Sensors and Actuators B 227 (2016) 92–99

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

An enzyme-free electrochemical sensor based on reduced graphene oxide/Co_3O_4 nanospindle composite for sensitive detection of nitrite

Yuvaraj Haldorai [a], Jun Yeong Kim [b], A.T. Ezhil Vilian [a], Nam Su Heo [b], Yun Suk Huh [b,*], Young-Kyu Han [a,*]

[a] Department of Energy and Materials Engineering, Dongguk University-Seoul, Seoul 100-715, Republic of Korea
[b] Department of Biological Engineering, Biohybrid Systems Research Center (BSRC), Inha University, Incheon 402-751, Republic of Korea

ARTICLE INFO

Article history:
Received 9 September 2015
Received in revised form
20 November 2015
Accepted 11 December 2015
Available online 14 December 2015

Keywords:
Graphene
Cobalt oxide
Nanocomposite
Nitrite
Non-enzymatic

ABSTRACT

Cobalt oxide (Co_3O_4) nanospindles-decorated reduced graphene oxide (RGO) composite is prepared via thermal decomposition of a three-dimensional coordination complex precursor, cobalt benzoate dihydrazinate, at 200 °C. Transmission electron microscopy reveals that Co_3O_4 nanospindles with an average particle size of <25 nm are decorated on the RGO surface. The low decomposition temperature and lack of residual impurities are significant aspects of this simple and facile method. The electrochemical performance of the proposed sensor is investigated using cyclic voltammetry and chronoamperometry. Under optimum conditions, anodic peak currents are linearly proportional to their concentrations, in the range of 1–380 μM for nitrite with a regression equation of I (μA) = 2.0660 C + 6.7869 (R^2 = 0.9992). The sensor exhibits a high sensitivity of 29.5 μA μM^{-1} cm^{-2}, a rapid response time of 5 s, and a low detection of limit of 0.14 μM. The proposed electrode shows good reproducibility and long-term stability. The sensor is used to determine the nitrite level in tap water with acceptable recovery, implying its feasibility for practical application.

1. Introduction

Graphene, a two-dimensional sp^2 carbon nanomaterial, has attracted increasing interest because of its unique physical and chemical properties, including high surface area, good chemical resistance, excellent electrical conductivity, extraordinary mechanical properties, high charge mobility, and thermal conductivity [1–3]. Transition metal oxides have attracted increasing attention due to their unique properties. Among the metal oxides most studied of late, cobalt oxide (Co_3O_4), a *p*-type semiconductor with a direct band gap of 1.5 eV and 2.19 eV [4]. Moreover, cobalt oxide has three well-known polymorphic structures: cobaltous oxide (CoO), cobaltic oxide (Co_2O_3), and Co_3O_4 [5]. The one-dimensional (1D) nanostructures of Co_3O_4 are inexpensive, environmentally friendly, and have good conductivity [6]. Due to its high surface area to volume ratio, high ratio of surface atoms, and good chemical stability, it should meet the requirements of future energy applications [7]. Considering the excellent properties, Co_3O_4 nanostructures have been used for a variety of applications [8–11]. Taking into account the excellent individual properties of graphene and Co_3O_4, a combination might yield enhanced performance.

Several studies have reported different approaches to synthesizing graphene/Co_3O_4 nanocomposites. Song et al. [12] fabricated graphene/Co_3O_4 nanosheet composites via a hydrothermal method. Choi et al. [13] synthesized three-dimensional (3D), porous graphene/Co_3O_4 composite films using replication and deposition processes for lithium ion batteries. Li et al. [14] reported a simple approach for preparing graphene/Co_3O_4 composites via a chemical deposition of Co_3O_4 nanoparticles onto GO followed by reduction of GO to graphene using $NaBH_4$ for high-performance lithium ion batteries. Ye et al. [15] fabricated graphene/Co_3O_4 composite using electrodeposition to determine tryptophan. Park and Kim [16] reported the synthesis of graphene/Co_3O_4 nanosheets using microwave-assisted method as supercapacitor electrodes. Dong et al. [17] prepared 3D graphene/Co_3O_4 nanowire composites for supercapacitors and non-enzymatic glucose detection. Kong et al. [18] fabricated interconnected 1D Co_3O_4 nanowires on graphene for non-enzymatic hydrogen peroxide detection. Shahid et al. [19] synthetized graphene/Co_3O_4 nanocube and graphene/Co_3O_4 nanocube@Pt composites for nitric oxide detection. Although graphene/Co_3O_4 composites have been used for various applications [12–19], few studies have investigated

* Corresponding authors.
E-mail addresses: yunsuk.huh@inha.ac.kr (Y.S. Huh), ykenergy@dongguk.edu (Y.-K. Han).

http://dx.doi.org/10.1016/j.snb.2015.12.032
0925-4005/

electrochemical sensors. Until now, no attempt has been made to use a graphene/Co_3O_4 composite for electrochemical non-enzymatic detection of nitrite.

In relation to such reported composite materials, it should be noted that the obtained Co_3O_4 is generally in the form of particle. It has been reported that the electrochemical performance of Co_3O_4 can be enhanced by processing 1D or 2D nanostructures such as nanowires, nanocubes, nanosheets [16–19], etc. It is therefore of interest to synthesize new1D or 2D Co_3O_4/graphene composites with a synergistic advantage between Co_3O_4 and graphene for electrochemical sensing. In this regard, a simple, reliable synthetic method needs to be developed because the size and morphology of Co_3O_4 have a significant effect on its chemical and physical properties as well as its applications.

Nitrite ions are important toxic inorganic pollutants found in food, soil, water, and physiological systems. High concentrations of nitrite ions can originate from caustic radioactive waste [20]. Excess nitrite ions are detrimental to the human body, and a high concentration in drinking water is a serious health risk for infants. In the human body, nitrites can combine with hemoglobin to form methemoglobin, which leads to a condition commonly called "blue baby syndrome." Nitrite can also be converted into nitrosamine, which causes cancer and hypertension [21]. Hence, it is essential to monitor toxic nitrite ions in the environment.

We report a facile synthesis of a reduced graphene oxide (RGO)/Co_3O_4 nanospindle composite using a 3D coordination complex as a precursor, and its application toward the electrochemical detection of nitrite. Electrochemical studies indicated that the composite exhibited a fast current response to nitrite, with a wide linear range and a low detection limit. In addition, the composite electrode showed excellent reproducibility and long-term stability. The fabricated electrochemical sensor exhibited significant sensitivity, selectivity and it was also applied to real sample analysis.

2. Experimental

2.1. Materials

Graphite, cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), hydrazine (N_2H_4), benzoic acid (C_6H_5COOH), sodium nitrate ($NaNO_3$), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), and sodium nitrite ($NaNO_2$) were purchased from Aldrich. All other reagents were analytical grade and were used as received.

2.2. Synthesis of Co_3O_4/RGO nanocomposite

Graphene oxide (GO) was synthesized from natural graphite using a modified Hummers' method [22]. The precursor complex was prepared by mixing an aqueous solutions of $Co(NO_3)_2{\cdot}6H_2O$ (0.01 mol) and of hydrazinium benzoate (0.02 mol) under constant stirring. The resulting mixture was concentrated to one-third of its total volume; the contents were cooled, filtered, washed with alcohol, and dried. 20 mg of GO was dispersed in 50 ml of ethanol under sonication for 1 h, then 100 mg of cobalt benzoate dihydrazinate complex precursor was added and the mixture was sonicated for another 1 h. The resulting mixture was transferred into a Teflon-lined reactor and the reaction was carried out at 200 °C for 8 h. The obtained product was separated, then washed with ethanol and distilled water by centrifugation. Finally, it was dried at 65 °C for 24 h in a vacuum oven.

2.3. Preparation of the modified electrode

The nitrite sensor was fabricated on a 3 mm diameter glassy carbon electrode (GCE) that was polished to a mirror finish using an alumina slurry (0.05 μm) sequentially, then washed ultrasonically in ethanol and deionized water and dried at room temperature. The electrode material was prepared by mixing 1.0 mg/ml of the Co_3O_4/RGO nanocomposite in ethanol under ultrasonication for 1 h to achieve a homogeneous dispersion. Then, 6 μl of the suspension was drop-casted on a GCE and dried at room temperature. The resulting electrode was denoted as Co_3O_4/RGO/GCE. The RGO/GCE electrode was also prepared similarly for comparison.

2.4. Characterization

Raman spectra of the samples were obtained using a HR800 UV Raman microscope (Horiba Jobin–Yvon, France). X-ray diffraction (XRD) patterns were collected using an X'Pert PRO MRD (Philips) diffractometer with Cu Kα radiation. Morphology of the composite was examined by a HITACHI SU8010 high resolution scanning electron microscope. Transmission electron microscopy (TEM, JEOL-2010F) was performed at an accelerating voltage of 200 kV. The TEM observation sample was prepared by depositing an ethanolic dispersion on a 200 mesh copper grid, followed by air drying. High-resolution TEM (HRTEM) recorded the selected area electron diffraction (SAED) image. X-ray photoelectron spectroscopy (XPS) measurements were obtained using a Thermo Scientific K-Alpha electron spectrometer with an Al X-ray source.

2.5. Electrochemical analysis

Electrochemical performance was evaluated using a three-electrode cell system. Cyclic voltammetry (CV) and chronoamperometry analyses were conducted on a CHI 660D electrochemical workstation at room temperature. A 1 M KOH solution was served as the electrolyte, while Co_3O_4/RGO nanocomposite represented the working electrode. A platinum wire was employed as a counter electrode, with calomel as the reference. Electrochemical impedance spectroscopy (EIS) was performed using an WonATech electrochemical workstation in 0.1 M KCl containing 5 mM $Fe(CN)_6{}^{3-/4-}$ at room temperature.

3. Results and discussion

The Co_3O_4/RGO nanocomposite was synthesized from GO and a 3D coordination complex precursor, cobalt benzoate dihydrazinate [$Co(C_6H_5COO)_2(N_2H_4)_2$], which was prepared according to the following reaction:

$$Co(NO_3)_2{\cdot}6H_2O + 2C_6H_5COON_2H_5 \rightarrow Co(C_6H_5COO)_2(N_2H_4)_2 + 2HNO_3 + 6H_2O \quad (1)$$

$$Co(C_6H_5COO)_2(N_2H_4)_2 + 15O_2 \rightarrow CoO + 2N_2H_4 + 14CO_2 + 5H_2O \quad (2)$$

$$6CoO + O_2 \rightarrow 2Co_3O_4 \quad (3)$$

Fig. 1 outlines the fabrication of Co_3O_4 nanospindles decorated RGO nanocomposite for nitrite sensing. Decomposition pathway of the precursor and the deposition of Co_3O_4 nanospindles on the RGO surface started at a relatively low temperature of ca. 200 °C. The precursor decomposed completely, losing N_2H_4, CO_2, and H_2O. The complex was stable in air and insoluble in water. The importance of using such a complex is the distribution of metal ions in a 3D coordination sphere so that the decomposition would results in very fine particles. The benzoate and hydrazine ligands enhance