



Development of a paper-based, inexpensive, and disposable electrochemical sensing platform for nitrite detection



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ABSTRACT

Electrochemical techniques are attractive for nitrite detection owing to their intrinsic advantages. However, traditional electrochemical sensors often suffer from the effects of fouling due to the adsorption of oxidation products on the electrode surface. In this work, a paper-based, inexpensive, disposable electrochemical sensing platform was developed for nitrite analysis based on a simple and efficient vacuum filtration system. Taking advantage of the physicochemical properties of graphene nanosheets and gold nanoparticles, the mass transport regime of nitrite at the paper-based electrode was thin layer diffusion rather than planar diffusion. In comparison with the electrochemical responses of commercial gold electrodes and glassy carbon electrodes (GCE), a considerably larger current signal was seen at the paper-based sensing interface, which significantly improved its sensitivity for nitrite detection. In particular, the paper-based electrode was a disposable sensing device, so that it effectively avoided the fouling effect arising from the adsorption of oxidation products. Moreover, the paper-based sensing platform made it possible to determine nitrite in environmental and food samples in an accurate, convenient, inexpensive, and reproducible way, indicating that the proposed system is promising for practical applications in environmental monitoring and public health.

1. Introduction

Nitrite ions are widely used as an additive in some foods and also as a corrosion inhibitor [1]. Moreover, they can be formed from the degradation of chemical fertilizers [2]. However, nitrite is an essential precursor for the formation of carcinogenic *N*-nitrosamines, which are extremely harmful for human health [2]. The detection of nitrite is therefore highly important for public health and in environmental monitoring [3]. A number of techniques have been used for the determination of nitrite, including chemiluminescence [4], fluorescent spectroscopy [5], colorimetric analysis [6], flow injection kinetic spectrophotometry [7], microfluidic Griess assay [8], and a liquid-phase microextraction method [9]. These techniques measured nitrite ions using different detection mechanisms, but often involved laborious operations, time-consuming pretreatments, or large background interference [4].

Electrochemical methods are ideal for nitrite detection because of their rapidity, sensitivity, and ease of operation [10–12]. Based on the direct oxidation behavior of nitrite, several electrochemical sensors have been designed to capture the current signal of nitrite [13–23]. These sensors have been shown to be useful tools for nitrite analysis

but, unfortunately, a challenge was encountered due to the fouling effect arising from the adsorption of reaction products. It was revealed that the oxidation products and intermediates of nitrite adsorbed irreversibly at the surface of traditional solid electrodes [24–26], which passivated the electrochemical activity of the sensing interface, resulting in poor sensitivity and reproducibility. Interestingly, Compton et al. presented an effective method for the elimination of surface adsorption based on ultrasonic cleaning [27]. This work enabled the amperometric detection of nitrite in a more accurate and reliable way, greatly improving the reproducibility and stability of sample analysis, although periodic sonication treatment was required.

Paper-based analytical devices (PADs), inspired by Whitesides et al. [28], represent a revolutionary methodology for conducting portable, low-volume, inexpensive on-site analysis [29–34]. In particular, electrochemical paper-based analytical devices (*e*-PADs) have recently attracted significant attention, with applications in immunoassay [35,36], biochemical analysis [37–42], and point-of-care clinical diagnosis [43,44]. In this communication, a paper-based electrochemical sensing platform was developed for environmental monitoring and food safety assessment. Based on an efficient vacuum filtration system coupled with an in situ electrodeposition technique, paper electrodes

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functionalized with graphene nanosheets and decorated with gold nanoparticles were fabricated for use in nitrite analysis. The paper-based electrodes were disposable sensing devices which could accurately detect the current signal of nitrite. Since the devices are disposable, the fouling effect resulting from the adsorption of oxidation products is effectively avoided and there is no need for sonication treatment. An improved electrochemical response for nitrite oxidation was demonstrated at the paper-based sensing interface compared with commercial gold electrodes and glassy carbon electrodes (GCE). In the present work the nitrite content of real samples was evaluated in a convenient, accurate, reproducible, and inexpensive way, confirming the practical applicability of the proposed sensing platform.

2. Experimental

Field emission scanning electron microscope (FE-SEM) images were acquired using an S-4800 microanalyzer (Hitachi, Japan). High-resolution transmission electron microscope (HR-TEM) images were obtained using a JEM-2100 transmission electron microscope (JEOL, Japan). Electrochemical experiments were performed on a CHI660E electrochemical workstation (CH Instruments, Austin, USA). The vacuum filtration operations were carried out on a KONTES Ultra-Ware system (Kimble Chase, Vineland, USA).

The preparation of functionalized paper chips is based on the method described by Wu et al. with improvements and modifications [45]. Prior to use, the mixed cellulose ester (MCE) filter papers were moistened and cleaned with deionized water. Reduced graphene oxide was dispersed in deionized water with the aid of sonication for 15 min, resulting in 8.0 mg L^{-1} uniform suspension. 9.0 mL of the above suspension was carefully transferred onto the MCE membrane, and under vacuum conditions a thin and homogeneous graphene-functionalized MCE film was formed. The resulting film was rinsed with deionized water five times to get rid of impurities associated with reduced graphene oxide and then vacuum-dried for 12 h at room temperature. For the preparation of paper-based electrodes, the vacuum-dried film was cautiously separated from the vacuum filtration system, and cut into 18 chips using a cutting template. These chips were linked with NTE copper wires using fast-drying silver paint, and wrapped with Parafilm to prepare the working electrodes (graphene/MCE). Gold nanoparticles were assembled on the graphene/MCE electrode using a convenient *in situ* electrodeposition technique. In brief, the three-electrode system consisted of a graphene/MCE working electrode, an Ag/AgCl wire reference electrode, and a platinum wire counter electrode. Gold nanoparticles were electrodeposited on the graphene/MCE at -0.2 V for 600 s in 0.1 M pH 7.0 PBS containing 0.6 mM HAuCl_4 . The resulting electrode was rinsed with deionized water, and denoted as GNPs/graphene/MCE. In control experiments, commercial GCE and gold electrodes were polished with 1.0, 0.3, and 0.05 μm alumina slurries, and cleaned with sonication for 10 min before use.

3. Results and discussion

3.1. Characterization of the paper-based system

The surface morphology of the paper-based system was characterized by FE-SEM (Fig. 1A). A typically interconnected network with a porous structure was clearly observed for the MCE paper, which provided sufficient internal surface area for material adsorption. The average diameter of the pores was about 100 nm, resulting in suitable flow rate for filtration. As a consequence, graphene nanosheets were uniformly and compactly distributed on the MCE surface through the driving force from vacuum filtration (Fig. 1B). The size of these graphene nanosheets was estimated to be about 3 μm . They were assembled to form a crumpled and partially vertical framework, which distinctly increased the roughness and edge-plane-like density of defect sites on the electrochemical interface. Based on a simple *in situ*

electrodeposition technique, gold nanoparticles with an average size of about 80 nm were homogeneously loaded onto the flexible graphene nanosheets (Fig. 1C). They assembled to form a three-dimensional structure, which further increased the electroactive surface area for sensing applications. The microscopic arrangement of the gold nanoparticles was further investigated by HR-TEM. As depicted in Fig. 1D, the lattice fringe spacing of the gold nanoparticles was measured to be 0.235 nm, which matches the d value for Au (111) [46].

3.2. Electrochemical oxidation and determination of nitrite

The direct oxidation behavior of nitrite was studied at graphene/MCE electrodes, GNPs/graphene/MCE electrodes, commercial gold electrodes, and commercial GCE in 0.1 M pH 4.75 acetate buffer. As shown in Fig. 2A, a well-defined nitrite oxidation peak was observed at 0.80 V for graphene/MCE (curve a), which was attributed to the conversion of NO_2^- to NO_3^- through a two-electron reaction mechanism ($\text{NO}_2^- + \text{H}_2\text{O} - 2e^- \rightarrow \text{NO}_3^- + 2\text{H}^+$). The favourable electrochemical response of nitrite further revealed that the graphene nanosheets were compactly assembled on the MCE surface. After the deposition of gold nanoparticles (curve b), the current density increased, and the peak potential shifted negatively, demonstrating that the GNPs/graphene/MCE electrode was more suitable for nitrite detection. In contrast, nitrite presented relatively weak oxidation peaks with higher overpotentials at the commercial gold electrode (curve c) and GCE (curve d), corresponding to the planar diffusion signature of the analyte [27,47,48]. The improved voltammetric response of GNPs/graphene/MCE electrodes compared with the electrochemical behavior of nitrite at the commercial gold electrode and GCE was attributed to a change in the mass transport regime [27,47,48], the planar diffusion signature at the bare electrodes switching to thin layer diffusion at the conductive GNPs/graphene film electrodes.

The calibration curve for sensitive determination of nitrite is given in Fig. 2B. As the concentration increased, the peak potential of NaNO_2 remained unchanged at 0.74 V, while the current density increased proportionally. The resulting linear regression equation was $j_{\text{pa}} (\mu\text{A cm}^{-2}) = 0.47c (\mu\text{M})$ ($n = 8$, $R^2 = 0.9984$), with a wide range of 0.3–720 μM . The detection limit was calculated to be 0.1 μM ($S/N = 3$). The analytical parameters of the developed sensing platform including linear range and detection limit were compared with various reference methods. As shown in Table 1, it was revealed that the proposed approach exhibited relatively wider linear range and lower detection limit, indicating that the paper-based system provided a promising platform for nitrite analysis.

3.3. Interference studies

The effect of foreign interfering species on the detection of 50 μM nitrite was investigated by adding various interferents into the system. The results revealed that common metal ions and acid radical ions (such as Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Zn^{2+} , Cl^- , NO_3^- , CO_3^{2-} , PO_4^{3-} , SO_4^{2-} , Ac^- and F^-) in environmental samples produced almost no interference at a 100-fold concentration (signal change < 2%). The influence of some redox-active substances, including environmental pollutants and biological molecules (such as Na_2SO_3 , dopamine, uric acid, hemoglobin, and glucose), was also evaluated. Although these electroactive species could generate oxidation currents at the electrode surface, their peak potentials were far from that of nitrite (0.74 V). It was also shown that the nitrite current changes were < 5% of the initial signal after the addition of the above substances at a 50-fold concentration, which demonstrated the high selectivity of the sensing platform.

3.4. Real sample analysis

In order to test the performance of the proposed system in practical

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