

# Nonenzymatic Electrochemical Sensor Based on PdAu Nanoflowers for the Detection of Hydrogen Peroxide

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In this work, PdAu nanoflowers was synthesized and used to fabricate hydrogen peroxide sensor. The sensor was fabricated by simple dropping of the mixed solution of chitosan and PdAu nanoflowers on a glassy carbon electrode. Using electrochemical impedance spectroscopy and cyclic voltammetry, we characterized the modified electrode. The proposed sensor exhibited a good performance due to the excellent electrocatalytic activity of PdAu nanoflowers toward H<sub>2</sub>O<sub>2</sub> in a wide linear range from 0.05 to 12 mM with a low detection limit of 1.5 μM (S/N=3). Moreover, the proposed sensor exhibited satisfying reproducibility and stability. The practical application of the nonenzymatic sensor was investigated via determination of H<sub>2</sub>O<sub>2</sub> in real disinfected fetal bovine serum samples.

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**Keywords:** PdAu nanoflowers; Electrocatalytical reduction; Hydrogen peroxide; Nonenzymatic sensor

## 1. INTRODUCTION

The rapid and sensitive detection of H<sub>2</sub>O<sub>2</sub> is very important because it has been applied in many fields, such as, foods safety [1], agriculture products [2], chemical and biochemical industry [3,4], clinical and environmental control [5,6]. Over the past years, the determination of H<sub>2</sub>O<sub>2</sub> was based on horseradish peroxidase [7-10]. Unfortunately, the enzyme-based methods have disadvantages including the high cost, instability of enzymes [11], demand on good microenvironment, and easy to lose their catalytic activity during measurements [12]. Because nanoparticles such as Ag, Pd, Au and Pt possess many advantages including catalytic activities, stability and convenience of electron transfer, they have been used as substitutes for enzymes in the fabrication of electrochemical sensor for H<sub>2</sub>O<sub>2</sub> [13-16]. Interestingly, due to the addition of the second metal, bimetallic nanoparticles are of superior

catalytic performances as compared to the monometallic counterparts [17-20]. Recently, enzyme-free, mediator-less amperometric sensors for H<sub>2</sub>O<sub>2</sub> based on bimetallic nanoparticle such as PdFe, PtAu, and PtPd was reported [21-23]. Furthermore, catalytic properties were critically dependent on the shape of bimetallic nanoparticle [24,25]. For example, AuPd nanodendrites exhibited much better catalytic activity than spherical AuPd catalysts [26].

In this work, we prepared bimetallic PdAu nanoflowers to fabricate an electrochemical sensor for the detection of H<sub>2</sub>O<sub>2</sub>. The sensor evaluation showed the Pd-Au nanoparticles have excellent electrocatalytic activity towards H<sub>2</sub>O<sub>2</sub>, and a good performance in the direct estimation of H<sub>2</sub>O<sub>2</sub> with high sensitivity, good reproducibility and stability.

## 2. EXPERIMENTAL

### 2.1. Materials

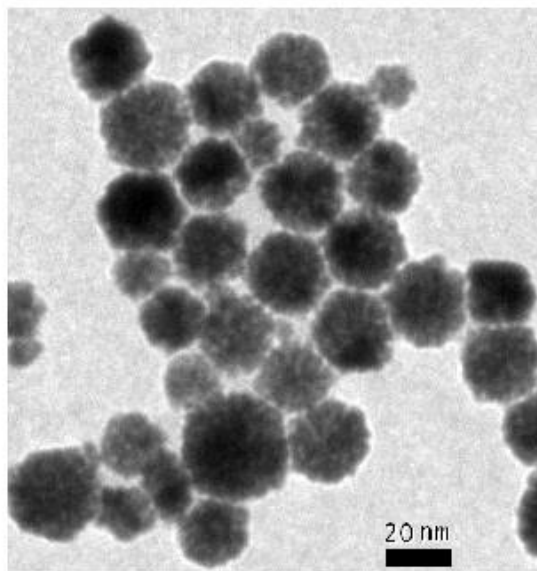
HAuCl<sub>4</sub>, ascorbic acid, K<sub>2</sub>PdCl<sub>4</sub>, chitosan (Chit) and poly(vinyl pyrrolidone) (PVP) were obtained from Sigma-Aldrich. H<sub>2</sub>O<sub>2</sub> (30%, v/v aqueous solution) was purchased from Jiangsu Tongsheng Chemical Reagent Company. The supporting electrolyte used was a 0.1 M phosphate buffer solution (PBS, pH 7.0), prepared using Na<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub>. A 5 mg/mL chitosan solution was prepared by dissolving 10 mg chitosan in 2.0 mL of 0.1 M acetic acid.

### 2.2. Apparatus

Electrochemical measurements including cyclic voltammetry (CV), electrochemical impedance spectra (EIS), and differential pulse voltammetry (DPV) were performed with a CHI 660A electrochemistry workstation (Shanghai CH Instruments, China). A three-electrode system which was made of a Pt electrode, a saturated calomel electrode (SCE), and a glass carbon electrode modified with PdAu nanoflowers–chitosan film was used. The sizes of the PdAu nanoflowers were estimated with transmission electron microscopy.

### 2.3. Preparation of bimetallic PdAu nanoflowers

The bimetallic PdAu nanoflowers were synthesized according to the method reported by Lee et al. with a slight modification [24]. In a typical synthesis, 1 mL of a 5 mM aqueous solution of HAuCl<sub>4</sub>/K<sub>2</sub>PdCl<sub>4</sub> mixtures in molar ratios of 1/1 was added to 47 mL of purified water. Then, 1 mL hydrazine with a concentration of 100 mM was added into the mixed solution. After 15 s, an aqueous solution of PVP (5 mg/mL, 1 mL) was added dropwise under vigorous stirring. The mixture was kept stirring at 25 °C for another 1 h. The resulted PdAu nanoflowers were collected by centrifugation at 12000 rpm for 10 min, washed three times with water. Then the product was redispersed into water for further use. The TEM image of PdAu nanoflowers was shown in Figure 1.



**Figure 1.** The TEM image of PdAu nanoflowers.

#### 2.4. Preparation of modified electrode

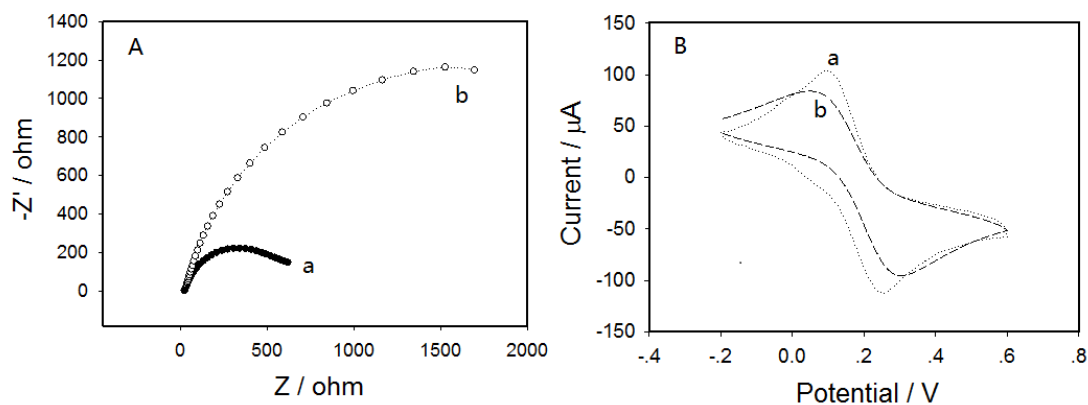
First, the glass carbon electrode (GCE, 4 mm) was polished repeatedly with 0.3 and 0.05  $\mu\text{m}$  alumina slurries sequentially, followed by successive sonication in doubly distilled and ethanol. Then the electrode was dried at room temperature. After that, 10  $\mu\text{L}$  homogeneous solution which was prepared by mixing PdAu nanoflowers (2 mg/mL) and chitosan (5 mg/mL) thoroughly (in a volume ratio of 1:1) with ultrasonication for 1 h was dropped on the surface of the cleaned GCE electrode.

### 3. RESULTS AND DISCUSSION

#### 3.1 Electrochemical characteristics of electrodes

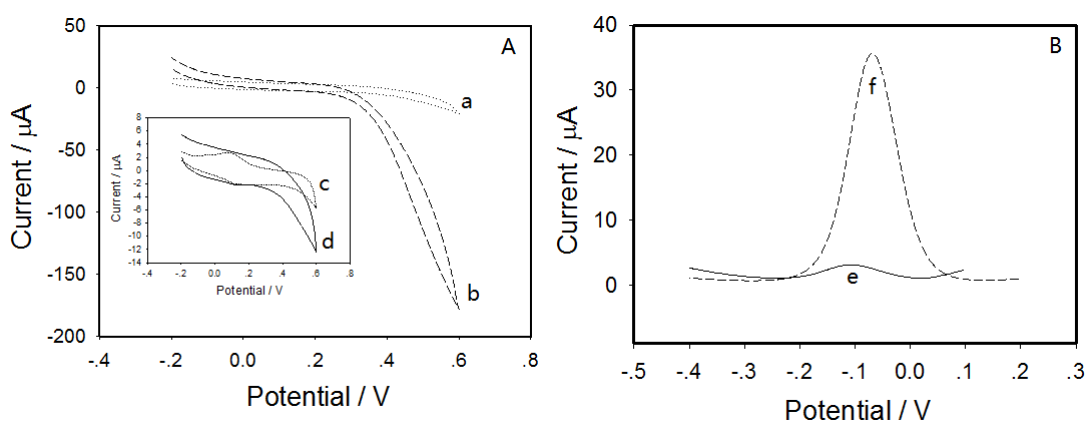
The various steps of modifying electrode were controlled by electrochemical impedance spectroscopy (EIS). Generally, the semicircle diameter of EIS equaled to the electron transfer resistance (Ret) [27]. EIS was measured in 5.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  containing 0.1 M KCl. Figure 2A shows the EIS of the bare electrode had a small semicircle diameter (curve a), implying low Ret to the redox probe dissolved in electrolyte solution. After electrode was modified with Chit-PdAu nanoflowers film, semicircle diameter increased (curve b) due to the increasing of Ret.

CV measurements were also used to characterize the modified electrode and performed in 5 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$  at a scan rate of 100  $\text{mV s}^{-1}$ . As shown in Figure 2B, the results were consistent with that resulting from EIS.



**Figure 2.** (A) EIS of bare electrode (a) and Chit-PdAu modified electrode (b). (B) CV profiles of bare electrode (a) and Chit-PdAu modified electrode (b). All measurements were processed in 5 mM  $\text{Fe}(\text{CN})_6^{4-/3-}$ .

### 3.2. Electrochemical behavior of different modified electrodes toward $\text{H}_2\text{O}_2$



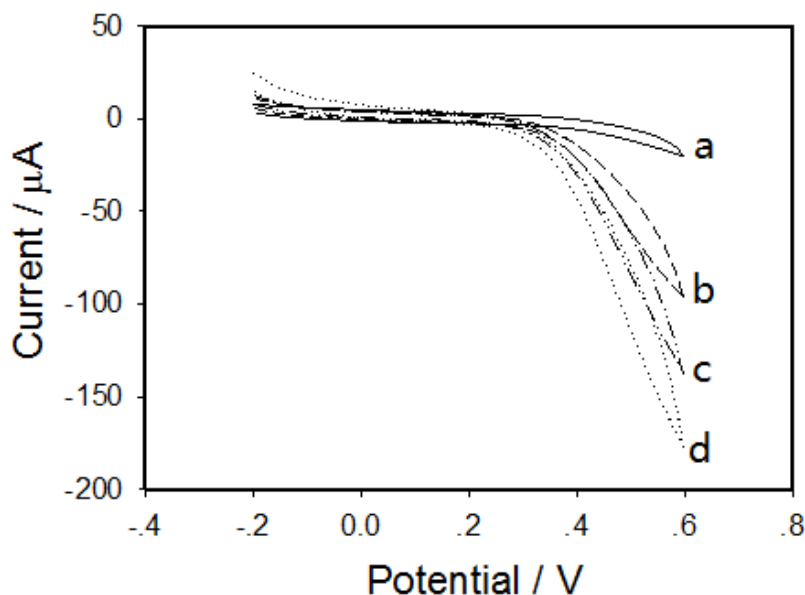
**Figure 3.** (A) CVs of chitosan modified GCE (a) and Chit-PdAu nanoflower modified GCE (b) in the presence of 10 mM  $\text{H}_2\text{O}_2$  (insert of A: CVs of chitosan modified GCE (c) and Chit-PdAu nanoflower modified GCE (d) in the absence  $\text{H}_2\text{O}_2$ ). (B) DPV responses of Chit-PdAu nanoflower modified GCE in the absence  $\text{H}_2\text{O}_2$  (e) and in the presence of 10 mM  $\text{H}_2\text{O}_2$  (f).

The cyclic voltammogram of different modified electrodes in 0.1 M PBS (pH 7.0) was shown in Figure 3A. In the presence of 10 mM  $\text{H}_2\text{O}_2$ , the reduction current of the chitosan modified GCE (Fig. 3A, curve a) were small. However, obvious increase of reduction current of the Chit-PdAu nanoflower modified GCE (Figure 3A, curve b) was observed. The increase of current indicated the electrocatalytic activity of PdAu nanoflowers toward  $\text{H}_2\text{O}_2$ . In the absence of  $\text{H}_2\text{O}_2$ , the reduction currents of the chitosan modified GCE (Figure 3A, curve c), and Chit-PdAu nanoflower modified GCE (Figure 3A, curve d) were also small. The phenomenon was in accordance with that reported by Qin [18]. Using differential pulse voltammetry (DPV) method, we also verified the electrocatalytic activity of PdAu nanoflowers toward  $\text{H}_2\text{O}_2$ . As can be seen from Figure 3B, in the absence of  $\text{H}_2\text{O}_2$ , the peak current of Chit-PdAu nanoflower modified GCE (Figure 3B, curve e) were small ( $3\mu\text{A}$ ). While the peak current of Chit-PdAu nanoflower modified GCE was substantial increase ( $37\mu\text{A}$ ) in the presence

of 10 mM H<sub>2</sub>O<sub>2</sub> (Figure 3B, curve f).

### 3.3. Comparison of electrocatalytic activity of different nanomaterials toward H<sub>2</sub>O<sub>2</sub>

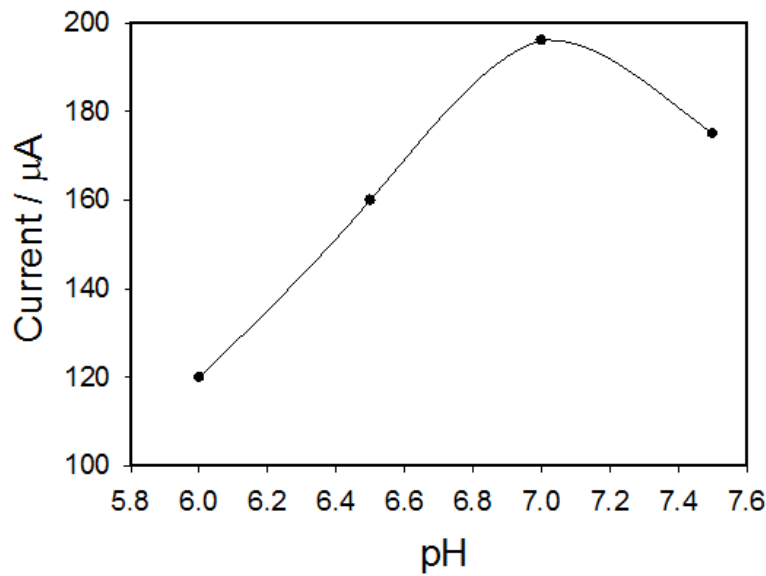
The bimetallic nanoparticles exhibit improved catalytic activity comparing with the monometallic components [21, 28]. The CV of Chit, Chit/Au nanoparticles, Chit/Pd nanoparticles, and Chit-PdAu nanoflowe modified electrodes was carried out in PBS solution containing 10 mM H<sub>2</sub>O<sub>2</sub>. Figure 4 shows that the reduction current gradually increased from curve a to d, indicating the electrocatalytic activity of PdAu nanoflowers toward H<sub>2</sub>O<sub>2</sub> is the highest among these different nanomaterials.



**Figure 4.** CV of chitosan modified GCE (a), Chit-Au nanoparticles modified GCE (b), Chit-Pd nanoparticles modified GCE (c), and Chit-PdAu nanoflower modified GCE (d) in the dpresence of 10 mM H<sub>2</sub>O<sub>2</sub>.

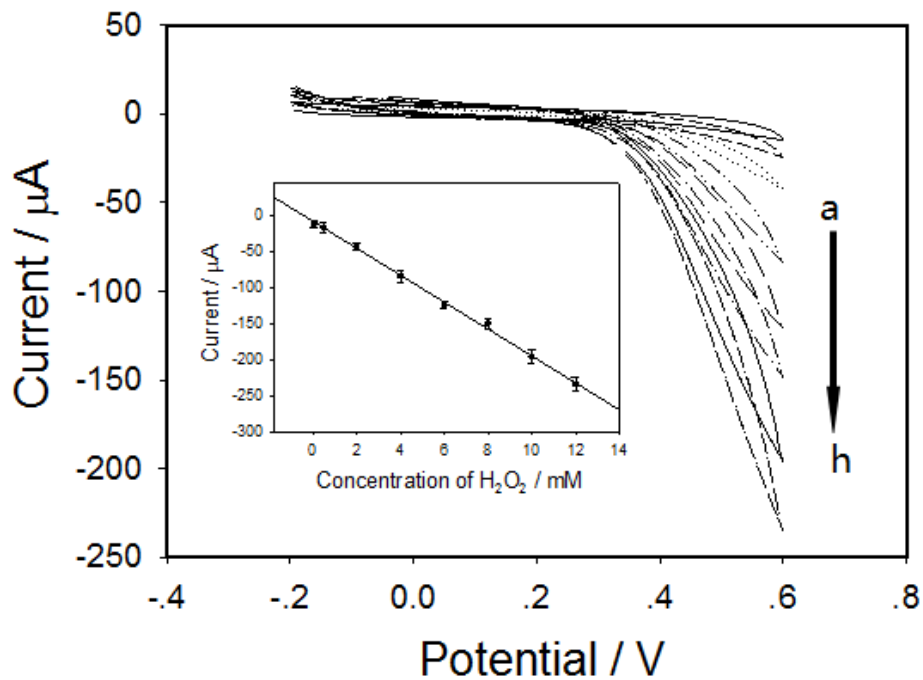
### 3.4. The effect of pH of PBS solution on the sensor response

The effect of pH of PBS solution on the reduction current of Chit-PdAu/GCE towards 10 mM H<sub>2</sub>O<sub>2</sub> was investigated. Figure 5 showed that the maximum current was obtained at 7.0. Thus, pH 7.0 PBS (0.1 M) buffer was selected for further use.



**Figure 5.** The effect of pH of PBS solution on the reduction current of the sensor toward 10 mM  $\text{H}_2\text{O}_2$ .

3.5. The detection of  $\text{H}_2\text{O}_2$



**Figure 6.** CV responses of the sensor to different concentrations of  $\text{H}_2\text{O}_2$  from a to h: 0.05, 0.5, 2.0, 4.0, 6.0, 8.0, 10.0, 12.0 mM. Insert: calibration curve of the sensor to different concentrations of  $\text{H}_2\text{O}_2$ ,  $n=3$ .

The signal of the fabricated sensor was resulted from the electrocatalytic activity of PdAu nanoflowers towards  $\text{H}_2\text{O}_2$ . Figure 6 presents the CVs of Chit-PdAu nanoflowers modified electrodes

in 0.1M PBS (pH 7.0) in the presence of different concentration of H<sub>2</sub>O<sub>2</sub>. The reduction currents corresponding to the potential value of 0.6 V enhanced with increasing of the concentration of H<sub>2</sub>O<sub>2</sub>. The linear range between catalytic current and concentration of H<sub>2</sub>O<sub>2</sub> was from 0.05 to 12 mM with a detection limit of 1.5 μM at a signal-to-noise ratio of 3 (S/N = 3).

A comparison of the sensor fabricated by us in this work with other nonenzymatic H<sub>2</sub>O<sub>2</sub> electrochemical sensors was presented in Table 1. As can be seen from Table 1, the electrode modified with Chit-PdAu nanoflower has favorable analytical performance.

**Table 1.** Comparison of the proposed sensor and other nonenzymatic H<sub>2</sub>O<sub>2</sub> sensors.

Modified electrode	Linear range (mM)	Detection limit (μM)	References
Ag/TiO <sub>2</sub> /GCE	0.1–60	1.7	29
Au/GCE	0.1–50	4	30
PtSnO <sub>2</sub> /C/GCE	0.001–0.1	0.1	16
SePt/GCE	0.01–15	3.1	31
PdFe/GCE	0.5–6	2.1	21
PdAu/GCE	0.05–12	1.5	This work

### 3.6. Reproducibility and stability of the sensor

In order to investigate the reproducibility of the sensor, an electrode modified with Chit-PdAu nanoflower was used to analyze 5 samples containing 10 mM of H<sub>2</sub>O<sub>2</sub>. The relative standard deviation of current responses was 5.3%, indicating a good reproducibility of the proposed sensor. The long-term stability of the H<sub>2</sub>O<sub>2</sub> sensor was also studied every 7 days for 10 mM of H<sub>2</sub>O<sub>2</sub>. The current decreased by 6.1% of the initial value after 4 weeks, which showed a good stability.

### 3.7. Real sample analysis

In order to investigate the practical application of the proposed sensor, a standard addition method was used to determine the concentration of H<sub>2</sub>O<sub>2</sub> in disinfected fetal bovine serum sample solution. The samples were prepared by diluting 100 times with 0.1 M PBS (pH 7.0). Each sample was measured three times. As can be seen from Table 2, satisfactory recovery was obtained, demonstrating the feasibility of the proposed sensor for detection of H<sub>2</sub>O<sub>2</sub> in real samples.

**Table 2.** Determination of H<sub>2</sub>O<sub>2</sub> added in disinfected fetal bovine serum with the proposed sensor (n=3)

Samples	Added (mM)	Founded (mM)	Relative deviation (%)
1	0.5	0.53	6.0
2	2	1.93	-3.5
3	6	6.28	4.7

#### 4. CONCLUSIONS

In summary, PdAu nanoflowers were synthesized and a nonenzymatic sensor for the determination of H<sub>2</sub>O<sub>2</sub> was fabricated. The sensor exhibited a wide linear concentration range and low detection limit due to the excellent catalytic ability of PdAu nanoflowers. Furthermore, the sensor exhibited a good reproducibility and long-term stability. It was applied to detect H<sub>2</sub>O<sub>2</sub> concentration of real samples and satisfactory results were obtained. This study may provide a feasible approach for sensing of clinical and environmental analytes.

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