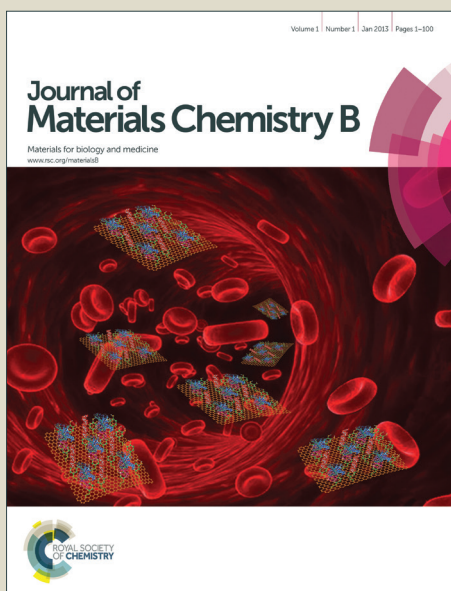


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ARTICLE TYPE

Journal of Materials Chemistry B Accepted Manuscript

Graphene oxide doped poly(3, 4-ethylenedioxythiophene) modified with copper nanoparticles for high performance nonenzymatic sensing of glucose

Ni Hui,^{ab} Wenting Wang,^a Guiyun Xu^a and Xiliang Luo^{*a}

Received (in XXX, XXX) XthXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX
DOI: 10.1039/b000000x

A highly stable and sensitive nonenzymatic glucose sensor was successfully constructed through a facile electrodeposition method. Graphene oxide (GO) doped poly (3,4-ethylenedioxythiophene) (PEDOT) was firstly electrodeposited onto a glass carbon electrode using cyclic voltammetry, and copper nanoparticles were then electrodeposited onto the rough surface of the PEDOT/GO nanocomposite through electrochemical reduction in a solution containing copper cations. The modified electrode was used for reliable nonenzymatic electrochemical detection of glucose, and under optimized conditions, it exhibited a high sensitivity up to 909.1 $\mu\text{A}/\text{mM}/\text{cm}^2$ and a very fast response time of less than 1 s, with a wide linear range of 0.1 μM to 1.3 mM and a low detection limit of 47 nM. This nonenzymatic glucose sensor was, furthermore, highly stable and unresponsive to potentially interfering substances, and it could be used for the assay of glucose in real human serum samples. These enhanced sensing performances were ascribed to the close contact of copper nanoparticles onto the rough surface of the PEDOT/GO conducting polymer nanocomposite, which has good conductivity and very high surface area that can act as excellent substrate for the growth and support of copper nanoparticles. All these results indicate that this electrochemical sensor is highly promising for nonenzymatic glucose detection.

1. Introduction

Glucose is a crucial metabolite for living organisms, especially in the case of millions of diabetics in the world. The detection of glucose is very important in biochemistry, fermentation industry, and clinical diagnosis¹⁻². Therefore, it is of urgency to develop fast, accurate and stable technologies to detect glucose levels³, not only in blood but also in other sources. In the 1960s, Clark and Updike developed the first enzyme electrode and amperometric enzymatic biosensors⁴⁻⁵. But glucose oxidase based biosensors often suffer from the disadvantages of complicated immobilization procedures, critical operating conditions, poor reproducibility, and high cost⁶⁻⁷. Thus, it is highly desirable to develop simple nonenzymatic glucose sensor. This kind of biosensor is based on the current response of glucose oxidation directly at the electrode surface, and the key factor that affects both the sensitivity and selectivity for the detection of glucose is the electrocatalytic activity of the electrode material⁸.

Recently, various noble metal nanoparticles such as Pt⁹⁻¹⁰, Pd¹¹⁻¹², Au¹³⁻¹⁴, Ag¹⁵⁻¹⁶ and alloy nanoparticles¹⁷⁻¹⁹ have been used for the fabrication of nonenzymatic glucose sensors. Despite the fact that these nanoparticles exhibit good electrocatalytic activities towards the oxidation of glucose, they are generally expensive and more importantly, very easy to get fouled by the chemisorbed intermediates and absorb ions such as chloride that led to poor stability²⁰. Compared with noble metal nanoparticles,

copper (Cu) based nanoparticles are attractive due to their advantages such as low cost and excellent catalytic activity for many different reactions²¹.

Copper based nanomaterials have been found to be able to catalyze the electrochemical oxidation of glucose for a long time. For example, metallic Cu²²⁻²³, cuprous oxide (Cu₂O)²⁴⁻²⁵, cupric oxide (CuO)²⁶, Cu_xO²⁷ and copper sulphide (Cu₂S)²⁸ have been used directly to modify electrodes for the fabrication of nonenzymatic glucose sensors, due to their outstanding catalytic ability and ready availability.

In order to improve their stability and dispersity, prior to the fabrication of glucose sensors, Cu based nanomaterials have been loaded onto different substrates, and among them are graphene and conducting polymers, mainly because graphene has extraordinary electrical properties, unusual mechanical strength and specific surface area²⁹, and conducting polymers possess high conductivity and can be easily synthesized³⁰. For instance, metallic Cu nanoparticles (CuNPs) have been incorporated on graphene sheets and used for the fabrication of a stable and sensitive nonenzymatic glucose sensor, and the obtained CuNPs/graphene nanocomposites demonstrated a synergistic combination of the advantages of CuNPs and graphene towards the electrochemical oxidation of glucose³¹. CuO nanoparticles have also been loaded on graphene and reduced graphene oxide (RGO) to form CuO/graphene³² and CuO/RGO³³ nanocomposites respectively, for glucose sensing. Glucose sensor based on the CuO nanocomposite could avoid the disadvantages of enzymatic

biosensors (low stability and limited linear range) and exhibited a low detection limit and a wide linear range³², and the other glucose sensor based on the CuO/RGO nanocomposite exhibited an excellent electrocatalytic activity towards glucose oxidation⁵ due to the synergistic effect of the high specific surface area of the RGO and the catalytic activities of CuO nanoparticles³³. Conducting polymers have been employed in various sensors to protect the electrode surface from fouling, immobilize a biocomponent, and extend the linear range of the sensor and to incorporate catalytic species³⁴⁻³⁶. Cu microparticles dispersed in polyaniline (PANI) have been used for the fabrication of amperometric sensors of amino acids and polyhydric compounds, and the Cu/PANI modified electrode offered good temporal stability and wide linear range³⁷. In another work, Cu nanoparticles were incorporated in poly-3-methylthiophene (CuNPs/P3MT) and the nanocomposite modified electrode was successfully applied for glucose electrochemical detection in NaOH solution³⁸.

Although graphene and conducting polymers, separately, have been used as supporting substrates for the loading of Cu based nanomaterials to fabricate nonenzymatic glucose sensors, the loading of Cu nanoparticles onto nanocomposites composed of conducting polymer and graphene have not been investigated so far. Very recently, we have prepared a novel poly(3,4-ethylenedioxythiophene)/graphene oxide (PEDOT/GO) nanocomposite through electrodeposition (the negatively charged GO will be doped into the formed PEDOT to neutralize the positively charged polymer backbone), and the nanocomposites modified electrode exhibited significantly enhanced catalytic activity³⁹. As the PEDOT/GO nanocomposite combines the excellent properties of both the conducting polymer and graphene oxide, it is our expectation that the loading of Cu nanoparticles onto this composite material may offer a unique platform for the electrocatalytic oxidation of glucose. In this work, a simple, two-step strategy was proposed to prepare the Cu nanoparticles modified PEDOT/GO (CuNPs/PEDOT/GO) nanocomposite, as shown in Scheme 1. Encouragingly, this new CuNPs/PEDOT/GO nanocomposite combines salient properties of CuNPs, PEDOT and GO, and the nanocomposite modified electrode allows highly sensitive, stable, and fast nonenzymatic sensing of glucose.

2. Experimental

2.1 Materials and apparatus

Graphene oxide was purchased from Nanjing Xian Feng Nanomaterials Technology Co., Ltd. (Nanjing, China). 3,4-Ethylenedioxythiophene (EDOT), D(+)-Glucose, ascorbic acid (AA), uric acid (UA), dopamine (DA) copper sulphate (CuSO₄), sodium sulfate (Na₂SO₄), Sodium hydroxide (NaOH) were obtained from Aladdin reagent (Shanghai, China). All used reagents were of analytical grade. Millipore water produced by a Milli-Q water purifying system was used throughout all experiments.

Electrochemical measurements were performed on a CHI630E Electrochemical Analyzer (Shanghai CH Instrument Co., China). A conventional three-electrode system was used with a saturated calomel electrode (SCE) as the reference

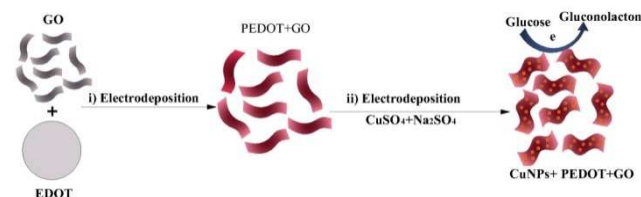
electrode, modified glassy carbon electrode (GCE) as the working electrode and a platinum wire as the counter electrode. Morphologies and nanostructures of CuNPs/PEDOT/GO and PEDOT/GO nanocomposites were characterized using a scanning electron microscope (SEM) (JEOL JSM-7500F SEM instrument Hitachi High-Technology Co., Ltd., Japan).

2.2 preparation of the CuNPs/PEDOT/GO modified electrode

According to a previous report⁴⁰, GCE was polished, washed and electrochemically pretreated in phosphate buffered saline (PBS). As shown in Scheme 1, PEDOT and GO nanocomposites were first electrochemically deposited onto the pretreated GCE in a solution containing 2 mg/mL GO and 0.02 M EDOT, using cyclic voltammetry (CV) scanning from -0.2 to 1.2 V at a scan rate of 100 mV/s for 15 cycles. For the further deposition of Cu nanoparticles, the PEDOT/GO nanocomposite modified electrode was immersed in a solution containing 10 mM CuSO₄ and 100 mM Na₂SO₄ and carried out electrodeposition at a potential of -1.0 V (vs. SCE) for 200s. GCEs modified with the PEDOT/GO nanocomposite and further electrodeposited Cu nanoparticles were denoted as PEDOT/GO/GCE and CuNPs/PEDOT/GO/GCE, respectively.

2.3 Electrochemical measurement

Electrochemical impedance spectroscopy (EIS) measurements were recorded in an electrolyte containing 0.1 mM KCl and equimolar of 50 mM [Fe(CN)₆^{4-/3-}] at the frequency range from 1 to 100000 Hz. The amplitude of the applied sine was 5 mV with the current potential set as 0.2 V. The electrochemical measurements for glucose oxidation at the CuNPs/PEDOT/GO/GCE were performed in a 0.1 mol/L NaOH solution. Amperometric curves were gained after adding desired concentration of glucose under the stirring constantly. All the measurements were carried out at room temperature.



Scheme 1. Schematic illustration of the formation of CuNPs/PEDOT/GO nanocomposite by a two-step method.

3. Results and discussion

3.1 Characterization of the CuNPs/PEDOT/GO nanocomposite

The surface morphologies of the CuNPs/PEDOT/GO and PEDOT/GO nanocomposites were characterized by SEM. As can be seen from Fig.1A, the electrodeposited PEDOT/GO film shows a very rough and wrinkled yet uniform microstructure due to the incorporation of GO sheets in the conducting polymer, which can provide a three dimensional space and larger surface

area for the deposition of Cu nanoparticles. Cu nanoparticles electrodeposited on the PEDOT/GO film are randomly distributed (Fig.1B and C), with a cubic shape and the average particle size of around 100 nm. Energy dispersive spectroscopy (EDS) has been used to investigate the component of the CuNPs/PEDOT/GO nanocomposite (Fig.1D), and it clearly indicated that the nanocomposite mainly contains Cu, C, and S elements, suggesting successfully electrodeposition of Cu onto the rough surface of PEDOT/GO nanocomposite.

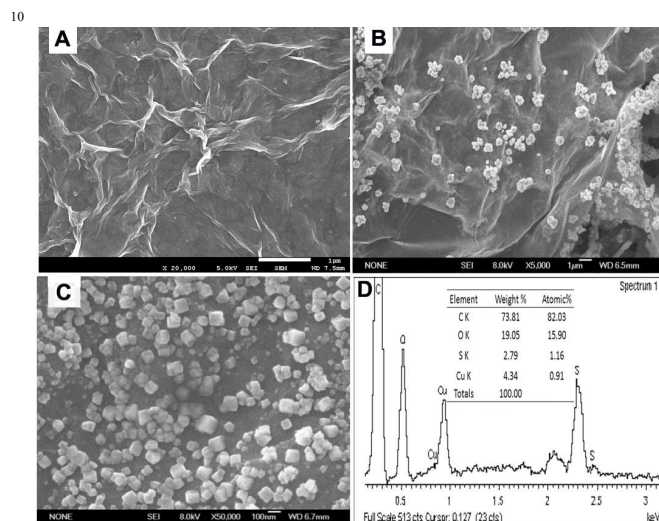


Fig. 1 SEM images of the PEDOT/GO (A) and the CuNPs/PEDOT/GO nanocomposite films at low (B) and high (C) magnifications; (D) EDS spectra of the CuNPs/PEDOT/GO nanocomposite film.

EIS, an effective method for probing the features of surface modified electrodes⁴¹, is used to monitor the preparation process of the electrodes. Fig.2 shows the Nyquist plots of the bare GCE (curve a), the PEDOT/GO/GCE (curve b) and the CuNPs/PEDOT/GO/GCE (curve c). It is known that the Nyquist plot is composed of a semicircle portion and a linear portion, with the former at higher frequencies corresponding to the electron transfer limited process and the latter at lower frequencies related to the diffusion process, and the semicircle diameter is equal to the charge transfer resistance (R_{ct})⁴². Clearly, the R_{ct} of the PEDOT/GO/GCE was much smaller than that of the bare GCE, indicating that a layer of conductive PEDOT/GO nanocomposite was formed on the electrode surface and it can promote the charge transfer. After the deposition of Cu nanoparticles, the obtained CuNPs/PEDOT/GO/GCE exhibited a markedly decreased R_{ct} value, manifesting that Cu nanoparticles with good electrical conductivity were successfully deposited and they can provide necessary conductive pathways to assist the charge/electron transfer.

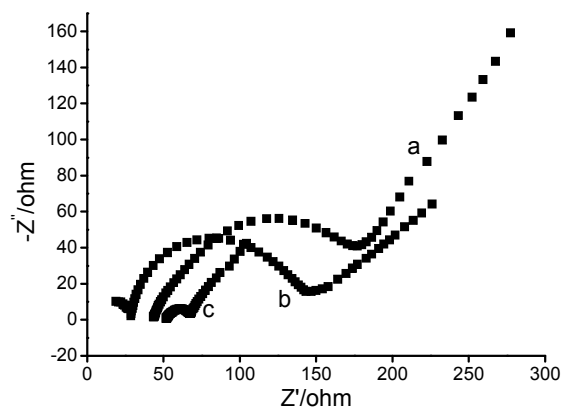
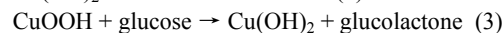
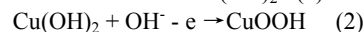
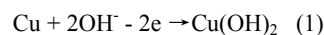


Fig. 2 Nyquist plots of (a) the bare GCE, (b) the PEDOT/GO/GCE and (c) the CuNPs/PEDOT/GO/GCE in 50 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$ solution containing 0.1 M KCl.

3.2 Response of glucose on the modified electrode

Responses of glucose on various modified electrodes are shown in Fig.3. Clearly, the PEDOT/GO/GCE showed little response towards the addition of glucose, while for the CuNPs/PEDOT/GO/GCE, a significant oxidation peak (starting at about 0.40V with the peak potential at around 0.55 V) was generated after the addition of glucose. The oxidation peak should be ascribed to the irreversible oxidation of glucose, which was similar to a previous report³¹. This result indicates that the CuNPs/PEDOT/GO/GCE has good catalytic activity towards the oxidation of glucose, and Cu nanoparticles play an important role. Pure Cu nanoparticles modified electrode (CuNPs/GCE) was also prepared and used for glucose oxidation. As shown in Fig.3 (curve c2), the CV of the CuNPs/GCE also showed an irreversible glucose oxidation peak at about 0.55 V, but it was much lower than that of the CuNPs/PEDOT/GO/GCE. Therefore, in this nanocomposite system, Cu nanoparticles can provide active site for the catalytic oxidation of glucose, while the PEDOT/GO offers a large surface area for nanoparticle loading and a highly conductive substrate that can enhance electron transfer. The synergistic effect makes CuNPs/PEDOT/GO an excellent nanocomposite for electrocatalytic glucose oxidation and sensing.

The mechanism of glucose electrochemical oxidation at copper based electrode is via multiple steps. In NaOH solution, Cu(0) is firstly oxidized into Cu(II), and Cu(II) is further oxidized into Cu(III). The Cu(III)/Cu(II) redox couple plays an important role for glucose oxidation in the present of the hydroxide solution. The process could be simply summarized as follow:^{37,43-44}



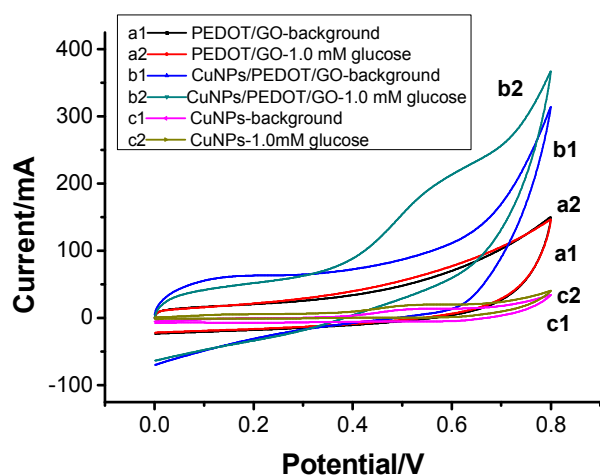


Fig. 3 Cyclic voltammograms of PEDOT/GO/GCE (curve a1, a2), CuNPs/PEDOT/GO/GCE (curve b1, b2), CuNPs/GCE (curve c1, c2) in the absence (a1, b1, c1) and presence (a2, b2, c2) of 1.0 mM glucose in 0.1 M NaOH solution at scan rate of 100 mV/s.

3.3 Optimization of conditions for glucose sensing

As Cu nanoparticles are essential for the catalytic activity of the CuNPs/PEDOT/GO/GCE, it is necessary to optimize the conditions for Cu nanoparticles electrodeposition. Effects of the electrochemical deposition time and potential for Cu nanoparticles on the catalytic activity of the CuNPs/PEDOT/GO/GCE towards glucose oxidation (catalytic oxidation current) are shown in Fig. 4 A and B, respectively. As can be seen clearly, when the electrodeposition potential was fixed at -1.0 V, the optimum deposition time was 200 s, as with a shorter deposition time, the deposited Cu nanoparticles are not enough, and with a longer deposition time, the Cu nanoparticles may grow bigger and aggregate, which will decrease their catalytic activities. When the electrodeposition time was fixed at 200 s, the optimum deposition potential was found to be -1.0 V, as this potential is considerably low but enough to effectively reduce Cu ions to form Cu nanoparticles that possess the highest catalytic activity.

Since the catalytic reaction of glucose involves OH⁻ ions, the influence of NaOH concentration on the glucose sensor was also investigated. As shown in Fig. 4 C, when the NaOH concentration was 0.1 M, the oxidation of glucose at the CuNPs/PEDOT/GO/GCE exhibited the highest peak current and the lowest peak potential. Therefore, 0.1 M NaOH was selected as the optimal supporting electrolyte for the sensing of glucose.

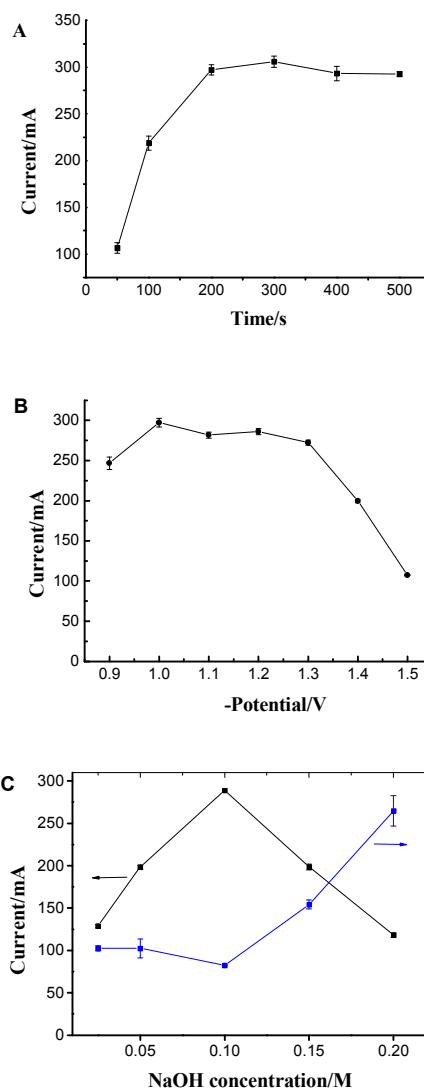


Fig. 4 Effects of deposition time (A) and deposition potential (B) on the oxidation peak current of the CuNPs/PEDOT/GO/GCE towards glucose oxidation. Error bars indicate the standard deviation of two measurements. (C) Effect of NaOH concentration on the peak current and peak potential for the oxidation of 1.0 mM glucose at the CuNPs/PEDOT/GO/GCE.

3.4 Amperometric detection of glucose

A typical amperometric response curve of glucose in 0.1 M NaOH at the CuNPs/PEDOT/GO/GCE is shown in Fig. 5. As expected, the CuNPs/PEDOT/GO/GCE showed extremely sensitive response towards the addition of glucose (even at a concentration down to 100 nM). More importantly, the response time of this sensor (reach the 95% steady state response, right inset of Fig. 5) is within 1.0 s, which is much faster than those reported for glucose sensors based on Cu nanoparticles/graphene (< 2 s)³¹, Cu nanobelt (< 100 s)⁴⁵, and SWCNTs/Cu/Nf (10 s)⁴⁶. The reason for this ultrafast response may be ascribed to the fast diffusion of glucose molecules to the CuNPs/PEDOT/GO that has a huge surface area, and the good conductivity that can assist the fast electron transfer. The CuNPs/PEDOT/GO/GCE exhibited a

linear response to glucose in the concentration range of 0.1 μM to 1.3 mM, with the regression equation of $I (\mu\text{A}) = 2.756 + 64.43c$ (mM) ($R=0.9986$). The sensitivity of this nonenzymatic glucose sensor was $911.96 \mu\text{A}/\text{mM}/\text{cm}^2$, and the detection limit was calculated to be 47 nM (at a signal-to-noise ratio of 3), which is lower than that of other similar glucose sensors based on copper based nanomaterials, such as CuNPs/MWCNTs (500 nM)⁴⁷, Cu film (500 nM)⁴⁸, and Cu₂O microcubes (800 nM)²⁵.

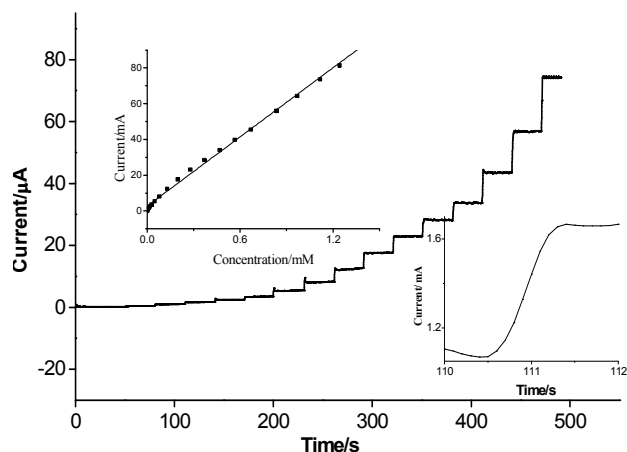


Fig. 5 Amperometric response of the sensor to successive addition of glucose into stirring NaOH (0.1 M). The working potential was 0.55 V, and the glucose concentration added were 0.1, 3.0, 5.0, 8.0, 10.0, 20.0, 30.0, 50.0, 70.0, 80.0, 90.0, 100.0, 200.0, 300.0 and 400.0 μM in sequence. Inset right, typical response time of the sensor; Inset left, the linear calibration curve of the glucose sensor.

3.5 Sensor stability and specificity

The reproducibility and stability of the sensor were carefully investigated. 7 different electrodes modified with CuNPs/PEDOT/GO nanocomposites were prepared independently and used to detect 0.1 mM glucose, and the relative standard deviation (RSD) of these sensor responses was 3.8%, indicating excellent reproducibility. The repeatability of the glucose sensor was investigated by measuring 0.1 mM glucose with a single modified electrode repeatedly for 10 times, and the RSD was just 3.3%. The long-term stability of the sensor was also evaluated by measuring its response to glucose within 30 days (Fig. 6), and it retained approximately 92% of its original response after 30 days, indicating very good stability.

The specificity of the sensor was evaluated using a number of interferents that possibly coexist with glucose in human blood serum and other samples, and the tested interferents are set at a higher concentration ratio compared with glucose (normally the physiological level of glucose is more than 30 times of that of certain interferents such as uric acid, ascorbic acid and dopamine), as shown in Fig. 7. Clearly, the sensor did not show significant increase in current response to all the added interferents (lower than 4.5% of the glucose response, even the concentration ratio of the interferent to glucose was set much higher). These results verified that the CuNPs/PEDOT/GO/GCE had very high specificity towards glucose in the presence of various interferents.

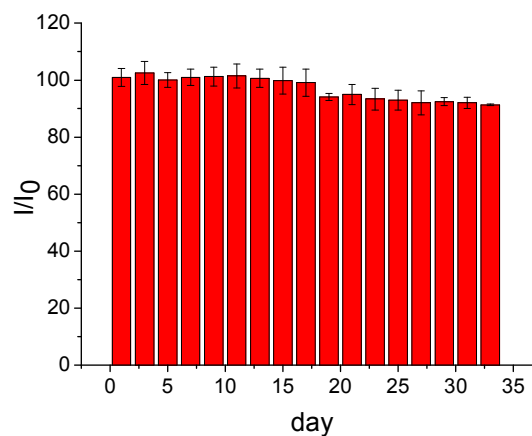


Fig. 6 Stability of the sensor stored at ambient condition over a month using 0.1 M NaOH at +0.55 V with 0.1 mM glucose (I/I_0).

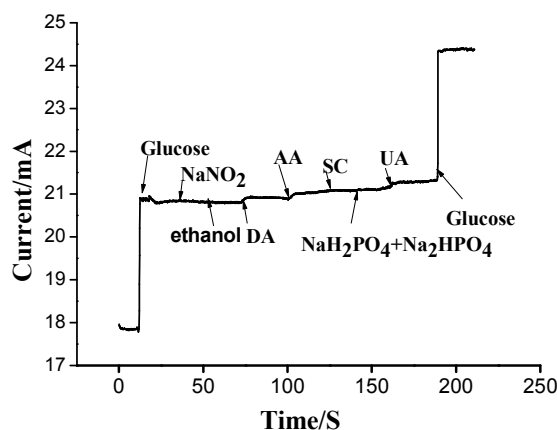


Fig. 7 Interference test of the sensor in 0.1 M NaOH at 0.55 V with 0.1 mM glucose and other interferents as indicated. Added substances: 0.01 mM dopamine (DA), 0.01 mM ascorbic acid (AA), 0.01 mM uric acid (UA), 0.02 mM sodium citrate (SC), 0.02 mM NaH₂PO₄ + Na₂HPO₄, 0.01 mM NaNO₂, and 0.02 mM ethanol.

3.6 Real sample analysis

To explore the Cu/PEDOT/RGO/GCE for possible practical application, it was used to determine glucose in human blood samples. Fresh serum samples were analyzed with an Automatic Analyzer (Hitachi 7600 automatic biochemical analyzer) and then detected with the prepared glucose sensor. 40.0 μL of serum sample was added to 10.0 mL 0.1 M NaOH solution, and then measured with the sensor at +0.55 V. As shown in Table 1, the measured results are very close to those of the hospital measurements, and the recovery is very satisfying.

Table 1. Determination of glucose in human blood samples

Samples	Glucose measured with Hitachi 7600 (mM)	Glucose measured with this sensor (mM)	RSD (%)
1	5.1	5.2	4.1
2	4.7	4.6	3.5
3	6.8	7.0	3.9
4	8.7*	8.9	4.6
5	12.5*	12.7	3.7

* Samples collected from patients that have already been diagnosed to be diabetic.

4. Conclusion

A novel nonenzymatic amperometric glucose sensor was fabricated via the electrodeposition of Cu nanoparticles onto the electrodeposited PEDOT/GO nanocomposite film. The results demonstrated that a synergistic combination of the advantages of Cu nanoparticles, grapheme oxide and PEDOT was achieved. The doping of the conducting polymer PEDOT with graphene oxide offered a rough and conductive substrate for the loading of Cu nanoparticles, which are stable and active sites for the electrochemical catalytic oxidation of glucose. The developed glucose sensor exhibited excellent sensitivity, high stability, fast response, and high specificity. The relatively low-cost and facile electrochemical fabrication of the nonenzymatic glucose sensor, combined with its many desirable advantages, has made this CuNPs/PEDOT/GO/GCE an excellent choice for routine glucose sensing.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (21422504, 21275087), the Natural Science Foundation of Shandong Province of China (ZR2012BM008), and the Taishan Scholar Program of Shandong Province, China.

Notes and references

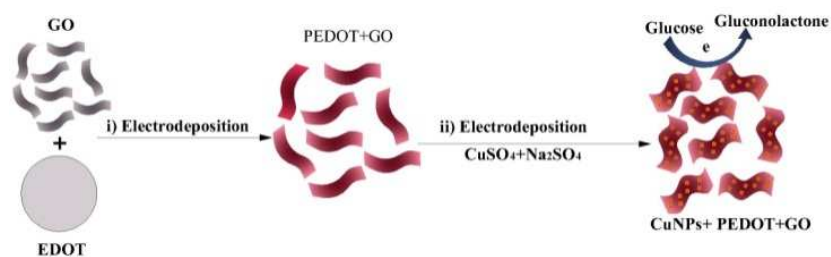
^a Key Laboratory of Sensor Analysis of Tumor Marker, Ministry of Education, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China. E-mail: xiliangluo@hotmail.com; Fax: (+86)53284022681; Tel: (+86)53284023927

^b College of Chemistry and Pharmacy, Qingdao Agricultural University, Qingdao 266109, China.

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Graphical abstract



A highly sensitive and stable nonenzymatic glucose sensor was developed through the electrochemical deposition of Cu nanoparticles onto the electrodeposited nanocomposite of conducting polymer PEDOT doped with graphene oxide.