



Sonochemical synthesis and characterization of Pt/CNT, Pt/TiO₂, and Pt/CNT/TiO₂ electrocatalysts for methanol electro-oxidation



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ABSTRACT

Pt electrocatalyst supported on composite formed of multi-walled carbon nanotubes and titanium oxide (CNT/TiO₂) was successfully synthesized by a sonochemical method without heat treatments, surfactants or additives. This electrocatalyst could be used for direct methanol fuel cells (DMFC) applications. For comparison, Pt/CNT and Pt/TiO₂ electrocatalysts were prepared as reference samples. Structural properties and morphology of the synthesized materials were examined by X-ray diffraction, transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and their specific surface areas were determined by the Brunauer-Emmett-Teller method. The Pt and acid-treated CNT contents were analyzed by inductively coupled plasma atomic emission spectroscopy and thermogravimetric analysis, respectively. The electrochemical properties of the synthesized electrocatalysts were evaluated by cyclic voltammetry (CV) and chronoamperometry in a three-electrode cell at room temperature. The evaluation performed using electrochemical techniques suggests that TiO₂ promotes the CO-tolerance due to TiO₂-Pt interaction. The CV tests demonstrated that 6 wt.% of acid-treated CNT increases significantly the current density when Pt selectively interacts with TiO₂.

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1. Introduction

Direct methanol fuel cells (DMFC) are being widely studied to satisfy the increasing demand of the power systems of portable electronic devices [1,2]. However, the main obstacles for the DMFC commercialization are the high cost of Pt-based electrocatalysts, as well as the sluggish kinetics of methanol electro-oxidation due to the Pt poisoning surface, caused by CO-like intermediates produced during methanol reaction. To solve this issue, Pt alloys have been extensively investigated to enhance the catalytic activity or to avoid the poisoning problems [3–5]. It has been established that the presence of Ru in the catalyst promotes the oxidation of CO by a bi-functional mechanism [6,7]. Nevertheless, the limited supply and the high cost of Ru prevent its use on a commercial

scale. On the other hand, the general requirements of the supporting materials for Pt-based electrocatalysts are: high surface area to allow a good dispersion of metal loading, good electrical conductivity to facilitate electron transport during the electrochemical reaction, a mesoporous structure in order to maximize the triple-phase boundary and a high corrosion resistance. Typically, multi-walled carbon nanotubes (CNT) have been used as promising supporting materials for DMFC electrocatalysts due to their good electrical conductivity [8,9]. However, the corrosion of carbon support under the harsh reaction conditions would lead to a rapid catalytic activity loss, and hence the reduction of the fuel cell life [10,11]. Recent researchers have reported the use of metal oxides as supports for DMFC electrocatalysts [12–18]. These studies have demonstrated that the incorporation of oxide nanoparticles can enhance their durability, catalytic activity, and CO-tolerance. Metal oxides as titanium oxide have attracted the attention as supports of catalysts due to their stability at fuel cell operation conditions, low cost, nontoxicity, and commercial availability.

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It is well known that the surface structure, electronic properties and catalytic performance of the electrocatalysts are related to the preparation methods of the supporting materials. One of the most promising methods to produce metallic nanoparticles and fuel cell electrocatalysts is using ultrasound. It has been demonstrated that the sonochemical production of carbon supported catalyst showed better electrochemical properties than materials prepared by chemical means since the ultrasonic vibration induces the nanoparticles dispersion on the support and hinders the agglomeration [19].

In this work, Pt/CNT/TiO₂ composite was prepared by the sonochemical method as anode electrocatalyst for DMFC with good CO tolerance. Pt/CNT and Pt/TiO₂ electrocatalysts were prepared as reference samples for electrochemical tests. Materials were characterized by X-ray diffraction (XRD), Raman spectroscopy, inductively coupled plasma atomic emission spectroscopy (ICP-AES), transmission electron microscopy (TEM) and nitrogen adsorption/desorption by the Brunauer-Emmett-Teller (BET) method. The electrochemical properties of prepared electrocatalysts were evaluated by cyclic voltammetry (CV) and chronoamperometric techniques allowing to distinguish the successful inclusion of TiO₂ to prevent CO poisoning.

2. Experimental procedures

2.1. Multi-walled carbon nanotubes synthesis and purification

Multi-walled carbon nanotubes (CNT) were synthesized in a modified spray pyrolysis system, previously reported by Aguilar et al. [20]. The Vycor tubing was heated into a tubular furnace (Lindberg Blue) until 925 °C under argon (Infra, 99.999%) flow at a rate of 0.2 L min⁻¹. Once the temperature was stabilized, the argon flow was adjusted at a rate of 4 L min⁻¹. Subsequently, a solution with toluene (Sigma-Aldrich, 99.8%) and 2.5 wt.% of ferrocene (Sigma-Aldrich, 98%) was sprayed into the Vycor tubing. After that, the system was cooled down to room temperature keeping the argon flow at a rate of 0.2 L min⁻¹.

The synthesized CNT were mechanically removed from the Vycor tubing and were purified with nitric acid (Sigma-Aldrich, 70%) in a reflux system during 12 h at 90 °C. After that, the acid-treated CNT were washed with deionized water (Milli-Q, 18 MΩ·cm) and dried at 100 °C for 12 h.

2.2. Synthesis of TiO₂ and CNT/TiO₂ supports

Herein, the synthesis method used for preparing the CNT/TiO₂ composite was based on a modified protocol to prepared TiO₂ previously reported by Yu et al. [21,22].

A direct immersion high-intensity ultrasonic probe (Sonics and Materials, VCX750, 20 kHz, 2 cm diameter) was used to prepare TiO₂ and CNT/TiO₂ supports.

The TiO₂ synthesis required the preparation of a precursor solution with 9 mL of titanium isopropoxide (TIP, Sigma-Aldrich, 97%) and 18 mL of isopropyl alcohol (Sigma-Aldrich, 99.5%). After the precursor solution was stirred during 15 min, the solution was injected into deionized water under sonication (3 s on, 1 s off, amplitude 40%) in air at controlled temperature (70 °C), the sonication was kept during 3 h [21,22]. The isopropyl alcohol: water volume ratio was remained constant 1:2. After sonication, the mixed solution was aged 10 h. Additional experiments were previously performed to show that a 3 h sonication followed by a 10 h aging time corresponds to optimized conditions for preparation. Subsequently, the mixed solution was stirred until dried appearance at 85 °C in a magnetic mixer-heater. Finally, a degassing treatment was done to eliminate any residual water under N₂ atmosphere at 120 °C for 3 h.

The CNT/TiO₂ support was prepared by hydrolysis of titanium isopropoxide (TIP) in the presence of acid-treated CNT and isopropyl alcohol: water (1:2). Acid-treated CNT (75 mg) were dispersed in deionized water during 30 min using the ultrasonic probe (3 s on, 1 s off, amplitude 40%) in order to achieve a final 6 wt % CNT loading. Meanwhile, 3 mL of TIP (Sigma-Aldrich, 97%) were dissolved in isopropyl alcohol (Sigma-Aldrich, 99.5%) under magnetic-stirring. During the ultrasonic vibration, the resulting TIP solution was injected into an acid-treated CNT suspension. To complete the crystallization of the TiO₂, the sonication was continued for 3 h at a controlled temperature (70 °C). Once the sonochemical synthesis ended, the mixed solution was aged for 10 h. Afterward, the precipitate was dried in a magnetic mixer-heater at 85 °C. This process was performed until the product showed dried appearance. A final degassing treatment was done to eliminate any residual water under N₂ atmosphere at 120 °C for 3 h.

2.3. Preparation of Pt/CNT, Pt/TiO₂ and Pt/CNT/TiO₂ electrocatalysts

To obtain Pt/CNT, Pt/TiO₂ and Pt/CNT/TiO₂ electrocatalysts, and 90 mg of the support (acid-treated CNT, TiO₂ or CNT/TiO₂) were dispersed in 15 mL of isopropyl alcohol under sonication with a direct immersion probe during 20 min (3 s on, 1 s off, amplitude 40%). In the meantime, a Pt precursor solution (H₂PtCl₆, Sigma-Aldrich, 99.999%) was prepared in an ultrasonic bath equipment (Branson, 2510). The metal loading of the electrocatalysts was calculated to obtain 10 wt.% of Pt. The metal precursor solution was added to each support suspension, and the sonication was kept during 20 min. Finally, 19.4 mg of sodium borohydride used as a reducing agent (Sigma-Aldrich, 99%) was added to the support suspension, and the sonication was maintained for 20 min. The black precipitates were filtered and washed several times with isopropyl alcohol, and then dried under N₂ atmosphere at 120 °C for 3 h.

2.4. Characterization and Electrochemical evaluation of the electrocatalysts

Powder-X-ray diffraction (XRD) was performed in a Philips X'Pert MPD diffractometer using Cu Kα (λ=0.154 nm) radiation source. The 2θ angular regions between 20° and 60° were studied. To determine the graphitization order, acid-treated CNT and CNT/TiO₂ samples were analyzed by Micro-Raman spectroscopy using a Horiba Jovin Yvon X'plora microscope applying a laser source with a wavelength of 532 nm. To determine the particle size, the transmission electron microscopy analysis (TEM) was performed in a JEOL JEM 2100F. The porosity of the synthesized materials was evaluated using a Micromeritics TriStar II 3020 and the specific surface areas (S_{BET}) were calculated by the Brunauer-Emmett-Teller (BET) method. Prior to measurement, the samples were outgassed under N₂ flow at 120 °C for 3 h. The Pt loading of the synthesized electrocatalysts was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) in a Varian Liberty 110 spectrometer. The amount of acid-treated CNT in the Pt/CNT/TiO₂ electrocatalyst was calculated by thermogravimetric analysis in a TA Instruments Q600 equipment. This analysis was performed under oxidant conditions from room temperature up to 800 °C with a heating ramp rate of 4 °C min⁻¹. To determine the chemical states of Ti and Pt in Pt/CNT/TiO₂ and Pt in Pt/CNT electrocatalysts, high-resolution X-ray photoelectron spectroscopy analysis were realized in an XPS-HR custom made SPECS PHOIBOS equipment using Al monochromatic X-ray source.

The electrochemical experiments were performed in a conventional three-electrode cell at room temperature, using 0.5 M H₂SO₄ and 0.5 M H₂SO₄+ 0.5 M CH₃OH as electrolytes. A glassy carbon (0.3 cm diameter) was used as the substrate to test different electrocatalysts. This assembly was used as a working electrode

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