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# Enhanced non-enzymatic glucose sensing based on copper nanoparticles decorated nitrogen-doped graphene



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## ABSTRACT

Copper nanoparticles (NPs) decorated nitrogen-doped graphene (Cu-N-G) was prepared by a facile thermal treatment, and further employed as a novel sensing material for fabricating the sensitive non-enzymatic glucose sensor. Compared with pure Cu NPs, the Cu-N-G showed enhanced electrocatalytic activity to glucose oxidation due to the integration of N-G, which exhibited the oxidation peak current of glucose ca. 23-fold higher than that of pure Cu NPs. The presented sensor showed excellent performances for glucose detection including wide linear range of 0.004–4.5 mM, low detection limit (1.3  $\mu\text{M}$ ,  $S/N=3$ ), high sensitivity (48.13  $\mu\text{A mM}^{-1}$ ), fast response time ( $< 5$  s), good selectivity to the general coexisted interferences, etc. Such properties would promote the potential application of the nitrogen-doped graphene as enhanced materials in fabricating sensors for chemical and biochemical analysis.

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## 1. Introduction

Efficient and highly sensitive detection of glucose concentration is of considerable importance in various fields ranging from medical applications in blood glucose sensing to ecological applications, and various approaches to glucose sensing have been developed including electrochemical, optical, thermometric, and fluorescent sensors (Steiner et al., 2011; Wu et al., 2011; Wang et al., 2013). Among these different types of sensors, amperometric glucose enzymatic sensors are promising due to their simple instrumentation and convenient operation, based on which good selectivity and high sensitivity have been achieved for glucose detection (Delvaux and Champagne, 2003; Qiu et al., 2009; Valentini et al., 2013). However, owing to the intrinsic nature of enzymes, enzymatic glucose sensors can easily be affected by temperature, pH value, humidity, and toxic chemicals (Sun et al., 2011). As an alternative strategy, several functionalized nanomaterials, such as gold nanowire (Cherevko and Chung, 2012), cobalt oxide nanorods (Kung et al., 2011), palladium nanoparticles/carbon nanotubes (Chen et al., 2009) and platinum nanoflowers/graphene oxide (Wu et al., 2013), have been designed and employed as sensing materials for fabricating non-enzymatic glucose sensors during recent years, which overcome the disadvantages of enzymatic glucose sensors to some extent.

Copper and copper oxides based nanomaterials have attracted great attention for non-enzymatic glucose sensor owing to their high electrocatalytic activity, and some other advantages of inexpensive, non-toxic, easily produced and readily stored (Yang et al., 2012). For example, Wang et al. (2010) have fabricated a sensitive non-enzymatic glucose sensor by employing CuO flowers and nanorods as the sensing material; Zhang et al. (2012) reported a sensitive and selective non-enzymatic glucose sensing platform based on the one-dimensional Cu nanowires. Furthermore, in order to improve their catalytic activity, great efforts have been made to combining copper or copper oxides with carbon-based nanomaterials (Kang et al., 2007; Luo et al., 2012; Zhou et al., 2012). For instance, Kang et al. (2007) fabricated a non-enzymatic glucose sensor based on Cu nanoclusters/multiwall carbon nanotube (MWCNT), which exhibited amplified and fast response for electrocatalytic oxidation of glucose by the introduction of MWCNT; Luo et al. (2012) developed a non-enzymatic glucose sensor based on Cu-graphene nanocomposites, and the sensor showed much higher current and more negative onset potential for glucose oxidation than Cu nanoparticles (NPs). All these studies indicated that combining copper or copper oxides with carbon-based nanomaterials could efficiently improve the performance of non-enzymatic glucose sensors, due to the increased electrocatalytic active area and the promoted electron transfer for glucose oxidation of carbon-based nanomaterials (Luo et al., 2012; Zhao et al., 2013).

Most recently, nitrogen-doped graphene (N-G), as a kind of novel carbonaceous derived materials, has received considerable interests by virtue of its excellent properties, such as large

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functional surface area, high ratio of surface active groups to volume, biocompatible C–N microenvironment, high electrical conductivity and much chemically active sites (Yang et al., 2013a). Furthermore, the latest studies indicated that N-G can provide excellent platforms for loading nanomaterials and improve their catalytic activity. According to Xiong's report (Xiong et al., 2013), Pt/N-G exhibited significantly enhanced catalytic activity for methanol electro-oxidation reaction compared to pure Pt. Borowiec et al. (2013) developed a sensor for electrochemical determination of chloramphenicol based on Au/N-G, which exhibited better electrocatalytic performance for chloramphenicol than Au/graphene. All these results indicated that N-G shows great potential as enhanced materials for fabricating the electrochemical sensing interface, and up to now, it is just the beginning of this fantastic topic.

In this paper, copper NPs decorated nitrogen-doped graphene (Cu–N-G) were prepared by a facile thermal treatment, using N-G as a novel substrate material. Due to the integration of N-G, the as-prepared Cu–N-G showed enhanced electrocatalytic activity to glucose oxidation, which exhibited the oxidation peak current ca. 23-fold higher than that of pure Cu NPs. Furthermore, combining the advantageous features of N-G and Cu NPs, a novel non-enzymatic glucose sensor has been constructed, which showed good performances for glucose sensing with high sensitivity, excellent selectivity, fast response, wide detection range and good stability. In addition, the prepared biosensor can be used for the detection of glucose in real samples with good accuracy, which may find practical applications in the future for the assay of blood glucose.

## 2. Experimental

### 2.1. Reagents and chemicals

Graphite was purchased from Qingdao Tianhe Graphite Co., Ltd. D-(+)-Glucose, L-Ascorbic (AA), dopamine hydrochloride (DA), 4-acetamidophenol (AP), uric acid (UA) and Nafion (5 wt%) were purchased from Sigma-Aldrich.  $\text{Cu}(\text{NO}_3)_2$ , glycine (Gly), NaOH and NaCl were purchased from Sinopharm Chemical Reagent Co., Ltd. Graphene oxide (GO) was prepared using modified Hummers method from graphite powders (Gilje et al., 2007). Unless otherwise stated, reagents were of analytical grade and used as received. All solutions were prepared with double distilled water.

### 2.2. Apparatus

Characteristics were performed via transmission electron microscopy (TEM, Hitach H800, Japan), scanning electron microscopy (SEM, JEOL JSM-6700, Japan) equipped with an energy-dispersive spectroscopy (EDS, Oxford Inca Energy 400, UK). X-ray diffraction spectra (XRD, Bruker D8 ADVANCE diffractometer, Germany) with  $\text{Cu K}\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation, Raman spectra (RM 2000 microscopic confocal Raman spectrometer, England), X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, Japan). Electrochemical impedance spectroscopy (EIS) was performed in 0.1 M KCl solution containing 5 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  with a frequency range from 0.01 Hz to 10 kHz, and the amplitude of the applied sine wave potential in each case was 5 mV which was taken with a ZENNIUM electrochemical workstation (Zahner Instruments, Germany). The electrochemical experiments were performed with a CHI660 B electrochemical analyzer (Chen Hua Instruments, Shanghai, China) in a conventional three-electrode system where glassy carbon electrode (GCE, 3 mm diameter) was used as working electrode, saturated calomel electrode (SCE) as reference electrode and platinum wire as counter electrode, respectively. Amperometric curves were obtained after adding a glucose solution of certain

concentration into 0.1 M NaOH electrolyte under stirring conditions, and then the current in each experiment was recorded when it reached the steady state.

### 2.3. Preparation of samples

GO was mixed with copper nitrate and Gly at a mass ratio of 1:1:8 (GO:copper nitrate:Gly) in water. The resulting mixture was sonicated for two hours and poured into an alumina crucible. The temperature of the mixture was gradually increased from room temperature to 500 °C under argon atmosphere and maintained for 2 h. Then, the final product was collected from the crucible directly. Similarly, N-G was prepared without adding copper nitrate. The Cu NPs were prepared according to the method described in our previous work (Xu et al., 2011).

### 2.4. Preparation of the modified electrodes

Prior to modification, the GCE was first polished with sand paper followed by 1.0, 0.3, and 0.05  $\mu\text{m}$  alumina slurry, respectively. After successive sonication in ethanol and double distilled water, the electrode was rinsed with double distilled water and allowed to dry at room temperature. 2 mg  $\text{mL}^{-1}$  Cu–N-G suspension was prepared by dispersing 1.0 mg Cu–N-G in 0.5 mL ethanol with ultrasonic agitation for about 2 min. Then, the as-prepared Cu–N-G suspension and 30  $\mu\text{L}$  of 5% Nafion were mixed with ultrasonic agitation for 2 min. After that, 6  $\mu\text{L}$  of the suspension was spread evenly onto the pretreated GCE surface and allowed to dry in ambient air for 24 h. Nafion/Cu–N-G modified GCE was thus successfully obtained (denoted as Nafion–Cu–N-G/GCE). For comparison, Nafion–N-G/GCE and Nafion–Cu/GCE were prepared using a similar procedure.

## 3. Results and discussion

### 3.1. Characterization of Cu–N-G

The TEM image of Cu–N-G is shown in Fig. 1, and it is obvious that the two-dimensional N-G sheets were well decorated by a large quantity of Cu NPs and both the outline of N-G and Cu NPs could be clearly observed. In addition, the synthesized N-G sheets (Fig. S1) showed a characteristically crumpled and overlapped multilayer surface structure. As shown in Fig. S2A, the Cu NPs with the size of 80–120 nm were uniformly decorated on the surface of N-G, and no free NPs were presented outside the N-G sheets. The morphologies of Cu–N-G were also characterized by SEM. Cu NPs were uniformly distributed on the N-G sheets as shown in Fig. 1B, and in some place, Cu NPs were deposited on both sides of the N-G sheets. EDS spectrum in Fig. S2B further confirmed that Cu NPs were formed on N-G sheets. Besides Cu, the elements of C, N, and O were detected as well. The peaks of C and N belonged to N-G and the existence of oxygen signal was due to the incomplete reduction from GO to N-G.

Further structural characterization of Cu–N-G was performed by XRD. As shown in Fig. 2A, the diffraction peak located at the  $2\theta$  value of  $\sim 26^\circ$  was ascribed to the hexagonal structure ((002) plane) of N-G (Xiong et al., 2013). The three major peaks at  $43.5^\circ$ ,  $50.5^\circ$  and  $74.5^\circ$  in the range of  $40\text{--}80^\circ$  correspond to the (111), (200) and (220) planes of Cu with cubic phase (JCPDS card no. 04-0836), respectively (Xu et al., 2011; Luo et al., 2012; Zhao et al., 2013). These results were consistent with the EDS results, which further confirmed that the Cu NPs were coated on the N-G sheets.

To characterize graphite and graphene materials, Raman scattering has been proved to be an essential tool, particularly for distinguishing ordered and disordered crystal structure of carbon

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