

Graphene-TiO₂ Nanocomposite-Modified Screen-Printed Electrode for Sensitive Nitrite Determination in Hot Spring Water

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In the present work, a TiO₂/reduced graphene oxide (RGO) nanocomposite-modified glassy carbon electrode (GCE) served as a highly sensitive electrochemical platform for the determination of nitrite. A simple wet chemical method was used for the synthesis of RGO-TiO₂. The electrocatalytic behavior of our proposed sensor for the oxidation of nitrite was studied using cyclic voltammetry (CV) and amperometric methods. Furthermore, our proposed sensor has been successfully applied for the determination of nitrite in real hot spring water samples.

Keywords: Reduced graphene oxide; Nanocomposite; Sensor; Hot spring; Nitrite

1. INTRODUCTION

The detection of nitrite ions has been gaining attention because it is extensively present in water, soils and food and has the potential to negatively influence human health (such as interfering in the oxygen availability for tissues, producing carcinogenic compounds in the digestive system, etc.) [1-4]. Thus, it is of great importance to control the concentration of nitrite through the evaluation of water and food quality. Many analytical techniques have been used, such as chromatographic, spectroscopic, electrophoretic and electrochemical methods [5-7]. Electrochemical methods are characterized by their portable instrumentation, low cost, easy use, and rapid response [8-10]. The electro-reduction and electro-oxidation of nitrite are categorized as electrochemical techniques, and the latter is better,

considering the sophisticated understanding of the reaction mechanism and the interference effects (especially with nitrate and molecular oxygen) demonstrated in the former method [11-16].

Unfortunately, some of these techniques could not cater to the maximum contaminant level (MCL) released by the Environmental Protection Agency (EPA; 1 ppm, 21.7 μM), whereas others require expensive and sophisticated equipment [17]. Scholars in the electrochemical community have shown substantial attention to the analysis of nitrite [18-24]. It has been known that nitrite shows electroactivity at glassy carbon, copper, gold, diamond, platinum, and transition metal oxide electrodes; however, the use of bare electrodes is limited because the surface of the electrode could be poisoned by certain species, causing a decrease in the accuracy and sensitivity [25, 26].

As an inorganic metal oxide with a high isoelectric point and a wide band gap, TiO_2 has been applied to the preparation of various electrochemical sensors [27-31]. In addition, its electrocatalytic feature was further improved after the incorporation of TiO_2 with graphene, considering the excellent electrical conductivity and large surface area of graphene. In the present work, a reduced graphene oxide-wrapped TiO_2 (RGO- TiO_2) nanocomposite was successfully prepared using a simple wet chemical technique. In addition, the electrochemical sensor that was prepared based on RGO- TiO_2 and used for the detection of nitrite exhibited a new electrocatalytic response to nitrite. The anti-interference feature, limit of detection (LOD), and linear range of our developed sensor toward nitrite were also studied in this work. In addition, the RGO- TiO_2 -based electrochemical sensor has been successfully applied to the analysis of nitrite in real hot spring water samples.

2. EXPERIMENTS

2.1. Chemicals

Acetic acid, ascorbic acid, 3-hydroxytyramine hydrochloride (DA), uric acid (UA), poly(diallyl dimethyl ammonium chloride) (PDDA, 20 wt.%), titanium butoxide, glucose and acetylcholine (Ach) were commercially available from Sigma-Aldrich. Graphene oxide powder was commercially available from JCNANO, Inc. All other reagents were of analytical grade and used without additional purification. For the preparation of the phosphate buffer solution (PBS), 0.1 M KH_2PO_4 and K_2HPO_4 solutions were mixed together until an appropriate pH value was obtained. All solutions used 18.2 M Ω cm Milli-Q water.

2.2. Preparation of RGO- TiO_2 nanocomposite

A simple hydrothermal method proposed by Lui et al. [32] was slightly modified and used for the preparation of TiO_2 nanoballs. A mixture obtained by mixing 20 mL of acetic acid with 2 mL of titanium butoxide under stirring for 30 min was introduced into a 50-mL Teflon-lined stainless-steel autoclave. This was followed by heat treatment at 150 $^\circ\text{C}$ in an oven for 10 h, and they were naturally cooled to ambient temperature. Then, the sediment was collected by centrifugation followed by washing. TiO_2 nanoballs were obtained after heating the product to 500 $^\circ\text{C}$. The RGO- TiO_2

nanocomposite was prepared by dispersing 100 mg of the TiO₂ nanoballs in 20 mL of water under sonication, which was then added with 2 mL of PDDA and stirred for 120 min. The PDDA-functionalized TiO₂ was collected by centrifugation by washing with water followed by additional dispersion in 20 mL of water. Afterwards, the PDDA-functionalized TiO₂ was then mixed with 2 mL of a 1 mg/mL GO dispersion. The as-prepared dispersion was stirred, mixed with ammonia solution (2 mL), and introduced into a 50-mL Teflon-lined stainless-steel autoclave, followed by heat treatment at 120 °C for 120 min. After centrifugation, the RGO-TiO₂ nanocomposite was produced.

2.3. Characterization

An X-ray diffractometer (D8 –Advance XRD, Bruker, Germany) with Cu K α radiation with Cu K α radiation was used for the structure characterization of the collected samples. Electrochemical measurements were carried out using an alumina-water slurry-polished GCE, which was rinsed using ethanol and water. The surface of the electrode was modified by dropping a catalyst dispersion (7 μ L, 1 mg/mL) onto the as-prepared GCE, followed by drying at ambient temperature. RGO, TiO₂ and RGO-TiO₂ were used for GCE modification and the resulting samples were denoted as RGO/GCE, TiO₂/GCE and RGO-TiO₂/GCE, respectively. Electrochemical experiments were carried out at ambient temperature on a CH Instruments 660A electrochemical workstation (CHI-660 A, CH Instruments, Texas, USA) with a three-electrode configuration, where the reference and auxiliary electrodes were an Ag/AgCl (3 M KCl) and a platinum wire, respectively. Differential pulse voltammetry (DPV) was carried out at a scan rate of 0.6 to 0.9 V, with the current referred to as a function of the potential (pulse width, 50 ms; pulse amplitude, 20 mV).

2.4. Collection and preparation of hot spring water specimens

Real hot spring water samples were collected using a 50 mL plastic tube from Aer Mountain, Inner Mongolia. Before determination, the samples were filtered through a 200-nm pore size filter paper. The standard addition method was used to analyze the environmental samples to evaluate the accuracy of the obtained results.

3. RESULTS AND DISCUSSION

The XRD characterization of RGO-TiO₂ is shown in Fig. 1. The typical peaks observed at 2θ of 25.2°, 37.2°, 47.7°, 54.3°, 54.5°, 62.7°, 68.4°, 70.6° and 75.0° suggest the (101), (004), (200), (105), (211), (204), (116), (200), and (215) crystallographic planes of anatase, respectively. In addition, a broad peak was observed to overlap with the (101) plane of anatase, which suggested the incorporation of the exfoliated RGO sheets with TiO₂.

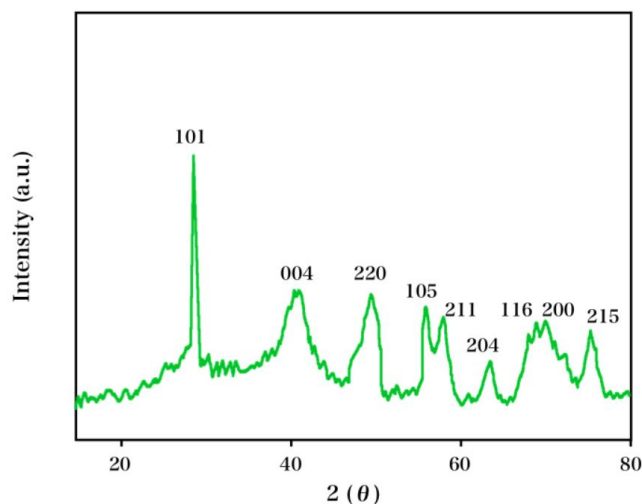


Figure 1. XRD characterization recorded for RGO-TiO₂.

The CV patterns of the bare GCE, the RGO-modified GCE, the TiO₂-modified GCE and the RGO-TiO₂-modified GCE for the oxidation of 1 mM nitrite are shown in Fig. 2. No redox peak was observed for the bare GCE when the potential ranged from 0.2 to 1.0 V. An obvious anodic peak was observed at the RGO-modified GCE, TiO₂-modified GCE and RGO-TiO₂-modified GCE, which suggested the oxidation of nitrite. At the RGO-modified GCE, TiO₂-modified GCE and RGO-TiO₂-modified GCE, the oxidation peak potentials of nitrite were obtained at 0.911, 0.889 and 0.831 V, which then shifted to the more negative potentials. Furthermore, the RGO-TiO₂-modified GCE displayed the highest peak current among these electrodes. The increased current response, along with the shift in the anodic peak to a more negative potential, suggested that the RGO-TiO₂-modified GCE served as a useful promoter to increase the kinetics of the electrochemical nitrite oxidation process[33].

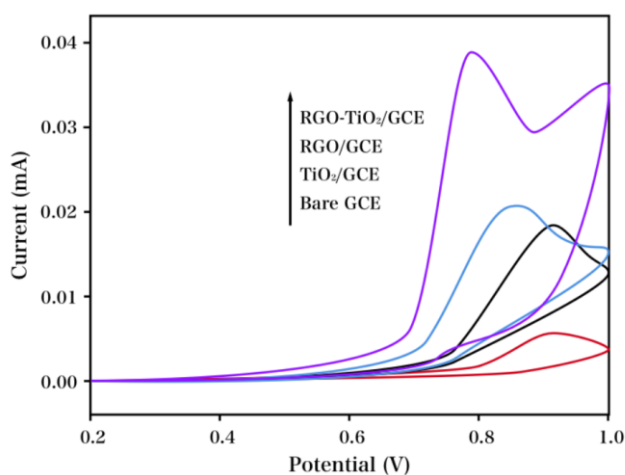


Figure 2. CVs of the bare GCE, RGO/GCE, TiO₂/GCE and RGO-TiO₂/GCE in 1 mM of a pH 7 nitrite solution at a scan rate of 50 mV/s.

The chronoamperometric response of the RGO-TiO₂-modified GCE in a 0.1 mM nitrite solution was recorded at a potential of 0.85 V. A straight line was plotted for the current vs. minus square root of time, which confirmed the diffusion controlled property of the nitrite oxidation.

The linear dependence of the current response of the nitrite oxidation on the scan rate was studied. The CVs of our proposed electrode in pH 7.0 PBS containing 1 mM nitrite over a scan rate of 20 - 150 mV/s is shown in Fig. 3A. The oxidation current of nitrite was found in proportion to the square root of scan rate, as shown in the following regression equation: $I_{pa} \text{ (mA)} = 0.00544 v^{-1/2} \text{ (mV}^{1/2}/\text{s}^{1/2}) - 0.00807$ ($R^2 = 0.9906$), which provided additional evidence that the overall electrochemical process was diffusion-controlled. As the scan rate was increased, the oxidation potential of nitrite obviously changed to a positive potential, as shown in the following linear regression equation: $E_{pa} \text{ (V)} = 0.10731 \log v \text{ (V/s)} + 1.02644$ ($R^2 = 0.9977$). Therefore, it could be concluded that the reaction between the redox sites of our proposed electrode and nitrite suffered from a kinetic limitation. The number of electrons involved in this reaction could be calculated by the Laviron's equation based on the above linear equation [34, 35]. The number of electron involved in the nitrite oxidation was obtained as $1.13 \approx 1$, which is consistent with the results reported previously [36, 37]. Based on these results, the mechanism for the electrocatalytic oxidation of nitrite using our proposed electrode could be described as follows [38-40]: first a complex of RGO-TiO₂(NO₂) was formed through the interaction between RGO-TiO₂ and nitrite. This was followed by the generation of NO₂ through the loss of one electron. Then, the amount of nitrogen dioxide was disproportionate to the production of nitrite and nitrate. Note that nitrate is the sole product.

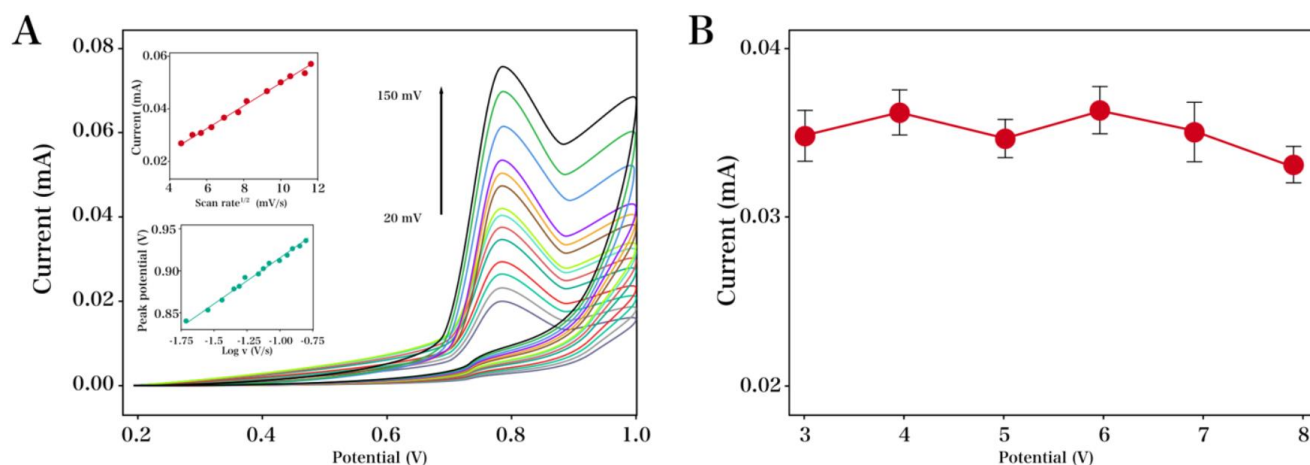


Figure 3. (A) CVs of the RGO-TiO₂-modified GCE in 0.1 M PBS containing 1 mM nitrite at varying scan rates. Inset (i) shows the linear dependence of the anodic peak current on the square root of the scan rate. Inset (ii) shows different peak potentials with the logarithm of scan rate. (B) The influence of the pH value on the current response of 1 mM nitrite using the RGO-TiO₂-modified GCE.

The effect of pH value on the anodic peak current response over a range of pH values from 3.0 to 8.0 is shown in Fig. 3B. As the pH value was increased, a gradual increase in the peak current was observed, which then reached a plateau at a pH of 7.0. The current response was decreased over the pH range of 7.0 to 8.0. The above result was consistent with those reported previously [41-44].

Subsequently, the nitrite was transformed into NO and NO_3^- , which possibly accounted for the lowered current response at acidic media [45]. In addition, the current response was also influenced by the lack of protons under higher pH conditions, due to the proton dependent property of nitrite oxidation [46]. In addition, the oxidization process would be inhibited by the oxide layer generated on the surface of the electrode under high pH conditions [47]. These results confirmed that a pH of 7.0 was the appropriate pH value for the analysis of nitrite.

Compared with CV, the DPV measurement is more sensitive, and has been extensively applied to electrochemical detection [48]. The DPV measurements of the RGO-TiO₂-modified GCE in nitrite over a concentration range of 1 - 1500 μM were recorded in Fig. 4, where the well-defined peaks denoted the oxidation of nitrite. There was a linear increase in the peak current with the nitrite concentration (1 - 1000 μM), as shown in the regression equation: $I (\mu\text{A}) = 0.02221 C(\mu\text{M}) + 0.3506$ ($R^2 = 0.9972$). The LOD was obtained as 0.21 μM , based on a signal-to-noise ratio of 3. The performance comparison of our proposed electrode with those reported previously was presented in Tab. 1. Therefore, our proposed electrode could be potentially applied to the practical determination of NO_2^- , due to the low LOD, high sensitivity, wide linear calibration range, and facile electrode preparation process.

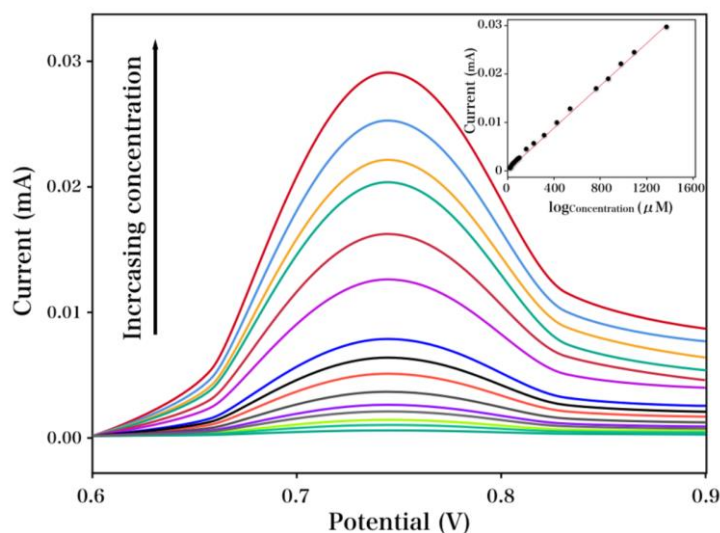


Figure 4. DPVs of the RGO-TiO₂-modified GCE in pH 7.0 solutions that contained 1, 2, 5, 15, 25, 45, 65, 85, 100, 150, 200, 300, 400, 500, 600, 700, 800, 900, 1000 and 1500 μM nitrite. Inset: calibration curve of nitrite concentrations against the peak current.

Table 1. Behavior comparison of our developed RGO-TiO₂-modified GCE and those proposed in other works.

Electrode	LOD (μM)	Linear range (μM)	Reference
GC/MC	0.1	0.5-100	[49]
(p-NiTAPc) modified GCE	0.9	2.5-1000	[50]
Thionine/ACNTs	1.12	3-500	[51]
GR/PPy/CS/GCE	0.1	0.5-722	[52]
RGO-TiO ₂ /GCE	0.21	1-1000	This work

The nitrite detection with the RGO-TiO₂-modified GCE was performed under laboratory conditions, using two real water samples from Aer Mountain, Inner Mongolia. Tab. 2 showed the equal determination of nitrite in the environmental samples. Our proposed electrode was confirmed to have excellent detection abilities for the 4 environmental samples. These results showed that the developed sensor could be potentially used for the preparation of portable electrochemical sensors for eco-friendly applications.

Table 2. Electrochemical analysis of nitrite quantity in the hot spring water samples collected from Aer Mountain, Inner Mongolia using RGO-TiO₂-modified GCE.

Sample	Added (μM)	Found (μM)	Recovery (%)
Sample 1	100	99.6	99.6
Sample 2	200	197.5	98.75
Sample 3	300	312.4	104.13
Sample 4	500	479.6	95.92

4. CONCLUSIONS

The present study reported the preparation of a novel and effective platform for nitrite determination based on the RGO-TiO₂-modified GCE. Our proposed sensor performed well for the determination of nitrite, with a linear range of 1 to 1000 μM and an LOD of 0.21 μM . Furthermore, our developed sensor could be potentially applied to the determination of nitrite in hot spring water samples.

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