



An enzyme-free electrochemical sensor based on reduced graphene oxide/Co₃O₄ 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 (Co₃O₄) 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 Co₃O₄ 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 $I(\mu\text{A}) = 2.0660C + 6.7869$ ($R^2 = 0.9992$). 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 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.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Graphene, a two-dimensional sp² 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 (Co₃O₄), 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 (Co₂O₃), and Co₃O₄ [5]. The one-dimensional (1D) nanostructures of Co₃O₄ 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, Co₃O₄ nanostructures have been used for a variety of applications

[8–11]. Taking into account the excellent individual properties of graphene and Co₃O₄, a combination might yield enhanced performance.

Several studies have reported different approaches to synthesizing graphene/Co₃O₄ nanocomposites. Song et al. [12] fabricated graphene/Co₃O₄ nanosheet composites via a hydrothermal method. Choi et al. [13] synthesized three-dimensional (3D), porous graphene/Co₃O₄ composite films using replication and deposition processes for lithium ion batteries. Li et al. [14] reported a simple approach for preparing graphene/Co₃O₄ composites via a chemical deposition of Co₃O₄ nanoparticles onto GO followed by reduction of GO to graphene using NaBH₄ for high-performance lithium ion batteries. Ye et al. [15] fabricated graphene/Co₃O₄ composite using electrodeposition to determine tryptophan. Park and Kim [16] reported the synthesis of graphene/Co₃O₄ nanosheets using microwave-assisted method as supercapacitor electrodes. Dong et al. [17] prepared 3D graphene/Co₃O₄ nanowire composites for supercapacitors and non-enzymatic glucose detection. Kong et al. [18] fabricated interconnected 1D Co₃O₄ nanowires on graphene for non-enzymatic hydrogen peroxide detection. Shahid et al. [19] synthesized graphene/Co₃O₄ nanocube and graphene/Co₃O₄ nanocube@Pt composites for nitric oxide detection. Although graphene/Co₃O₄ 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), ykenegy@dongguk.edu (Y.-K. Han).

electrochemical sensors. Until now, no attempt has been made to use a graphene/Co₃O₄ composite for electrochemical non-enzymatic detection of nitrite.

In relation to such reported composite materials, it should be noted that the obtained Co₃O₄ is generally in the form of particle. It has been reported that the electrochemical performance of Co₃O₄ can be enhanced by processing 1D or 2D nanostructures such as nanowires, nanocubes, nanosheets [16–19], etc. It is therefore of interest to synthesize new 1D or 2D Co₃O₄/graphene composites with a synergistic advantage between Co₃O₄ and graphene for electrochemical sensing. In this regard, a simple, reliable synthetic method needs to be developed because the size and morphology of Co₃O₄ 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)/Co₃O₄ 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(NO₃)₂·6H₂O), hydrazine (N₂H₄), benzoic acid (C₆H₅COOH), sodium nitrate (NaNO₃), sulfuric acid (H₂SO₄), hydrochloric acid (HCl), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂), and sodium nitrite (NaNO₂) were purchased from Aldrich. All other reagents were analytical grade and were used as received.

2.2. Synthesis of Co₃O₄/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(NO₃)₂·6H₂O (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 Co₃O₄/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 Co₃O₄/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 Co₃O₄/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 a WonATech electrochemical workstation in 0.1 M KCl containing 5 mM Fe(CN)₆^{3–/4–} at room temperature.

3. Results and discussion

The Co₃O₄/RGO nanocomposite was synthesized from GO and a 3D coordination complex precursor, cobalt benzoate dihydrazinate [Co(C₆H₅COO)₂(N₂H₄)₂], which was prepared according to the following reaction:

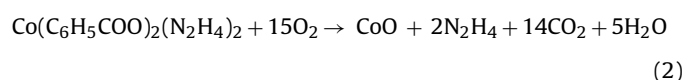
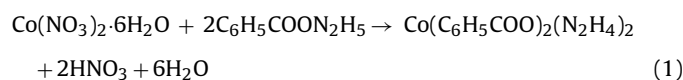


Fig. 1 outlines the fabrication of Co₃O₄ nanospindles decorated RGO nanocomposite for nitrite sensing. Decomposition pathway of the precursor and the deposition of Co₃O₄ nanospindles on the RGO surface started at a relatively low temperature of ca. 200 °C. The precursor decomposed completely, losing N₂H₄, CO₂, and H₂O. 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

Download English Version:

<https://daneshyari.com/en/article/7144336>

Download Persian Version:

<https://daneshyari.com/article/7144336>

[Daneshyari.com](https://daneshyari.com)