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Highly sensitive amperometric sensing of nitrite utilizing bulk-modified MnO_2 decorated Graphene oxide nanocomposite screen-printed electrodes

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ABSTRACT

A screen-printed amperometric sensor based on a carbon ink bulk-modified with MnO_2 decorated graphene oxide (MnO_2/GO-SPE) nanocomposite was investigated for its ability to serve as a sensor towards nitrite. The composite was prepared by simple ultrasonication and reflux methodology and was characterized by FT-IR spectroscopy, transmission electron microscopy, scanning electron microscopy, Raman spectroscopy, atomic force microscopy and electrochemically using cyclic voltammetry, chronoamperometry and differential pulse voltammetry techniques. The MnO_2/GO-SPE was found to exhibit an electro-catalytic activity for the electrochemical oxidation of nitrite in 0.1 M phosphate buffer solution (pH 7.4). The electrochemical oxidation of nitrite occurs at +0.55 V (Vs. Ag/AgCl) with a limit of detection (3σ) found to be 0.09 μM and with two linear ranges of 0.1 μM to 1 μM and 1 μM to 1000 μM with sensitivities of $1.25\ \mu A \mu M^{-1}\ cm^{-2}$ and $0.005\ \mu A \mu M^{-1}\ cm^{-2}$ respectively. Furthermore, the MnO_2/GO-SPE showed an excellent anti-interference ability towards a range of commonly encountered electroactive species and metal ions. Additionally, the fabricated MnO_2/GO-SPE nitrite sensor presented an excellent selectivity, reproducibility and stability. The presented study widens the scope of applications of graphene-based nanocomposite materials for on-site monitoring of nitrite.

1. Introduction

The last decades have witnessed an expansive interest in the detection and quantification of nitrite (NO_2^-) owing to the actuality of formation of carcinogenic nitrosamines by the interaction of nitrites with amines and also the oxidation of hemoglobin to methemoglobin, causing health issues such as methemoglobinemia [1,2]. Additionally, nitrite is customarily used as a preservative, dyeing agent, fertilizer and food additive. Thus, there is an imminent need for the sensitive and rapid determination of NO_2^- for public health and environmental safety. Several approaches have been made for NO_2^- determination, such as spectrophotometry [3], chemiluminescence [4], ionic chromatography [5], high performance liquid chromatography [6,7], gas chromatography-mass spectrometry [8], capillary electrophoresis [9], spectrofluorimetry and electrochemical methods [10–12]. However, most of the predominantly reported techniques suffer from flaws such as the use of toxic reagents, time consuming sample preparations, and susceptibility to potential interferences. Amongst all, the electrochemical mode has grabbed significant attention due to its high sensitivity, reliability, ease of operation, low cost, good selectivity, fast procedure, low detection limits and high accuracy [13,14]. However, the electrochemical oxidation of nitrite at most common electrodes suffers from large over-potentials decreasing the sensitivity and accuracy of the electrodes which are easily affected by electroactive interferences. The surface modification of electrodes has been adopted to obtain a higher current response at a lower overpotential. In this context, the composites based on engineered carbon nano-materials are nowdays being principally used for designing electrochemical sensors/biosensors due to excellent electrochemical properties [15–19].

Graphene, a planar sheet of one-atom thickness sp^2 bonded carbon structure, due to its remarkable properties such as high specific surface area ($2630\ m^2\ g^{-1}$), high electronic conductivity ($106\ Scm^{-1}$), extraordinary electronic properties and a wide electrochemical window is foremost choice for electrochemical applications compared with those of other carbon based nano-

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materials, such as graphite and carbon nanotubes [20,21]. Moreover, graphene oxide (GO), a decorated form of graphene with certain oxygen functionalities on the basal plane and edges provides strong hydrophilic properties and good dispersibility in water and other polar solvents. The reported hindrance in the use of GO is due to the oxygen containing functional groups which result in loss in electrical conductivity as compared to graphene. This can be overcome by coupling GO with metal [22,23], metal oxide [24,25], metal hydroxide [26], metal sulfide [27] and noble metal nanoparticles [28–30] where GO provides large surface area for the immobilization of inorganic nano-particles to form composites with enhanced electrocatalytic performance. Amongst the library of many metal oxides, manganese dioxide (MnO_2) has gained much attention from researchers due to its low-cost, abundance and non-toxicity compared to other inorganic oxides such as cobalt, nickel and vanadium etc. [31,32]. Moreover, MnO_2 has superb electro-catalytic properties and fast response times and these properties have been utilized in super-capacitors but much less reports available in the field of electrochemical sensors and biosensors [33,34]. The properties of MnO_2 depend on the manganese oxidation state and on the structural type of MnO_2 crystal; so great efforts have been made to prepare nano-crystalline MnO_2 with different structures.

In this presented work, we have successfully exploited the unique features of GO and MnO_2 nano-particles to design a nanocomposite by simply decorating MnO_2 nanoparticles over GO sheets. The GO-wrapped MnO_2 nanocomposites were synthesized by the co-assembly between MnO_2 nano-particles and GO sheets. The process is thought to be driven by Van der Waals interactions [35]. More importantly, the presence of nano-structured MnO_2 is able to efficiently prevent the aggregation of GO sheets caused due to the Van der Waals interactions, consequently leading to an increase in the available electrochemical active surface area and a suitable porous structure of MnO_2 nano-particles [36] facilitating improvements in the sensing of the target analyte. The electrochemical properties of the MnO_2 decorated graphene oxide nanocomposite (hereafter referred to as MnO_2/GO) were investigated in detail, and obtained results revealed that the composite material has a good electrochemical performance as electrode material. The as-fabricated MnO_2/GO nanocomposite was further incorporated in graphite ink into graphite inks and used for the bulk production of screen-printed electrodes which are simple and disposable, yet sensitive, selective, and have lower the over-potential for the detection of nitrite (compared to a bare GC electrode) in sub-millimolar levels as compared to prior reported works which suffer from low sensitivity, selectivity and lack of on-site applications [37–49].The selectivity, operational stability and practicality of the developed nitrite sensor has also been critically accessed and demonstrated.

2. Experimental Section

2.1. Chemicals and reagents

Graphene oxide flakes, chitosan (MW: 15000-20000), $KMnO_4$, oleic acid ($C_{18}H_{34}O_2$), sodium nitrite ($NaNO_2$), acetic acid (AcOH) were used and these chemicals were of analytical grade and purchased from Alfa-Aesar. All experiments were carried out in triple distilled water (tdw).

2.2. Methods

2.2.1. Preparation of dendrite shaped MnO_2

Dendrite shaped MnO_2 was prepared as reported in literature [36] with slight modifications. In a typical synthesis, 6.3 mmol of $KMnO_4$ was dissolved in 500 mL of triple distilled water and stirred for 30 mins. Then, 10.0 mL of oleic acid (a capping agent) was added in the molar solution of $KMnO_4$, and a steady emulsion was formed by vigorous stirring. The emulsion was transferred to a 1 L separating funnel and allowed to stand at room temperature for 24 hrs. A brown-black precipitate were collected on the organic layer which was separated from the aqueous layer and washed several times with ethanol to remove excess of oleic acid and then washed several times with distilled water. Finally, the precipitate was dried under a vacuum at 60 °C for 10 hrs.

2.2.2. Synthesis of the MnO_2/GO nanocomposite

For the preparation of nanocomposite, GO was prepared by chemical oxidation and exfoliation of natural graphite performed according to modified Hummers method [50].To an aqueous GO solution (1 mg/mL) prepared by ultrasonication, an equivalent amount of MnO_2 was added (for optimization data *cf.* Table 1) and ultrasonicated for 2–3 hrs and then refluxed at high temperature for 10–12 h and the solid product was collected by centrifugation at 13,000 rpm and was dried under vacuum at 70 °C for 12 hrs.

2.2.3. Fabrication of modified GC electrodes

The casting of MnO_2/GO nanocomposite on glassy carbon electrodes (GCE) was performed in a chitosan matrix (Chit) for which 0.1 g chitosan powder was mixed in 20 mL (0.2 M) AcOH solution and ultrasonicated for 30 mins. Then, 1 mg of MnO_2/GO nanocomposite was added to the Chit solution. The GCE was polished upto mirror finish using 0.05 μm alumina powder and was ultrasonicated in tdw and ethanol for 5 mins. 10 μL of the prepared MnO_2/GO/Chit nanocomposite was drop-casted on the GCE and dried for 4–5 hrs and used further for electrochemical studies.

2.2.4. Preparation of Screen Printed Electrodes (SPE)

The in-house fabrication of screen-printed carbon electrodes were performed using suitable stencil designs using a micro-DEK1760RS screen-printing machine (DEK, Weymouth, UK). Firstly a carbon–graphite ink formulation was screen-printed onto a flexible polyester film (Autostat, 250 micron thickness), then the layer was stored in a fan oven at 60 °C for 30 min. Ag/AgCl paste was screen printed for fabricating Ag/AgCl reference electrode (Gwent Electronic Materials Ltd, UK) onto the plastic substrate and the SPE was ready to use after a final coating of dielectric paste ink layer (Gwent Electronic Materials) to cover the connections and to define the graphite working electrode diameter to be 3 mm and cured for 30 min at 60 °C. The MnO_2/GO were incorporated into the SPEs according to % weight of M_P and M_I, where M_P is the mass of particulate and M_I is the mass of the carbon ink formulation used in the printing process. The weight per cent of M_P and M_I typically

Table 1
Optimization of ratio of GO and MnO_2 nano for preparation of nanocomposite by varying the concentration of GO, and MnO_2 nano in MnO_2/GO.

Systems	GO (mg)	MnO_2 nano (mg)	Nanocomposite ratio
I			
A	0.5	1.0	1:2
B	1.0	1.0	1:1
C	1.5	1.0	1.5:1
D	2.0	1.0	2:1
II			
A	1.0	0.5	1:0.5
B	1.0	1.0	1:1
C	1.0	1.5	1:1.5
D	1.0	2.0	1:2