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# One-step electrodeposition of graphene loaded nickel oxides nanoparticles for acetaminophen detection

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## ABSTRACT

An electrochemical sensor of acetaminophen (AP) based on electrochemically reduced graphene (ERG) loaded nickel oxides ( $\text{Ni}_2\text{O}_3\text{-NiO}$ ) nanoparticles coated onto glassy carbon electrode (ERG/ $\text{Ni}_2\text{O}_3\text{-NiO}$ /GCE) was prepared by a one-step electrodeposition process. The as-prepared electrode was characterized by scanning electron microscopy, X-ray photoelectron spectroscopy and Raman spectroscopy. The electrocatalytic properties of ERG/ $\text{Ni}_2\text{O}_3\text{-NiO}$  modified glassy carbon electrode toward the oxidation of acetaminophen were analyzed via cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The electrodes of  $\text{Ni}_2\text{O}_3\text{-NiO}$ /GCE, ERG/GCE, and  $\text{Ni}_2\text{O}_3\text{-NiO}$  deposited ERG/GCE were fabricated for the comparison and the catalytic mechanism understanding. The studies showed that the one-step prepared ERG/ $\text{Ni}_2\text{O}_3\text{-NiO}$ /GCE displayed the highest electro-catalytic activity, attributing to the synergetic effect derived from the unique composite structure and physical properties of nickel oxides nanoparticles and graphene. The low detection limit of  $0.02 \mu\text{M}$  ( $S/N=3$ ) with the wide linear detection range from  $0.04 \mu\text{M}$  to  $100 \mu\text{M}$  ( $R=0.998$ ) was obtained. The resulting sensor was successfully used to detect acetaminophen in commercial pharmaceutical tablets and urine samples.

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## 1. Introduction

Graphene has attracted immense attention owing to its unique 2D structure, high mechanical strength, tunable optical properties and electrical conductivity since it was discovered in 2004 (Novoselov et al., 2004). Traditionally, graphene is mainly produced via the chemical reduction method, which causes the concern of chemical contamination of the resulting product for practical application. The green approach or in-situ reduction method like direct electrochemical reduction of graphite oxide (GO) into graphene has been becoming interesting recently and received a large amount of attention (Chen et al., 2011; Guo et al., 2009). The electrochemically reduced graphene (ERG) provides a lot of flexibility in preparation and easy usage, showing the great application potential in many fields, such as sensors (Alwarappan et al., 2009; Chen et al., 2011; Devadas et al., 2012; Guo et al., 2009; Palanisamy et al., 2012; Shao et al., 2010), supercapacitors (Liu et al., 2011), and fuel cells (Zhou et al., 2010).

For electrochemical sensing application, it has been greatly agreed that the additional modification of nanomaterials, for example, metal or metal oxide nanoparticles, may bring in the benefits of larger specific surface areas, higher conductivity, and better biocompatibilities which will enable the high sensitivity and high stability of the graphene-nanomaterials based electrochemical sensors for different chemical/biological species detection (Q. Chen et al., 2012). Recently, the application of graphene-based nanocomposite electrodes for acetaminophen has become an interesting research topic owing to the practical need of acetaminophen monitoring (X. Chen et al., 2012; Kang et al., 2010; Song et al., 2011). Acetaminophen, also named as paracetamol or N-acetyl-p-aminophenol, is a widely used antipyretic and analgesic drug for cold fever, joint pain, neuralgia, migraine pain, and acesodyne after surgery operation (Chu et al., 2008). Generally, the routine dosage of acetaminophen exhibits no harmful side effects. However, the excess usage of this drug will lead to the formation of some liver and nephron toxic metabolites (X. Chen et al., 2012; Kang et al., 2010; Song et al., 2011), which put a strong request on developing highly sensitive and accurate analytical methods for the determination of acetaminophen. The recent studies of using graphene-based nanocomposites for acetaminophen detection have well demonstrated the advantage of electrochemical techniques over other analytical methods, such as

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spectrophotometry, titrimetry, and chemiluminescence, in terms of high sensitivity, less time-consumption and low cost. For example, X. Chen et al. (2012) report a high performance electrochemical sensor based on single-walled carbon nanotube (SWCNT)–graphene nanosheet (GNS) hybrid films. Hossein (2012) reports the construction of graphene-modified carbon-paste electrode for acetaminophen detection, while Fan et al. (2011) report the fabrication of Nafion/TiO<sub>2</sub>–graphene modified glassy carbon electrode (GCE) for acetaminophen detection. The achievement of high sensitivity, stability, selectivity, and low detection limit as well as wide linear range has been attributed to the extraordinary electronic transport properties and high electrocatalytic activities of graphene and the unique 2D crystal structure of graphene which serve as the substrate support for metal or metal-oxide catalyst nanoparticles (Ng et al., 2010).

In the present work, a novel modified electrode is prepared for electrochemical detection of acetaminophen by electrochemically reducing graphite oxide and depositing graphene together with nickel oxides onto glassy carbon electrode simultaneously, and is named ERG/NiO/GCE. The key consideration of directly depositing electrochemically reduced graphene is that the high quality graphene can be prepared by electrochemical reduction of GO at  $-1.5$  V (vs. SCE, Saturated Calomel Electrode), which eliminates the use of excessive reducing agents and thus addresses the concern of contaminating resultant products (Hilder et al., 2011). Since the deposition of nickel oxides nanoparticles (NPs) can be achieved via a cathodic current in a bath containing nickel salt (Bayandori Moghaddam et al., 2008; Giovanelli et al., 2003; Oriňáková et al., 2006; Streinz et al., 1995), it is expected that electrochemical reduction of GO and electrodeposition of Ni<sub>2</sub>O<sub>3</sub>–NiO NPs can be simultaneously performed at  $-1.5$  V (vs. SCE) in a solution containing both nickel ion and graphite oxide. Different kinds of modified electrodes such as ERG/GCE, Ni<sub>2</sub>O<sub>3</sub>–NiO/GCE, and ERG/Ni<sub>2</sub>O<sub>3</sub>–NiO/GCE, were prepared for the comparison study. The electrocatalytic activity and selectivity of the composite electrode toward the acetaminophen oxidation were also evaluated. The analytical performance of the prepared ERG/Ni<sub>2</sub>O<sub>3</sub>–NiO/GCE with respect to the detection limit, linear range, and stability is discussed in detail.

## 2. Experimental

### 2.1. Apparatus

All electrochemical experiments including cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) were performed with a CHI660C electrochemical workstation (Chen Hua Instruments Co., Shanghai, China) using a conventional three-electrode system which consists of a platinum wire auxiliary electrode, a SCE reference electrode, and a working electrode of modified glassy carbon electrode.

Surface morphology analysis of the electrodes was performed by a field-emission scanning electron microscope (FE-SEM) using a Hitachi S-4800 field emission scanning electron microanalyzer. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a PHI 5000 ESCA system (Perkin Elmer) with Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV). Raman spectroscopic characterization was performed with a confocal microprobe Raman system (LabRam II, Dilor, France).

### 2.2. Chemicals and reagents

Graphite powder (spectral pure), acetaminophen (AP), ascorbic acid (AA), NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NiSO<sub>4</sub>·6H<sub>2</sub>O, KMnO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, KCl, H<sub>2</sub>O<sub>2</sub> (30%), HCl, Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O and NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O were all

purchased from Sinopharm Chemical Reagent Co. Ltd. Dopamine (DA) and uric acid (UA) were purchased from Sigma. K<sub>3</sub>[Fe(CN)<sub>6</sub>] was obtained from Shanghai LingFeng chemical reagent Co. Ltd. All the chemicals were used as received without any further purification. All solutions were prepared with deionized (DI) water ( $\geq 18$  M $\Omega$  cm).

### 2.3. Synthesis of graphite oxide

Graphite oxide was synthesized via the modified Hummers method (Chen et al., 2009; Hummers Jr and Offeman, 1958) by using the graphite powder (SP). Typically, after the synthesis, filtration and drying under vacuum at the temperature of 40 °C, the graphite oxide was obtained as a gray powder.

### 2.4. Preparation of ERG/Ni<sub>2</sub>O<sub>3</sub>–NiO modified GC electrode

80 mg graphite oxide was dispersed in 20 mL DI water and the dispersion was ultrasonicated to form a homogeneous 4 mg/mL GO suspension solution. Before the electrodeposition, the glassy carbon electrode was polished with 0.3  $\mu$ m alumina powders, and then sequentially sonicated in DI water, hydrous ethanol and DI water, and allowed to dry under ambient condition.

Two methods have been employed to prepare ERG/Ni<sub>2</sub>O<sub>3</sub>–NiO/GCE composite substrate. The first method is to electrodeposit nickel oxide nanoparticles and electrochemically reduced graphene simultaneously onto the GCE surface via one-step process by dipping glassy carbon electrode in the solution of 4 mg/mL GO, 40 mM NiSO<sub>4</sub> and 0.1 M Na<sub>2</sub>SO<sub>4</sub> followed by applying a constant potential of  $-1.5$  V (vs. SCE) for 150 s. The same method was also used to prepare the Ni<sub>2</sub>O<sub>3</sub>–NiO/GCE in the solution of 40 mM NiSO<sub>4</sub>+0.1 M Na<sub>2</sub>SO<sub>4</sub>. The second method is to first prepare an ERG modified GC electrode (ERG/GCE) and then further electrodeposit Ni<sub>2</sub>O<sub>3</sub>–NiO onto the ERG modified glassy carbon electrode (noted as Ni<sub>2</sub>O<sub>3</sub>–NiO deposited ERG/GCE). Typically, a 5  $\mu$ L of 4 mg/mL GO dispersion was firstly coated onto GCE surface. The GO modified electrode was then dried in the air and electro-reduced into ERG in the solution of 0.1 M Na<sub>2</sub>SO<sub>4</sub> with the constant potential of  $-1.5$  V (vs. SCE) for 150 s. The as-prepared electrode was further electrodeposited with Ni<sub>2</sub>O<sub>3</sub>–NiONPs in the solution of 40 mM NiSO<sub>4</sub> and 0.1 M Na<sub>2</sub>SO<sub>4</sub> with the constant potential of  $-1.5$  V (vs. SCE) for 150 s. The electrode was used for electrochemical study without further treatment.

## 3. Results and discussion

### 3.1. Surface characterization of as-prepared electrodes

The ERG/Ni<sub>2</sub>O<sub>3</sub>–NiO nanocomposite prepared with the one-step method is first characterized by Raman spectroscopy. As can be seen in Fig. 1A, the Raman spectrum (curve a) of ERG/Ni<sub>2</sub>O<sub>3</sub>–NiO nanocomposite is dominated by two strong peaks at 1352 and 1599 cm<sup>-1</sup> corresponding to the D and G modes respectively, which are obviously observed in the Raman spectra of GO recorded before (curve c) and after (curve b) the reduction. The D peak is the defect peak due to the intervalley scattering (Ferrari, 2007) and the strong G peak is the characteristic peak of the graphene. The 2D peak of graphene is clearly observed in the Raman spectrum of reduced graphene, while it is absent in the spectrum of GO. In addition, the D/G intensity ratio in the spectrum of ERG is higher than that of GO, indicating a decrease of the size of the in-plane sp<sup>2</sup> domains and the increase of the number of smaller graphene domains upon reduction of GO as well as a partially ordered crystal structure of the ERG (Guo et al., 2009). The above evidences indicate the successful reduction of

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