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Enzyme-free sensing of glucose on a copper electrode modified with nickel nanoparticles and multiwalled carbon nanotubes

Anni Zhong · Xiaoli Luo · Liping Chen · Shanshan Wei · Yonghong Liang · Xinchun Li

Abstract We describe a new electrochemical platform for direct sensing of glucose. The electrode was prepared by controlled electrodeposition of nickel nanoparticles onto carbon nanotubes on a copper electrode. The sensor was optimized by investigating the effects of the concentration of nickel precursor, electrolysis time and acidity of the medium. The nanocomposite was characterized by scanning electron microscopy and energy dispersive spectroscopy. Cyclic voltammetry of glucose in 0.1 M NaOH solution gives a well-defined anodic wave with a peak potential at 0.53 V (vs. Ag/AgCl) that indicates the direct electrooxidation of glucose at the nanomaterial. The electrode responds to glucose over a wide linear range (from 2 μM to 10 mM), with high sensitivity (3.8 mA mM^{-1} cm^{-2}) and a low detection limit (0.7 μM). The sensor was applied to the determination of glucose in blood samples, and the results were in good agreement with data obtained by a commercially available glucometer. The method holds promise due to the ease of sensor fabrication and its robust performance and longevity.

Keywords Nickel nanoparticle · Multiwalled carbon nanotubes · Enzyme-less sensor · Glucose · Electrochemistry

Introduction

Glucose is a crucial element for life activity, which maintains the essential biochemical and physiological function.

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However, glycometabolism disorder usually occurs in a considerable multitude of population worldwide, resulting in clinically relevant disease such as diabetes mellitus, which commonly engenders a series of complications including cardiovascular disease, kidney failure, and blindness, and has become a major cause of death [1]. Therefore, exploring simple, rapid, reliable and cost effective methods toward glucose assay in biological specimen is highly demanded with respect to clinical diagnostic [2]. Thus far, tremendous analytical methods have been developed. Among them, electrochemical methods by immobilization of glucose oxidase (GOx) on solid electrodes represent a prevailing strategy [3], while diverse polymer films [4, 5], conducting matrix [6, 7] or redox mediators [8, 9] were usually used to bind GOx. Measurement by electroreduction of dissolved oxygen [6, 10], or by electrooxidation of hydrogen peroxide [7], an enzymatic product, have been the routine methodology toward electroanalysis of glucose. Besides, direct electrochemistry of GOx is another research topic for detection of glucose, which is generally based on the oxidation/reduction of FADH$_2$/FAD moiety in the enzyme center [2, 11].

Enzyme electrodes have witnessed massive progress and commercially available glucose meters have also opened broad opportunities for monitoring glucose level in real time [12]; however, notable drawbacks and disadvantages have been extensively interrogated [13, 14], which originate mainly from the nature of GOx. Principally, the activity of enzyme is prone to be affected by temperature, acidity, and toxic chemicals, resulting in poor reproducibility and stability. Besides, most enzymes are expensive and thus incur high cost in usage. Additionally, laborious and complicated protocols are required to immobilize enzyme on electrode [15]. Because of these flaws aforementioned, fabrication of enzyme-free glucose sensors has continuously been motivating research interests [16].

It is well recognized that direct electrooxidation of glucose on ordinary electrodes generally encounters several

challenges. For example, the analytical sensitivity is commonly restricted by the sluggish kinetics and high overpotential [12]. Moreover, the activity of metal electrodes is likely to be impaired by the adsorbed oxidation intermediates of glucose [17]. Therefore, a large number of nanomaterials have been used to enhance the electrocatalytic ability and improve antifouling property of the modified electrodes [14]. Noble metals such as gold [18], platinum [19], palladium [20], and silver [21], metal oxides [22], and bimetallic materials [15, 23, 24] have been intensively studied. These researches are bound to increase the cost of sensors, thus making design of economical glucose sensors eagerly pursued.

Nickel and copper are ideal alternatives for the fabrication of electrochemical glucose sensors [25, 26], owing to their distinctive electroactivity toward glucose as well as the abundant resource in nature. Sun [27] described a nonenzymatic glucose sensor based on copper film modified indium tin oxide (ITO) electrode, which gained a linear relationship from 1 μM to 0.5 mM. Liu [28] reported on Ni nanoparticle-loaded carbon nanofiber paste (NiCFP) electrode; the NiCFP nanocomposite was prepared by combination of electrospinning technique with thermal treatment. This method apparently relied on rather complicated electrode processing. Mu [29] presented nano nickel oxide modified electrode for nonenzymatic determination of glucose, with a detection limit of 1 μM being obtained; however, the linear response only covered the concentration range of 1–100 μM. Ni nanowire arrays were prepared by Lu [30] using a template-directed electropolymerization technique, which was used for glucose assay. The quantification capacity was up to 7 mM, and the limit of detection (LOD) was down to 0.1 μM; nevertheless this method was also carried out at the expense of sophisticated electrode fabrication. Another appealing work was demonstrated by Nie [26], where nickel nanoparticles-carbon nanotubes nanohybrid was synthesized by a precipitation reaction combined with pyroprocessing in H_2/N_2 mixture atmosphere, which was also somewhat inconvenient. Yang [31] et al reported chitosan-reduced graphene oxide–nickel nanoparticles decorated screen-printed electrode coupled to a microfluidic device for the determination of glucose; the LOD was 4.1 μM as regards the analysis of urine samples. Very recently, Choi [32] presented atomic layer deposition carbon nanotube–nickel nanocomposite modified glassy carbon electrode; the linear response window was from 5 μM to 2 mM, with the detection limit of 2 μM. This work although was elegant, the exceedingly complex process would make it less applicable for ordinary work.

Copper electrode can provide procedural advantages and simplification that make it more accessible for routine analysis [33]; the practical applications however, are sparse compared to other solid electrodes. We present here a simple, facile, and cost effective nonenzymatic glucose electrochemical sensor that utilized copper electrode modified with nickel

nanoparticles (NiNPs)-multiwalled carbon nanotubes (MWCNTs). The sensor can be easily fabricated, thus circumventing laborious material synthesis and manufacturing procedure. In addition, the sensor showed excellent sensitivity that achieved a current density up to 3.8 mA mM^{-1} cm^{-2}, and the linear range was from 2 μM to 10 mM. Furthermore, the use for glucose assay in a considerable volume of clinical samples revealed the reliability and practicability of the prepared sensor.

Materials and methods

Chemicals and reagents

All reagents were of analytical grade and used as received otherwise specified statement. Sodium phosphate monobasic, sodium hydroxide, absolute alcohol, nickel sulfate heptahydrate (guarantee reagent), were obtained from Sinopharm reagent (Shanghai, China, http://www.reagent.com.cn/). D-(+)-Glucose, ascorbic acid (AA), uric acid (UA) and urea (UE) were purchased from Aladdin (Shanghai, China, http://www.aladdinreagent.com/). MWCNTs (>95 % purity) with 5–15 μm length and 10–20 nm internal diameter were purchased from Nanotech Port (Shenzhen, China, http://www.nanotubes.com.cn/). Blood samples were kindly provided by department of laboratory medicine, the first affiliated hospital of Guangxi Medical University. 100 mM glucose stock solution was prepared in water, and diluted with supporting electrolyte to desired concentrations for analysis. Ultrapure water was prepared with a Milli-Q system (18.2 MΩ cm, MA, USA) and used throughout the experiments.

Preparation of electrochemical sensor

MWCNTs were continuously stirred in 3 M HNO$_3$ at 60 °C for 10 h to remove the impurities, then filtered and rinsed to neutral pH value with copious amount of water, followed by drying in a vacuum oven. A portion of 5 mg of the processed MWCNTs was added into 5 ml of 0.1 % Nafion solution (in ethanol), and treated with ultrasonic agitation for 10 min. Copper disk electrode (2 mm in diameter) was polished carefully with 0.05 μm alumina slurry to a mirror finish, followed by ultrasonic cleaning in water and ethanol, each for 3 min. After drying with nitrogen, 2 μL of MWCNTs dispersion was dropped onto the surface of the electrode and allowed to dry at room temperature.

MWCNTs coated copper electrode was subjected to electrodeposition in 5 mM NiSO$_4$ solution (0.1 M phosphate buffer, pH 5.0) at −1.2 V (vs. Ag/AgCl) for 10 min with constant nitrogen bubbling and magnetic stirring. Then prepared electrode was rinsed thoroughly with water after the

electrochemical processing, and stored at 4 °C in refrigerator when not in use. Copper electrode and MWCNTs modified copper electrode were used for comparison.

Electrochemical measurement and characterization

All of electrochemical analyses were carried out with a three-electrode system, in which a platinum wire and a Ag/AgCl (*Sat*. KCl) electrode were used for counter electrode and reference electrode, respectively. Electrochemical measurements were performed on a CHI810 electrochemical analyzer (Shanghai, China, http://www.instrument.com.cn/) at ambient temperature. Field emission scanning electron microscopy (FESEM, Hitachi-SU8020, Japan) equipped with energy dispersive spectroscopy (EDS) was used to characterize the modified electrode.

Results and discussion
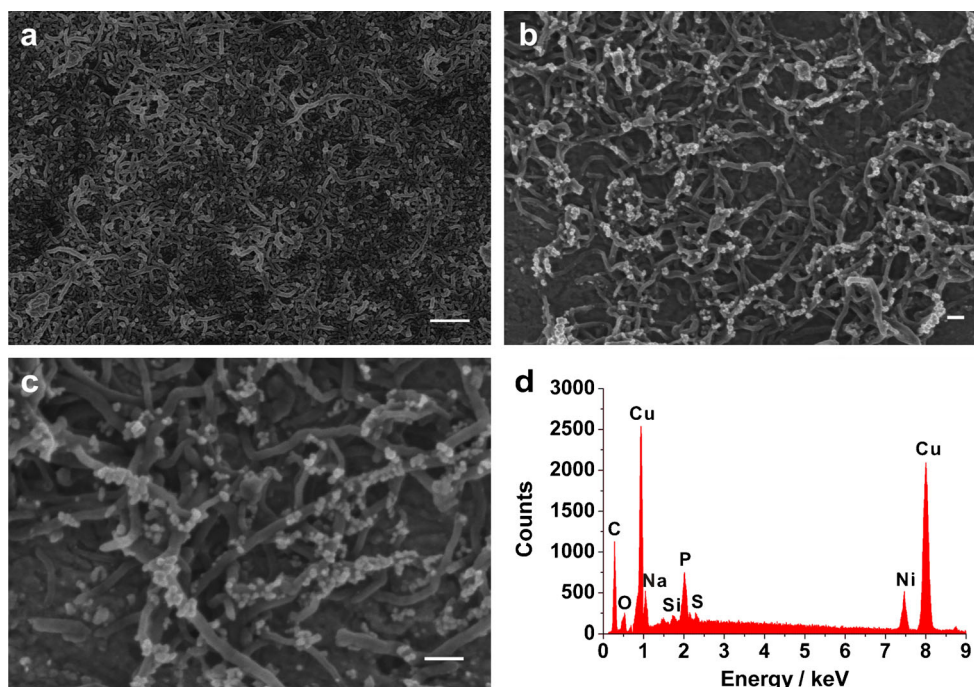
Characterization of NiNPs-MWCNTs modified Cu electrode

The nonenzymatic glucose sensor was constructed by MWCNTs decorated Cu electrode, followed by electrochemical reduction of $NiSO_4$ to produce nickel nanoparticles. As shown in Fig. 1, Nafion-dispersed MWCNTs formed basal conducting network on Cu electrode. Upon the electrodeposition of nickel precursor in 0.1 M phosphate buffer (pH 5.0), highly uniform NiNPs adhered to the MWCNTs and assembled to form nanocluster, with a diameter of about 18 ± 2.1 nm.
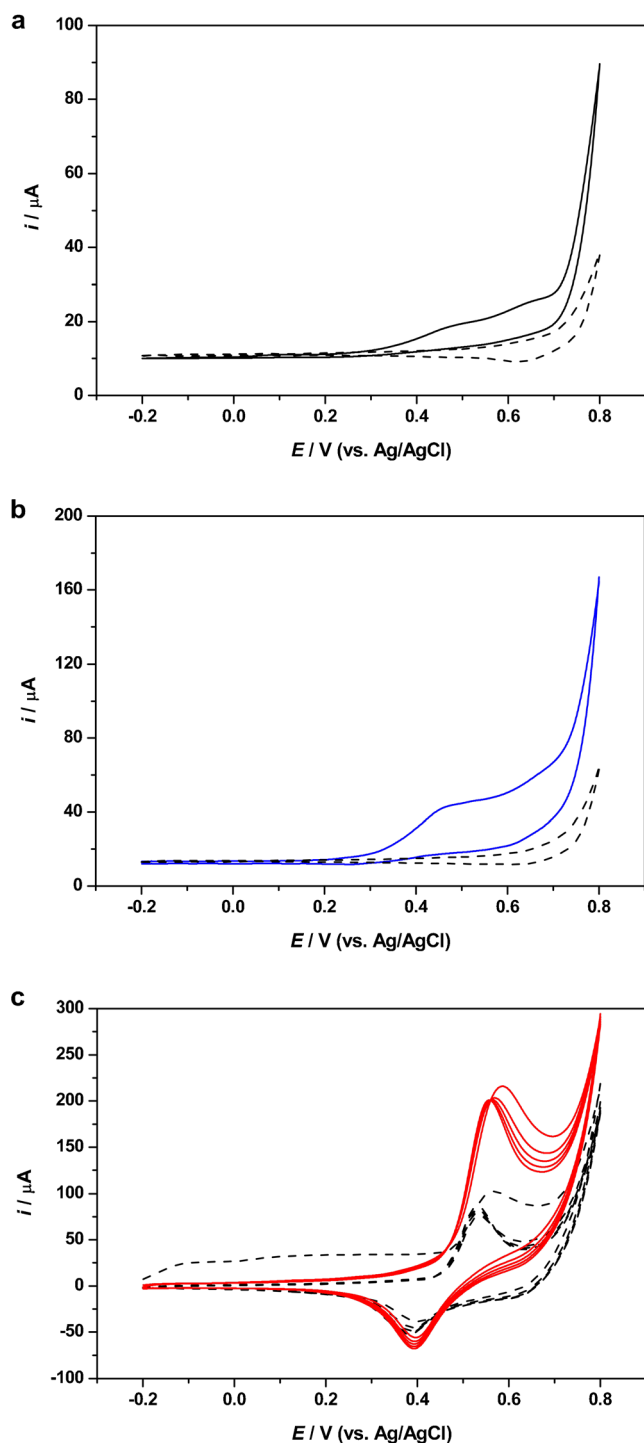
Such well-arranged nanoparticles ought to endow the modified electrode with more fascinating electron-transfer ability and electrocatalytic function. Additionally, EDS revealed the principal constituents (Cu, C, and Ni), while other peaks including O, Na, and P were totally attributed to the solvent used.

Electrochemical behavior of glucose

To investigate the electrochemical property of glucose on the prepared sensor, cyclic voltammetry (CV) was employed over the potential range from −0.2 to 0.8 V in 0.1 M NaOH solution. Figure 2 depicted the details. For comparison, bare Cu electrode and MWCNTs modified Cu electrode were used. Obviously, Cu electrode manifested slightly electrocatalytic activity toward glucose in alkaline environment; gradually increased oxidation current was observed in the potential region of 0.35~0.7 V (Fig. 2a). Similar voltammetric curve was found on the MWCNTs/Cu electrode, which however, behaved fairly improved electrochemical response due to the distinct conducting power of MWCNTs (Fig. 2b). In contrast, remarkable electrolytic current of glucose emerged on the NiNPs-MWCNTs modified copper electrode (Fig. 2c), with the onset potential of 0.32 V, which then evolved to a distinct oxidation peak at 0.53 V. Such an enhanced electrocatalytic performance was exactly a result from the synergic effect of carbon nanotubes and the loaded Ni nanoparticles that feature with favorable electron transfer ability and large surface active sites. To be noted that, at the anodic process, the peak potential of the first cycle was a bit higher than that of the subsequent

Fig. 1 SEM images of Nafion/MWCNTs **a** and NiNPs-Nafion/MWCNTs **b** modified copper electrodes. **c** An enlarged view of b. Accelerating voltage, 10 kV; scale bar, 100 nm. **d** EDS data of the as-prepared NiNPs-Nafion/MWCNTs modified copper electrode
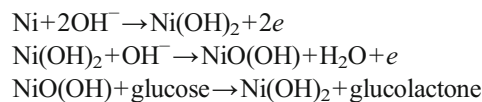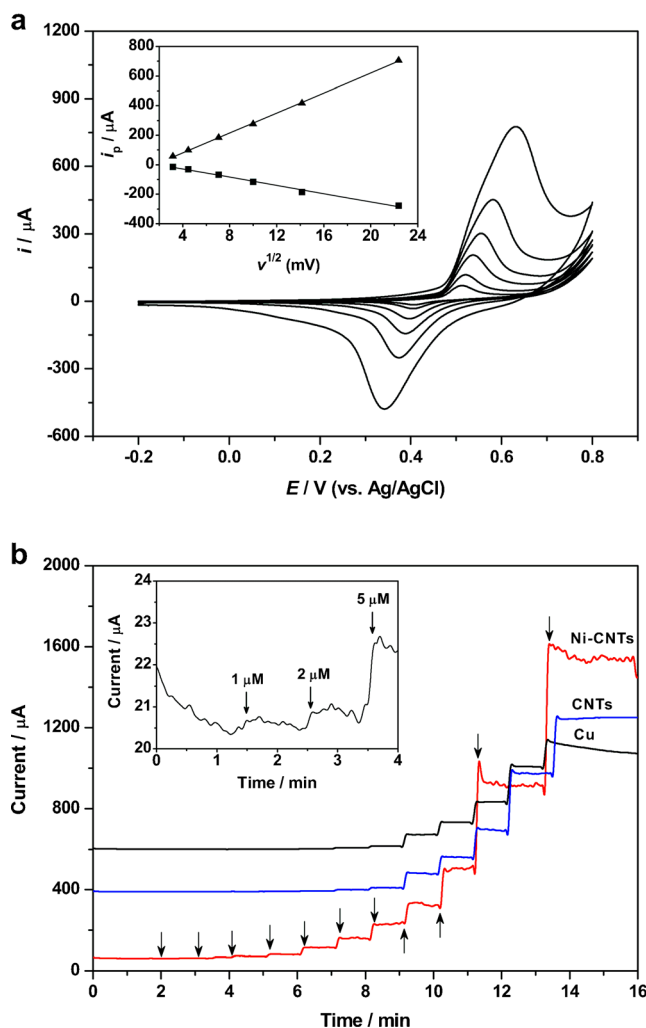
based surface in alkaline condition commonly pertains to the following electrochemical reactions.

$$Ni + 2OH^- \rightarrow Ni(OH)_2 + 2e$$
$$Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e$$
$$NiO(OH) + glucose \rightarrow Ni(OH)_2 + glucolactone$$

First, Ni is oxidized to form Ni^{2+}. Then, the hydroxide phase $Ni(OH)_2$ can be readily transferred to NiO(OH), which indeed functions as a highly-efficient catalyst and rapidly oxidizes glucose to give rise to oxidation current. Based on the above electrochemical mechanism, we can elucidate that the more positive oxidation peak in the first potential cycle

Fig. 2 CVs of glucose (1 mM, solid line) obtained at bare Cu electrode **a**, MWCNTs modified copper electrode **b**, and NiNPs/MWCNTs modified copper electrode **c**. Curves in dashed lines represented the CVs of the blank electrolyte. Conditions: supporting electrolyte, 0.1 M NaOH; scan rate, 50 mV s^{-1}

Fig. 3 a Serial cyclic voltammograms of glucose (1 mM in 0.1 M NaOH) on the prepared sensor at scan rate of 10, 20, 50, 100, 200, and 500 mV s^{-1} (from inner to outer). Inset, the relationship of anodic and cathodic peak currents versus the square root of scan rate, respectively. **b** Amperometric current-time curves by successive addition of glucose at bare Cu electrode, MWCNTs modified copper electrode, and the prepared sensor. Arrows indicated the concentration of glucose solutions from 2, 5, 10, 20, 50, 100, 500, 1000, 2000, 5000, 10,000 μM. Inset, *i-t* curve showing the electrochemical response upon addition of low concentration of glucose. Operating potential, 0.55 V (vs. Ag/AgCl)

scans (Fig. 2c). This was also a case when blank electrolyte was subject to cyclic voltammetry. As has been reported in the literature [34], direct electrochemistry of glucose on nickel-

differing from the succeeding scans is probably ascribed to the initial conversion from Ni to Ni^{2+}. In the absence of glucose, a well-characteristic redox peaks can be observed, with the peak potential (E_p) of 0.38 and 0.53 V, respectively; corresponding to the redox couple of Ni^{3+}/Ni^{2+}, which was in good agreement with the previous researches [26, 30, 31].

To achieve optimal performance of the sensor, we investigated the preparation conditions (Fig. S1, Electronic Supplementary Material, ESM). Along with the increase of electrolytic time of $NiSO_4$, the oxidation peak current (i_p) of glucose displayed an ever-increasing tendency, suggesting incremental quantity of nickel nanoparticles loaded on the electrode that directly contributed to the electrocatalytic activity. However, intensive electrolysis beyond 10 min resulted in decreased current response (Fig. S1a), mainly due to the increscent size and/or aggregation of nanoparticles, which in turn, diminished the active surface area of the sensor [24]. The effect of media acidity was also investigated (Fig. S1b); an optimal acidity was found to be pH 5. Besides, the precursor concentration was examined (Fig. S1c). Low concentration of $NiSO_4$ (0.1 mM) generated negligible electrochemical response toward glucose, whereas pronounced augment on catalytic current was observed in the range from 0.5 to 5 mM, and then leveled off. According to these results, electrodeposition of 5 mM $NiSO_4$ in pH 5.0 phosphate buffer for 10 min was implemented. Note that such a procedure is controllable, thus enabling the preparation of reproducible sensors and improving the practicability.

Amperometric determination of glucose

Further, cyclic voltammetry of glucose at the modified electrode with different potential scan rate (v) was tested. As shown in Fig. 3a, both anodic and cathodic peak current (i_p) raised clearly with the increase of scan rate. It is calculated that i_p is proportional to the square root of v, signifying a diffusion-controlled process of glucose electrooxidation on the prepared sensor. Additionally, the anodic peak shifted positively while the cathodic peak became more negative along with the scan rates, leading to much larger peak-to-peak separation.

The current-time curves by successive addition of glucose solution to 0.1 M NaOH at constant potential of 0.55 V were depicted in Fig. 3b. Consistent with the above CVs, both Cu electrode and MWCNTs/Cu electrodes generated relatively evident current response just until the introduction of 0.1 mM of glucose. In contrast, NiNPs-MWCNTs/Cu electrode produced notable current variations at very low concentration level of glucose (inset of Fig. 3b). The steady-state current can be achieved within 5 s, and responded linearly to glucose concentration, indicative of favorable electrocatalytic oxidation toward glucose. Plotting the current against the concentration yielded well-characteristic linear relationship ranging from 2 mM to 50 μM, and 0.05 to 10 mM; respectively (Fig. S2, ESM). The regression equations were correspondingly expressed as $i=0.1902C+0.9740$ ($R^2=0.982$), and $i=0.0822C+1.770$ ($R^2=0.999$). Such a broad quantification domain would be beneficial to the analytical utility. Moreover,

Table 1 Comparison of typical Cu/Ni-related nonenzymatic glucose electrochemical sensors

Material	Sensitivity (μA mM^{-1} cm^{-2})	Linear range	LOD (μM)	Operability	Reference
NiNPs-MWCNTs/Copper	3822	2 μM~10 mM	0.7	Easy	This work
Pt-Ni NPs-graphene/GCE [a]	20.42	~35 mM	10	Moderate	24
Cubic CuNPs-CNTs/GCE	922	500 μM~7.5 mM	2.0	Complex	25
NiNPs-SMWNTs/GCE	1438	1 μM~1 mM	0.5	Complex	26
Copper film/ITO [b]	699.4	1 μM~0.5 mM	0.5	Easy	27
Electrospun NiNPs/CNPE [c]	420.4	2 μM~2.5 mM	1.0	Complex	28
Nano NiO/CPE [d]	6600	1 μM~0.11 mM	0.16	Easy	29
Ni nanowire array/GCE	1043	0.5 μM~7 mM	0.1	Complex	30
NiNPs-CS-rGO/SPE [e]	318.4	200 μM~9 mM	4.1	Moderate	31
ALD Ni-CNTs/GCE [f]	1384.1	5 μM~2 mM	2	Complex	32
Porous Cu foams/SPE [g]	2570	2 μM~5 mM	0.95	Moderate	35
NiNPs-rGO/GCE	10,200	2 μM~2.1 mM	0.1	Moderate	36

[a] *GCE: glassy carbon electrode*

[b] *ITO: indium tin oxide*

[c] *CNPE: carbon nanofiber paste electrode*

[d] *CPE: carbon paste electrode*

[e] *CS: chitosan; rGO: reduced graphene oxide*

[f] *ALD: atomic layer deposition*

[g] *SPE: screening printed electrode*

the sensitivity was found to approach 3.8 mA mM^{-1} cm^{-2}, and the limit of detection (LOD) was calculated to be 0.7 μM at signal-to-noise ratio of 3, which was advantageous to that on PtNi nanoparticle-graphene modified glassy carbon electrode [24], porous Cu foam modified screen-printed electrode [35], electrospun Ni nanoparticle-carbon nanofiber paste electrode [28], and nickel nanoparticle-chitosan-reduced graphene oxide modified screen-printed electrode [31]. This further verified the outstanding analytical performance of the prepared sensor. A comparison of representative nonenzymatic glucose sensors was listed in Table 1.

Interference and stability

The interfering electrochemical signal stemming from coexisting electroactive substances is a critical concern when
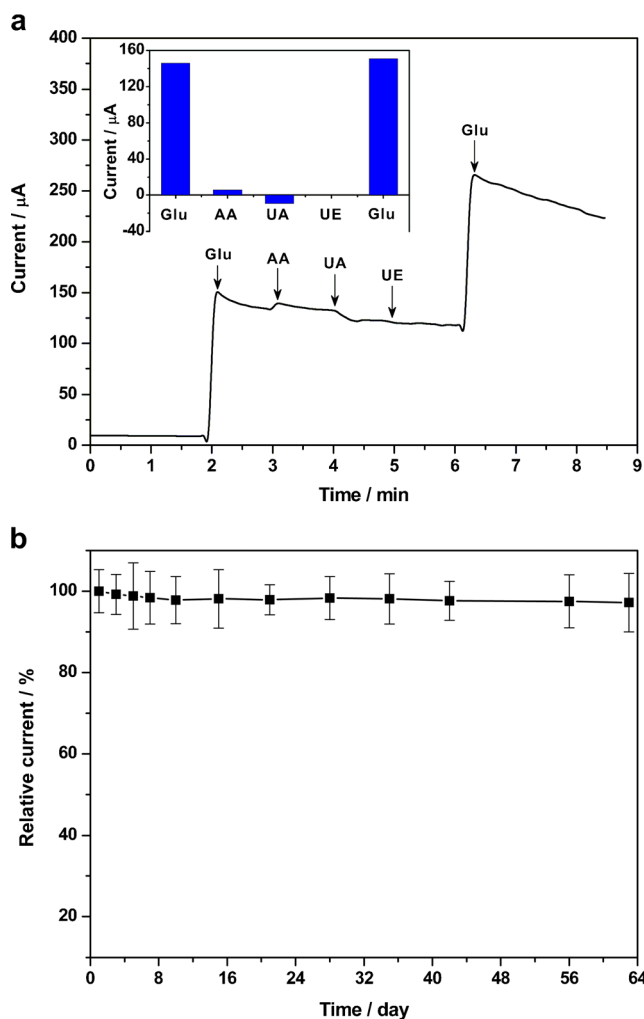
Fig. 4 **a** Electrochemical response upon alternate addition of glucose (Glu), ascorbic acid (AA), uric acid (UA), and urea (UE). Inset, the steady-state current corresponding to glucose and the potential interferents. Condition was as in Fig. 3. **b** Long-term stability of the sensor. The peak current originating from cyclic voltammograms was normalized ($n=3$)

fabricating a nonenzymatic glucose sensor [25]. The selectivity of the prepared sensor was examined by consecutive addition of diverse endogenous species such as ascorbic acid (AA, 0.1 mM), uric acid (UA, 0.1 mM) and urea (3 mM) by means of amperometry at the operating potential of 0.55 V. As can be seen, urea almost displays negligible current change, while AA and UA merely produce slight electrochemical response, causing 3.9 and 5.2 % signal disturbance, respectively, compared to the addition of 1 mM glucose (Fig. 4a). Considering the physiological concentration of glucose in blood (3.5~6.1 mM) [24], such variations of current actually would not affect the detection of glucose. Interestingly, under this condition, UA led to the decline of the current terrace, which has been previously observed on a nickel-based glucose sensor [36]. The exact cause of such a phenomenon remains unclear, probably due to the electrostatic repulsion of negatively charged UA by nafion-decorated electrode surface in strong alkaline condition. Additionally, it is worthwhile to mention that dopamine has not been taken into account for the interfering test, since it has extremely low concentration level (0.01~1 μM) in biological matrix [37], thus exclusion of potential influence.

The stability was another important factor in view of the practicality. The experiment was performed by cyclic voltammetry of glucose in 0.1 M NaOH solution at different time interval. It can be seen that the peak current of glucose can retain 97.2 % initial value for at least 2 months (Fig. 4b), indicating a robust lifetime of the prepared sensor. This can be substantially ascribed to the rational nanostructured nickel-CNTs composite interface.

Real samples analysis

The applicability was estimated by measurement of clinical biological samples. A portion of 0.1 mL blood sample was
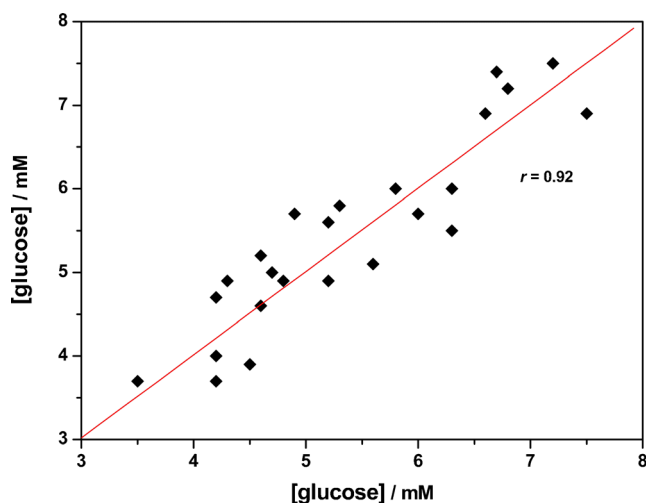
Fig. 5 Scattering diagram showing the correlation of glucose concentration in blood samples measured by the present electrochemical method (*y* axis) and a reference method (*x* axis)

diluted with 10-fold using blank electrolytic solution prior to electrochemical determination. The methodological validation was also carried out (Table S1, ESM). The recovery was found to be from 93.5 to 106 %, and the relative standard deviation (RSD) was less than 5.2 %, showing favorable accuracy and precision. Moreover, a blood sugar biochemical analyzer adopted in hospitals was used for reference; a total amount of 26 samples were tested (Fig. 5), and the concordant results stated clearly that the developed method was feasible for glucose assay.

Conclusion

In conclusion, we have demonstrated a novel and simple nonenzymatic glucose amperometric sensor, which is based on nickel nanoparticles/multiwalled carbon nanotubes/ copper sensing interface. The sensor can be easily fabricated at very low cost, and exhibits eminent performance with respect to sensitivity and specificity. The quantitative region spanned three orders of magnitude, and the stability was also appealing, which added much flexibility for analytical application. Furthermore, the utility was authenticated by analyzing a considerable amount of real samples; the results were in good agreement with commercial analyzer used in hospitals. This work offers great possibility for development of economical glucose electrochemical sensor.

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