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# A novel enzyme-free hydrogen peroxide sensor based on polyethylenimine-grafted graphene oxide-Pd particles modified electrode

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ABSTRACT

A novel enzyme-free hydrogen peroxide ($H_2O_2$) sensor was fabricated by coating graphene oxide (GO), branched polyethylenimine (PEI) and Pd particles in sequence on the surface of glassy carbon (GC) electrode (Pd-PEI/GO/GC). A layer-by-layer method was used, which involved π–π interactions, covalent bonding through 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide/*N*-hydroxysulfosuccinimide (EDC/NHSS) chemistry, electrostatic adsorption and electroreduction. The Pd-PEI/GO/GC electrode exhibited high electrocatalytic activity, a low detection limit, and good stability for the detection of $H_2O_2$. The sensor's practical application was tested via determination of $H_2O_2$ in real water samples.



## 1. Introduction

The accurate and rapid detection of hydrogen peroxide ($H_2O_2$) has attracted great attention due to its increasing significance in many fields [1]. For example, in biological systems, $H_2O_2$ is associated with many different intracellular pathways and biological processes, which can be related to several diseases [2]. Among the various analytical methods for $H_2O_2$ detection [3–6], electrochemical sensors have the advantages of simplicity, easy operation, high sensitivity, and low cost. Electrochemical sensors for $H_2O_2$ identification are basically classified into two major types, namely, enzyme based and enzyme-free sensors. Most enzymatic sensors encounter problems during complicated immobilization procedures, instability and the expensive use of enzymes. In contrast, with the development of nanoscience and nanotechnology, enzyme-free $H_2O_2$ sensors based on various nanomaterials are receiving more and more research interest due to their simplicity, low cost, high stability and reproducibility [1].

Graphene is a single layer of $sp^2$ hybrid carbon atoms with closely-packed, conjugated hexagonal lattices. The unique structure endows it with desirable properties such as high electrical and thermal conductivities, great mechanical strength, good transparency, and inherent flexibility [7]. A highly oxidized derivatives of graphene, graphene oxide (GO), has a similar layered structure to graphene although the basal plane and edges of the carbon atoms in GO are heavily decorated with oxygen-containing groups (C═O, C—O—C, —OH, —COOH) [8]. This oxygen rich surface provides a vast platform for further modification allowing for construction of novel electrochemical sensors or biosensors. Recently, electrochemically modified GO electrodes were developed for the electrocatalytic oxidation of glutathione (GSH) [9], dopamine (DA) and ascorbic acid (AA) [10,11], and reduction of $Cu^{2+}$ [12]. Unlike graphene, the conductivity of GO is poor, however, the oxygen-containing groups present on GO play an important part in electrocatalysis [9–12]. In addition, nickel oxide nanoparticles [13], Au nanorods [14], Au nanoparticles [15], mercaptophenyl boronic acid (MBA) terminated Ag@AuNPs [16], DNA [17], peptides [18], proteins [19], peptide nucleic acids (PNA) [20], poly(amidoamine) dendrimer (PAMAM) [21–23], poly (diallyldimethylammonium chloride) (PDDA) [24,25], ionic liquid [26,27], triphenylamine [28], 3-carboxyphenylboronic acid [29], aminothiophenol [30] and polyacrylic acid [31] were anchored to GO for the fabrication of novel sensors with high stability. Branched polyethyleneimine (PEI) is a positively charged polyamine that contains abundant amine groups and has been used as a polyvalence ligand to modify

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or stabilize metallic nanoparticles due to a strong interaction between amine groups and metal atoms. Herein, a novel $H_2O_2$ sensor based on Pd-GO/PEI modified glassy carbon electrode (Pd-PEI/GO/GC) was developed using a layer-by-layer method. The presented $H_2O_2$ sensor exhibited high reduction potential, good stability, a low detection limit, and wide linear range.

## 2. Experimental

### 2.1. Chemicals and solutions

PEI, $K_2PdCl_6$, $H_2O_2$ (30 wt.%), 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide (EDC), *N*-hydroxysulfosuccinimide (NHSS), uric acid (UA), AA, DA, GSH and glucose (GLU) were acquired from Sigma–Aldrich. GO was obtained from Nanjing XFNano Materials Tech Co., Ltd. All other chemicals used were of analytical reagent grade, and the aqueous solutions were prepared with double-distilled water.

### 2.2. Apparatus

Electrochemical experiments were performed on a CHI 842C electrochemical workstation (Austin, TX, USA) with the conventional three-electrode system including GC (or GO/GC, PEI/GO/GC, and Pd-PEI/GO/GC) working electrode, platinum coil auxiliary electrode, and Ag/AgCl (saturated KCl) reference electrode. The morphology of the GC, GO/GC, or Pd-PEI/GO/GC electrode was directly characterized using a field emission scanning electron microscope (LEO1530 FESEM) with special GC electrodes (3 mm) (Wuhan Gaossunion Tech Co., Ltd.) for SEM.

### 2.3. Preparation of Pd-PEI/GO/GC electrode

Fig. 1 illustrates the fabrication process for Pd-PEI/GO/GC electrode. Firstly, to prepare the GO/GC electrode, 1.0 mg GO was dispersed in 1.0 mL $H_2O$, creating a suspension following sonication. Prior to coating, the bare GC electrodes were polished with 1, 0.3, and 0.05 μm alumina slurry respectively. 5.0 μL of the suspension was dip-coated onto GC electrodes and the electrodes were then dried at room temperature in the air. Secondly, the GO/GC electrode was soaked in 10.0 mM EDC/NHSS solution (pH = 7) for 40 min, followed by rinsing the electrode with excess water. Thereafter, the electrode was dipped in 10.0 mg/mL PEI solution for 40 min, and branched PEI was covalently linked to the GO/GC electrodes via an amide bond to form PEI/GO/GC electrode. Thirdly, the resulting PEI/GO/GC electrodes were immersed into 1.0 mM $K_2PdCl_6$ solution for 40 min to capture $PdCl_6^{2-}$ through electrostatic interaction, and then the electrodes were washed thoroughly with water. Finally, Pd particles were loaded on the surface of the PEI/GO/GC electrodes (Pd-PEI/GO/GC) by in situ electrochemical reduction in pH 7.2 PBS by CV in the range between 0 and −0.8 V. In addition, as a comparison, Pd modified GC (Pd-GC) electrodes were prepared via electrodeposition in 1.0 mM $K_2PdCl_6$ solution (pH 7.2) using CV in the same range.

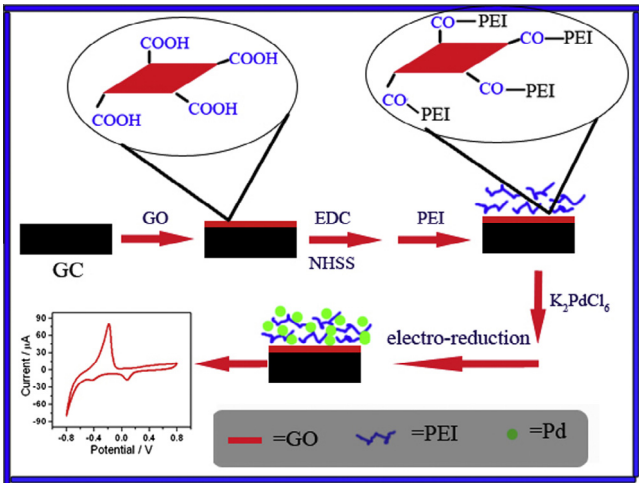


**Fig. 1.** Schematic representation for the fabrication processes of Pd-PEI/GO/GC electrode.

## 3. Results and discussion

### 3.1. Characterization of modified electrodes

A promising electrochemical sensor not only exhibits high electrocatalytic activity towards analyte but also possesses high stability. The stability of an electrochemical sensor depends on the fabrication method. In this study, a layer-by-layer method was used to construct the Pd-PEI/GO/GC electrode (Fig. 1). As shown in Fig. 1, the interactions in the layer-by-layer construction were composed of π–π interactions between GO and GC electrode, covalent bonds between GO and PEI, and electrostatic interactions between PEI and $PdCl_6^{2-}$, which improves the stability of each layer, indicating high stability of the Pd-PEI/GO/GC electrodes. In order to confirm the fabrication procedures, the morphologies of GC, GO/GC, and Pd-PEI/GO/GC electrodes were characterized by SEM, as shown in Fig. 2. Compared with bare GC electrode (Fig. 2A), GO/GC electrode exhibited a wrinkle surface structure (Fig. 2B), suggesting that the GC electrode was successfully modified via π–π interactions. In order to confirm the bonding of PEI to GO/GC electrodes which were activated in EDC/NHSS solution, the resulting electrodes were

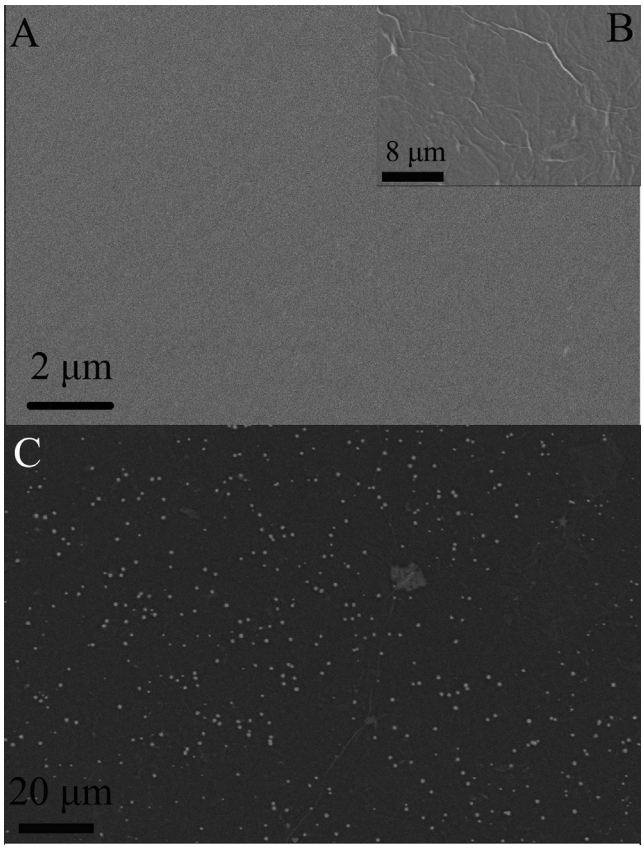


**Fig. 2.** SEM images of GC (A), GO/GC (B), and Pd-PEI/GO/GC (C) electrodes.