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Seed-mediated synthesis of copper nanoparticles on carbon nanotubes and their application in nonenzymatic glucose biosensors

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ABSTRACT

In this paper, for the first time, Cu nanoparticles (CuNPs) were prepared by seed-mediated growth method with Au nanoparticles (AuNPs) playing the role of seeds. Carbon nanotubes (CNTs) and AuNPs were first dropped on the surface of glassy carbon (GC) electrode, and then the electrode was immersed into growth solution that contained $CuSO_4$ and hydrazine. CuNPs were successfully grown on the surface of the CNTs. The modified electrode showed a very high electrochemical activity for electrocatalytic oxidation of glucose in alkaline medium, which was utilized as the basis of the fabrication of a nonenzymatic biosensor for electrochemical detection of glucose. The biosensor can be applied to the quantification of glucose with a linear range covering from 1.0×10^{-7} to 5×10^{-3} M and a low detection limit of 3×10^{-8} M. Furthermore, the experiment results also showed that the biosensor exhibited good reproducibility and long-term stability, as well as high selectivity with no interference from other oxidable species.

1. Introduction

Glucose detection is essential in clinical diagnostics, biotechnology and the food industry [1,2]. Several methods for the determination of glucose, including the optical techniques [3], coulometric measurement [4], capacitive detection [5] and the amperometric method [6] have been proposed. Among these techniques, the amperometric biosensor has attracted significant attention and has become a promising method for its simplicity, high reliability, sensitivity and selectivity, low detection limit, promising response speed, low cost, compatibility for miniaturization and ease of use. Glucose oxidase (GOx) has been widely used to construct various amperometric biosensors for glucose detection, due to its high sensitivity and selectivity to glucose. However, the most common and serious problems with enzymatic glucose biosensors are insufficient long-term stability and unsatisfactory reproducibility originating from the nature of the enzymes as well as the activity of the immobilized enzymes [7]. Therefore, considerable attention has been paid to develop nonenzymatic biosensors to solve these problems.

In the fabrication of nonenzymatic biosensors, the electrocatalytic activity of the electrode material for electrochemical oxidation of glucose is crucial. The direct electrooxidation of glucose on noble metals such as platinum [8,9], gold [10], alloys (containing Pt, Pb, Au, Pd and Rh) [11] has been explored in the hope of exploring effective nonenzymatic biosensors. However, low sensitivity, poor selectivity and poisoning by adsorbed intermediates are main drawbacks of Au and Pt electrodes [12,13]. In contrast to Au and Pt, copper-based electrodes show an excellent electrocatalytic activity for glucose oxidation without observable self-poisoning [14–17]. It has been speculated that nonenzymatic electro-oxidation of glucose is greatly enhanced at Cu compared with the other electrodes as a result of its electrocatalytic effect mediated by Cu(II)/Cu(III) redox couples [18–20].

With the development of nanotechnology, nanostructured Cu is promising in the development of nonenzymatic glucose biosensors due to its highly specific surface area, good electrochemical activity, and the possibility of promoting electron-transfer reactions [21–25]. Most recently, various nanostructured CuNPs with different sizes have been synthesized by reverse micelles, microemulsions, and radiation techniques [26–36]. However, the synthesis of these nanostructured Cu is time-consuming and complicated. So there still remains a need to develop a simpler fabrication of nanostructured Cu with superior catalytic property. Seed-mediated growth is a popular approach of fabricating nanostructures such as nanorods and nanoparticles on substrate surfaces in order to control their sizes [37–39]. The seed nanoparticles are first deposited onto the surface of electrode in order to provide nucleation sites for target nanostructures to grow, and then the

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target nanostructures can attach the surface firmly through aggregation.

Here we report the seed-mediated method to the growth of CuNPs, using 3.5 nm AuNPs as seeds and CNTs as growth scaffold. Our synthetic protocol simply involves the reduction of $CuSO_4$ by hydrazine in the presence of Au nanocrystal seeds in the growth solution. The CuNPs modified electrode shows high electrocatalytic ability to glucose oxidation in alkaline solution and exhibits good linear dependence and selectivity to glucose concentration change.

2. Experimental

2.1. Reagents and chemicals

Carbon nanotubes (CNTs) (purity, 95%) with the average diameters and lengths were 20–30 nm and 10–30 μm, respectively, were obtained from Shenzhen Nanotechnologies (Shenzhen, China). Chloroauric acid ($HAuCl_4{\cdot}3H_2O$), trisodium citrate, and sodium borohydride ($NaBH_4$) were all purchased from Sinopharm Chemical (Shanghai, China). Chitosan (chit, MW $\sim 1 \times 10^6$; ~80% deacetylation) were purchased from Sigma. Bluestone ($CuSO_4$) and hydrazine ($N_2H_4{\cdot}H_2O$) were purchased from Shanghai Chemical Reagent Factory (Shanghai, China). D-Glucose and sodium hydroxide were purchased from Beijing Chemical Plant (Beijing, China). All chemicals were of analytical grade and distilled water was used in experiment.

2.2. Apparatus

Cyclic voltammetric and amperometric measurements were carried out on CHI 760B electrochemical workstation (Shanghai, China). Scanning electron microscopy (SEM) images of the electrodes were obtained using JSM-5600LV SEM (JEOL, Ltd., Japan). Transmission electron microscope (TEM) images of the AuNPs were obtained by JEM-3010 TEM (JEOL, Ltd., Japan). X-ray diffraction (XRD, Rigaku, Tokyo, Japan) was used for characterizing the structure of Cu nanoparticles. A three-electrode cell (10 mL) was used, with the modified glassy carbon (GC) electrode as the working electrode, a SCE as a reference electrode, and platinum foil electrode as a counter electrode. All potentials were measured and reported versus the SCE. All experiments were carried out at room temperature and performed in 0.1 M NaOH solutions under nitrogen atmosphere.

2.3. Preparation of Au nanoparticles

The 3.5-nm Au nanoparticle (AuNP) was synthesized by the method reported previously [39]. Typically this involved the preparation of a 20 mL aqueous solution containing 2.5×10^{-4} M $HAuCl_4$ and 2.5×10^{-4} M trisodium citrate. 0.6 mL of ice-cold 0.1 M $NaBH_4$ was added to the solution, which was then stirred. The solution immediately turned orange-red, indicating the formation of gold nanoparticles.

2.4. Preparation of the electrodes

Glassy carbon (GC, 4-mm diameter) electrodes were first polished with emery paper and alumina slurry, then cleaned using bath sonication for 10 min, and finally thoroughly rinsed with distilled water. The CNTs was first purified as reported previously [40,41] and then dispersed in 0.5% chit at a concentration of 2 mg mL^{-1} by sonicating for 60 min. GC was first covered by 5 μL CNTs solution and then by 8 μL of 3.5 nm aqueous AuNP solution. After drying, the GC was immersed into the growth solution containing 0.05 M $CuSO_4$ and 0.05 M $N_2H_4{\cdot}H_2O$ for 4 h in order to attach the CuNPs. Finally, the electrode (CuNPs/AuNPseed/CNTs/chit electrode) was coated with an extra 2.5 μL layer of 0.5% nafion. For comparison with the nafion/CuNPs/AuNPseed/CNTs/chit electrode, chit electrode, CNTs/chit electrode and AuNPseed/CNTs/chit electrode were prepared with the same procedures as described above.

3. Results and discussion

3.1. Characterization of the nafion/CuNPs/AuNPseed/CNT/chit surface

The TEM image in Fig. 1A confirms that the size of AuNPs is successfully controlled as previous reported, the diameter of which is around 3.5 nm. Fig. 1B shows the SEM micrographs of the CNTs/chit surface. The CuNPs/AuNPseed/CNTs/chit was prepared by a one-step seed growth protocol. As can be seen from Fig. 1C, the Cu nanoparticles could be attached to the surface of GC having a moderate dispersion and the diameters of the sphere nanoparticles were around 50 nm. The CuNPs feature was also demonstrated by using power XRD determination (Fig. S1). The XRD results clearly indicate that the layers of CuNPs were introduced on the surface of AuNPseed/CNTs/chit.

3.2. Electrochemical characterization of the nafion/CuNPs/AuNPseed/CNTs/chit electrode

Cyclic voltammetry of ferricyanide system is a valuable and convenient tool to characterize the modified electrode. Fig. 2 represents the cyclic voltammograms (CVs) of chit (a), CNTs/chit (b), AuNPseed/CNTs/chit (c), CuNPs/AuNPseed/CNTs/chit (d) and nafion/CuNPs/AuNPseed/CNTs/chit (e) electrodes in 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) containing 0.1 M KCl at 100 mV s^{-1}. A well-defined CV was observed at the chit electrode (curve a). An increase in peak current was observed when CNTs was covered onto the electrode (curve b). When AuNPseed was anchored on the CNTs/chit film, the peak current further increased (curve c). This could be ascribed to the excellent conductivity of AuNPseed. By immersing AuNPseed/CNTs/chit electrode into the growth solution containing Cu^{2+} and N_2H_4, CuNPs could be grown on the surface of AuNPseed/CNTs/chit. The CuNPs greatly enhanced the active area of the surface and the peak current further increased again (curve d). In contrast, a peak current decrease was observed at the nafion/CuNPs/AuNPseed/CNTs/chit modified electrode due to the poor electrical conductivity of nafion (curve e).

Fig. 3 shows the CVs of the nafion/CuNPs/AuNPseed/CNTs/chit electrode recorded in 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) containing 0.1 M KCl at different scan rates. It was found that both the anodic and cathodic peak current clearly increased with increasing potential scan rate. Besides, the redox peak currents were proportional to the square root of scan rate, $\nu^{1/2}$ (inset of Fig. 3), indicating a diffusion electron-transfer process.

3.3. Electrocatalysis of glucose at the nafion/CuNPs/AuNPseed/CNTs/chit electrode

The electrocatalytic activity of the nafion/CuNPs/AuNPseed/CNTs/chit electrode toward glucose was investigated. Fig. 4 shows the CV of the nafion/CuNPs/AuNPseed/CNTs/chit in 0.1 M NaOH between −1.0 V and +1.0 V with a scan rate of 100 mV s^{-1} in the presence and absence of glucose, respectively. Upon the addition of glucose, a remarkable enhancement of the anodic current was observed, indicating that the nafion/CuNPs/AuNPseed/CNTs/chit electrode possessed excellent electrocatalytic activity for glucose oxidation. As indicated in literatures [42,43], the oxidation of glucose to glucolactone

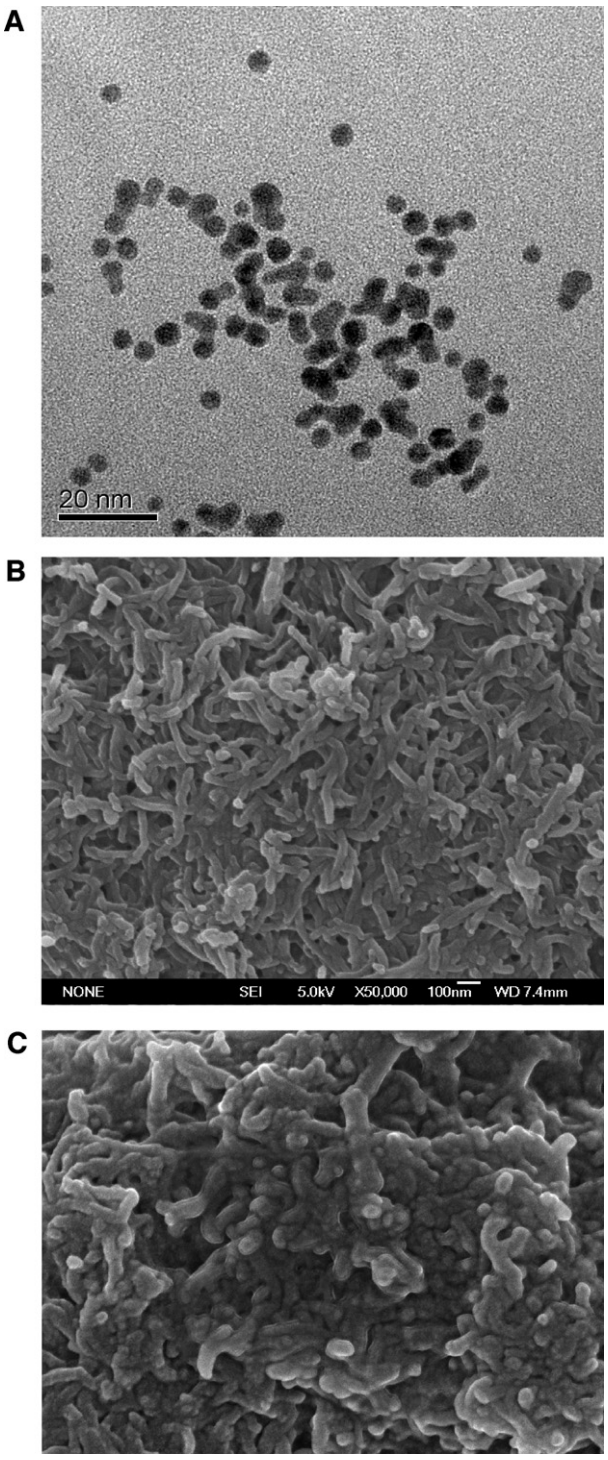

Fig. 1. Transmission electron micrographs of 3.5 nm Au nanoparticle (A); SEM images of CNTs/chit (B) and CuNPs/AuNPseed/CNTs/chit (C).

was catalyzed by the Cu(II)/Cu(III) redox couple. For comparison, various electrodes were prepared and tested, and the amperometric responses for successive addition of 0.5 mM glucose at an applied potentials +0.65 V were obtained as shown inset of Fig. 4. It can be seen that there was no obvious increase in current response for the chit (a) and CNTs/chit (b). The AuNPseed/CNTs/chit (c) electrode only displayed slight increases in current response to successive addition of glucose. In contrast, the nafion/CuNPs/AuNPseed/CNTs/chit (d) electrodes exhibited dramatic increases in current response to

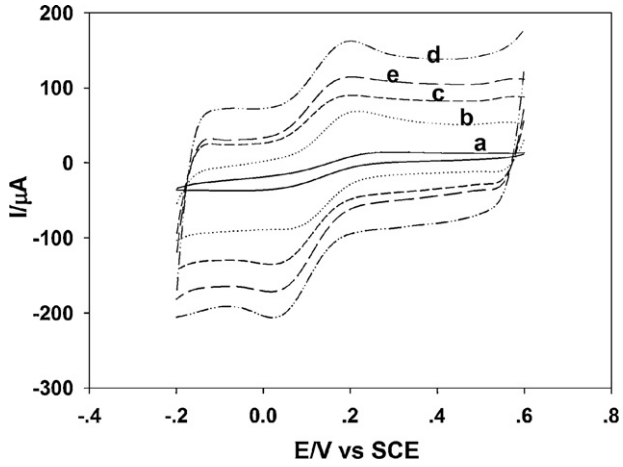

Fig. 2. The cyclic voltammograms of the chit (a), CNTs/chit (b), AuNPseed/CNTs/chit (c), CuNPs/AuNPseed/CNTs/chit (d) and nafion/CuNPs/AuNPseed/CNTs/chit (e) electrodes in 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) containing 0.1 M KCl at 100 mV s^{-1}.

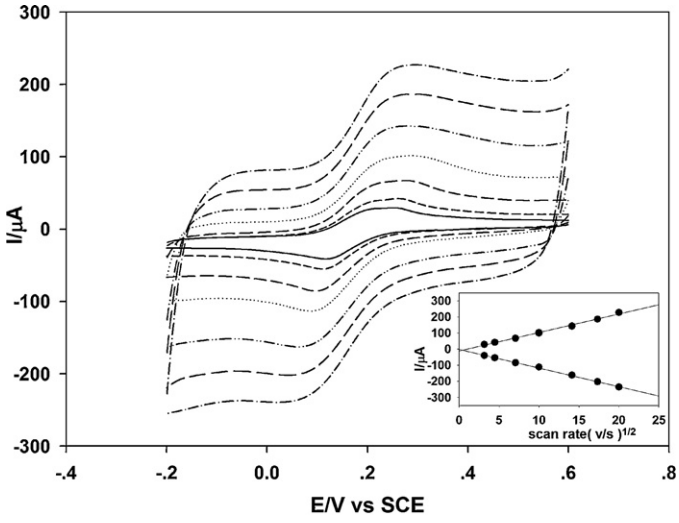

Fig. 3. The cyclic voltammograms of the nafion/CuNPs/AuNPseed/CNTs/chit electrode recorded in 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) containing 0.1 M KCl at different scan rates (inner to outer): 10, 20, 50, 100, 200, 300 and 400 mV s^{-1}. Inset: plots of peak current vs. $v^{1/2}$.

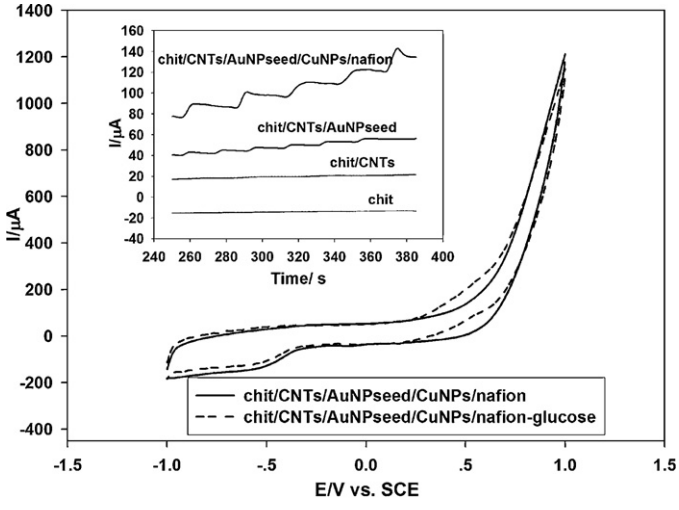

Fig. 4. The cyclic voltammograms of nafion/CuNPs/AuNPseed/CNTs/chit electrode in 0.1 M NaOH between −1.0 V and +1.0 V with a scan rate of 100 mV s^{-1} in the presence and absence of 5 mM glucose. Inset: steady-state current–time response of various modified electrodes to 0.5 mM glucose at +0.65 V.

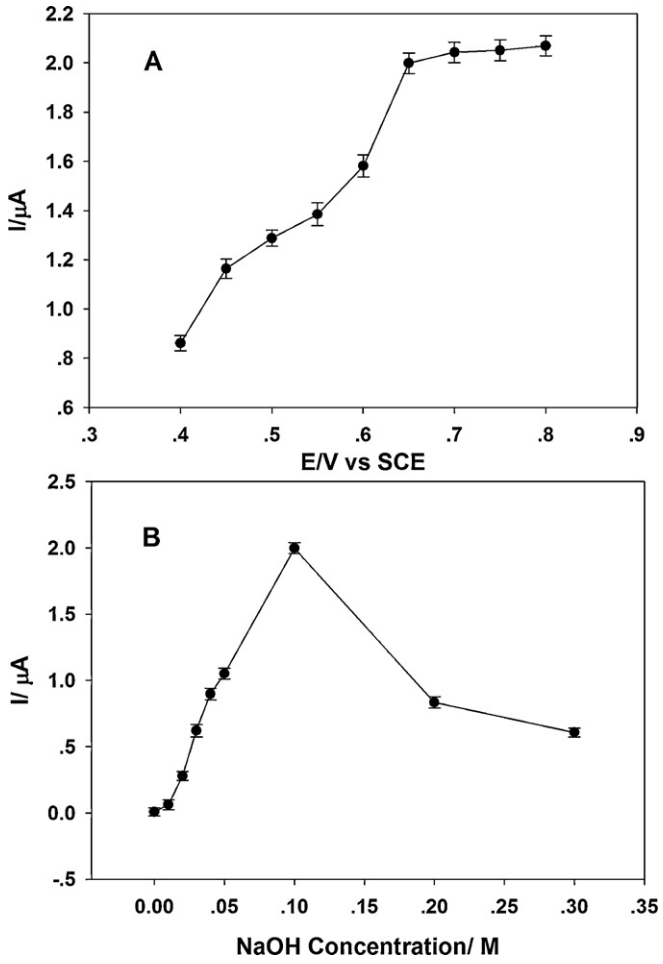

Fig. 5. Effects of applied potential (A) and pH (B) on amperometric response of the nafion/CuNPs/AuNPseed/CNTs/chit electrode to 0.1 mM glucose.

successive addition of glucose. Such excellent catalytic activity of nafion/CuNPs/AuNPseed/CNTs/chit nanohybrids might be attributed to the synergistic reaction of CuNPs and CNTs. The well-distributed CuNPs on the surface of CNTs with a high density would provide more active sites for the catalytic redox reaction and greatly increase the electrocatalytic activity.

3.4. Optimization conditions for the biosensor

It is well known that the applied potential strongly affects the amperometric response of a biosensor. We have systemically investigated the impact of applied potentials on the amperometric response of the nafion/CuNPs/AuNPseed/CNTs/chit electrode to glucose. Amperometric response was performed by varying the potential of the nafion/CuNPs/AuNPseed/CNTs/chit electrode between 0.35 V and 0.8 V in the presence of 0.1 mM glucose. As shown in Fig. 5A, the current response increased with the increase of applied potential. When the potential reached +0.65 V, the current response almost became steady. In addition, high potential would oxidize some interfering species which were stable under relatively low potential. Thus, +0.65 V was chosen as the optimal potential for amperometric glucose sensing.

An alkaline medium is required for enhancing the electrocatalytic activity of several transition metals for oxidation of carbohydrate compounds. Therefore, we investigated the influence of hydroxide concentration on the performance of the biosensor over the hydroxide concentration range of 0–0.3 M. As shown in Fig. 5B, no response current of the oxidation of glucose was acquired

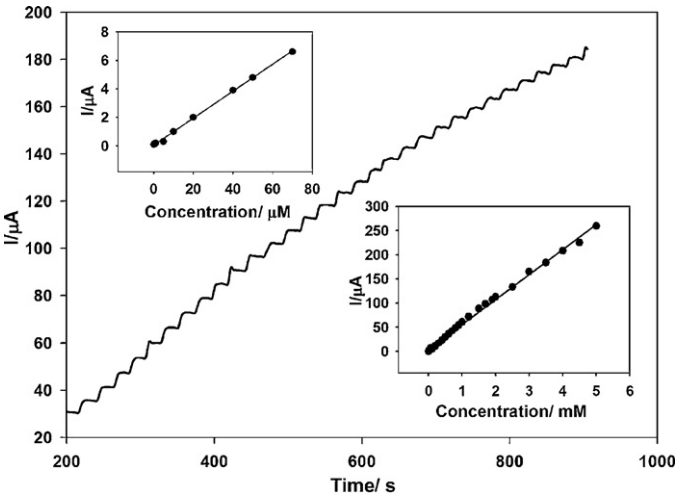

Fig. 6. Typical current–time response curve of nafion/CuNPs/AuNPseed/CNTs/chit electrode toward 0.1 mM glucose at +0.65 V (Inset: the relationship of catalytic current with the concentration of glucose).

in the absence of NaOH. The response current first increased and then decreased when NaOH concentration was between 0.01 M and 0.3 M. When the NaOH concentration was 0.1 M, the current response reached the maximum. The result is consistent with that reported in literatures [44,45]. Thus, a 0.1 M NaOH solution was chosen as the medium.

3.5. Amperometric detection of glucose

The amperometric response of the nafion/CuNPs/AuNPseed/CNTs/chit electrode to successive additions of glucose was further evaluated under the optimized experimental conditions. Fig. 6 shows the typical current–time dynamic response of the nafion/CuNPs/AuNPseed/CNTs/chit electrode toward glucose. The electrode responded quickly to the change of glucose concentration and reached about 95% of the steady-state current within 7 s, which was faster than those reported for the CuO nanorods modified electrodes (10 s) [46], the PtPb nanoparticle/MWCNT nanocomposite electrode (12 s) [47] and Cu nanoparticle/SWCNT/Nafion modified glassy carbon electrode (10 s) [48] and mesoporous platinum–modified platinum rod electrode (100 s) [49]. The amperometric signal showed linear correlation to glucose concentration in the range from 1×10^{-7} M to 5×10^{-3} M with a correlation coefficient of 0.999, which covered five orders of magnitude of glucose concentrations. It was much wider than that of the electrospun Ni nanoparticle-loaded carbon nanofiber paste electrode (2×10^{-6} to 2.5×10^{-3} M) [50], nickel oxide microfibers modified electrode (1×10^{-6} to 2.70×10^{-4} M) [51], CuO nanowires electrode (4×10^{-7} to 2.0×10^{-3} M) [52] and Cu nanocluster/MWCNT modified GC electrode (7×10^{-4} to 3.5×10^{-3} M) [40]. The detection limit was estimated to be 3×10^{-8} M (based on S/N = 3) for glucose, which was lower than that of 2.06×10^{-6} M at the over-oxidized polypyrrole modified Pd/Si microchannel plate electrode [53], 5×10^{-7} M at the MWCNT/Polyethyleneimine/Cu nanoparticles electrode [54], 1×10^{-5} M at the copper nanobelt electrode [55] and 2×10^{-7} M at the Cu nanoparticles/ZnO composite modified electrode [56].

3.6. Selectivity, reproducibility and stability

One of the most important analytical factors for an amperometric biosensor is the ability of the biosensor to discriminate the interfering species having electroactivities similar to the target analyte. The oxidizable compounds such as ascorbic acid (AA) and uric

Table 1
The interferences to glucose oxidation.

Substate	Response current (μA)
Glucose (1 mM)	60.38
Ascorbic acid (0.1 mM)	1.81
Uric acid (0.1 mM)	1.15

Table 2
Amperometric determination of glucose in human blood serum samples.

Sample	Concentration (mM)	R.S.D. (%)[a]	Added (mM)	Found (mM)	Recovery (%)
1	4.1	2.9	0.5	4.46	97
2	4.9	3.1	0.5	5.56	103

[a] R.S.D. (%) calculated from three separate experiments.

acid (UA) are normally co-existed with glucose in real samples. The normal physiological level of glucose is about 3–8 mM, which is much higher than the concentrations of interfering species like AA (0.1 mM) and UA (0.1 mM). In the present work, we studied the interference effect of AA (0.1 mM) and UA (0.1 mM) on the amperometric response of 1 mM glucose and the response was shown in Table 1 and Fig. S2. As shown, the biosensor showed excellent selectivity to glucose in the presence of AA and UA. Such excellent selectivity may be attributed to negatively charged nafion, which can electrostatically repel the negatively charged AA and UA.

The reproducibility and repeatability of the developed biosensor were determined. In a series of 10 sensors prepared in the same way, a relative standard deviation of 4.5% was obtained toward 0.2 mM glucose, indicating the reliability of the method. A set of 10 different amperometric measurements for 0.2 mM glucose with a single biosensor yield a R.S.D. of 3.4%.

The stability of the glucose biosensor was explored. The proposed biosensor was stored in air at ambient conditions. The response to 0.2 mM glucose was tested each week, after 65 days of storage, the response of the biosensor only decreased 8% compared to the initial response, which showed long-term stability.

3.7. Real sample analysis

To illustrate the feasibility of the nafion/CuNPs/AuNPseed/CNTs/chit electrode in practical analysis, it was applied to detect glucose in human serum. 40.0 μL of serum sample was added in 10.0 mL of 0.1 M NaOH solution, and the current response at +0.65 V was recorded. The recovery of glucose was determined by standard addition of pure glucose to the solutions containing the serum samples and the corresponding results were given in Table 2. One can see that the nafion/CuNPs/AuNPseed/CNTs/chit electrode gives good recoveries, indicating that potential interfering species in serum do not affect its detection of glucose.

4. Conclusions

In this paper, we introduced the seed-mediated method to the growth of CuNPs, using 3.5 nm gold nanoparticles as seeds and CNTs as growth scaffold. The nafion/CuNPs/AuNPseed/CNTs/chit electrode showed high electrocatalytic ability to glucose oxidation in alkaline solution and was used to construct a novel nonenzymatic glucose biosensor, which presented many attractive analytical features, such as superb electrocatalytic activity, high sensitivity, strong stability, good reproducibility, and excellent selectivity as well as quick response. The nafion/CuNPs/AuNPseed/CNTs/chit electrode can also be used as an amperometric biosensor for routine analysis of glucose in human serum samples.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.aca.2011.12.011.

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