



Electrocatalytic performance of silica nanoparticles on graphene oxide sheets for hydrogen peroxide sensing

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ABSTRACT

Graphene oxide–silica nanoparticles composite was successfully synthesized for the nonenzymatic detection of H_2O_2 . Characterization was performed by FT-IR, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The composite consisting of graphene oxide and silica nanoparticles exhibited good electrochemical activity for the detection of H_2O_2 in alkaline medium. Low detection limit ($2.6 \mu\text{M}$), good reproducibility ($R^2 = 0.997$) and a wide linear range ($5.22 \mu\text{M}$ – 10.43 mM) were obtained based on amperometric study. These results suggest that the catalytic property of silica nanoparticles towards H_2O_2 could be enhanced with graphene oxide, making these composites promising novel materials for the development of nonenzymatic sensors.

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1. Introduction

Hydrogen peroxide (H_2O_2) is a simple compound in nature but of great importance in clinical, sterilization, pulp and paper bleaching, food production and many other fields. In biological system, H_2O_2 is involved in intracellular pathways and several biological events, which can be linked to several diseases [1]. It is also a side product generated from some classic biochemical reactions catalyzed by enzymes. Therefore, the investigation on H_2O_2 detection is essential for both academic and industrial purposes. Many conventional methods have been developed for H_2O_2 determination, including chemiluminescence [2], fluorescence [3] and spectrophotometry [4], which are either costly, complex or time consuming. In contrast, electrochemistry can be cost effective, simple, rapid, sensitive and portable [5–9].

In recent years, the renewed interest in H_2O_2 detection is related to the new application of graphene on electrochemical sensor [6]. Graphene is reported as an ideal platform for electrochemical research because of its 2-D structure, unique optical, electronic and chemical properties. In addition, graphene oxide (GO) is one of the most important derivatives of graphene. With a large specific surface area and oxygen functional groups on the basal planes and edges, GO is well suited for the immobilization of large amounts of substances like metal or metal dioxide nanoparticles, polymer, and biomolecules [7–9]. Much attention has been focused on the fabrication of graphene related nanocomposites starting

from GO to extend the application of graphene in H_2O_2 detection. For example, Liu's group reported an ultrasensitive H_2O_2 biosensor, which is fabricated by immobilizing graphene–gold nanocomposite, CdTe–CdS, gold nanoparticles and horseradish peroxidase on the gold electrode [9]. This biosensor demonstrated a high sensitivity at a low concentration range from 0.1–12 nM because of the electrocatalytic synergy of graphene–gold nanoparticles, CdTe–CdS and peroxidase. However, there are several disadvantages of enzymatic sensor, such as complicated immobilization procedure, instability and high cost of enzyme. In order to overcome these problems, nonenzymatic electrodes have been developed by functionalizing graphene with metal alloys, metal or metal oxide nanoparticle and semiconductor nanoparticles [7,8,10,11]. For example, Wang's group fabricated a graphene/Prussian blue (PB) composite modified glassy carbon electrode. The PB nanomaterial combined with graphene exhibited great catalytic performance in the detection of H_2O_2 at a positive potential, with a high sensitivity and a good linear response in the range of 0.02–0.2 mM [10]. The size and shape of PB were reported to be important to the electrocatalytic performance for H_2O_2 reduction. Manganese dioxide (MnO_2) anchored on the surface of graphene oxide sheets was reported to show good electrocatalytic activity to H_2O_2 in alkaline medium, which showed a linear range from 5 to 600 μM [8]. Sun's group successfully synthesized silver nanoparticles (Ag NPs)–GO composite, and reported its good catalytic activity toward H_2O_2 reduction [11]. It was noted that the nanoparticles attached on GO toward H_2O_2 determination were almost all metals and metal oxides. It was reported that silica nanoparticles had been successfully attached on graphene oxide sheets (GO) via “loading from” [12,13] or “loading to” approaches [14,15]. Generally, the “loading

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from” approach means silica nanoparticles grow from the active sites on the surfaces of graphene oxide sheets through an in situ growth process, while the “loading to” approach indicates silica nanoparticles formed separately prior to the coupling to GO through physical and chemical linkage. The “loading to” approach is considered superior in the control over silica nanoparticles effects such as particle size and density. Herein, uniform spherical silica nanoparticles were prepared and attached on GO by “loading to” approach and further investigated. Currently in the literature, the “loading to” approach though chemical linkage has been demonstrated via an aqueous synthesis method with EDC/NHS (N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride/N-hydroxysuccinimide) as a coupling agent, or an organic phase synthesis method via DCC (N,N'-dicyclohexylcarbodiimide) as a coupling agent in DMF (dimethylformamide). Liu et al. found the high concentration of EDC (>0.1 mM) could cause the aggregation of GO [14]. Therefore, we proposed an organic phase synthesis method, since a high concentration of coupling agent could be employed. Moreover, the coupling reaction between acyl-chloride of GO and amine group of silica had not been attempted previously. The method developed in this study could be an alternative approach to combine GO and uniform silica nanoparticles which may overcome the problem of aggregation of GO.

In addition, there are limited reports on the modification of GO with non-metallic oxides (e.g. silica nanoparticles), which has been only demonstrated in the application of solid phase extraction [14]. In this study, the performance of GO modified with silica nanoparticles in an electrochemical sensor toward hydrogen peroxide was investigated. Silica NPs possess several advantages such as good water solubility, no toxicity, biocompatibility and stability, which were commonly employed as a support for loading biomolecules or metal nanoparticles in sensing application. To the best of our knowledge, there are limited reports on the electrocatalytic study of silica nanoparticles (silica NPs) in the electrochemical sensor. In this paper, we prepared GO/Silica NPs composite (GSnano) for H₂O₂ detection. Furthermore, GSnano with chitosan (CS) modified glassy carbon electrode (GCE) was also investigated and found to exhibit good electrocatalytic activity to H₂O₂, which offer great promise for new class of nonenzymatic biosensor.

2. Experiment

2.1. Chemicals and apparatus

All chemicals were of analytical grade. Natural graphite flake (~325 mesh, 99.8%) was purchased from Alfa Aesar (Ward Hill, MA) and used to prepare GO. Sodium nitrate, concentrated sulfuric acid (95%), potassium permanganate, hydrogen peroxide (30%), hydrogen chloride (HCl), ethanol, ammonium hydroxide, tetraethoxysilane (TEOS), (3-aminepropyl)triethoxysilane (APTES), thionyl chloride (SOCl₂), dimethylformamide (DMF), triethylamine, chitosan, acetic acid were acquired from Sigma Aldrich (St. Louis, MO). All the solutions were prepared by using ultrapure water, and pH values of the buffer solutions were determined with Metrohm 827 pH lab meter (Herisau, Switzerland).

The scanning electron microscopic (SEM) images were carried out by JEOL_JSM 6701F field-emission microscope (Tokyo, Japan). The transmission electron microscopic (TEM) images were performed on JEOL JEM 3010 microscope (Tokyo, Japan). The C 1s and Si 2p spectra of the X-ray photoelectron spectroscopy (XPS) were measured by Kratos AXIS Ultra^{DL} (Kratos Manchester, UK) under a pressure of 5×10^{-9} Torr using mono Al K α radiation (15 kV/5 mA). The position of the most intense C—C peak was taken as 284.5 eV. Electrochemical experiments were performed

at room temperature on an IviumSoft (Fernandina Beach, FL) electrochemical workstation with a conventional three-electrode system. A bare or modified glassy carbon electrode was used as the working electrode. The Ag/AgCl electrode and a platinum wire were used as the reference electrode and auxiliary electrode, respectively. All the measurements were carried out at room temperature (25 ± 0.5 °C).

2.2. Preparation of GSnano

Firstly, GO containing the carboxylic acid groups was synthesized from the graphite by a modified Hummers method according to Zhang et al. [16,17]. The powder flake graphite (1.0 g) and sodium nitrate (0.5 g) was mixed with 24 ml of concentrated sulfuric acid (95%) in a 500 ml round-bottom flask under constant vigorous stirring. The mixture was continuously stirred for 30 min in ice bath. Then potassium permanganate (3.0 g) was added to the mixture slowly over 2 h to keep the reaction temperature lower than 20 °C. The ice bath was removed and the mixture was stirred at room temperature overnight. The mixture is homogeneous and pasty with a light brownish color. Then, 45 ml water was slowly added to the paste. The mixture was stirred for 30 min as the temperature was increased to 98 °C. The diluted mixture was stirred for 1 day under 98 °C. Finally, 10 ml of 30% H₂O₂ was added to the mixture. The color of the suspension changed from light brown to more deep brown. For the purification, the suspension was washed and centrifuged with 5% HCl and then distilled water several times. GO samples were dried in a vacuum oven and obtained as a small piece of film.

Uniform spherical silica NPs with diameters of 64 ± 6 nm were then prepared by the STÖBER method [18,19]. 80 ml of ethanol, 4.85 ml of H₂O and 3.6 ml of NH₃H₂O were added into a 250 ml flask and heated gradually to 55 °C under constant stirring. It is important to note that the NH₃ gas was used as a catalyst to maintain the spherical particles. Subsequently, a mixture solution

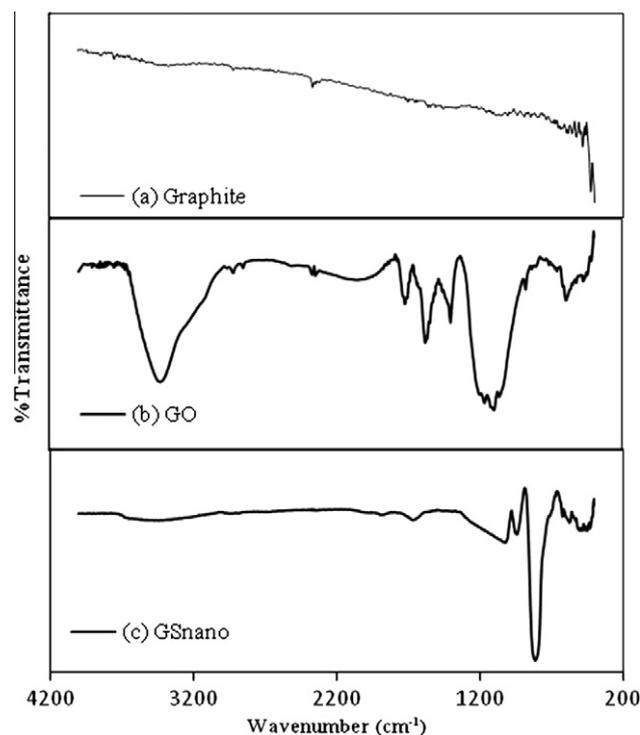


Fig. 1. FT-IR spectrum of graphite (a), GO (b) and GSnano material (c).

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