Preparation of a Cu$_2$O/rGO porous composite through a double-sacrificial-template method for non-enzymatic glucose detection

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ABSTRACT

We report a double-sacrificial-template method for the fabrication of a Cu$_2$O and a reduced graphene oxide (rGO) porous nanocomposite (Cu$_2$O/rGO), which has great potential in non-enzymatic glucose detection. Firstly, an aqueous graphene oxide (GO) solution was dispersed in a polystyrene (PS)/cyclohexane (CH) solution to prepare a water-in-oil emulsion at 50 °C. Then, the emulsion was cast onto a glass substrate to evaporate solvents and cooled down to room temperature. During that time, the self-assembly of the GO sheets and the PS chains takes place at the interface. The cooling of the emulsion below the θ temperature of the system PS/CH (34.5 °C) facilitates the precipitation of the PS chains at the interface to form microcapsules. A sponge-like PS/GO composite film was thus obtained after complete evaporation of solvents, where the water droplets in the emulsion served as the first sacrificial template. The PS/GO composite was loaded with copper compounds and was then carbonized to remove the second template of the polymer. In this manner, a free-standing porous nanocomposite of Cu$_2$O/rGO was fabricated, and its structure was carefully characterized. The composite was applied as the working electrode in order to take advantages of its porous microstructure, the conductivity of rGO, and the electrochemical performance of crystalline nano-Cu$_2$O. The electrochemical responses of the composite to glucose were evaluated at glucose concentration ranging from 20 to 1000 μM. The results evidence that the porous nanocomposite of Cu$_2$O/rGO exhibits fast and linear amperometric responses to glucose with excellent sensitivities. Moreover, the stability of the Cu$_2$O/rGO composite in the electrolyte solution and its selective response to glucose have been demonstrated to indicate its practical potential.

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Introduction

Glucose detection is highly important in the clinical diagnosis of the diabetes mellitus [1, 2]. To develop effective methods for rapid, sensitive and reliable detection of glucose in blood is thus of key significance for diabetes patients to receive timely treatments. Among the many approaches [1–6] established for that purpose, the electrochemical method [1, 2, 7] has received particular attention due to its characteristics of high sensitivity, fast response, outstanding accuracy, low cost and easy operation. It has been reported [7] that there are two types of electrochemical sensors for glucose detection, i.e., the enzymatic and the non-enzymatic glucose sensors. However, the enzymatic glucose sensor suffers from inevitable disadvantages such as requirement for expensive enzyme, tedious enzyme immobilization process and unsatisfactory chemical and thermal stabilities [8], whereas the non-enzymatic glucose sensor can overcome those drawbacks to some extent through direct electrocatalytic oxidation of glucose.

During the past few decades, a lot of metals or alloys and metal oxides at nanometer scale have been explored for the non-enzymatic glucose detection, and the unique features and architecture of the nanomaterials were carefully designed and utilized [7]. In comparison with the noble metals and alloys, copper oxide (CuO)- and cuprous oxide (Cu_2O)-based nanomaterials have superiorities of inexpensiveness together with high activity of non-enzymatic direct electrooxidation of glucose [7, 9, 10]. The Cu-based oxides were fabricated into different kinds of nanoscaled architectures in order to make utilization of their exceptional optical and electrical properties [9, 10]. During glucose detection, Cu_2O generates Cu(III)/Cu(II) redox couple, which can then transform glucose into glucolactone through catalytic reaction to realize glucose detection [7]. Lately, the well-known two-dimensional material of graphene oxide (GO) has been widely employed to prepare Cu-based composite sensors [11]. The large surface area and excellent conductivity of GO [12] will greatly improve the electrochemical performances of the prepared composite or hybrid materials [6, 7, 11, 13–17]. In order to take advantage of the characteristics of GO, metal oxides are anticipated to grow on the matrix of GO to expose more active sites of the obtained sensor to improve its electrochemical performances [11]. However, GO can hardly form framework of a porous material [12] to provide firm matrix for the growth of the metal oxides.

It has been reported [18] that there is strong $\pi-\pi$ stacking interaction between the aromatic groups of polystyrene (PS) and GO sheets. In this work, a water-in-oil emulsion was prepared by dispersing GO aqueous solution in PS/CH solution, and self-assembly of the PS chains and the GO sheets was expected to take place at the interface of the emulsion. Meanwhile, the PS chains would be precipitated at the interface during the cooling step of the preparation process, which facilitated formation of a firm framework. After complete solvent evaporation of the emulsion, a porous composite of PS/GO was thus prepared, where water droplets in the emulsion served as sacrificial templates. Copper compounds were then loaded on the PS/GO composite. After carbonization to remove the polymer matrix, a free-standing and porous Cu_2O/rGO nanocomposite film was thus obtained. The preparation and the microstructures of the obtained materials were carefully analyzed and discussed. The electrochemical performances of the Cu_2O/rGO composite were characterized, and its amperometric responses to glucose were evaluated. Moreover, the stability of the porous Cu_2O/rGO composite and its selective amperometric responses to glucose were measured to indicate its potential application in non-enzymatic glucose detection.

Experimental section

Materials

Polystyrene (PS, weight-average molecular weight $M_w = 240$ kg/mol, polydispersity index $d = 1.80$) was obtained from the former Hüls AG. Analytical grade reagents of copper sulfate, sodium hydroxide, cyclohexane (CH), sodium dodecyl benzene sulfonate (SDS), glucose, uric acid (UA), ascorbic acid (AA), sodium chloride (NaCl) and dopamine (DA) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China) and were used directly without further purification. Deionized water was used throughout. Graphene oxide (GO) was synthesized from graphite powder using an improved Hummers method [19]. The obtained GO is about 1.2 nm in thickness according to our previous work [20].

Preparation of PS/GO composite

PS was firstly dissolved in CH under 50 °C with a concentration of 20 mg/mL. GO and SDS were ultrasonic oscillated in water for 15 min under 50 °C to obtain a mixture having GO content of 2 mg/mL and SDS content of 50 mg/mL. Then, the mixture was dropped into the PS/CH solution having twice volume of the former under vigorously stirring. A water-in-oil emulsion was obtained after stirring for 4 h, during which the slurry was naturally cooled down to 25 °C. The emulsion was thereafter cast onto a clean glass substrate to evaporate CH at room temperature and then completely dried in a ventilation oven at 50 °C. The obtained sponge-like composite was washed thoroughly with water and ambient-dried.

Preparation of porous Cu_2O/rGO composite

The PS/GO composite was soaked in a 50 mM copper sulfate aqueous solution for 12 h and then dipped into a 100 mM sodium hydroxide aqueous solution. After drying at ambient conditions, it was washed with water until neutral and heat-treated at 500 °C in a tube furnace (GSL-1500X, Kejing, China) under argon atmosphere for 3 h. During the thermal treatment, the polymer template of PS was removed, the GO was reduced into reduced graphene oxide (rGO) [19], and Cu_2O was formed at the same time. In this manner, the Cu_2O/rGO composite was fabricated.

Characterizations

The obtained samples were sputter-coated with a thin layer of gold (about 2 nm) and then examined with a scanning electron microscope (SEM, SU-70, Hitachi, Japan). X-ray diffraction (XRD) patterns of the obtained materials were recorded using a Bruker D8 ADVANCE X-ray diffractometer (Bruker, Germany) with Cu-Kα radiation. The samples were continuously scanned from 10° to 80° (2θ) at a speed of 0.0167° s^{-1}.

Electrochemical performances and glucose detection

All electrochemical experiments were performed on an Autolab PGSTAT302N electrochemical work station (Metrohm, Switzerland). The electrochemical properties of the obtained composite were evaluated using a three-electrode system at room temperature, where the counter and reference electrodes were Pt foil and saturated calomel electrode (SCE), respectively. The working electrode was glass carbon electrode (GCE) modified with the Cu_2O/rGO composite. The GCE (3 mm in diameter) was in turn polished by 1, 0.3 and 0.05 μm alumina powder and then washed repeatedly with ethanol and water. Four mg of the as-prepared Cu_2O/rGO composite was dispersed in 1 mL 0.5% Nafion (Aldrich, USA) solution and then sonicated for 10 min to obtain a homogeneous black suspension. Four μL of the suspension was dropped onto the aforementioned GCE. After air-dried, the GCE modified with the Cu_2O/rGO composite was served as the working electrode.

Cyclic voltammetry (CV) experiments for the detection of glucose were carried out in the potential window of −0.8 to 0.8 V with a series of scan rates (10, 20, 50, 80, 100, 150 and 200 mV/s) using 0.1 M NaOH solution as the electrolyte. Chronoamperometry experiments were implemented at a constant potential of 0.6 V in 0.1 M NaOH electrolyte.

Results and discussion

Preparation of the porous Cu_2O/rGO composite

For the purpose of the fabrication of the final Cu_2O/rGO porous composite material, a water-in-oil emulsion slurry was firstly prepared. Based on the strong π–π stacking interaction between the aromatic groups of PS and the GO sheets [18], the PS chains and the GO sheets assemble at the interface of the emulsion. The PS chains are in a relatively extended conformation in CH at 50 °C, which is much higher than the θ temperature (about 34.5 °C) of the PS/CH binary system [21]. With the temperature of the emulsion gradually decreasing during stirring, the PS chain coils start to shrink. As the temperature of the emulsion decreases below the θ temperature, the PS chains are precipitated and enriched at the interfaces [21]. After complete evaporation of the solvents (CH and water) of the casting slurry, a sponge-like film containing PS and GO was obtained. Figure 1 shows the morphology of the PS/GO composite film and indicates an irregular microparticle randomly packed microstructure.
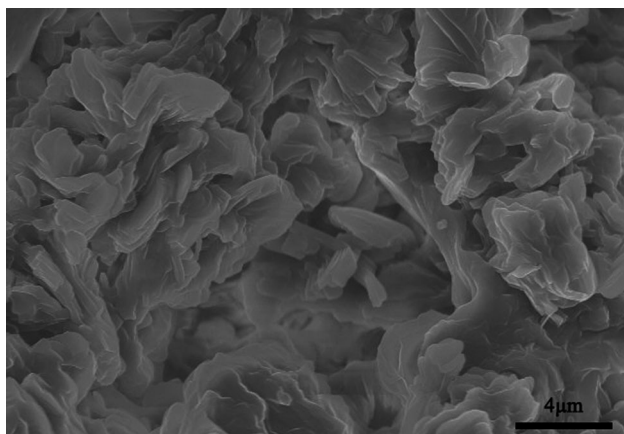
Figure 1 SEM image of the surface of the PS/GO film.

According to the above analysis, the obtained PS/GO composite has a hollow microcapsular microstructure, where the PS and the GO sheets form the walls of the microcapsules. This is confirmed by the SEM images illustrated in Fig. 2, which shows the microstructure of the PS/GO composite after thermal treatment at 500 °C in Argon for 3 h. Figure 2a shows a porous microstructure of the obtained material, and Fig. 2b reveals that the microcapsules constitute the matrix of the material. The microcapsules have a scale at hundreds of nanometers to several micrometers. It is interesting to note that most of the microcapsules are to some extent collapsed, which is attributed to evaporation of the water-droplet templates during drying of the PS/GO composite and to the removal of PS during the following thermal treatment. Therefore, the GO remained to form framework of the obtained material after carbonization of the PS/GO composite film. It is worth

mentioning that the obtained material is a free-standing film.

Through immersing the as-prepared PS/GO composite film in an aqueous solution of copper sulfate and subsequent drying under ambient conditions, Cu^{2+} was loaded on the framework in order to take advantage of the specific microstructure. Then, it was soaked in sodium hydroxide aqueous solution to transfer the Cu^{2+} into $Cu(OH)_2$. After washing until neutral, the $Cu(OH)_2$-loaded film was thermally treated at 500 °C in argon atmosphere for 3 h to remove the polymer template. During the thermal treatment, the GO was reduced to reduced graphene oxide (rGO) [18] and Cu_2O was formed [22] simultaneously, so that the Cu_2O/rGO composite was prepared.

Figure 3 shows the SEM images of the obtained Cu_2O/rGO composite. As illustrated in Fig. 3a, the composite retains its microporous morphology. More detailed observations (Fig. 3b) suggest that numerous nanoparticles at the scale of 100 nm decorate the matrix of the composite. Figure 4 displays the XRD pattern of the obtained composite. The peaks at 29.5°, 36.3°, 42.4°, 61.5° and 73.8° can be indexed to the (110), (111), (200), (220) and (311) crystal faces of Cu_2O [8, 13], respectively. The sharp and strong peaks indicate that the Cu_2O is highly crystalline, which may have positive influence on the electrochemical activity of the composite [23]. The weak peaks at 43.4°, 50.6° and 74.2° are corresponding to the crystalline planes of (111), (200) and (220) for Cu metal. However, there is no peak for crystalline CuO in the pattern. The results demonstrate that the loaded copper compounds have mainly been transferred
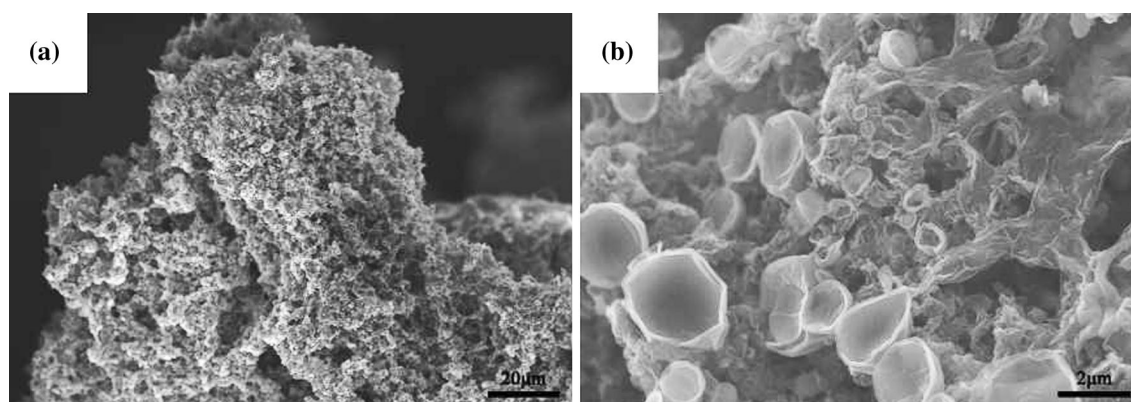

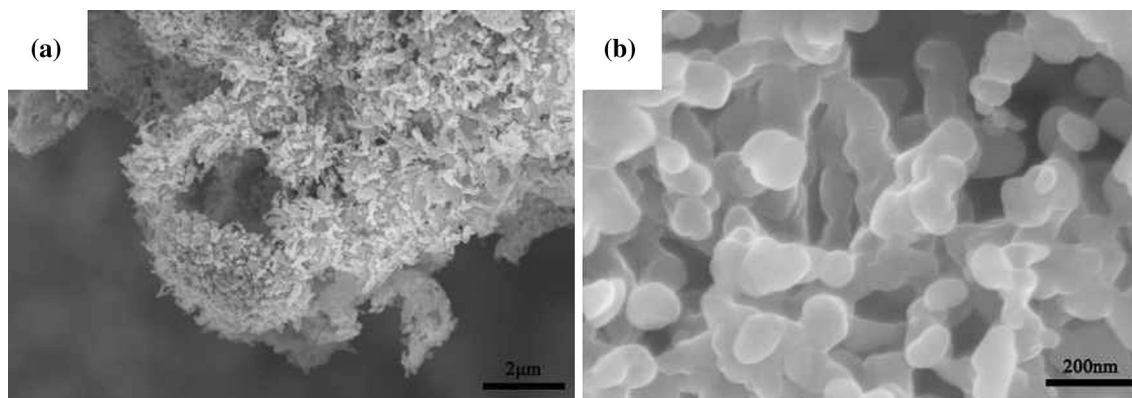**Figure 2** SEM images of the PS/GO composite after thermally treated at 500 °C in Argon for 3 h.

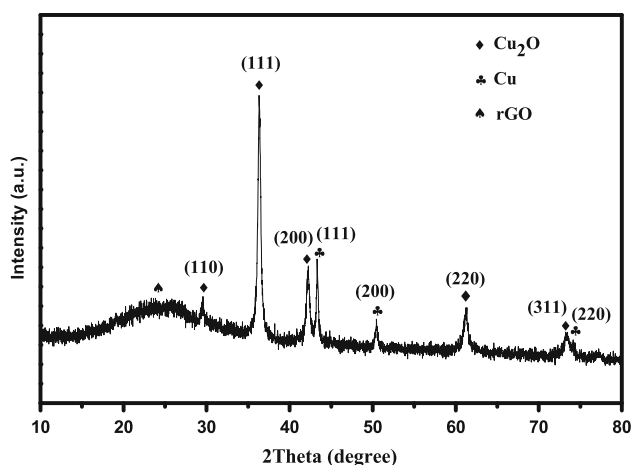**Figure 3** SEM images of the Cu_2O/rGO composite under different magnification.

Figure 4 XRD pattern of the Cu_2O/rGO composite.

into Cu_2O during the thermal treatment, which is known as the carbothermal reaction procedure [24–26]. The wide band centered around 23.8° is attributed to the layered rGO, which was reduced from GO during the thermal treatment [19]. Therefore, the Cu_2O/rGO composite was successfully prepared to combine the advantages of the microporous structure, the conductivity of rGO, and the electrochemical performance of nano-Cu_2O, implying excellent potential application in electrochemical sensing.

Glucose detection

The porous Cu_2O/rGO composite was used to modify the GCE to serve as the working electrode. Figure 5 displays the CV curves of the electrode in 0.1 M NaOH aqueous solution in the absence and in the presence of 5 mM glucose at a scan rate of 50 mV/s. The CV curve in the absence of extra
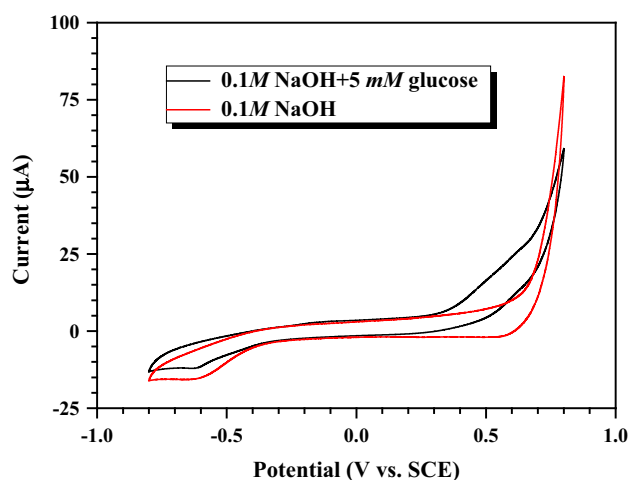

Figure 5 CV curves of the Cu_2O/rGO composite in 0.1 M NaOH aqueous solution in the absence and in the presence of 5 mM glucose at scan rate of 50 mV/s.

glucose has a sharp peak loop at the potential over 0.6 V, which could be attributed to the oxidation of copper ions [13, 27, 28]. After addition of 5 mM glucose in the electrolyte, the CV curve exhibits an obvious cathodic stage in the range of 0.3–0.7 V, which is considered to be due to the oxidation of glucose. It has been widely reported that the oxidation of glucose could be catalyzed by Cu_2O, and the most acceptable mechanism is that Cu^{3+} ions produced from the oxidation of Cu^{2+} may act as electron transmitter to oxidize glucose into glucolactone [7, 11, 27, 28]. As illustrated in the CV curve, the present composite material has an obvious amperometric response to glucose.

Figure 6a shows the CV curves of the Cu_2O/rGO composite material in 0.1 M NaOH aqueous solution in the presence of 5 mM glucose under different scan
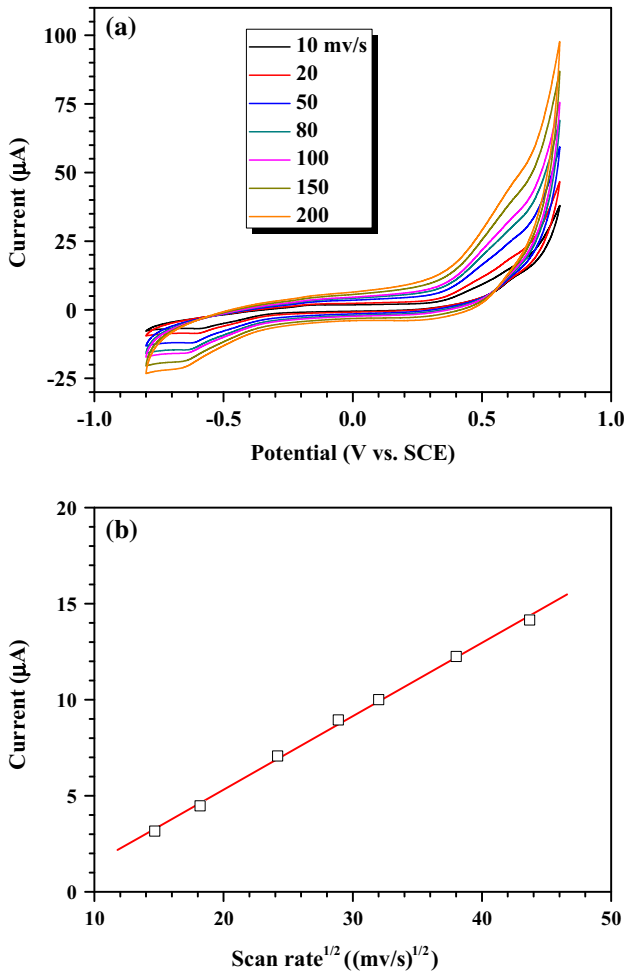
Figure 6 CV curves of the Cu₂O/rGO composite material in 0.1 M NaOH aqueous solution with 5 mM glucose under different scan rates (**a**), and dependence of the glucose oxidation current at 0.6 V on square root of scan rate (**b**). The *line* in **b** is the linear fitting of the experimental data with a correlation coefficient (*R*) of 0.9991.

Figure 7 Amperometric responses of the Cu₂O/rGO composite to the successive addition of glucose with various concentrations in 0.1 M NaOH at 0.6 V (**a**), and dependence of the current on glucose concentration (**b**). The *data points* in **b** are linearly fitted in glucose concentration below and over 200 μM, respectively.

rates (10–200 mV/s). It is obvious that the profiles of the CV curves are similar under the investigated scan rates. Moreover, it is found that the glucose oxidation current increases with increasing the scan rate, so the current at 0.6 V has been correlated with the square root of the corresponding scan rate. As shown in Fig. 6b, the experimental data points can be linearly fitted with a correlation coefficient (*R*) of 0.9991. The linear dependence suggests that the oxidation of glucose is determined by its diffusion to the electrode [8]. This means that the composite has electrochemical response to glucose in a wide range of scan rates.

The sensitivity of the composite to glucose has been evaluated. Figure 7a shows the amperometric
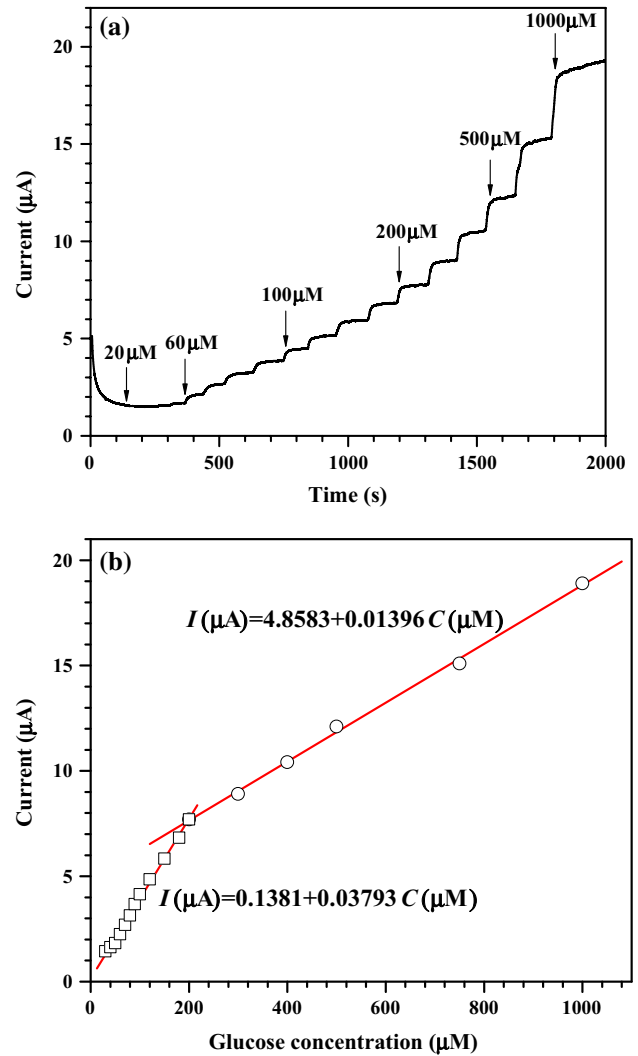
responses of the Cu₂O/rGO composite to successive addition of glucose at various concentrations under a constant working potential of 0.6 V. In order to eliminate the diffusion effect, the electrolyte was magnetically stirred to realize homogeneous distribution of glucose in the electrolyte. A well-defined and stable amperometric response has been observed during the successive addition of glucose. Moreover, it took within 10 s to achieve constant current upon addition of glucose, suggesting fast detection of glucose by the Cu₂O/rGO material. The high electrocatalytic activity of Cu₂O/rGO toward glucose could be attributed to the large surface area and high

conductivity as well as fast electron transfer provided by graphene.

The dependence of the current on the glucose concentration is illustrated in Fig. 7b. It is interesting to see that the data points below and above 200 μM of glucose can be linearly fitted, respectively. The linear fitting of the data points in the glucose concentration window between 20 and 200 μM gives the dependence of I (μA) = 0.1381 + 37.93C (mM) with a correlation coefficient (R) of 0.9977. The sensitivity is thus obtained to be 525.1 μA/mM cm^2, and the detection limit is calculated to be 4.74 μM ($S/N = 3$) of glucose. For the glucose concentration over 200 μM, the dependence reads I (μA) = 4.8583 + 13.96C (mM) ($R = 0.9992$) with a sensitivity of 198.2 μA/mM cm^2. It is noted that the sensitivity in the higher glucose concentration region is much lower. This could be ascribed to the intermediates absorbed onto the surface of the electrode due to high concentration of glucose, leading to less direct contact between glucose and the sensor [17]. The observation of multiple linear response of the present Cu$_2$O/rGO composite to glucose is similar as those reported in literatures [7, 13, 17]. The glucose detection performances of the present material is compared with those reported in some literature works, as collected in Table 1. The comparison indicates that the present sensor has relatively large linear range and low detection limit and provides satisfactory sensitivity.

In addition, the specific response of the Cu$_2$O/rGO composite to glucose is important for the practical condition. For that purpose, the electrochemical signal of the electrode to glucose was measured by successive addition of additional interferents such as AA, DA, UA and NaCl, which are the main electrolytes in human blood. Figure 8 shows the amperometric responses of the Cu$_2$O/rGO composite to

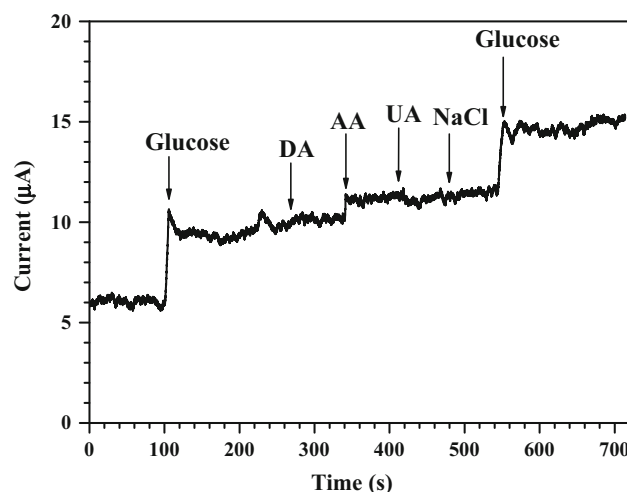Figure 8 Amperometric responses of the Cu$_2$O/rGO composite upon successive addition of 0.1 mM glucose, 0.05 mM DA, 0.05 mM AA, 0.05 mM UA, 0.05 mM NaCl and 0.1 mM glucose again under the working potential of 0.6 V in 0.1 M NaOH.

successively addition of 0.1 mM glucose, 0.05 mM DA, 0.05 mM AA, 0.05 mM UA and 0.05 mM NaCl under the working potential of 0.6 V in 0.1 M NaOH. It can be seen that the signals for DA, AA, UA and NaCl are all far less than that for glucose, indicating satisfactory selectivity toward glucose. Furthermore, 0.1 mM glucose was added after the interferents, and the response intensity was comparable with that of the first addition of glucose, suggesting excellent interference resistance. The stability of the Cu$_2$O/rGO composite was tested by storing it in 0.1 M NaOH solution and to check its response to 0.1 mM glucose after specific intervals. It has been found that the amperometric responsive current retained 92% of its initial value after two weeks, indicating high stability. Therefore, such a porous Cu$_2$O–rGO composite would be feasible for the fabrication of non-

Table 1 Comparison of the performances of the Cu$_2$O-based non-enzymatic glucose sensors

Electrode material	Linear range (μM)	Detection limit (μM)	Sensitivity (μA/mM cm^2)	References
Cu$_2$O nanoparticles	50–1100	47.2	190	[29]
Cu$_2$O nanocubes	0–500	38	121.7	[30]
Hollow Cu$_2$O nanospheres	1.25–37.5	0.4	2038.2	[8]
Carbon quantumdots/octahedral Cu$_2$O	20–4300	8.4	298	[31]
Cu$_2$O microsphere-rGO	1–419	0.73	–	[16]
Graphene-wrapped Cu$_2$O nanocubes	300–3300	3.3	285	[14]
Cu$_2$O NPs/rGO	0–700	0.1	–	[17]
Cu$_2$O/rGO porous nanocomposite	20–1000	4.7	525.1/198.2	This work

enzymatic glucose sensor with high stability, sensitivity and specificity.

Conclusions

In this work, a double-sacrificial-template method was employed to successfully prepare a free-standing Cu_2O/rGO porous nanocomposite. The results indicate that the rGO sheets constitute the walls of the matrix of the composite material and highly crystalline Cu_2O nanoparticle at the scale of 100 nm decorates the rGO walls. The porous Cu_2O/rGO composite was applied to modify the GCE to serve as the working electrode, which shows fast amperometric response to glucose. The Cu_2O/rGO composite exhibits linear amperometric responses to glucose, which reads I (μA) $= 0.1381 + 37.93C$ (mM) in the glucose concentration range of 20–200 μM, and I (μA) $= 4.8583 + 13.96C$ (mM) when the glucose concentration is over 200 μM. The sensitivities are 525.1 and 198.2 μA/mM cm^2 in the two glucose concentration regions, respectively. The satisfactory electrochemical response of the Cu_2O/rGO porous nanocomposite to glucose can be attributed to the porous microstructure, the conductivity of rGO, and the electrochemical performance of crystalline nano Cu_2O. Moreover, the Cu_2O/rGO composite displays selective amperometric response to glucose and excellent stability in electrolyte solution, suggesting its feasibility for fabrication of non-enzyme electrochemical sensors for glucose detection.

Acknowledgements

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