Multi-walled carbon nanotubes supported Pd composite nanoparticles hydrothermally produced from technical grade PdO precursor

Keqiang Ding, Yongbo Zhao, Lu Liu, Yuan Li, Likun Liu, Yiran Wang, Hongbo Gu, Huige Wei, Zhanhu Guo

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Palladium (Pd) composite nanoparticles (NPs) supported on multi-walled carbon nanotubes (MWCNTs) (denoted as Pd/MWCNTs) are fabricated by a very simple process of hydrothermal reaction (HR) using the technical grade PdO as the precursor. With a HR period of 3 h, the Pd NPs with an average size of ~5.0 nm are found to be quite uniformly dispersed on the surface of MWCNTs. The electrocatalytic activity towards ethanol oxidation reaction (EOR) of the synthesized catalysts is probed by using cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). The 3-h prepared catalyst has demonstrated 6.7 times better EOR activity than 5-h prepared sample (159.7 mA mg\(^{-1}\) vs. 23.8 mA mg\(^{-1}\)) at an applied potential of −0.24 V (vs. SCE) in the CA test. The excellent electrocatalytic activity of the 3-h Pd/MWCNTs catalyst toward EOR is mainly ascribed to its easier hydrogen evolution, lower electrode potential and the existence of PdO as compared to other catalysts prepared.

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1. Introduction

Due to the relatively simple handling, storage and transportation of fuels, direct alcohol fuel cells (DAFCs) based on liquid fuels such as methanol and ethanol have attracted enormous attention as compact electrochemical power sources for portable applications [1]. Compared to direct methanol fuel cells, direct ethanol fuel cells (DEFCs) have some superior merits, such as less toxicity, easier storage and transportation, higher energy density [2]. More importantly, ethanol can be produced in large quantities from farm products by biological process [2]. All the aforementioned properties make DEFCs a promising electrochemical power source, therefore, numerous works concerning ethanol oxidation reaction (EOR), an anodic reaction to generate electrons, have been widely carried out. However, recent works have demonstrated that the sluggish rate of EOR on the electrode was the main obstacle hindering further implementation of DEFCs [3]. Thus, developing effective anodic catalysts has become an attractive topic in the research field of EOR.

Although platinum (Pt) has been utilized as a catalyst for EOR, the high price and limited supply of Pt have constituted a major barrier for the deployment of DEFCs [4]. Thereby, a lot of efforts have been devoted to creating Pt-free catalysts. Among the developed catalysts for EOR, palladium (Pd) is thought as a promising catalyst for EOR especially in alkaline media [5]. Recently, many kinds of Pd or Pd based catalysts such as Pd-Ni [6], Pd-Sn [7], Pd-Pt [8] and Pd-Cu [9] catalysts have been fabricated with an intention to reduce the catalyst cost while maintaining the higher electrocatalytic activity towards EOR as compared to the Pt-based catalysts. For instance, Behmenyar et al. [10] prepared carbon supported Pd and bimetallic Pd-Cu nanoparticles (NPs) through a modified polyl method by using palladium acetate as the metal precursor. Mech and co-workers [11] successfully prepared Co-Pd alloys through an electrodeposition method where the electrolyte contained [Co(NH\(_3\))\(_6\)]\(^{3+}\) and [Pd (NH\(_3\))\(_4\)]\(^{2+}\) complexes. Hong et al. [12] have just released their work on a rapid synthesis of porous Pd NPs with superior catalytic activity toward ethanol/formic acid electrooxidation, in which Na\(_2\)PdCl\(_4\) was used as the precursor of Pd. Meanwhile, various methods have been developed to prepare Pd NPs. For example, Shen et al. addressed the synthesis of a carbon supported Pd-Ni catalyst via a high-temperature calcination and chemical etching method [13], Maiyalagan et al. [14] prepared the carbon supported Pd electrocatalysts by a wet chemical reduction method, in which
PdCl₂ and NaBH₄ were employed as the starting material and the reducing agent, respectively. Modibedi et al. [15] reported the fabrication of Pd nanostructured catalysts by surface-limited redox replacement reactions using the electrochemical atomic layer deposition technique, in which the plating solution contained PdCl₂ and HClO₄.

Actually, PdO has been utilized as a catalyst in the research field of catalysis. For example, Weaver’s group [16] investigated the molecular adsorption and dissociation of n-butane on a PdO (10 1) thin film using temperature-programmed reaction spectroscopy (TPRS) experiments and density functional theory (DFT) calculations, and found that the formation of relatively strongly-bound complexes on PdO (10 1) serves to electronically activate C—H bonds in addition to prolonging the surface lifetime of these reactive precursors. Lu et al. [17] studied the influence of the synthesis method on the structures of Pd-substituted perovskite catalysts for methane oxidation, and reported that the exposure of PdO on the perovskite oxide surface was crucial for the catalytic activity. Chin and his co-worker [18] studied the diverse pathways, by which the C—H bonds in CH₄ reacted on the bare Pd clusters, and the Pd cluster surfaces saturated with chemisorbed oxygen (O²⁻), and PdO clusters by using mechanistic assessments and density functional theory. The aforementioned reviews strongly indicate that PdO has the catalysis for some peculiar organic reactions. To the best of our knowledge, there was no paper reporting on the synthesis of Pd NPs by using the technical grade PdO as the metal precursor.

Carbon nanotubes (CNTs), a kind of carbon that was created by Iijima [19] about two decades ago, still attract the attention of numerous scientists due to its unique properties such as high specific surface area, electrical conductivity, and good thermal and chemical stability [20], though many novel kinds of carbon such as carbon nanofibers [21] and graphene [22] have been developed recently. Above superior properties make CNTs a good catalyst support candidate for fuel cells [23]. Therefore, immobilizing metal nanoparticles onto CNTs has become a hot topic due to the significant roles of CNTs and metal nanoparticles in the fields of electrocatalysis, biosensors and so on [24]. Although many works concerning the immobilization of Pd NPs onto CNTs have been published every year, to our knowledge, no paper reporting the anchoring of Pd NPs onto carbon nanotubes (CNTs) by a facile method of hydrothermal reaction (HR) using PdO as the precursor was published so far.

In this work, Pd nanoparticles supported on the multi-walled carbon nanotubes (MWCNTs) were prepared by using a very simple process of hydrothermal reaction (HR). In the preparation system, only technical grade PdO, MWCNTs and doubly-distilled water were utilized. Among all the resultant nanocomposites, the 3-h prepared catalysts have displayed the best electrocatalytic activity towards EOR in alkaline media. The possible reasons to give the excellent electrocatalytic activity of the 3-h catalyst towards EOR were also discussed.

2. Experiment

2.1. Materials

Except the technical grade PdO, all other chemicals were of analytical grade and used as received without any further treatment. MWCNTs (purity=95%) with an average diameter of 10—20 nm were purchased from Shenzhen nanotech port Co., Ltd. (China). All the electrodes were purchased from Tianjin Aida Co., Ltd. (China). Doubly distilled water was used to prepare the aqueous solutions.

2.2. Preparation of Pd nanocomposite particles

Firstly, 4.1 mg PdO and 15 mg MWCNTs were dissolved in 3 mL distilled water to prepare a suspension solution, and then the resulting solution was ultrasonicated for 30 min. Secondly, the resulting suspension was placed in a home-made autoclave at room temperature, and then the well-sealed autoclave was transferred to a muffle furnace. The temperature of the muffle furnace was maintained at 200 °C for a period of time. It should be noticed that this process was accomplished in an SRXJ-8-13 muffle furnace equipped with a KSY 12-16 furnace temperature controller. The samples prepared by this process for 1, 2, 3, 4 and 5 h, were denoted as H1, H2, H3, H4 and H5, respectively. After cooling down to the room temperature, the filtered samples were washed copiously with distilled water and dried in an ambient condition to generate MWCNTs supported catalysts (denoted as Pd/MWCNTs).

2.3. Fabrication of Pd/MWCNTs modified electrode

Firstly, the working electrode, i.e., a glassy carbon (GC) electrode with a cross-sectional area of 0.07 cm², was polished to a mirror finish with 50 nm alumina nanopowder suspensions. And then, the catalyst ink was prepared by dispersing 1 mg catalyst in 1 mL Nafton ethanol solution (0.1 wt.%). And after 20 min ultrasonication, 15 μL of ink was added on the surface of the GC electrode. After drying in air, the Pd/MWCNTs-coated GC electrode was fabricated. The loading of catalysts on the GC electrode was about 0.276 μg cm⁻².

2.4. Characterizations

The XRD analysis of the catalysts was carried out on a Bruker D8 ADVANCE X-ray diffractometer equipped with a Cu Kα source (λ = 0.154 nm) at 40 kV and 30 mA. The 2θ angular region between 10 and 90° was explored at a scan rate of 1°/step. The particle morphology was examined by scanning electron microscopy (SEM, HITACHI, S-570) and transmission electron microscopy (TEM, HITACHI, H-7650). The crystalline structure of the samples has been achieved by high resolution transmission electron microscopy (HRTEM FEI Tecnai G2 F20 twin). The samples for TEM analysis were prepared by adding a drop of the solution of as-prepared products on a carbon-coated copper grid. Fourier transform infrared spectrum (FT-IR) measurements were carried out on a Hitachi FT-IR-8900 spectrometer (Japan). Energy dispersive X-Ray spectroscopy (EDS) spectrum analysis was conducted on an X-ray energy instrument (EDAX, PV-9900, USA).

Electrochemical measurements, including cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) were carried out on a CHI 660B electrochemical working station (Shanghai Chenhua Apparatus, China) connected to a personal computer. The EIS was performed in the frequency range from 0.1 to 10⁵ Hz with an amplitude of 5 mV at the open circuit potential.

A conventional three-electrode system was employed, in which a Pd/MWCNTs modified GC electrode and a platinum wire were used as the working electrode and counter electrode, respectively. Additionally, the reference electrode was a saturated calomel electrode (SCE, 0.245 V vs. NHE), and the potentials in this paper were reported with respect to this reference electrode. A solution of 1.0 M KOH containing 1.0 M C₆H₄OH was used to study ethanol oxidation reaction activity. Prior to each electrochemical test, the electrolyte was bubbled with high purity nitrogen for 30 min to avoid the influence of oxygen dissolved in the electrolyte. All the experiments were carried out at room temperature.
proven that the HR period was a key factor that can directly affect the compositions of the resultant samples. Meanwhile, compared to the XRD patterns of pure MWCNTs, the intensity of the (002) diffraction facet for the Pd/MWCNTs sample was not much attenuated, as shown in the red-circled part, implying that the crystal structure of MWCNTs was not destroyed during the HR process.

For a clear comparison, the XRD patterns of the MWCNTs, H3 and starting material of PdO are plotted in Fig. 2A. In pattern c, the (101) and (112) crystallographic planes corresponding to PdO (JCPDS, Card No.00-041-1107) are presented, confirming the existence of PdO. However, the lower intensities of these diffraction peaks suggested a poor crystallinity as compared to the H3 catalyst (pattern b). For the H3 sample (pattern b), except the diffraction peak at 26° belonging to MWCNTs, four diffraction peaks assigned to the fcc crystalline Pd are markedly exhibited, indicating the formation of metallic Pd on the surface of MWCNTs.

According to the Scherrer formula using Eq. (1) [29], the average crystallite size of the catalysts was estimated based on the Pd (111)

$$d(A) = \frac{k\lambda}{\beta \cos \theta}$$  

where k is a coefficient (0.9), \(\lambda\) the wavelength of X-ray used (1.54056 Å), \(\beta\) the full-width half maximum (FWHM) and \(\theta\) is the angle at the position of peak maximum. The calculated crystallite particle sizes, based on (111) plane for 1, 2, 3, 4 and 5 h treated catalysts, are 67.0, 97.2, 38.0, 40.1 and 50.5 nm, respectively. Therefore, among all the prepared samples, the crystal size of H3 catalyst is the smallest one. The crystallite particle sizes calculated are much larger than those obtained from TEM images (Fig. 3). The difference between the mean particle sizes obtained by TEM and XRD could be attributed to the fact that XRD reflects crystalline particles rather than the actual morphology of the catalysts. In the XRD measurement, only large particles are selected, while most of the small particles could be counted in the TEM measurement [30].

The EDS spectra for above three typical samples are presented in Fig. 2B. For the starting material of technical grade PdO (pattern c), the atomic contents of Pd, O and Cl elements were 33, 36 and 30%, respectively. While for the resulting H3 catalyst (pattern b), only elements of C, O and Pd were detected. Evidently, the element of Cl was originated from MWCNTs. And element of Pd was from the Pd NPs formed or from the un-reacted PdO, element of O was from the PdO left or from the Pd oxides or Pd hydrous oxides (POHOs) prepared. Thus, it was reasonable to think that the element Cl has been consumed in the HR process probably by the means of

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the as-prepared samples are depicted in Fig. 1A. For the pure MWCNTs, only a diffraction peak centered at around 26°, assigned to the (002) facet of MWCNTs [25], is displayed (pattern a). While for other samples, four typical peaks at 2\(\theta\) of about 39.9, 47, 68 and 82°, corresponding to the plane (1 1 1), (2 0 0), (2 2 0) and (3 1 1), respectively are presented clearly, characteristics of the face centered cubic (fcc) crystalline Pd [JCPDS, Card No.01-089-4897] [14]. This result substantially indicates that Pd NPs could be produced via this very simple method of HR process using technical grade PdO as the precursor. A closer inspection revealed that the intensities of all the diffraction peaks are altered with the preparation time. Obviously, the XRD pattern (pattern d) for the H3 sample, as shown by the black circled part, shows the highest diffraction peak among all the patterns, indicating that the NPs of H3 catalyst have the best crystallinity among all the catalysts [26]. To one’s surprise, for the H3 sample, a novel peak appearing at about 34° (green circled part) is clearly observed. It was reported that the diffraction peak of 34° can be ascribed to the presence of Pd oxides or Pd hydrous oxides (POHOs) [27,28]. Nevertheless, this diffraction peak was not markedly observed in the case of other catalysts. This result effectively

\[\text{Intensity (a.u.)} \quad 01-089-4897\]

\[\text{2}\theta(\text{degree})] 20 \quad 40 \quad 60 \quad 80\]

\[\text{Fig. 1. XRD patterns of (a) bare MWCNTs and the synthesized Pd/MWCNTs with a HR time of (b) 1.0, (c) 2.0, (d) 3.0, (e) 4.0 and (f) 5.0 h. (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)}\]

\[\text{Intensity (a.u.)} \quad \text{Energy (keV)}\]

\[\text{2}\theta(\text{degree})] 20 \quad 40 \quad 60 \quad 80\]

\[\text{Fig. 2. (A) XRD patterns and (B) corresponding EDS spectra of (a) MWCNTs, (b) 3-h Pd/MWCNTs and (c) technical grade PdO.}\]
volatilization. In such a system, a reductive environment may be produced by the reaction between carbon and water according to reaction [31], \( C + H_2O = CO + H_2 \). Thus, during the process of HR, the following reaction probably may occur, i.e., \( PdO + C \) (or \( H_2 \)) → Pd+
CO (or H2O), consequently, most elements of O were consumed and the Pd NPs were fabricated on the surface of MWCNTs. This result strongly indicates that it was feasible to prepare Pd NPs by this simple process of HR developed here using technical grade PdO as Pd precursor. The formation process of Pd NPs on the surface of MWCNTs may be described by the Scheme 1.

3.2. Morphology characterization

The SEM images of five samples are presented by the insets of Fig. 3. It is evident that some white dots were anchored on the outer surface of MWCNTs after the HR process, indicating the formation of NPs on the surface of MWCNTs. It seems that the amount of NPs immobilized on the surface of MWCNTs decreased with increasing the HR period (when comparing the inset of image b with other insets). The TEM microstructures for all the samples are depicted by Fig. 3. No particles are found on the surface of pure MWCNTs (image a). After the HR process, the produced NPs (black dots) with negligible agglomerations, roughly in the spherical shape, are observed to be dispersed on the outer walls of the MWCNTs. The characteristic diameters of the MWCNTs supported NPs were evaluated from an ensemble of 200 particles in an arbitrarily chosen area of the TEM images. The particle sizes for the H1, H2, H3, H4 and H5 catalysts were estimated to be approximately 10, 18, 5, 8 and 12 nm, respectively. That is to say, the catalyst of H3 has the smallest particle size among all the samples, which may provide a larger specific surface area relative to other catalysts at the same particle loadings.

To confirm the formation of metallic Pd particles, the surface structure of the samples was further characterized with HRTEM. A typical HRTEM image for the H3 sample is presented by image (g) and (h) in Fig. 3. Obviously, highly crystalline nanocrystals with apparently resolved lattice fringes were exhibited in image (h). The interplanar spacing of the lattice fringes was measured to be 0.118 nm, which matched well with the (311) planes of face centered cubic (fcc) metallic palladium. Previous work [32] has indicated that Pd (311) stepped surface had a special property for CO adsorption. Thus, along with the XRD patterns shown in Fig. 1 and the presence of EOR peaks displayed in Fig. 4, it was convinced that metallic Pd nanoparticles were prepared by using the very facile method of HR using PdO as the precursor.

3.3. Electrochemical characterization

The cyclic voltammograms (CVs) of the as-prepared catalysts in a solution of 1.0 M KOH containing 1.0 M C2H5OH are illustrated in Fig. 4. An oxidation peak (peak f) centered at around −0.27 V in the anodic sweep curve and an abnormal oxidation peak (peak b) located at −0.37 V in the cathodic sweep curve, are observed clearly. The shape of these two oxidation peaks is very similar to that reported in the previous work [33], indicating that the EOR can proceed on all the prepared catalysts facilely. That is to say, the particles, prepared via a HR process using the technical grade PdO as the precursor in the presence of MWCNTs, have the electrocatalytic activities toward EOR. Interestingly, in terms of peak f, the largest peak current density was displayed in the H4 catalyst, while for peak b, the highest peak was observed in the case of H1 sample. This indicates that it is not appropriate to evaluate the electrocatalytic ability of a catalyst only using the peak current in CV curves. Also, it should be mentioned that although the largest peak current (about 1472 mA mg−1) of peak b was still lower than the reported value (2361 mA mg−1) [34] of EOR, the preparation method presented here was much simpler than the reported method [34]. It has been widely accepted that the forward oxidation current peak f is related to the oxidation of the freshly chemisorbed species coming from ethanol adsorption, and the reverse oxidation peak b is primarily associated with the removal of carbonaceous species not completely oxidized in the forward scan, rather caused by freshly chemisorbed species [35]. Thus, it can be concluded that the process of EOR on the H4 catalyst is rather different from that occurring on the H1 catalyst. In addition, a careful inspection reveals that the shape of the CVs of the anodic peak for H3 catalyst is rather different from those of other catalysts, as shown by the red-circled part. It should be noted that this abnormal shape of CVs for EOR was not reported so far. Probably, the existence of PdO, confirmed by the XRD pattern d in Fig. 1, has varied the oxidation mechanism of EOR on the H3 catalyst, though the exact mechanism of EOR cannot be clarified by CV test alone.

Interestingly, a small oxidation peak appeared at the potential of 0.025 V in terms of H3 catalyst. To the best of our knowledge, this interesting result was not reported in the previously published works. The presence of this strange oxidation peak was probably resulted from the differed composition of the H3 catalyst when compared with other catalysts. That is to say, as shown by the pattern d in Fig. 1, the novel substance appearing at the 34° probably has altered the electrochemical oxidation process of

![Scheme 1. A schematic representation for the synthesis of MWCNTs stabilized Pd nanocatalysts.](image-url)
ethanol on the Pd/MWCNTs catalyst. Generally, the ratio of the forward anodic peak current (peak f) to the reverse anodic peak current (peak b), i.e., \( i_f/i_b \), could be used to evaluate the poisoning tolerance of a catalyst [35]. A larger \( i_f/i_b \) ratio indicates a better oxidation of ethanol during the anodic scan. Approximately, the values of the \( i_f/i_b \) ratio for the H1, H2, H3, H4 and H5 samples were estimated to be around 0.468, 0.764, 0.827, 0.889 and 0.908, respectively. Unfortunately, the order of the \( i_f/i_b \) ratio values did not accord with that of the results obtained from electrochemical measurements. In the CA test (Fig. 5), H3 sample displayed the best electrocatalytic activity towards EOR though the value of \( i_f/i_b \) ratio for H1 sample is the smallest one among all the prepared catalysts.

According to the electrochemical theory, except the temperature and the number of electrons transferred, the value of current is proportional to the electrode reaction rate, \( \text{ca. } \nu = i/nFA \) [36], in which, \( \nu \), \( i \), \( n \), \( F \) and \( A \) correspond to the electrode reaction rate, current passed, the number of electrons transferred, Faraday constant and electrode surface area, respectively. That is to say, when other parameters are identical, a larger peak current density corresponds to a quicker electron transfer rate of an electrode reaction occurring at the interface between the electroactive substances (ethanol and the carbonaceous species) and the electrode. Therefore, it is reasonable to employ the total current of peak f and peak b at a potential scanning rate to evaluate an electrochemical reaction rate. Generally, the area of the peak presented in the CV curves stands for an electric quantity consumed, from which the accurate surface area of a Pt or Pd electrode could be evaluated [37]. Meanwhile, it has been accepted that both peak f and peak b are all resulted from the electro-oxidation of ethanol molecules or the intermediates produced in the process of EOR, though peak f and peak b correspond to different oxidation mechanisms. In other words, the area sum of the forward and backward peak in CVs of EOR should correspond to the total amount of electro-oxidized substances.

The electrochemical stability of all the as-prepared catalysts toward EOR was investigated by chronocapacitometry (CA) at an applied potential of -0.24 V in the electrolyte of 1.0 M KOH + 1.0 M C2H5OH. It is clear that for all the CA curves, the polarization currents decreased sharply in the initial stage of 15 s. Generally, this decrease is associated with the charging/discharging behavior of a double-layer. And the gradual decrease in the current with the passage of time (from 15 to 100 s) could be ascribed to the poisoning of the electrocatalysts, likely due to the formation of intermediates and some poisoning species during the ethanol oxidation reaction [38]. The steady currents, exhibited in the left testing periods and denoted as Faraday current, are mainly originated from the electrochemical oxidation of ethanol. It is evident that the current density in the H3 catalyst (blue curve) decays more slowly than other catalysts, indicating that H3 catalyst is the most stable one among all the prepared samples. It is observed from Fig. 5 that the current densities in the H1, H2, H3, H4 and H5 catalysts modified electrodes are about 42.5, 43.2, 159.7, 116.5 and 23.8 mA mg\(^{-1}\) at 350 s, respectively. Hence, the EOR close-steady current densities decreased in an order of H3 > H4 > H1 ≈ H2 > H5, indicating that the H3 sample is the most active catalyst among all the resulting catalysts. Therefore, the H3 sample was much more efficient and poisoning tolerant electrocatalyst than other catalysts studied. Meanwhile, it should be noted that steady current density for the H3 catalyst (159.7 mA mg\(^{-1}\) at 350 s) was comparable to the value obtained on the Pd/C catalyst [34]. However, in the previous report [34] PdCl2 and ethylene glycol (EG) were employed as the precursor and reducing agent, respectively. That is to say, the developed method for preparing Pd nanoparticles in this work was rather different from that previously reported.

The ethanol oxidation kinetics on the as-prepared catalysts in alkaline media was further probed under the quasi-steady-state conditions. Fig. 6 shows the linear sweep voltammograms (LSVs) of the EOR obtained on the resultant electrodes at a scan rate of 1 mVs\(^{-1}\) in 1.0 M KOH containing 1.0 M ethanol. The onset potentials of EOR were about 30, and 75 mV lower on the H3 catalyst coated GC electrode than those of H4 and H2 catalyst, respectively. Also, the peak current density in the H3 catalyst is about 397 mA mg\(^{-1}\), which is the largest peak current density among all the samples. Therefore, it is further confirmed that among all the catalysts, the H3 catalyst showed the highest kinetics in terms of both onset potential and the peak current density.

As one typical curve of the electrochemical impedance spectroscopy (EIS), Nyquist plot has been widely employed in probing the electrochemical performance of a working electrode. According to the previous report [39], the semicircle appearing at the high frequency region corresponds to a circuit having a resistance element parallel to a capacitance element. The line with a 45° slope appearing at the lower frequency region corresponds to the Warburg resistance [30]. And the length of the diameter for the semicircle, generally, corresponds to the value of the charge transfer resistance (Rct) of the electrochemical reaction occurring at the working electrode. A bigger diameter stands for a larger value of Rct. Prior to the analysis of the plots, it should be mentioned that all the plots were recorded at their open circuit.

![Fig. 5. CA curves of the synthesized Pd/MWCNTs with a HR time of (a) 1.0, (b) 2.0, (c) 3.0, (d) 4.0 and (e) 5.0 hours performed in 1.0 M KOH solution containing 1.0 M C2H5OH at an applied potential of -0.24 V vs. SCE. (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)](image1)

![Fig. 6. Linear sweep voltammetry (LSV) curves of the synthesized Pd/MWCNTs with a HR time of (a) 1.0, (b) 2.0, (c) 3.0, (d) 4.0 and (e) 5.0 hours recorded in 1.0 M KOH solution containing 1.0 M C2H5OH at a scan rate of 1 mVs\(^{-1}\).](image2)
potentials. As illustrated in Fig. 7A, the Nyquist plots were constructed by a semicircle at high-to-middle frequency range and a tilted line at the low frequency region, whose shape is very consistent with the previous report on a system containing MnO2 and CNTs [40]. It was also reported that the sequential x-intercepts of semicircle stand for the bulk electrolyte solution resistance (Rb) and the electron-transfer resistance (Rct) between the active materials and the electrode, respectively. The straight line indicates a pure capacitive behavior [40]. The similarity in Nyquist plots for all the prepared catalysts effectively indicates that all the catalysts modified GC electrodes have a similar structure at the interface between the working electrode and electrolyte. Nevertheless, the slight variation in the values of Rb and Rct also illuminates that the microstructures of these catalysts were different from each other. The values of Rb and Rct estimated from those spectra for the H1, H2, H3, H4 and H5 samples were approximately 4.0 and 5.0, 5.0 and 6.0, 11.0 and 3.0, 6.0 and 4.0, 6.0 and 6.0 Ω, respectively. The smallest value of Rct was exhibited by the H3 catalyst, demonstrating the highest electrocatalytic property among all the samples, being consistent with the results obtained from Figs. 5 and 6 very well.

Bode modulus plots of electrochemical impedance for all the prepared catalysts modified electrodes were recorded. Fig. 7B. It is visible that when the frequency is above 10^4 Hz, the electrode impedances do not differ much, indicating that the values of electrode conductivity are close to each other. Also, this result proves that the immobilization of as-prepared catalysts on the surface of the GC electrodes did not influence the impedance behavior of each electrode at high frequency region. However, as the frequency was lower than 10^4 Hz, the values of impedance for the electrodes became distinct from each other. For example, the value of impedance at 10 Hz for the H3 sample is about 3981.07 Ω, which is significantly larger than that of H2 sample (31.62 Ω). Evidently, the value of impedance for H3 catalyst is the largest one among all the catalysts, which is probably due to the existence of Pd oxides or Pd hydrous oxides (pattern d in Fig. 1).

Bode phase angle plots for all the prepared catalysts coated GC electrodes are compared, Fig. 7C (phase angle vs. log f), with an intention to acquire more useful information of the electrical properties of the as-prepared catalysts. It is evident that only the H3 catalyst coated GC electrode exhibits a symmetric peak in the frequency region from 3.98 to 100 Hz, corresponding to a relaxation process of the electrode/solution interface [41]. Generally, the appearance of this peak is indicative of complex and irregular surface properties of a bulk electrode. In other words, the presence of a symmetric peak has effectively demonstrated that the composition of the H3 sample was rather different from that of other catalysts. Meanwhile, the largest phase angles for H1 and H4 catalysts at 0.1 Hz are −86° and −72°, respectively. Interesting, the values of the highest phase angle for H2, H3 and H5 catalyst are very close to each other (−77°). The slight variation in the highest phase has indicated different microstructures of these catalysts coated GC electrodes [42].

Why did the catalysts prepared with various HR periods show such different electrocatalytic activity toward EOR? To disclose the possible reasons, the CVs of five catalysts in 1.0 M KOH are plotted in Fig. 8. Generally, multiple peaks corresponding to the hydrogen absorption/desorption (Hab) process and hydrogen adsorption/desorption (Had) process [43] should appear at the hydrogen evolution region, however, in this case, only the hydrogen evolution peaks were observed at the potential lower than −1.10 V. The magnified hydrogen evolution peaks were presented by the inset of Fig. 8. It is clear that among all the samples, the highest hydrogen evolution peak current and the most positive onset potential of the hydrogen evolution were all displayed by the H3 catalyst (curve c). Thus, it can be deduced that the hydrogen evolution on the H3 catalyst proceeded more easily than those occurring on other catalysts.

Fig. 7. Nyquist (A), Bode modulus (B) and Bode phase angle (C) plots of the synthesized Pd/MWCNTs with a HR time of (a) 1.0, (b) 2.0, (c) 3.0, (d) 4.0 and (e) 5.0 hours in 1.0 M KOH solution containing 1.0 M C2H5OH solution.
The huge reduction peak at around −1.10 V corresponds to the hydrogen evolution. According to the previous report [43], this huge peak was resulted from the reduction of water, leading to the hydrogen evolution, i.e.,

$$\text{Pd} + \text{H}_2\text{O} + e^- \rightarrow \text{Pd} - \text{H}_2\text{ads} + \text{OH}^- \quad (1)$$

$$\text{Pd} - \text{H}_2\text{ads} + \text{Pd} - \text{H}_2\text{ads} \rightarrow 2\text{Pd} + \text{H}_2 \quad (2)$$

Thus, more OH⁻ ions were generated in the vicinity of Pd atoms due to the evolution of hydrogen gas. It has been reported that in the potential region for hydrogen evolution, the dissociative adsorption of ethanol may take place on the surface of Pd, as described below.

$$\text{Pd} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{Pd} - (\text{CH}_3\text{CH}_2\text{OH})_{\text{ads}} \quad (3)$$

And during the process of electrochemical oxidation of ethanol in an alkaline media, the following reaction may take place based on the former report, i.e.,

$$\text{Pd} - (\text{CH}_3\text{CH}_2\text{OH})_{\text{ads}} + 3\text{OH}^- \rightarrow \text{Pd} - (\text{CH}_3\text{CO})_{\text{ads}} + 3\text{H}_2\text{O} + 3e^- \quad (4)$$

Also, according to the previously published work [44], the adsorption of OH⁻ may occur at the far negative potential from the onset potential of EOR, namely.

$$\text{Pd} + \text{OH}^- \rightarrow \text{Pd} - \text{OH}_{\text{ads}} + e^- \quad (5)$$

Meanwhile, it has been widely accepted that the cleavage of the C—C bond is rather difficult on the Pd catalyst and the main product of EOR is acetate ions, as expressed as follows:

$$\text{Pd} - (\text{CH}_3\text{CO})_{\text{ads}} + \text{Pd} - \text{OH}_{\text{ads}} \rightarrow \text{Pd} - \text{CH}_3\text{COOH} + \text{Pd} \quad \text{(rate-determining step)} \quad (6)$$

$$\text{Pd} - \text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{Pd} - \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \quad \text{(fast step)} \quad (7)$$

Therefore, on the basis of the chemical equilibrium shifting principle of Le Chatelier’s principle [45], more number of OH⁻ ions can favor the Reactions of (4)/(5), (6) and (7). Consequently, compared to other catalysts, more ions of OH⁻ were generated on the H3 catalyst, generating an enhanced polarized current (Fig. 5).

Although the electrocatalytic ability of a metallic catalyst was strongly influenced by the added second or the third metal, the electrochemical properties of a catalyst were mainly determined by its nature according to the Nernst equation [46]. The value of open circuit potential (OCP) can be used to reflect the ability of oxidation and reduction of a catalyst. Fig. 9 displays the curves of open circuit potential (OCP) against time. For all the OCP curves, an increment of OCP value is observed in the initial period of testing, and then the value of OCP reaches a relatively stable constant. The values of OCP for various catalysts are different. For example, at the working time of 1000 s, the values of OCP for the catalysts of H1, H2, H3, H4 and H5 are about −0.64, −0.58, −0.67, −0.31 and −0.44 V, respectively. The significant difference in the values of OCP strongly testified that the composition and structure of the as-prepared catalysts were different from each other. In the whole testing period, the value of OCP for H3 catalyst was the lowest one (blue curve), implying that the electrons can be released from the catalyst of H3 easier than the other catalysts based on the Nernst Equation [46]. In other words, protons (H⁺), released from water, can obtain electrons from H3 catalyst easily, leading to the generation of hydrogen atoms or hydrogen gas. This conjecture was strongly supported by the results of CV curves, Fig. 8.

According to our previous work [33], in the hydrogen evolution potential region, the newly generated hydrogen atoms can reduce PdO to form Pd atoms, and thus more “fresh Pd atoms” were released, on which EOR can proceed very well. According to the results obtained from Figs. 8 and 9, H3 catalyst can be easily “cleaned” to produce fresh Pd atoms due to its easier hydrogen evolution process as compared to other catalysts. This may lead to an increased oxidation peak current of EOR.

From the viewpoint of electrochemistry, the standard electrode potentials of PdO is different from that of metallic Pd, thus, for the H3 sample, a micro-cell may form due to the existence of PdO, in which the metallic Pd may work as a negative electrode and PdO as the positive electrode. Thus, the microenvironment of the interface between the H3 catalyst and ethanol, due to the formation of micro-cell, should differ from those of other catalysts. This new concept, i.e., forming a micro-cell, may provide a novel concept to explain the fact that compared to the pure metal catalyst, binary or ternary composite catalysts always have better electrocatalysis towards small organic molecules reactions occurring in the fuel cells.

To discuss the mechanism of the HR process, photos of the solution before and after the process are shown by the insets of Fig. 10. For the solution containing the starting material of PdO, a light brown color was observed, indicating the existence of Pd²⁺. Interestingly, even after the 2-h HR process, a colorless solution was displayed, demonstrating that the metal ions in the solution have been consumed in the HR process. This result can only be attributed to the reaction between the metal ions and MWCNTs since no color changes were found in the above process in the absence of MWCNTs. This result impressively indicates that MWCNTs themselves were employed as the reducing agents in the HR process.
Ultraviolet–visible (UV–vis) absorption spectra for the solution before and after HR process are presented in Fig. 10. As shown by curve a, for the starting solution, an absorption peak located at around 305 nm was observed, indicating the presence of Pd²⁺ [47]. It was claimed that the spectra in the far-UV region (200–250 nm) corresponded to the peptide n–π* electronic transition [48]. For the solution after being treated for 2 h, curve c, the absorption peak at around 258 nm disappeared, suggesting that the n–π* electronic transition was greatly inhibited by the HR treatment. Also, it strongly demonstrates that Pd²⁺ ions have been consumed in the HR process. Evidently, the band intensity of the curves decreased with increasing the treatment period. However, when the HR period was 5 h, the intensity of the curve, instead, was increased to some extent (curve f). The slight difference in the intensities of these curves effectively indicates that the compositions of the filtered solution varied from each other. That is to say, the components of the as-prepared Pd composite NPs differed from each other.

The FT-IR spectra of three typical samples, i.e., MWCNTs, the starting material of PdO and the H3 sample, are presented in Fig. 11. It is evident that for pure PdO, no bands were found in the whole wavenumber region, but for the starting material of technical grade PdO, six bands, centered at 3462, 2352, 1639, respectively, 1383, 659, 573 cm⁻¹ were observed clearly. The weak peak at 3462 cm⁻¹ can be attributed to H-O stretching vibration of the absorbed water on PdO according to the previously published work [49]. The band at 659 cm⁻¹ can be assigned to the stretching band of (Pd-O) based on the prior report [49]. As for the resultant sample of H3, above six bands disappeared completely, indicating that PdO has been consumed by the reaction between PdO and introduced MWCNTs. It should be mentioned that in the absence of MWCNTs, no change was found before and after the HR treatment in the FT-IR spectra for the starting material of PdO. The analysis of the FT-IR spectra strongly demonstrates that there were some reactions between PdO and MWCNTs in the process of HR treatment. To clarify the formation of Pd NPs, a scheme was proposed as shown in Scheme 1, in which the light brown cycles stand for the PdO particles, and the green cycle represents the formed Pd NPs. As discussed above, H₂ or CO, that was produced by the reaction between MWCNTs and water, was utilized as the reducing agent to reduce PdO. As a result, Pd NPs were produced.

4. Conclusions

For the first time, Pd composite nanoparticle catalysts were prepared using technical grade PdO as the precursor by a hydrothermal reaction in the presence of MWCNTs. Due to the smaller particle size and higher crystallinity, the 3h-Pd/MWCNTs catalyst exhibited the best electrocatalytic ability toward EOR among all the prepared samples. Most importantly, the existence of PdO with a well-defined crystal structure in the 3-h catalyst was verified by the XRD pattern. In the electrolyte of 1.0 M KOH, a larger hydrogen evolution peak with more positive onset potential was displayed in the catalyst of 3-h Pd/MWCNTs when compared to other catalysts. This may lead to a facilitated generation of OH⁻ ions, which was considered as a possible reason for the enhanced peak current of EOR. Presenting a novel method to prepare NPs of Pd by a HR process using technical grade PdO as the starting material is the main contribution of this work, which is thought to be helpful to the development of novel catalysts towards EOR or other small organic molecule oxidation reactions.

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