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Multi-walled carbon nanotubes supported palladium nanoparticles: Synthesis, characterization and catalytic activity towards methanol electro oxidation in alkaline media

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Abstract

Palladium nanoparticles supported on multi-walled carbon nanotubes (Pd/MWCNTs) have been synthesized using a modified polyol reduction method and its performance in methanol oxidation reactions has been evaluated. The morphology of palladium on MWCNTs was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The catalytic performance of the synthesized catalyst was examined for methanol oxidation in a N_2- saturated solution of 1 M KOH and 1 M CH_3OH. Cyclic voltammetry (CV) analysis demonstrated that the Pd/MWCNTs catalyst exhibits lower catalytic activity compared to the commercial Pt/C, but because of its relatively low-cost, the prepared Pd/MWCNTs might be an economically viable alternative for methanol oxidation. The chronoamperometry technique is an effective method to evaluate the electrocatalytic activity and stability of the alcohol oxidation reaction. The chronoamperometry results showed that Pd supported on MWCNTs has better long-term stability in comparison to Pt/C which is related to the good dispersion of Pd nanoparticles on the surface of support.

1. Introduction

Direct methanol fuel cells (DMFCs) have attracted considerable attention in recent years due to their high energy efficiency, convenient transportation and storage of methanol fuel, as well as being environmentally friendly, etc. [1-3]. They are considered as a promising power source for portable electronic devices and electric vehicles. However, widespread application is difficult due to several technical barriers such as the relatively low kinetics of methanol electro-oxidation (MEO) on the anode and the poisoning of anode catalyst, etc. Hence, considerable efforts must be made in order to enhance the catalytic efficiency of the electrode catalysts for the MEO [1].

Until now, the majority of the DMFCs used as electrocatalysts have contained platinum (Pt) and platinum alloys because of their excellent

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electrocatalytic activities. Pt cannot be used for large-scale applications, however, because of its high price and the fact that it is readily poisoned by carbon monoxide (CO), so alternative materials are therefore needed [4-6].

Previous studies have shown that using an alkaline electrolyte in DMFCs rather than an acidic media leads to significant improvement in methanol oxidation and Pt-free electrocatalysts can be used [6-8]. Although palladium (Pd) possesses very similar properties (i.e. same group of the periodic table, same fcc crystal structure and similar atomic size) to Pt, the cost of Pd is currently lower than that of Pt, and therefore it could be used as a good substitute for Pt as the catalyst in alkaline fuel cells [9-12]. For these reasons, many researchers have devoted their efforts to investigate the application of Pd-based catalysts in fuel cells. Naked palladium has a tendency towards aggregation which can have an adverse impact on its electro-catalytic activity, so for these applications template supports with large superficial areas, such as MWCNTs, have been adopted to disperse the palladium nanoparticles and prevent aggregation.[13, 14]. However, more studies are needed to further enhance the electro-catalytic activity, stability and CO tolerance of these catalysts. Recently Amin et al. [15] prepared bimetallic Pd-Ni/C using the borohydride reduction method and observed that the Pd-Ni/C displayed better catalytic activity and more stability than Pd/C and Ni/C towards MOR in alkaline medium. Lingzhi et al. [3] synthesized Pd-Ag supported on reduced graphene oxide (RGO) with different Pd/Ag ratios in an easy process without the use of any reducing or dispersing agents and investigated the electrochemical activity and stability of the synthesized catalysts toward methanol oxidation in alkaline media. They found that Pd/Ag (1:1)/RGO had the best catalytic activity and stability.

In this study Pd nanoparticles were precipitated on the surface of MWCNTs by a modified polyol reduction method and characterized by various techniques. The catalytic performance of the synthesized catalyst was examined for methanol oxidation in a N_2- saturated solution of 1M KOH and 1M CH_3OH.

2. Experimental

2.1. Materials

Ethylene glycol (EG, Merck), palladium chloride ($PdCl_2$, Merck), Nafion (perfluorosulphonic acid-PTFE copolymer, 5 wt. % mixture of aliphatic alcohol and water, ElectroChem), potassium hydroxide (KOH, Merck), sodium hydroxide (NaOH, Merck), nitric acid (HNO_3, Merck), methanol (CH_3OH, Merck), de-ionized (DI) water, commercial Pt/C and modified MWCNTs were used in this experiment.

2.2. Instruments

Ultrasonic Homogenizers (sonopuls HD 2000 series), probe (KE 76), vacuum oven (Wise Ven®, Fuzzy Control System), pH meter (EcoMet, P25) and digital scale (KERN, ALJ160-4NM) were used in this work.

2.3. Functionalization of MWCNTs

MWCNTs (purity min. 95%; diameter 5-20 nm; length 1-10 mm) were purchased from PlasmaChem GmbH. MWCNTs were used as support for the electrocatalysts. Firstly, MWCNTs were functionalized with -C=O, -COO and -COH groups by refluxing in 65% nitric acid solution at about 110-120ºC for 6 h.

2.4. Synthesis of Pd/MWCNTs electrocatalyst

After functionalization of MWCNTs, Pd was deposited on MWCNTs support with 30 wt% Pd loading by a modified polyol method [16-18]. Initially, 20 mg of MWCNTs was dispersed in a 40 mL solution of EG and water by ultrasonication followed by stirring. To ensure the uniform dispersion of MWCNTs in the solution, the mixture was sonicated for 30 min in an ice bath. For sonication, Ultrasonic Homogenizers and a probe were used. Processing frequency 20 kHz and 30% power were used. Also, to regulate the temperature to room temperature, an ink vessel was held in an ice bath, because sonication of catalyst ink makes it hot. Then, the proper quantity of $PdCl_2$ solution was added to the suspension drop by drop and stirred continuously for 12 h. Before refluxing at 90°C for 6 h, the pH of the entire solution was adjusted to 11 by adding NaOH (2.5 M) solution. During the entire reaction, the water to EG ratio was maintained at 1:3. Lastly, the final product was filtered and washed with DI water and dried at 60°C for 8 h in a vacuum oven [17].

2.5. Physical characterization of electrocatalyst

2.5.1. Scanning electron microscopy

The morphology of the MWCNTs sample was determined using scanning electron microscopy (SEM, Hitachi S-4160) operated at an accelerating voltage of 20 kV.

2.5.2. Transmission electron microscopy

The nanostructure of the sample and distribution of nanoparticles supported on MWCNTs were investigated using transmission electron microscopy (TEM; ZEISS 900) with an accelerating voltage of 50-80 kV.

2.5.3. Inductively coupled plasma mass spectrometry

The mass content of Pd in the synthesized sample was estimated by inductively coupled plasma mass spectrometry (ICP-MS) measurements using a PerkinElmer (NexION 350D ICP-MS) Spectrometer.

2.6. Electrochemical characterization

The electrochemical properties of the catalysts were measured at room temperature in a conventional three-electrode system with a potentiostat/galvanostat (biologic sp-150). The working electrode was a pre-polished glassy carbon electrode (2 mm in diameter) coated with the catalyst layer. A platinum foil was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. To prepare the working electrode, the catalyst ink was made by dispersing 2 mg of catalyst powder in a mixture of 1 mL DI water and 100 µL Nafion solution (5wt%) by ultrasonication for 1 h to form a homogeneous ink, and followed by dropping 6µl of the catalyst ink on to the surface of glassy carbon electrode (GCE). Finally, the working electrode was dried in the air. The electrochemical measurements were carried out in a solution of 1M KOH and 1M CH_3OH which was saturated with high-purity nitrogen gas for about 30 min. The catalytic activity of the catalysts was characterized by cyclic voltammetry (CV) with a potential range from -1 to 0.2 V at a scan rate of 50 mV s^{-1}. The chronoamperometry test was recorded at a constant potential of -0.2V. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 10 mHz to 100 kHz at the constant potential of -0.2 V.

3. Results and discussion

3.1. Physical characterization of MWCNTs

The SEM image of functionalized MWCNTs used as a support for Pd nanoparticles in the next step is shown in Figure 1. The carbon nanotubes must be functionalized before being used as an electrocatalyst support in order to anchor and precipitate the metal nanoparticles because of the chemical inertness of the MWCNTs surface.

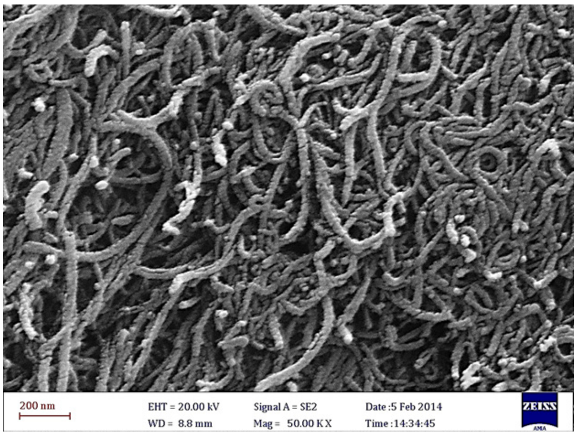

Fig. 1. SEM image of functionalized MWCNTs.

Figure 2 shows the IR spectra, the treated CNTs specimen has many functional groups, such as carboxyl at 1500-1800 cm^{-1}, phenyl at 2250-2500 cm^{-1} and hydroxyl at 3500-3700 cm^{-1}.

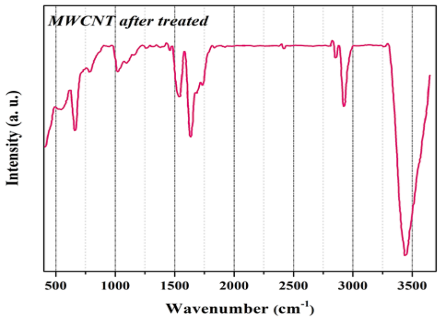

Fig.2. IR spectrum of treated CNTs.

3.2. Physical characterization of Pd/MWCNTs

ICP-MS measurements confirmed the amount of metals by weight in the Pd/MWCNTs sample to be 30 wt% Pd. FESEM and TEM images of Pd/MWCNTs are shown in Figure 3. The Pd nanoparticles are well-dispersed on the functionalized MWCNTs, demonstrating the formation of supported electrocatalysts (Fig. 3b). The small black spots and low degree of Pd nanoparticles agglomeration results from the preparation process. Since ethylene glycol is a reducing, stabilizing, and dispersing agent in the modified polyol reduction method, the distribution of Pd nanoparticles was uniform and had a narrow size distribution. It can be clearly seen that the Pd nanoparticles were uniformly loaded on MWCNTs in the size of 2 to 5 nm.

3.3. Electrochemical properties of catalysts

Typically, the electrochemical active surface area (ECSA) is one of the crucial factors to evaluate the catalytic activities of electrocatalysts [19]. Fig.4 (a) shows the cyclic voltammograms of Pd/MWCNTs and commercial Pt/C in a N_2-saturated solution of 1 M KOH at a scan rate of 50 mVs^{-1} in the potential region from -1 to 0.2 V vs. Ag/AgCl at 298 K was used to determine the electrochemically surface areas (ECSAs) of the electrocatalysts. As can be seen, the weak peaks in the potential region from -1 to approximately -0.6 V are associated with the adsorption/desorption of hydrogen from the surface of the electrode by the following reactions [20, 21]:

$$Pd - H_{ads} + OH^- \rightarrow Pd + H_2O + e^- \qquad (1)$$

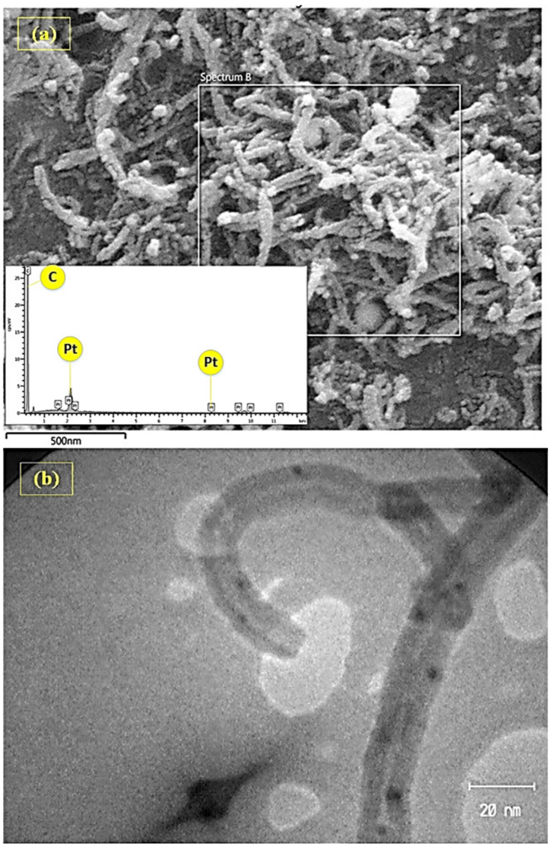

Fig. 3. FESEM and TEM images of Pd/MWCNTs.

$$Pd + H_2O + e^- \rightarrow Pd - H_{ads} + OH^- \qquad (2)$$

An observed increasing current at the potential higher than -0.3 V on the positive going scan, is attributed to the transformation of Pd metal on the surface film in to Pd(II) oxide, which can be explained as follows [20, 21]:

$$Pd + OH^- \rightarrow Pd - OH_{ads} + e^- \qquad (3)$$

$$Pd - OH_{ads} + OH^- \rightarrow Pd - O + H_2O + e^- \qquad (4)$$

$$Pd - OH_{ads} + Pd - OH_{ads} \rightarrow Pd - O + H_2O \qquad (5)$$

Furthermore, a strong reduction peak at the potential range of -0.1 to -0.5 V on the negative going scan can be attributed to the reduction of Pd(II) oxide to Pd metal, as described by [20, 21]:

$$Pd - O + H_2O + 2e^- \rightarrow Pd + 2OH^- \qquad (6)$$

The ECSA of the catalysts has been determined by calculating the area under the curve of Pd(II) oxide reduction (Q_p) using the following equation [10, 22]:

$$ECSA = \frac{Qp}{0.405 * l} \tag{7}$$

Where Q_p is the columbic charge in mC and determined by calculating the area under the curve of the Pd(II) oxide reduction. A proportionality constant, 0.405 mC cm^{-2}, is assumed for the charge required for reduction of Pd(II) oxide monolayer and L is the loading of Pd on the surface of the electrode in g. ECSA values were found to be 36.42 and 77.9 $m^2.g^{-1}$ for Pd/MWCNTs and Pt/C, respectively. The results show that the ECSA of Pt/C is higher than Pd/MWCNTs, indicating higher electrocatalytic activities and more effective utilization of Pt nanoparticles over the surface.

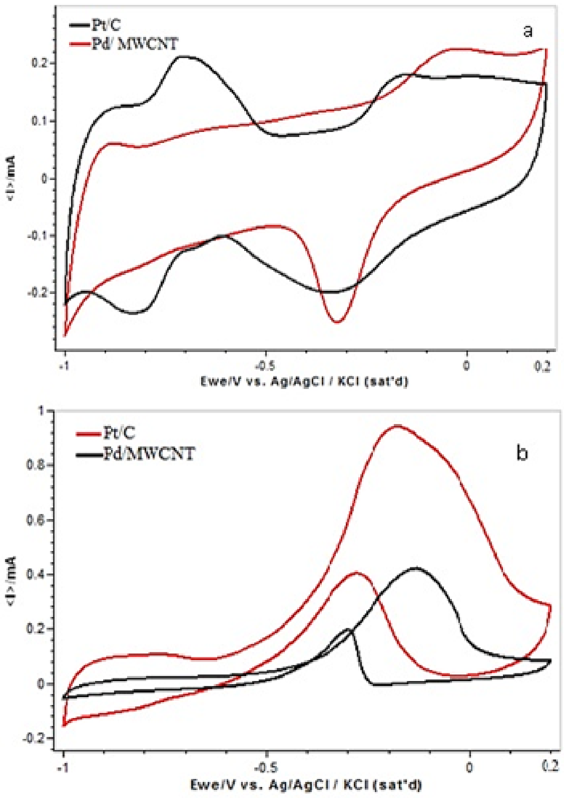

Fig. 4. CVs of Pd/MWCNT and Pt/C in a) 1M KOH, b) 1M KOH and 1M CH_3OH at scanning rate of 50 mVs^{-1}.

Figure 4 (b) shows the catalytic activities of Pd/MWCNTs and commercial Pt/C for methanol oxidation by CV in an electrolyte solution of 1 M CH_3OH and 1 M KOH. Two typical peaks for MOR can be observed. The forward peak current (I_f), around -0.18 V (vs Ag/AgCl), can be related to the oxidation of methanol species, leading to the formation of carbon species such as CH_3OH, CH_3O, CHO, CO and CO_2 on the electrode surface. The adsorbed carbonaceous species on the surface of the electrode can reduce the ECSA of the synthesized catalysts, resulting in a reduction in performance of electrocatalysts toward MOR. The mechanism of the methanol oxidation process is described in other works [23-25]. The backward peak current (I_b), about -0.3 V (vs. Ag/AgCl), may be due to the oxidation of the residual carbon species produced during the incomplete oxidation of methanol in the forward scan [23-25].

As can be observed, the I_f of methanol oxidation for Pd/MWCNTs is about 0.42 mA which is lower than that for Pt/C (0.92 mA), but Pd/MWCNTs can be a promising catalyst in DMFCs in alkaline media. Because of the high cost, low abundance and susceptibility of Pt to CO-like intermediates formed during the methanol oxidation, the use of Pt in DMFCs has been limited. One catalyst that has received a great deal of attention is Pd because of its super catalytic activity and stability in DMFCs and it is about 50 times more abundant than Pt [4-6]. Also, NG has been significantly regarded as a support material for fuel cell electrocatalysts due to its unique physical and chemical properties such as high surface to volume ratio, high electrical conductivity, and its excellent chemical, mechanical and thermal stability [26, 27]. So, Pd nanoparticles supported on NG can be a promising catalyst in DMFCs in alkaline media, but the catalytic activity of Pd-based catalysts need the addition of other metals such as Ag, Ni, Co, Ru, Sn etc,. The significantly higher anodic current of Pt/C could be attributed to the high dispersion and small size of Pt/C, in agreement with the higher ECSA of this catalyst.

The chronoamperometry (CA) technique is an effective method to evaluate the electrocatalytic activity and stability of the alcohol oxidation reaction on the surface of Pd/NG and Pd/MWCNTs catalysts. A CA test was recorded for 6 h at -0.2 V (vs Ag/AgCl) in 1 M KOH and 1 M CH_3OH (shown in Figure 5). It was found that the methanol oxidation current on all electrocatalysts rapidly decreased in the initial stage corresponding to the formation of intermediate species such as CO_{ads}, CH_3OH_{ads} and CHO_{ads} during methanol oxidation reaction [23, 28-30]. After that, the current decay became more gradual and eventually stabilized. Thereafter, the current gradually decreased until it reached a constant value. It is well known that the Pt/C catalyst shows a higher steady-state current density (0.022 mA) compared to Pd/MWCNTs (0.01 mA), indicating that Pt/C achieves better stability for methanol oxidation. This is probably due to the fact that the Pt/C catalyst has a larger active surface area in comparison to Pd/MWCNTs.

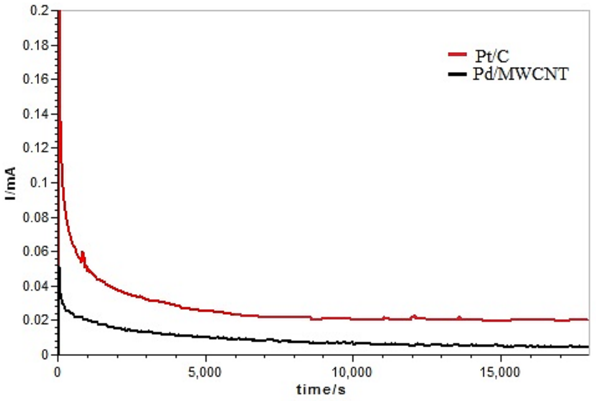

Fig. 5. Chronoamperometric responses of Pd/MWCNTs and Pt/C catalysts in N_2- saturated solution of 1 M KOH and 1 M CH_3OH at -0.2 V vs Ag/AgCl.

Electrochemical impedance spectroscopy (EIS) is a powerful tool for under-standing the mechanism of electrode reactions. The complex plane (Nyquist) impedance plots of the electro-catalysts at potentials of -0.2 V in 1.0 M methanol and 1 M KOH aqueous solution are presented in Figure 6. All the plots presented two typical features, a semicircle in the high frequency region corresponding to the charge-transfer resistance and a straight line in the low frequency region corresponding to the capacitive behavior of the electrodes [1, 31]. According to Figure 6, the semicircle diameter of Pd/MWCNT is 7.3 Ω, which is larger than that of around 2.35 Ω for Pt/C, indicating the lower charge transfer resistance of Pt/C.

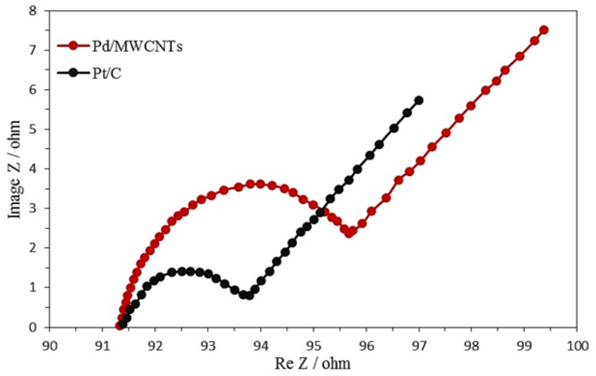

Fig. 6. Nyquist plots of Pd/NG and Pd/MWCNTs in a N_2-saturated solution of 1M KOH and 1M CH_3OH.

4. Conclusion

Uniform Pd nanoparticles supported on the surface of MWCNTs have been successfully prepared by a modified polyol reduction method. Herein, ethylene glycol was employed as a reducing, stabilizing, and dispersing agent, resulting in better dispersion and less agglomeration of Pd nanoparticles over the surface of MWCNTs. Physical characterization revealed that well-dispersed Pd nanoparticles supported on the surface of MWCNTs were obtained. Electrochemical characterization demonstrated that the catalytic activity of as-prepared Pd/MWCNTs for methanol oxidation is lower than the commercial Pt/C, but the performance of Pd/MWCNTs catalyst can be improved by increasing the loading level of metal on the surface of MWCNTs and modifying the synthesis process.

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