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Glucose biosensor based on highly dispersed Au nanoparticles supported on palladium nanowire arrays

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ABSTRACT

A glucose biosensor was constructed by using highly dispersed gold nanoparticles supported on palladium nanowire arrays (Au-PdNWs) as sensing interface. The property of the biosensor was detected by cyclic voltammetry and chronoamperometry and the use of composite nanomaterial led to an efficient enzyme loading, showing a perfect catalytic activity towards the oxidation of glucose. The biosensor exhibited excellent sensitivity (detection limit was down to 0.001mM), short response time (about 5 sec) and wide linear range (from 0.05 to 5mM). Furthermore, the biosensor exhibited long-term stability and good reproducibility.

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KEYWORDS

Glucose biosensor;
Pd nanowire array;
Nano-Au;
Electrochemical method.

INTRODUCTION

The development of sensing devices for the fast and reliable monitoring of glucose and the carbohydrates for the treatment and control of diabetes has been a focal subject in analytical chemistry for the past few decades^[1]. Recent advances from the convergence of nanotechnology and biotechnology are accelerating the development of sensor research. Nanostructured materials, for example metal nanowires, have the properties of novel optical, electrical, catalytic, and magnetic properties, which make the nanowires the promising sensing materials for ultrasensitive, trace-level biological and chemical nanosensors^[2].

As a highly active noble metal, the role of palladium in catalysis and electrochemical analysis have been recognized extensively and studied intensively.

Especially in the recent years, as the nano-technology advances continuously, studies and applications on palladium nanowire have been reported frequently, including the palladium nanowire^[3] prepared by electroless deposition and palladium alloy nanowires, such as Pd-Ni^[4] and Pd-Co^[5] nanowires produced by electro-deposition. These researches mainly concentrated on the catalysis research of alcohols and the preparation of hydrogen micro-sensor. As far as we know, there are few reports on the application of PdNWs in the area of glucose detection.

Here, we report Pd nanowire arrays based on the highly ordered NWA architecture using an anodized aluminum oxide (AAO) template electro-deposition^[6]. With the palladium nanowire array loaded by the gold nano-particles as the substrate, the amperometric glucose sensor was prepared. The Au colloids could increase the specific surface area and adsorb more en-

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zymes, and it could make the modified electrode to adsorb lots of enzymes and keep their bioactivities in good condition. And Pd NWAs have an extremely high electrochemical active surface area and are highly active toward the electro-oxidation of glucose. The biosensor obtained shows electro-catalytic activity, good accuracy, and a low cost.

EXPERIMENTAL

PdNWs were prepared in my lab and the fabrication method has been described in the previous reports^[6]. GCE was polished and thoroughly cleaned. A piece of as-prepared AAO template was attached to the polished surface of the GCE. Electro-deposition was carried out in an aqueous solution containing $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 + \text{NH}_4\text{Cl}$. The pH value of the solution was adjusted to 8 with $\text{NH}_3 \cdot \text{H}_2\text{O}$. At last a PdNWs electrode embedded in AAO were dipped into NaOH solution of 2 M for 1 h to remove the AAO completely and then washed by distilled water for several times.

The GOD electrode was prepared as follows: The 10 μL GOD (2g L^{-1}) and 0.3 ml Au colloid were mixed, and 3ml anhydrous ethanol (2%, w/v) with PVB was added to the mixed solution. Then the Pd nanowire electrode was dipped into the above mixed solution for 10 min. After it was dry, the GOD electrode (denoted as GOD/nano-Au/PdNWs/GCE) was obtained, and it was suspended in PBS with pH 6.86 and stored at 4°C. Nano-Au/PdNWs/GCE, GOD/PdNWs/GCE and GOD/GCE, which were used in the control ex-

periments, were prepared by the same method.

Electrochemical experiments were performed on a PARSTAT 2273 electrochemical workstation (Princeton, USA). A standard three-electrode cell was used and was controlled at 25°C using a water bath during the experiment. A platinum wire and saturated calomel electrode (SCE, 0.241 V versus SHE) were used as counter and reference electrodes, respectively. Scanning electron microscopic (SEM) analysis was performed with a Hitachi S-5200.

RESULTS AND DISCUSSION

Figure 1a and 1b showed the typical images of the PdNWs, and the AAO template was dissolved completely.

It could be seen that a large amount of Pd nanowires had been assembled in the AAO template. Though some nanowires aligned together, forming several clusters of aggregates, a large area of Pd nanowires had good orientation and was highly ordered, perpendicular to the surface of the substrate. It could be clearly observed from figure 1b that the Pd nanowires were highly ordered with uniform diameters of 30 nm, maintaining the size and shape close to cylinder of the pores of the AAO template. The hexagonal shape of the Pd nanowires was due to the AAO porous structure during anodization. The nanowires were uniform, well isolated, parallel to one another, and stood vertically to the electrode substrate surface.

The cyclic voltammogram of GOD/GCE, GOD/PdNWs/GCE and GOD/nano-Au/PdNWs/GCE in

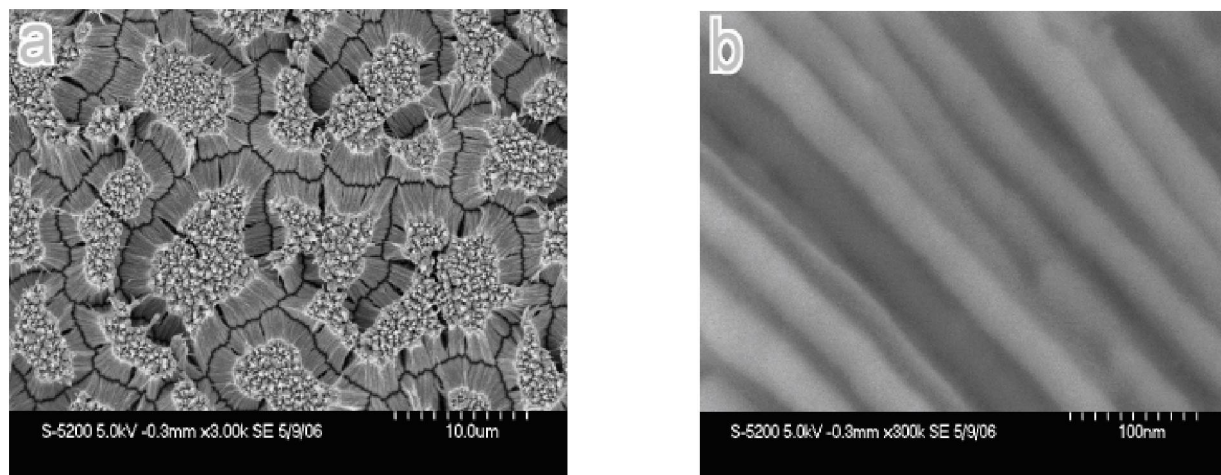


Figure 1 : SEM image of PdNWs(a) and (b).

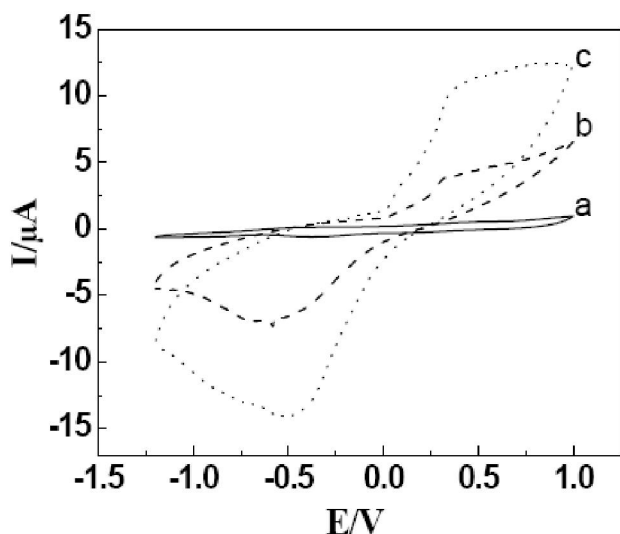


Figure 2 : CVs of 1mmol L^{-1} glucose at different electrodes in a 0.1mol L^{-1} PBS (pH 6.86) at a scan rate 100mV s^{-1} , (a) GOD/GCE; (b) GOD/PdNWs/GCE; (c) GOD/nano-Au/PdNWs/GCE.

1mmol L^{-1} glucose solution was shown in figure 2.

The results revealed that there were no apparent redox peaks of glucose in GOD/GCE (a). Under the same conditions, apparent peaks were observed on GOD/PdNWs/GCE (b) and GOD/nano-Au/PdNWs/GCE (c), suggesting that PdNWs, as a carrier, played an important role in electron transfer. Though GOD/PdNWs/GCE without Au colloid had the similar response during the scanning, its cathodic peak current was small compared with GOD/PdNWs/GCE with Au colloid. It was indicated that gold nanoparticles loading on PdNWAs with good bio-compatibility and conductivity played a significant role in the catalysis of GOD to produce H_2O_2 , which enhanced the immobilization of the enzyme and accelerated electron transfer in the active center of the electrode and enzyme. Consequently, the current response to glucose in nano-Au/PdNWs/GCE, which possessed the properties of PdNWAs and nano-Au, was significantly boosted.

The investigation of the effect of pH on the performance of biosensor is of great importance. The solution acidity had a significant influence on the activity of immobilized GOD and the redox process with proton participation, thereby affecting the properties of GOD/nano-Au/PdNWs/GCE. The pH dependence of the sensor was evaluated at 1mmol L^{-1} glucose solution over the pH ranging from 4 to 9. The current response was weaker when the acidity was stronger, and the reaction

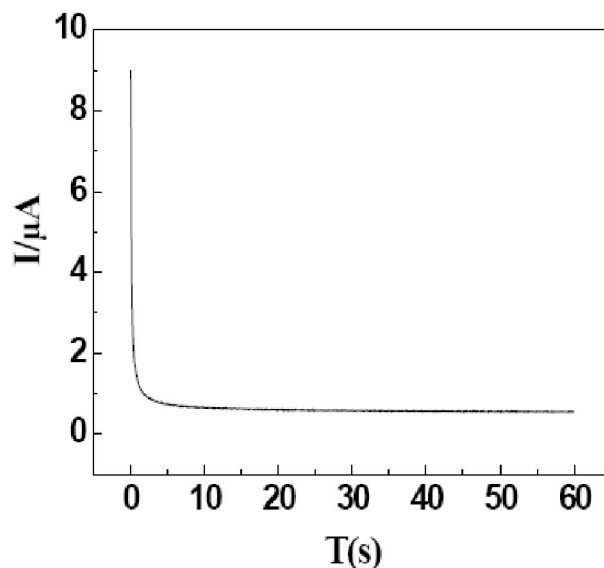


Figure 3 : Current-time responses of the glucose on GOD/nano-Au/PdNWs/GCE.

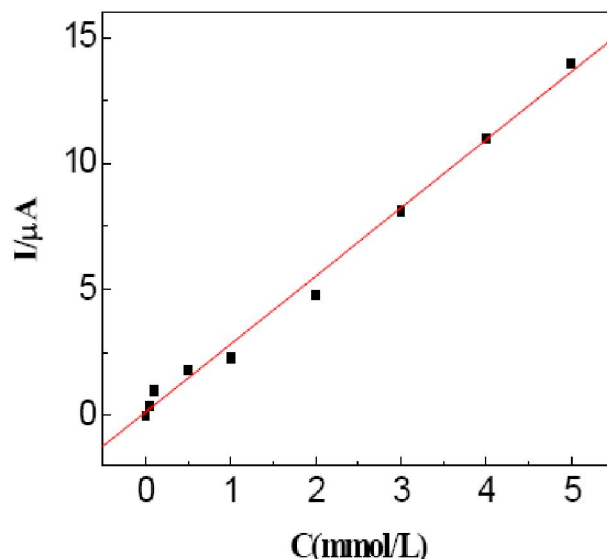


Figure 4 : Linear measurements of glucose on GOD/nano-Au/PdNWs/GCE.

hardly proceeded forward due to plenty of H^+ . With pH increasing, H^+ concentration decreased and current response became strengthened gradually. When $\text{pH}=6.86$, the response reached the maximum. And then it declined gradually as pH further increased, as high pH might prevent transformation between oxidation and reduction states of GOD. Therefore, pH was determined as 6.8 in the experiment.

The response time of biosensor relied on electron transfer rate. Pd nanowire array and gold nanoparticles served as a bridge between the electron acceptor and the donor, and it improved the transfer rate to

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a great extent, thus shortening the response time. It was determined by chronoamperometry that response time was less than 5s generally when the current was stable (Figure 3). It was greatly shorter than that of electrodes made by other methods (0.5-1.5 min, in general).

It was detected in the optimal working condition (pH=6.8, T=35°C). There was a linear relationship between current response and glucose concentration within the range of $5.0 \times 10^{-5} \sim 5.0 \times 10^{-3} \text{ mol L}^{-1}$ (Figure 4). The linear equation was $i_p = 1.26 \times 10^{-7} + 2.7 \times 10^{-6} C$, with relative coefficient $R=0.9964$ and the detection limit of $1.0 \times 10^{-6} \text{ mol L}^{-1}$. The results indicate that the sensor shows higher enzymatic activity and implies that the present enzyme electrode exhibits a higher affinity for glucose than the reported biosensors^[7,8].

The reproducibility of the current response of the enzyme electrode was examined at a glucose concentration of 0.5 mmol L^{-1} and the relative standard deviation was 3.6% (n=5). The sensitivity of the electrode response maintained about 75% of the original value after 1 month testing. This could be due to the good biocompatibility of nano-Au thus the lifetime of the glucose biosensor could be prolonged.

The biosensor was not only required to sensitive to glucose but also to be insensitive to other electro-active substances. Interference studies were performed with the present biosensor. The results show that 0.01 mmol L^{-1} ascorbic acid and 0.01 mmol L^{-1} uric acid do not interfere with determination of glucose 0.05 mmol L^{-1} .

CONCLUSION

In this study, we have demonstrated that, nanostructuring using the prepared nano-Au and PdNWAs improves the analytical performance of the corresponding sensors. The sensitivity of the GOD electrode toward glucose is much better than that of conventional electrode. The biocompatibility of nano-Au and the large surface area of the nanowire make it suitable for the adsorption of enzyme and applied in the fabrication of biosensor. It is no doubt that the biosensor fabrication method offers a promising platform for various bio-sensing applications.

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