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Microwave synthesis 3D rambutan-like CuO and CuO/reduced graphene oxide modified electrode for non-enzymatic glucose detection

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Abstract: A novel type of cupric oxide (CuO) particles-reduction graphene oxide (r-GO) modified electrode has been fabricated through a facile, simple and fast microwave method. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET), and X-ray diffraction (XRD) were employed to characterize the morphologies and structures of the as-prepared samples. The results reveal that the CuO/r-GO composite was porous 3D rambutan-like microstructure with high surface area. Then the CuO and CuO/r-GO electrodes were constructed for high-performance and sensitivity non-enzymatic glucose biosensor in alkaline conditions. The proposed biosensor exhibits glucose concentrations in a range from 0.50 μM to 3.75 mM. Besides, chronoamperometry demonstrates a desirable sensitivity of 52.1 μA mM^{-1} at an applied potential of 0.50 V (vs. Ag/AgCl), with a detection limit of 0.10 μM (signal/noise=3). Most importantly, this non-enzymatic glucose biosensor was highly stable characteristics and can be manufactured into long-term stability electrode for the application in various complicated circumstances. All these results confirm that this CuO/r-GO biosensor is a promising active material for non-enzymatic glucose detection with excellent analytical properties.

Keywords: Cupric oxide; Reduction graphene oxide; Non-enzymatic biosensor; Glucose

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1. Introduction

Diabetes is one of the most common chronic diseases in the world that seriously affects normal life of hundreds of millions of people.[1-3] Blood glucose level is a basic issue in the diagnosis and treatment of diabetes, hence great efforts have been made to develop for a reliable and fast determination of glucose in clinical diagnostics applications.[4-7] Glucose oxidase (GOx) based on the immobilization of glucose oxidase on various substrates are the topics of the most previous studies on this subject, which exhibits high sensitivity and selectivity to be used as biosensors for glucose detection.[8-12] However, these established enzyme-modified electrodes generally suffer from one or more limitations, such as instability, requirement of low temperature storage, and critical operating situation.[13-14] Therefore, a strong need remains for development of non-enzymatic amperometric glucose biosensor, which can provide a unique set of physical and practical properties and may be able to be exploited in blood glucose detection.[15-17] In this context, much effort has been made over the recent several decades to develop electrochemical glucose biosensor.

Recently, graphene oxide has been extensively studied due to its unique structures, and excellent electrical conductivity, as well as it strong application potential in various fields.[18-21] Its potential applications thus have stimulated considerable efforts aimed at exploring efficient methods towards the preparations of two-dimensional graphene-based hybrid networks, in which graphene not only act as a template or scaffold for assembly other materials but also achieve their multiple functionalities.[22-23] Alternatively, as a well-known materials of p-type semiconductor, cupric oxide (CuO) and CuO-composites have become a significant topic in many fields of science and technology involving catalysis, superconductors and lithium-ion batteries, mainly due to their characteristic of biocompatibility, reliability, nontoxicity and compatibility.[24-31] More than that based on cupric-based hybrid materials were extensively investigated for their applications in non-enzymatic glucose sensing with high sensitivity and fast response. Such activities have been documented in recent literature. For example, CuO-multi-walled carbon nanotubes (MWCNTs) array electrode for detection of glucose with high sensitivity;[32] hybrids

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of CuO-carbon fiber fabric was constructed for sensitive glucose detection.[33] Selective non-enzymatic glucose sensing platform based on copper decorated nitrogen-doped graphene.[34] All above studies indicated that copper-based/carbon composites could be chosen as glucose electroactive materials and the conductive substrates for fabricating a highly sensitive non-enzymatic glucose sensing. Up to the present, studies on the development of sensors towards CuO-based hybrid materials have been abundant conducted, however, to our best knowledge, related experimental work about based on 3D rambutan-like CuO and CuO/r-GO glucose biosensor has not been reported so far.

Herein, we demonstrate a simple and fast synthesis of 3D rambutan-like CuO/reduced graphene oxide (CuO/r-GO) through microwave-promoted synthetic approach, the positively charged CuO will be doped into a thin layer of r-GO by the electrostatic attraction, the modified glassy carbon electrode greatly improved the electrocatalytic property and broadens the range of detection. Moreover, as is an environmental friendly material, chitosan is one of the most popular materials to immobilize reagents for preventing the samples from dispersing into electrolyte, which has been widely used for the modification of electrode surfaces and for preparation of biosensors.[35,36] The sensing system is also free from the interference of biomolecule and other distractions, which is promising for the development of nonenzymatic glucose biosensor.

2. Experimental

2.1. Reagents and materials

Cuprous chloride, ammonia, ethanol, ethylene glycol, glucose and sodium hydroxide were purchased from Xilong Chemical Co., Ltd. P123 was purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Deionized water (18 MΩ cm^{-1}) was used for all solutions' preparation. Healthy human bloods were provided by Zhangzhou Hospital. Human procedures were in agreement with the guidelines of the Nuremberg Code, Declaration of Helsinki, the Belmont Report and the regional ethics committee for human experiments. Human experiments were approved by the Zhangzhou Department of Health. All other reagents were of analytical grade and used without

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further purification. The electrochemical measurements were performed in 0.1 M NaOH solution.

2.2. Apparatus

Rambutan-like CuO and CuO/r-GO were synthesized by monowave 300 (Anton Paar, Austria). The sizes and morphologies of the samples were characterized using a field-emission SEM (JEM-6010La) operating at 20 kV. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G20 electron microscope (FEI Company, USA) operating at 300 kV. X-ray powder diffraction (XRD) patterns were recorded on the Bruker D8 Advance (Bruker AXS, Germany), X-ray diffractometer at a scan rate of 0.05 deg s^{-1} using Cu Kα radiation. Nitrogen adsorption/desorption isotherm was measured on Belsorp-MAX (Bel Japan, Inc.). All samples were outgassed at 130 $^{\circ}$C for 12 h under vacuum before measurement. The specific surface areas were calculated using the Brunauer-Emmet-Teller (BET) method. Electrochemical measurements were performed on a CHI660E electrochemical workstation. The glassy carbon electrode (diameter 3mm) was used as working electrode. The Ag/AgCl electrode and platinum wire were used as reference and auxiliary electrode, respectively.

2.3. Preparation of the CuO/r-GO composite

The graphene oxide (GO) was synthesized from natural graphite by a modified Hummers' method, which has been reported previously.[37] The CuO/r-GO composite was prepared by monowave technique: 5 mL of cuprous chloride (0.2 M) was dissolved into 10 mL of ethanol, 5 mL ethylene glycol and 0.05 g of P123 mixed solution at room temperature. After stirring for 10 min, the mixed solution was treated with 0.45 mL $NH_3 \cdot H_2O$ solution and the blue $Cu(OH)_2$ precursor were observed. The dispersed 0.4 mL of GO (10 wt%) was added to the $Cu(OH)_2$ solution under constant stirring, which was then sealed in 30 mL reaction vial (G30) and transferred to a microwave (monowave 300) and heated to 130 ^{o}C for 10 min at under stirring (1000 ppm) by automatically adjusting the microwave power. Then, transformed the $Cu(OH)_2$ into the uniform-sized mesoporous CuO particles. The color of the solution

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changed from sky blue to brownish. Finally, the product was cleaned by repeated washing with ethanol and distilled water, and then centrifuged. The synthesis yields of CuO and CuO/r-GO composites are 71.4 % and 68.7%, respectively.

2.4. Preparation of modified electrodes

The different powders (1 mg) were mixed with deionized water (1 mL) and 1 mL chitosan solution (0.5 wt.%) and then ultrasonically treated to form the inks (KQ2200DE, 40 kHz and 300 W). Approximately 10 μL of each ink was dropped onto a clean surface of glassy carbon (GC) electrode and dried at room temperature to form the modified GC electrode.

3. Results and discussion

3.1. Characterization of the materials

Fig. 1A shows the SEM image of the CuO with spherical irregular structure, which can be clearly observed that the CuO nanoparticles with an average size of 0.5 μm exhibit a hierarchical profile of three-dimensional (3D) rambutan-like microstructure. The image of TEM (**Fig.1B**) further confirmed the results from the SEM image. **Fig.1C** shows the high-resolution TEM (HRTEM) image of CuO particle, indicates that the well-defined rambutan-like 3D CuO microstructures. The nanocrystal with clear lattice fringes with the lattice spacing of the (111) planes, d≈ 2.1 Å. **Fig. 1D** shows the morphology of the produced GO sheets resembling a thin wrinkled paper. TEM image in **Fig. 1E** displays that the rambutan-like CuO particles are decorated onto r-GO sheets. The dark rambutan-like structure on the graphene sheets are high-density CuO. TEM image observations in **Fig. 1F** gives more detailed structural characteristics of the CuO/r-GO composite. It can be observed that the CuO/r-GO assembled with many densely and randomly arranged nano needlelike grown from the center of the rambutan and CuO are obviously thin and dispersive after being coated. The rambutan-like CuO on graphene surfaces are nearly homogeneous distribution. As far as we know, the rambutan-like CuO and CuO/r-GO composites have not been reported in the literature.

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Fig. 1

The structures of the rambutan-like CuO and CuO/r-GO composite were identified by the XRD pattern**.** The diffraction peaks of XRD patterns corresponding to CuO are broad and lower in intensity, which suggests that the CuO particles with relatively low crystallization. As shown in **Fig. 2**. All of the reflection XRD patterns identify that the products are monoclinic CuO (JCPDF 44-0706). The presence of some functional groups on the growth and crystallization of metal oxide nanoparticles and renders them with irregular shapes. None of obvious typical peaks belonging to r-GO are observed in the XRD pattern of CuO/r-GO composite. It can be ascribed to the low amount and low diffraction intensity of r-GO.

Fig. 2

The N_2 adsorption-desorption isotherms and pore size distributions of CuO and CuO/r-GO are studies. **Fig.3.** shows that both as-obtained materials exhibit typical V type curve, suggesting that the samples are mesoporous materials. Moreover, the CuO and CuO/r-GO exhibit a hysteresis loop at the P/P_0 range of 0.5-1.0. The hysteresis loop of all materials resemble the H3 type (based on the IUPAC classification), which verified that 3D rambutan-like CuO and CuO/reduced graphene oxide are composed of ultrathin porous nanosheets. The BET surface area of CuO and CuO/r-GO are calculated to be 131.94 m^2 g^{-1} and 116.46 m^2 g^{-1}, respectively. In addition, the pore size distributions are calculated using the Barrett-Joyner-Halenda (BJH) model from the desorption branches of the isotherms. According to the corresponding pore size distribution curve (inset of **Fig. 3A** and **3B**), the pore size of CuO and CuO/r-GO are measured to be 14.46nm and 10.38 nm, respectively. It is interesting that when GO is added to prepared hybrid CuO/r-GO, the pore size is much smaller. It can be concluded that r-GO successfully wrapping CuO up in r-GO sheets with homogeneous distribution. These results agreed very well with the results of SEM and TEM.

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Fig. 3

3.2. Cyclic voltammetric response of the modified electrode

Fig. 4A displays cyclic voltammetric behavior on the bare GCE, r-GO/GCE, CuO/GCE and CuO/r-GO/GCE were examined by CV in the 0.1 M NaOH solution containing 0.1 mM glucose at the scan rate of 0.1 V s^{-1}. For bare GCE and reduced graphene modified electrodes, small response currents can be observed. However, the as-prepared CuO exhibit strong electrocatalytic activity towards glucose oxidation, which might due to the conversion of Cu(III) to Cu(II).[38-39] For the CuO/r-GO electrode, a substantial negative shift of the oxidation peak potential and increase of current response was observed. The oxidation process starts at approximately +0.30 V with broad peak at around +0.50 V. The oxidation peak current of glucose remarkably increased at CuO/r-GO, which may be attributed to the large specific surface area, and strong electron transfer rate of r-GO sheets from electrode can accelerate the electron transfer rate to glucose. The corresponding sensing mechanism schematic is shown in **Scheme 1**.

Furthermore, we have also investigated the influence of scan rate on the oxidation current of glucose, as shown in **Fig. 4B**. The anodic peak current (I_{pa}) of oxidation of glucose was exhibited a linear response to the scan rate. A good linearity between scan rate and peak current was obtained: I_{pa} (μA) = -20.95 - 425.51V (V s^{-1}), with the correlation coefficient (R) of 0.996. The result indicates that the electrochemical kinetics is controlled by the adsorption of glucose.[40]

Scheme 1

Fig. 4

3.3. Amperometric detection of glucose at CuO/r-GO modified GC electrode

Fig. 5 shows the amperometric measurement of the CuO/r-GO electrode in 0.1 M

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NaOH solution at detection potential of 0.50 V, with successive additions of glucose. The steady-state current was obtained at a 4 s response time and plotted as the calibration curve, which shows the lowest concentration of detection 0.5 μM for glucose. This observation may be attribute to the enhanced nano-size effect realized by the highly well dispersed self-assembly nanostructure. The biosensor electrode exhibits linearity for glucose sensing that ranged from 0.50 μM to 3.75 mM, and the correlation coefficient was 0.9970 (illustrated by the inset in **Fig. 5**). The electrode sensitivity calculated from the slope of the calibration curve is 52.1 μA mM^{-1}. The performance of our CuO/r-GO biosensor was compared with those of other published nonenzymatic glucose biosensors in **Table 1**. All the data demonstrate that the CuO/r-GO modified electrode has a good electrocatalytic ability, which can make an excellent electrochemical biosensor for glucose detection.

Fig. 5

Table 1

3.4. Interference study

As shown in **Fig. 6**, to evaluate the selectivity of the CuO/r-GO electrode, the current responses to several possible co-exist interfering biomolecules, such as Ascorbic acid (AA), dopamine (DA), and inorganic salt such as NaCl, which are the most important interferences for nonenzymatic glucose biosensor. Considering the interfering materials in the human blood were at low least 30 times concentrations. The interference experiment was conducted at CuO/r-GO electrode by successive injection of 0.1 mM glucose and 0.02 mM interfering species in 0.1 M NaOH solution. A well-defined glucose response was obtained, No such an effect was observed in presence of these interferences on the glucose determination, Hence it can be concluded that the CuO/r-GO/GCE presented good selectivity toward glucose detection.

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Fig. 6

3.5. Reproducibility and stability

The reproducibility and stability of response current of the developed CuO/r-GO electrode was further evaluated, as shown in **Fig. 7A**. Cyclic voltammograms responses to succession addition of 0.1 mM glucose were evaluated by using six different CuO/r-GO electrodes prepared. The relative standard deviation (R.S.D) under the same condition was 1.94%, confirming that the preparation method was highly reproducible. Meanwhile, the current responses to the addition of 0.1 mM of glucose at the same CuO/r-GO electrode for eight times only changed a little, indicating that the sensor was very stable. In order to investigate the long-term stability of the sensor, the current response to 0.1 mM glucose was also measured during 1 month (**Fig. 7B**). The biosensor was tested every six days. The current response of the CuO/r-GO was approximately 98.7% of its original counterpart, which demonstrated that the electrode can be applied a long time. The long-term stability and good reproducibility of CuO/r-GO electrode may be attributed to the terrific chemical stability of the composite themselves in the base solution.

Fig. 7

3.6 Real blood analysis

In order to verify the reliability of the non-enzymatic glucose biosensor for routine analysis, the CuO/r-GO electrode is also employed to detect the concentration of glucose in human blood. The results, as listed in **Table 2**, reveal that the recoveries of CuO/r-GO electrode were in the range of 94.8–101.4%, RSD listed indicate that the as-prepared CuO/r-GO electrodes were credible and accurate. Thus, it can be concluded that the developed biosensor performs very well in the detection of glucose in serum samples.

Table 2

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4. Conclusions

The rambutan-like CuO and CuO/r-GO composite were fabricated by monowave synthetic method in the alkaline environment. The reaction of CuO on r-GO layer only ten minutes to be integrated, which was high efficiency and the enzyme-free glucose sensor displays substantially excellent electrocatalytic activity to glucose oxidation. It offers high sensitivity of 52.1 μA mM^{-1} and a low detection limit of 0.1 μM. These excellent performance characteristics are combined with ease of fabrication, good reproducibility, long-term stability and perfect specificity to glucose in the presence of complex interferent. In a word, the CuO/r-GO electrode could be an extremely promising candidate applicable for a wide range of glucose detection.

Acknowledgments

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Figure and table captions

Scheme 1. Illustration of glucose biosensing mechanism based on CuO/r-GO composite.

Fig. 1. SEM (A), TEM (B) and HRTEM (C) images of rambutan-like CuO. SEM images of GO (D) and CuO/r-GO composite (E). TEM (F) image of CuO/r-GO composites.

Fig. 2. XRD patterns of 3D rambutan-like CuO and CuO /r-GO composite.

Fig. 3. Nitrogen adsorption desorption isotherms of rambutan-like CuO and CuO/r-GO composite. Insets show the pre-size distributions of the corresponding samples.

Fig. 4. (A) CV of 0.1 mM glucose on the bare GCE, r-GO/GCE, CuO/GCE and CuO/r-GO/GCE in 0.1 M NaOH (scan rate: 0.1 V s^{-1}). (B) CV of 0.1 mM glucose on the CuO/r-GO/GCE at different scan rate (0.01, 0.05, 0.10, 0.20, 0.30, and 0.40 V s^{-1}). Inset: the redox peak current relation with the scan rate.

Fig. 5. Amperometric response of CuO/r-GO/GCE upon the successive addition of glucose from 0.5 μM to 3.75 mM into 0.1 M NaOH at 0.50 V. (B) The calibration curve of current vs. concentration of glucose at the CuO/r-GO electrode.

Fig. 6. Amperometric response of the CuO/r-GO modified electrode prepared by injections of 0.1 mM of glucose, 0.02 mM interferents of dopamine, NaCl and ascorbic acid at an applied potential of 0.50 V.

Fig. 7. (A) The different CuO/r-GO electrodes of its current response at a potential value of +0.50 V in 0.1 M NaOH. (B) Stability of the biosensor stored at ambient conditions in one month.

Table 1. Analytical performances of our proposed CuO/r-GO biosensor with other published glucose biosensors.

Table 2 Determination of glucose in plasma samples, average of four determinations.

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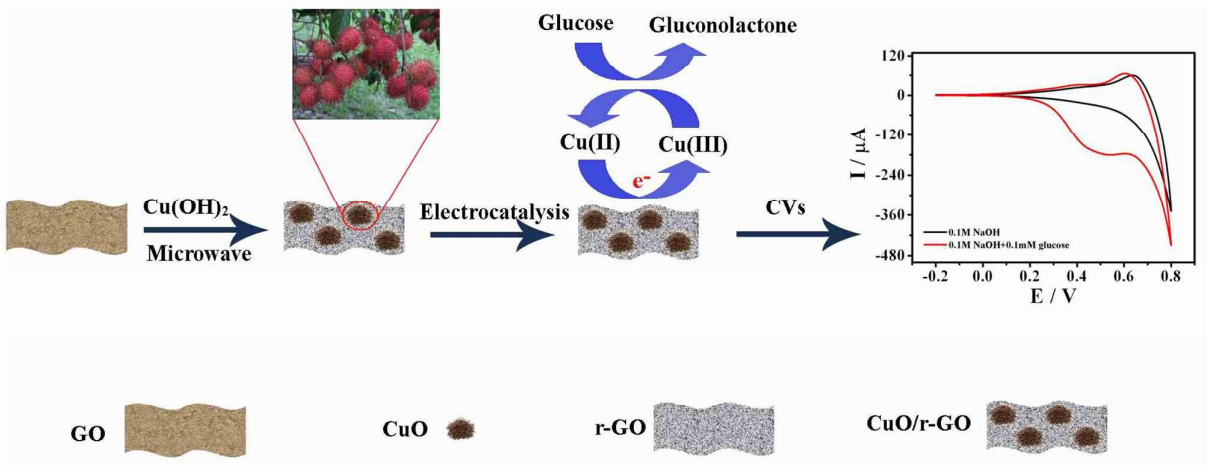

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368 **Scheme 1.** Illustration of glucose biosensing mechanism based on CuO/r-GO

369 composite.

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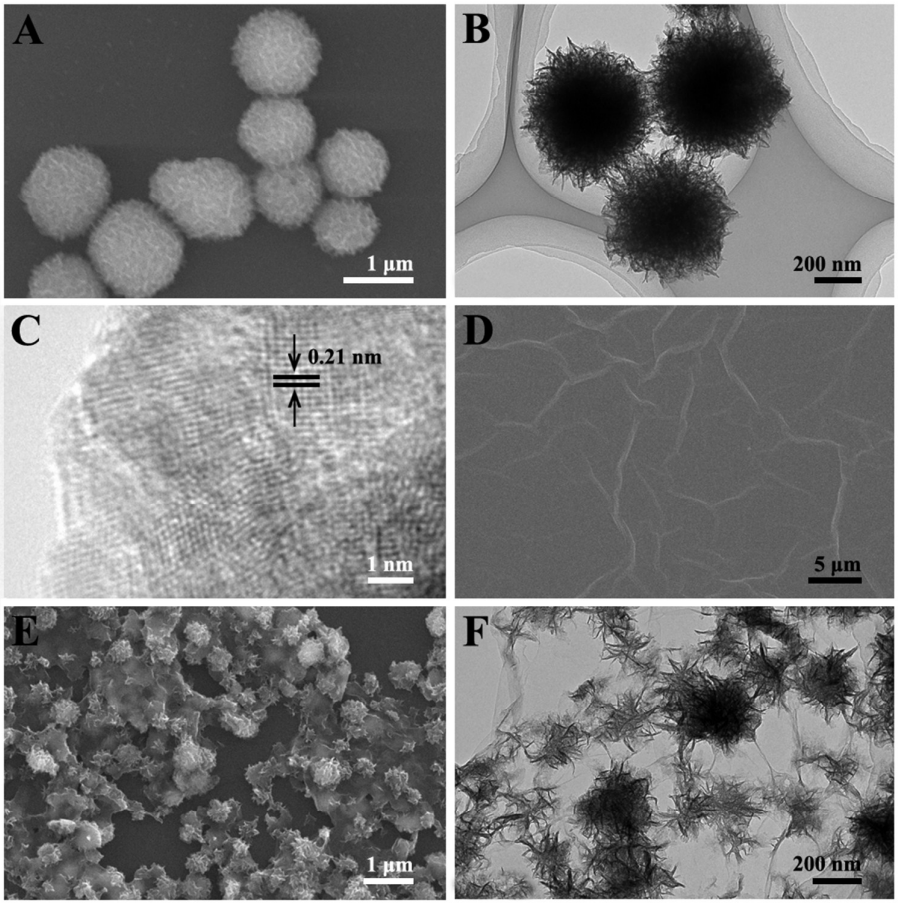

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372 **Fig. 1.** SEM (A), TEM (B) and HRTEM (C) images of rambutan-like CuO. SEM
373 images of GO (D) and CuO/r-GO composite (E). TEM (F) image of CuO/r-GO
374 composite.
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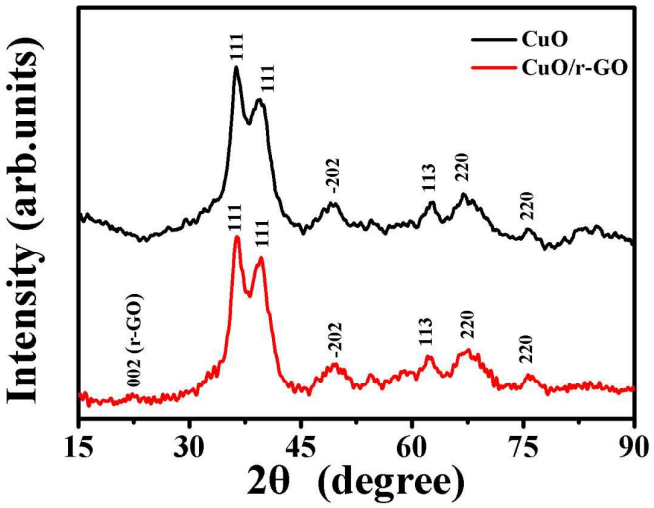

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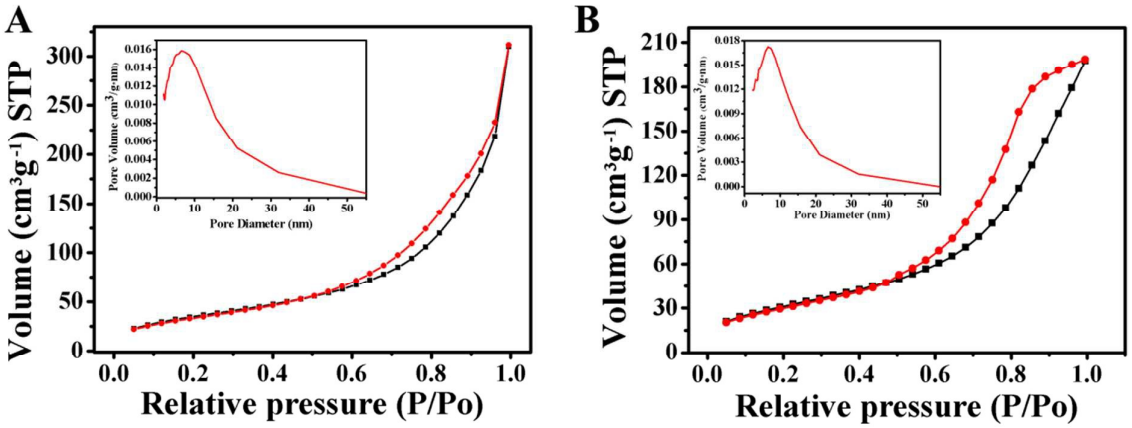

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Fig. 3. Nitrogen adsorption desorption isotherms of (A) rambutan-like CuO and (B) CuO/r-GO composite. Insets show the pre-size distributions of the corresponding samples.

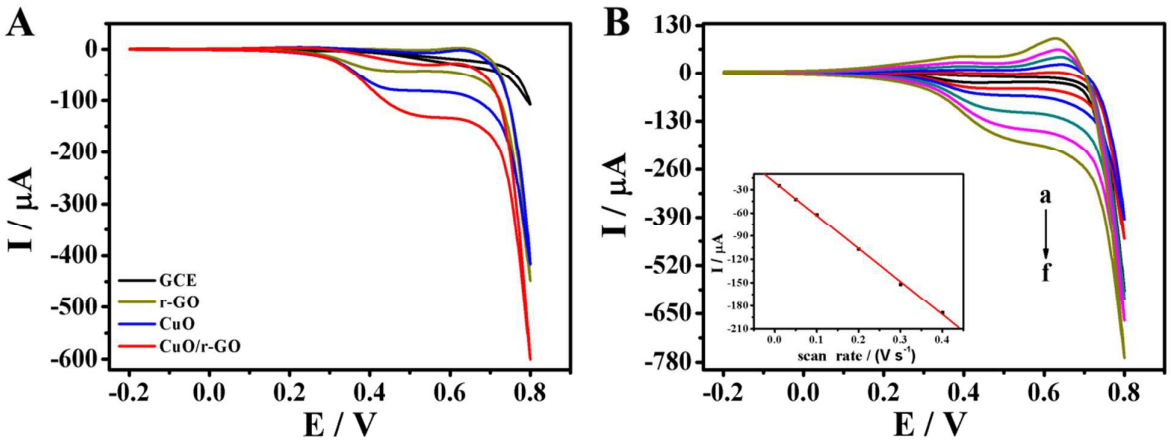

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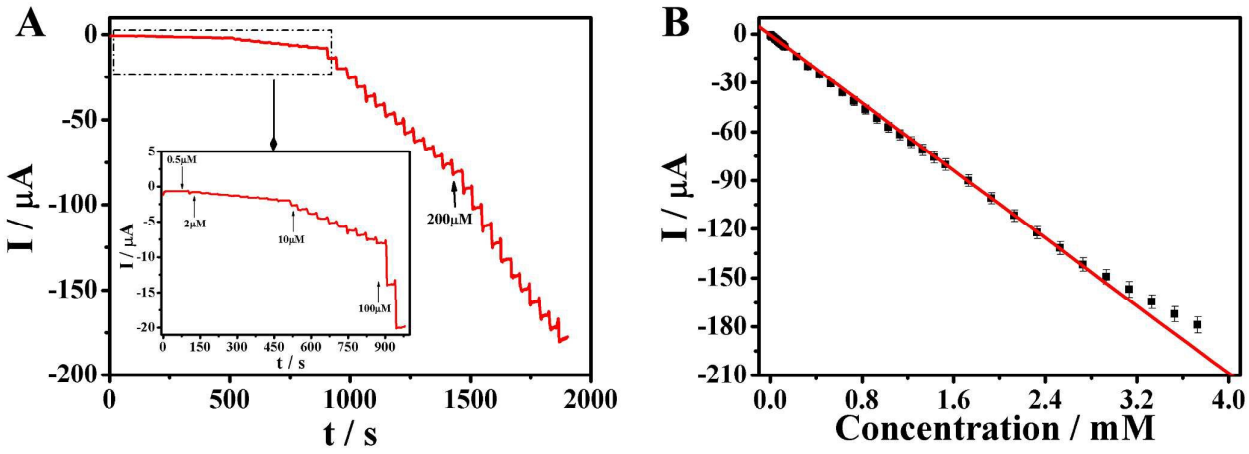
Fig. 4. (A) CV of 0.1 mM glucose on the bare GCE, r-GO/GCE, CuO/GCE and CuO/r-GO/GCE in 0.1 M NaOH (scan rate: 0.1 V s^{-1}). (B) CV of 0.1 mM glucose on the CuO/r-GO/GCE at different scan rate (0.01, 0.05, 0.10, 0.20, 0.30, 0.40 V s^{-1}).



Inset: the redox peak current relation with the scan rate.

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390 **Fig. 5.** Amperometric response of CuO/r-GO/GCE upon the successive addition of
391 glucose from 0.50 μM to 3.75 mM into 0.1 M NaOH at 0.50 V. (B) The calibration
392 curve of current vs. concentration of glucose at the CuO/ r-GO electrode.
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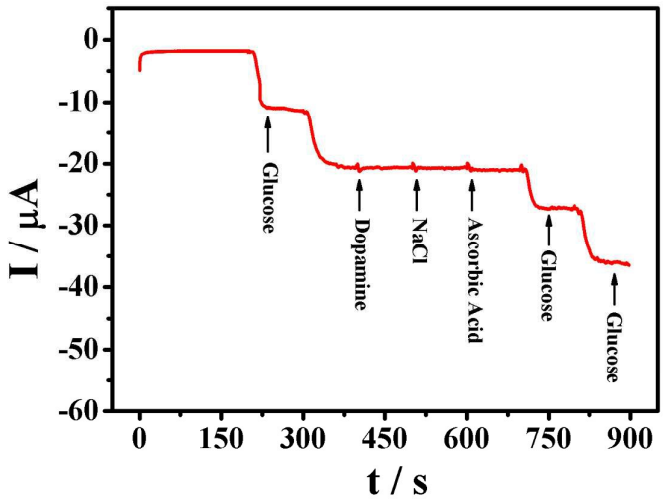

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395 **Fig. 6.** Amperometric response of the CuO/r-GO modified electrode prepared by
396 injections of 0.1 mM of glucose, 0.02 mM interferents of dopamine, NaCl and
397 ascorbic acid at an applied potential of 0.50 V.

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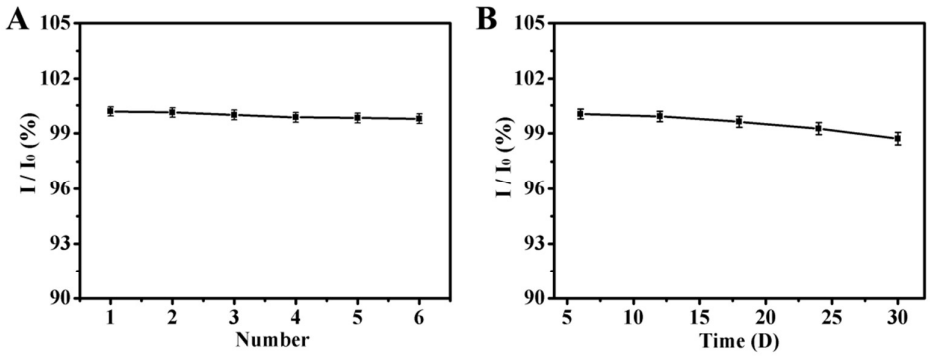

Fig. 7. (A) The different CuO/r-GO electrodes of its current response at a potential value of +0.50 V in 0.1M NaOH. (B) Stability of the biosensor stored at ambient conditions in one month.

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404 **Table 1** Analytical performances of our proposed CuO/r-GO biosensor with other
405 published glucose biosensors.

Electrode	Potential	Linear range	Sensitivity	Detection limit	Reference
Graphene-CuO	0.40V	2 μM to 0.06 mM	1480 μA mM^{-1} cm^{-2}	0.29 μM	8
CuO/GO_x/Nafion	0.58V	10 μM to 10.0 mM	47.19 μA mM^{-1} cm^{-2}	1.37 μM	9
CuO–Graphene	0.59V	2.0 μM to 4 mM	1360 μA mM^{-1} cm^{-2}	0.7 Mm	26
CuO/MWCNTs	0.40V	0.4 μM to 1.2 mM	2596 μA mM^{-1} cm^{-2}	0.2 μM	32
Cu/N-Graphene	0.50V	4.0 μM to 4.5 mM	48.13 μA mM^{-1}	1.3 μM	34
MnO_2/MWCNTs	0.30V	10 μM to 28 mM	33.19 μA mM^{-1}	—	40
CuO/r-GO	0.50V	0.50 μM to 3.75 mM	52.1 μA mM^{-1}	0.10 μM	This work

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408 **Table 2** Determination of glucose in plasma samples, average of four determinations.

Sample	Spiked (mM)	Found (mM)	Recovery (%)	RSD (%)
Serum 1	0	0.54	—	—
	0.3	0.79	94.8	3.65
	0.6	1.08	96.6	4.43
Serum 2	0	0.77	—	—
	0.3	1.04	97.3	3.18
	0.6	1.46	101.4	2.82

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Graphical abstract

Microwave synthesis 3D rambutan-like CuO and CuO/reduced graphene oxide modified electrode for non-enzymatic glucose detection

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Abstract: A novel type of cupric oxide (CuO) particles-reduction graphene oxide (r-GO) modified electrode has been fabricated through a facile, simple and fast microwave method. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET), and X-ray diffraction (XRD) were employed to characterize the morphologies and structures of the as-prepared samples. The results reveal that the CuO/r-GO composite was porous 3D rambutan-like microstructure with high surface area. Then the CuO and CuO/r-GO electrodes were constructed for high-performance and sensitivity non-enzymatic glucose biosensor in alkaline conditions. The proposed biosensor exhibits glucose concentrations in a range from 0.50 μM to 3.75 mM. Besides, chronoamperometry demonstrates a desirable sensitivity of 52.1 μA mM^{-1} at an applied potential of 0.50 V (vs. Ag/AgCl), with a detection limit of 0.10 μM (signal/noise=3). Most importantly, this non-enzymatic glucose biosensor was highly stable characteristics and can be manufactured into long-term stability electrode for the application in various complicated circumstances. All these results confirm that this CuO/r-GO biosensor is a promising active material for non-enzymatic glucose detection with excellent analytical properties.

Keywords: Cupric oxide; Reduction graphene oxide; Non-enzymatic biosensor; Glucose

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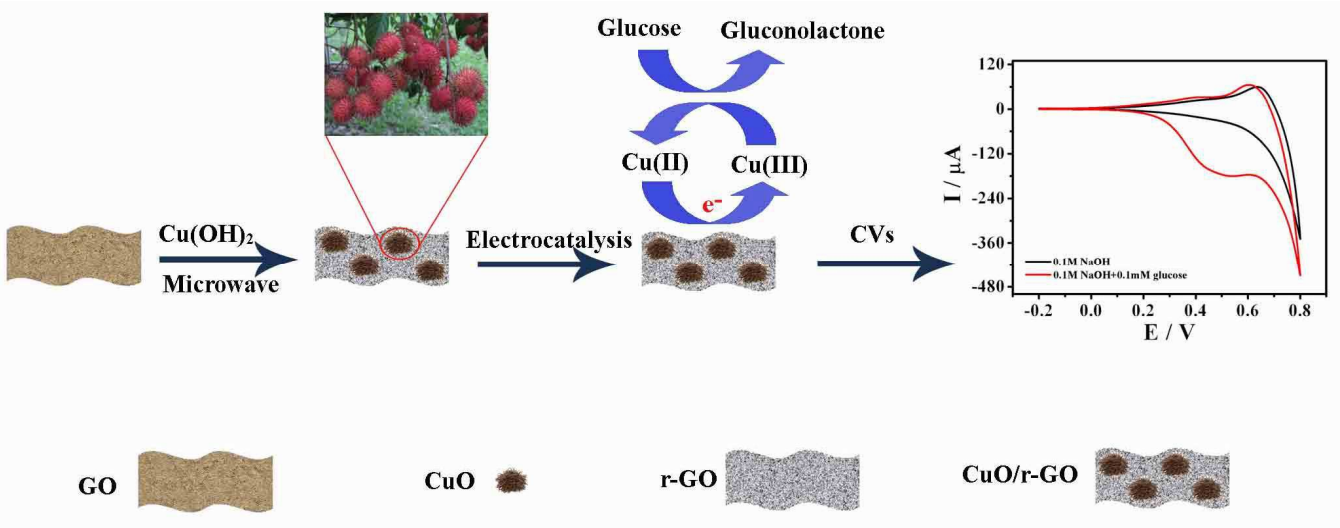

Scheme 1. Illustration of glucose biosensing mechanism based on CuO/r-GO composite.