Electrochimica Acta 172 (2015) 52–60

Contents lists available at ScienceDirect

Electrochimica Acta

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

Facile Synthesis of Boron-doped Graphene Nanosheets with Hierarchical Microstructure at Atmosphere Pressure for Metal-free Electrochemical Detection of Hydrogen Peroxide

Min-Hsin Yeh [a], Yan-Sheng Li [b], Guan-Lin Chen [b], Lu-Yin Lin [c], Ta-Jen Li [a], Hui-Min Chuang [a], Cheng-Yu Hsieh [d], Shen-Chuan Lo [d], Wei-Hung Chiang [b,**], Kuo-Chuan Ho [a,e,*]

[a] Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan
[b] Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan
[c] Department of Chemical Engineering and Biotechnology, National Taipei University of Technology (Taipei Tech), Taipei 10608, Taiwan
[d] Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu 30140, Taiwan
[e] Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

ARTICLE INFO

Article history:
Received 30 October 2014
Received in revised form 31 January 2015
Accepted 31 January 2015
Available online 2 February 2015

Keywords:
Boron-doped
Electrochemical sensor
Graphene
Hydrogen peroxide reduction reaction
Koutecký–Levich equation

ABSTRACT

Hydrogen peroxide (H_2O_2) is an essential mediator for most of the oxidative biological reactions in enzyme-based biosensor systems, such as glucose oxidase, cholesterol oxidase, and alcohol oxidase. Synthesis of new catalysts to detect the concentration of H_2O_2 more precisely is indispensable for enzyme-based electrochemical biosensors. In this study, boron-doped graphene nanosheets (BGNs) with 2.2 atomic percentage (at%) boron doping level and a hierarchical microstructure were synthesized by an atmospheric-pressure carbothermal reaction as a noble-metal free catalyst for sensing H_2O_2. The isolated boron atoms on the BGNs surface act as the electrocatalytic sites by transferring charges to neighbor carbon atoms, and the hierarchical microstructure provides multidimensional electron transport pathways for charge transfer and therefore enhances the electrocatalytic ability. BGNs possess a higher reduction current in the cyclic voltammetry (CV) measurement than that of pristine graphene nanosheets (GNs) over the detection range of 0.0 to 10.0 mM at −0.4 V (*vs.* Ag/AgCl). The BGNs modified electrochemical sensor shows a linear range from 1.0 to 20.0 mM of H_2O_2 with a sensitivity of $266.7 \pm 3.8\ \mu A\ mM^{-1}\ cm^{-2}$ and limit of detection (LOD) of 3.8 μM at a signal-to-noise (S/N) ratio of 3. The beneficial hierarchical microstructure and the synergetic effects arising from doping boron in GNs accomplish the better performance of the BGNs modified electrochemical sensor.

1. Introduction

Hydrogen peroxide (H_2O_2) is one of the products in vivo metabolism and an important mediator in physiological processes, where it serves as a messenger during cellular signal transduction [1–4]. H_2O_2 can be quantitatively analyzed by several techniques, including spectral analysis [5], chemi-luminescence-based methods [6], and electrochemical methods [7]. The electrochemical method is the most promising technique because of its rapid response, cost effectiveness and real-time monitoring abilities [8]. Electrochemical sensors for detecting H_2O_2 have thus gained remarkable attention owing to their practical applications in clinical diagnosis, biomedical and environmental monitoring. The design of electrochemical sensors with excellent electron transduction and favorable selectivity relies upon the use of suitable chemicals and matrices [9–14].

There are many advantages for applying noble metallic nanoparticles as the catalyst for electrochemical sensors, *e.g.*, high electrochemical surface area, good electron conductivity, and reduced over-potential, which can suppress the interference from other species [15]. Also, nanoparticle-based sensors are able to cope with diverse working conditions and retain the electrocatalytic activity of the catalyst after repeated usage. Self-

* Corresponding author at: National Taiwan University, Department of Chemical Engineering, No. 1, Sec. 4, Roosevelt Road, Taipei 10617, Taiwan. Tel.: +886 2 2366 0739; fax: +886 2 2362 3040.
** Corresponding author at: National Taiwan University of Science and Technology, Department of Chemical Engineering, No.43, Sec. 4, Keelung Road, Taipei 10607, Taiwan. Tel.: +886 2 2737 6647; fax: +886 2 2737 6644.
E-mail addresses: whchiang@mail.ntust.edu.tw (W.-H. Chiang), kcho@ntu.edu.tw (K.-C. Ho).

http://dx.doi.org/10.1016/j.electacta.2015.01.210
0013-4686/

assembled Pt-based electrodes, such as Pt nanoparticles [16], Pt black [17], Pt nanowires [18], PtPd [19] and PtIr [20] bimetallic nanoparticles, possess high activity and stability, but Pt is very expensive in considering of the cost-effective fabrication of electrochemical sensors. Therefore, replacement of Pt with other cheaper materials, including other kind of relatively cheaper metals [21], carbonaceous materials [22–24], inorganic compounds [25,26], conducting polymers [27], and composites with metallic-based materials on carbon supports [28–38], is required for reducing the production cost, especially when the production is in mass scale. Table 1 is a partial list on the performances of H_2O_2 sensors with noble metal-free catalysts and the comparisons are also made with our current study. Therefore, improving the electrocatalytic property and electrical conductivity of noble metal free catalyst is essential for realizing the low-cost and effective electrochemical sensors.

Ever since Nobel laureates Novoselov and Geim have discovered the two dimensional graphene in 2004 [39], it has been introduced in various electrochemical devices, such as sensors [40], lithium-ion batteries [41], dye-sensitized solar cells [42–44], and capacitors [45], owing to the remarkable electrical, optical, thermal, and mechanical properties of graphene as well as its extraordinarily high surface area ($\sim$2,630 $m^2 g^{-1}$) [46]. Doping graphene with foreign heteroatoms, *e.g.*, nitrogen, boron, sulfur and phosphorus, is one of the effective approaches to tailor its electronic properties and electrochemical activities [47]. Chemical doping of boron is effective because boron can create defects in the nearby sites and induce the uneven charge distribution, which can facilitate the charge transfer between neighboring carbon atoms and enhance the electrochemical performance [48]. Adjizian *et al.* illustrated boron-doped multi-wall carbon nanotubes as a potential candidate for gas detection [49]. Kim *et al.* prepared substitutionally boron-doped single-layer graphene by using the mechanical exfoliation of boron-doped graphite [50]. Recently, Yang *et al.* synthesized nitrogen and boron co-doped graphene as the catalyst for H_2O_2 detection by using a microwave-assisted synthesis method to obtain enhanced H_2O_2 electrocatalytic activity [51]. However, it is still lacking a facile synthesis of B-doped graphene at atmospheric-pressure and a systematic study on the electrochemical detection of H_2O_2 using B-doped graphene.

In this work, a noble-metal free catalyst, boron-doped graphene nanosheets (BGNs) of 2.2 atomic percentage (at%) boron doping level, with a hierarchical microstructure was synthesized using an atmospheric-pressure carbothermal reaction for sensing H_2O_2. Pristine graphene nanosheets (GNs) was also synthesized as the comparison for investigating its electrochemical performance without boron doping effect. The isolated boron atoms provide electrocatalytic sites and the hierarchical microstructure acts as multidimensional electron transport pathways to enhance the charge transfer and improve the electrocatalytic ability. A higher hydrogen peroxide reduction reaction (HPRR) current density for BGNs was obtained by using the cyclic voltammogram (CV) measurement over the detection range of 0.0 to 10.0 mM at −0.4 V (*vs.* Ag/AgCl). The kinetic properties of reducing H_2O_2 on GCE modified with GNs and BGNs films were investigated quantitatively in terms of heterogeneous rate constant (k) and effective electroactive surface area (A), by using a Koutecký–Levich equation through the rotating disk electrode (RDE). The BGNs modified electrochemical sensor shows a linear range from 1.0 to 20.0 mM of H_2O_2 with a good sensitivity of 266.7 ± 3.8 μA mM^{-1} cm^{-2} and limit of detection (LOD) of 3.8 μM at a signal-to-noise (S/N) ratio of 3, compared to GNs modified one (sensitivity of 118.5 ± 3.0 μA mM^{-1} cm^{-2} and LOD of 129.8 μM). The chemical and physical properties of BGNs and GNs were characterized by using high resolution transmission electron microscopy (HR-TEM), scanning electron microscopy (SEM), electron energy loss spectrum (EELS), X-ray photoelectron spectroscopy (XPS), and micro Raman spectroscopy. It is also noteworthy from a practical point of view that the developed atmospheric-pressure BCN synthesis method is amenable to industrial-scale production since it avoids the need for a vacuum system.

2. Experimental

2.1. Materials

Boron trioxide powder (B_2O_3, ACS reagent, ≧99%) was purchased from Alfa Aesar, A Johnson Matthey Company (Lancashire, United Kingdom). Absolute ethanol (≧99.8%), hydrogen peroxide (30 wt%, PERDROGEN™), Nafion® 117 solution (5 wt% in a mixture of lower aliphatic alcohols and H_2O), potassium chloride (KCl, ≧99%), sodium phosphate monobasic monohydrate ($NaH_2PO_4{\cdot}H_2O$, ACS reagent, 98.0–102.0%), and sodium phosphate dibasic heptahydrate ($Na_2HPO_4{\cdot}7H_2O$, ACS reagent, 98.0–102.0%) were purchased from Sigma–Aldrich, Inc. (St. Louis, MO, USA). All chemicals were used as received without further treatment. Deionized water with a resistivity ≧18.2 MΩ-cm was produced by

Table 1
A partial list of H_2O_2 sensors with noble metal-free catalysts and their performance parameters.

Modified electrodes	Sensitivity (μA mM^{-1} cm^{-2})	Linear Range	LOD	Reference
GN/MWCNT[a]	32.91	0.02∼2.1 mM	9.4 μM	[24]
Fe_2O_3/CP[b]-epoxy	N.A.	0.2∼5.5 mM	3.5 μM	[28]
MnO_2/CP-epoxy	N.A.	0.12∼10.3 μM	1.4 μM	[29]
GN/PB[c]	196.6	0.02∼0.2 mM	1.9 μM	[30]
rGO[d]/nitrobenzene/PB	300.16	1.2 μM∼15.25 mM	0.4 uM	[31]
MWCNT/PB	153.7	0.01∼0.4 mM	0.57 uM	[32]
rGO/ZnO	13.49	1.0∼22.48 μM	0.02 μM	[33]
rGO/Fe_3O_4	688.0	0.1∼6.0 mM	3.2 μM	[34]
Exfoliated GO/Co_3O_4	560.0	1∼5000 μM	0.3 μM	[35]
Polydopamine/GN form	169.7	0.4∼660 μM	80 nm	[36]
GN/Fe_3O_4	132.0	5∼3810 μM	0.6 μM	[37]
CuO/MWCNT	N.A.	0.5∼82 μM	0.16 μM	[38]
GNs	118.5 ± 3.0	1∼20 mM	128.9 μM	This work
BGNs	266.7 ± 3.8	1∼20 mM	3.8 μM	This work

N.A. = not available.
[a] MWCNT = multi-walled carbon nanotube.
[b] CP = carbon powder.
[c] PB = Prussian blue.
[d] rGO = reduced graphene oxide.