



Electrocatalytic performance of Pd nanoparticles supported on TiO₂-MWCNTs for methanol, ethanol, and isopropanol in alkaline media



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ABSTRACT

A Pd/TiO₂-multi-walled carbon nanotubes (MWCNTs) catalyst has been synthesized for use in direct alcohol fuel cells using an *in situ* chemical method. TiO₂ pretreated with HNO₃ and HF was applied as a support material between the Pd nanoparticles and MWCNTs template. Transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy analysis indicated that the metallic-state Pd nanoparticles were uniformly dispersed onto the TiO₂ particles anchored onto the MWCNTs. Electrochemical characterizations using cyclic voltammetry and chronoamperometry measurements demonstrated that the Pd/TiO₂-MWCNTs catalyst showed higher electro-catalytic activity, durability, and stability for methanol, ethanol, and isopropanol oxidation than the Pd/MWCNTs catalyst. Furthermore, the electro-catalytic activity and durability for alcohols was of the order ethanol ≥ methanol ≥ isopropanol. The effect of the scan rate was also studied. The results indicated that the alcohol oxidation process on the Pd/TiO₂-MWCNTs modified electrode was irreversible and controlled by the diffusion of the alcohols. Taken together, these results demonstrated that the Pd/TiO₂-MWCNTs electrode has good potential for significant application in fuel molecular oxidation.

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1. Introduction

Direct alcohol fuel cells (DAFC) have attracted increasing attention as powerful and clean electrochemical energy converters for electric vehicles and portable electronic devices [1,2], because of the advantages associated with the simplicity of their system, low-to-zero pollutant emissions, and high energy densities [3,4]. However, there are still some obstacles limiting the application of alcohol fuel cells, with the main problem being the low electro-catalytic activity and facile deactivation of the catalysts when it is applied to the molecular oxidation [5,6]. The noble metal and noble metal based alloy catalysts widely used in fuel cells exhibit great electro-catalytic activity [7–9]. Among noble metal group, Pd represents the most cost-effective choice and is also relatively abundant in the earth [10,11]. In addition, Xu et al. have found that the Pd-based catalysts show better activity and steady-state performance for alcohols electrooxidation than Pt-based catalysts in alkaline media [7,12]. Unfortunately, naked palladium nanoparticles tend to aggregate and this can have an adverse impact on their electro-catalytic activity [13]. Template

supports with a large superficial area are therefore needed to disperse the palladium nanoparticles, preventing aggregation [5,14].

In recent years, significant research efforts have been devoted to investigating the effects of metal oxides catalysts based on noble metals for the molecular oxidation of fuel cell [15–17]. The introduction of metal oxides can improve the catalytic activity, corrosion resistance, and reduce any degradation of the active surface area [18,19]. In addition, the combination of transition metals with noble metal group can improved catalyst's oxygen reduction reaction overpotentials and reduced noble group metals loadings [20,21]. Among all transition metal oxides, TiO₂ nanoparticles show good potential on account of their commercial availability, long-term stability, and nontoxic nature [22]. Besides, the application of TiO₂ as a support can enhance the performance of Pd-based catalysts [23,24]. However, the utilizing of TiO₂-CNTs supports to disperse catalytic nanoparticles is common in the optoelectronic and photocatalysis fields [25,26]. This is due to the low conductivity of semiconductor TiO₂ [27]. Pretreatment is required to enhance the electronic conductivity of TiO₂.

In this work, we developed a facile method to synthesize Pd/TiO₂-MWCNTs catalyst, which applied pretreated TiO₂ as a support between Pd and MWCNTs to increase the electro-catalytic activity, poison resistance and stability of the Pd nanoparticles. And then

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we adopted this catalyst to the oxidation of methanol, ethanol, and isopropanol in alkaline system. The catalysts were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analyses. Electrochemical experiments were conducted using cyclic voltammetry and chronoamperometric measurements.

2. Experimental

2.1. Raw materials

All the chemicals employed in this study were of analytical grade. Tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, TBT), palladium chloride (PdCl_2), concentrated nitric acid (HNO_3), concentrated sulfuric acid (H_2SO_4), sodium borohydride (NaBH_4), hydrogen fluoride (HF), sodium hydroxide (NaOH), methanol, ethanol, ethylene glycol, and isopropanol were used without any further purification. Commercial MWCNTs (Nanotech Port Co., Shenzhen, China) were used. The used water was ultrapure ($18.2 \text{ M}\Omega \text{ cm}^{-1}$).

2.2. Treatment of the MWCNTs

Treatment was required to remove any impurities from the MWCNTs and increase the surface area of the available functional groups. Typically, MWCNTs were added with concentrated HNO_3 and H_2SO_4 (1:3, v/v) to a 50 mL flask and ultrasonicated for 10 h at 80°C . The resulting mixture was filtered and the filter-cake washed several times with ultrapure water until the rinse water achieved neutral.

2.3. Fabrication and pretreatment of TiO_2

Tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, TBT) was used as a titanium source. TBT was added to ethanol and several drops of water added with ultrasound treatment. Upon completion of the hydrolysis reaction, the mixture was dried at 110°C for 4 h before being washed and filtered several times with ethanol and ultrapure water. The residues were dried at 500°C in a muffle furnace for 4 h to obtain anatase TiO_2 .

A 0.5 M HNO_3 solution was then added to the synthesized TiO_2 and dried at 200°C for 2 h. Following this treatment, the sample was dispersed in a 0.2 M HF solution with strong stirring for 4 h to improve its electronic conductivity. The precipitate was then separated by filtration and washed several times with ultrapure water, and dried at 70°C .

2.4. Preparation of the TiO_2 -MWCNTs and Pd/ TiO_2 -MWCNTs catalysts

The TiO_2 -MWCNTs were synthesized using the *in situ* chemical method. Pretreated TiO_2 (0.1 g) was dispersed in ultrapure water (in a 100 mL beaker) and vigorously stirred for 1 h. Functional MWCNTs (0.05 g) were then added and the resulting mixture was stirred for 1 h. Isopropanol (15 mL) was then added and the resulting mixture stirred for 30 min. Ethylene glycol (5 mL) was then added, and the resulting mixture stirred for 6 h to ensure that the reaction proceeded to completion. The sample was filtered and washed several times with ultrapure water before being dissolved in ultrapure water.

The Pd/ TiO_2 -MWCNTs catalyst was synthesized using the borohydride reduction method. PdCl_2 was ultrasonicated in ultrapure water at 50°C for 1 h to obtain a uniform solution. The TiO_2 -MWCNTs (Pd: TiO_2 -MWCNTs = 1:5, w/w) were then dissolved in ultrapure water with stirring over a period of 30 min. The Pd solvent was then added and the resulting mixture was stirred for a period of 1 h. Aqueous NaBH_4 (Pd: NaBH_4 = 1:70, w/w) was then

added to the solution in a drop-wise manner. The resulting solution was then stirred for another 8 h before being filtered and washed several times with ultrapure water. The resulting residues (about 0.18 g) were then dissolved in ultrapure water (10 mL).

2.5. Electrochemical instrumentation and characterization

The catalysts were characterized by TEM (JEOL JEM-200CX), XRD with Cu $K\alpha$ radiation (ARL X'TRA), and XPS (ULVAC-PHI PHI 5000 VersaProbe). The mass ratio of Pd in the catalyst was detected by the ICP (Optima 5300DV). The Model CHI 660D electrochemical workstation was applied for the electrochemical experiments. A three-electrode cell was used for the electrochemical measurements. Glassy carbon (GC, with a diameter of 3 mm), platinum foil (1 cm^2) and saturated calomel electrode (SCE) were used as the working, counter and reference electrodes, respectively. The catalyst solution ($6 \mu\text{L}$) was dropped onto the GC electrode, and then dried using infrared light. Prior to the electrochemical test, the GC electrode was polished mechanically with alumina powder of size 5 and $0.05 \mu\text{m}$ successively, and cleaned in an ultrasonic water bath before catalyst deposition.

Meanwhile, the electrocatalytic activity of the synthesized catalyst is represented by the current density. All current densities in the present study were normalized by the electrochemical active surface area (ESA) of Pd nanoparticles. The electrochemical active surface area of Pd nanoparticles was measured through the integration of charges in the reduction of palladium oxide formed over the top layer of the Pd particles that has been reported previously [28–30]:

$$\text{ESA} = \frac{Q_H}{[\text{Pd}] \times 0.405}$$

where Q_H is the calculated charge for hydrogen desorption (mC cm^{-2}), $[\text{Pd}]$ is the palladium mass based electrode loading ($\text{mg}_{\text{Pd}} \text{ cm}^{-2}$), and 0.405 (mC cm^{-2}) is the charge value assumed for the reduction of the PdO monolayer.

3. Results and discussion

3.1. Physical characterizations

3.1.1. TEM analysis

The micro-surfaces of the catalysts are shown in Fig. 1. It is clear from Fig. 1(a) that the tubes of the MWCNTs had clean surfaces after the pretreatment process. The TEM pictures of the Pd/MWCNTs (Fig. 1(b)) and TiO_2 -MWCNTs (Fig. 1(c)) confirmed the successful dispersion of Pd nanoparticles and TiO_2 particles onto the MWCNTs. From Fig. 1(d), it is exhibited that the Pd nanoparticles were uniformly dispersed on the TiO_2 particles anchored onto the MWCNTs. Furthermore, there is no significant difference in particle size of the Pd catalysts between Pd/MWCNTs (Fig. 1(e)) and Pd/ TiO_2 -MWCNTs (Fig. 1(f)). However, Pd agglomerations were more obviously in the Pd/MWCNTs catalyst, likely because of the lack of surface functional groups on the MWCNTs to facilitate Pd ion nucleation and subsequent particle growth [28]. The results demonstrated that the pretreatment method of TiO_2 effectively increased the activity sites on its surface, and promoted the Pd dispersion.

3.1.2. Crystallographic analysis

The XRD profiles were used to investigate the crystal form of the catalysts. In all the MWCNTs catalysts, the broad peaks around 26.0° corresponding to the (002) plane of the graphitized CNTs could be found. In the TiO_2 -MWCNTs and Pd/ TiO_2 -MWCNTs catalysts, the graphitized CNT peaks were overlapped by the anatase

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