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# Electrocatalytic performance of Pd/PANI/$TiO_2$ nanocomposites for methanol electrooxidation in alkaline media

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ABSTRACT

An electrochemical method was successfully used for the Pd nanoparticles deposition on the Polyaniline/titanium dioxide (PANI/$TiO_2$) modified glassy carbon (GC) electrode. The electrochemical activity of fabricated palladium/Polyaniline/titania (Pd/PANI/$TiO_2$) electrocatalyst was investigated for methanol electrooxidation by cyclic voltammetry (CV) and chronoamperomtery (CA) in alkaline media. Also, the effect of different methanol concentrations and potential sweep rates were in two separate set of experiments. The prepared samples were characterized by field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX) and Fourier transform infrared spectroscopy (FTIR) techniques. Obtained results indicated that the synthesized Pd/PANI/$TiO_2$ catalyst not only possessed much higher electrochemically active surface area (EASA) than that of the pure Pd catalyst, but also enhanced the forward anodic peak current density ($J_f$) for methanol electrooxidation reaction. These observations are extracted from the combination of high charge transfer of the PANI/$TiO_2$ nanocompsites and excellent catalytic characteristic of the Pd catalyst.

## 1. Introduction

During the last decades, direct methanol fuel cells (DMFCs), electrochemical devices which directly convert chemical energy to electricity via electrooxidation of methanol as fuel, have become attractive due to their advantages including high efficiency, low operating temperature, and low/zero emission. But for commercialization of this technology, some barriers should be overcome. The slow reaction kinetics of methanol electrooxidation has been widely noticed as one of the most important challenges which strongly depends on the used catalysts [1].

Platinum (Pt) has been commonly implemented in DMFCs as catalyst layer on both anode and cathode side. Howevere, because of high cost and catalyst posioning towards methanol oxidation, many researchs have been done to find an alternative [2–4]. Pt alloy catalysts such as Pt/Ru, Pt/Ni, Pt/Co, Pt/Cu, Pt/Au and Pt/Ru/Ni have been demonstrated high activity and stability for application as anode catalyst in DMFCs [5–7]. Thus, Palladium-based catalysts with a lower cost than Pt and high catalytic activity in methanol oxidation reaction in alkaline media has been considered as a substitute for commonly-used Pt electrocatalysts [3,8–10].

In order to enhance the activity of pure Pd catalyst, Pd alloy catalysts such as PdSn, PdRu, and PdNi have been suggested because of their effect on oxidation of adsorbed CO intermediates to $CO_2$ during methanol oxidation at lower potentials [11]. Another method for improving electrocatalytic activity in methanol oxidation is usage of support materials including 1) carbon-based materials such as carbon nanotube (CNT), carbon nano-fiber (CNF) and graphene, and 2) metal oxides like $TiO_2$, $SnO_2$, $RuO_2$, MnO and $CeO_2$ [12–17]. As among, Pd/$TiO_2$ nanocomposites have been shown high electrochemical activity and excellent stability in methanol oxidation [11,18].

In recent years, conducting polymers have been enormously used in various applications including catalysis, energy storage, electronic nanodevices bio-sensors and biomedical engineering due to their good mechanical, optical and electrical properties [19–25]. Between different conducting polymers, poly(o-phenylenediamine), polyaniline (PANI) and polypyrrole (PPy) has been broadly reported for improving the DMFCs performance [26–29]. Among them, PANI has attracted a lot of attention because of its low cost, easy synthesis methods and excellent electrical properties [30]. In addition, the modification effect of PANI on methanol oxidation reaction has been confirmed by several papers [4,31–36].

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In the current study, Pd nanoparticles was electrochemically deposited on the PANI/$TiO_2$ nanocomposites modified glassy carbon electrode to form the Pd/PANI/$TiO_2$/GC working electrode and was used as anode catalyst for methanol oxidation. Field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDX) analyses were subsequently performed with the porpuse of morphological and elemental characterization of the fabricated Pd/PANI/$TiO_2$ catalyst. Moreover, functional groups of prepared catalyst were identified by means of Fourier transform infrared spectroscopy (FTIR). Then, electrochemical measurement techniques comprising cyclic voltammetry (CV) and chronoamperomtery (CA) were conducted to investigate the electroacivity of the Pd/PANI/$TiO_2$ modified GC electrode towards methanol oxidation in an aqueous solution consisting of potassium hydroxid (KOH). Based on the experimental results, the Pd/PANI/$TiO_2$ catalyst dramatically increased the catalytic activity of pure Pd catalyst by enlarging the elechtrochemical active surface area.

## 2. Experimental

### 2.1. Materials and apparatus

In the current study, aniline ($C_6H_5NH_2$) was purchased from Sigma-Aldrich. Commercial $TiO_2$ nanoparticles were supplied from nanosabz Co. Ammonium persulfate (APS) with the chemical formula of $(NH_4)_2S_2O_8$, HCl, methanol, $PdCl_2$ and KOH were purchased from Merck. All reagents were used without any further purification. In all experimetns, double distlited water was used.

All electrochemical experiments including cyclic voltammetry and chronoamperometry were conducted using a potentiostat/galvanostat instrument (Metrohm Autolab, PGSTAT204, Netherlands) at room temperature. A three-electrode cell was conducted in all electrochemical tests. A glassy carbon (GC) electrode with the diameter of 2 mm and surface area of 0.0314 $cm^2$ and a Pt wire were used as working and counter electrodes, respectively. A saturated Ag/AgCl, (3 M KCl) system was served as the reference electrode. Hence, all potentials mentioned in this paper are against standard Ag/AgCl electrode.The structure of three-electrode system and mechanism of methanol oxidation on the surface of the Pd/PANI/$TiO_2$ modified glassy carbon is schematically depicted in Fig. 1. In terms of electrochemical measurements, Initialy, in absence of methanol, cyclic voltammetry experiments were performed to determine the electrochemical surface area of the Pd/PANI/$TiO_2$ and Pd catalyst loaded on GC electrode in a solution of 0.5 M KOH at a potential sweep rate of 50 mV/s between −0.8 and 0.5 V. Cyclic voltammetry measurements were carried out to evaluate the electrocatalytic activity of aforementioned catalysts towards methanol oxidation in a solution containing 0.5 M KOH and 1 M methanol at 50 mV/s scan rate. Then, the effects of methanol concentration and potential sweep rate were investigated by changing the scan rate from 10 to 1000 mV/s and varying the concentration of methanol from 0.05 M to 4.5 M in the two separate set of experiments. Chronoamperometry measurement was carried out in a solution of KOH (0.5 M) and methanol (1 M) at a constant potential of −0.1 V for 1000 s.

### 2.2. Synthesis of PANI/$TiO_2$ nanocomposites

PANI/$TiO_2$ nanocomposites were synthesized via an in-situ emulsion polymerization method. In this method, 0.1 M aniline monomer and 1 M HCl were vigorously stirred, and a certain amount (20 wt%) of commercial $TiO_2$ nanopowder was added. Then, APS as an oxidant reagent was poured dropwise to the aniline–HCl–$TiO_2$ mixture under constant stirring. The reaction was performed at a temperature of 5 °C. When polymerization reaction started, the color of the mixture turned light blue, proving the formation of PANI via an oxidation reaction. The stirring was maintained for 4 h to ensure complete polymerization. As a consequence, dark green PANI/$TiO_2$ nanocomposites were formed, followed by a color change to dark blue. After that, the prepared nanocomposites were filtered and washed with distilled water to remove oligomers and excess acid. Finally, the product was dried out for 24 h at room temperature.

### 2.3. Fabrication of Pd/PANI/$TiO_2$/GC electrode

The thin-film electrode was prepared as follows: 2 mg of PANI/$TiO_2$ nanocomposites was dispersed via an ultrasonic instrument in 1 mL of nafion + ethanol for a period of 10 min. Then, 12 microliters of the dispersed suspension were transferred onto the glassy carbon disk using a micropipette and then dried at room temperature. A potentiostatic technique was chosen to fabricate the Pd/PANI/$TiO_2$/GC electrode, in which the Pd nanoparticles were electrodeposited from a solution containing 0.05 M $PdCl_2$ and 0.5 M $H_2SO_4$. To achieve desirable samples, applied potential and process duration were set to −0.35 V and 300 s, respectively. Eventually, prepared Pd/PANI/$TiO_2$/GC electrode was rinsed with double distlilled water prior to electrochemical measurements.

## 3. Result and discussion

### 3.1. Characterization of Pd/PANI/$TiO_2$ catalyst

FESEM, EDX and FTIR techniques were successfully performed to analyze the fabricated Pd/PANI/$TiO_2$ electrocatalyst. FESEM image and EDX spectra are presented in Fig. 2. As shown in Fig. 2A, pure PANI has smooth surface and flakes morphology. Moreover, the morphology of PANI/$TiO_2$ nanocomposite was reformed with the presence of $TiO_2$ nanoparticles (Fig. 2B) that indicated $TiO_2$ is dispersed within PANI structure during the preparation of PANI/$TiO_2$ nanocomposite. From Fig. 2C, it can be observed that a metallic layer of Pd nanoparticles is coated on the surface of the PANI/$TiO_2$/GC electrode. As expected from chronoamperometry technique, this image also shows the agglomeration of metallic Pd particles forming a rough semi-spherical morphology on the electrode surface [37]. The EDX spectra presented in Fig. 2D prove the existence of palladium and titanium, and also oxygen and carbon species in the fabricated electrode.

Fig. 3 demonstrates the FTIR spectra of three samples including pure $TiO_2$ nanoparticles, PANI and the synthesized $TiO_2$/PANI nanocompsites. From the $TiO_2$ spectra, the bands related to Ti—O bending vibration are observed at 540 and 680 $cm^{-1}$ (as expected, in the region between 400 and 800 $cm^{-1}$). In this plot, moreover, the band at around 1630 $cm^{-1}$ is the characteristic of O—H bending mode stemming from water molecules absorbed on the surface of $TiO_2$ nanoparticles. From the PANI IR pattern, the bands occur at 1570 and 1490 $cm^{-1}$ are attributed to C═N and C═C stretching mode, respectively. The peaks correspond to the C—N stretching mode are observed at 1294 and 1245 $cm^{-1}$. Furthermore, the peaks located at 1134 and 818 $cm^{-1}$ can be assigned to C—H bending vibration. Totally, from the repetition and existence of $TiO_2$ and PANI characteristic absorption bands in the spectra of the PANI/$TiO_2$ nanocomposite, the successful synthesis of the $TiO_2$/PANI nanocompsites can be interpreted.

### 3.2. Electrochemical measurements

#### 3.2.1. Cyclic voltammetry studies

Fig. 4 shows the cyclic voltammograms of Pd/GC and Pd/PANI/$TiO_2$/GC electrodes in a solution containing 0.5 M KOH by sweeping the potential between −0.8 V and 0.5 V at a scan rate of 50 mV/s. As can be seen in Fig. 4, there are two anodic peaks in the forward scan and a cathodic one in the reverse potential scan. The first anodic peak, which appears in the voltage range between −0.6 V and −0.4 V, can be attributed to the hydrogen adsorption or desorption [38]. The second anodic peak, at the potential about −0.2 V, is ascribed to Pd oxide (PdO) formation [38]. In the cathodic scan, a well-defined peak

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