

Construction of a non-enzymatic glucose sensor based on copper nanoparticles/poly(*o*-phenylenediamine) nanocomposites

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Abstract An electrochemical non-enzymatic glucose sensor was fabricated by electrodeposition of copper nanoparticles (CuNPs) onto a poly(*o*-phenylenediamine) (PoPD) film-modified glassy carbon electrode (CuNPs/PoPD/GCE). We had studied some factors such as the pH value of supporting electrolyte, the amount of PoPD and applied potentials and optimize the experiment conditions. Under the optimum conditions, the as-obtained sensor for glucose sensing had achieved a wide linear range, low detection limit, and fast response time. The current response of the as-obtained sensor towards electrochemical oxidation of glucose was linear with the concentration of glucose in the range of 5.0 μM to 1.6 mM ($R=0.998$) in the solution of 0.1 M NaOH at the applied potential of 0.5 V. The detection limit is 0.25 μM and the fast response achieves within 1 s. The sensor exhibits good sensitivity, selectivity, and reproducibility. The proposed non-enzymatic glucose was successfully employed to determine glucose in blood samples.

Keywords Non-enzymatic glucose sensor ·
Copper nanoparticles · Electrodeposition ·
Poly(*o*-phenylenediamine) · Chronoamperometry

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Introduction

Diabetes mellitus is a metabolic diseases and a major public health problem affecting millions of people. In order to achieve accurate diagnosis and good management of diabetes mellitus, tremendous efforts have been devoted into seeking an efficient, sensitive, and reliable method to determine glucose. Glucose sensing also plays an important role in food industries [1] Owing to good sensitivity, selectivity, and simplicity, electrochemical methods have become the main technique in glucose sensing. Most studies had focused on glucose oxidase (GOx)-based and glucose dehydrogenase (GDH)-based electrochemical glucose sensors [2–4] so as to cater to the demand of reliable blood glucose monitoring in clinical practice. However, due to the natural instability of enzymes, strict experimental conditions, and complicated immobilization procedures [4, 5], enzyme-based sensors usually obtain unsatisfactory results such as unsatisfactory reproducibility and insufficient long-term stability [6]. Another drawback of enzyme-based electrochemical glucose biosensor is the serious interference induced by other electroactives species in blood samples such as ascorbic acid and uric acid [7]. Therefore, the development of non-enzymatic glucose biosensors is of great significance and has attracted considerable attention.

The good performance of non-enzymatic glucose sensor is attributed to the efficient electron transfer electrode and excellent catalytic material [8, 9]. In recent years, nanotechnology has offered many research opportunities on fabrication nanostructured materials and multi-component nanomaterials. There had been many studies that improve the performance of non-enzymatic glucose sensors by incorporating various nanostructured metals or metal oxides [7, 8, 10–15]. Recent advances indicate that nanostructured copper and copper oxides (Cu/CuOx) is very promising [8, 10–14, 16–20] due to their excellent property of high electrocatalytic activity and some advantages, which are inexpensive, non-toxic, and

easily produced. Copper NPs can efficiently enhance the electron transfer process and decrease the overpotentials of the investigated electrochemical reaction, which is attributed to its properties such as excellent conductivity and catalytic properties [21, 22]. Multi-component nanomaterials have a synergistic effect that takes advantage of their hybrid properties [23]. The synergistic effects of the composite nanomaterials lead to broad applications in different analytical fields, especially in fabrication of sensor. Electrodeposition is a particularly simple and effective approach that consists in introducing nanoparticles (NPs) into polymer matrices or mixing them with the polymer [24]. Cu NPs-based nanocomposites in the electrochemical enzymeless glucose detection have attracted interest. As for polymers, conducting polymers are used as a coating or encapsulating material on an electrode surface and are developed towards interdisciplinarity [25]. Whereas a majority of polymers are unable to conduct electricity, a non-conducting polymer is being used for the immobilization of specific receptor agents on the sensor device, and their insulating properties are utilized in the electronic industry [26]. *o*-Phenylenediamine (*o*-PD), a non-conducting polymer, is usually electropolymerized over electrodes, which widely act as a support for immobilizing enzymes and a charge-transfer mediator or as a barrier to interference. Because the film is permselective, *o*-PD polymer film is being increasingly electrosynthesized over enzyme electrodes in order to avoid or minimize interferences from endogenous electroactive species in biological samples [27].

In this paper, we developed a non-enzymatic glucose sensor based on CuNPs/poly(*o*-phenylenediamine) (PoPD) film that was obtained from electrodepositing CuNPs onto PoPD film electropolymerized on glassy carbon electrode (GCE). The CuNPs/PoPD/GCE exhibited remarkable catalytic activity for glucose oxidation with a fast amperometric response, a low detection limit, and a wide linear range in alkaline solution.

Experimental

Materials

Glucose, *o*-phenylenediamine (*o*-PD) and other chemicals were obtained from the Chemical Reagent Company of Shanghai (Shanghai, China). All the reagents were of analytical grade and used without further purification. The water used in this study was deionized by milli-Q Plus system (Millipore, France) having 18.2-M Ω electrical resistivity.

Apparatus

Electrochemical experiments were performed with a CHI 1232 electrochemical workstation (Chenhua Instruments

Company, Shanghai, China) with a conventional three-electrode system. A modified electrode, an Ag/AgCl, and a platinum electrode were used as the working electrode, reference, and the auxiliary electrode respectively. Atomic force microscopy (AFM) images were carried out in the AFM (Nanoscope III, Waeco, USA). Scanning electron microscope (SEM) measurements were conducted on an S-4800 II FESEM (Hitachi High-Technologies Corporation, Japan) and energy-dispersive X-ray spectroscopy (EDS) was performed on an EDAX instrument (Genesis XM2, USA). The accelerating voltage and working distance were 20.0 kV and 15 mm, respectively. Magnetic stirrers (85–1; Keeler Instruments Company, Nanjing, China) and a Mettler-Toledo FE20 pH meter (Shanghai, China) were adopted. All experiments were carried out at room temperature (25 °C).

Cu NPs/PoPD composite sensor preparation

GCE (Φ 3 mm) was polished with alumina paste (0.3 and 0.05 μ m) on a soft polishing cloth, and then GCE was cycled in the potential range of -0.2 to 0.8 V at a scan rate of 100 mV/s in 0.1 M H_2SO_4 until the stable cyclic voltammograms (CVs) were obtained. Thereafter, the PoPD film was fabricated on a GCE surface by electropolymerizing *o*-PD in an aqueous solution of 80 mM *o*-PD solutions with 0.1 M H_2SO_4 . Figure 1 shows the cyclic voltammograms (CVs) of GCE in 0.1 M H_2SO_4 solution containing 80 mM *o*-PD. This is the process that *o*-PD electropolymerization onto the surface of GCE. In the first anodic scan, there were two irreversible anodic peaks at 0.55 V (O1) and 1.08 V (O2), respectively, which were ascribed to the oxidation of *o*-PD that resulted in the polymerization of *o*-PD [25, 28].

Next, Cu-NPs were electrodeposited onto the PoPD film in 0.1 M H_2SO_4 solution containing 0.01 M $CuSO_4$ under a fixed applied potential of 0.5 V (vs. Ag/AgCl) for 400 s. Figure 2 shows an obvious Cu peak is detected by energy-dispersive X-ray spectroscopy (EDS), which indicated that Cu

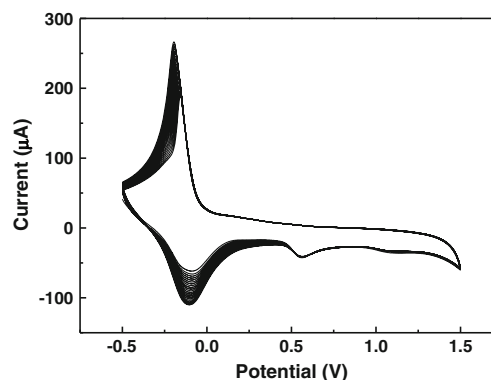


Fig. 1 CVs of bare GCE in 0.1 M H_2SO_4 containing 80 mM *o*-PD in the potential range of -0.5 and 1.5 V. Scan rate, 100 mV/s

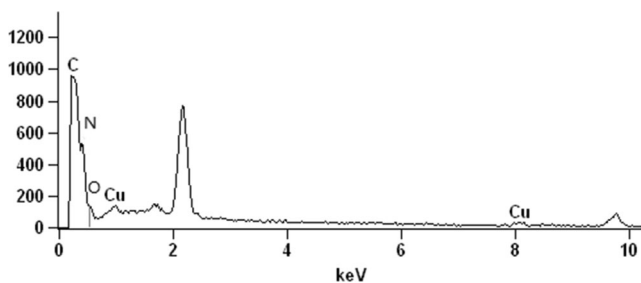


Fig. 2 EDS spectra of the CuNPs/PoPD composite film

had been successfully electrodeposited onto PoPD film-modified electrode.

Electrochemical test

The electrochemical characterization of the modified electrode was evaluated using cyclic voltammetry (CV) in 0.1 M NaOH. The current response measurements were performed in NaOH with a potential of 0.50 V, and then detected glucose concentration in human blood under the same conditions.

Results and discussion

Characterization of the CuNPs/PoPD-modified electrode

Figure 3 shows the AFM and SEM images of a bare GCE (a), a PoPD/GCE (b), and a CuNPs/PoPD/GCE (c) composite-modified electrode. In the AFM image (b), there are PoPD films covered on the electrode surface, and Cu nanoparticles are dispersed onto the PoPD films uniformly. The SEM images clearly indicated that Cu NPs were uniformly attached to the electrode surface, with an average diameter in the range of 5 to 30 nm. From AFM and SEM images, it was confirmed that PoPD films and CuNPs were attached to the electrode surface.

Electrocatalytic activity of CuNPs/PoPD/GCE towards glucose oxidation

To understand electrocatalytic activity of the Cu NPs/PoPD-modified GCE towards glucose oxidation, cyclic voltammograms (CVs) of the bare GCE (curve a), PoPD/GCE (curve b), and Cu NPs/PoPD/GCE (curve c) in 0.10 M NaOH containing 0.65 mM glucose were investigated, and the result was shown in Fig. 4. As can be seen in Fig. 4, compared with other two electrodes, the Cu NPs/PoPD/GCE led a dramatic increase of current response at 0.5 V, which indicated that the Cu NPs/PoPD modified electrode caused an increased electrocatalytic activity towards the oxidation of glucose. Meanwhile, we can

also observe that the Cu NPs/PoPD/GCE produced an evident increase of current signal at 0.2 V compared with the bare GCE and PoPD/GCE, which is attributed to the oxidation of Cu. The possible mechanism for the oxidation of glucose in alkaline media at Cu NPs/PoPD/GCE is that Cu (III) species such as CuOOH or $\text{Cu}(\text{OH})_4^-$ are considered as the strong oxidizing agent for electrocatalyzing glucose [8, 29, 30]. The first is that Cu is electrochemically oxidized into CuO in NaOH solution. And then CuO is electrochemically oxidized into strong oxidizing agent of Cu(III) species such as CuOOH or $\text{Cu}(\text{OH})_4^-$. Finally, glucose is catalytically oxidized by the Cu(III) species and forms hydrolyzate gluconic acid.

Figure 5 shows the CVs of the Cu NPs/PoPD modified electrode in 0.1 M NaOH in the absence and the presence of glucose by sweeping the potential between -0.8 and 0.5 V at a scan rate of 100 mV/s. The CVs shows that the CuNPs/PoPD modified electrode led an increasing current response with the concentration of glucose at around 0.5 V, which also indicated that glucose could be irreversibly oxidized at the CuNPs/PoPD modified electrode. In the case of the CuNPs electrodeposited onto PoPD layer, CuNPs grown on the surface of the non-conducting polymer film, through the inert polymer matrix, remained in electronic contact with the underlying substrate and acted as an electrocatalytic center for glucose oxidation.

Effect of the applied potential on the current response

Applied potential is an important parameter in chronoamperometry. Figure 6 shows the effect of the applied potential on the amperometric response to 60 μM glucose. From Fig. 6, it can be seen that the glucose oxidation exhibited strong electrocatalytic activity at an applied potential of 0.50 V. It was evident that Cu NPs electrodeposited on PoPD film showed strong electrocatalytic activity towards glucose oxidation. So the potential of 0.50 V was chosen as the optimum applied potential in our experiments.

Selection of the optimal operation conditions

Figure 7 shows the effect of the amount of PoPD on the response current for glucose oxidation in 0.1 M NaOH containing glucose of 60 μM . Firstly, we had investigated that the CuNPs/PoPD/GCE was constructed by electropolymerizing *o*-PD in a solution with different concentrations of *o*-PD and then electrodepositing Cu NPs onto the PoPD film surface. From Fig. 7a, we could see an obvious rise in the response current with the increase of *o*-PD concentration, and reaching the maximum value at 80 mM. This can be explained that lower *o*-PD concentration resulted in few PoPD electropolymerized on the electrode surface and prevented more CuNPs from depositing on the PoPD film, which reduced the electrocatalytic activity [29]. With the continuous

Fig. 3 AFM and SEM images of bare GCE (a), PoPD/GCE (b), and Cu NPs/PoPD/GCE (c)

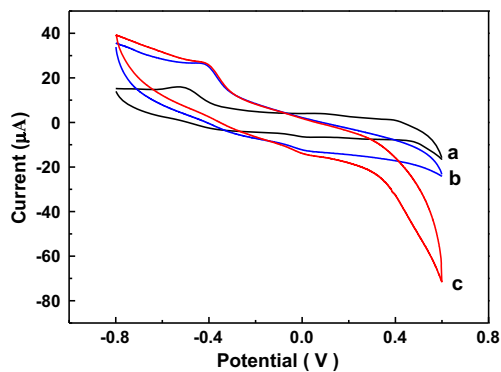
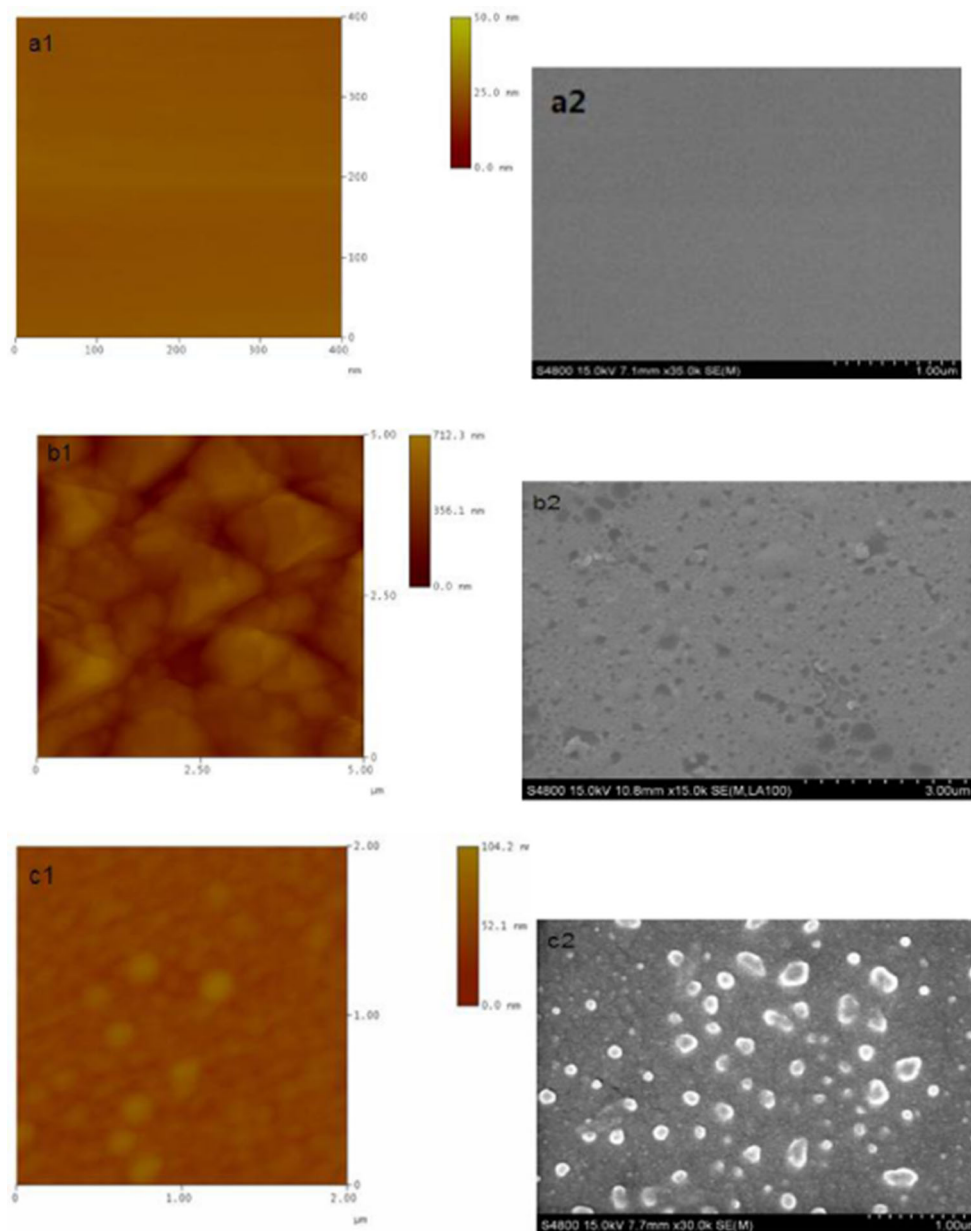


Fig. 4 The CVs of a bare GCE (curve a), PoPD/GCE (curve b), and Cu NPs/PoPD/GCE (curve c) in a solution of 0.1 M NaOH containing 0.65 mM glucose in the potential of -0.8 – 0.6 V. Scan rate, 100 mV/s

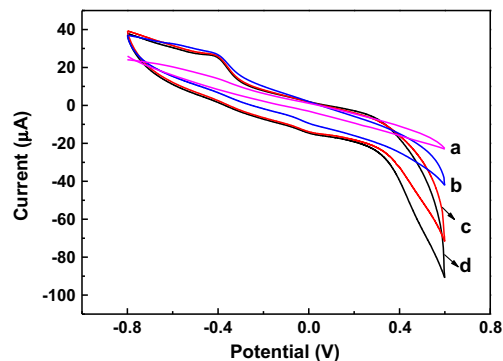


Fig. 5 Cyclic voltammograms of Cu NPs/PoPD modified electrode in PBS containing different glucose concentrations: a, b, c, and d are 0, 0.25, 0.55, and 0.75 mM, respectively. The potential: -0.8 to 0.6 V; scan rate, 100 mV/s

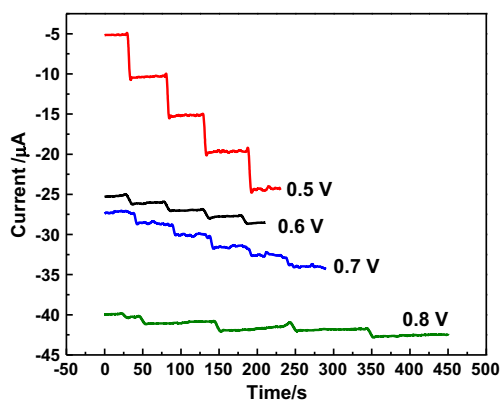


Fig. 6 Effect of the potential on the Cu NPs/PoPD modified electrode response. Steady-state currents were measured in 0.1 M NaOH containing 60 μM glucose

increase of *o*-PD, the current decreased gradually, which produced compact PoPD film on the electrode surface and decreased the active area of CuNPs. So 80 mM *o*-PD was selected as the optimal concentration. The number of scanning cycles affects the uniformity, porosity, permeability, and thickness of the PoPD film on GCE [26]. Figure 7b shows the effect of the PoPD scanning cycles on the response current. With the increase of scanning cycles, the response currents of glucose rose. This is because less scanning cycles formed a smaller amount of thin PoPD film on the GCE surface, which reduced the deposition of CuNPs on the films and produced a poor catalytic activity to glucose. While the number of scanning cycles increased the thickness of PoPD film, the porosity decreased accordingly, diminishing the exposed copper particles surface available for the glucose molecules. As shown in Fig. 7b, 25 cycles was chosen as the optimal number of scanning cycles.

Figure 8 shows the effect of the electrodeposition time of CuNPs on the response current. The glucose oxidation signal rises with the increase in the amount of deposited copper, which is due to the increase of the exposed metal surface [31]. When the electrodeposition time increased to 400 s, the response current reached maximum value. Then the response

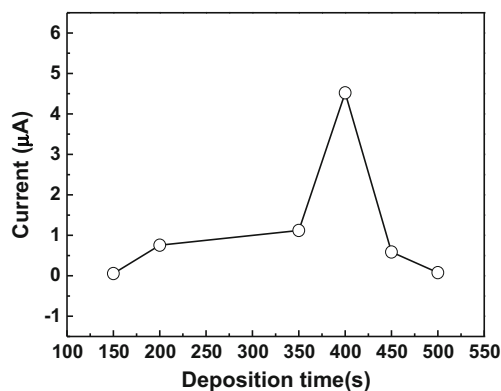


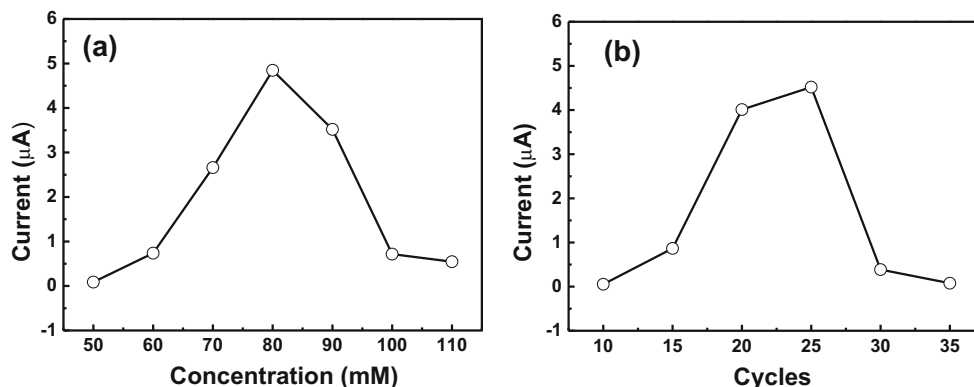
Fig. 8 Effect of the electrodeposition time of CuNPs on the response current at CuNPs/PoPD/GCE. Steady-state currents were measured in 0.1 M NaOH at the applied potential of 0.5 V under gently stirring

current began to decrease when the electrodeposition time increased further, which might obtain bigger CuNPs and decrease the electrocatalytic ability. Thus, 400 s was chosen as the optimal electrodeposition time.

Amperometric determination of glucose

The amperometric response measurements of Cu-NPs/PoPD modified electrode were performed for the successive addition of 1.0 μM glucose in 0.1 M NaOH at 0.50 V under gently stirring. Figure 9a shows a typical current–time plot for the CuNPs/PoPD/GCE upon the consecutive addition of glucose. The response current increased with the successive addition of glucose. The response currents reached a steady-state current signal within 1 s, indicating a fast response of the sensor. Figure 9b displays the corresponding calibration curve for glucose. The linear response range of the biosensor to glucose was from 5.0 μM to 1.6 mM and the corresponding linearity (*R*) was 0.998, and the detection limit was 0.25 μM. The response speed, detection limit, and linear range of the proposed glucose sensor were compared with non-enzymatic glucose sensors based on nanostructured Cu that had reported in recent two years, as summarized in Table 1. From the

Fig. 7 The amperometric responses of 60 μM glucose in the 0.1 M NaOH solution at the CuNPs/PoPD/GCE. **a** Effect of *o*-PD concentration on the Cu-NPs/PoPD modified electrode response; **b** effect of sweep cycles for electropolymerization *o*-PD on current response



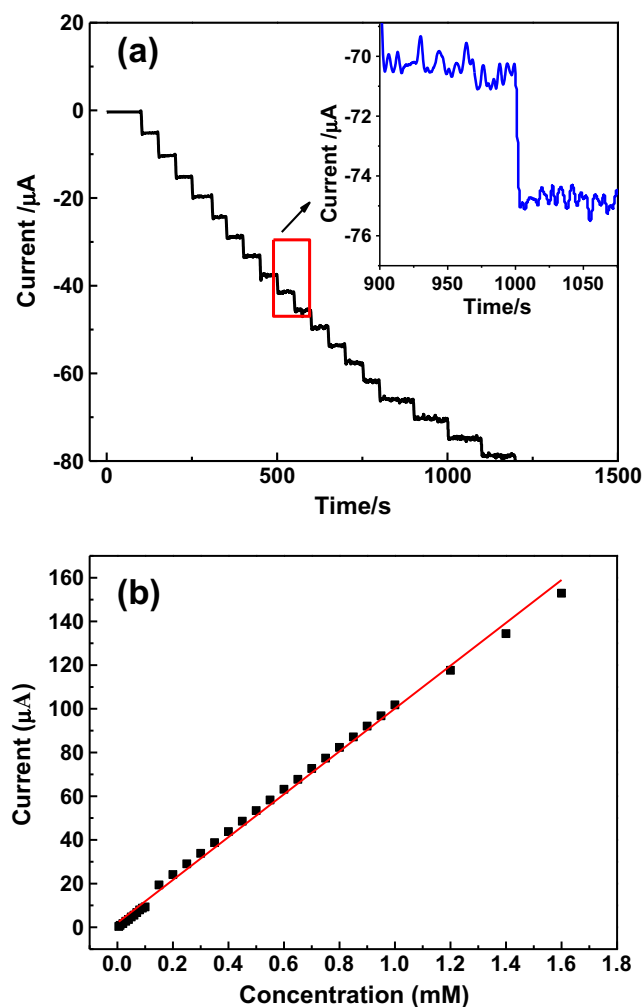


Fig. 9 **a** The amperometric response of Cu-NPs/PoPD/GCE for the successive addition of 60 μM glucose in 0.1 M NaOH at 0.50 V under gently stirring. **b** The corresponding calibration curve for glucose

presented data in Table 1, our proposed sensor exhibits relatively fast response speed, low detection limits, and wide linear range.

Table 1 Comparison of several reported non-enzymatic glucose sensors

| | Modified electrode | Response time(s) | Detection limit (μM) | Linear range | Reference |
|---|----------------------------------|------------------|-----------------------------------|---|-----------|
| | CNT-Ni ³ /GCE | 3 | 2 | 5 μM –2 mM | [8] |
| | Cu nanowires/GTE | <2 | 1.6 | 5 μM –6 mM | [8] |
| ^a Carbon-nanotube-nickel nanocomposites | Cu flowers/GCE | – | 1 μM | 2 μM –75 μM | [10] |
| | Cu octahedral cages/GCE | – | 4 μM | 8 μM –93 μM | |
| ^b Copper/porous silicon nanocomposite | Cu/Psi ^b /CPE | <4 | 0.2 | 1.0 μM –190 μM 190 μM –2.3 mM | [11] |
| ^c Cubic Cu nanoparticles and multi-walled carbon nanotubes | Cu-MWCNTs ^c electrode | 1 | 2.0 | 0.5 mM–7.5 mM | [12] |
| ^d TiC/C nanofiber arrays decorated with Cu nanoparticles | Cu@TiC/C ^d electrode | <5 | 0.2 | 1.0 μM –1.7 mM 1.7 mM–5.2 mM | [13] |
| ^e Copper nanoparticles decorated nitrogen-doped graphene | Nafion-Cu-N-G ^e /GCE | <5 | 1.3 | 4 μM –4.5 mM | [14] |
| | Proposed sensor | <1 | 0.25 | 5.0 μM –1.6 mM | This work |

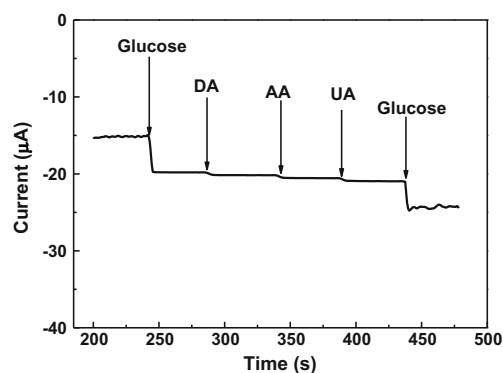


Fig. 10 Effect of interferences on the amperometric response of the CuNPs/PoPD/GCE to 60 μM glucose, 6 μM DA, 6 μM AA and 6 μM UA at +0.50 V, respectively

Anti-interference study

Ascorbic acid (AA) and uric acid (UA) are well-known main interferences on the amperometric response of glucose. To evaluate the selectivity of the proposed biosensor, AA and UA were examined. Considering that the concentration of glucose in the healthy human blood is more 30 times that of AA and UA [32], 60 μM glucose, 6 μM DA, 6 μM AA, and 6 μM UA were successively added to 0.1 M NaOH for the amperometric response measurement of the CuNPs/PoPD/GCE, and the results were shown in Fig. 10. As can be seen in Fig. 10, insignificant responses were observed for interfering electroactive species. These small responses for DA, AA, and UA can be neglected. In other words, the CuNPs/PoPD/GCE shows good selectivity for glucose detection. Furthermore, some main coexist ions in human blood (Na^+ , K^+ , NH_3^+ , Ca^{2+} , Fe^{2+} , Cl^- , PO_4^{3-}), maltose, icodextrin, galactose, and xylose were also examined, and all the effects could be ignored. The results indicated our electrode has high selectivity. Therefore, the sensor can be used for blood glucose detection effectively.

Table 2 The determination results of glucose in human blood samples

| Sample | Glucose concentration ($n=6$) (mM) | Added (mM) | Found (mM) | RSD% ($n=6$) | Recovery % |
|--------|--------------------------------------|------------|------------|----------------|------------|
| 1 | 5.17 | 3.00 | 2.89 | 3.3 | 96.3 |
| | | 4.00 | 4.11 | | 102.8 |
| | | 5.00 | 4.91 | | 98.2 |
| 2 | 5.98 | 3.00 | 3.05 | 3.8 | 101.7 |
| | | 4.00 | 4.08 | | 102.0 |
| | | 5.00 | 4.92 | | 98.4 |

Reproducibility, repeatability, and stability of the sensor

The response reproducibility of six electrodes, prepared under the same optimum conditions, was estimated in 0.1 M NaOH at 0.50 V by the response to 60 μ M glucose. A mean current response of 4.89 μ A and a relative standard deviation (R.S.D.) of 3.8 % were yielded. The repeatability of the determination was investigated at 0.50 V and 25 °C in 0.10 M NaOH containing 60 μ M glucose, which yielded a relative standard deviation of 3.5 % for ten continuous determinations of the same sample by using one proposed electrode. The results indicated that the proposed electrode has good reproducibility and repeatability. The proposed electrodes were stored at room temperature, and their long-term stability was tested over 4 months. The measurements were taken under the same conditions, which yielded a relative standard deviation of 3.7 %. The measurement results indicated that the response current did not show obvious decrease, thereby exhibiting long-term stability.

Determination of glucose in human blood samples

The sensor was used to determine the glucose in human blood samples. Blood samples were obtained from healthy humans who complied with fasting blood test requirements. Human blood samples were mixed and diluted in NaOH, and the amperometric response measurements were performed under the optimum conditions at an applied potential of 0.50 V. The results of glucose concentrations in blood samples are listed in

Table 2. Recoveries in blood samples were from 96.3 to 102.8 %.

The glucose concentrations in fresh human blood samples obtained from our experiments were compared with those measured by the hospital with an YSI Model 2300 Glucose Analyzer (Yellow Springs Instruments, Yellow Springs, OH). The YSI analyzer uses a GO based method to measure glucose. The results are listed in Table 3. The bias for each sample is less than 0.3 mM. This comparison clearly shows that our results satisfactorily agree with those obtained in the hospital.

Conclusions

In conclusion, a non-enzymatic glucose sensor based on Cu-NPs and PoPD was developed. The response of the proposed electrode to glucose concentrations presented a good linearity over the range of 5.0 μ M to 1.6 mM. The study provided an easy way for the determination of glucose in human blood. The current response time for steady-state current was within 1 s. The applicability of the method to the determination of glucose in human blood was demonstrated. As a non-enzymatic sensor, the analytical results were satisfactory for the detection of glucose in human blood. The newly developed non-enzymatic glucose sensor shows various excellent characteristics such as low cost, fast response, acceptable sensitivity, reproducibility, selectivity, and long-time stability.

Table 3 Comparison between the values obtained in the hospital and those obtained by using proposed sensor for the determination of glucose in human blood samples

| Sample number | Determined in the hospital (mM) | Determined by our biosensor (mM) | Bias (mM) |
|---------------|---------------------------------|----------------------------------|-----------|
| 1 | 4.86 | 4.79 | -0.07 |
| 2 | 5.58 | 5.74 | +0.16 |
| 3 | 5.89 | 5.62 | -0.27 |
| 4 | 6.83 | 6.98 | +0.15 |
| 5 | 7.07 | 7.31 | +0.30 |

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