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Electrocatalytic oxidation of nitrite using metal-free nitrogen-doped reduced graphene oxide nanosheets for sensitive detection

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ABSTRACT

Nitrite can become poisonous to animals and human beings as it can lead to generation of carcinogenic *N*-nitrosamines. Metal-free nitrogen-doped reduced graphene oxide (NrGO) exhibited a good electrocatalytic activity toward oxidation of nitrite with the relatively low oxidation potential of 0.68 V (v.s. saturated calomel electrode), thus, a facile electrochemical sensor based on metal-free NrGO was fabricated for sensitive detection of nitrite for the first time. The novel sensor showed a wide linear concentration range from 0.5 to 5000 μM and a low detection limit of 0.2 μM at the signal-to-noise ratio of 3 with good selectivity, stability, and reproducibility. This fabricated sensor was used for the determination of nitrite in pickled garlic and river water. These results demonstrate that the facile metal-free NrGO-modified electrochemical sensor has promising applications for the determination of nitrite in food and environment.

1. Introduction

Highly sensitive detection of nitrite (NO_2^-) is of great importance due to its harmful effect on food, environment, and human health. It has shown that nitrite can become poisonous at high concentrations to animals and human beings as it can lead to generation of carcinogenic *N*-nitrosamines through the reactions with various amines and amides [1,2]. Due to the potential toxicity of nitrite, many techniques have been used to determine nitrite, including spectroscopy [3,4], chromatography [5], chemiluminescence [6], electrochemistry [7], and capillary electrophoresis [8]. The electrochemical methods are desirable owing to the ease of operation, real-time detection, rapid response, and high sensitivity. In general, the electrochemical methods result from either anodic oxidation or cathodic reduction of nitrite on the surfaces of chemically modified electrodes [9–11]. The anodic oxidation of nitrite is desirable because nitrate (NO_3^-) is the ultimate product without interference, but occurs at relatively high overpotential [12]. The primary disadvantages of the cathodic reduction of nitrite are the interferences from a few products depending on the condition of electrodes and the nature of electrocatalysts [13]. Therefore, it is important to exploit readily available and effective electrode materials for the oxidation of nitrite to fabricate highly selective sensors.

Carbon-based nanostructured materials have the good features, such as small residual currents, wide potential windows, and excellent chemical stability, and have been widely employed in electrochemistry. Among them, graphene is an ideal two-dimensional layered material and has been extensively used for growth and anchoring of precious metal and transition metal oxide nanoparticles because of its unique physical and chemical properties, including excellent electronic conductivity, large surface area, high mechanical strength, and good electrocatalytic activity. A variety of graphene or reduced graphene oxide (rGO)-based electrochemical sensors, decorated with precious metal nanoparticles (Au [14], Pd [15], and Au-Pd [16]), metal/transition metal oxide nanoparticles (K [17], ZnO [18], Fe_2O_3 [19], Fe_3O_4 [20], Co_3O_4 [21]), metalloproteins (hemoglobin [22] and myoglobin [23]), and polyelectrolytes (poly(diallyldimethylammonium chloride), PDDA [24]) have been fabricated toward oxidation of nitrite. In recent years, it has been shown that the electronic property, chemical activity, and optical characteristics of graphene can be tailored by chemical doping with heteroatoms such as boron and nitrogen [25–32]. It is highly desirable to develop non-precious metal or even metal-free electrocatalysts with excellent catalytic performances because of low cost, long-term stability, and resistance to catalyst poisoning. Metal-free boron-doped graphene exhibited a good electrocatalytic activity toward oxygen reduction reaction in alkaline solutions for fuel cells [25,30–32]. Nitrogen-doped graphene, with and without metal/metal oxide nanoparticles, also displayed good electrocatalytic activities toward oxygen reduction reaction [25–30]. However, metal-free nitrogen-doped graphene was used

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to fabricate the electrochemical sensor for simultaneous determination of ascorbic acid, dopamine, and uric acid in neutral aqueous solutions [33]. To the best of our knowledge, no work has been reported for sensitive detection of nitrite using metal-free nitrogen-doped graphene nanosheets.

Herein, a facile electrochemical sensor based on metal-free nitrogen-doped rGO (NrGO) nanosheets was fabricated for the sensitive detection of nitrite for the first time. The NrGO nanosheets exhibited a good electrocatalytic activity toward oxidation of nitrite at a relatively low oxidation potential (0.68 V). The newly fabricated nitrite sensor showed a wide linear concentration range (0.5–5000 μM) and a low detection limit (0.2 μM) even in comparison to the rGO-based electrochemical sensors mentioned above [14–24], as well as satisfactory selectivity, stability, and reproducibility. The developed electrochemical sensor was further applied for the determination of nitrite in pickled garlic and river water.

2. Experimental

2.1. Materials

Graphite powder and *N*,*N*-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium nitrite ($NaNO_2$) was obtained from Shanghai Sinpeuo Fine Chemical Co., Ltd. Aqueous ammonia ($NH_3 \cdot H_2O$, 28%), hydrazine hydrate ($N_2H_4 \cdot H_2O$, 85%), and other inorganic salts ($NaNO_3$, Na_2CO_3, Na_2SO_4, Na_3PO_4, NaCl, and KBr) were purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Phosphate buffered solution (PB, 0.1 M, pH 7.0) was prepared from NaH_2PO_4 and Na_2HPO_4 without addition of NaCl. All other reagents were of analytical grade and used as received. Double-distilled water was used in all of the experiments.

2.2. Instrumentation

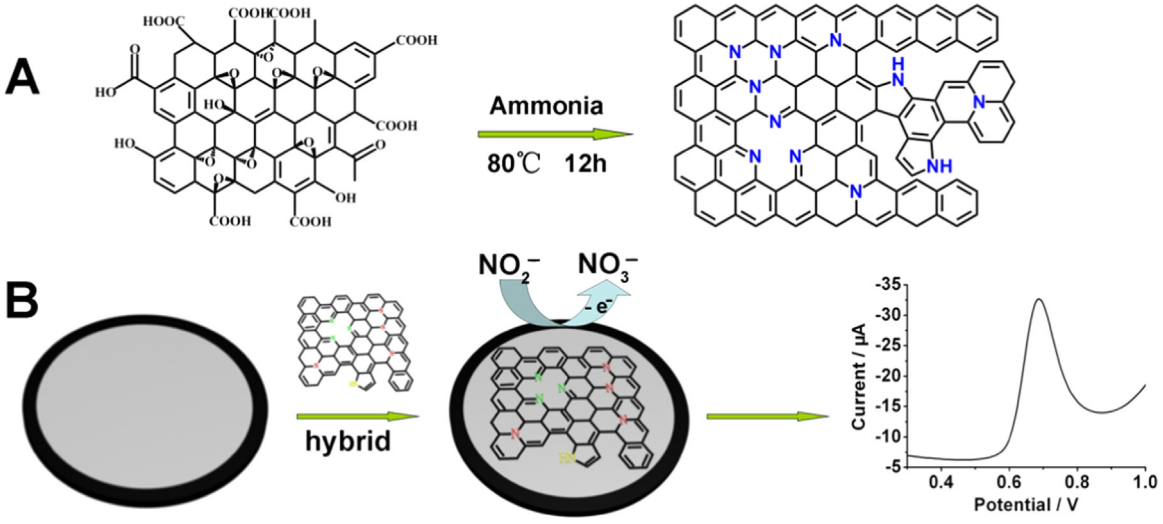
UV–vis absorption spectra were recorded on a UV-3600 spectrophotometer (Shimadzu, Japan). Transmission electron microscope (TEM) images were acquired using a JEM-2100 microscope (JEOL, Japan) with an accelerating voltage of 200 kV, and scanning electron microscope (SEM) images using a Hitachi S-4800 microscope (Hitachi, Japan). X-ray diffraction (XRD) measurements were performed on a PANalytical diffractometer (Philips, Netherlands) with Cu-Kα radiation (λ=0.15418 nm). X-ray photoelectron spectroscopy (XPS) experiments were operated on an ESCALAB 250 spectrometer (Thermo-VG, USA) with an ultrahigh vacuum generator. Raman spectra were collected on a LabRAM Aramis HJY Raman spectrometer (HORIBA Jobin Yvon, France) equipped with a CCD detector using a laser source at an excitation line of 532 nm. All electrochemical measurements were carried out on a CHI 660C electrochemical workstation (Shanghai Chenhua Instruments, Inc., China) using a conventional three-electrode system. A modified glassy carbon electrode (GCE, 3 mm in diameter) was used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire electrode as the counter electrode. Prior to electrochemical measurements, the solutions were deoxygenated by bubbling nitrogen gas at least for 15 min.

2.3. Preparation of NrGO

Graphite was first oxidized to GO via a modified Hummers and Offeman method [34]. The as-synthesized GO was used to prepare NrGO according to the reported procedure [35]. As shown in Scheme 1(A), 0.16 g of GO was dispersed in 20 mL of double-distilled water under the assistance of ultrasonication for 1 h. The well-dispersed solution was adjusted by aqueous ammonia (28%) to pH 10.0, and then 2.3 mL of hydrazine hydrate (85%) was added to the dispersion. The mixture was stirred for 15 min at room temperature followed by transferring to a Teflon-lined autoclave at 80 °C for 12 h. After cooling in the air, the precipitate was collected by centrifugation, washed repeatedly with water and ethanol, and finally dried at 70 °C in vacuum. rGO was synthesized by adding 0.02 mL of hydrazine hydrate (85%) and 0.14 mL of aqueous ammonia (28%) to 20 mL of aqueous GO solution (0.5 mg mL^{-1}) under continuous stirring for 15 min, followed by heating in an oil bath at 95 °C for 12 h.

2.4. Fabrication of NrGO-modified electrodes

Different alumina slurries (1.0, 0.3, and 0.05 μm) were used in turn to polish a bare GCE up to a mirror-like surface and then sequentially sonicated in ethanol and double-distilled water for cleaning. After the electrode was purged with nitrogen stream, 6 μL of NrGO dispersion (0.1 mg mL^{-1}), which was prepared by dispersion of NrGO powder in DMF under ultrasonication, was cast onto the pretreated GCE surface and dried at room temperature (Scheme 1(B)). The rGO-modified GCE was fabricated with the



Scheme 1. Illustration of preparations of NrGO (A) and NrGO-modified electrode for detection of nitrite (B).