Journal of Colloid and Interface Science 468 (2016) 51–56

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

Editor's Choice

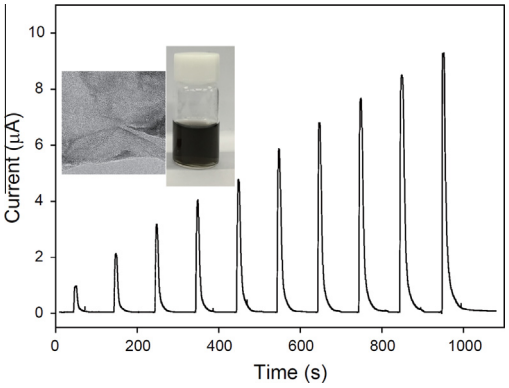
Polyoxometalate-grafted graphene nanohybrid for electrochemical detection of hydrogen peroxide and glucose

MinHo Yang [a], Dong Seok Kim [b], Tae Jae Lee [a], Seok Jae Lee [a], Kyoung G. Lee [a,*], Bong Gill Choi [b,*]

[a] Department of Nano Bio Research, National NanoFab Center (NNFC), Daejeon 34141, Republic of Korea
[b] Department of Chemical Engineering, Kangwon National University, Samcheok 25913, Republic of Korea

GRAPHICAL ABSTRACT

Highly efficient electrocatalytic polyoxometalate was directly deposited on polymeric ionic liquid (PIL)-functionalized reduced grapheme oxide, leading to high electrocatalytic activity for the electrochemical detection of H_2O_2 and glucose in flow-injection biosensor device.



ARTICLE INFO

Article history:
Received 16 December 2015
Revised 18 January 2016
Accepted 20 January 2016
Available online 22 January 2016

Keywords:
Polyoxometalate
Graphene
Nanohybrid
Ionic liquid
Electrochemical sensor

ABSTRACT

The electrochemical performances of electrochemical biosensors largely depend on electrode characteristics, such as size, composition, surface area, and electron and ion conductivities. Herein, highly efficient electrocatalytic polyoxometalate (POM) was directly deposited on polymeric ionic liquid (PIL)-functionalized reduced graphene oxide (rGO) in a simple manner. The nano-sized POM with PIL functional groups was uniformly distributed on the surface of rGO sheets. The unique nanostructure of the resultant POM-g-rGO nanohybrids enabled well-defined multiple redox reaction of POMs and rapid electron transfer. In particular, as-prepared nanohybrids demonstrated high electrocatalytic activity for the electrochemical detection of H_2O_2 and glucose molecules in flow-injection biosensor device with high sensitivity, rapid response time, and low detection limit.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Nanostructured materials have been extensively employed to prepare an electrode for electrochemical devices due to their large surface areas, high mass transport rate, and excellent

* Corresponding authors.
E-mail addresses: kglee@nnfc.re.kr (K.G. Lee), bgchoi@kangwon.ac.kr (B.G. Choi).

http://dx.doi.org/10.1016/j.jcis.2016.01.047
0021-9797/© 2016 Elsevier Inc. All rights reserved.

electrocatalytic properties [1,2]. Recently, the integration of conductive carbon materials and metal (or metal oxide) nanoparticles is of great interest in the material science and practical applications [3–6]. Such nanohybrid materials provide great opportunities for the fine tuning multiple functionalities [7]. In particular, nanoparticles anchored on graphene sheets are one of the most widely used nanohybrid materials for electrochemical biosensor applications targeting hydrogen peroxide, NADH, ascorbic acid, dopamine, and others [8–12]. Graphene acts as an excellent support on which to deposite nanoparticles and a conducting pathway to assist a fast electrochemical kinetics during electrocatalytic reactions [13]. On the other hand, of the various electrocatalytic nanoparticles, polyoxometalates (POMs) are considered as versatile nano-building blocks for the construction of nanohybrid materials due to their multiple charge transfer reactions and unique structural, electronic, and optical properties [14]. POM-based nanohybrid materials are particularly effective electrochemical catalysts in the detection of nitrate, iodate, bromate, and H_2O_2 [15–18]. Owing to this electrocatalytic effect of POMs toward reduction of H_2O_2, POM-based nanohybrid materials are also suitable for use in electrochemical glucose biosensors. Despite these attractive features of POMs, high solubility of POMs in aqueous solution limit their direct use in electrochemical systems [19], and thus, main strategy is to prepare POM-based nanohybrid materials.

Herein, we describe the electrocatalytic characteristics of a POM-grafted reduced graphene oxide (POM-g-rGO) nanohybrid for development of electrochemical sensors for detection of H_2O_2 and glucose molecules. In preparation of POM-g-rGO nanohybrids, a polymeric ionic liquid (PIL) was employed to link POMs to rGO. This process not only prevents rGO sheet aggregation, which commonly occurs during the reduction of GO sheets, but also facilitates charge transfer at the electrode/electrolyte interface. The electrochemical sensing performances of POM-g-rGO nanohybrids were thoroughly examined by incorporating them as electrodes in a injection-flow system. The POM-g-rGO nanohybrids showed high electrocatalytic activities toward H_2O_2 and glucose with high sensitivity, low detection limit, and rapid response time.

2. Material and methods

2.1. Materials

All chemicals were used a received without further purification. The GO was synthesized from natural graphite (Sigma Aldrich, <20 μm) using a modified Hummers methods [20]. The rGO was prepared by the chemical reduction of GO using hydrazine hydrate. The PIL, poly(1-vinyl-3-ethylimidazolium bromide), was prepared according to previously reported procedure [21]. Hydrazine monohydrate (64–65%), phosphomolybdic acid hydrate ($H_3[PMo_{12}O_{40}]\cdot xH_2O$, denoted by POM), potassium hexacyanoferate (III) ($K_3Fe(CN)_6$), and potassium hexacyanoferate (II) trihydrate ($K_4Fe(CN)_6\cdot 3H_2O$), glucose oxidase (GOx, EC1.1.3.4, from *Aspergillus niger*, ~200 U/mg), β-D-(+)-glucose, ascorbic acid (AA), and uric acid (UA) were obtained from Sigma–Aldrich. Hydrogen peroxide (H_2O_2, 30% w/w) was purchased from Junsei.

2.2. Preparation of the POM-g-rGO nanocomposites

To prepare POM-g-rGO, aqueous a PIL-GO suspension was prepared by mixing GO (5 mg) with PIL (10 mg) in 20 mL of deionized (DI) water. Chemical reduction of GO was conducted by adding 20 μL of hydrazine monohydrate and heating at 85 °C for 24 h. The stable black-colored PIL-rGO suspension obtained was filtered through an Anodisc membrane filter (pore size 0.20 μm, Whatman) and washed extensively with DI water to remove any residual hydrazine and unbound PIL. After drying under ambient conditions, the PIL-rGO was re-dispersed in DI water and mixed with excess POM. The resulting suspension was vigorously stirred overnight to yield POM-g-rGO by anion exchange. Finally, POM-g-rGO was collected by filtration and thoroughly washed with DI water to remove any unbound POM.

2.3. Preparation of nanohybrid-modified electrode and immobilization of GOx

Before surface modification, glassy carbon electrode (GCE, dia 3 mm) was polished with 0.05 μm alumina sequentially, rinsed with DI water, sonicated in water bath and dried in air. Then, 5 mg of POM-g-rGO was first suspended in 10 mL of DI water and sonicated for 1 h. Next, a 5 μL of POM-g-rGO suspension was dropped onto the surface of GCE. After drying in air, an aliquot of 5 μL Nafion solution (1 wt% in propanol) was casted on the layer of POM-g-rGO in order to entrap POM-g-rGO. The as-prepared electrode was immersed in DI water for 1 h to wet the Nafion layer thoroughly before use. For immobilization of GOx, 6 μL of 3 mg/mL GOx was dropped on the surface of the POM-g-rGO electrode. A 5 μL Nafion solution was dropped on the enzyme electrode (GOx/POM-g-RGO) and dried for 24 h at 4 °C to form a uniform structure. After drying, the prepared enzyme electrode was washed with copious PBS to remove the non-immobilized GOx.

2.4. Fabrication of microfluidic electrochemical sensor

Microfluidic sensor was fabricated by integrating a fluidic channel substrate with POM-g-rGO or GOx/POM-g-RGO nanohybrids. The microfluidic device was based on plastic substrates with an oval-shaped flow channel. The device was equipped with two holes of inlet and outlet, an Ag/AgCl reference electrode, and a Pt counter electrode. A syringe pump (KD scientific, KDS 100) and injection valve (Rhoedyne, model 7725i) with a HPLC-grade sample loop was used to pump the carrier solution (20 μL) and to inject H_2O_2 and glucose for the microfluidic detection system, respectively.

2.5. Characterization

Transmission electron microscopy (TEM) images were obtained using a field-emission TEM (JEM2100F, JEOL Ltd.) operated at 200 kV. Scanning electron microscopy (SEM) images were obtained using a field emission scanning electron microscope (S-4800, Hitachi). X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo MultiLab 2000 system. An Al Mgα X-ray source at 200 W was used with pass energy of 20 eV and a 45° takeoff angle in a 10^{-7} Torr vacuum analysis chamber. All electrochemical measurements were performed on a CHI 760E electrochemical workstation (CH Instruments) using a conventional three-electrode system. Flow injection mode in microfluidic sensor was performed with chronoamperometric technique. All flow injection measurements were carried out at a flow rate of 1 mL/min. All potentials were collected at room temperature, and the as-obtained data were within the error range of ±1%.

3. Results and discussion

Fig. 1a displays typical photographs of rGO and POM-g-rGO dispersed in aqueous solution. The rGO was not dispersed in water, but the POM-g-rGO was well dispersed in water, because of its abundant hydrophilic anionic sites of POMs. In addition, the imidazolitum cations of PIL were interacted with rGO sheets through cation–π interaction, while Br^- anions of PIL were exchanged with

Download English Version:

https://daneshyari.com/en/article/606385

Download Persian Version:

https://daneshyari.com/article/606385

Daneshyari.com