



On-Off Ratiometric Electrochemical Biosensor for Accurate Detection of Glucose



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ABSTRACT

A highly selective and accurate on-off ratiometric electrochemical biosensor to detect glucose was proposed based on gold nanoparticles (AuNPs)-glucose oxidase (GOD) nanocomposites as the catalyst for both the oxidation of glucose and the electrochemical reduction of O_2 and the thionine as the inner reference signal for the first time. The reduction peak of O_2 catalyzed by AuNPs-GOD at -0.45 V decreased in GOD-glucose reaction in which the O_2 was consumed gradually to produce H_2O_2 . While, the reduction peak of the produced H_2O_2 catalyzed by thionine at -0.24 V increased gradually. By using the ratiometric peak current as detection signal, a novel on-off ratiometric electrochemical biosensor for glucose detection was developed and exhibited an acceptable detection limit of $11.66 \mu\text{M}$ and a wide linear range from $35.43 \mu\text{M}$ to 15 mM. The biosensor also exhibited high accuracy, high selectivity, good reproducibility and high sensitivity. The ratiometric electrochemical approach not only developed a new method for highly selective and accurate detection of glucose but also provided a good idea for accurate and selective analysis of other analytes.

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1. Introduction

Electrochemical biosensors are attracting extensive interest owing to their simple instrument, easy operation, etc [1–6]. Lots of electrochemical biosensors have been constructed for various applications in food industry, environmental analysis, medical diagnosis, etc [3,7–11]. However, the reproducibility of electrochemical biosensors is always a very serious disadvantage due to the change of the electrode area or the modified layer, which limits their extensive application. It will cause the variation of the background current for different electrodes, which makes the determination of analytes unreliable. Furthermore, the selectivity of electrochemical biosensors is another important issue needs to be resolved because the potential is always applied to the working electrode, which will cause some interference for complex samples.

Although the fluctuation of electrode area can be effectively overcome by normalizing the electrode area, the change of modified layer for regenerated electrode is inevitable. To improve the poor reproducibility originated from the change of modified

layer, a solution strategy was introduced into electrochemical biosensors where enzymes or other materials existed in the solution, only an bare or simply modified electrodes were used [12]. The reproducibility, regeneration and stability of electrochemical biosensors were improved greatly, but it was not suitable for some specific analysis such as in-vivo analysis and on-line analysis.

Recently, great attention has been paid to ratiometric electrochemical biosensors because they can overcome the environmental and personal factors and the change of modified layer to enhance the reproducibility and accuracy greatly [13–25]. For example, Tian et al. constructed a ratiometric electrochemical biosensor for Cd^{2+} detection by simultaneously modifying 6-(ferrocenyl) hexanethiol (FCHT) and protoporphyrin IX on the Au nanoparticles (AuNPs) modified electrode [24]. The protoporphyrin IX was used as a selective recognition element for Cd^{2+} over other metal ion such as Cu^{2+} , Fe^{3+} , Ca^{2+} owing to its high affinity for Cd^{2+} . The electroactive FCHT was used as the reference signal. Wei et al. used thionine and Ketjen to construct a ratiometric electrochemical biosensor for determination of vitamin C in living brains [25]. The assembled electroactive thionine acted as an inner reference and the Ketjen black was used to catalyze vitamin C. The ratiometric electrochemical biosensors actually demonstrated a reliable reproducibility and high accuracy, but the selectivity of

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electrochemical biosensors was not improved greatly because the reference signal was independent on the detection signal. Once the detection signal or the reference signal was affected by the interference, the detection results would be inaccurate.

In this work, a novel on-off ratiometric electrochemical biosensor to selectively and accurately determine glucose was developed by co-immobilizing thionine (Thi) and gold nanoparticles (AuNPs)-glucose oxidase (GOD) on AuNPs/three-dimensional kenaf stem-derived porous carbon (3D-KSC) [26–29]. As we all know, GOD could catalyze the oxidation of glucose accompanied by the reduction of O_2 into H_2O_2 [30–32]. The reduction of O_2 at -0.45 V was used as the detection signal, while the reduction of the produced H_2O_2 catalyzed by Thi at -0.24 V was employed as the internal reference to construct a novel on-off ratiometric electrochemical biosensor for selective and reliable detection of glucose. Our result showed that the proposed on-off ratiometric electrochemical biosensor exhibited acceptable stability, high selectivity, good accuracy and reproducibility for glucose detection.

2. Experimental section

2.1. Chemicals and reagents

The chloroauric acid ($HAuCl_4$) was obtained from Aladdin. Thionine (Thi) was purchased from Alfa Aesar. Glucose oxidase

(GOD) (EC 1.1.3.4, 140 U mg^{-1}) was purchased from Sigma-Aldrich. Glucose, $NaBH_4$, galactose, mannose, sucrose, NaCl, KCl, ascorbic acid (AA), dopamine (DA), urea, cysteine and uric acid (UA) came from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The kenaf stem (KS) was obtained from Futian farm (Ji'an, China). Other reagents were obtained from Guangdong Xilong Chemical Reagent Factory (Guangdong, China). The supporting electrolyte was 0.2 M NaH_2PO_4/Na_2HPO_4 (PBS, pH 6.0–8.0). Ultra-pure water purified by a Millipore-Q System (18.2 M Ω cm) was used.

2.2. Preparation of AuNPs-GOD nanocomposites

The AuNPs-GOD nanocomposites were prepared by one-pot reaction in which the $HAuCl_4$ was reduced by $NaBH_4$ in the presence of GOD [33]. The detail on the preparation of AuNPs-GOD nanocomposites was shown in Fig. S1 (Supporting Information). Since the GOD molecules contained $-SH$ and $-NH_2$ group, they could be assembled on AuNPs surface via Au-S or Au-N bond to form AuNPs-GOD nanocomposites. From the typical atomic force microscopy (AFM) image of AuNPs-GOD nanocomposites (Fig. S1A, Supporting Information), these AuNPs-GOD were found to be almost spherical and their diameter was around 28 nm. The UV–vis absorption spectrum of AuNPs-GOD nanocomposites (Fig. S1B, Supporting Information) showed two absorbance peaks at around 276 nm and 532 nm, corresponding to GOD (278 nm) [34] and AuNPs (525 nm) [35,36], respectively. The above results clearly

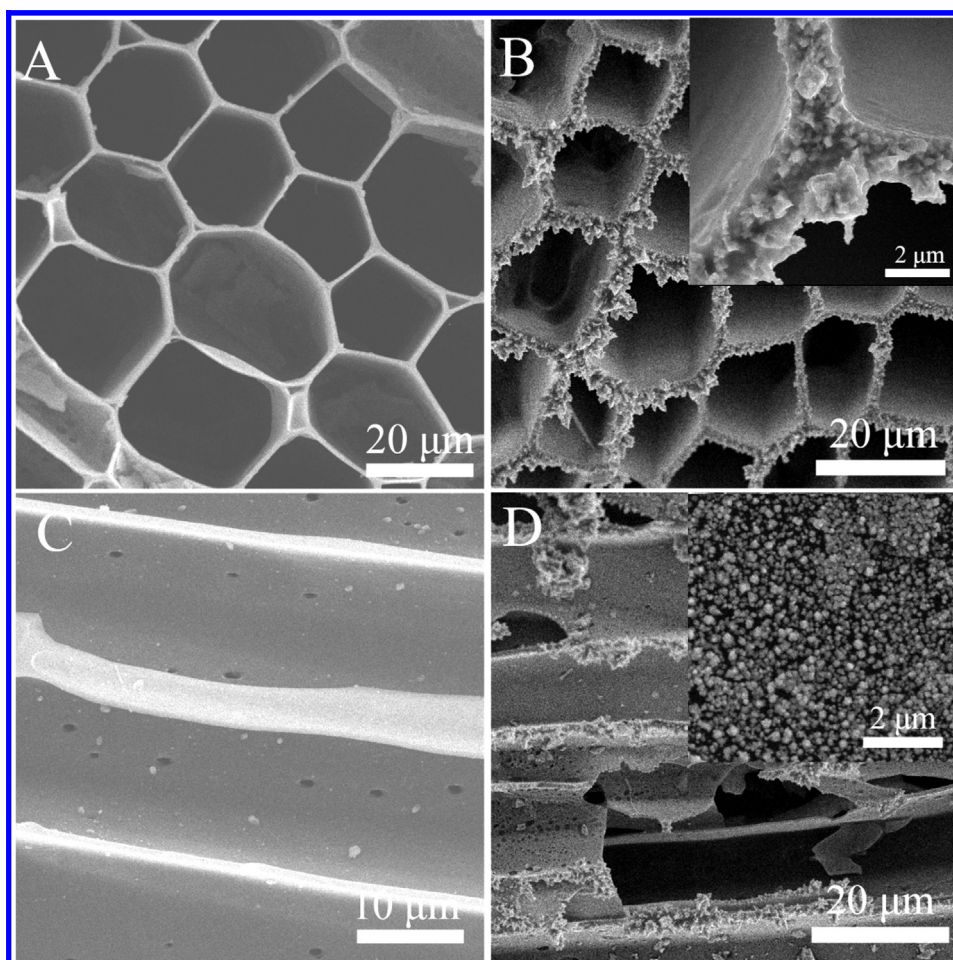


Fig. 1. SEM images of 3D-KSC (A, C) and 3D-KSC/AuNPs (B, D). Insets were the high-magnification SEM images.

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