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# Ethanol electrooxidation at carbon paste electrode modified with Pd–ZnO nanoparticles

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ABSTRACT

The electrocatalytic and analytical performance of palladium–zinc oxide nanoparticles modified carbon paste electrode (Pd–ZnO/CPE) for determination and oxidation of ethanol were studied in alkaline media. X-ray diffraction (XRD) and transmission electron microscopy (TEM) was used to characterize Pd–ZnO nanoparticles. The electrochemical characterizations were performed using cyclic voltammetry (CV) and chronoamperometry techniques. The results show that the electrode reveals excellent electrocatalytic characteristics for ethanol oxidation such as high catalytic activity, stability and tolerance toward poisoning effects. Also, the excellent analytical performance for ethanol determination confirms the applicability of this electrode as a nonenzymatic amperometric ethanol sensor. This sensor has the advantages of low detection limit (20.3 μM), two wide linear range (1.99–490.90 mM and 0.491–3.355 M), and good long-term stability (more than 120 days) for ethanol determination. All results showed that palladium–zinc oxide nanoparticle is a good candidate for application in ethanol sensor and ethanol fuel cells.



## 1. Introduction

Direct liquid fuel cells, such as direct alcohol fuel cells (DAFCs), have attracted much attention as one of the most viable candidates to replace batteries as a source of portable power. Among the various liquid fuels, ethanol is less toxic, has higher energy density and is easier to store and handle than methanol [1,2].

Among the electrocatalysts for alcohols oxidation, Pd-based catalysts are promising candidates and have comparable or even better electrocatalytic activities than the Pt-based catalysts for alcohol oxidation in alkaline media [3]. So, more efforts have been done for improvement of electrocatalytic performance of Pd-based catalysts. Main strategies to improve the performance of the Pd-based catalysts are: supporting Pd on materials with large surface areas such carbonaceous material, metal oxides and combining Pd with other metals such as Ag [2], Ni [4,5], Pb [6], Sn [7], etc. Transition metal oxides such as $CeO_2$, NiO, $Co_3O_4$, $Mn_3O_4$ [8], NiO/MgO [9], $MoO_x$ [10] and $TiO_2$ [11] as supporting materials for Pd significantly improve the electrode performance by enhancing the electrochemical activity. Among the metal oxide nanoparticles, ZnO nanoparticles have been extensively investigated due to their unusual but favorable properties such as high surface area, high catalytic efficiency, non-toxicity, chemical stability and strong adsorption ability [12]. The modification of ZnO with noble metals such as Ag [13], Au [14], Pt [15], and Pd [13,16] has attracted significant attention. As a noble metal, palladium, whose ionic radius (0.080 nm) is close to that of $Zn^{2+}$ (0.074 nm), has been widely used in the gas sensors and industry catalysis especially for methanol synthesis [17].

The detection of ethanol concentration is important for medicine, brewing, beverage, traffic safety and etc. Analytical techniques, such as gas/liquid chromatography [18] and mass spectroscopy [19] have been proposed for ethanol determination but they are expensive and not suitable for portable use. Also, application of semiconductor-based ethanol sensors is limited due to some drawbacks such as high working temperature (≥300 °C), complicated fabrication and high cost [20,21]. In general, the electrochemical ethanol sensors have the highest sensitivity and accuracy among all of the sensors that in which response currents resulted from the ethanol oxidation. There are two types of these sensors: enzymatic sensors and nonenzymatic sensors. Because of loss of enzyme and/or mediator loading and degradation of enzyme activity in critical temperature or solution pH, it is reasonable and practical to develop nonenzymatic sensors for the detection of ethanol. Generally, metal or alloy was usually the basic element for nonenzymatic electrodes [22]. Several nonenzymatic sensors

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have been reported to detect the ethanol such as Pd [23], NiPd [22], Ni foil [24], Ni/Pt/Ti on an $Al_2O_3$ substrate [25], $RuO_2$ modified Ni electrode [24], Pd–Ni/Si NWs [21] and the cobalt nickel oxide electrode [26]. Nonenzymatic ethanol sensors were relatively rare in comparison with the other nonenzymatic sensors.

In this work, we applied palladium–zinc oxide nanoparticles (Pd–ZnO) used in carbon paste electrode for analytical determination and electrocatalytic oxidation of ethanol in alkaline media. The results show that the Pd–ZnO/CPE provides high electrocatalytic activity and good tolerance toward poisoning species for ethanol oxidation reaction in an alkaline media. Also, this electrode shows excellent analytical performance as a nonanzematic sensor for determination of ethanol. The electrochemical behaviors of this electrode were investigated using cyclic voltammetry (CV) and chronoamperometry.

## 2. Experimental

### 2.1. Materials and reagents

Potassium hydroxide (KOH, 85%), ethanol ($C_2H_5OH$, 99.9%), formic acid, 2-propanol, glucose, fructose, formaldehyde, and methanol were obtained from Merck. For determination of ethanol, the stock solution of ethanol (10.0 M) and KOH (2.5 M) were prepared daily in a 100.0-mL flask. Graphite powder (particle size <100.0 μm) and paraffin oil used for constructing electrodes were purchased from Fluka and Merck, respectively. Human serum samples were obtained from Fars Blood Transfusion Organization, Shiraz, Iran.

### 2.2. Apparatus

Electrochemical measurements were carried out with an electrochemical analyzer Autolab PGSTAT 302N (Metrohm Autolab B.V., Ultrecht and The Netherlands). A conventional three-electrode system was used throughout the experiments at room temperature. The working electrode was Pd–ZnO/CPE and the auxiliary electrode was a platinum wire. Besides, an Ag/AgCl was taken as the reference electrode. Measurements of pH were made with a Denver Instrument Model 780 pH meter equipped with a glass electrode. Transmission electron micrograph (TEM) was taken with Zeiss-EM10C −80 kV and XRD spectra were obtained by D8ADVANCE type (BRUKER-Germany).

### 2.3. Synthesis of palladium–zinc oxide nanocomposite

The Pd–ZnO catalyst was synthesized as described elsewhere [27]. Briefly, palladium nitrate (0.027 g/mL) and zinc nitrate (0.267 g/mL) solutions were mixed and then an aqueous solution of sodium carbonate (1.0 M) was added to this solution at room temperature to produce a final pH of 8.0. The mixture was aging for 2 h at 70–80 °C. The precipitate was then filtered and washed with ethanol and water several times and dried overnight in an oven at 80 °C. The product was calcinated at 723 K for 2 h.

### 2.4. Modified electrode preparation

Unmodified carbon paste was prepared by hand mixing of 70% of graphite powder and 30% of paraffin oil thoroughly to form a homogeneous paste. A modified carbon paste electrode was prepared in a similar method, except that the graphite powder, paraffin oil and Pd–ZnO with a ratio of 70:20:10 (%w/w), respectively were mixed thoroughly to form a paste. The resulting pastes were packed firmly into the cavity (3-mm diameter) of a Teflon holder. The electric contact was established *via* a stainless steel rod connected to the paste. A new surface was obtained by smoothing the electrode onto a weighing paper.

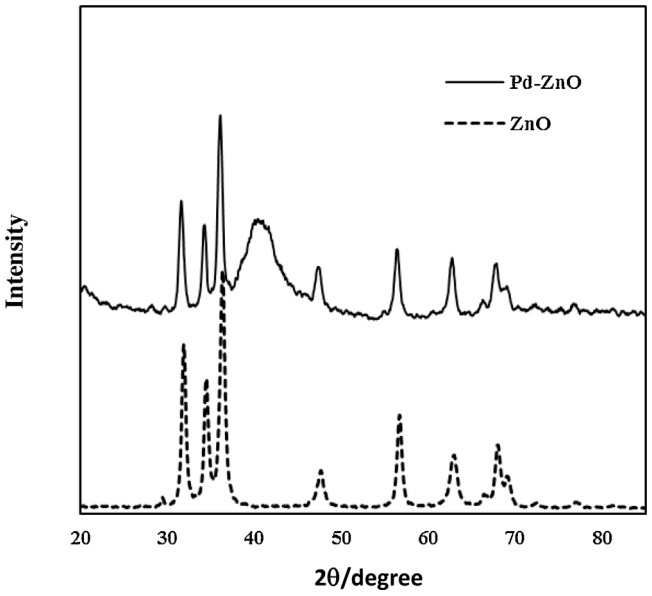


**Fig. 1.** XRD pattern of ZnO, and Pd–ZnO nanoparticles.

## 3. Results and discussion

### 3.1. Characterization of ZnO and Pd/ZnO nanoparticles

X-ray diffraction patterns of ZnO and Pd/ZnO nanoparticles are presented in Fig. 1. As shown in Fig. 1, all the XRD peaks are indexed by a hexagonal Wurtzite phase of ZnO (JCPDS card no. 36-1451). The absence of characteristic impurity peaks such as $Zn(OH)_2$ and unhydrolyzed Zn(II)–acetate indicate a high-quality ZnO nanoparticles. The XRD patterns of Pd/ZnO exhibit one additional broad peak appearing at a Bragg's angle of 41.2° originating from the diffraction of (1 1 1) planes that agree well with the face-centered cubic (fcc) morphology of palladium (JCPDS Card File No. 05-0681) that confirms the formation of palladium nanoparticles on ZnO surface. Also, the crystallite size of nanoparticles of Pd and ZnO estimated from Scherrer's formula are about 5 and 22 nm respectively [28]. The morphology of the Pd/ZnO particles were characterized by TEM images (Fig. 2). As shown in low magnification TEM image (Fig. 2A), the Pd/ZnO nanoparticle were undefined (shapeless) nanoparticles with average particle size of 26 nm. The average size of Pd nanoparticles on the surface of ZnO which was obtained from higher magnification TEM (Fig. 2B) image was found lower than 6 nm.

### 3.2. Preliminary study

Fig. 3 shows the cyclic voltammograms of modified electrode before (a) and after (b) reduction step (100 s in −1.0 V). As shown in Fig. 1a, there is no significant response to ethanol oxidation on the electrode surface before applied potential step. However, after applied potential step, the current was specifically increased. This is due to the fact that partially oxidized Pd on the ZnO surface reduced to Pd nanoparticles. So, this optimum time and potential were used before each analysis.

### 3.3. Electrocatalytic studies of ethanol oxidation at Pd–ZnO/CPE

Fig. 4 shows the cyclic voltammograms (CVs) of 1.0 M KOH solution at different electrodes containing Pd or Pd/ZnO-nanoparticles.