



Sensitive nonenzymatic detection of hydrogen peroxide at nitrogen-doped graphene supported-CoFe nanoparticles

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ABSTRACT

In this work, a new enzymeless sensor for hydrogen peroxide (H_2O_2) was constructed by supporting CoFe nanoparticles on the nitrogen-doped graphene (CoFe/NGR). In this preparation, the graphene oxide (GO) is first used as substrate for the growth of CoFe layered double hydroxides (CoFe LDHs) through hydrothermal reaction. Then, the pyrolysis of CoFe LDHs/GO under NH_3 produces CoFe/NGR. By supporting CoFe nanoparticles on NGR support, the electrocatalytic performance of CoFe is dramatically improved because of high electric conductivity of NGR. Consequently, the combination of CoFe and NGR allows the nonenzymatic detection of H_2O_2 . Compared with the unsupported CoFe nanoparticles, the CoFe/NGR displays high electrocatalytic activity towards H_2O_2 , enabling a high sensitivity of $435.7 \mu\text{A mM}^{-1} \text{cm}^{-2}$ and low detection limit of $0.28 \mu\text{M}$ towards the reduction of H_2O_2 . Especially, the attractive feature of low cost and outstanding analytical performance of CoFe/NGR suggest it great potential in electrochemical sensor and biosensor fabrication.

1. Introduction

Hydrogen peroxide (H_2O_2), described as the simplest peroxide, finds wide use in for pulp- and paper-bleaching, medical field, waste-water treatment processes, and production of various organic peroxides [1]. In biological system, H_2O_2 is also a byproduct of large number of oxidase enzymes and is a ubiquitous oxidant present in all aerobic organisms. Accordingly, sensitive and accurate detection of H_2O_2 is important for biomedical and environmental monitoring. To achieve this goal, several analytical techniques, such as chemiluminescence [2,3] and fluorimetric method [4], have been used for H_2O_2 determination. In addition to these aforementioned ways, electrochemical sensors or biosensors are found to be capable for sensitive detection of H_2O_2 because of particular interest for their easy operation, portability, simplicity, and low-cost [1,5–12]. The enzyme-based H_2O_2 biosensors are one example for electrochemical sensors, which were constructed by immobilization of enzymes on the electrode surface [5,7]. As a result of specific enzyme activity, these enzyme-based H_2O_2 biosensors showed high performance, such as high sensitivity and excellent selectivity. Despite their high intrinsic activity, such H_2O_2 biosensors often suffer from poor stability due to the inherent instability and high cost of enzyme molecules. To address this problem, alternative H_2O_2 electrochemical sensors based on inorganic nanomaterials are reported to offer potential economic advantages and provide a desired way to overcome

the high cost of enzymes and low stability. Recent rapid development in H_2O_2 electrochemical sensors has demonstrated the capability and stability of inorganic nanomaterials [1,2,13–22]. Among these alternative H_2O_2 sensors, transition metal nanomaterials are the very promising candidates for H_2O_2 electrochemical sensors because of their low cost, earth abundance and relatively easy preparation methods [8,13,14,17,21,23–33].

As mentioned above, transition metal nanomaterials have been widely used in H_2O_2 electrochemical sensors because of low cost and earth abundance. For example, CuO with dumbbell and grass-like morphologies were used as an electrode material for electrochemical sensing of H_2O_2 [34]. The result indicated that the nanostructuring method of CuO materials dramatically increased its performance by synergistically enhancing the effective electrode surface area and facilitating mass transport during electrochemical processes. In another work, Ni_7S_6 with flower-like morphology synthesized by a facile one-pot hydrothermal method were shown to be active for H_2O_2 sensing, exhibiting a wide linear range from 0.005 to 20.5 mM with a low detection limit of $0.15 \mu\text{M}$ and high sensitivity of $37.77 \mu\text{A mM}^{-1} \text{cm}^{-2}$ [30]. Other transition metal nanomaterials, including Fe_2O_3 [28,35], spinel [8,36,37], CuS [38], Cu oxides [32,39,40], perovskite [11,20], Mn oxides or hydroxides [16,25,29,41], CoP [42], NiO [17], Co_3N [43] and Cu_3N [44], also exhibited high activity toward the detection of H_2O_2 . Although these transition metal nanomaterials show high

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activity, their low electrical conductivity limits the charge transfer through the electrode surface and thereby restricts their analytical performance. Therefore, transition metal nanomaterial-based electrodes with higher electrical conductivity are preferred.

Noting the low electrical conductivity of transition metal nanomaterials, the electrical conductivity of transition metal nanomaterials can be improved by the synthesis of a composite containing a conductive additive, such as graphene (GR) [1,23–25] and carbon nanotubes [45]. The combination of the transition metal nanomaterials with a carbon support usually results in improvements in both stability and performance because directly anchoring the electrocatalyst to a conducting support allows a low-resistance electrical transport pathway. The electronic coupling between the conducting support and catalyst materials for synergistically improving the activity has been clearly demonstrated for MoS₂ nanoparticles synthesized directly on GR sheets [46], which exhibited enhanced performance and intrinsic electrocatalytic activity towards folic acid compared to unsupported MoS₂ particles. Similarly, the glucose oxidation and H₂O₂ reduction of Cu₂O/GR composites greatly exceeds that of Cu₂O nanocubes alone due to the superior electrical conductivity of GR support, resulting in linearity ranges of 0.3–3.3 mM and 0.3–7.8 mM for glucose and H₂O₂, respectively [40]. Building on the same principle, the activity of NiCo₂O₄ [47], FeN [48], ZrO₂ [49], Co₃O₄ nanoparticles [50], and CuO [24] is substantially enhanced when they are prepared as nanoparticles supported on carbon nanomaterials. The differences between transition metal nanomaterials and their composites in these recent studies highlight the electrochemical activities and stabilities of transition metal-based electrode materials can be improved by preparing on conductive support.

In addition to the enhancement of electric conductivity, alloying or mixing multiple transition metals is another attractive way to modify the electrochemical activity of transition metal-based electrode materials [51]. Generally, alloying or blending of transition metals has been demonstrated to tune the electronic states, interatomic spacing, and Fermi level energy, all of which could in turn affect the activity of the alloyed electrocatalyst toward the target analyte of interest [52,53]. This strategy has been experimentally exemplified in transition metal nanomaterials. For example, NiO/CuO/polyaniline exhibit significantly higher activity than NiO/polyaniline and CuO/polyaniline towards the oxidation of glucose, owing to favorable interactions between metal oxides and more active sites for electrocatalysis [54]. Similarly, CoCu alloyed nanoparticles grown on vertically aligned TiO₂ nanotube [55] and GR [56] possessed a high density of catalytic sites and benefitted from the excellent charge transport properties of alloyed nanoparticles, leading to high electrocatalytic activity towards glucose. Other transition metal alloys or mixed oxides, including CuCo alloyed dendrite [57], Cu₂O/NiO_x [58], Cu-Ag [59], NiO/CuO [60] also showed high analytical performance compared with their corresponding controls. As has been shown for the transition metal alloyed electrode materials, the incorporation of additional metal or metal oxide to a host compound is expected to alter the electrocatalytic performance due to alteration in its electronic properties, modifying their intrinsic activity.

In this work, a simple method is reported for preparation of CoFe nanoparticles/nitrogen-doped GR (CoFe/NGR) composites. First, the graphene oxide (GO) is used as substrate for the growth of CoFe layered double hydroxides (CoFe LDHs) through hydrothermal reaction. Under the NH₃ atmosphere, pyrolysis of CoFe LDHs/GO under NH₃ results in the formation of CoFe nanoparticles supported on NGR. Through the preparation of CoFe nanoparticles on NGR support, the electrocatalytic activity of CoFe is dramatically enhanced because of synergistic effects of Co and Fe elements and the high conductivity of NGR. The combination of CoFe and NGR ensures the nonenzymatic detection of H₂O₂ with high sensitivity, fast response, and low detection limit. Although GR or NGR have been reported as support for various nanoparticles, our methodology is special because: (1) alloying of the two transition metals modifies the electronic properties of CoFe nanoparticles,

consequently leading to high intrinsic activity; (2) Additional attractive feature is the low cost and high earth-abundance of CoFe alloyed nanoparticles. Although the low cost and earth abundance of transition metal is not an important factor for use of small amount of nanomaterials, the cost the electrochemical sensor can be alleviated by using the less expensive transition metal-based nanomaterials compared with noble metal-based electrochemical sensors. The low cost, high earth-abundance and high activity endow CoFe/NGR as an electrochemical sensor for H₂O₂.

2. Experimental

2.1. Reagents and apparatus

CoCl₂·6H₂O, FeCl₃·6H₂O, Nafion and NaOH were purchased from Sigma-Aldrich. All other reagents (analytical grade) are used as received without further purification. The phosphate buffer saline (0.1 M, pH 7.4, PBS) was used as a supporting electrolyte. PBS was prepared with Na₂HPO₄, NaH₂PO₄ and 0.1 M KCl. The pH value of PBS solutions was adjusted by 0.1 M H₃PO₄ or 0.1 M NaOH. A stock solution of H₂O₂ (1.0 M) was prepared daily by diluting 30% (v/v) H₂O₂ into 10 mL with distilled water. The serum sample was obtained from the Hospital Attached to Northeast Normal University. The serum sample was diluted 2 and 10 times for electrochemical detection and titration method, respectively.

The X-ray diffraction (XRD) patterns were measured on the instrument of Rigaku X-ray D/max-2200vpc (Japan) operated at 20 mA and 40 kV using Cu K α radiation (λ = 0.15406 nm). The structure and morphology of samples are characterized by transmission electron microscopy (TEM, JEM-2100F TEM) and scanning electron microscope (SEM, Philips XL-30 ESEM) images. The Fe, Co, C, and N elements were tested by X-ray photoelectron spectroscopy (XPS, Thermo ESCA LAB spectrometer, USA). Electrochemical detection of H₂O₂ was performed on a CHI 660 C electrochemical workstation (CH Instruments, China) with a three-electrode configuration. The modified glassy carbon (GC, 3 mm diameter) electrode serves as a working electrode; Ag/AgCl in saturated KCl solutions works as reference electrode and a platinum wire is used as counter electrode. The electron transfer ability was characterized by electrochemical impedance spectroscopy (EIS) using a Par 2273 Potentiostats-Electrochemistry Workstation in 5 mM Fe (CN)₆^{4−/3−} and 0.1 M KCl solutions from 0.1 Hz to 10.0 kHz at + 0.25 V. The calibration curve was constructed by plotting current versus concentration for standard solutions. The analytical results of CoFe/NGR-2 were validated by those determined by the classical potassium permanganate titration method. The sensor stability was evaluated by checking the current response or sensitivity before and after three weeks. The living cells were cultured according to our previous method [61].

2.2. Preparation of CoFe LDHs/GO and CoFe/NGR

GO was synthesized according to modified Hummers' method [62]. The preparation method of CoFe/NGR is illustrated in Scheme 1. The CoFe LDHs/GO was prepared by coprecipitation and aging method in the presence of GO. Then, the calcination of CoFe LDHs/GO reducing atmosphere of ammonia gas leads to the decomposition of CoFe LDHs, nitrogen doping, and reduction of both CoFe LDHs and GO, yielding the product of CoFe/NGR. The CoCl₂·6H₂O and FeCl₃·6H₂O with different Co/Fe ratios were added into 30 mL of GO solutions (1.6 mg L^{−1}). The total amount of 10 mM for CoCl₂·6H₂O and FeCl₃·6H₂O is kept same. After ultrasonication for 2 h, the pH value of above mixture was adjusted to 10.00 with 0.1 M NaOH. Then, the solution was transferred into autoclave with capacity of 60 mL and the autoclave was maintained at 100 °C for 6 h. The product was collected by configuration and frozen drying. Finally, the product was calcined in NH₃ flow at 800 °C for 3 h. The NGR was prepared with same procedure

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