

The Nonenzyme Ethanol Sensor Based on Pt NPs and Fe₃O₄ MNPs Modified Au Electrode

JUN WAN*, XIUJU MA, LING XING AND GUANG YIN

*College of Environment and safety Engineering, Key Laboratory of Eco-chemical Engineering,
Ministry of Education, Qingdao University of Science and Technology,
Qingdao 266042, China.*

wanjundz@sohu.com*

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Summary: The none enzyme ethanol sensor was prepared using Pt nanoparticles (NPs) and Fe₃O₄ magnetic nanoparticles (MNPs) modified Au electrode. Pt NPs were deposited on the gold plated electrode through the method of potentiostatic deposition. Fe₃O₄ magnetic nanoparticles were added to the surface of Pt NPs modified Au electrode to obtain the Au/Pt/Fe₃O₄MNPs electrode. The as-prepared Au/Pt/Fe₃O₄MNPs electrode was used for the detection of liquid ethanol without using enzyme. Cyclic voltammetry and differential pulse voltammetry were used to study the behavior of ethanol electro-catalytic oxidation on Pt/Au/Fe₃O₄ electrode. It was found that Pt NPs played strong catalytic oxidation role of ethanol with the presence of Fe₃O₄ MNPs. The linear range of Au/Pt/Fe₃O₄MNPs electrode for the detection of ethanol was of $2 \times 10^{-5} \sim 1.1 \times 10^{-4}$ mol·L⁻¹ and the detection limit was of 3.2×10^{-6} mol·L⁻¹ when signal to noise ratio was 3 σ . The sensibility of the sensor is 420.4 μ A·mmol⁻¹·cm². The simple method provided an effective means for fabricating the novel sensors.

Keywords: Fe₃O₄ magnetic nanoparticles; Pt nanoparticles; Ethanol sensor; nonenzyme sensor.

Introduction

Direct ethanol fuel cells (DEFCs) have attracted researchers' concern because of its high energy conversion efficiency and low operating temperature. Ethanol is used in DAFCs with its significant features, for example, low toxicity, low permeability through the proton exchange membrane [1] and high energy density [2]. In particular, ethanol is a kind of easily available and mass-produced fuel.

Although ethanol has many advantages, the broken of C-C bond is essential to determine the fuel efficiency and power output. Considerable effort has been made to improve the activity and durability of anode catalyst. These electrocatalysts include Pt [3-5], Pt-based alloys [6-8] and oxide crystals [9-13]. Therefore, the development of relatively inexpensive, anti-toxic catalysts is an important research direction in electrochemical area and energy area. Electrochemical deposition is an important method for preparation of electrode materials. It can achieve the optimal preparation of electrode materials by controlling the deposition potential or current, deposition time, electrolyte concentration and composition.

Currently, two kinds of detection methods of ethanol are enzyme-based detection and nonenzymatic detection. Enzyme-based detection methods are based on the application of alcohol dehydrogenase, alcohol oxidase and other natural

enzyme applications. However, the natural enzyme has some serious shortcomings. For example, the catalytic activity of natural enzymes is susceptible to be inactively. Natural enzymes can also be broken down by proteases. Although magnetic nanoparticles (MNPs) were generally considered with biological and chemical inertness [14], the latest research reports have confirmed the Fe₃O₄ MNPs can simulate the enzyme activity [15]. The activity of magnetic nanoparticles is similar to the natural peroxidase. As the magnetic nanomaterials are generally considered to be chemically and biologically inert, they are usually coated with metal catalysts, enzymes or antibody to increase their functionality.

In this paper, Pt nanoparticles (PtNPs) were deposited on the gold plated with the methods of potentiostatic deposition, then adsorbed Fe₃O₄ MNPs on the modified electrode. Cyclic voltammetry and differential pulse voltammetry were used to investigate the ethanol electro-catalytic oxidation of Pt/Au/Fe₃O₄ electrode. The simple method provided an effective means for fabricating the novel sensors.

Results and Discussion

The Oxidation of Ethanol

A dual path mechanism for small organic molecules (C₁-C₄) oxidation on platinum electrode

*To whom all correspondence should be addressed.

has been proposed and developed [16]. The dual path is reactive surface intermediate and chemisorbed intermediate ('poison'). Strong interaction of small organic molecules and the electrode surface include the strongly chemisorbed, fracture dissociation, poisoning intermediate (mainly is an adsorbed carbon monoxide species which can be bonded in more than one configuration to the platinum surface) and a series of surface process.

Characterization of NPs

TEM image of Fe_3O_4 MNPs in Fig. 1 shows good dispersive Fe_3O_4 MNPs were prepared. A uniform distribution of Fe_3O_4 MNPs is about 20 ~ 30 nm in diameter, and the good dispersive nanoparticles with a narrow particle size distribution. The sizes of Fe_3O_4 MNPs were small enough to be firmly adsorbed on Pt film which was deposited on gold films, in subsequent experiments also confirmed.

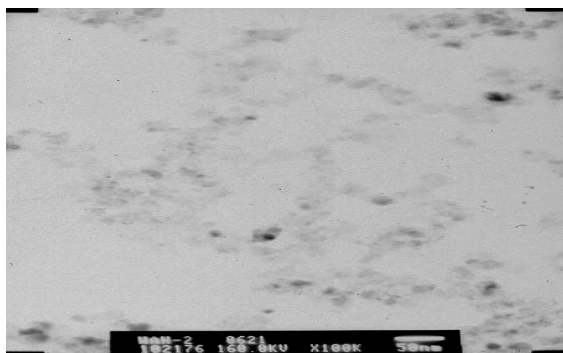


Fig. 1: TEM image of the Fe_3O_4 MNPs.

Fig. 2 is the SEM image of the deposited platinum nanoparticles on gold films. Due to the long time deposition and higher concentration of depositing liquid, Pt nanoparticles assembled together tightly. The sediment particle size is generally less than 100 nm while the maximum particle diameter is about 100 nm. From the Fig. 2, we can see clearly that the deposition of Pt film has high surface roughness and surface area, so it is very beneficial to the catalytic oxidation of ethanol.

Fig. 3 shows the cyclic voltammetry (CV) curves of different electrode. The curve a is CV of Au/Pt electrode in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, and we can see a peak separation of 0.394V, which is the characteristic peak in H_2SO_4 solution. The curve b is the CV of Au/Pt electrode in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution containing $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ethanol shows

three peaks separation of 0.380 V, 0.699 V and 1.054 V, but only 0.380V peak position is the characteristic peak of ethanol oxidation. And curve c is the CV of Au/Pt/ Fe_3O_4 MNPs decorate electrode in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution containing $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ethanol, compared with curve b at the peaks of 0.380V ethanol oxidation was significantly increased, while the peak current also increased significantly. This confirmed that Fe_3O_4 MNPs significantly promote ethanol oxidation, in turn, confirmed that the Fe_3O_4 MNPs in strong acidic solution did not dissolve, in this conditions also performed similar with natural peroxidases [17], but also in rough conditions remains a good activity, shows that Fe_3O_4 MNPs strong environmental adaptability, also indicates that it has broad applications.

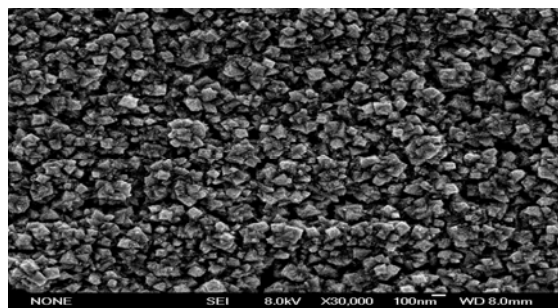


Fig. 2: SEM image of the deposited Pt NPs.

CV Behavior of the Modified Electrodes

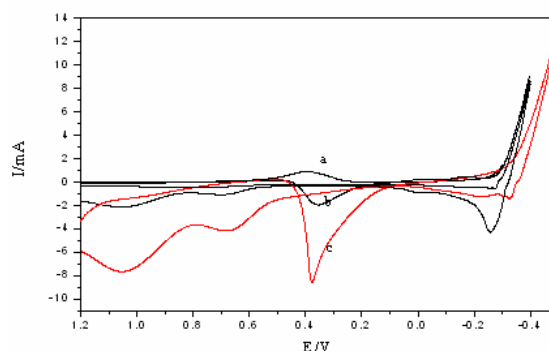


Fig. 3: Cyclic voltammetry curves of different electrode in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution: (a), (b) Au/Pt electrode absence or presence $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ethanol; (c) Au/Pt/ Fe_3O_4 MNPs electrode presence $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ethanol.

Optimization of Deposition Conditions

The deposition condition and the dosage of

Fe_3O_4 MNPs can impact the electrochemical characteristics of electrodes significantly. Here we studied the influence of the deposition solution concentration, deposition time and electrolyte pH on the electrochemical characteristics of electrodes. Fig. 4a shows the influence of chloroplatinic acid in concentration range from 0.001 mol L^{-1} to 0.01 mol L^{-1} on the electrochemical characteristics of electrodes. It can be seen that the modified electrode displayed the best electrochemical properties when H_2PtCl_6 is $7.0 \times 10^{-3} \text{ mol L}^{-1}$. Fig. 4b shows the influence of the deposition time. It shows that the optimal deposition time is 14 min.

The gold film electrode was deposited in $7.0 \times 10^{-3} \text{ mol L}^{-1}$ chloroplatinic acid solution for 14 min to obtain the Au/PtNPs electrode, and $4 \mu\text{L}$ Fe_3O_4 MNPs solution was dropped on the as prepared electrode. Then the modified electrode was dried. When the pH values range from 1.0 to 7.0, the CV curves were obtained in $\text{H}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ solution containing $1.0 \times 10^{-4} \text{ mol L}^{-1}$ ethanol (Fig. 4c). It demonstrated the maximum response at the pH value of 2.0 in $\text{H}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ solution containing $1.0 \times 10^{-4} \text{ mol L}^{-1}$ ethanol. Thus, the optimal deposition pH is 2.0.

Fig. 4d shows the influence of the quantities of the Fe_3O_4 . When the quantities of Fe_3O_4 MNPs range from 0.0256mg to 0.128mg, the CV curves were obtained in $\text{H}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ solution containing $1.0 \times 10^{-4} \text{ mol L}^{-1}$ ethanol (pH = 2). The results showed that a $0.384 \mu\text{g}$ Fe_3O_4 MNPs had the best CV curve (Fig. 4d).

Influence of the Scan Rate

Typical CV curves of Au/Pt/ Fe_3O_4 MNPs in 0.5 mol L^{-1} H_2SO_4 containing $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ethanol at different scan rates are shown in Fig. 5. The peak-to-peak separation also increased with the scan rate. A good linear relationship was found for the peak current and square root of scan rate, with the results shown in Fig. 5 (inset). Obtained straight line has regression equation: $I(mA) = 3.633 E^{1/2}(V/s)^{1/2} - 0.576$ ($n = 8$, $r = 0.994$). This indicates that the reaction is a quasi-reversible diffusion-controlled process. Mainly is ethanol molecules diffusion to the Au/Pt/ Fe_3O_4 MNPs electrode surface.

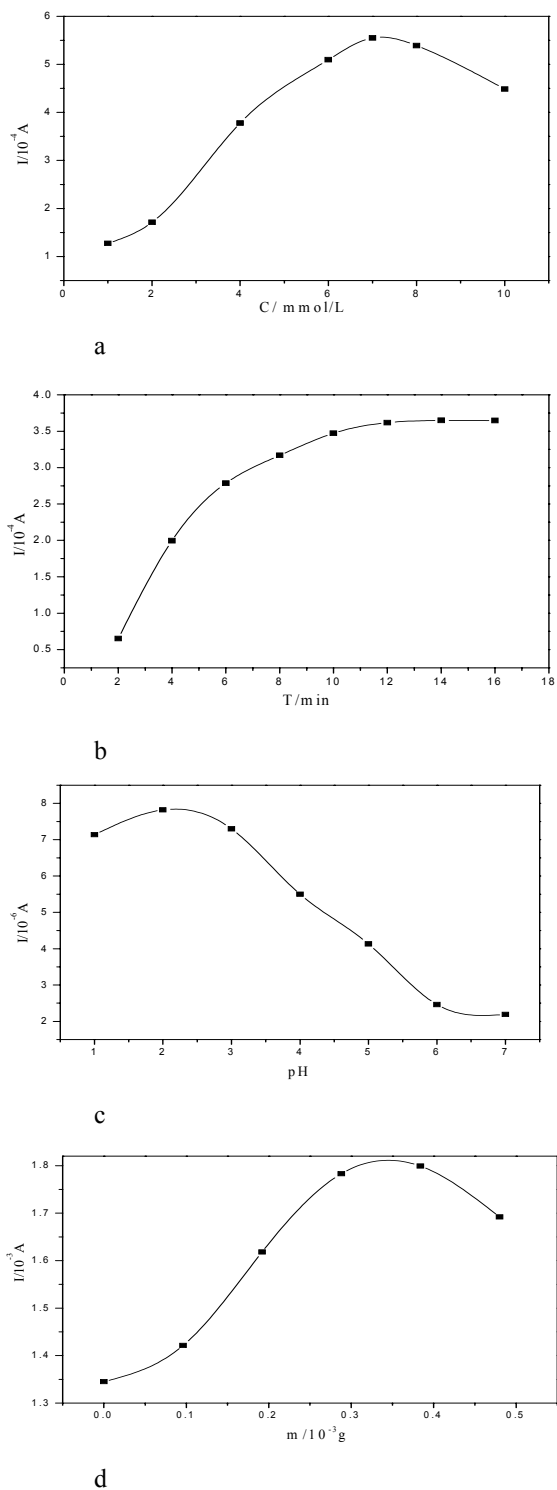


Fig. 4: Effects of (a) concentration of electrolytic solution, (b) deposited time, (c) pH values of deposited condition and (d) quantities of Fe_3O_4 MNPs

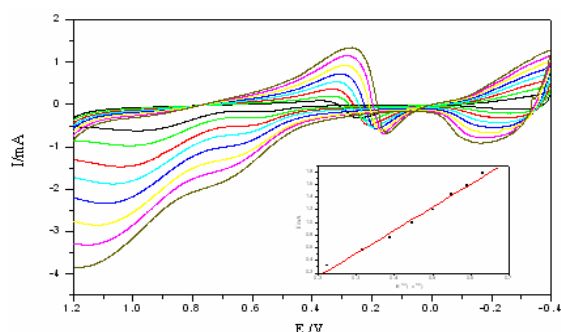


Fig. 5: CV curves of Au/Pt/Fe₃O₄ MNPs electrode in 0.5 mol·L⁻¹ H₂SO₄ solution of 1.0 × 10⁻³ mol L⁻¹ ethanol at different scan rates (V s⁻¹): (a) 0.05; (b) 0.1; (c) 0.15; (d) 0.2; (e) 0.25; (f) 0.3; (g) 0.35; (h) 0.4. Inset shows a calibration plot of peak current versus scan rate.

Prepared Au/Pt/Fe₃O₄ MNPs Electrode Detection of Ethanol

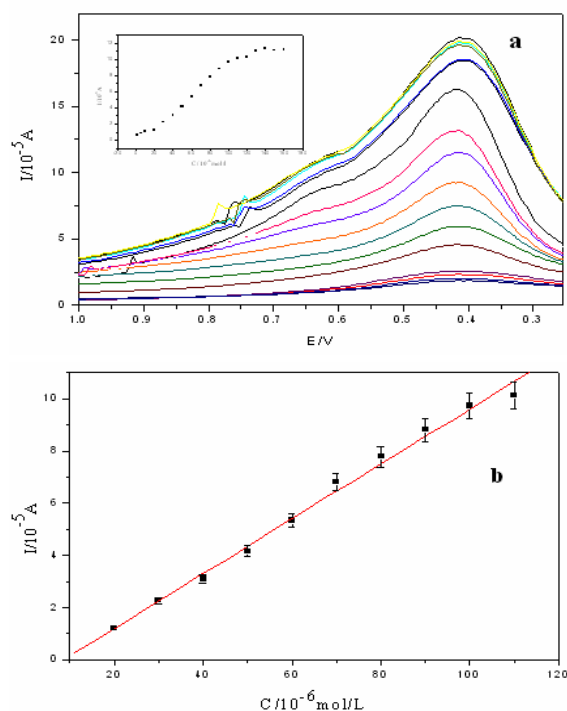


Fig. 6: (a): DPV curves obtained with different concentration of ethanol in 0.1 mol·L⁻¹ H₂SO₄-Na₂SO₄ solution of Au/Pt/Fe₃O₄ MNPs electrode. The inset shows the plot of catalytic oxidation peak current versus the concentration of ethanol. (b) Linear relationship between the value of current and the concentration of ethanol.

In order to examine the applicability of Au/Pt/Fe₃O₄ MNPs, differential pulse voltammetry method was used for ethanol detection. The differential pulse voltammetry curves were obtained under the optimal conditions shown in Fig. 6a. A linear calibration graph was obtained in the ethanol concentration range from 2.0 × 10⁻⁵ mol L⁻¹ to 1.1 × 10⁻⁴ mol L⁻¹ with the regression equation (Fig. 6b): $I (\mu A) = 0.1051 C (\mu mol L^{-1}) - 0.9010$ ($n = 10$, $r = 0.9964$), with a detection limit of 3.2 × 10⁻⁶ mol L⁻¹ when signal to noise ratio was 3σ. The sensibility of the sensor is 420.4 μA·mmol⁻¹·cm⁻².

To demonstrate the performance of the developed ethanol sensor, a comparison of the linear range, and detection limit obtained by several enzyme-based electrodes for ethanol detection was made in Table-1. From the table we know that the sensor based on PtNPs and Fe₃O₄ MNPs exhibit excellent performance.

Experimental

Materials and Reagents

Chloroplatinic acid (H₂PtCl₆) and Ethanol were purchased from the Tianjin Reagent Company and Yantai Chemical Reagent Ltd respectively. The other chemicals were used without further purification. All solutions were prepared with doubly distilled water. The H₂SO₄-Na₂SO₄ solutions at various pH values were prepared by diluting the sulphuric acid (wt 98%) to 0.5 mol L⁻¹ with doubly distilled water and then adjusting the pH with dropping of 2 mol L⁻¹ NaOH, using a pH meter control.

Instruments

Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV) were performed on a CHI832B electrochemical analyzer (Shanghai Chenhua Instrument, China) with a conventional three-electrode system composed of platinum wire as auxiliary electrode, Ag/AgCl as reference electrode, and a gold slice as working electrode. Scanning electron microscopy (SEM) measurements was carried out on a JSM-6700F scanning electron microscope (Japan Electro, Japan). Transmission electron microscope (TEM) measurements were carried out on a JSM-2000EX transmission electron microscope (Japan Electro, Japan).

Table-1: Comparison of developed ethanol sensor with other sensors.

Ethanol Sensor	Linear range(mol·L ⁻¹)	Detection limit(mol·L ⁻¹)
Nonenzyme ethanol sensor based on PtNPs and Fe ₃ O ₄ MNPs (this work)	2×10 ⁻⁵ ~ 1.1 × 10 ⁻⁴	3.2×10 ⁻⁶
Chemiluminescence ethanol sensor based on nanosized ZrO ₂ [18]	3.4×10 ⁻² ~ 3.4	1.3×10 ⁻²
Electrochemical biosensor based on dehydrogenase enzymes and AuNPs [19]	5×10 ⁻⁴ ~ 3.5×10 ⁻³	2 × 10 ⁻⁵
Ethanol biosensor based on Au nanoparticles[20]	7.3×10 ⁻⁵ ~ 2.9×10 ⁻⁴	4.9×10 ⁻⁵
Ethanol biosensor based on alcohol dehydrogenase[21]	0 ~ 1.25×10 ⁻²	1×10 ⁻⁴

Preparation of Fe₃O₄ MNPs

The Fe₃O₄ MNPs were prepared *via* a coprecipitation method. Firstly, FeCl₃·H₂O : FeCl₂·H₂O = 1.8 : 1.0 (n : n) were dissolved with doubly distilled water, then 0.4 mol L⁻¹ NH₃·H₂O was added gradually to the above solution with violent stirring, resulting in a change of color from brown to black, which indicated the formation of Fe₃O₄ nanoparticles. Secondly, 0.4 mol L⁻¹ NH₃·H₂O was added slowly to the mixture continuously until whose value was pH = 9, then the mixture was heated to 70 °C and sustained for 30 min.

Preparation of Working Electrode

Electrochemical deposition of Pt was carried out in a conventional three-electrode cell with a Ag/AgCl as a reference, a platinum wire as the counter electrode and the gold slice as the working electrode. The solution was not stirred during deposition. The electrochemical experiments were performed using a potentiostat method (Potentiostat/Galvanostat model 263A, Princeton Applied Research). Prior to deposition, the gold slice was ultrasonic for 3min immersing in the acetone, ethanol and doubly distilled water respectively, after that the gold plate was coated a thin layer insulating oil above the deposition area. Following deposition, Fe₃O₄ hydrosol was dipped onto the film of depositing Pt.

Conclusions

The Au/Pt/Fe₃O₄MNPs electrode was prepared by using Fe₃O₄ magnetic nanoparticles attachment to the surface of Pt NPs modified Au electrode, and used for the determination of liquid ethanol without using enzyme. It was found that PtNPs played strong catalytic role for oxidation of ethanol with the presence of Fe₃O₄ MNPs. The response of Au/Pt/Fe₃O₄MNPs electrode on ethanol was linear in ethanol concentration range from 2.0 × 10⁻⁵ mol·L⁻¹ to 1.0 × 10⁻⁴ mol·L⁻¹ and the detection limit was of 3.2 × 10⁻⁶ mol·L⁻¹. The sensibility of the sensor is 420.4 μA·mmol⁻¹·cm⁻². This nonenzyme ethanol sensor display more excellent characteristics:

easy to operate, long-term stability, low cost, high alcohol sensitivity and much lower detection limits. It can find good prospects for practical applications and can provide a new approach for direct ethanol fuel cell applications.

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