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Electrochemical sensing platform based on Pd–Au bimetallic cluster for non-enzymatic detection of glucose

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ABSTRACT

Bimetallic Pd–Au cluster was synthesized through a direct chemical reduction method and utilized for the fabrication of electrochemical sensing platform. Scanning electron microscopy (SEM) characterization indicated the obtained Pd–Au cluster displays branch-type structure that composed of nanowires. As a demonstration of the application of the sensing platform, the performance of the platform toward non-enzymatic electrochemical detection of glucose was studied. Analytical results show improved activity of the Pd–Au cluster toward glucose oxidation with high sensitivity, wide linear range and good stability. When the electrode was used for the detection of glucose in blood samples, the glucose contents detected by the electrode was in good agreement with those from the hospital. The proposed electrochemical sensing platform can certainly be expanded to the fabrication of other kinds of electrochemical sensors and biosensors.

1. Introduction

Metallic nanomaterials, due to their interesting physical and chemical properties, have found wide applications in various sensing and biosensing areas [1–3]. Among the reported properties, the catalytic activity of metal nanomaterials has drawn special attention. Metal nanomaterials display significantly improved catalytic activity when compared to their bulk counterpart [4–6]. For example, when used as signal tags for signal amplification in biosensing, metal nanomaterials were usually act as catalysts to trigger the detectable signal [7–9]. In electrochemical sensing, the electrocatalytic activity of meal nanomaterials toward different molecules, such as hydrogen peroxide, glucose, ascorbic acid, uric acid and dopamine has been widely studied [10–13].

Various structured metallic nanomaterials, such as nanoparticles, nanorod and nanoclusters have been synthesized by different strategies [14–16]. Besides the nanomaterials composed of a single metal, bimetallic alloys have also been widely studied. Bimetallic nanomaterials based on the bifunctional mechanism and the electronic effect usually exhibited improved properties than nanomaterials composed of single metal. The bimetallic nanomaterials reported include, but not limited to bimetallic nanoclusters, bimetallic aerogels, core–shell bimetallic nanoparticles and bimetallic nanocrystals [17–20].

Due to the rising requirement for clinical diagnosis and personal care, sensitive and precise detection of glucose in blood samples has always been the hot research subject [21–23]. Although different techniques that have been reported for glucose detection, electrochemical sensors are still recognized as the most successful analytical tool for glucose testing due to their high sensitivity, low cost and simple instrumentation. Typically, the enzyme, glucose oxidase (GOx) is immobilized onto electrode surface to catalyze glucose reaction and thus enable the biosensor with high sensitivity and good selectivity toward glucose detection [24–26]. However, the enzymes are suffered from poor stability, which inhibited the application of the biosensors in some areas, such as food monitoring and bioprocess control. In these areas, extreme conditions are required (e.g., high temperature and extreme pH values) [27]. On the contrary, non-enzymatic glucose biosensors based on the direct electrocatalytic oxidation of glucose could circumvent such issues [28,29]. To enhance the catalytic activity of the electrode toward glucose, various nanomaterials, especially metal based nanomaterials, including gold, palladium, platinum and nickel have been used to modify the electrodes to achieve non-enzymatic glucose detection [30–33]. Despite the reported studies, searching for highly-efficient and stable nanomaterials for glucose oxidation is still of great interest.

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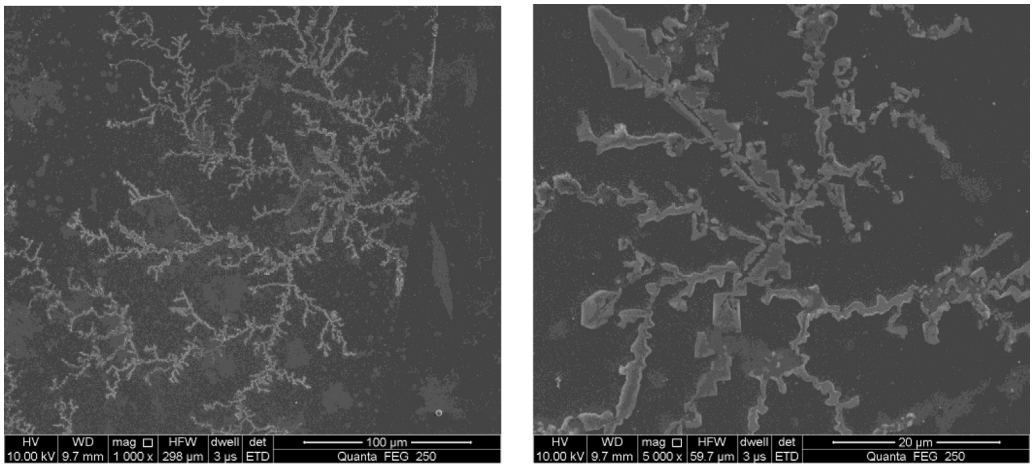

Fig. 1. SEM characterization of the synthesized Pd–Au bimetallic cluster.

Here, in this paper, we synthesized Pd–Au bimetallic clusters and then developed electrochemical sensing platform based on the clusters for non-enzymatic detection of glucose. The Pd–Au bimetallic clusters were synthesized simply by reducing the mixture of K_2PdCl_4 and $HAuCl_4$ together with $NaBH_4$. The sensor preparation process is rather simple. For the modification of the electrode, the clusters were directly dropped onto the electrode surface. The electrochemical response of the modified electrode toward glucose was characterized in detail. The modified electrode displays high sensitivity as well as good selectivity and stability to glucose detection. The synthesized Pd–Au bimetallic cluster may be used as catalyst in different areas and the reported electrochemical sensing platform could also be applied for the fabrication of various electrochemical sensors and biosensors.

2. Experimental

2.1. Reagents and apparatus

Potassium tetrachloropalladate(II) (K_2PdCl_4) (99.9%), chloroauric acid ($HAuCl_4$) (99.9%), glucose and sodium hydroxide (NaOH) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Uric acid (UA), ascorbic acid (AA), chitosan (MW 140,000–220,000) and sodium borohydride ($NaBH_4$) were purchased from Sigma–Aldrich. For real sample analysis, the blood samples were obtained from the Second Xiang-ya Hospital affiliated to Central South University. All other reagents were of analytical grade and deionized water (MilliQ, 18.2 MΩ) was used for preparing aqueous solutions throughout the experiments.

Electrochemical measurements were performed on a CHI-650D electrochemical workstation (Shanghai CH Instruments Co., China). A conventional three-electrode system was used with a glassy carbon (GC, 3 mm in diameter) as the working electrode, a saturated calomel electrode as the reference electrode and a platinum wire as the auxiliary electrode. Scanning electron microscopy (SEM) images were obtained on Nova NanoSEM230 (FEI, USA).

2.2. Synthesis of Pd–Au bimetallic cluster

The synthesis of the Pd–Au bimetallic cluster was according to reference reports with minor revisions [18]. Freshly prepared K_2PdCl_4 and $HAuCl_4$ solution were mixed together with the final concentration of K_2PdCl_4 and $HAuCl_4$ both 1 mM. After stirring for about 10 min, 375 μL of 40 mM $NaBH_4$ solution was quickly added into above mixture solution. The color of the solution was immediately turned from light yellow to dark gray. The solution was kept stirred for another 30 min and then settled at room temperature still for about 3 days. Finally, the Pd–Au cluster was separated through centrifuge.

The Pd and Au clusters were synthesized in a similar way by reducing 1 mM K_2PdCl_4 or $HAuCl_4$ with $NaBH_4$.

2.3. Electrode preparation

For the modification of the electrode, 20 μL of the synthesized Pd–Au cluster solution was added onto the GC electrode surface. After dried, another 7.5 μL of chitosan solution (1%, w/w) was dropped onto the electrode surface. The electrode was then dried under infrared lamp.

3. Results and discussion

The synthesis of the Pd–Au bimetallic cluster was simple and efficient [18]. $NaBH_4$ was used as reductant and was directly added into the mixture containing both K_2PdCl_4 and $HAuCl_4$. The obtained Pd–Au bimetallic cluster were then collected and characterized by SEM. As shown in Fig. 1, the cluster composed mainly of nanowires that fused and interconnected to form a branch-type structure. The diameter of the nanowires is around 500 nm. The corresponding energy dispersive X-ray spectroscopy (EDX) data indicated the presence of Pd and Au in the cluster (Supporting Information, Fig. S1).

To modify the electrode, the cluster was directly dropped onto the electrode surface. After dried, another chitosan layer was coated onto the electrode to prevent the leakage of the cluster from the electrode surface and improve the stability of the electrode. The resulting electrode was then characterized by cyclic voltammetry (CV) in detail. First, the characterization of the electrodes in $K_3Fe(CN)_6$ indicated no obvious increase of the electrode surface area after the modification of the Pd–Au cluster (Supporting Information, Fig. S2). Fig. 2 shows the CV curves of the electrode in 0.1 M NaOH in the absence and presence of glucose. Without glucose, the curve shows a pair of strong current peaks, typical characteristics of metal Pd in base solutions (curve a). The peak at around −0.3 V was ascribed to the formation of Pd oxide, while the peak at −0.4 V was due to the stripping of Pd oxide [34]. After the addition of 5 mM glucose, another sharp current peak was appeared at −0.05 V, which was ascribed to the oxidation of glucose at the