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A Novel Non-Enzymatic Glucose Sensor Based on CuO-Graphene Nanocomposites

Hong-Ying Yu[2], *Miao-Qing Xu*[1], *Shu-Hong Yu*[1], *Guang-Chao Zhao*[1,*]

[1]College of Environmental Science and Engineering, Anhui Normal University, Wuhu, 241000, P R China
[2] Department of Automation Control, Wuhu Institute of Technology, Wuhu 241000, P R China
[*]E-mail: gczhao@mail.ahnu.edu.cn

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Copper oxide (CuO) graphene nanocomposites were prepared by a one-step chemical procedure using copper acetate-adsorbed graphene oxide (GO) as precursors and their potential application in non-enzymatic glucose sensing were also evaluated. The morphology of the as-prepared nanocomposites was characterized by Scanning Electron Microscopy. The electrochemical performance of the CuO-graphene modified glassy carbon electrode for glucose sensing was investigated by cyclic voltammetry (CV) and amperometric I-t Curve. The CuO-graphene modified electrode shows good electrocatalytic activity toward the oxidation of glucose in 0.1M NaOH solution. The amperometric response current of glucose on the electrode is linear to the concentration of glucose in the range from 2.0×10^{-6} to 5.0×10^{-4} M with a low detection limit of 6.7×10^{-7} M. The novel glucose sensor also exhibits good reproducibility, long-term stability, as well as no interference from L-ascorbic acid, uric acid, and dopamine.

Keywords: Graphene, Copper oxide nanoparticles, Glucose, Non-enzymatic sensor

1. INTRODUCTION

Glucose determination plays a significant role in many fields including clinical diagnostics, biotechnology and the food industry [1-5]. In the past, there had been many approaches to measure glucose concentration, such as fluorescence [5], the continuous glucose monitoring system (CGMS) [6] and electrochemical determination [7-10], etc. Among these techniques, the electrochemical approach has attracted significant attention for its simplicity, high reliability, sensitivity and selectivity, low detection limit. Enzymatic electrochemical sensors based on glucose oxide (GOx) have advantages for good performance and high selectivity. However, the most serious problem of enzymatic sensors is lack of stability due to the intrinsic nature of enzyme. Environmental conditions also can easily affect the performance of GOx sensors. So development of glucose non-enzyme sensor holds a leading position among various electrochemical sensors by virtue of their highly improved stability and sensitivity.

Metal and metal oxides, including Pt-Pd nanoflakes, Ni-titania nanotube, NiO/OMC, Cu-Cu_2S nanocomposite and CuO-SWCNT nanocomposite [11-15], are often used as effective catalysts towards glucose. CuO, a p-type semiconductor with a narrow band gap of 1.2 eV, is promising in the development of non-enzymatic glucose sensor because of its highly specific surface area, good electrochemical activity and the capacity of promoting electron transfer reactions at a lower overpotential [16-18]. For instance, CuO nanowires were used as electrode for glucose sensing with high sensitivity [19]. Since the existence of CuO as impurity in carbon nanotubes was claimed to be responsible for electrocatalytic activity of glucose oxidation, CuO-carbon nanomaterials has been rapidly becoming the attractive electrode materials [20]. Zhang' group fabricated a novel type of CuO nanoparticles-modified multi-walled carbon nanotubes (MWCNTs) array electrode for sensitive glucose detection [21]. Kim's group had also constructed a high performance non-enzymatic glucose sensor with CuO-SWCNT nanocomposites [15].

Graphene (GR) is a new form of carbon material with carbon atoms parked in a two-dimensional honey lattice, which has attracted a tremendous amount of attention due to their extraordinary physical, chemical and mechanical properties. Besides, due to its low-cost, large specific surface area and strong interactions with metal clusters, graphene is a promising material for catalytic applications [22]. The dispersion of metal nanoparticles on graphene sheets potentially provide a new way to develop catalytic materials [23] and to construct non-enzymatic sensors, such as oxygen sensors [24, 25] and methanol sensors [26, 27]. There also had been a few studies about CuO-graphene nanocomposites for measuring glucose with good performance [28-30]. Herein, we report a simple one-step synthesis procedure to prepare CuO graphene nanocomposites. The as-prepared nanocomposites material displays an obvious promotion for electrocatalytic oxidation of glucose. Based on this, a non-enzymatic glucose sensor can be constructed for sensitive detection of glucose.

2. EXPERIMENTAL

2.1 Apparatus and chemicals

Electrochemical experiments were performed with CHI660 electrochemical analyzer (CHI, USA) with a conventional three-electrode cell. CuO-GR modified glass carbon electrode (GCE) was used as the working electrode. An Ag/AgCl electrode and a platinum wire electrode were used as the reference and the auxiliary electrodes, respectively.

Graphite, glucose, copper(II) nitrate and ammonium hydroxide were purchased from Shanghai Chemical Reagent Co., Ltd. C_2H_5OH (99%) , D-(+)-glucose and sulfuric acid(95%) were obtained from Sinopharm Chemical Reagent Co. Ltd. All reagents were of analytical grade and used as received. All aqueous solutions were prepared with doubly distilled water. Scanning electron microscopy (SEM) image was obtained using an S-4800 Scanning Electron Microscopy (Hitachi, Japan).

2.2 Synthesis of copper oxide-graphene nanocomposites

Graphene oxide used in this experiment was synthesized from graphite power according to Hummers method [31]. The obtained graphene oxide was washed with deionized water six times to remove the remaining metal ions and acid and stored for use. The preparation procedure of copper oxide nanoparticles-graphene (CuO-GR) nanocomposites using copper acetate-adsorbed graphene oxide (GO) as precursors can be described as follows: Copper (II) nitrate aqueous solution (10 mL, 0.02M) was added into graphene oxide aqueous solution (10 mL, 0.5 mg mL^{-1}) and mixed by magnetic stirring for 10 min. Then, ammonium hydroxide (10 mL, 2M) was added into above solution and mixed by magnetic stirring for 5 min. The mixture was displaced into a 60mL steel autoclave and maintained at 100℃ for 10 h. The color of resulting solution changed from yellow to black. The product was washed with distilled water and ethanol for several times to remove the impurities by centrifugation and dried to get the CuO-GR nanocomposites.

2.3 Preparation of CuO-GR/GC modified electrode

Initially, the bare glassy carbon electrode was polished successively with emery paper and alumina slurries (0.3μm and 0.05 μm). After a short rinse with acetone and water (each for 5 min), the electrode was allowed to dry at room temperature. Then, 10μL of CuO-GR-ethanol suspension (5 mg mL^{-1}) was cast on the pretreated GC electrode surface with a microsyringe and the solvent (ethanol) was allowed to evaporate at ambient temperatures. The electrode was denoted as CuO-GR/GC electrode. Prior to electrochemical experiments, the modified electrode was rinsed thoroughly with doubly distilled water and stored at 4^{o}C.

3. RESULTS AND DISCUSSION

3.1 SEM characterization of CuO-GR composites

The morphologies of graphene oxide, graphene and CuO-GR were characterized by SEM. Fig. 1 depicts the typical SEM imagines of graphene oxide (A), graphene (B) and as-prepared copper oxide-graphene nanocomposites (C) respectively. It can be observed that the graphene oxide film looks like a thin wrinkling paper on electrode surface. The chemically reduced graphene film shows a flake-like shape, which is significantly different from that of the graphene oxide. As can be seen in Fig.1C, a number of small dots are uniformly deposited on the graphene sheets with a mean diameter less than 85 nm, indicating that the graphene as a large surface area provider was fit for the formation of CuO nanoparticles. In other words, CuO-GR nanocomposites were successfully prepared.

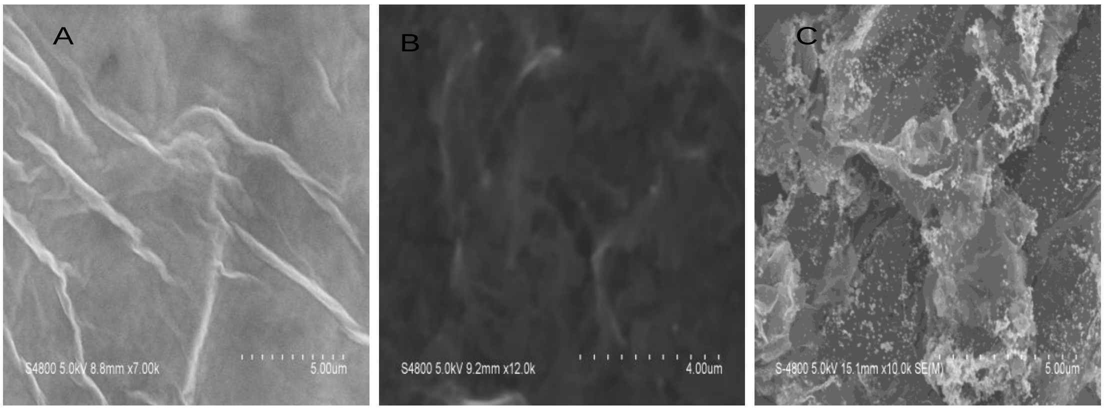


Figure 1. SEM image of graphene oxide (A), graphene (B) and copper oxide nanoparticles-graphene nanocomposites (C).

3.2 Direct electrochemistry of glucose on CuO-GR/GCE

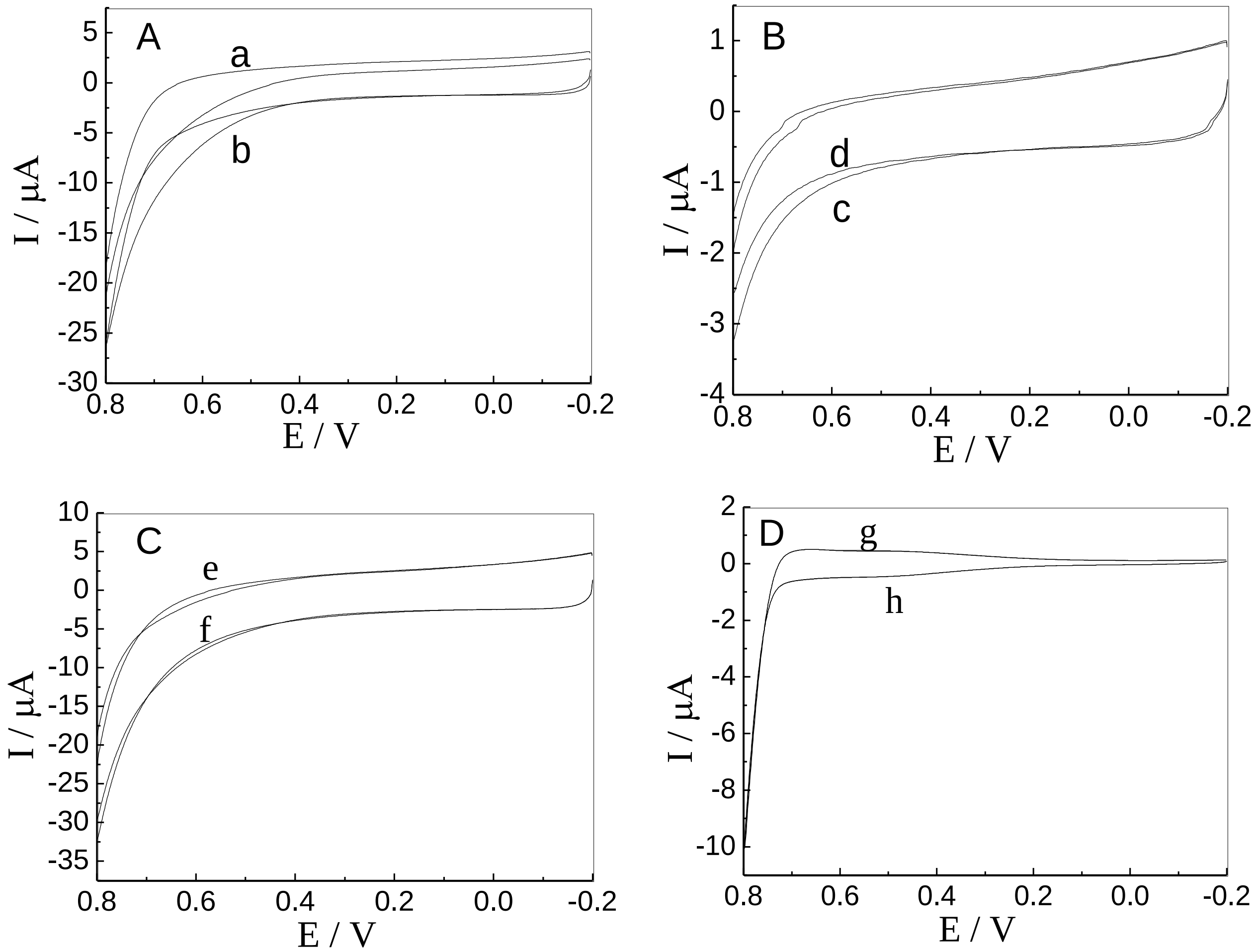
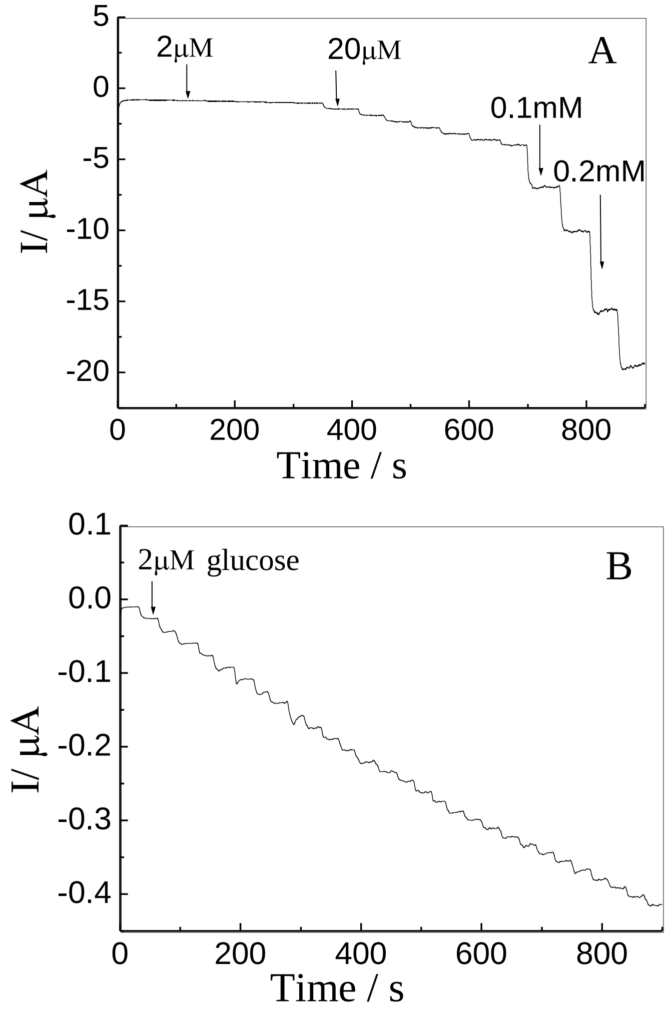


Figure 2. Typical CVs of CuO-GR/GCE (A), bare GCE (B), GR/GCE (C) and CuO/GCE (D) in 0.1M NaOH solution with (a, c, e and g) or without 4.0×10^{-4} M glucose (b, d, f, and h).

The electrochemical performances of different modified electrodes were measured by cyclic voltammograms (CVs) in 0.10 M NaOH with or without 0.4 mM glucose. Fig.2 shows the typical CVs of CuO-GR/GCE (A), bare GCE (B), GR/GCE (C) and CuO/GCE (D) in 0.1M NaOH solution respectivly. Curve a, c, e and g in Fig.2 stand for CVs of as-prepared four electrodes in 0.1M NaOH solution in the absence glucose. Curve b, d, f, and h stand for CVs of as-prepared four electrodes in 0.1M NaOH solution in presence of 4.0×10^{-4} M glucose, respectively. As shown in Fig.2, no obvious increase of the oxidation current was observed at bare GCE (B), GR/GCE (C) and CuO/GCE (D) in present of 0.4 mM glucose. But for CuO-GR modified electrode, when 0.4 mM glucose was present, the oxidation current remarkly increased at positive potential owning to the electro-oxidation of glucose to gluconolactone [32]. The results indicate that the combination of graphene and CuO nanoparticles has a significant catalytic activity towards glucose oxidation in alkaline solution.

3.3 Amperometric responses of CuO-GR/GCE towards glucose

The amperometric response of the CuO-GR/GCE to glucose was investigated through successively adding glucose to a continuous stirring NaOH solution. In this process, a potential of 0.55V was applied to the working electrode.



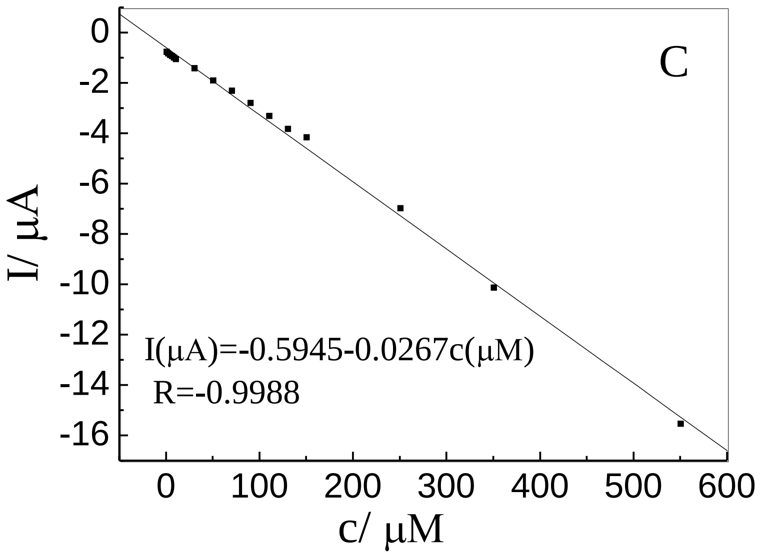


Figure 3. (A) Amperometric i-t Curve of CuO-GR/GCE at 0.55V with successive addition of 2μM, 20μM, 0.1mM and 0.2mM glucose into 0.1M NaOH solution. (B) Amperometric i-t Curve of CuO-GR/GCE at 0.55V with successive addition of 2μM glucose into 0.1M NaOH solution. (C) Calibration curve for glucose sensing corresponding to A and B.

Fig. 3(A and B) illustrates the amperometric response of CuO-GR/GCE to successive addition of glucose. It was found that during successive addition of 2μM (Fig. 3B), 2μM, 20μM, 0.1 and 0.2mM (Fig. 3A) glucose into 0.1M NaOH solution, an evident current response was observed. The oxidation current increases to reach a stale plateau within 3 s when adding glucose into NaOH solution. This suggested that the response of the electrode to glucose should be a quick responsive process [33-34].

The calibration plot for the glucose determination was constructed (Fig 3C). The proposed electrode exhibits excellent linear response to glucose in the concentration range from 2.0×10^{-6} to 5.0×10^{-4} M with a correlation coefficient of -0.9988 and a low detection limit of 6.7×10^{-7} M (S/N=3) for glucose sensing. The result suggests that the CuO-GR/GCE can be used as non-enzyme sensor to detect glucose.

3.4 Interference study

One of the major challenges in non-enzymatic glucose detection is the interfering electrochemical signals caused by the oxidation of electroactive compounds normally coexisting with glucose in real samples such as L-ascorbic acid (AA), uric acid (UA), and dopamine (DA). Under optimal experimental conditions, the potential interferences have been carefully examined (as shown in Fig. 4). It can be found that 4 mM AA, UA and DA did not interfere obviously in the determination of 0.15mM glucose.

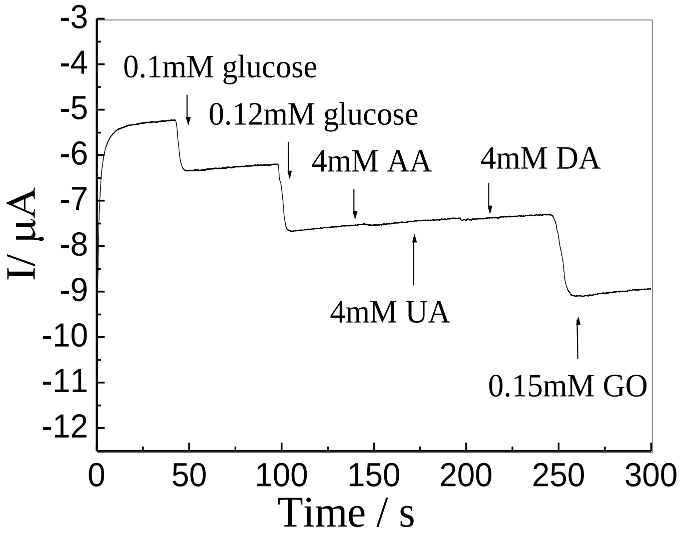


Figure 4. Amperometric i-t Curve of CuO-GR/GCE to 0.12 mM glucose, 4mM AA, 4 mM UA, 4 mM DA and 0.15 mM glucose in 0.1M NaOH solution. Work potential is 0.55V.

3.5 Reproducibility and stablitiy

The reproducibility of the modified electrode was measured at the same CuO-GR/GCE by eight repetitive amperometric measurements which carried out with the 0.1M NaOH solution containing 8 µM glucose. The relative standard derivation for eight repetitive measurements was found to be 1.9%. The long-term stability of the sensor was also evaluated by measuring the current response to glucose within 3 weeks. The results show that the CuO-GR/GCE retained 88% of its initial current response to glucose which could be mainly ascribed to the chemical stability of CuO [35]. Therefore, we conclude that the proposed sensor has a good reproducibility and high high stability which enable the monitoring of trace levels of glucose.

4. CONCLUSIONS

In conclusion, we have demonstrated a simple one-step synthesis of well-defined CuO-GR nanosheets and their subsequent use as electrode modify for determination of glucose. The GCE modified with CuO-GR nanocomposites exhibits good analytical performance towards glucose with a linear range from 2.0×10^{-6} to 5.0×10^{-4} M, low detection limit (6.7×10^{-7} M) at 0.55 V and fast response. No severe interference and good stability of CuO-GR/GC electrode can be obtained in amperometric current-time measurements. Based on these, a new glucose non-enzyme sensor was constructed and CuO-GR nanocomposites hold great promise for electrochemical applications.

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