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# Electrodeposition of nickel oxide and platinum nanoparticles on electrochemically reduced graphene oxide film as a nonenzymatic glucose sensor

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ABSTRACT

We report the facile electrochemical fabrication of NiO nanoparticles (NPs)/Pt NPs/electrochemically reduced graphene oxide (NiO/Pt/ERGO) ternary composite modified electrode. The NiO/Pt/ERGO film was characterized by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectrometry (EDS), atomic force microscopy (AFM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Cyclic voltammetry (CV) measurements reveal that NiO/Pt/ERGO can directly catalyze the oxidation of glucose and display enhanced current responses. This nonenzymatic sensor shows an excellent sensitivity of 668.2 $\mu A\,mM^{-1}\,cm^{-2}$ (476 $mM^{-1}\,cm^{-2}$), a linear range of 0.05–5.66 mM ($R = 0.9996$), a fast response time (2.5 s), and a low detection limit (S/N ratio = 3) of 0.2 μM in alkaline medium. The nonenzymatic glucose sensor also exhibits superior stability and good anti-interference properties. The electrochemical detection results demonstrate that NiO/Pt/ERGO/GCE is a good candidate for glucose quantification.

## 1. Introduction

Quick and effective determination of glucose is of considerable interest in a number of areas including the food industry, clinical diagnostics, and biotechnology [1,2]. Many studies have involved the use of glucose oxidase to detect glucose. These glucose biosensors show the advantages of excellent selectivity and high sensitivity. However, glucose oxidase-based biosensors are hindered by the thermal and chemical instabilities of the enzyme [3,4]. Therefore, direct electrocatalytic oxidation of glucose at nonenzymatic electrode seems to be an attractively alternative technique.

The electrochemical nonenzymatic glucose sensors (such as alloys, noble metal platinum (Pt)-based nanocomposites, metal oxides, etc.) have been widely reported [5]. Cu and Ni based catalysts are worth of developing and have been broadly used in the fabrication of nonenzymatic glucose sensors [6–13]. As is well known, large-scale commercial nonenzymatic glucose sensors are Pt-based materials. However, they are limited by their poor operational stability, low reserves, high cost, and low antitoxic ability. In order to enhance the stability, antitoxic ability and reduce the Pt usage, a lot of Pt-based binary catalysts in a general format of PtM (M = Ag, Co, Pb, Ni, etc.) have been studied [14–17], and most of them show good electrocatalytic property, non-toxicity, and long-term stability. Especially, the Pt–Ni alloy catalyst has been prepared by one-step electrochemical synthesis [18], and this catalyst shows a wide linear range, but the sensitivity and high usage of Pt could be improved. A template-based electrodeposition of Pt/Ni nanowires is prepared for glucose oxidation and shows high stability [19]. However, the catalyst is a bit complicated and high Pt usage still has a room for improvement.

The incorporation of noble metal nanoparticles (NPs) and conducting matrix materials is another efficient procedure to decrease the usage of noble metal and improve the electrocatalytic activity and stability [20,21]. As a kind of matrix material, graphene (GN) has received significant attention in the preparation of electrochemical sensors [22–24]. Generally, the synthesis of GN involves the oxidative exfoliation of pristine graphite to graphene oxide (GO), and subsequent chemical reduction by hydrazine hydrate, $NaBH_4$, etc. Unfortunately, the chemical reduced GO tends to form irreversible agglomerates. Aggregated RGO has the total surface area less than twenty percent of GNs, which is a fatal flaw of RGO for the dispersion of metals [25]. Electrochemically reduced graphene oxide (ERGO) has been reported, and is turn out to be a simple, efficient, and eco-friendly method to produce pure RGO [26]. So we expect to produce pure and little aggregated RGO for metal NPs dispersion by the electrochemical reduction.

Electrodeposition is a kinetic-controlled process involving preferential nucleation and subsequent growth of metal NPs on an appropriate electrode surface [20,21], and is widely used in the preparation of catalysts due to advantages of high purity of deposits

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and simple procedure of deposition. We think that electrodeposition is an effective way to prepare the Pt/Ni catalyst.

Based on those reasons mentioned above, herein, using electrodeposition as preparation method, NiO/Pt/ERGO is successfully prepared on glassy carbon electrode (GCE). When NiO/Pt/ERGO/GCE is used as an enzyme-free glucose sensor, it exhibits excellent catalytic activity, selectivity, and high stability. Real sample analysis shows that NiO/Pt/ERGO/GCE can be potentially used in detection of glucose in practical blood. This work is of great significance because it not only develops a simple and effective method to prepare NiO/Pt/ERGO nanocomposites, but also the material may be used as nonenzymatic glucose biosensor.

## 2. Experimental

### 2.1. Reagents and apparatus

Glucose, $Ni(NO_3)_2{\cdot}6H_2O$, $H_2PtCl_6{\cdot}6H_2O$, uric acid (UA), dopamine (DA), ascorbic acid (AA), lactic acid (LA), glutaric acid (GA), and acetaminophen (AP) were purchased from Sinopharm Chemical Reagent C. All reagents were of analytical grade and used as received without further purification.

The morphology and composition of products were studied by Philips XL-30 ESEM equipped with an EDX analyzer. X-ray photoelectron spectroscopy (XPS) was measured using Thermo ESCA LAB spectrometer (USA). Raman spectra were obtained using a confocal microprobe Raman system (HR800, Jobin Yvon). Atomic force microscopy (AFM) images were recorded using Atomic force microscope (SPA400, SEIKO).

All electrochemical experiments were performed on a CHI 830B electrochemical workstation (CH Instruments, China) in a conventional three-electrode cell. Ag/AgCl electrode (in saturated KCl solution), platinum electrode, and modified GCE (3 mm diameter) were applied as reference, counter, and working electrodes, respectively. All potentials mentioned in this paper are referred to Ag/AgCl.

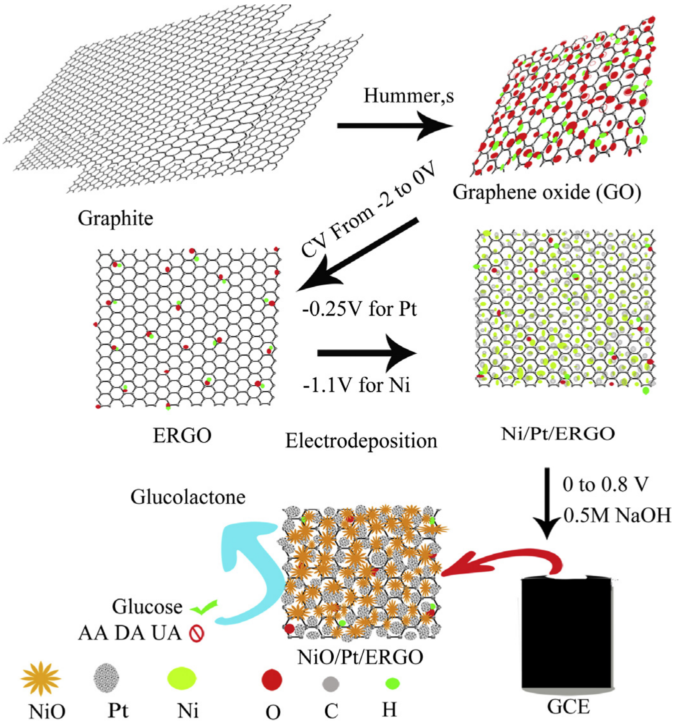
### 2.2. Preparation of NiO/Pt/ERGO/GCE

Before the electrochemical preparation, GCE was polished carefully with 1.0, 0.3, and 0.05 μm alumina powders, respectively; and then it was cleaned with $HNO_3$ (1:1), ethanol, and deionized water sequentially; finally, it was dried at room temperature. GO was prepared from purified natural graphite by the modified Hummer's method [27]. 2 mg GO was exfoliated in 2 mL water to form a homogeneous suspension after 15 min ultrasonication. 10 μL of 1 mg $mL^{-1}$ GO suspension was transferred onto the cleaned GCE surface and reduced in 10 mM $KH_2PO_4$ solution; thus, ERGO/GCE was obtained. Pt NPs are electrodeposited on ERGO/GCE for 50 s in 10 mM $KH_2PO_4$ aqueous solution containing 0.01 mM $H_2PtCl_6{\cdot}6H_2O$ at −0.25 V. And Ni NPs were electrodeposited on Pt/ERGO/GCE for 150 s in 0.1 M acetate buffer solution (pH 4.0) containing 5 mM $Ni(NO_3)_2$ at −1.1 V. The obtained Ni/Pt/ERGO/GCE was scanned by CV from 0 to 0.8 V in 0.05 M NaOH solution until a steady state CV appeared [28]. For comparison, NiO/GCE, Pt/GCE, ERGO/GCE, Pt/ERGO/GCE, and NiO/ERGO/GCE were prepared in the similar way.

## 3. Results and discussion

### 3.1. Electrochemical reduction of GO sheets and electrodeposition of Pt and NiO NPs

Scheme 1 shows a simple and feasible strategy for fabrication of NiO/Pt/ERGO/GCE. The reduction process of GO is shown in Fig. S1. Fig. S2 reveals the dispersion processes of Pt and Ni on the ERGO sheets. The amounts of Pt and Ni deposited on ERGO are of $1.3 \times 10^{-6}$ g and $9.9 \times 10^{-6}$ g (Fig. S2A and C), showing a mass ratio (Ni:Pt) of 7.4:1.0. When scanning in 0.05 M NaOH solution from 0.0 to 0.8 V, a pair of redox peaks originating from the conversion of Ni NPs to NiO NPs appeared. The total reaction could be simply described as following [29]:



**Scheme 1.** Assembly of NiO/Pt/ERGO nanocomposite by electrochemical reduction.

$$Ni + 2OH^- - 2e^- \rightarrow Ni(OH)_2 \quad (I)$$

$$Ni(OH)_2 + OH^- - e^- \rightarrow NiO(OH) + H_2O \quad (II)$$

Herein, $Ni(OH)_2$ roots in the oxidation of Ni(0) to Ni(II). The anodic peak and cathodic peak at 0.6 V and 0.4 V are corresponding to the Ni(III)/(II) redox couple.

### 3.2. Characterization

Fig. 1A and B illustrates the surface morphologies and structures of GO and ERGO films by SEM, respectively. It is clear that the morphology of GO consists of thin stacked flakes and has a model multilayer structure. ERGO layers keep the multilayer structure, but little irreversible agglomerates appear. Fig. 1C shows highly dispersed Pt NPs on the surface of ERGO, but there are also partial metal aggregations appearing. After the electrodeposition of Ni NPs and scanning in 0.05 M NaOH, plenty of interconnected NiO NPs are deposited on Pt/ERGO (Fig. 1D). In order to investigate the element constituents, EDS spectra of Pt/ERGO (Fig. 1E) and NiO/Pt/ERGO (Fig. 1F) were measured respectively. The peaks of F, Si and other elements in ITO are also found in the EDS spectra as thin layers of nanocomposites are deposited on ITO. The comparison of two hybrids shows that a small number of O elements in Pt/ERGO comes from the oxygen-containing functional groups of ERGO. However, abundant Ni and O elements appeared in EDS of NiO/Pt/ERGO, indicating the presence of NiO instead of Ni. The mass ratio (Ni:Pt) of 7.3:1.0 is consistent to that (Ni:Pt = 7.4:1.0) calculated from the charge consumption.