cell controlled by Electrochemical Work Station (CHI 660D, CH Instruments, Inc.). A modified glassy carbon (GC) disk (3 mm in diameter) was used as the working electrode, with Ag/AgCl and platinum foil serving as the reference and counter electrodes, respectively. All potential values given below refer to Ag/AgCl.

2.3. Synthesis of IL-rGO

IL-rGO was synthesized by an epoxide ring-opening reaction between graphene oxide (GO) and the IL-NH_2 according to the previous report [22]. Firstly, IL-NH_2 (10 mg) was added into 10 mL of GO homogeneous dispersion in water (0.5 mg mL^{-1}), Secondly, KOH (10 mg) was added into the above turbid mixture and then the mixture was subjected to ultrsonication for 30 min. Finally, the homogeneous solution was vigorously stirred at 80 °C for 24 h. The resulting IL-rGO was subsequently centrifuged, washed with ethanol and water, dried under room temperature in the air, and re-dispersed in ultrapure water (0.5 mg mL^{-1}).

2.4. Preparation of the IL-rGO/AuNDs/Nafion modified electrode

Prior to use, the GCE was polished using aqueous alumina slurry (0.3 and 0.05 μm), washed with deionized water thoroughly, and then ultrasonicated for 1 min. The IL-rGO suspensions (10 μL) were added on the surface of GCE and dried using an infrared lamp to get the IL-rGO composite modified electrode(GCE/IL-rGO). The modified electrode was then immersed in a 1.0 mmol L^{-1} chlorauric acid solution containing 0.2 mol L^{-1} of sodium sulfate to electrodeposit gold with constant potential at −0.2 V for 60s. Lastly, 6 μL of 0.5% Nafion solution was dropped on the GCE/IL-rGO/AuNDs and dried at room temperature to form a uniformly coated electrode (GCE/IL-rGO/AuNDs/Nafion). The obtained GCE/IL-rGO/AuNDs/Nafion was washed carefully with deionized water and then dried at room temperature. The schematic illustration of the stepwise self-assembly procedure is shown in Scheme 1. In order to compare with the electrochemical behavior for different electrodes, three



Scheme 1. The schematic illustration of the stepwise self-assembly procedure.