Journal of Colloid and Interface Science 509 (2018) 153–162

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

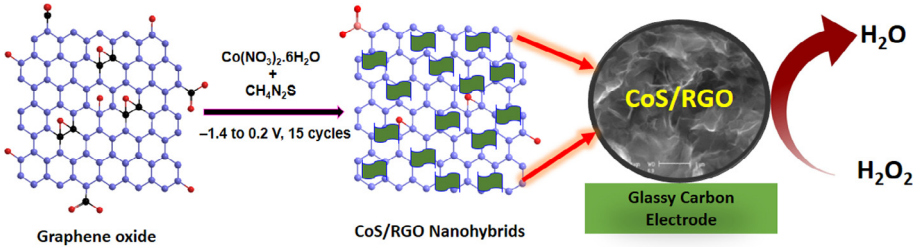
Regular Article

Electrochemical co-preparation of cobalt sulfide/reduced graphene oxide composite for electrocatalytic activity and determination of H_2O_2 in biological samples

Subbiramaniyan Kubendhiran [a], Balamurugan Thirumalraj [a], Shen-Ming Chen [a,*], Chelladurai Karuppiah [b]

[a] Electroanalysis and Bioelectrochemistry Lab, Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei 106, Taiwan, Republic of China
[b] Battery Research Center of Green Energy, Ming Chi University of Technology, New Taipei City 24301, Taiwan, Republic of China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 July 2017
Revised 18 August 2017
Accepted 27 August 2017
Available online 30 August 2017

Keywords:
Cobalt sulfide
Reduced graphene oxide
Electrochemical method
H_2O_2 sensor
Electrocatalytic activity
Real sample analysis

ABSTRACT

In this work, we describe a simple approach for the preparation of cobalt sulfide/reduced graphene oxide (CoS/RGO) nanohybrids via single step electrochemical method. The electrocatalytic activity of the CoS/RGO nanohybrids was evaluated towards the detection hydrogen peroxide (H_2O_2). The physiochemical properties of the prepared composite was characterized by means of field emission scanning electron microscopy, high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy and X-ray powder diffraction patterns. The CoS/RGO modified electrode showed superior electrocatalytic activity towards the detection of H_2O_2. The amperometric (*i-t*) studies revealed that the CoS/RGO performed well by attaining a wide linear response range of H_2O_2 from 0.1 to 2542.4 μM with a lower detection limit 42 nM and the sensitivity of 2.519 μA μM^{-1} cm^{-2}. Meanwhile, the CoS/RGO nanohybrids exhibited good selectivity, rapid and stable response towards H_2O_2. The practical applicability of the sensor was successfully evaluated in human serum and urine samples with satisfactory recoveries.

1. Introduction

Transition metal sulfides/oxides are act as a highly efficient and low cost material for various potential applications particularly in the field of electrocatalysis and energy storage devices [1–5]. Specifically, cobalt sulfide (CoS), is a phase dependent catalyst e.g., $Co_{1-x}S$, CoS, CoS_2, Co_9S_8, and Co_3S_4, have been widely used in different potential applications such as lithium-ion batteries [6–12], solar cells [13–15], supercapacitors [16–18], electrochemical sensor [19,20] hydrogen evaluation and oxygen reduction reaction [21–28]. Besides, cobalt sulfides have also been considered as an important material due to their distinctive magnetic, catalytic, electrical properties and their potential applications for

* Corresponding author.
E-mail address: smchen78@ms15.hinet.net (S.-M. Chen).

http://dx.doi.org/10.1016/j.jcis.2017.08.087
0021-9797/

hydrodesulfurization and hydrodearomatization in many industrial fields [6–8]. Moreover, various methods have been adapted for the synthesis of CoS nanohybrids such as hydrothermal synthesis, plasma treatment, solvothermal synthesis, pyrolysis and so on. However, these methods have some drawbacks, such as high cost, hazardous chemicals usage, doing experiments in higher temperature, time consuming and following the tedious protocol. On the other hand, the electrochemical method has tremendous advantage for material synthesis, because it is very simple and low cost method also it is less time consuming process and do not required high temperatures. Hence, in this work, we aims to use electrochemical method for the single step preparation of CoS/RGO nanohybrids [17].

Carbon based materials such as carbon aerogel [29], activated carbon [30], porous carbon [31], graphene [32], etc., offers several advantages over decades due to their specific high surface area, good conductivity, low cost and environmental friendly. Reduced graphene oxide (RGO), is a two dimensional sp^2 graphitized carbon nanosheets, provides ultrahigh surface area with strong mechanical strength and good chemical stability [33]. In addition, the functionalities that present in the RGO can be used for the nucleation and anchoring the nanocrystals to achieve the covalent attachment of the hybrid nanomaterials [34,35]. Previous studies proved that graphene supported metal oxides, hydroxides, and sulfides exhibited superior electrochemical performance for various potential applications including electrochemical sensors [26–28,36]. Moreover, the metal sulfide based H_2O_2 sensor has been reported previously, but few reports are available in the literature using CoS modified electrode. Based on these, we used CoS and RGO as an active material for the effective and enhanced the electrocatalytic activity towards the detection of H_2O_2. Hence, in this work, we prepared the CoS/RGO nanohybrids and used it for the non-enzymatic hydrogen peroxide sensor application.

Hydrogen peroxide (H_2O_2) is simplest colorless peroxide and play a crucial role in biological system. Besides, it is widely applicable in pharmaceutical industries, clinical studies, environmental protection, food, and many other clinical process [37]. In addition, H_2O_2 is a reactive oxygen species and induced some disorders such as cancer, Alzheimer's disease and Parkinson's disease [33,38]. Therefore, the detection of H_2O_2 in industrial and biological samples is inevitable. To date, numerous analytical methods have been utilized for the rapid and accurate detection of H_2O_2 including fluorescence, chemiluminescence, fluorimetry, photometry, spectrophotometry and electrochemical methods [38]. Among them, the electrochemical methods are more suitable for the low level and accurate detection of H_2O_2 because of their remarkable properties such as fast response, simple and low cost, higher sensitivity and user friendly. Hence, in this study, we focus to use the electrochemical method for the detection of H_2O_2.

In the present work, we report a facile approach for the preparation of CoS/RGO nanohybrids as an effective electrode material for non-enzymatic H_2O_2 sensor. The CoS/RGO nanohybrids were prepared by simple step electrochemical process, where cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), and thiourea (CH_4N_2S) used as cobalt and sulfide precursor, respectively. To improve the electrocatalytic activity of the prepared material, we have optimized the deposition cycles and concentration of cobalt precursor. Interestingly, the optimized CoS/RGO nanohybrid exhibited an excellent electrocatalytic activity towards the H_2O_2 determination. In addition, the as-prepared CoS/RGO nanohybrids could be used for the detection of H_2O_2 in human serum and urine samples for practical applications.

2. Experimental

2.1. Materials

Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), thiourea (CH_4N_2S), monosodium phosphate (NaH_2PO_4) and disodium phosphate (Na_2HPO_4) were purchased from Aldrich. Hydrogen peroxide (H_2O_2) was obtained from Wako chemical industries, Taiwan. Human serum was collected from valley biomedical, Taiwan product & services, Inc and urine sample was collected from one healthy person in Taipei Tech. The supporting electrolyte, 0.05 M phosphate buffer saline (PBS) was prepared by using 0.05 M Na_2HPO_4 and NaH_2PO_4 solutions in double distilled water. All other chemicals used were of analytical grade.

2.2. Instruments

The crystallographic structure of as-prepared CoS and CoS/RGO nanohybrids were examined by powder X-ray diffraction (XRD) using XPERT-PRO (PANalytical B.V., The Netherlands) with CuKα radiation (λ = 1.5406 Å). The surface morphological of the prepared composites were characterized using HitachiS-3000H field emission scanning electron microscope (FE-SEM) scanning electron microscope, and the elemental mapping was performed using a HORIBA EMAX X-ACT equipped with a HitachiS-3000H microscope and high resolution-transmission electron microscopy (HR-TEM, JEOL, JEM-3000F) operated at 300 kV. Raman spectrometer (Dong Woo 500i, Korea) equipped with a 50× objective and a charge-coupled detector used to record the Raman spectra. The X-ray photoelectron spectroscopy (XPS) was recorded using a XPS ULVAC-PHI PHI 5000 Versa Probe. Electrochemical measurements (CV, LSV and amperometry) were recorded using a computerized CHI410a and CHI1205b analyzer at room temperature using a three electrode system which containing GCE as working electrode; Ag/AgCl (sat. KCl) as reference electrode; platinum wire as a counter electrode. Electrochemical impedance spectra were recorded using IM6ex ZAHNER (Kroanch, Germany).

2.3. Electrochemical preparation of CoS/RGO nanohybrids

Graphite oxide (GO) was synthesized using modified Hummer's method [33]. The CoS/RGO nanohybrids were prepared by simple electrochemical co-preparation method. Briefly, the GCE was polished using alumina slurry (0.03 μm) with an assist polishing kit and washed with ethanol followed by double distilled water. About 6 μL of GO dispersion (1 mg/mL) was drop coated on the surface of pre-cleaned GCE and dried at room temperature. Then, the GCE was transferred into a solution containing 5 mM $Co(NO_3)_2{\cdot}6H_2O$ and 0.75 mM CH_4N_2S for 15 consecutive cycles with an applied potential range of −1.4 to 0.2 V vs. Ag/AgCl at 50 mV/s. Finally, the CoS/RGO modified GCE was washed with double distilled water and allowed to dry at room temperature. In addition, the preparation method was optimized by varying the solution concentration and deposition cycles and the detail discuss is provided in the results and discussion. For the comparison, the RGO and CoS modified electrodes were prepared individually using the same procedure. The schematic representation of overall procedure for the preparation of CoS/RGO nanohybrid was illustrated in Scheme 1. In addition, the electrochemical mechanism of CoS deposition is described in the following equations [17].

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (1)$$

$$SC(NH_2)_2 + 2OH^- \rightarrow S^{2-} + OC(NH_2)_2 + H_2O \quad (2)$$