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Novel glucose sensor with Au@Ag heterogeneous nanorods based on electrocatalytic reduction of hydrogen peroxide at negative potential

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ABSTRACT

A novel electrochemical glucose sensor based on Au@Ag heterogeneous nanorods (Au@Ag heterogeneous NRs) was developed. The Au@Ag heterogeneous NRs exhibited favorable electrocatalytic ability to reduce H_2O_2 at negative potential of about −0.6 V (vs. SCE). Further, the glucose oxidase (GOx)/Au@Ag heterogeneous NRs modified electrode was constructed as a glucose sensor, which exhibited wide linear range of 0.02–10 mM glucose in O_2-saturated phosphate buffered saline (PBS) at an applied potential of −0.4 V. Additionally, the glucose sensor showed good reproducibility and stability. Further, the proposed sensor showed good selectivity to common interferents (ascorbic acid, uric acid and dopamine), other saccharides, and 0.15 M chloride ions, which could be applicable for real human serum sample analysis.

1. Introduction

Blood glucose monitoring systems are important for the diabetics to manage their conditions, which attracted much attention in the field of clinical analysis and individual monitoring [1]. Many kinds of amperometric glucose sensors have been developed and commercialized in the past few decades [2–5]. On the one hand, lots of nonenzymatic glucose sensors were developed with good thermal and chemical stability [6,7], nevertheless, they usually work in alkaline solution, which is not suitable for the *in vivo* application. In addition, some nonenzymatic sensors can be seriously poisoned by the presence of chloride ions (Cl^-) [8–10]. On the other hand, the enzyme based glucose sensors have been widely used and exhibited excellent selectivity and high sensitivity, utilizing glucose oxidoreductase as catalyst [11]. For example, an enzyme based glucose sensor was developed by immobilizing glucose oxidase (GOx) in a poly (*o*-phenylenediamine) film, and a low response time was observed [12]. GOx was one of the most widely used enzymes in amperometric glucose sensors because of its high thermostability and good selectivity [13–16]. GOx could catalyze glucose oxidation to gluconolactone in the aid of O_2, resulting in the producing of H_2O_2. So the glucose detection could be achieved by measuring the produced H_2O_2 [17,18]. However, the oxidation of H_2O_2 needs a high positive potential [19], which might be severely involved in many interferents. So far, there have been some reports on the development of glucose based on H_2O_2 reduction at negative potential [20–23]. In addition, these sensors still had some disadvantages such as low current response and low stability. Therefore, materials with good electrocatalytic activity for H_2O_2 and excellent stability have attracted substantial interest.

With the development of nanotechnology, numerous novel nanomaterials especially noble metal nanomaterials were found to have catalytic activity towards H_2O_2 reduction, due to their high effective surface areas, size controlled electrical properties and excellent stability [24]. To date, pure Au nanoparticles [25,26]

Abbreviations: Au@Ag heterogeneous NRs, Au@Ag heterogeneous nanorods; SCE, saturated calomel electrode; GOx, glucose oxidase; PBS, phosphate buffered saline; TEM, transmission electron microscopy; GCE, glassy carbon electrode; CV, cyclic voltammogram; AA, ascorbic acid; UA, uric acid; DA, dopamine; PDDA, poly (diallyldimethylammonium) chloride; EG, ethylene glycol.

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and Ag nanoparticles [27–29] have been reported to be good electrocatalyst for H_2O_2. However, they still have some disadvantages, such as exhibiting activity only at alkaline pH condition[7] and experiencing serious poison in the presence of excess Cl^- [6]. Considering excellent catalytic activity of Au [20,30] and Ag [20,21], the Au@Ag heterogeneous nanorods (Au@Ag heterogeneous NRs) were synthesized and had been proved to be of good stability and biocompatibility according to our previous work [31]. In this work, the electrocatalytic activity of the Au@Ag heterogeneous NRs for H_2O_2 reduction was investigated. Then, the Nafion/GOx/Au@Ag heterogeneous NRs modified electrode was constructed as a glucose sensor and experiments were performed in neutral pH condition at a low potential of −0.4 V. The prepared sensor had good reproducibility, stability, and selectivity for common interferents, which could be used for the sensitive determination of glucose in the presence of 0.15 M Cl^-. Finally, the sensor was used to detect glucose in human blood serum successfully.

2. Experimental

2.1. Chemicals and reagents

Ascorbic acid (AA), uric acid (UA), dopamine (DA), glucose, xylose (Xyl), galactose (Gal), lactose (Lac), sorbitol (Sor), sucrose (Suc), arabinose (Ara), maltose (Mal), and H_2O_2 (30%) were purchased from Sinopharm Chemical Reagent Co. Nafion (perfluorinated ion-exchange resin, 5 wt% solution in a mixture of lower aliphatic alcohols and water) and GOx was purchased from Sigma–Aldrich. 0.05 wt% Nafion was diluted from 5 wt% Nafion. Ultrapure water was prepared using a Millipore Milli-Q system and used throughout. Phosphate buffer saline (PBS, pH 7.4 containing 0.15 M NaCl) was used as the supporting electrolyte. All other reagents were of the highest grade and all solutions were prepared with ultrapure water.

2.2. Preparation of Au@Ag heterogeneous NRs

Au@Ag heterogeneous NRs were synthesized according to our previous publications [32,33] with minor modification. Briefly, 0.25 mL of 0.5 M $HAuCl_4$ (0.125 mM) aqueous solution, 1 mL of poly (diallyldimethylammonium) chloride (PDDA) (1.25 mM), and 0.25 mL of 0.5 M $AgNO_3$ (1.25 mM) aqueous solution were introduced into 49 mL of ethylene glycol (EG) solution in a brown glass vial. The mixture solution was vigorously stirred for about 30 s at room temperature and ambient conditions. The as-prepared mixture solution was subsequently reacted at 200 °C for 60 h in air in an oil bath. The final product was collected by centrifugation at 14,500 rpm and washed repeatedly with pure water and ultrasound to remove any residual EG or PDDA.

2.3. Preparation of Nafion/GOx/Au@Ag heterogeneous NRs composite films modified glassy carbon electrode

The glassy carbon electrode (GCE) was polished to a mirror using 0.3- and 0.05-μm alumina slurry, followed by rinsing thoroughly with deionized water. After ultrasonic processing in a hydrous ethanol solution and ultrapure water successively, the electrode was rinsed with ultrapure water and dried at room temperature. In preparation of Nafion/Au@Ag heterogeneous NRs/GCE, 10 μL of Au@Ag heterogeneous NRs suspension solution was dropped onto the surface of pretreated GCE and left to dry at room temperature to get the Au@Ag heterogeneous NRs/GCE. Subsequently, 5 μL of Nafion solution (0.05 wt%) was syringed to the modified GCE surface to prevent the NRs from running off the electrode. The fabrication of Nafion/GOx/Au@Ag heterogeneous NRs/GCE was similar with that of Nafion/Au@Ag heterogeneous NRs/GCE, except that 10 μL of GOx and Au@Ag heterogeneous NRs mixture (2:1 in volume) was dropped onto the inverted bare GCE rather than Au@Ag heterogeneous NRs suspension solutions and dried overnight at 4 °C in refrigerator, and 5 μL of Nafion solution (0.05 wt%) was added afterwards to immobilize the enzyme and to shield the possible influence of negatively charged interferents. The modified electrode was stored at 4 °C in refrigerator when not in use. Before measurements, the as-prepared electrodes were immersed into PBS buffer to remove any loosely combined composite.

2.4. Apparatus and measurements

Electrochemical measurements were performed using a CHI660E potentiostat (CH Instruments, Chenhua, Shanghai, China). The electrochemical response was measured in a conventional three-electrode system using a chemically modified GCE as working electrode, a Pt wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. All potentials were reported in this context with respect to this reference. All measurements were performed at room temperature (~25 °C). The synthesized Au@Ag heterogeneous NRs were characterized by transmission electron microscopy (TEM, Hitachi, H-7650).

3. Results and discussion

3.1. Characterization of Au@Ag heterogeneous NRs

The surface morphology of the as-prepared Au@Ag heterogeneous NRs was observed by TEM. As displayed in Fig. 1, the NRs are average 200 nm long and 65 nm wide. The average aspect ratio of these NRs was 3.1. It must be mentioned that the Au@Ag heterogeneous NRs used in this report were quite different from the gold/silver core–shell nanorods (Au@Ag core–shell NRs) in the previous report [34]. The Au nanoparticles were fully embedded into Ag and the clear boundaries of Ag and Au were seen, leading to the formation of the Au@Ag heterogeneous NRs instead of alloy or core–shell NRs. The molar ratio of Ag to Au in the as-synthesized Au@Ag heterogeneous NRs was above 10:1, that is, the main composition of Au@Ag heterogeneous NRs was silver (>90%) [33]. Whereas, the composition of Ag in Au@Ag core–shell NRs was generally lower than 50% [34]. Meanwhile, Au@Ag core–shell NRs used in the previous paper was synthesized through the multi-steps seed-mediated growth procedure using Au NRs as seeds in the cetyltrimethylammonium bromide (CTAB) aqueous solution. The length of Au@Ag core–shell NRs was strongly limited by that of

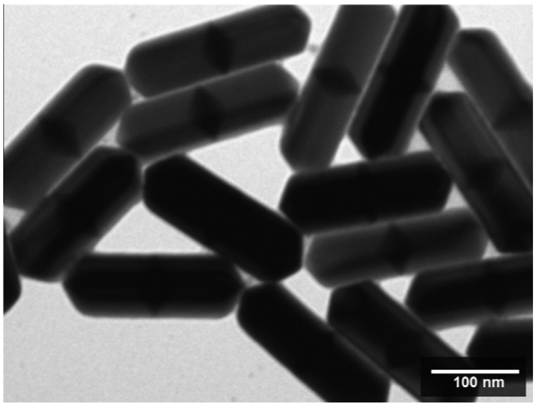

Fig. 1. The TEM images of synthesized Au@Ag heterogeneous NRs.