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Electrodeposited Gold Nanoparticles Modified Screen Printed Carbon Electrode for Enzyme-Free Glucose Sensor Application

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Abstract: An enzyme-free glucose sensor has been developed based on electrodeposited gold nanoparticles modified screen-printed carbon electrode (SPCE). The combination of electrodeposited gold nanoparticles and SPCE, makes the device compact, low cost, and reliable enzyme-free glucose sensor. Gold nanoparticles were directly synthesized via electrochemical deposition method on carbon surface from $HAuCl_4$ solution. The gold nanoparticles electrodeposited on the surface of SPCE was observed by SEM. The gold nanoparticles modified SPCE were successfully used for the sensing of glucose. This enzyme free sensor showed wide linear range with the glucose concentration from 0.5 ÷ 8.5 mM and sensitivity 9.12 μA/mA.cm^2 with a limit of detection of 200 μM.

Keywords: Enzyme Free Glucose Sensor, Screen-Printed Carbon Electrode, Electrodeposited Gold Nanoparticles.

1. Introduction

Accurate, rapid, inexpensive and stable sensor for glucose detection in biological fluids is nowadays extremely important for the diagnosis and management of diabetes mellitus. The majorities of well-known amperometric biosensors for glucose monitoring are based on immobilized specific oxidase and electrochemical detection of enzymatically liberated hydrogen peroxide, or redox mediators such as derivatives of ferrocene, hydroquinone and other redox organic dyes [1]. Although enzymatic glucose sensors usually shows good selectivity and sensitivity, the main drawback of these sensors is natural instability of immobilized enzyme with temperature, pH, humidity, ionic detergents leading to lack of stability and accuracy during the storage and use [2] and the oxidation of enzymatically generated H_2O_2 requires a high overpotential and is prone to interference due to other redox-

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active molecules such as ascorbic acid (AA), uric acid (UA) [3].

Enzyme-free glucose sensor, the next generation of glucose sensors, have advantages over enzymatic glucose sensors such as stability, simplicity, reproducibility and free from oxygen limitation. They are expected to overcome this problem for practical uses with principle based on the direct oxidation of glucose on the electrode surface without using a fragile enzyme [4]. These sensors are modified with nanomaterials such as nanostructured Pt [5], Cu_xO [6], Ni [7], nanoparticles modified carbon nanotube [8] and porous nanomaterial [9]. Especially, nanoparticles with high surface area, stable components have received much attention because of their wide application as absorbents, catalysts. With advantages of fast time, simple, not required the post synthesized process and green, the electrochemical deposition is beneficial to become simpler and quicker methods to prepare nanoparticles modified electrode in the application for the enzyme-free glucose sensor. Among nanostructured materials, gold is an attractive metal since gold electrodes present higher activity and their oxidation potential in the neutral and alkaline medium are more negative compared with other metals [10].

Screen printed carbon electrode (SPCE), a disposable three-electrode system, have successfully prepared in our laboratory with the strong advantage of fabricating a large number of near identical electrodes at a low-cost [11]. SPCE is printed on the insulator substrates as plastic or ceramics. The difference with other materials such as Cu, Au, Pt, stainless steel used as electrode substrates make the challenges in experimental set-up and non-friendly for end-user in practical application. The SPCE is the compact three electrode system, disposable and ease to modify. It can become the reliable solution for an enzyme-free glucose sensor in practical use.

In this work, we report the fabrication of a non-enzymatic electrode based on electrodeposited gold nanoparticles modified SPCE. In this way, a highly stable, fast time and disposable sensor could be fabricated for highly sensitive amperometric detection of glucose. The enzyme-free glucose sensor is also compact compared with previous ones.

2. Experimental

2.1. Reagents

$HAuCl_4$, D-glucose and ascorbic acid (AA) were purchased from Sigma-Aldrich. $NaH_2PO_4.2H_2O$, Na_2HPO_4, NaCl and KH_2PO_4 were purchased from Wako (Japan). SPCE with working electrode area of 2.64 mm^2 was purchased from Biodevice Technology (Japan). Other reagents were of analytical grade, and all solutions were prepared and diluted using ultra-pure water (18.2 MΩ.cm) from the Milli-Q system (Millipore, USA).

2.2. Instrument

Scanning electron microscopy (SEM) images were obtained using Hitachi S-4100 with accelerating voltage 20 kV. Electrochemical measurements were performed on an Autolab 30 (Metrohm, Netherland). A drop of 35 μL of the electrolyte solution was applied to the three electrodes of SPCE (see figure 1b). All experiment was conducted at room temperature (25 ^{0}C).

2.3. Preparation of gold nanoparticles modified SPCE and glucose measurement

Gold nanoparticles were electrodeposited on SPCE (figure 1a) using cyclic voltammetry technique with a drop (35 µL) of a solution containing 5 mM $HAuCl_4$ through a modification of the previously reported procedures. Briefly, CV was sweep from -0.7 V to 0.4 V vs. AgCl/Ag in 10 cycles, scan rate 50 mV/s. Then the modified SPCE was washed with pure water and dried naturally at room temperature. Electrochemical measurements of glucose sensor were performed in which a three-electrode system was used with a printed carbon as the counter, a printed Ag/AgCl as the reference and electrodeposited gold modified SPCE as working electrode (see figure 1b). KOH 0.1M solution was used as electrolyte during all electrochemical measurements. Prepared D-glucose solutions were allowed to mutarotate overnight at room temperature before use.

3. Results and discussion

The photograph of SPCE in the figure 1a illustrates that this three-electrode system is very compact with mm in size and convenience for handling and electrochemical measurement (figure 1b) compared with conventional electrodes like glassy or carbon paste electrode. Figure 1c shows the SEM image of Au nanoparticles were electrodeposited on the surface of SPCE electrode. The Au nanoparticles have a size approximately 50 nm, high density, and well distribution. The results indicate electrochemical deposition method has a lot of advantages such as simple, onsite, no post-treatment requirement and very quick to prepare nanoparticles.

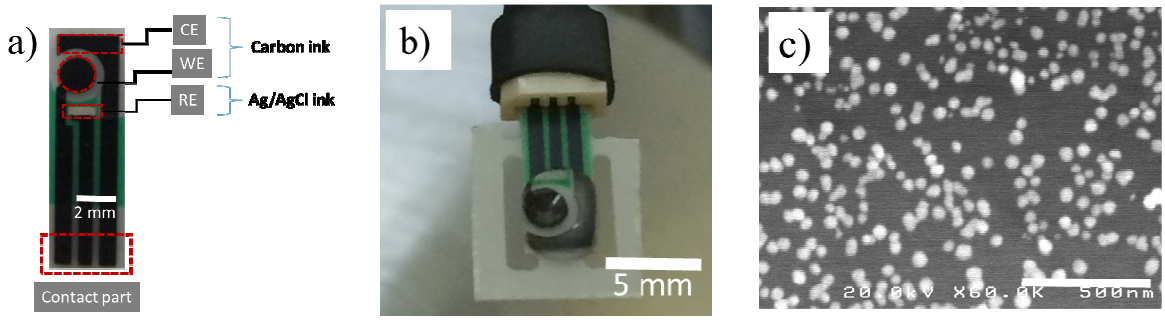

Figure 1. a) Photograph of Screen printed carbon electrode, b) electrochemical measurement set-up of SPCE c) SEM image of electrodeposited Au nanoparticles on the surface of SPCE.

The electrochemical properties of Au nanoparticles modified SPCE compared with bare SPCE in typical benchmark redox couple $K_3[Fe(CN)_6]$/ $K_4[Fe(CN)_6]$ in 0.1M KCl is shown in figure 2a. The Au nanoparticles modified SPCE enhanced the electron transfer rate and current intensity with the anode and cathode peak separation ΔE = 130 mV, and current intensity ratio i_a/i_c = 0.77, while for bare SPCE, the anode and cathode peak separation is ΔE = 200 mV, and peak current ratio i_a/i_c = 0.66. The formed surface area of electrodeposited Au nanoparticles on the surface of SPCE can be estimated by simple

sweep the modified SPCE in H_2SO_4 0.5M solution using cyclic voltammetry technique. The result shows in the figure 2b with two peaks around 1.0 V and 0.7 V vs. AgCl/Ag corresponding to the oxidation of gold to gold oxide and the reduction of gold oxide to gold again. According to [12] the real surface area of electrodeposited Au nanoparticles modified SPCE is calculated by assuming that the reduction of a monolayer of Au oxide requires 386 µC.cm^{-2}. The Q_c (shade area) for reduction of gold oxide to gold obtained from CV curve is 22.1 µC. The real active surface area of the gold nanoparticles electrodeposited on the SPCE is calculated to be 5.72 mm^2.

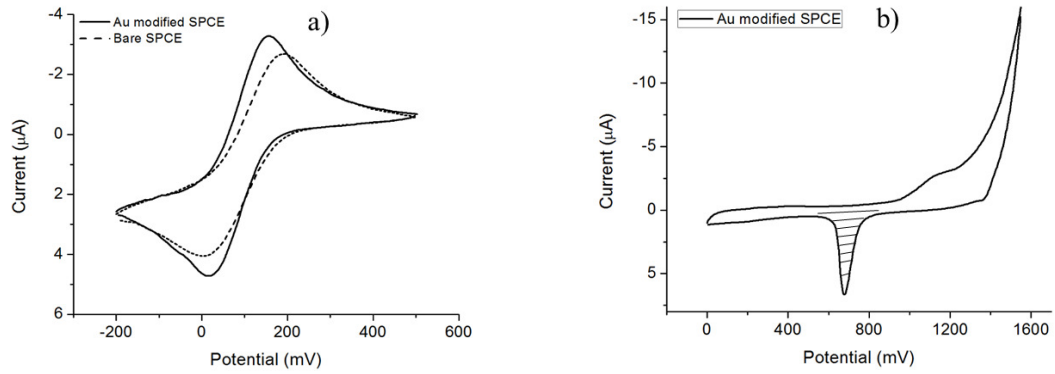

Figure 2. a) Cyclic voltammogram curves (CVs) of bare SPCE and Au nanoparticles modified SPCE in 1 mM $K_3[Fe(CN)_6]$/ $K_4[Fe(CN)_6]$ in 0.1M KCl, scan rate 50 mV/s. b) CV curve of electrodeposited Au nanoparticle modified SPCE in H_2SO_4 0.5M, scan rate 50 mV/s.

The electrochemical properties of Au nanoparticles modified SPCE in KOH 0.1M is shown in figure 3 (solid line). According to M. Pasta [13], the cyclic voltammogram (CV) of electrodeposited Au nanoparticles modified SPCE in KOH 0.1M in the absence of glucose one can see two electrochemical processes related to gold hydroxide formation and reduction. Peak around -0.3 V is attributed to the electrochemical adsorption of hydroxide ion on the surface of Au nanoparticles and the peak at 0.3 V is the formation of gold oxide. On the backward scan two peaks at -0.15V and -0.5V corresponding to the reduction of gold oxide and de-adsorption of hydroxide ion.

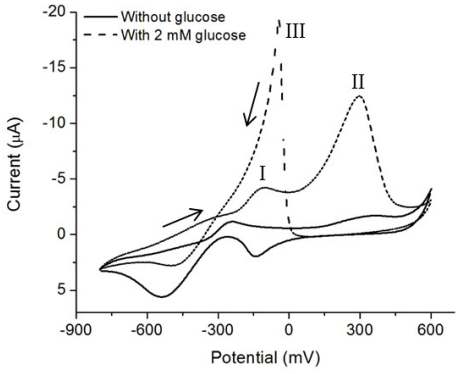

Figure 3. CV curves of Au nanoparticles modified SPCE in KOH 0.1M without and with 2 mM glucose, scan rate 50mV/s.

In the presence of glucose (2mM), the usual peaks of glucose electrooxidation at gold electrode are present (broken line in figure 3). Peak I is attributed to the molecules electrochemically adsorbed at the surface of the

electrode by dehydrogenation. The dehydrogenated molecule can be transformed to gluconate either by direct oxidation or through a δ-gluconolactone intermediate step, indistinguishable at room temperature (peak II). During the cathodic scan, gold hydroxide is reduced, and therefore glucose can be re-adsorbed and oxidized, generating an oxidative peak in the cathodic scan (peak III) used in a previous study to develop a new approach to glucose sensing. This cyclic voltammetric measurement shows that electrodeposited gold nanoparticles modified SPCE can be used to sense glucose in alkaline solution.

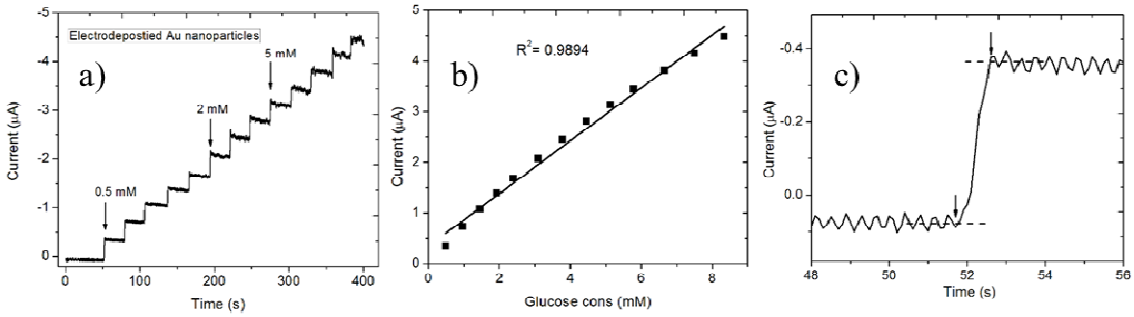

Figure 4. Amperometric of electrodeposited Au nanoparticles on SPCE in KOH 0.1M with a) different concentration of glucose from 0.5 mM to 8.5mM, b) linear relationship of glucose concentration vs. current intensity, c) the response time of current to added glucose.

Figure 4 shows the typical amperometric response of the gold nanoparticles modified SPCE to glucose oxidation in a stirring 0.1M KOH solution at applied potential of -0.2V vs. Ag/AgCl by successive addition of certain concentration of glucose. The selected applied potential was optimized and showed that in 0.1M KOH solution the best potential should be -0.2V vs. Ag/AgCl (data not shown). When an aliquot of glucose solution was dropped into the stirred KOH solution, the anodic current rose steeply to reach a stable value. The sensor could reach the steady state current within 1.0 s (see the arrows on figure 4c), indicating a very fast amperometric response behavior. The amperometry is widely used in a commercial product such as handheld glucose sensors due to its simple in electronic circuits and low cost compared with other electrochemical techniques as CV or differential pulse voltammetry. The sensor also illustrates the wide dynamic range of glucose concentration from 0.5 mM to 8.5 mM. Figure 4b shows the calibration curve for this oxidation process, indicating the relation between current intensity (i) vs. glucose concentration (C) on a linear plot. The calibration curve illustrates wide linear range from 0.5÷ 8.5 mM glucose with regression equation between glucose concentration (mM) and current intensity (μA) $y = 0.5216x + 0.3425$ ($R^2 = 0.9894$), which is overlap the normal physiological level of glucose 3÷8 mM (54-144 $mg.dL^{-1}$). The sensitivity of this fabricated sensors is 9.12 $\mu A/mA.cm^2$ and limit of detection was estimated about (LOD) 200 μM.

4. Conclusion

We have demonstrated that electrodeposited gold nanoparticles modified SPCE, the compact three electrode system, efficiently catalyze the oxidation of glucose in the absence of any enzymes and redox mediators. Gold

nanoparticles structure on SPCE has been successfully synthesized via simple electrochemical deposition technique. This sensor exhibits high sensitive properties with limit of detection as low as 200 µM and wide dynamic range from 0.5 mM to 8.5 mM. Our enzyme free sensor would extend clinical indices for glucose as indices for fitness not only to people with diabetes but also to general population.

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Cảm biến đường huyết không sử dụng enzyme dựa trên nền hạt nano vàng biến tính hệ ba điện cực thu nhỏ

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Tóm tắt: Một cảm biến glucose không sử dụng enzyme đã được phát triển dựa trên hạt nano vàng được tổng hợp bằng phương pháp kết tủa điện hóa trên bề mặt của hệ ba điện cực thu nhỏ (SPCE). Sự kết hợp của hạt nano vàng với hệ ba điện cực thu nhỏ làm cho cảm biến trở nên nhỏ gọn, giá thành rẻ

và có thể hiện thực việc đo đường huyết trong thực tế. Trong nghiên cứu này hạt nano có kích thước cỡ 50 nm được kết tủa điện hóa trực tiếp trên bề mặt điện cực từ dung dịch axit vàng, $HAuCl_4$. Sự có mặt của hạt nano vàng được khẳng định qua ảnh SEM. Hạt nano vàng biến tính bề mặt hệ ba điện cực thu nhỏ đã thành công trong việc xác đinh glucose. Cảm biến glucose không sử dụng enzyme này có khoảng hoạt động tuyến tính rộng từ 0.5 mM tới 8.5 mM và độ nhạy 9.12 $\mu A/mA.cm^2$ với giới hạn phát hiện đạt 200 µM.

Từ khóa: Cảm biến đường huyết không sử dụng enzyme, Hệ ba điện cực thu nhỏ, Điện phân hạt nano vàng.