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ORIGINAL PAPER

Glucose biosensor based on a platinum electrode modified with rhodium nanoparticles and with glucose oxidase immobilized on gold nanoparticles

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Abstract We have developed an enzymatic glucose biosensor that is based on a flat platinum electrode which was covered with electrophoretically deposited rhodium (Rh) nanoparticles and then sintered to form a large surface area. The biosensor was obtained by depositing glucose oxidase (GOx), Nafion, and gold nanoparticles (AuNPs) on the Rh electrode. The electrical potential and the fractions of Nafion and GOx were optimized. The resulting biosensor has a very high sensitivity (68.1 μA mM^{-1} cm^{-2}) and good linearity in the range from 0.05 to 15 mM (r = 0.989). The limit of detection is as low as 0.03 mM (at an SNR of 3). The glucose biosensor also is quite selective and is not interfered by electroactive substances including ascorbic acid, uric acid and acetaminophen. The lifespan is up to 90 days. It was applied to the determination of glucose in blood serum, and the results compare very well with those obtained with a clinical analyzer.

Keywords Blood glucose · Biosensor · Rh nanoparticle · Gold nanoparticle · Nafion

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Introduction

Diabetes mellitus is a global health problem with devastating social and economic impact, especially in newly industrialized and developing nations. Type 2 Diabetes is poised to become one of the major challenges to public health in the 21st century and will result in a huge burden, through premature morbidity and mortality. The number of persons with diabetes worldwide is approximate 171 million in the year 2000, and will increase to 366 million in the year 2030 [1]. Diabetes mellitus is one of the leading causes of death and disability in the world. There are more than 3.8 million people worldwide die every year from diabetes related causes. The blood glucose level is usually used as a clinical indicator of diabetes, rapid and accurate determination of glucose concentration of blood is essential in diagnosis and management of diabetes [2].

Many technologies are used to measure glucose concentrations, such as colorimetric method [3, 4], enzyme electrode method [5–7] and fluorescence spectrum [8, 9]. Enzyme electrodes have several advantages including rapid determination, high sensitivity, high selectivity and facile procedure, and play a key role in providing a powerful analytical tool for blood glucose concentration measurement. However, there continues to be several challenges related to the achievement of accurate and reliable glucose monitoring. One of the challenges is the electroactive interferences. The amperometric measurement of hydrogen peroxide produced by GOx catalyzed reaction at the working electrode requires application of a relatively high potential at which some species, such as ascorbic and uric acids and some drugs (e.g., acetaminophen), are also electroactive [10, 11]. The current contributions of electroactive species can compromise the selectivity and hence the overall accuracy of the measurement. One useful method in eliminating electroactive interferences is to employ a selectively-permeable membrane coating that prevents interferences from the access of the electrode with transport properties based on electric charge, size, or polarity. The

negatively charged Nafion has been used to exclude interfering anions [12]. Poly (vinyl chloride) [13], cellulose acetate [14] and poly (o-phenylenediamine) [15] are extremely useful in imparting high selectivity by rejecting interferences based on size exclusion. Hydrophobic alkanethiol [16] and thioctic acid self-assembled monolayers [17] are also used to eliminate the interference. Another avenue to avoid interfering reactions is using low electrode potentials at which interferences are not efficiently oxidized or reduced. Numerous metal complexes, such as of iridium, rhodium, ruthenium or osmium and their oxides, ferrocene and its derivatives have been shown to lower the oxidation overpotential. Recent reports show that Rh nanoparticles or its compounds modified electrodes produced by electrochemical deposition [10] or screen printing [18] can lower the oxidation overpotential and minimize the interferences from relevant electroactive species, especially acetaminophen which is difficult to eliminate by selectively-permeable membranes. It should be noted that Pt nanoparticles which are quite commonly used in glucose biosensors can improve the sensitivity but can't reduce the operation potential [19].

We produced rhodium nanoparticle modified electrode by electrophoretic deposition rhodium nanoparticles on the surface of flat Pt electrodes. Rhodium nanoparticle modified electrodes have high electrocatalytic activity due to large surface areas active sites and hence can eliminate interferences by low operating potential without sacrifice of the sensitivity and linearity. In addition, selectively-permeable membrane, Nafion film was also used to modify the electrode and immobilize the GOx enzyme.

On the other hand, it should be noticed that selectively-permeable membranes can eliminate electroactive interferences but will decrease the electrical current response of the electrode due to the limitation of glucose flux. Increasing the current response of the electrode with nanoparticle-enzyme hybrid system is a feasible way to enhance the sensor's sensitivity. Nobel metal nanoparticles have excellent catalytic and conductivity properties, which make them suitable for acting as catalysts to increase electrochemical reactions [20, 21] and enhance the electron transfer between enzyme redox centers and electrode surfaces [22]. In our study, we also utilize gold nanoparticles which are excellent biocompatible to enhance the sensitivity of our glucose biosensor [23]. In summary, a glucose biosensor with high sensitivity and wide linear range under low operation potential has been prepared. This electrode construction can also be used to build biosensors based on other enzymes, such as horseradish peroxidase, urease, and lactate oxidase.

Experimental

Reagents and apparatus

GOx(108 Umg^{-1}, from Aspergillus niger), dioctyl sulfosuccinate sodium salt (AOT), 2,2,4-Trimethylpentane (C_8H_{18}), Nafion (5 wt% solution in lower aliphatic alcohol), chlorauric acid hydrated ($HAuCl_4 \cdot 4H_2O$), uric acid (UA) and acetaminophen(AP) were purchased from Sigma-Aldrich (http://www.sigmaaldrich.com). Rhodium trichloride ($RhCl_3$) and ascorbic acid (AA) were purchased from Baker (http://www.avantormaterials.com). Other reagents like D-(+)-Glucose, sodium borohydride ($NaBH_4$) and trisodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) were purchased from Sangon Biotech (Shanghai, China, http://sangon.bioon.com.cn) and were reagent grade. Deionized-ultrafiltered (18MΩ · cm) water was used for all aqueous solutions.

Electrochemical measurements were carried out on a CHI660 electrochemical work station (Co., CHI, China, http://www.chinstr.com). All experiments were performed with a three-electrode system using a rhodium nanoparticle modified electrode as the working electrode, a platinum wire as the auxiliary electrode and an Ag/AgCl (3 M KCl) as the reference electrode.

Preparation of nanoparticles

Rh nanoparticles have been prepared by reverse micelle method which was widely used in nanoparticle preparation due to its advantages such as simple equipment, facile operation and controllability of particle sizes [24]. Synthesis of Rh nanoparticles was carried out as follows. Firstly, 0.1 M $RhCl_3$ aqueous solution, 0.1 M $NaBH_4$ aqueous solution and 0.1 M AOT-C_8H_{18} solution was prepared respectively. Then, $RhCl_3$ aqueous solution and $NaBH_4$ aqueous solution were added into AOT-C_8H_{18} solution respectively to prepare $RhCl_3$ microemulsion and $NaBH_4$ microemulsion. Finally, the same volume of $RhCl_3$ microemulsion and $NaBH_4$ microemulsion were mixed, keeping stirred till the solution turned to be brownish black. TEM micrographs confirmed that the diameters of the Rh nanoparticles are about 10 nm and have a narrow size distribution (Fig. 1).

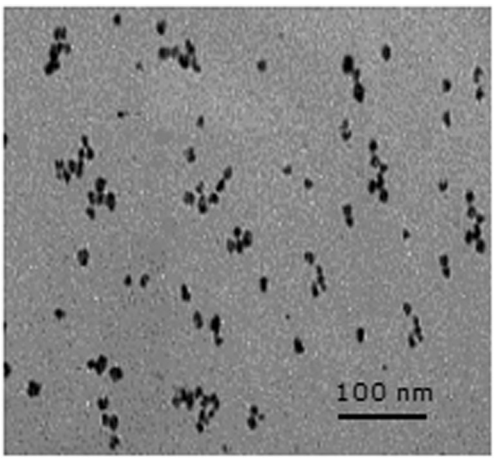

Fig. 1 TEM image of Rh nanoparticles prepared by reverse-micelle synthesis

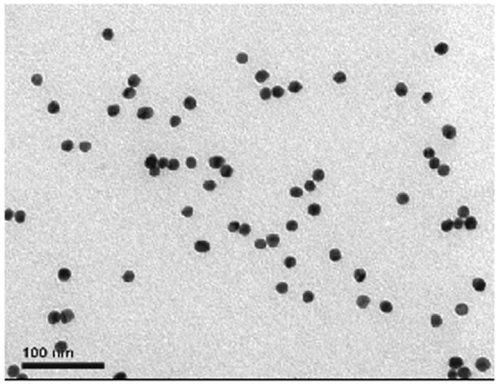

Fig. 2 TEM image of gold nanoparticles prepared by chemical reduction

Gold nanoparticles (AuNPs) have been prepared by reduction of chlorauric acid ($HAuCl_4$) aqueous solution with trisodium citrate [25]. Synthesis of AuNPs was carried out as follows. 50 mL of 0.01 wt. % $HAuCl_4$ solution was heated to boiling while stirring in a 100 mL beaker. Then 25 μL of 1 wt. % trisodium citrate solution was quickly added to the $HAuCl_4$ solution. The solution changed color within several minutes from yellow to black and then to purple color, and finally came into orange red. After a stirring for 15 min with heating, this solution was ceaselessly stirred without heating until it was cooled. TEM micrographs confirmed that the diameters of the AuNPs are nearly 15 nm (Fig. 2).

Preparation of rhodium nanoparticle modified electrodes

The rhodium nanoparticle modified electrodes were prepared by electrophoretic deposition [26]. Two flat Pt electrodes were polished to have a mirror like surface and then rinsed thoroughly with deionized ultra-filtered water. Subsequently the two electrodes were immersed into the Rh nanoparticle reverse micellar solution and applied with a potential of 300 V (electric field intensity was about 100 $V \cdot mm^{-1}$). Driven by the electric field, Rh nanoparticles were electrophoretically deposited onto the cathode Pt electrode. Finally, the Pt electrode deposited with Rh nanoparticles was sintered at 450 °C to obtain the rhodium nanoparticle modified electrode. Figure 3 showed the SEM of

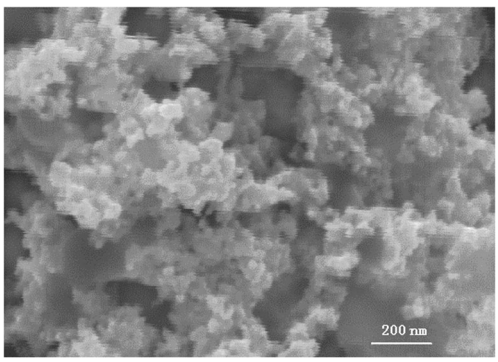

Fig. 3 SEM image of a rhodium nanoparticles modified electrode

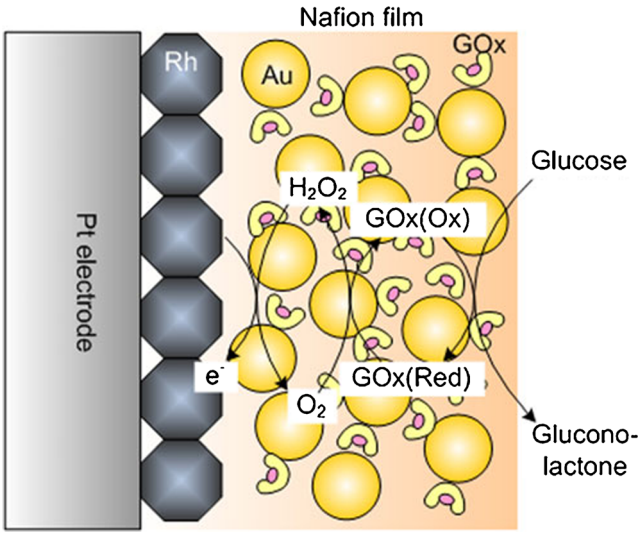

Fig. 4 Schematic cross section of the glucose biosensor

the rhodium nanoparticle modified electrode. As shown, the size of Rh nanoparticles on the electrode is about two fold of that in reverse micellar solution (Fig. 1). This may be due to the agglomeration of Rh nanoparticles caused by sintering process.

Preparation of glucose biosensors

Nafion, a negatively charged sulfonated tetrafluoroethylene based fluoropolymer-copolymer, has both hydrophobic fluorinated groups and strong hydrophilic sulfonic groups at its chains, and has been extensively used in glucose biosensors due to its excellent selectively permeability and durability. In a typical procedure, a glucose biosensor was prepared as follows. 3.2 mg GOx was dissolved in 0.5 mL PBS. The enzyme solution was mixed with 0.5 mL gold sol and a certain amount of Nafion, and was sonicated for 5 min to get a composite solution. 5 μL GOx, AuNPs and Nafion composite solution was cast onto the rhodium nanoparticle modified electrode surface and dried at room temperature. Figure 4 schematically illustrates the cross section of the glucose biosensor. Rh

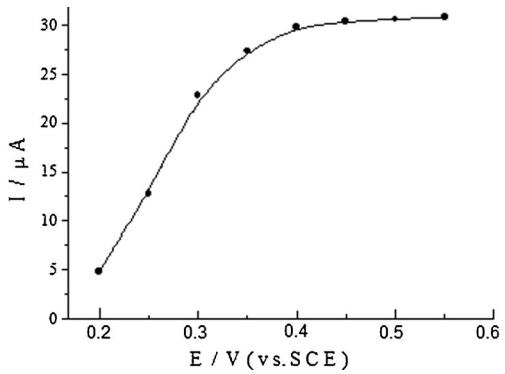

Fig. 5 The effect of applied potential on the response of biosensor to 5 mM glucose

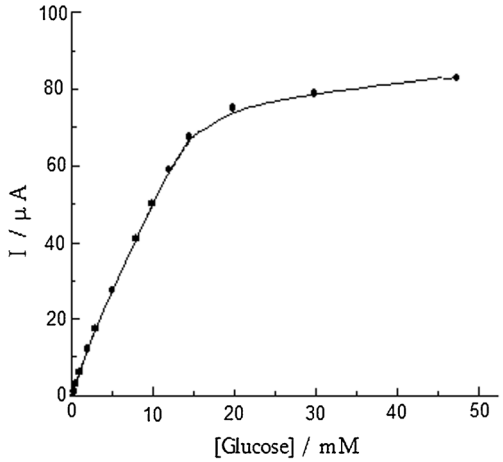

Fig. 6 The relationship between the current response of biosensor and glucose concentrations

nanoparticles were electrophoretically deposited on the Pt flat electrode. AuNPs and GOx were distributed in Nafion film which was cast on the rhodium nanoparticle modified electrode. The prepared glucose biosensors were stored in PBS at 4 °C when not in use.

Results and discussion

Effect of the potential on the response current

Figure 5 shows the effect of the operation potential on the amperometric response to 5 mM glucose at the enzyme electrode. The response current increases rapidly when the potential is moved from 0.2 to 0.35 V (vs. Ag/AgCl). However, when the potential is further moved towards the positive direction, the response current doesn't increasing remarkably. Considering that the low operating potential of the sensor can eliminates the interference from common interferents, such as acetaminophen, ascorbic acid etc., a potential of 0.35 V was preferred in the following experiments.

Optimization of Nafion and GOx concentrations

We know that the contents of Nafion in modified electrode will influence the morphology and performance of the biosensor. In our experiments, we found that increasing the Nafion concentration will improve the linearity of detection, while the response current decreased due to its diffusion limitation of glucose. The optimized Nafion concentration was 3 wt% with consideration to both linearity and sensitivity. The influence of GOx concentration on the biosensor sensitivity has also been studied. The biosensor response was improved by raising the concentration of GOx. However, this improvement was not obvious when the GOx concentration over 3.2 mg · mL^{-1}. So, the GOx concentration of 3.2 mg · mL^{-1} (505 U · mL^{-1}) was thus chosen for the following experiments.

Amperometric determination of glucose of the sensor

The rhodium nanoparticle modified electrode based glucose sensor was highly sensitivity to glucose. Figure 6 shows the calibration curve of the amperometric response of the sensor as a function of glucose concentration. The sensor have a linear response to glucose in the range from 0.05 to 15 mM (corresponding linearity (R) is 0.989), with a detection limit estimated at 0.03 mM, at an SNR of 3. The sensitivity of the sensor is about 68.1 μA·mM^{-1}·cm^{-2}, which is one order of magnitude larger than that of other reported glucose enzyme electrodes [27–30]. Moreover, the detection potential is lower than most reported enzymatic electrodes [29, 31–33]. Compared to enzymatic glucose biosensors based on metal oxide

Table 1 Comparison of the present biosensor with different glucose sensors

Modified electrode	Linear range (mM)	Detection limit (μM)	Sensitivity (μA mM^{-1} cm^{-2})	Detection potential (V)	Ref.
Pt/PVF-Au-GOx	1–36	–	4.17	0.6	[27]
Teflon-Au-CNT-GOx	0.05–1	17	2.6	0.5	[28]
Pt/PAA/AuNP/GOx	0.5–16	7	2.77	0.6	[29]
AuE/AuNP/GOx	0.02–5.7	8.2	8.8	0.3	[30]
GCE/Chitosan-AuNP/GOx	0.05–1.3	13	–	0.7	[31]
Graphene/AuNPs/GOx/Chits	2–14	180	17.5	0.5	[32]
Fc@NaY/GOx	0.0008–4.0	0.2	68.1	0.4	[33]
CS-GNPs-Fe_3O_4/GOx	0.003–0.57	1.2	–	−0.4	[35]
GCE/Chits/HGNs/GOx	0.002–0.046	1.6	–	0.15	[36]
PET/Ti/Au/ZnO:Co/GOx	0.2–4	20	13.3	−0.5	[37]
GCE/TiO2–GR/GOx	0–8	–	6.2	−0.6	[38]
MWCNT/TiO_2/HAP/GOx	0.01–15.2	2	57	0.3	[39]
Pt/Rh/AuNP-GOx-Nafion	0.05–15	30	68.1	0.35	This work

nanoparticles [34], our sensor has wider linear range than most of them. Some metal oxide nanoparticle based glucose sensors have much lower detection potential [35–39], that's because metal oxide nanoparticles facilitate the direct electron transfer from GOx to electrodes. However, the linear range and sensitivity of those sensors [35–37] are inadequate for practical clinical applications, since the general range of glucose concentrations in human blood is 80–120 mg · dL^{-1} (4.4–6.6 mM). The analytical performance comparison between the present glucose biosensor and other sensors was displayed in Table 1. The high sensitivity and wide linear range might be attributed to the enhancement of AuNPs which were close to the active sites of enzymes and directly catalyze H_2O_2 oxidation, and the low detection potential should be due to the nanostructured Rh electrode with high specific surface area. AuNPs also act like an electron shuttle between FAD and the Rh nanoparticles modified electrode.

Compared to non-enzymatic glucose sensors based on the use of the metals platinum, gold, nickel, copper, of alloys and bimetals, of carbon materials [40], our glucose sensor has a higher sensitivity. Although some non-enzymatic glucose sensors [41–45] exhibit greater sensitivity, their linearity is unsatisfactory for blood glucose detection. Also, most of the non-enzymatic glucose sensors were studied in buffer solutions rather than real biological samples, and the clinical application of non-enzymatic glucose sensors still has tremendous challenges [40]. For now, the enzymatic glucose sensors are widely used for practical application.

Interference tests

Selectivity is important in the practical use of biosensors. The compounds such as uric acid (UA), ascorbic acid (AA) and acetaminophen (AP) are usually coexisted with blood glucose in real samples, which may interfere with the determination of glucose.

Figure 7 shows the amperometric response of the nanostructured rhodium based glucose sensor to the consecutive addition of AA, AP and UA to the measuring cell in concentrations corresponding to their relevant clinical levels. The percentages of the interference of ascorbic acid and uric acid are decreased to 8.9 % and 5.3 % respectively. The interference of acetaminophen is nearly eliminated. The high selectivity should be attributed to the low operation potential (0.35 V vs. Ag/AgCl) and the SO_3^- in Nafion.

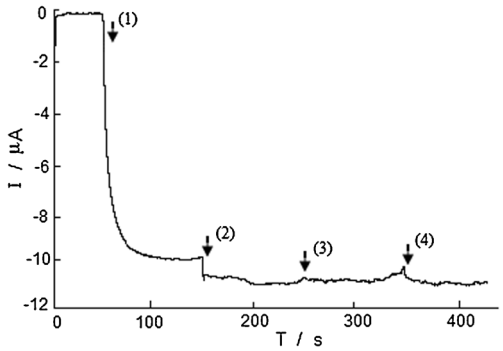

Fig. 7 Current-time responses of biosensor to glucose and electroactive interfering substances, (1) 2 mM glucose, (2) 0.1 mM ascorbic acid, (3) 0.2 mM acetaminophen, (4) 0.2 mM uric acid

Table 2 Measurement results of glucose contents in blood samples

Sample No.	Determined by hospital (mM)	Measured by biosensor (mM)	Relative error
1	4.4	4.5	+0.1
2	6.1	5.9	−0.2
3	8.6	8.8	+0.2
4	12.5	12.3	−0.2
5	15.4	15.1	−0.3

Determination of glucose in serum

In order to demonstrate the practical usage of the biosensor, serum samples were assayed. The serum samples and their glucose concentrations were provided by a local hospital (The serum samples were first analyzed in the hospital with HITACHI 7020 chemistry analyzer system). 0.5 mL serum sample was added into 2 mL phosphate buffer solution (pH 7.2), and the response was obtained at 0.35 V. The glucose concentration of the serum can then be calculated from the calibration curve in Fig. 6. The results of the as-prepared sensor are averaged with 7 measurements. The analytical results provided by the hospital and those determined by the as-prepared biosensor are listed in Table 2. The results are satisfactory and agree closely with those measured by the HITACHI 7020 chemistry analyzer system in hospital. Thus, the biosensor can be used for the actual detection of glucose in serum.

Long term stability

The long term stability of the glucose biosensors has been investigated. The biosensors were immerged in PBS and stored

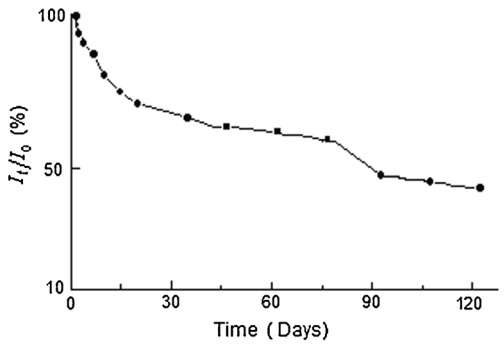

Fig. 8 The lifespan of the as-prepared blood glucose biosensor

at 4 °C in the refrigerator. The biosensor response to 2 mM glucose was measured intermittently. Result shows that the biosensors have a lifespan of 90 days with 50 % of the initial response (Fig. 8). The long lifespan might be attributed to three-dimensional distribution of gold nanoparticles and GOx in Nafion film. The gold nanoparticles in the network can catalyse the oxidation of H_2O_2, the by-product of the enzymatic reaction, preventing H_2O_2 accumulation which will accelerate loss of the enzyme activity [46].

Conclusions

We have described a glucose biosensor based on rhodium nanoparticles modified electrode covered with gold nanoparticles, GOx and Nafion hybrid film. The biosensor has high sensitivity, wide linear range, good selectivity and long term stability. The determination of glucose in real blood serum samples have been investigated, and the result were consistent with the HITACHI 7020 chemistry analyzer system in hospital. Further investigation for clinical practice application is on the way.

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