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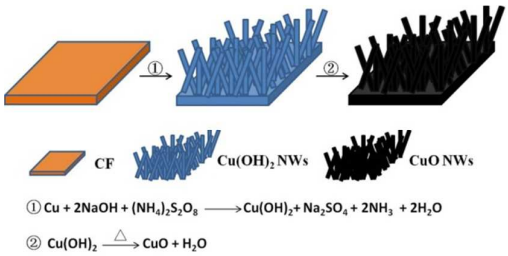

A facile method to fabricate a non-enzymatic glucose sensor based on CuO nanowires is developed.

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PAPER

Facile fabrication of CuO nanowires modified Cu electrode for non-enzymatic glucose detection with enhanced sensitivity

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In this paper the fabrication of CuO nanowires (CuO NWs) by a facile two-step method is reported. $Cu(OH)_2$ nanowires ($Cu(OH)_2$ NWs) on a copper surface was prepared at room temperature by a simple solution-based procedure, and subsequent calcinations of $Cu(OH)_2$ NWs led to the formation of CuO NWs. The morphologies and structures of $Cu(OH)_2$ NWs and CuO NWs were characterized by scanning electron microscopy and X-ray diffraction. Electrochemical measurements showed that the CuO NWs modified Cu electrode exhibited good electrocatalytic behavior for the detection of glucose with a wide linear range from 2 μM to 3.56 mM (R^2= 0.9984), a low detection limit down to 0.05 μM, and a high sensitivity of 1886.3 μA mM^{-1} cm^{-2}. The sensor also displayed a high selectivity, an acceptable reproducibility, an excellent long-term stability and good repeatability. Moreover, the as-prepared sensor has great potential in the practical applications.

1. Introduction

Nowadays, diabetes has become one of the major health care problems. Glucose, an essential bioactive substance, is often used as clinical indicator of diabetes.[1] Therefore, the reliable, accurate, and rapid determination of glucose is of practical importance in biological and clinical analysis.[2] So far, various techniques such as electrochemistry, fluorimetry, surface plasmon resonance and capillary zone electrophoresis have been developed for glucose determination.[3-6] Compared to other analytical techniques, electrochemistry methods have attracted more attention due to their intrinsic simplicity, good selectivity, high sensitivity and easy operation.[7-10] The widely employed glucose sensors are enzyme-based because of their high sensitivity and excellent selectivity to glucose detection.[11-15] However, most enzyme-based sensors suffer from high costs, short lifetimes and stability problems, which limit their further use.[16] To overcome these disadvantages, numerous efforts have been made to develop non-enzymatic glucose sensors. Noble metals (Pt, Au, Pd) and their alloys (Pt-Pd, Pt-Au, Au-Pd) with large specific surface, excellent conductivity and electrocatalytic activities have been widely used for non-enzymatic glucose detection.[17-24] However, these noble metals-based sensors have displayed the drawbacks of high cost that limit their practical application.[9] Accordingly, it is crucial to develop cost-effective, enzyme-free glucose sensors.

CuO, an important *p*-type semiconductor with a narrow band gap of 1.2 eV, has shown its potential applications in various fields, such as electrochemical sensors, photoelectric chemical materials, gas sensing and lithium ion batteries.[25-28] Among these applications, electrochemical sensors have been intensively investigated. Recently, a few attempts have been made to amperometrically detect glucose based on CuO nanomaterials.[8,10,29,30] Wang prepared the CuO nanofibers by electrospining technique and used it for non-enzymatic glucose determination.[31] Cherevko fabricated a CuO electrode by hydrogen bubble evolution and investigated its application in non-enzymatic glucose detection.[32] However, the complex and time-consuming fabrication process limit their application. Therefore, it's still greatly demanded to develop simpler processes to synthesize novel CuO nanostructures with superior catalytic property for fast, sensitive, and stable detection of glucose.

In this paper, we reported a facile way to directly grow CuO NWs on a copper surface. Firstly $Cu(OH)_2$ NWs on the copper surface was fabricated through a simple, template-free, solution-based procedure.[33] The facile transformation of $Cu(OH)_2$ NWs to CuO NWs without obvious morphological change has been achieved by heat treatment. The whole process is simple without using complicated and expensive equipment. The obtained CuO NWs modified Cu electrode exhibits good electrocatalytic performance toward the electrooxidation of glucose. Moreover, the proposed sensor has great potential in the practical applications.

2. Experimental Section

2.1 Materials and apparatus

Copper foil and malt dust were purchased from Sangon Biotech Co., LTD (Shanghai, China). Glucose, sucrose, NaOH and $(NH_4)_2S_2O_8$ were obtained from Beijing Chemical Co. (Beijing, China). Ascorbic acid (AA), uric acid (UA) and dopamine (DA) were supplied by Sigma-Aldrich. All of these reagents were of analytical grade and used without further purification. The ultrapure water used throughout this work was produced by a Milli-Q system. The copper foils were used after ultrasound

cleaning in 3 M HCl, ethanol and deionized water.

Scanning electron microscopy (SEM) characterizations were carried out using a S-4800 FE-SEM scanning electron microscope equipped with an accelerating voltage of 20 kV. The X-ray diffraction (XRD) patterns were recorded with a Rigaku-D/max 2500 V X-ray diffractometer equipped with a Cu Kα radiation source (λ=1.54178 Å). Electrochemical measurements were performed on a CHI660a electrochemical workstation in a conventional three-electrode cell containing 0.1 M NaOH at room temperature, using a platinum foil as the counter electrode, a saturate calomel electrode (SCE) as the reference electrode and Cu electrode, $Cu(OH)_2$ NWs modified Cu electrode and CuO NWs modified Cu electrode as the working electrodes.

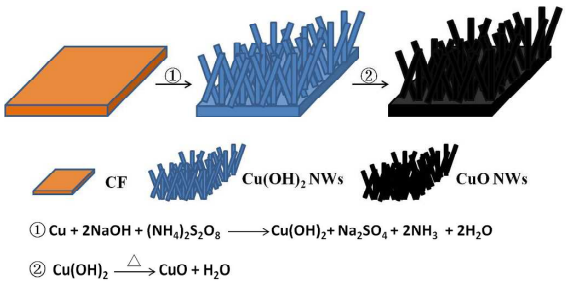
2.2 Preparation of $Cu(OH)_2$ NWs and CuO NWs

The formation mechanism of the CuO NWs is shown in Scheme 1. A typical fabrication of $Cu(OH)_2$ NWs was carried out as follows. Briefly, a piece of clean copper foil (5 mm×5 mm) was immersed into a solution containing 80 μL of 10 M NaOH, 180 μL H_2O and 40 μL of 1 M $(NH_4)_2S_2O_8$. After immersing for 30 minutes, the copper foil was taken out from the solution, washed with distilled water and dried in the air. It can be seen clearly from Fig. S1 that a deep blue film is formed on the surface of copper foil. For the synthesis of CuO NWs, the $Cu(OH)_2$ NWs modified Cu electrode was loaded into an alumina boat, which was then put in a tube furnace. After purging with Ar gas for 30 minutes, the furnace was heated to 120 ℃ for 3 h for complete dehydration. Then the temperature was raised to 180 ℃ and maintained at this temperature for 2 h to promote crystallization. As shown in Fig. S1, the original blue color of the film turns into black after the heat treatment.

3. Results and discussion

3.1 Characterization of copper foil, $Cu(OH)_2$ NWs and CuO NWs

Fig. 1A and 1B show the SEM images of the cooper foil taken at different magnifications. It can be obviously seen that the surface of copper foil is coarse. The XRD peaks of the copper foil are displayed in Fig. 1C and the standard diffraction pattern for Cu (JCPDS no. 04-0836) is also presented for comparison. The peaks positions are in good agreement with the standard file, indicating the obtained copper foil has a high crystalline purity. The SEM images of $Cu(OH)_2$ NWs are shown in Fig. 1D and 1E. It can be seen from the low-magnification SEM image (Fig. 1D) that the as-prepared $Cu(OH)_2$ NWs shows a wire-like morphology and uniformly and compactly covers the copper foil. Fig. 1E reveals the wire-like structure of the $Cu(OH)_2$ NWs with 50-500 nm in diameter. The XRD of $Cu(OH)_2$ NWs (Fig. 1F) is attributed to the orthorhombic $Cu(OH)_2$ phase. The peaks positions match well with the standard XRD data (JCPDS no. 13-0420), confirming the $Cu(OH)_2$ NWs have been successfully grown on the copper foil. Fig. 1G and 1H display the low and high magnification SEM images of the CuO NWs. The wire-like morphology of the CuO NWs is well-preserved and the CuO NWs uniformly covers the copper foil surface. The XRD peaks of the CuO NWs are displayed in Fig. 1I. Except the small broad peak around 30 degrees from $Cu(OH)_2$, no other peaks from impurities are



Scheme 1 Schematic illustration for preparation of the CuO NWs modified Cu electrode.

observed compared with standard file (JCPDS no. 45-0937), demonstrating that the $Cu(OH)_2$ NWs have been almost completely converted to CuO NWs after the heating treatment.

3.2 Electrocatalytic ability of CuO NWs modified Cu electrode towards glucose oxidation

It was reported that CuO-based materials displayed excellent ability to catalyze the oxidation of glucose.[34] In this study, the CuO NWs modified Cu electrode was fabricated and applied as an electrochemical sensor to investigate its catalytic performance on glucose oxidation with Cu electrode and $Cu(OH)_2$ NWs modified Cu electrode as comparison. CV curves of different electrodes in 0.1 M NaOH in the potential window ranging from 0 to 0.8 V in the absence and presence of glucose are shown in Fig. 2A. In the absence of glucose, no obvious current signal is observed at Cu electrode (curve a), while a dramatic current signal is found at $Cu(OH)_2$ NWs modified Cu electrode (curve c) and CuO NWs modified Cu electrode (curve e), respectively. After injecting 2 mM glucose in the electrolyte, a weak oxidation peak at *ca.* +0.58 V is observed for the Cu electrode (curve b) and a more significant oxidation signal of glucose at *ca.* +0.53 V is found at $Cu(OH)_2$ NWs modified Cu electrode (curve d). For CuO NWs modified Cu electrode (curve f), a noticeable increase of the oxidation current starting at *ca.* +0.20 V with a shoulder peak at *ca.* +0.42 V is present. That may be attributed to the proposed involvement of Cu(II) and Cu(III) surface species in the oxidation of glucose though the exact mechanism for the oxidation of glucose in alkaline medium at the Cu-based modified electrode remains some-what controversial.[25,35] The oxidation potential of glucose at CuO NWs modified Cu electrode is more negatively shifted than that at $Cu(OH)_2$ NWs

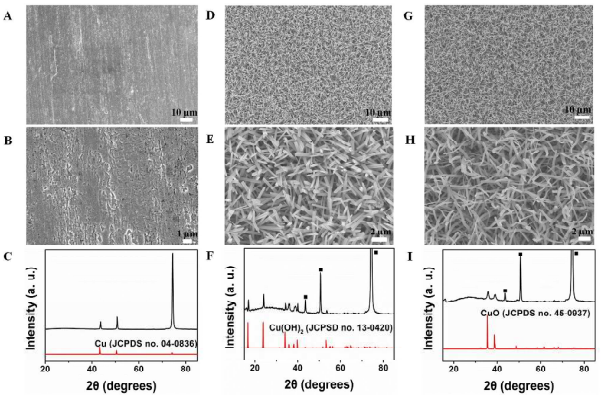


Figure 1 SEM images and XRD patterns of Cu electrode (A, B, C), $Cu(OH)_2$ NWs (D, E, F), and CuO NWs (G, H, I). Peaks marked with ■ are from the copper foil.

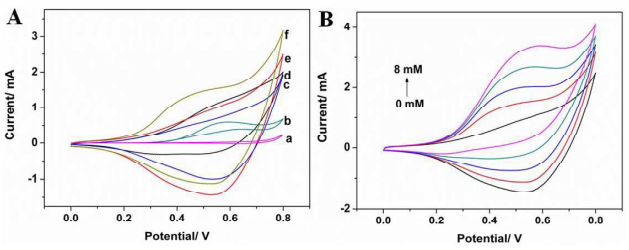


Figure 2 (A) CVs of Cu electrode (a, b), $Cu(OH)_2$ NWs modified Cu electrode (c, d), CuO NWs modified Cu electrode (d, e) in 0.1 M NaOH in the absence (a, c, e) and presence of 2 mM glucose (b, d, f) at the scan rate of 50 mV s^{-1}. (B) CVs of the CuO NWs modified Cu electrode in the absence and presence of glucose with different concentrations (from the bottom to top: 0, 2, 4, 6, 8 mM). Scan rate: 50 mV s^{-1}.

modified Cu electrode and Cu electrode. Furthermore, the oxidation current of glucose at CuO NWs modified Cu electrode is 1.5 times and 2.5 times than that at $Cu(OH)_2$ NWs modified Cu electrode and Cu electrode, respectively. The more negative reduction potential and larger current response indicate that the CuO NWs modified Cu electrode has much higher catalytic activity towards the oxidation of glucose than $Cu(OH)_2$ NWs modified Cu electrode and Cu electrode. As shown in Fig. 2B, a series of CVs are recorded in the absence and presence of glucose with different concentrations in the range of 2 mM to 8 mM. It can be clearly observed that the oxidation current increases with the increase of glucose concentration, indicating the CuO NWs modified Cu electrode has a good catalytic ability for the oxidation of glucose. To understand whether the dissolved oxygen involved in the electrocatalytic oxidation process, the amperometric responses of the CuO NWs modified Cu electrode to the successive injections of 0.2 mM glucose in 0.1 M NaOH with or without N_2 degassing operation were investigated. Fig. S2 shows that the current responses to glucose remain the same magnitude when the solution is saturated with N_2, suggesting the oxygen does not involve in this reaction.

3.3 Amperometric performance of the CuO NWs modified Cu electrode to glucose

3.3.1 Selection of the optimal measurement conditions for the sensor

In order to improve the electrocatalytical performance of CuO NWs modified Cu electrode, various factors that may affect the current response were investigated, such as the concentration of NaOH and the applied working potential. Previous reports have shown that alkaline electrolyte is indispensable for the electrooxidation of carbohydrates on Cu substrates as a result of its electrocatalytic effect mediated by $Cu(OH)_2$/CuO(OH) redox couples.[18,31] Therefore, the effect of NaOH concentration on the response of CuO NWs modified Cu electrode to glucose was investigated. As shown in Fig. 3A, no distinguishable oxidative current is observed when the concentration of NaOH is less than 50 mM. While, an obvious oxidative peak is obtained, the oxidative potential negatively shifts and the oxidative current increases with the increase of NaOH concentration. It is obviously seen that the oxidative current changes a little from 0.1 mM to 0.2 mM, to avoid high alkaline in glucose detection, 0.1 M NaOH was applied as the supporting electrolyte.

In order to ensure enough sensitivity and a lower background current, the effect of applied potential was also investigated by

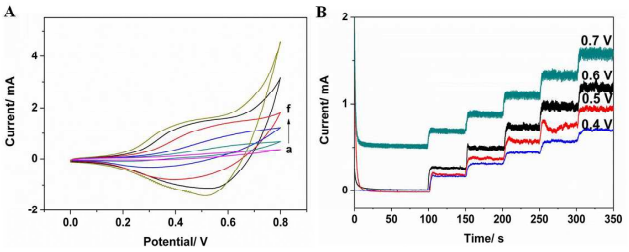


Figure 3 (A) Electroanalytical effect of different concentrations of NaOH ((a) 5 mM, (b) 10 mM, (c) 20 mM, (d) 50 mM, (e) 0.1 M, (f) 0.2 M) in the presence of 2 mM glucose. (B) Amperometric current responses of the CuO NWs modified Cu electrode under different working potentials upon successive additions of 0.25 mM glucose into 0.1 M NaOH.

five successive amperometric measurements of 0.25 mM glucose into a stirring 0.1 M NaOH at different potentials ranging from 0.4 V to 0.7 V. As shown in Fig. 3B, the largest response sensitivity is obtained at 0.6 V. As a result, 0.6 V was applied as the working potential for the subsequent amperometric measurements.

3.3.2 Amperometric determination of glucose at CuO NWs modified Cu electrode

The simple fabrication procedure makes the as-prepared CuO NWs modified Cu electrode a good platform for the amperometric determination of glucose. A typical amperometric

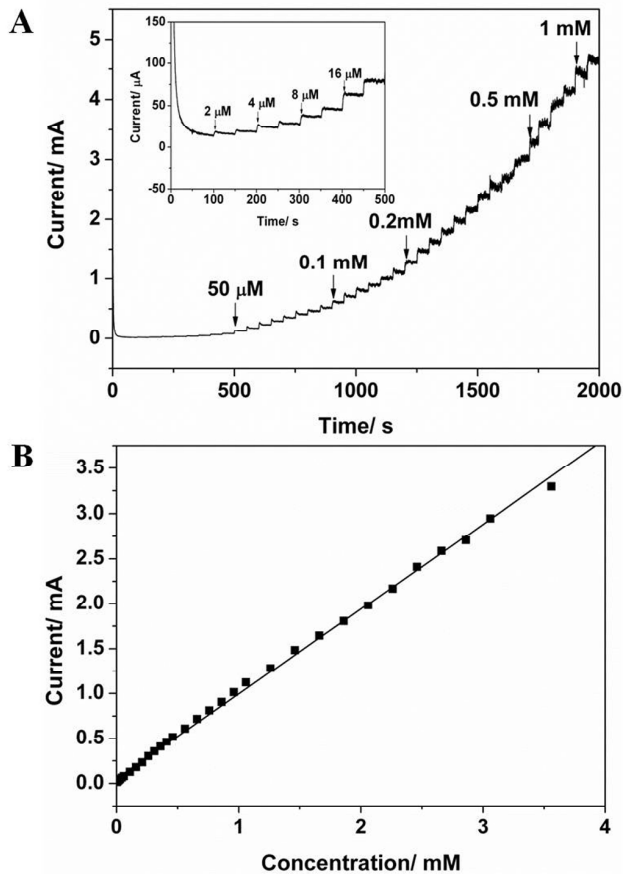


Figure 4 (A) Typical amperometric current responses of CuO NWs modified Cu electrode with successive additions of glucose (2 μM, 4 μM, 8 μM, 16 μM, 50 μM, 100 μM, 200 μM, 500 μM, 1 mM) into a stirring 0.1 M NaOH at 0.6 V. Inset shows the enlarged response to 2 μM, 4 μM, 8 μM, 16 μM glucose. (B) The relationship of oxidation current *versus* glucose concentration

response of the CuO NWs modified Cu electrode upon the successive injections of a certain concentration of glucose into a stirring 0.1 M NaOH at an applied potential of 0.6 V is displayed in Fig. 4A. Once glucose is added into the stirring electrolyte solution, the prepared sensor shows a fast response and achieves the maximum steady-state current within 5 s. As shown in Fig. 4B, the catalytic current is linear with the concentration of glucose in the range from 2 μM to 3.56 mM with a coefficient of 0.9984. The sensitivity is as high as 1886.3 μA mM^{-1} cm^{-2}. The detection limit can reach as low as 0.05 μM based on a signal to noise ratio of 3 (S/N = 3), which is even lower than certain enzyme-based glucose sensors.[13,15] In order to assess the analytical performance of the proposed sensor, we compared the characteristics of the sensor with other glucose sensors based on CuO nanomaterials reported previously, as shown in Table 1. It can be clearly seen that the detection limit, linear range and sensitivity of the as-prepared sensor are comparable or even better than other glucose sensors. These results make the CuO NWs modified Cu electrode a promising sensor for the detection of glucose.

3.3.3 Stability, repeatability, reproducibility and anti-interfering activity of the CuO NWs modified Cu electrode

The stability, repeatability and reproducibility of the CuO NWs modified Cu electrode were investigated by determining 0.2 mM glucose in 0.1 M NaOH. Three CuO NWs modified Cu electrodes were fabricated independently under optimal condition and a relative standard deviation (RSD) of 1.78% was obtained, confirming the fabrication method was extraordinarily reproducible. In addition, six successive amperometric measurements of 0.2 mM glucose on the same CuO NWs electrode yielded a RSD of 4.75%, indicating that the sensor was stable and could be used repeatedly for the detection of glucose. The long-term stability of the sensor was studied by amperometric measurements in the presence of 0.2 mM glucose periodically. It was found that the current response retained 92.1% of its initial response after a 7-day storage under ambient conditions, demonstrating the sensor is remarkably stable.

Previous reports have shown that glucose sensors based on Cu electrodes may easily lose their electrochemical activity due to the chloride poisoning effect.[8,25] Therefore, the amperometric responses of CuO NWs modified Cu electrode to the successive injections of 0.2 mM glucose into 0.1 M NaOH with or without 0.2 M NaCl were investigated. As shown in Fig. 5A, the current responses of CuO NWs modified Cu electrode to glucose oxidation remain almost constant after adding NaCl into the electrolyte, indicating the electrode could be used in the presence of high concentration chloride ions.

Table 1 A comparison of glucose sensor based on CuO nanomaterials.

Type of electrode	Detection Limit (μM)	Sensitivity (μA mM^{-1} cm^{-2})	Linear range (mM)	Reference
CuO Nanosphere	1	404.53	0-2.55	8
CuO Flowers	4	709.52	0.004-8	10
CuO Nanofibers	0.8	431.3	0.006-2.5 0-	31
CuONL[a]/MWCNTs[b]	5.7	664.3	0.9	36
CuO Nanourchins	1.52	2682	0.1-3	37
Cu_xO/Cu	49.0	1620	-	38
CuO nanobelt	<1	582.0	0.01-7.3	39
CuO NLs	5	26.6 μA mM^{-1}	0.1-3	40
CuO/TiO_2	1	79.79	0-2.0	41
CuO NWs	0.05	1886.3	0.002-3.56	This work

[a] Nanoleave-shaped copper oxide
[b] Multiple-walled carbon nanotube

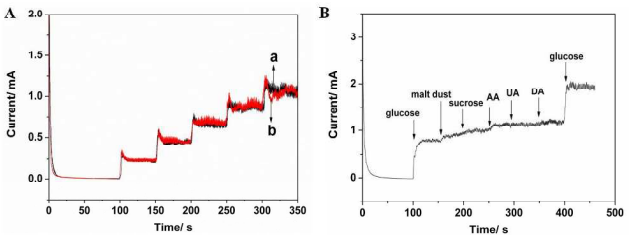


Figure 5 (A) Amperometric responses of CuO NWs modified Cu electrode with successive additions of 0.2 mM glucose to (a) 0.1 M NaOH solution and (b) 0.1 M NaOH solution containing 0.2 M NaCl at an applied potential of 0.6 V. (B) Amperometric responses of the CuO NWs modified Cu electrode at 0.6 V to 1 mM glucose and different interfering species: 0.2 mM malt dust, 0.2 mM sucrose, 0.2 mM AA, 0.2 mM UA and 0.2 mM DA, , in a stirring 0.1 M NaOH.

Table2 Determination of glucose in human blood serum samples.

Sample	Spectrophotometric Method/ mM	Proposed Method/ mM	Recovery(%)	[a]RSD(%)
1	5.00	5.21	104.20	5.46
2	9.30	9.08	97.63	1.04

[a] Relative standard deviation (RSD) of 3 measurements.

The selectivity of the CuO NWs modified Cu electrode was also investigated because the co-existing electroactive species might affect the detection of glucose in real sample analysis. UA, DA and AA are the major interferences normally co-existing with glucose in real samples. Moreover, other carbohydrate compounds may also affect the determination of glucose. Considering that the normal physiological level of glucose is about 30 times than that of the interfering agents,[42-44] the anti-interference effect of the as-prepared CuO NWs modified electrode was tested by successive addition of 1 mM glucose, and 0.2 mM of each of five relevant interfering species including sucrose, malt dust, AA, UA and DA. Figure 5B shows that no obvious interference is observed, suggesting the sensor exhibits high selectivity to the detection of glucose.

3.3.4 Human serum samples measurement

To verify the feasibility of the proposed glucose sensor in practical applications, the determination of glucose in the human blood serum was carried out. Human blood was collected from volunteers, the supernatant of which was blood serum was obtained after the blood was coagulated. 40 μL serum sample was added into 3.96 mL 0.1 M NaOH, the amperometric current response was recorded at 0.6 V and each sample was measured three times. Table 2 shows that the results obtained from the proposed method are in a good agreement with the results from a spectrophotometric method. Therefore, the proposed sensor is effective on glucose detection and could be used in practical applications.

4. Conclusions

In summary, we have successfully synthesized CuO NWs on a cooper surface by a simple two-step method. The CuO NWs were used to construct a non-enzymatic glucose sensor. The newly developed sensor displays good catalytic activity for glucose oxidation, with a wide linearity range, high sensitivity, good selectivity and low detection limit. In addition, the sensor also

shows excellent stability and good selectivity to glucose detection. Moreover, the fabrication technique is simple and can be easily used for the mass production.

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Notes and references

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