



Preparation and characterization of Pt/TiO₂ nanofibers catalysts for methanol electro-oxidation



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ABSTRACT

Pt/TiO₂ nanofibers (Pt/T-NFs) composite catalysts are prepared through the combination of an electrospinning technique with a reductive impregnation method. Obtained samples are analyzed by various techniques, such as transmission electron microscopy and X-ray diffraction, which reveal that 21 wt.% Pt/T-NFs sample has a homogeneous distribution of smaller Pt nanoparticles of about 4.5 nm in size on the TiO₂ nanofibers surface without large aggregations. Electrochemical studies are carried out using cyclic voltammetry, chronoamperometry and CO stripping voltammetry, which indicate that 21 wt.% Pt/T-NFs catalyst has higher electrochemical surface area and much better activity for methanol electro-oxidation. All Pt/T-NFs catalysts have enhanced stability and CO tolerance for methanol electro-oxidation than commercial Pt/C. The results suggest that Pt/TiO₂ nanofibers catalysts exhibit the better activity for methanol oxidation and are favorable for improving the tolerance to poisoning species.

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1. Introduction

Direct methanol fuel cells are receiving more and more attention as power sources for portable electronic devices and electric vehicles [1,2]. Methanol has unique advantages to be a promising option as fuel, such as high energy density, good kinetics of oxidation compared to other alcohols at low temperatures and it could be oxidized completely to CO₂, resulting in the maximum transfer of electrons [3]. Consequently, oxidation of methanol has been studied extensively over the past several decades.

Platinum is generally considered to be the best monometallic catalyst for the electro-oxidation of small organic molecules. Most researches focused on Pt-based catalysts and many achievements have been obtained including identifying the intermediates, elucidating the reaction mechanism and enhancing the catalyst activity [4–14]. However, the price of pure platinum is relatively high and it is a poor anode catalyst for methanol electro-oxidation at room temperature because CO is generated as an intermediate during methanol oxidation reaction and strongly adsorbed on platinum active sites [15–18]. The electro-catalytic activity of Pt nanoparticles for methanol reaction is dependent on various factors such as preparation methods, supporting materials, size, dispersion of the particles and their surface conditions, and so on.

Generally, the high dispersion of Pt nanoparticles on a support is very significant for its electro-catalytic activity [19,20].

Various studies have been focused on the development of novel Pt-based electro-catalysts, for example, Pt/transition metal oxide composite systems. TiO₂ [21,22], MoO_x [23], SnO₂ [24], CeO₂ [25,26], and WO₃ [27,28] have been employed as supports to enhance the activity and stability of the electro-catalysts for methanol oxidation. The transition metal oxides have high chemical stability, good corrosion resistance and strong metal-support interaction, which can enhance the activity of the catalysts. As catalyst supports, they are able to stabilize and disperse adequately a number of active phases. Among different metal oxides titanium dioxide has caused more and more attention because of low cost, high durability, non-toxic nature and high stability in acidic and oxidative environments [29,30]. Above all, it is easier to disperse Pt nanoparticles on TiO₂ rather than on carbon supports which are characterized by their hydrophobicity [31]. However, the electric conductivity of TiO₂ is relatively lower, which limits its practical application in fuel cells [32,33].

Pt/TiO₂ electrodes reported in the papers were prepared by gas phase decomposition, electro-deposition, thermal decomposition [31] and magnetron sputtering [34–41], etc. Different preparation techniques result in different properties of the electrode materials [42]. Electrospun nanofibers have been proven to be efficient catalytic supports owing to the large surface areas and high porosity, which are preferable to the dispersion of Pt nanoparticles

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on the surface of the TiO₂ nanofibers (T-NFs) support, leading to the low electrical resistance to facilitate electron transport during the electrochemical reactions, maximum contact with fuel or oxidant, and strong interaction between the metal Pt and the support, increasing the catalytic activity of Pt/T-NFs for methanol oxidation.

In the present study, we propose a flexible approach to the preparation of Pt/TiO₂ hybrid electrodes with different Pt contents by combining electrospinning technique with reduction impregnation method. The catalysts were characterized by transmission electron microscopy, electron diffraction spectroscopy and X-ray diffraction. Their electrocatalytic activities for methanol oxidation were investigated by cyclic voltammetry, chronoamperometry and CO stripping voltammetry at 30 °C in acidic solutions.

2. Experimental

Electrospinning of the T-NFs was carried out in air at room temperature with a standard syringe and grounded collector plate configuration, as described in the literature [43,44]. Firstly, an electrospinning solution was prepared by mixing 0.3 g polyvinyl pyrrolidone (PVP, $M_w \approx 1,300,000$) and 4.5 mL anhydrous ethanol and stirred until it was completely dissolved. Then 3 mL acetic acid (CH₃COOH, $M_w = 60.05$) and 2.5 mL titanium (IV) isopropoxide (TIIP, $M_w = 284.22$) were added into the above mixed solution. After that, this precursor solution was fed at a constant feed rate of 0.5 mL h⁻¹ through a stainless steel needle with a flat outlet. The distance between the tip of the needle and the collector plate was about 18 cm, and the applied voltage was 16 kV. After a period of time, a large amount of white nonwoven nanofibers were obtained. Later the electrospun fibers were exposed to air at room temperature for several hours to allow for the complete hydrolysis of the polymer. Finally, the nanofibers were followed by calcination in air at 600 °C for 3 h to decompose continuously and remove the precursor residues. The T-NFs were obtained without further modification.

The Pt/T-NFs catalysts were synthesized using the impregnation method [45]. For example, in order to produce 10 wt.% Pt/T-NFs catalysts, 0.5 g T-NFs was mixed with 6.25 mL 20 g L⁻¹ hexachloroplatinic acid (H₂PtCl₆·6H₂O, $M_w = 517.92$) solution. The

mixture was ultrasonically treated for 1 h and then stirred for 2 h. After that 200 mL 0.4 mol L⁻¹ sodium borohydride (NaBH₄, $M_w = 37.83$) at 80 °C was added to the mixture under vigorous stirring. Then, the catalytic powder was filtered and washed with a large amount of water and dried under vacuum at 110 °C for 4 h. Similarly other stoichiometric Pt/T-NFs catalysts were synthesized.

The morphology of the prepared catalysts was studied by transmission electron microscopy (TEM, JEOL JEM 2000EX) and the microscope with an accelerating voltage of 200 kV. The sample specimens for TEM experiment were prepared by dispersing the catalyst powder in ethanol by ultrasonic treatment for several minutes, dropping onto a holey carbon film supported by a copper grid. The elemental composition and the Pt weight percentage of Pt/T-NFs catalysts were determined by electron diffraction spectroscopy (EDS, FEI GENESIS 60S). The crystal structure was investigated with X-ray diffraction (XRD, SHIMADZU XD-3A) using Cu K radiation. Data were recorded at a scanning rate of 5° min⁻¹ with a scanning step size of 0.02°.

Electrochemical measurements were carried out at 30 °C in a three-electrode cell using CHI 760D electrochemical workstation (CH Instruments, Shanghai Chenhua Instrument Corp. China). The counter electrode was a Pt wire while the reference electrode was a reference saturated calomel electrode (SCE). All the potentials in this study were related to SCE. A 0.5 mol L⁻¹ sulfuric acid (H₂SO₄, $M_w = 98.08$) was used for preparing the electrolytic solution and 1 mol L⁻¹ methanol (CH₃OH, $M_w = 32.04$) + 0.5 mol L⁻¹ H₂SO₄ solution for methanol oxidation activity test. The working electrode was a glassy carbon disk with a 3 mm diameter (geometric surface area is 0.071 cm²). It was polished with Al₂O₃ powder and washed carefully before catalyst deposition. An ink was prepared by ultrasonically dispersing 5 mg catalytic powder with 5 mg conductive graphite powder in 0.5 mL ultrapure water (Millipore, 18.2 MΩ cm). The solution was sonicated for 15 min. The conductive graphite powders were added in order to ensure a good electronic conductivity of the catalytic layer. A drop of 4.0 μL catalyst ink was deposited onto the working electrode surface with a micropipette. A Nafion film was cast by pipetting 2.0 μL 0.5 wt.% Nafion solution onto the catalytic layer. Before the cyclic voltammetry measurements, nitrogen was bubbled in the supporting electrolyte for 30 min. Cyclic voltammetry was carried out

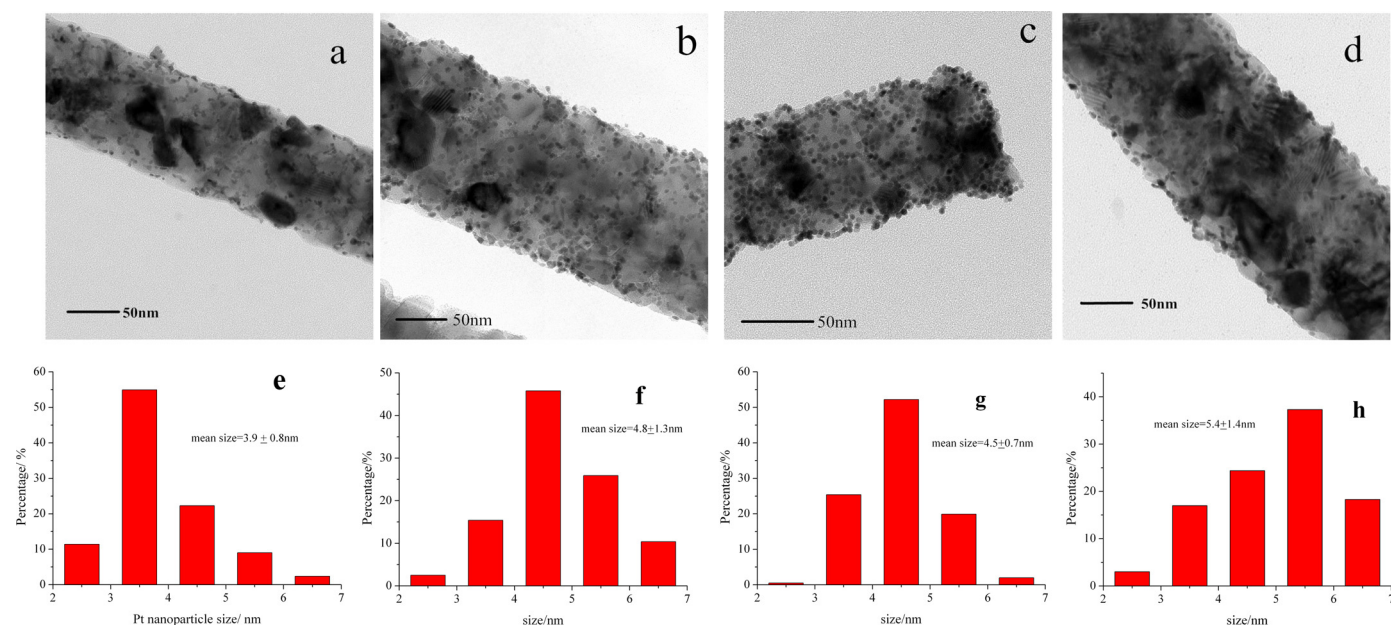


Fig. 1. TEM images (a–d) and Pt particles size distribution (e–h) of samples (a, e) 10% Pt/T-NFs (b, f) 16% Pt/T-NFs (c, g) 21% Pt/T-NFs (d, h) 27% Pt/T-NFs.

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