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Synthesis of Cuprous Oxide (Cu_2O) Nanoparticles/Graphene Composite with an Excellent Electrocatalytic Activity Towards Glucose

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The development of nanoscience and nanotechnology has inspired scientists to continuously explore new electrode materials for enhancing electrocatalytic activity and constructing electrochemical platform for sensing. In this study, we proposed a simple and effective approach to the *in situ* decoration of Cu_2O nanoparticles on the surface of graphene nanosheets (Cu_2O@CRG). The resulting microstructure and morphology were characterized by atomic force microscopy (AFM), transmission electron microscopy (TEM), energy-dispersive X-ray (EDX), X-ray powder diffraction (XRD) spectroscopy and electrochemical technique. The results confirm that the high dispersion of crystal Cu_2O nanoparticles with the uniform size distribution could be easily obtained via using sodium citrate as reductant and stabilizer. Moreover, the as-prepared Cu_2O@CRG which modified glassy carbon electrode (GCE) exhibit better non-enzymatic electrocatalytic responses to glucose than the chemically reduced graphene (CRG) or Cu_2O in alkaline media. This new findings demonstrate Cu_2O@CRG is a promising candidate of advanced electrode material in electrochemical sensing and other electrocatalytic applications.

Keywords: Synthesis; Cuprous oxide (Cu_2O) nanoparticles; Chemically Reduced Graphene (CRG) ; Non-enzymatic electrocatalysis.

1. INTRODUCTION

Graphene nanosheet (GN), which is a monolayer of carbon atoms tightly packed into a honeycomb lattice[1], has opened a new avenue for utilizing two-dimensional (2D) carbon material as a support because of its high conductivity (10^3-10^4 S/m), tremendous surface area (theoretically calculated value, 2630 m^2/g), unique graphitized basal plane structure, high thermal and chemical stability, and potential low manufacturing cost[1-3]. These unique structure make graphene a promising additive or supporting component for potential applications in various fields [4-9], such as nanoelectronics [10,11], batteries [12], nanocomposites [13,14], supercapacitors [15] , and sensors [16,17] solar cells [18,19] fuel cells [20, 21] etc. Especially the metals or metal oxides are distributed onto the surface of graphene or between the graphene layers, as substrates for immobilizing metal or metal oxide catalysts , have been fabricated by restacking graphene sheets in the presence of guest nanoparticles or corresponding precursors. For example, Pt [22], Co_3O_4 [23] nanoparticles supported by chemically converted graphene were found to be an excellent electrocatalyst for oxygen reduction reaction (ORR). Palladium nanoparticles on graphite oxide and its functionalized graphene derivatives showed high catalytic activities for the Suzuki-Miyaura coupling reaction [4]. TiO_2 nanoparticles decorated graphene exhibited high photocatalysis performance[24]. MnO_2/graphene, SnO_2/graphene and ZnO/graphene hybrids or composites have been demonstrated to reveal special features in new hybrids that can be widely utilized in supercapacitors [25,26]. Compared to other carbon matrices such as graphite[27], carbon black [28], and carbon nanotubes [29], graphene sheets preserve the high electrical conductivity of the overall electrode.

Copper-based and its oxide-based nanomaterials were of great interest for their extensive applications in catalysis, gas sensor, Li ion battery, gas sensor, field-effect transistors and biosensors for a long time [30-32]. Especially, there is a great amount of interest on copper-based nanocomposites for the non-enzymatic detection of glucose [31, 33]. Luo[34] developed a non-enzymatic glucose sensor by prepared from copper nanoparticles and graphene which can be prepared by one-setp electrochemical reduction using graphene oxide (GO) and copper ion as the starting materials. Kang[35] fabricated a Cu-carbon nanotubes composite sensor by electrochemically depositing copper nanoclusters on MWNTs modified glass carbon electrode (GCE). Yang[36] reported that copper nanoparticles could load easily on the sidewall of MWNTs via polyelectrolyte coat on MWNTs and exhibited high electrocatalytic activity, and so on.

Herein, a facile and straightforward strategy is designed to deposit Cu_2O nanoparticles on graphene sheets at a low temperature using sodium citrate as reductant and stabilizer. The as-prepared Cu_2O@CRG show higher sensitivity and more excellent selectivity than CRG or Cu_2O in alkaline media. To the best of our knowledge, little research on the fabrication of Cu_2O@CRG hybrids in a water-sodium citrate system has been reported so far. Our study opens a novel and insightful way to develop electrocatalyst for sensing application.

2. EXPERIMENTAL

2.1 Raw materials

Graphite powder was obtained from Alfa Aesar (Shanghai Carbon Co., Ltd., China), with a particle size of 100 μm, and sodium citrate were bought from Shanghai Chemical Factory (Shanghai, China). All chemicals were of analytical grade and solutions were prepared with deionized water from a pure system (>18 MΩ, Purelab Classic Corp., USA).

2.2 Synthesis of GO

The graphene oxide (GO) was synthesized from natural graphite powder according to the literature [37]. Briefly, graphite powder (3.0 g) were gradually added into 98% H_2SO_4 (140 mL) with vigorous stirring in an ice-water bath. After the graphite forms a black slurry, $NaNO_3$ (3.0 g) was slowly added for about 25 min. The mixture was then placed to room temperature and stirred for 1 h. Then 250 mL water was added to the solution followed by stirring at 80 ^{o}C for 30 min. The mixture was poured into 800 mL water, next slowly adding 20 mL H_2O_2. The solution was filtered after the color of the solution changed from dark brown to yellow. The resultant material was redispersed in water and filtered several times until the pH of the filtrate was neutral. Finally, a homogeneous aqueous GO dispersion (about 1 mg/mL) was obtained.

2.3 Synthesis of Cu_2O@CRG

In a typical procedure, 50 mg GO, 25 mg $CuCl_2$ and 200 ml deionized (DI) water were mixed in a 500 ml three-necked flask, and the mixture was ultrasonicated at low energy for 1 h at room temperature. Sodium citrate solution (120 ml, 10%) was then added slowly to the above mixture solution under continuous stirring at 100◦C for 24 h. Subsequently, the mixture was filtered and washed several times with DI water to remove byproducts. The resulting product dried at 80◦C for 24 h under vacuum to obtain the chemically reduced graphene supported Cu_2O nanoparticles (Cu_2O@CRG) hybrids. For comparison, Cu_2O was prepared by the same procedure without GO, and CRG was also synthesized by chemically reduction.

2.4 Characterization

TEM images were obtained from JEM-2100 (Japan) with a 200 kV accelerating voltage. The TEM samples were prepared by drying a droplet of the chemically reduced graphene (CRG) or Cu_2O@CRG suspensions on a Cu grid. AFM images were obtained on an Agilent 5500 AFM/SPM system with Picoscan v5.3.3 software in tapping mode under ambient conditions. An X-ray powder diffractometer (XRD, Shimadzu, X-6000, Cu Kα radiation) was used to determine the phase purity and crystallization degree.

2.5 Electrochemical experiment

1.5 mg Cu_2O@CRG powder was dispersed in 300 μL dimethylformamide (DMF). Nafion solution (1.5%) was prepared by diluting 5% Nafion solution (Aldrich) with ethanol. 2.5 μL Cu_2O@CRG composite in DMF was cast on a well-polished glassy carbon electrode (φ= 3 mm) twice under atmosphere. After the film was dried, Nafion solution (1.5% in ethanol) was pipetted on the catalyst surface for protection. Electrochemical measurements were performed at a standard three-electrode electrochemical cell on a CHI 800 electrochemical Station (CH Instrument, USA) with a modified electrode as the working electrode, a platinum foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode, respectively.

3. RESULT AND DISCUSSION

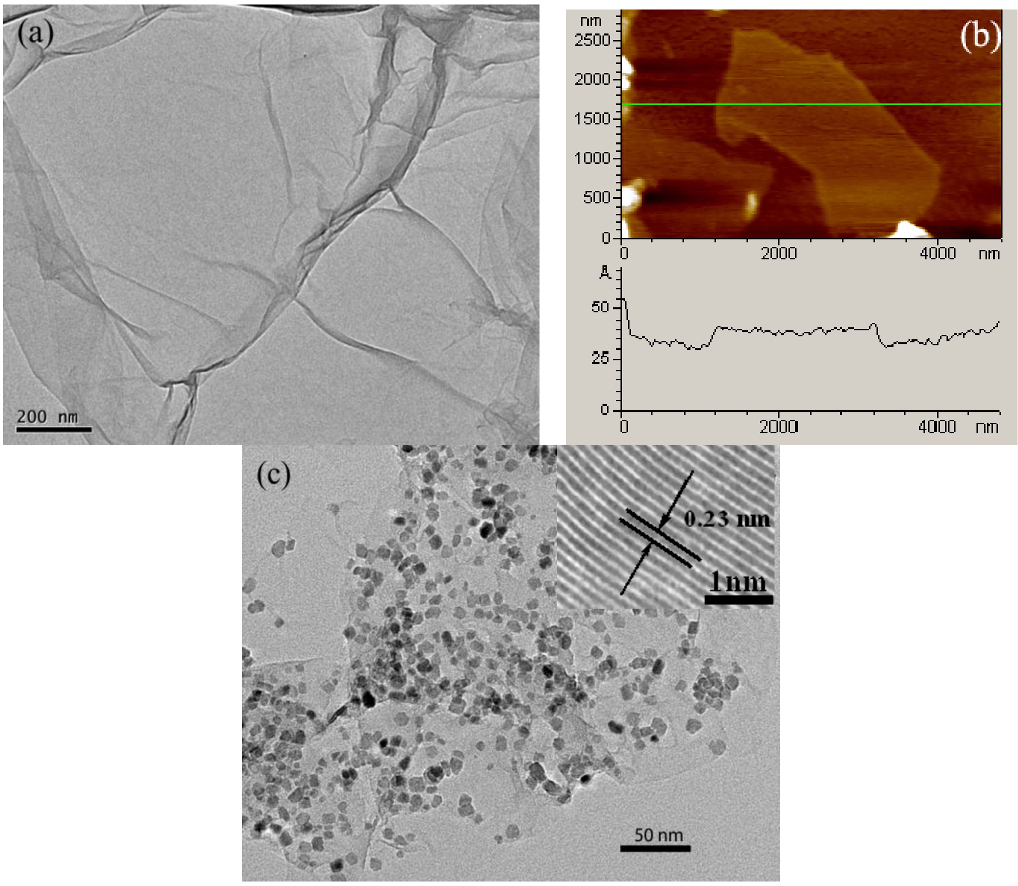


Figure 1. (a and b) Typical low-resolution TEM and tapping-mode AFM image of as-prepared CRG, (c) TEM image of Cu_2O@CRG composites and the upright inset is its part magnified image.

The morphologies of chemical reduction graphene (CRG) and the as-prepared Cu_2O/CRG were characterized using TEM and AFM. As shown in Fig. 1a, the CRG nanosheets are randomly compact and stacked together, showing uniform laminar morphology like crumpled silk veil waves. Atomic force microscopy (AFM) can directly characterize the morphologies and layers of CRG. The AFM samples were prepared by dropping CRG dispersed in DMF onto clean silicon wafers and dried at room temperature. Fig.1b displays the typical AFM image of the chemically reduced graphene oxide. Planar graphene nanosheets with an average thickness of about 1.0 nm appeared, corresponding to less than three single graphene layers by considering the theoretical thickness of a single-layer graphene (around 0.34 nm), indicating CRG is a few-layered nanostructure.

The highly dispersed nanoparticles on supports with larger surface areas have unique properties with advantages for catalytic activity and sensor sensitivity [38]. As shown in Fig. 2c, the anchored crystal Cu_2O NPs distributed evenly on the graphene nanosheets without obvious aggregations. These two or three layer graphene nanosheets possess huge surface areas, and particles can deposit on both sides and surfaces of these sheets [39, 40]. Thus, such integration of two-dimensional supports with large surface areas and the highly dispersed nanoparticles can be an exciting material for use in future nanotechnology. Moreover, the corresponding high-resolution TEM (HRTEM) image in the top right insets of Fig. 1c shows a clear interplanar spacing of 0.23 nm, corresponding to the (111) plane of the Cu_2O [41].

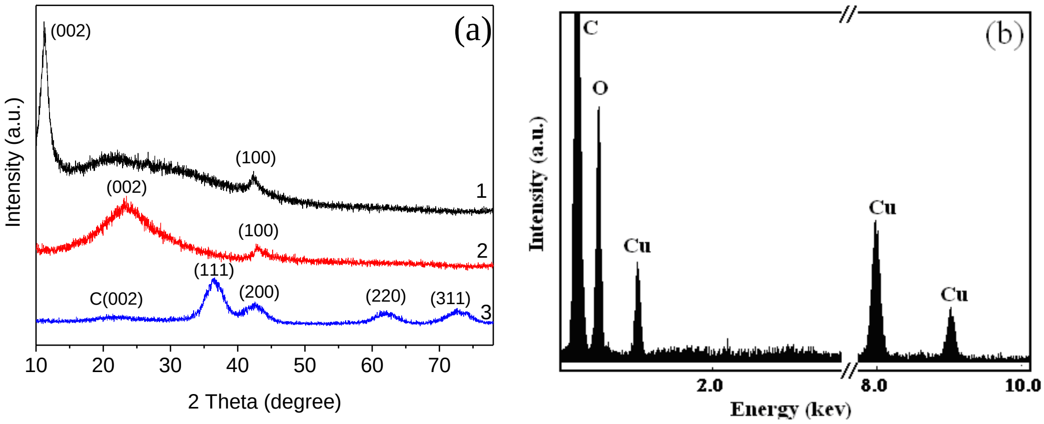
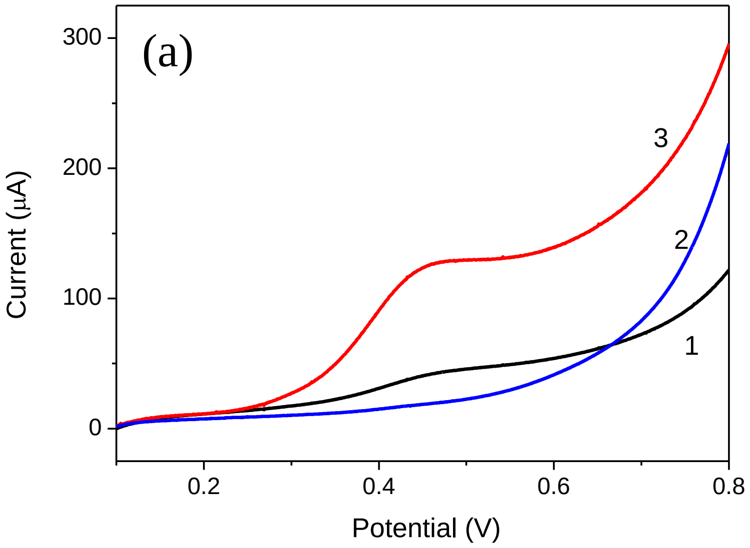


Figure 2. (a) XRD patterns of as-prepared (1: GO, 2: CRG and 3: Cu_2O@CRG. (b) EDX spectrum was obtained from graphene-supported Cu_2O nanoparticles

Fig. 2a shows XRD patterns of graphene oxide (GO), graphene nanosheets (CRG) and Cu_2O@CRG. In Fig. 2a-1, the characteristic diffraction peak (002) of GO at around 11°, corresponding to a d-spacing of 0.784 nm. In contrast, the interlayer distance of the (002) peak for graphite powder is 0.337 nm ($2\theta=26.3°$) [42]. This could be ascribed to the introduction of oxygenated functional groups, such as epoxy, hydroxyl (–OH), carboxyl (–COOH) and carbonyl (–C=O) groups attached on both sides and edges of carbon sheets. These surface functional groups will subsequently act as anchoring sites for metal oxides [43]. The diffraction peak at around 43°is associated with the (100) plane of the hexagonal structure of carbon [44]. It can be seen in Fig. 2a-2 that the typical diffraction peak (002) of GO shifts to higher angle after reduction in a water-sodium citrate system under heating at 100°C for 24 h. This could be attributed to fact that GO nanosheets are partially reduced to graphene and restacked into an ordered crystalline structure. X-ray diffraction of Cu_2O@CRG as displayed in Fig. 2a-3, it is obvious that the position of the strong diffraction peaks at 25.9° is attributed to the plane of (002), of graphene. Four characteristic diffraction peaks positioned at 36.4°, 42.5°, 61.4° and 73.4°could be corresponding to the (111), (200), (220) and (311) crystalline planes of the cubic phase Cu_2O [42] with cubic phase (JCDS 78–2076), respectively. Moreover, there is no peaks of impurities are detected, indicating that the Cu_2O nanostructures are pure and well crystallined. To further confirm it is Cu_2O nanoparticles loaded on the graphene sheets, we undertook the energy-disperse X-ray spectrum (EDX) measurement on the hybrids on carbon grid. The results further reveals that the samples contain elements of copper and oxygen and exhibit an oxide state.



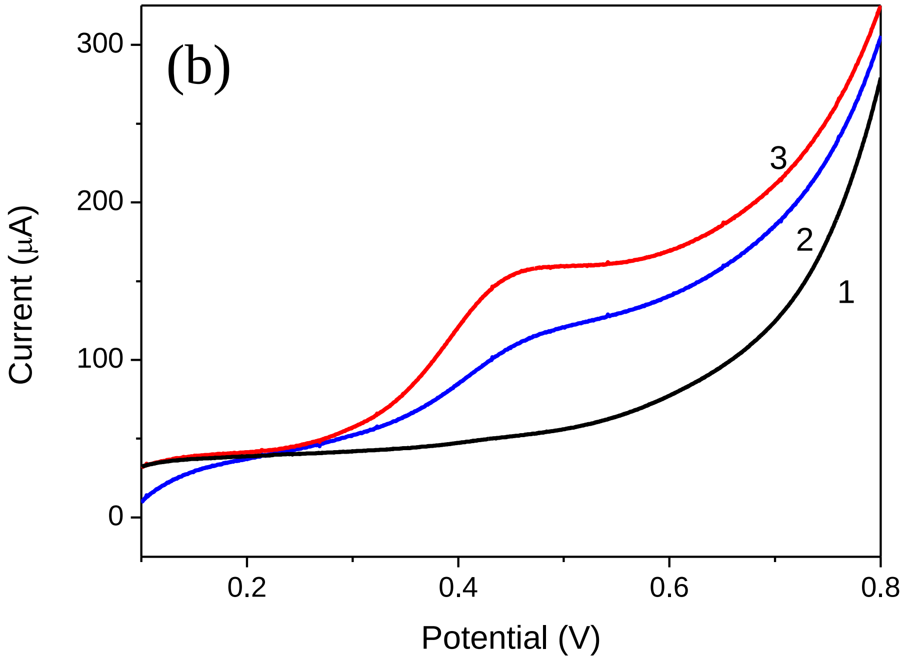


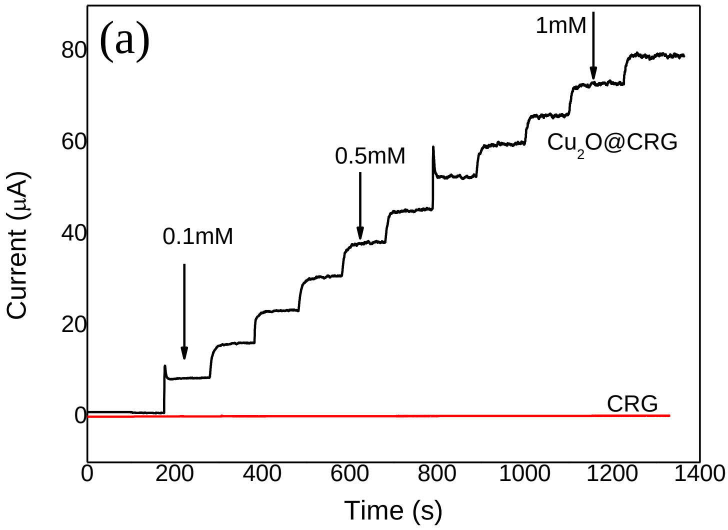
Figure 3. Linear sweep voltammetry (LSV) of (a): the Cu_2O (curve 1), CRG (curve 2), and Cu_2O@CRG (3) modified GC electrodes in 50mM NaOH solution containing 2mM glucose at a scan rate of 50 mV s^{-1}, and (b) the Cu_2O@CRG electrode in 50mM NaOH solution containing different concentration of glucose (curve 1: 0 mM, curve 2: 1 mM, curve 3: 2 mM) at a scan rate of 50 mV s^{-1}.

Decoration of metal or metallic oxide nanoparticles on CRG can be an alternative strategy for the construction of two-dimensional graphene-based hybrids. Their rough surfaces probably endow them with a higher electrochemical active area, resulting in a higher turnover for heterogeneous catalytic reactions or electrochemical reactions. Herein, glucose was selected as the model analyte using the typical Linear sweep voltammetry (LSV) methods. The electrocatalytic activity of the Cu_2O@CRG was compared with the CRG or Cu_2O alone as the electrode modifying material for oxidation of glucose in 50mM NaOH solution, as shown in Fig. 3a. From the current response, the nanohybrids exhibit typical current response for the oxidation of glucose (curve 3). However, no obvious oxidation peak for glucose can be found at the CRG (curve 2) and Cu_2O nanoparticles (curve 1) modified electrodes. Such excellent electrocatalytic activity of the Cu_2O@CRG nanohybrids may be attributed to high catalytic active sites for the glucose oxidation provided by the Cu_2O nanoparticles and the introduction of the CRG plays an important role in the increase of the efficient electroactive surface area and providing the conductive bridges for accelerating the electron-transfer.

The electrocatalytic activity of the as-prepared Cu_2O@CRG nanocomposites modified electrodes towardss oxidation of glucose was investigated by LSV. Fig. 3b presents the LSV responses obtained at the Cu_2O@CRG modified electrode in 50 mM NaOH solution containing different concentrations of glucose at a scan rate of 50 mV s^{-1}. No oxidation peak appears in the absence of glucose as shown in curve 1 of Fig.3b, With 1 mM glucose being added (curve 2), notable enhancement of oxidative peak current corresponding to the irreversible oxidation of non-enzymatic glucose is observed, and the amperometric response increased with a rising concentration of glucose (curve a) at about +0.43 V, where the oxidation peak is due to the conversion of Cu (II) to Cu (III) [36]. These results illustrate that the Cu_2O@CRG nanocomposites exhibit excellent electrocatalytic activity towards the oxidation of glucose. The oxidation mechanism of glucose in alkaline media may be that copper species could make C-C bond of glucose cleave easily. Some documents believe that the electrocatalytic activity of Cu-based hybirds towardss glucose may be attributed to the involvement of Cu(II) and Cu(III) surface species in the oxidation of glucose in alkaline medium [36, 45, 46].

Electrocatalysts are generally estimated by measuring current response at a fixed potential after addition of the analyte for chemical sensing applications. Fig. 4a displays the amperometric responses at the Cu_2O@CRG modified glassy carbon electrode for a successive addition of glucose at about 100 s in 50mM NaOH at optimal potential of 0.45 V. It is observed that notable enhancement of current responses was obtained and the steady-state current was achieved less than 3 s after each addition of glucose solution, which indicates an extraordinarily fast rapid and sensitive response to glucose. Moreover, the Cu_2O@CRG electrode yielded a much larger current response than CRG electrode. The results indicate that the as-synthesized Cu_2O@CRG nanohybrids exhibit very sensitive and rapid response characteristics, which is ascribed to the highly electroconductivity and large active surface area of the nanohybrids.

Fig. 4b shows that the correlation between the amperometric responses and glucose concentration range from 0.1 mM to 1.1 mM at CRG and Cu_2O@CRG modified electrode. As seen in Fig. 4b, the current response of Cu_2O@CRG exhibited a good linear dependence on glucose concentration (R^2=0.999) and the detection limit was 1.2μM (at signal/noise = 3). This is owing to the nanocomposite nature of as-prepared Cu_2O@CRG modified electrode based on CRG with huge active surface area, which facilitates high catalytic activity towardss glucose.



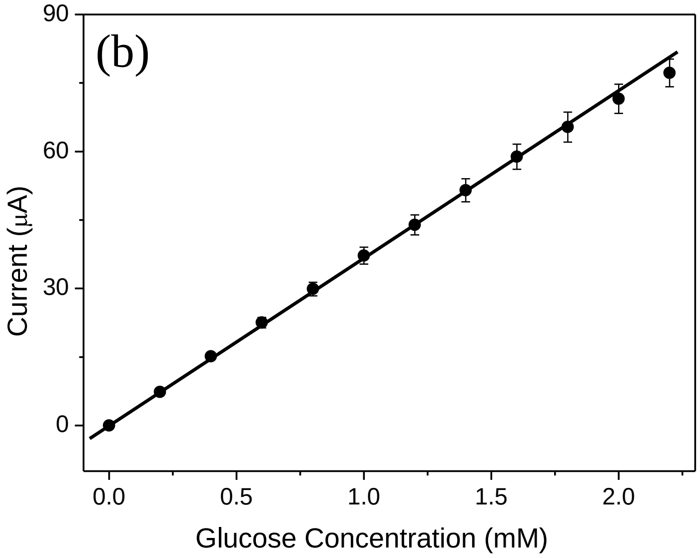


Figure 4. (a) Current–time responses at +0.45V with an successive increasing glucose concentration of 0.1mM per 100 s for the CRG and Cu_2O@CRG modified GC electrode respectively. (b) The dependence of the current response vs. Glucose concentration at Cu_2O@CRG modified GC electrode. Error bars indicate standard deviations of five measurements.

Ascorbic acid (AA), dopamine (DA), and uric acid (UA) usually coexist together and are considered as important molecules for physiological processes in human metabolism. To estimate the selectivity of Cu_2O@CRG towards glucose detection, three possible interfering biomolecules (AA, DA and UA), which normally coexist with glucose were examined. Considering that the concentration of glucose in the human blood is about 30 times of AA, DA or UA [47,48], the amperometric responses towards the addition of 0.5mM glucose, 0.1mM AA, DA and UA were examined in 50 mM NaOH solution at +0.45 V. As shown in Fig. 5a, well-defined glucose responses were obtained, whereas very small responses were observed for interfering species, which can be neglected compared to glucose.

These results indicate that Cu_2O@CRG modified GCE has high selectivity for glucose detection. In addition, several electroactive compounds (such as NaCl, NaH_2PO_4 and sodium citrate) normally coexist with glucose in human blood. the current responses towards the successive addition of glucose, NaCl, NaH_2PO_4 and sodium citrate were examined.

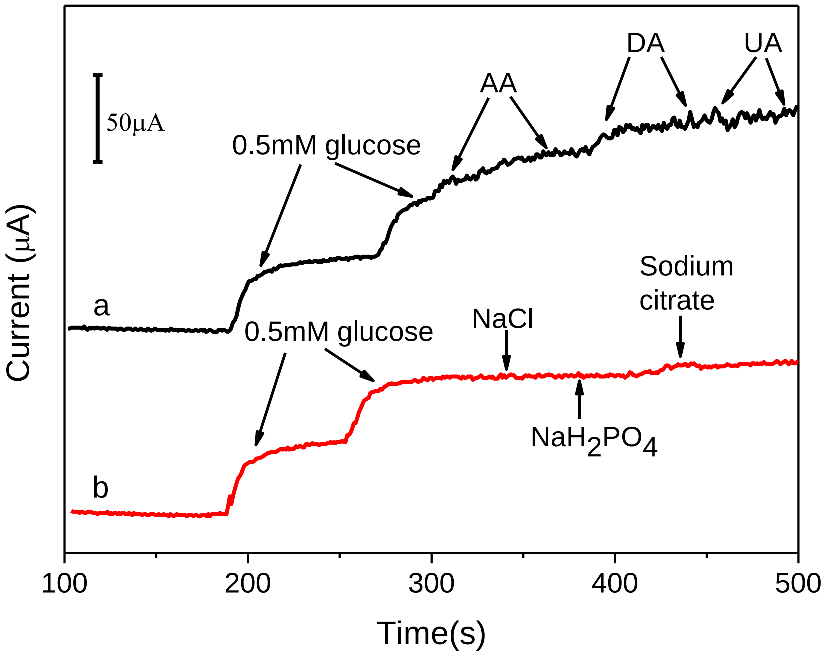


Figure 5. Interference measurement of the Cu_2O@CRG modified GC electrode in 50 mM NaOH at +0.45 V, (a) successive additions of 0.5 mM glucose and 0.1 mM other interferents (ascorbic acid (AA), dopamine (DA) and uric acid (UA)), (b) successive additions of 0.5 mM glucose, 0.1 mM NaCl, 0.1 mM NaH_2PO_4 and 0.1 mM sodium citrate.

The results show that the foreign substances did not interfere significantly on the glucose determination. These results indicate good selectivity of the Cu_2O@CRG nanostructure modified electrodes, which makes as-obtained Cu_2O@CRG hybrids as a promising candidate for glucose analysis.

4. CONCLUSIONS

In summary, we have developed a simple and effective procedure to the decoration of Cu_2O nanoparticles on graphene nanosheets by using sodium citrate as eco-friendly reducing agent and stabilizer for the first time. Moreover, the as-prepared Cu_2O@CRG modified GCE exhibit better non-enzymatic electrocatalytic responses to glucose than the CRG or Cu_2O in alkaline media. We believe that such a facile and low-cost assembly approach will provide a new avenue for the large-scale production of various functional hybrid materials for electrochemical sensing and other electrocatalytic applications.

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