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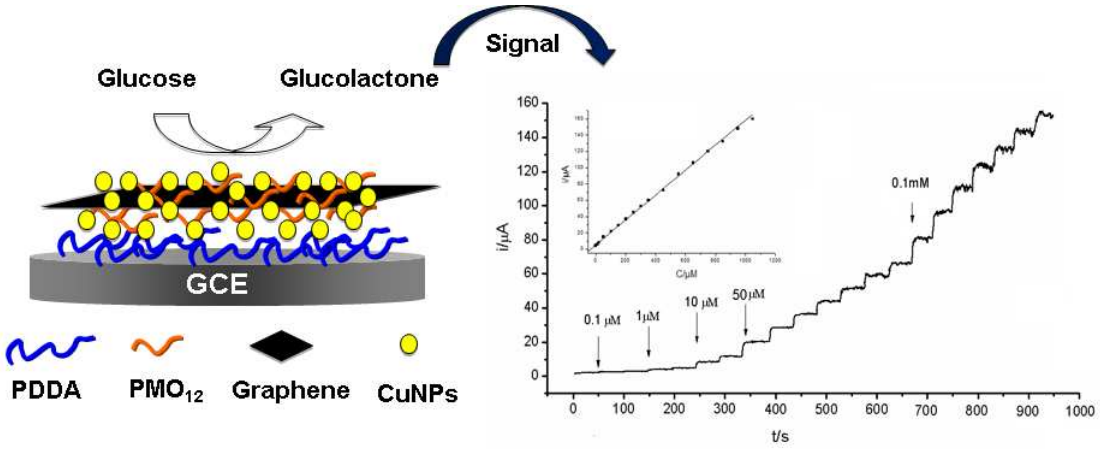

Phosphomolybdic acid Functionalized Graphene Loading Copper Nanoparticles Modified Electrodes for Non-Enzymatic Electrochemical Sensing of Glucose

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Abstract: A sensitive non-enzymatic glucose electrochemical biosensor (Cu/PMo_{12}-GR/GCE) was developed based on the combination of copper nanoparticles (CuNPs) and phosphomolybdic acid functionalized graphene (PMo_{12}-GR). PMo_{12}-GR films were modified on the surface of glassy carbon electrode (GCE) through electrostatic self-assembly with the aid of poly diallyl dimethyl ammonium chloride (PDDA). Then CuNPs were successfully decorated onto the PMo_{12}-GR modified GCE through electrodeposition. The morphology of Cu/PMo_{12}-GR/GCE was characterized by scanning electron microscope (SEM). Cyclic voltammetry (CV) and chronoamperometry were used to investigate the electrochemical performances of the biosensor. The results indicated that the modified electrode displayed a synergistic effect of PMo_{12}-GR sheets and CuNPs towards the electro-oxidation of glucose in the alkaline solution. At the optimal detection potential of 0.50 V, the response towards glucose presented a linear response ranging from 0.10 μM to 1.0 mM with a detection limit of 3.0×10^{-2} μM (S/N=3). In addition, Cu/PMo_{12}-GR/GCE possessed a high selectivity, good reproducibility, excellent stability and acceptable recovery, which indicating the potential application in clinical field.

Keywords: Phosphomolybdic acid; Graphene; Copper nanoparticles; Non-enzymatic glucose sensing; Amperometric detection

1. Introduction

The electrochemical approach for glucose detection has attracted significant attention for its simplicity, high reliability, sensitivity, selectivity and low cost. Since the first enzyme electrode was reported in 1962 [1], most researches on glucose sensing have involved the use of glucose oxidase. Although these biosensors express a highly sensitive performance, the lack of stability originating from the intrinsic nature of the enzymes has limited their applications. The activity of these enzymes can be easily affected by temperature, pH, humidity, toxic chemicals and so on. Considering these drawbacks, non-enzymatic electrochemical sensors have become a highly desirable project for glucose detection [2]. The majority of these nonenzymatic electrochemical glucose sensors rely on the current response of glucose oxidation directly at solid electrode surface. However, the traditional electrodes have poor analytical performance due to their slow electrode kinetics and high over-potential. And the electrocatalytic surfaces of the electrodes are always blocked by the accumulation of chemisorbed intermediates, which resulted in a lose of electrocatalytic activity. In addition, the electrodes often suffer from the influence coming from some electroactive species during electrochemical detection of glucose under physiological conditions.

In recent years, a variety of nanomaterials [3,4], especially the carbon-based nanocomposites [5-8], have been introduced to the fabrication of non-enzymatic electrochemical glucose sensors due to their desirable chemical, physical and electronic properties, which can enhance the sensing performance. Among these

materials, graphene-based nanocomposites [9-11] have aroused extensive interest and become attractive choices for glucose non-enzymatic sensing. The reason is that graphene-based nanocomposites could provide large electrochemically active surface areas and enhance the electron transfer between electrode and glucose effectively, leading to a more rapid and sensitive current response. Up to now, various metal-graphene and metal oxide-graphene nanocomposites have been reported for the fabrication of non-enzymatic glucose sensor, including of Pd nanoparticles-graphene oxide [12], Ag nanoparticles-graphene [13], Fe_3O_4-graphene [14], MnO_2-graphene [15], Co_3O_4-graphene [16], SnO_2-graphene [17], copper oxide-graphene [18,19], ZrO_2-graphene [20] and so on. And the performance of the graphene-based non-enzymatic glucose biosensor relies not only on the properties of the individual components, such as the electron transport ability of the substrates and the catalytic activities of metal or metal oxide nanoparticles, but also on the effective structural integration and electrical communication of the components. Therefore, it is important to develop methods to improve the intimate contact between the components.

The addition of intermedium is an important strategy to improve electrical communication. Using this strategy, many multi-component glucose biosensors have been reported, such as Pd nanoparticles/nafion/graphene [21], Ni/quercetin/graphene [22], polyvinylpyrrolidone/graphene/nickel nanoparticles/chitosan [23] and so on [24]. But, many additions like nafion and chitosan are mainly not chosen as electron intermedium but as stabilizer. Because they are not active materials for glucose sensing, they may degrade the sensitivity of glucose detection. Polyoxometalates

anions (POMs), a type of well-known polynuclear metal-oxo cluster compounds represented by Keggin-type phosphomolybdate (PMo_{12}) [25], can be introduced to fabricate metal nanoparticles/graphene-based glucose biosensor as intermedium. One of the most important properties of PMo_{12} is the potential for reversible multi-electron redox reactions, which makes it to be an attractive candidate for electrocatalysis and electroanalysis [26,27]. We have reported a novel phosphomolybdic acid/graphene composite modified electrode for determination of folic acid [28]. The synergistic effect of phosphomolybdic acid and graphene improved the analytical performances of the electrode. Additionally, PMo_{12} can also act as a dispersant and stabilizer to prevented the hydrophobic graphene from agglomerating [29]. Therefore, PMo_{12} is suitable to fabricate graphene-based glucose electrochemical sensor as active materials. In order to immobilize PMo_{12} on electrode surface effectively and maintain its beneficial properties, a variety of methods have been used, including of Langmuir-Blodgett (LB) technique [30], electrodeposition [31] and so on [32-34]. In this research, electrostatic self-assembly is used with the assistance of Poly(diallyldimethylammonium chloride) (PDDA), a positively charged polyelectrolyte [35]. And the PDDA can enhance the conductivity further [36,37], which is beneficial for the performance improvement of the electrocatalyst.

Herein, we report a novel non-enzymatic glucose electrochemical sensor based on cooper nanoparticles (CuNPs) and graphene (GR). To make intimate contact between CuNPs and GR, which can improve analytical performance of the sensor, PMo_{12} is introduced to the modified electrode through electrostatic self-assembly with the

assistance of PDDA. With the synergistic effect of PMo_{12}, GR sheets and CuNPs, this proposed glucose sensor exhibits excellent electrocatalytic activity towards the glucose with a fast amperometric response, low detection limit and wider linear range. It is capable to assay the glucose in human serum samples contained other coexisting interferences.

2.Experimental

2.1. Chemicals and materials

Glucose was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Keggin-type phosphomolybdic acid $H_7PMo_{12}O_{42}$ xH_2O (denoted briefly as PMo_{12}) was ordered from Tianjin Regent Co., Ltd. (Tianjin, China). Graphite was provided by Qingdao Fujin Graphite Co., Ltd. (Qingdao, China). Dopamine (DA) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Ascorbic acid (AA) was obtained from Shanghai Reagent Factory (Shanghai China). Uric acid (UA) was purchased from Sinogharm Chemical Reagent. PDDA was ordered from Sigma-Aldrich (St. Louis, MO, USA). $CuSO_4$, NaOH and other reagents were of analytical grade.

2.2. Apparatus

Scanning electron microscopy (SEM) and transmission electron microscope (TEM) images were obtained by JEOL JSM-7001F and JEOL JEM-2100, respectively. Cyclic voltammetry (CV) and amperometric measurements were performed using a CHI-660C electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) with a conventional three-electrode cell. A glassy carbon electrode (GCE) was

used as bare electrode, and the modified GCE (Cu/PMo_{12}-GR/GCE) was used as the working electrode. A platinum wire was used as the auxiliary electrode. All the potentials quoted here were referred to a saturated calomel electrode (SCE) as the reference.

2.3. Preparation of the Cu/PMo12-GR/GCE

GR was prepared according to our previously reported method [38]. 10 mg GR was fully dispersed in 10 mL of PMo_{12} solution by ultrasonicating for 30 min. Then the PMo_{12} functionalized GR (PMo_{12}-GR) was obtained.

A GCE was first sequentially polished with 0.3 μm and 0.05 μm alumina powders. Then the GCE was ultrasonically cleaned in ethanol and double-distilled water respectively followed by drying at room temperature before use. The as-prepared GCE was soaked in PDDA (10 wt%) for 15 min, and then took it out to dry by air. After that, a PDDA/GCE was obtained. Then we put the PDDA/GCE in the suspension liquid of PMo_{12}-GR for 15 min, and then took it out and dried it in room temperature. Repeated the same process, we could obtain multilayer PMo_{12}-GR modified electrode.

Subsequently, the electrodeposition of CuNPs on the PMo_{12}-GR modified electrode was conducted in a solution consisting of 0.040 M $CuSO_4$ at -0.40 V for 400 s. After that, the Cu/PMo_{12}-GR/GCE was obtained. For comparison, CuNPs deposited on GR/GCE were prepared by a similar method as stated above without the addition of PMo_{12}, which was denoted as Cu/GR/GCE.

2.4. Analytical procedure

0.10 M NaOH solution was employed as the supporting electrolyte. CV measurements were performed with the potential range of 0.0 V-1.0 V at a scan rate of 50 mV/s. Amperometric detection of glucose was carried out by continuously adding glucose every 50 s under magnetic stirring with the applied potential of 0.50 V. All measurements were carried out at room temperature. And the electrolyte was purged with highly purified N_2 to eliminate the O_2 before conducting the analytical experiments.

3. Results and discussion

3.1. Fabrication and characterization of the Cu/PMo_{12}-GR/GCE

The detailed preparation procedure was illustrated in Scheme 1. The PMo_{12} was immobilized onto the GR through the non-covalent bonding, made of weak π-π stacking interactions between PMo_{12} and graphene due to the 3D/2D dimensionality nature of PMo_{12} and graphene [39]. Then the sensor was prepared with the immobilization of PMo_{12}-GR onto the GCE through electrostatic self-assembly with the assistance of the positively charged PDDA. PMo_{12}-GR with different layers were prepared by repeating the electrostatic self-assembly procedure. The electron transfer ability between electrolyte and electrode surface with different PMo_{12}-GR layers (4, 6, 8, 10 layers, respectively) was investigated using CVs in 0.10 M H_2SO_4 at 100 mV/s over a range from -0.40 V to 1.4 V. As shown in Fig. 1, the characteristic peaks of phosphomolybdic acid were observed, indicating that PMo_{12}-GR was modified in electrode successfully. The increased CV peak currents were observed with the PMo_{12}-GR layers from 4 to 8. When the layer increased from 8 to 10, the peak

currents only had a little change. Therefore, eight layers were chosen as the optimal thickness of the PMo_{12}/GR film for electron transfer. The currents of Cu/PMo_{12}-GR/GCE with different PMo_{12}-GR layers towards glucose also verified the optimal thickness of 8 layers. The whole process was illustrated by following reaction equations:

$$PMo_{12}{}^{VI}O_{40}{}^{3-}+2e^{-}+2H^{+}\rightarrow H_2PMo_2{}^{V}Mo_{10}{}^{VI}O_{40}{}^{3-} \quad (1)$$

$$H_2PMo_2{}^{V}Mo_{10}{}^{VI}O_{40}{}^{3-}+2e^{-}+2H^{+}\rightarrow H_4PMo_4{}^{V}Mo_8{}^{VI}O_{40}{}^{3-} \quad (2)$$

$$H_4PMo_4{}^{V}Mo_8{}^{VI}O_{40}{}^{3-\ -}+2e^{-}+2H^{+}\rightarrow H_6PMo_6{}^{V}Mo_6{}^{VI}O_{40}{}^{3-} \quad (3)$$

Subsequently, CuNPs were immobilized on the PMo_{12}-GR modified electrode using the electrodeposition method according to the previously reports [40,41]. The deposition potential, which had great influences on the catalytic activity of CuNPs, was investigated by chronoamperometry with adding 1.0 mM glucose in 0.10 M NaOH solution under different deposition potentials of -0.30, -0.35, -0.40, -0.45 V. The corresponding current-time curves were shown in Fig. 2A. The current response increased significantly with the increase of deposition potential from -0.30 V to -0.40 V. When the deposition potential was -0.45 V, a slight decline of the current response was shown. The effect of deposition time was also studied by chronoamperometry at different time of 200, 300, 400, 480 s and the results were shown in Fig. 2B. With the increase of the deposition time, the oxidation peak current increased and the maximum peak current appeared in the 400s. Therefore, we have chosen -0.40 V and 400 s as reaction deposition potential and deposition time, respectively.

Scheme 1.

Fig. 1.

Fig. 2.

The introduction of PMo_{12} could effectively disperse GR. Fig. 3A and 3B showed the images of the dispersion of GR and PMo_{12}-GR in aqueous solution, respectively. After placing for 12 h, the PMo_{12}-GR solution was still a homogeneous black dispersion. But the GR solution produced black precipitation at the bottom of the bottle, which indicating the aggregation of GR. The results indicated that PMo_{12} could act as the dispersant to prevent the hydrophobic graphene from agglomerating.

The morphologies of the GR, PMo_{12}-GR and Cu/PMo_{12}-GR were characterized using SEM. The top views of the GR (Fig. 3C) clearly illustrated the typically flake-like nanosheets. And the TEM image of the GR (inset of Fig. 3C) also clearly presented the crumpled and wrinkled flake-like structure. As shown in Fig. 3D, 8 layers of PMo_{12}-GR illustrated the three-dimensional and multilayer incompact morphology. The results signified that PMo_{12} had been successfully deposited on GR, and that the surface of GR was fully covered by a PMo_{12} continuous film with an incompact structure, which was eligible for fast transportation of electrons and ions. After the electrodeposition of CuNPs, it could be observed that abundant CuNPs were immobilized on the surface of PMo_{12}-GR (Fig. 3E). It was evident that spherical CuNPs with uniform diameters were dispersed on the surface of multilayer PMo_{12}-GR. As a comparison, CuNPs were immobilized on the surface of GR without the assistance of PMo_{12}. As can be seen in Fig. 3F, CuNPs tended to form agglomerates on the surface of GR. However, the CuNPs were uniform and had a well dispersion on

the surface of PMo_{12}-GR. The histogram of the CuNPs size distribution showed that the average diameter of CuNPs supported on PMo_{12}-GR was measured to be 80 nm (Fig. 4A), which was smaller than that supported on GR without PMo_{12} (Fig. 4B, 120 nm). Furthermore, the size distribution of CuNPs on PMo_{12}-GR was narrow compared to that on GR. Thus, the structural integration of PMo_{12} and GR onto electrodes could effectively promote the uniform growth of CuNPs with smaller size, which was beneficial for the electro-oxidation of glucose. The PMo_{12} contained negative charges which should be balanced by the dopant counter ions, and the PMo_{12}-GR had an incompact nanostructure. Therefore the Cu^{2+} can easily diffuse into the surface of the composite film, which results in homogeneous shaping of CuNPs.

Fig. 3.

Fig. 4.

3.2. Electrocatalysis of glucose at the Cu/PMo_{12}-GR/GCE

The electrocatalysis of glucose at different electrodes was investigated using CV. The CVs of Cu/PMo_{12}-GR/GCE, Cu/GR/GCE and PMo_{12}-GR/GCE in the glucose solution and 0.10 M NaOH solution without glucose were shown in Fig. 5. In the absence of glucose, there was no any oxidation peak appeared at Cu/PMo_{12}-GR/GCE (curve d). But after the addition of glucose, an irreversible redox peak was observed. As shown in curve a, b and c, the maximum current response was observed on the surface of Cu/PMo_{12}-GR/GCE. This could be ascribed to the effects of graphene, PMo_{12} and PDDA. Firstly, the existence of graphene, PMo_{12} and PDDA improved the electrical conductivity of the modified electrode to some extent due to their intrinsic

conductivity. Secondly, the PMo_{12} could form an electronegative surface for the immobilization of PMo_{12}-GR on GCE and promote the uniform growth of CuNPs with smaller size, which was beneficial for the electrocatalysis of glucose. In addition, the PMo_{12} prevented the aggregation of graphene, which increased specific surface area for the adsorption of targets.

The mechanism of electrocatalytic oxidation of glucose in NaOH solution by Cu/PMo_{12}-GR/GCE could be represented by the following reactions based on previous reports. The Cu could be oxidized to Cu (II) and then to Cu (III) in alkaline solution. After that, glucose could be electrocatalytic oxidized to gluconolactone by the Cu (III) species [41]:

$$Cu + 2OH^- - 2e \rightarrow Cu(OH)_2 \quad (1)$$

$$Cu(OH)_2 + OH^- - e \rightarrow CuOOH + H_2O \quad (2)$$

$$CuOOH + glucose \rightarrow Cu(OH)_2 + gluconolactone \quad (3)$$

Fig. 5.

3.3. Amperometric detection of glucose

In order to obtain an accurate testing result of glucose, the effect of detection potential in electrochemical workstation was explored under different potentials (0.30, 0.40, 0.45, 0.50, 0.55 V, respectively) with dropwise addition of 0.10 mM glucose into 0.10 M NaOH solution at 50 s interval. As shown in Fig. 6, the response current increased with the detection potential from 0.30 to 0.50 V. But when the detection potential was increased to 0.55 V, the response current had an obvious decrease.

Hence, 0.50 V was selected as the optimal detection potential for the detection of glucose.

Fig. 6.

The current-time response curve of Cu/PMo_{12}-GR/GCE upon the dropwise addition of glucose into 0.10 M NaOH solution with a detection potential of 0.50 V was presented in Fig. 7. After the continuous addition of glucose solution with different concentrations at 50 s interval, the sensor represented a stable current-time response. And the current reached 95% of steady-state current within 5 s, indicating that the Cu/PMo_{12}-GR/GCE could provide a rapid and steady detection of glucose. As shown in Fig. 7 (inset), the oxidative peak current increased linearly with the increase of glucose concentration in the range from 0.10 μM to 1.0 mM and the regression equation was I = 0.1532 c (μM) + 5.2363 (R=0.9990). The detection limit could reach 3.0×10^{-2} μM (S/N=3), which was lower than that of CuNPs-GR/GCE [42,43]. The reason was that the introduction of PMo_{12}, which was efficient for the uniform growth of CuNPs and electron transport. Compared to some other Cu-based non-enzymatic electrochemical glucose sensors, this proposed biosensor was superior or equal in sensitivity and linear range (Table 1). In addition, the innovative advantage of this method was the exploration for the multi-elements (GR, PMo_{12} and Cu NPs) modified strategies.

Fig. 7.

Table 1

3.4. Anti-interference property, stability and reproducibility of the Cu/PMo_{12}-GR/GCE

Anti-interference property was an important factor for measuring the performance of the non-enzymatic electrochemical sensor. In this work, the anti-interference ability was tested by successive addition of glucose and other common coexisting interferences, such as dopamine (DA), urinary (UA) and ascorbic acid (AA). As shown in Fig. 8, a significant amperometric response was observed rapidly with the addition of 0.20 mM glucose, owing to the fast oxidation of glucose by Cu/PMo_{12}-GR/GCE. However, there were no obvious current response changes after the addition of 0.20 mM of DA, UA and AA. The reseults indicated that the Cu/PMo_{12}-GR/GCE had a good anti-interference ability.

Fig. 8.

In this work, the stability and reproducibility of Cu/PMo_{12}-GR/GCE were also investigated. The stability of this sensor was investigated by storing it at 4 °C and measuring the current response in 0.010 mM and 0.10 mM glucose solution once a day over a period of 2 weeks. The relative standard deviations (RSD) were 5.2% and 3.6% respectively. These results demonstrated that this proposed sensor had a satisfactory stability. Furthermore, the reproducibility of Cu/PMo_{12}-GR/GCE was investigated by measuring the current response in 0.10 mM glucose solution with five different Cu/PMo_{12}-GR/GCEs prepared under the same conditions. The RSD was 4.1%, indicating the good reproducibility of the developed sensor.

3.5. Determination of glucose in real sample with the Cu/PMo_{12}-GR/GCE

The applicability of the proposed non-enzymatic glucose electrochemical biosensor was evaluated by using standard addition method. The standard solutions of glucose were added into the human serum to obtain serum samples with different concentrations of glucose. Then the serum samples were added into 0.10 M NaOH solution and detected using the proposed electrochemical biosensor. According to the procedure of spiked standards, the spiked recoveries were 93.91-106.2% for different concentrations of glucose, which were shown in Table 2. These results clearly indicated the applicability of the proposed biosensor.

Table 2

4. Conclusions

In conclusion, a novel non-enzymatic glucose electrochemical sensor was fabricated successfully based on Cu NPs and PMo_{12} functionalized GR with the aid of PDDA. Owing to the synergistic effect of porous multilayer structure of PMo_{12}/GR and the catalytic activity of CuNPs, the fabricated electrochemical sensor exhibited an excellent performance in non-enzymatic detection of glucose with high sensitivity, excellent selectivity, and good stability. This non-enzymatic glucose electrochemical sensor could be a promising technique for the practical determination of glucose. In addition, this work offered a promising candidate for non-enzymatic electrochemical interface construction and electrochemical biosensing.

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Tables

Table 1

Comparison of the linear range and detection limit between this biosensor and other non-enzymatic Cu-based glucose biosensors.

Table 2

Determination of glucose in human serum using the proposed biosensor.

Figure legends:

Scheme 1. Fabrication process of non-enzymatic glucose electrochemical sensor based on GR, PMo_{12} and CuNPs.

Fig. 1. Cyclic voltammograms of the PMo_{12}-GR/GCE with various thicknesses (4, 6, 8, 10 PMo_{12}-GR layers, respectively) in 0.10 M H_2SO_4, scanned at applied potential from -0.20 v to +1.2 v at 100 mV/s.

Fig. 2. Current-time responses of Cu/PMo_{12}-GR/GCE prepared with different deposition potentials (A) and deposition time (B) in 0.10 M NaOH solution with addition of 1.0 mM glucose.

Fig. 3. The images of the dispersion of GR (a) and PMo_{12}-GR (b) in aqueous solution after 0 h (A) and 12 h (B). SEM images of GR (C), 8 layers of PMo_{12}-GR (D), Cu/PMo_{12}-GR (E) and Cu-GR (F). The inset of (C) is the TEM image of GR.

Fig. 4. Histograms of CuNPs size distributions for Cu/PMo_{12}-GR (A) and Cu-GR (B).

Fig. 5. Cyclic voltammograms of different electrodes (a) Cu/PMo_{12}-GR/GCE, (b) Cu/GR/GCE, (c) PMo_{12}-GR/GCE in 1.0 mM glucose solution and (d) Cu/PMo_{12}-GR/GCE in 0.10 M NaOH solution without glucose, scanned at applied potential from 0.00 V to +0.90 V at 100 mV/s.

Fig. 6. Current-time responses of Cu/PMo_{12}-GR/GCE at different potentials in 0.10 M NaOH with addition of 0.10 mM glucose at 50 s interval.

Fig. 7. Current-time of response at +0.50 V with an increase concentration of glucose per 50 s for Cu/ PMo_{12}-GR/GCE. The insets show the linear increase of the oxidative

peak current with the glucose concentration (A) and the amplified current-time curve for 0.1μM (B).

Fig. 8. Interference test of the sensor in 0.10 M NaOH at +0.50 V with 0.20 mM glucose and 0.20 mM interfering species.

Table 1

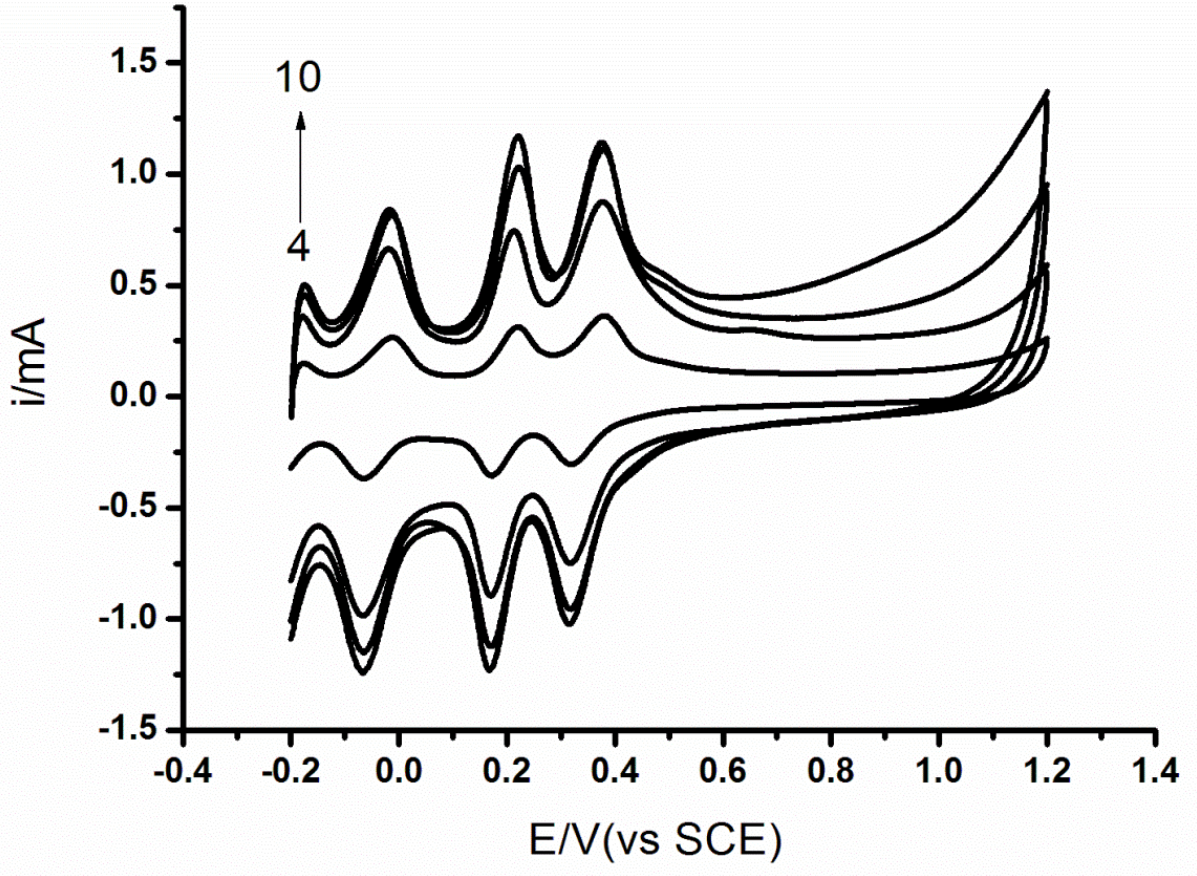
Comparison of the linear range and detection limit between this biosensor and other non-enzymatic Cu-based glucose biosensors.

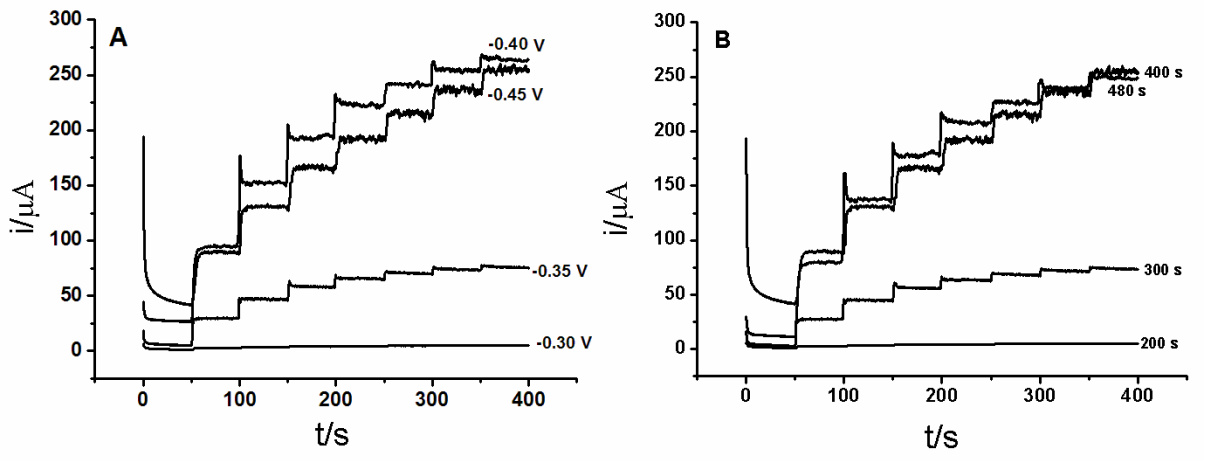
Biosensor	Linear range (mM)	Detection limit (μM)	Ref.
CuNP/GO/SWCNT	0.001-4.538	0.34	[41]
CuNPs-GR/GCE	0.005-1.4	0.20	[42]
CuNPs/rGO	0.01–1.2	3.4	[43]
Cu/PMo_{12}-GR/GCE	0.0001-1.0	0.03	This work
CuO-rGO	0.0004-3	0.1	[18]
CuO-GR/GCE	0.002-4	0.7	[44]
Porous Cu-NiO	0.5–5	0.5	[45]
CuO nanorods/graphite	0.004–8	4.0	[46]
Cu_xO/Ppy-rGO/GCE	0.1-100	0.03	[47]
CuO/MWCNTs	0.0004-1.2	0.2	[48]
CuONPs/CSs	0.0005-2.3	0.1	[49]

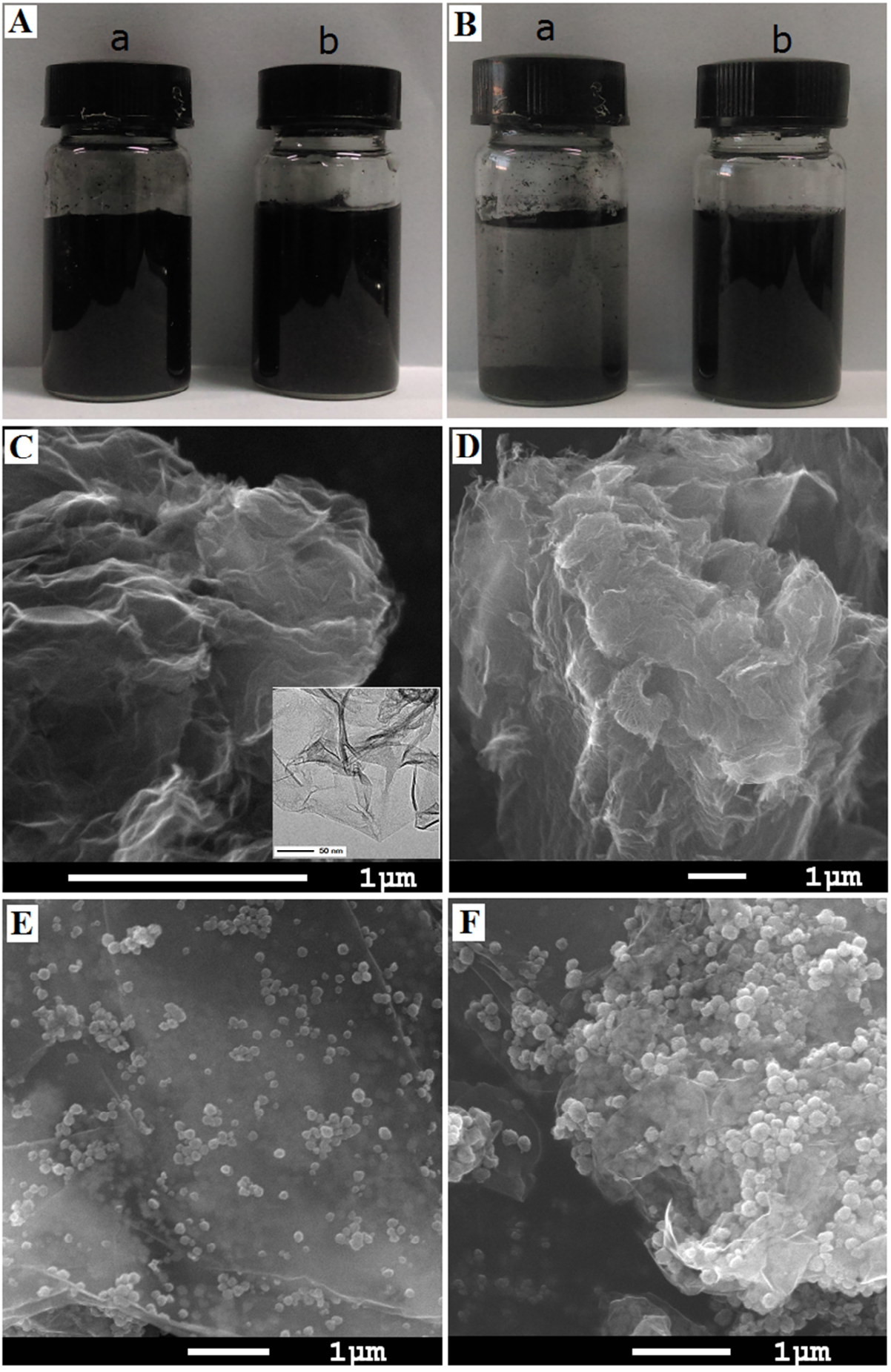
Table 2

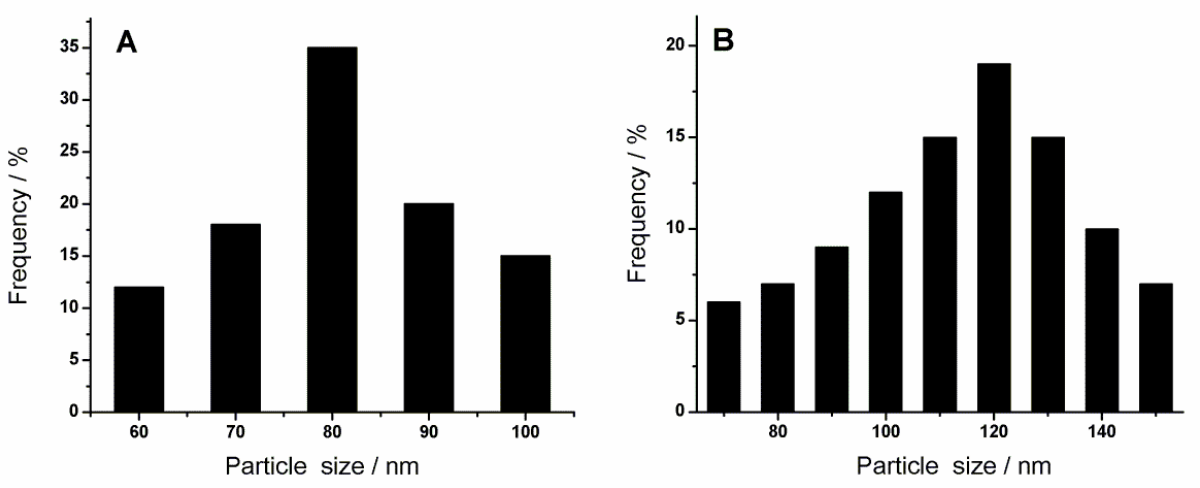
Determination of glucose in human serum using the proposed biosensor.

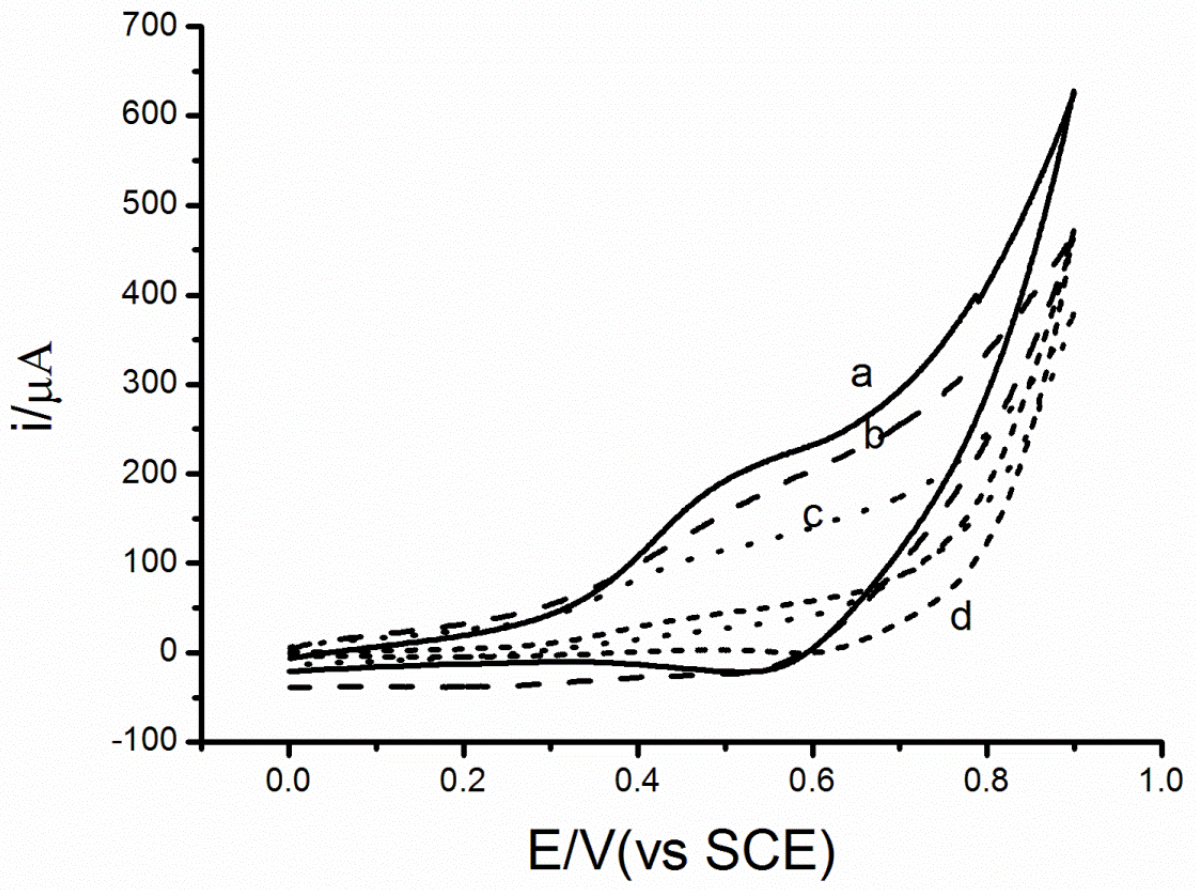
Sample	Concentration (mM)	Added (mM)	Found (mM)	Recovery (%)	RSD (%)
1	5.08	1.00	5.71	93.91	3.2
2	5.08	5.00	9.48	94.05	2.1
3	5.08	10.00	16.02	106.2	3.6

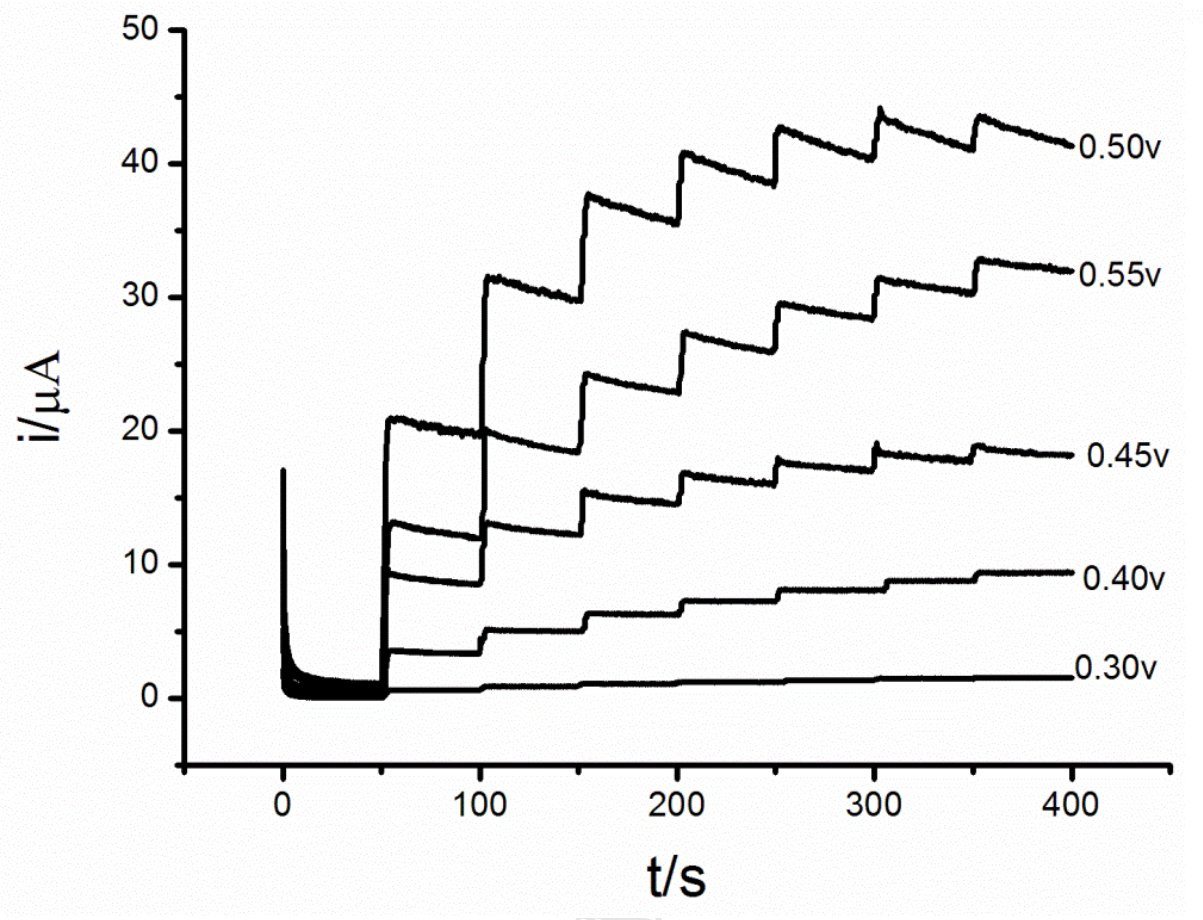


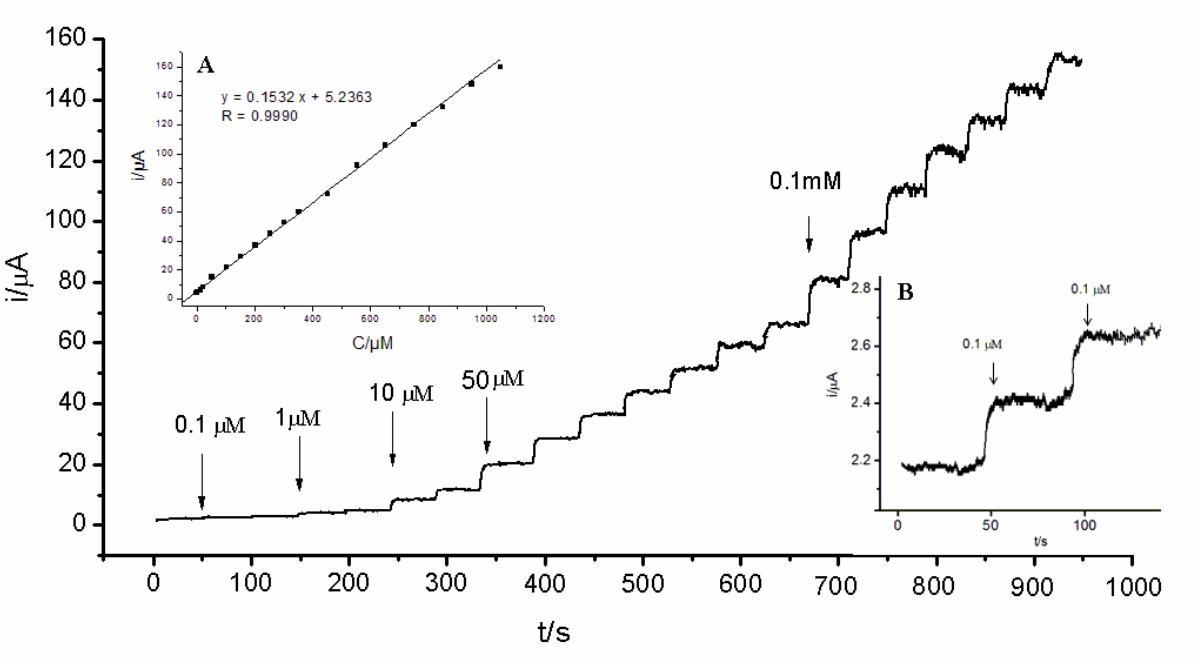


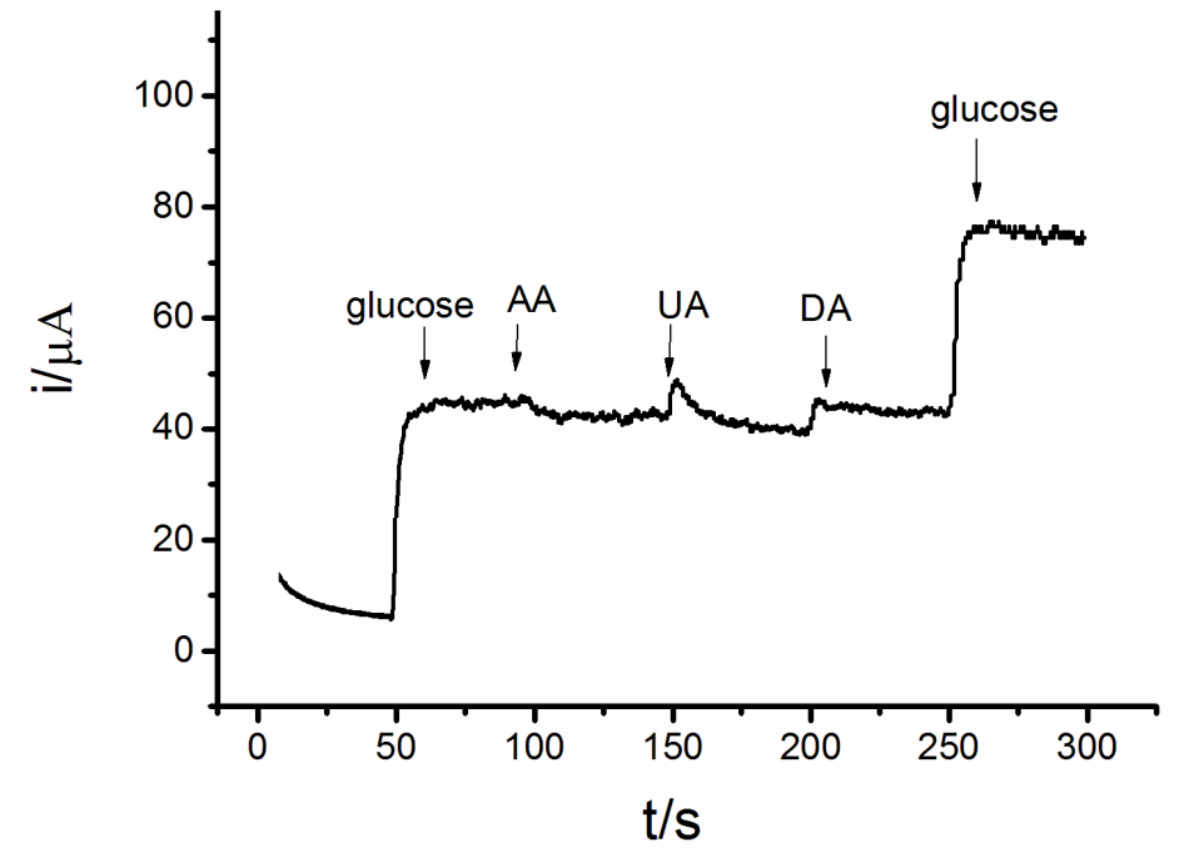

A
a
b
B
a
b
C
50 nm
1 µm
D
1 µm
E
1 µm
F
1 µm

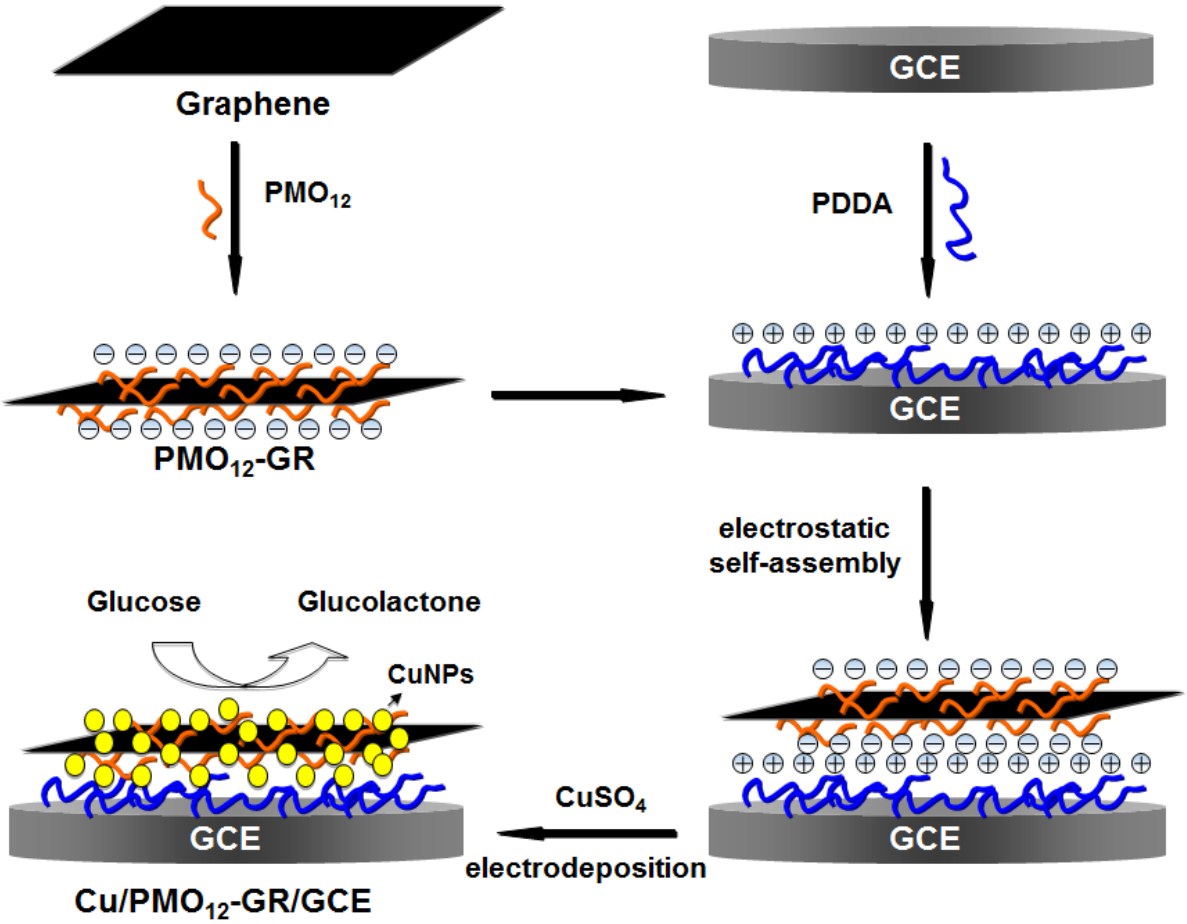












1. Cu/PMo_{12}-GR/GCE as a non-enzymatic glucose electrochemical sensor.
2. PMo_{12} is efficient for the uniform growth of Cu-NPs and electron transport.
3. The sensor exhibits good sensitivity and specificity towards glucose.