

Sonochemical synthesis of Pt/CNT/TiO₂ anode catalyst for direct methanol fuel cells

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ABSTRACT

Pt/CNT/TiO₂ anode catalyst was prepared by sonochemical method using a high-intensity probe. Multi-walled carbon nanotubes (CNT) was obtained by spray pyrolysis method, purified and then characterized by Raman spectroscopy. The graphitization order of CNT was evaluated by I_D/I_G ratio, the value obtained was 0.39. The CNT/TiO₂ system was synthesized at controlled temperature under ultrasonic conditions. Finally, about 7 wt.% of Pt nanoparticles were incorporated to CNT/TiO₂ using NaBH₄ as reducing agent. Pt/CNT and Pt/TiO₂ catalysts were prepared as reference samples. The chemical composition of the systems were determined by ICP and EDS analysis. Structural properties and specific surface area of anode catalysts were examined by XRD and nitrogen adsorption by BET method, respectively. The electrochemical study was performed by cyclic voltammetry in a three-electrode half-cell at room temperature. Pt/CNT/TiO₂ anode catalyst was successfully synthesized by sonochemical method without heat treatment, surfactants or additives. The synthesized catalyst was obtained with a narrow pore size distribution and specific surface area of 193 m² g⁻¹. The results of cyclic voltammetry tests for methanol oxidation suggest that the incorporation of TiO₂ improves the catalyst tolerance to carbonaceous species. The Pt/CNT/TiO₂ anode catalyst exhibited better oxidation of methanol to carbon dioxide than Pt/CNT.

Keywords: Carbon nanotubes; Titanium dioxide; Methanol oxidation



1. Introduction

Direct methanol fuel cell (DMFC) is being widely studied in order to satisfy the increasing demand of power systems of portable electronic devices [1]. However, the main obstacles for DMFC commercialization are the high cost of Pt-based electrocatalyst and the sluggish kinetic of methanol electro-oxidation, because of the Pt poisoning surface by CO-like intermediates produced during methanol electro-oxidation. To solve this problem, Pt alloys have been extensively investigated to enhance the catalytic activity or prevent the poisoning problems [2, 3]. Pt-Ru alloy is considered the benchmark anode catalyst for DMFC. The presence of Ru in the catalyst promotes the oxidation of CO by a bi-functional mechanism [4]. Nevertheless, the limited supply and high cost of Ru prevent its use on commercial scale.

The surface structure, electronic properties and catalytic performance of electrocatalysts are related to the preparation methods of the support. Typically, carbon nanotubes (CNT) are used as promising supports for DMFC due to their good electrical conductivity [5], however, the corrosion of carbon support under the harsh reaction conditions would lead to quick loss catalytic activity, and hence the reduction of fuel cell life [6]. In general, the requirements of support materials of Pt-based electrocatalyst are a high surface area to good dispersion of metal loading, good electrical conductivity to facilitate electron transport during electrochemical reaction, mesoporous structure in order to maximize the triple-phase boundary and high corrosion resistance. Recent researches have been reported the use of metal oxides as support for DMFC [7-10], these studies have demonstrated that the incorporation of oxide nanoparticles can enhance the durability and catalytic activity of the electrocatalyst, and also their corrosion resistance. Among many metal oxides (MO), titanium oxide has been attractive as support because of its stability in fuel cell operation conditions, low cost, nontoxicity and commercial availability.

In order to obtain electrocatalytic stability, high CO tolerance and good electrical conductivity, we prepared the Pt/CNT/TiO₂ electrocatalyst by sonochemical method. On the other hand, Pt/CNT and Pt/TiO₂ were prepared as reference samples. Selected materials were characterized by X-ray diffraction (XRD), Raman spectroscopy, Inductively Coupled Plasma (ICP), Energy Dispersive Spectroscopy (EDS) and nitrogen adsorption by BET method. The CO tolerance of Pt/CNT/TiO₂ electrocatalyst due to TiO₂ presence was analyzed by Cyclic Voltammetry (CV) test.

2. Experimental

2.1 Carbon nanotubes synthesis

Multi-walled carbon nanotubes (CNT) were synthesized in a modified spray pyrolysis system, previous reported by Aguilar *et al.* [11]. In our synthesis system an additional valve was added to avoid the access of solution mist inside Vycor tubing (9 mm outer diameter) during the heating and cooling processes. The Vycor tubing was heated into a tubular furnace (Lindberg Blue) up to 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. Immediately, a solution with toluene (Sigma Aldrich, 99.8%) and 2.5 wt.% of ferrocene (SigmaAldrich, 98%) was sprayed inside Vycor tubing. Thereafter, the system was cooled up to room temperature under 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 CNT were washed with deionized water (Millipore, 18 MΩ) and dried at 100 °C for 12 h.

2.2. Preparation of CNT/TiO₂ and Pt/CNT/TiO₂ catalyst

CNT/TiO₂ and Pt/CNT/TiO₂ were synthesized by sonochemical method employing a direct immersion high-intensity ultrasonic titanium probe with 19 mm diameter (Sonics and Materials, VCX750, 20 kHz).

Sonochemical preparation of CNT/TiO₂ with mesoporous and bicrystalline TiO₂ framework was synthesized at controlled temperature by means of thermocouple attached to VCX750 equipment.

The CNT/TiO₂ was prepared by hydrolysis of titanium isopropoxide (TIP) in the presence of isopropyl alcohol and water. The volume ratio of alcohol:water remains constant in 1:2.

Acid treated CNT (75 mg) were dispersed in deionized water during 30 min using a direct immersion titanium probe in the sonication glass vessel (3 s on, 1 s off, amplitude 40%). Meanwhile, 3 mL of TIP (Sigma Aldrich, 97%) were dissolved in isopropyl alcohol (Sigma Aldrich, 99.5%) under magnetic stirring.

During ultrasonic irradiation, the resulting TIP solution was injected into CNT suspension. The sonication was continued for 3 h, in order to complete the crystallization of TiO₂. Once the sonochemical synthesis ended, the mixed solution was aged 10 h. Afterwards, the precipitate was dried in a magnetic mixer-heater at 85 °C. The drying process was performed until the product had dry appearance.

Pt/CNT/TiO₂ composite was synthesized by reduction method under ultrasonic irradiation. The metal loading of the catalyst was calculated to obtain 10 wt.% of Pt. In an ultrasonic bath equipment (Branson, 2510) 90 mg of CNT/TiO₂ were dispersed in 10 mL of isopropyl alcohol during 1 h. Subsequently, a direct immersion high-intensity probe was placed into the solution glass vessel. After, metal precursor solution (H₂PtCl₆, Sigma Aldrich, 99.999%) was added to the mixture, followed by high-intensity sonication for 30 min. To reduce the Pt precursor, 19.4 mg of NaBH₄ (Sigma Aldrich, 99%) was added into the solution. The sonication was continued for 30 min. The black precipitate was filtered and washed several times with isopropyl alcohol and then dried under N₂ atmosphere at 120 °C for 3 h.

TiO₂, Pt/TiO₂ and Pt/CNT were prepared as samples references following the procedures previously described.

2.3 Characterization methods

The elemental composition of synthesized electrocatalyst was investigated by dispersive X-ray spectroscopy (EDS) in a JEOL JSM-5300 microscope. In addition, the amount of platinum and titanium in the electrocatalyst was determined by inductively couple plasma-atomic emission spectrometry (ICP-AES) in a Varian Liberty 110 spectrometer. Powder XRD diffraction were performed in a Philips X'Pert MPD diffractometer using Cu K_α (λ=0.154 nm) radiation source. The 2θ angular regions between 20° and 60° were analyzed. Selected samples were analyzed by Raman spectroscopy in a HORIBA Jovin Yvon X'ploRA microscope applying a laser source with wavelength at 532 nm. The porosity of materials was evaluated using a Micromeritics TriStar II 3020. The specific surface area (S_{BET}) of synthesized materials



was calculated by Brunauer-Emmet-Teller (BET) method. Prior to measurement, the samples were outgassed under N_2 flow at 120 °C for 3 h.

The electrochemical experiments were made in a conventional three-electrode half-cell at 25 °C in 0.5 M H_2SO_4 and 0.5 M CH_3OH electrolyte. Glassy carbon electrode (0.3 cm diameter) was used as working electrode (WE); Ag/AgCl [Sat NaCl] and Pt coiled were used as reference and counter electrode, respectively. Inks were prepared with 10 mg of electrocatalyst ultrasonic dispersed in 1 mL of ethanol and 60 μ L of a solution 3:1 of Nafion (Sigma Aldrich, 5% in aliphatic alcohols) and deionized water. 10 μ L of electrocatalyst ink were placed on the WE surface. The three electrodes were connected to an AUTOLAB PGSTAT302N potentiostat, subsequently, Cyclic Voltammetry (CV) tests were plotted by performing thirty cycles at a scan rate of 0.02 V s^{-1} . Prior to each test, the electrolyte was purged with argon during 30 min.

3. Results and discussion

The crystalline structure of selected samples was analyzed by XRD. Fig. 1a shows the XRD patterns of TiO_2 , CNT/ TiO_2 and Pt/CNT/ TiO_2 . In all patterns the presence of anatase (JCPDS, no. 21-1272) and brookite (JCPDS, no. 29-1360) structures are determined. The XRD patterns of TiO_2 and CNT/ TiO_2 are similar, indicating that the CNT incorporation during the catalyst synthesis did not modify the formation of TiO_2 . Pt/CNT/ TiO_2 pattern exhibited two Pt diffraction peaks at 39.8° and 46.2° (2 θ), demonstrating that Pt is in the metallic form. In CNT/ TiO_2 and Pt/CNT/ TiO_2 patterns there are no (002) the peak of graphite 2H associated with CNT about at 26° (2 θ), due to the CNT peak overlaps with the (101) peak of anatase phase.

The presence of CNT in the system was confirmed by Raman spectroscopy. Fig. 1b shows the Raman spectra of CNT and CNT/ TiO_2 . The spectra exhibit two characteristic bands at approximately 1572 and 1342 cm^{-1} , corresponding to first order G mode (E_{2g} symmetry) assigned to regular sp^2 graphitic network and D mode (A_{1g} symmetry) corresponds to sp^3 hybridized carbons, indicating the disorder and defects of graphite on CNT surface. The I_D/I_G ratio was used as graphitization degree indicator of CNT [12]. For CNT the I_D/I_G ratio was calculated as 0.39 whereas for CNT/ TiO_2 it is equal to 0.48. This indicates that the graphitic order of CNT in the system CNT/ TiO_2 is reduced. This effect may be attributed to the ultrasonic treatment during the synthesis and the interaction between CNT and TiO_2 . Although the graphitic order was reduced, the crystalline nature of CNT was conserved.

The EDS spectra of CNT/ TiO_2 and Pt/CNT/ TiO_2 are presented in Fig. 1c, where the presence of C, Ti and Pt is confirmed. In the spectrum of Pt/CNT/ TiO_2 also Na is observed as impurity from borohydride reduction method.

The Pt and Ti loadings determined by ICP-AES are presented in Table 1. The synthesis was calculated to obtain 10 wt.% of Pt loading. However, the achieved metal loading was about 7 wt.%. Although the Pt loading was lower than the theoretically calculated, all samples had similar values of metal loading. It is expected that if the amount of $NaBH_4$ as reducing agent increases, more metal nanoparticles will be deposited on CNT surface.



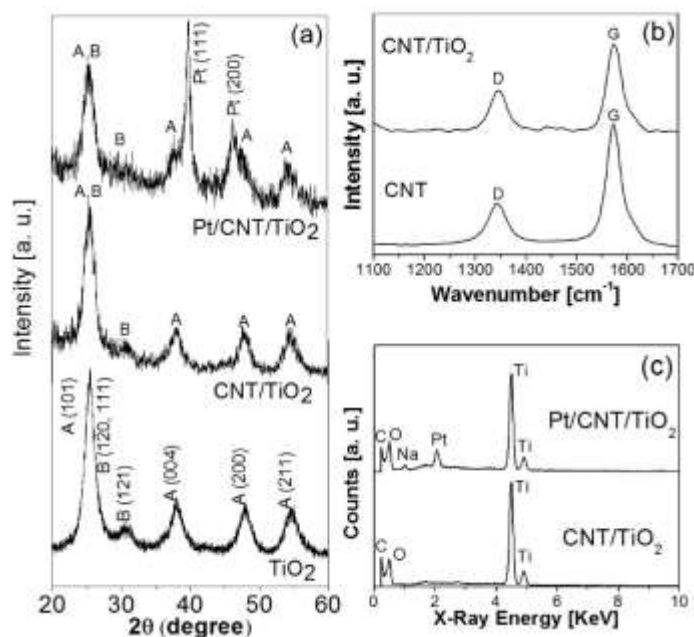


Fig 1. (a) XRD diffraction patterns of TiO₂, CNT/TiO₂ and Pt/CNT/TiO₂. (b) Raman spectra of CNT with and without TiO₂. (c) EDS spectrum of CNT/TiO₂ and Pt/CNT/TiO₂.

On the other hand, the specific surface area (S_{BET}) of prepared materials is presented in Table 1. Where is observed that Pt/CNT/TiO₂ system has larger surface area than Pt/CNT, this fact can improve the dispersion of Pt and enhance the anode catalyst properties.

Table 1. Metal loading of catalysts and specific surface area (S_{BET}) of synthesized materials.

Materials label	Weight % Pt	Weight % Ti	S_{BET} [m ² g ⁻¹]
CNT	----	----	42.5 ±6
Pt/CNT	7.1	----	35.0±6
TiO ₂	----	----	261±6
CNT/TiO ₂	----	----	233±6
Pt/TiO ₂	7.4	36.2	195±6
Pt/CNT/TiO ₂	6.9	33.7	193±6



Nitrogen adsorption/desorption isotherms of TiO_2 , CNT/TiO_2 and $\text{Pt}/\text{CNT}/\text{TiO}_2$ and inset pore size distribution of TiO_2 and CNT/TiO_2 are presented in Fig. 2. The isotherms for all samples are type IV, characteristics of mesoporous materials. Also, the materials exhibit type H3 hysteresis-loop.

The type H3 loop does not present limiting adsorption at high P/P_0 , it is observed with aggregates of plate-like particles to give rise to slit-shaped pores [13].

As show in the insets of Fig. 2a and 2b, TiO_2 and CNT/TiO_2 samples have a narrow pore size distribution with average pore diameter of 4.2 and 5.4 nm, respectively.

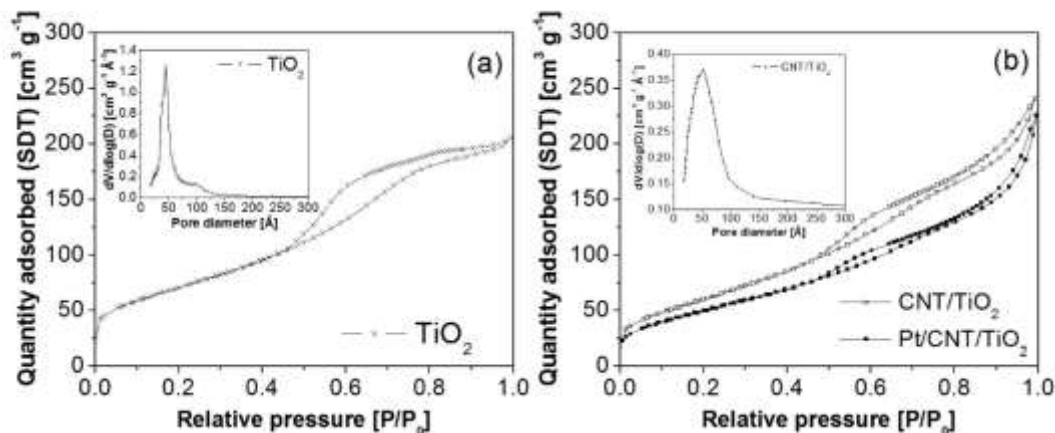


Fig. 2. Nitrogen adsorption/desorption isotherms of (a) TiO_2 , (b) CNT/TiO_2 and $\text{Pt}/\text{CNT}/\text{TiO}_2$. The insets shows pore size distribution calculated by Barret-Joyner-Halenda (BJH) method.

In order to investigate the effect of TiO_2 on methanol oxidation, the CV tests of electrocatalysts Pt/CNT , $\text{Pt}/\text{CNT}/\text{TiO}_2$ and $\text{Pt}/\text{CNT}/\text{TiO}_2$ are compared in Fig. 3. The voltammograms of all materials have similar shape, in agreement with previous reports [7, 8]. There are two main anodic peaks in the forward (I_f) and backward (I_b) scans; I_f is associated to methanol oxidation and I_b is related with the oxidation of CO-like intermediates on the pathways of methanol oxidation, such as formaldehyde (HCHO), formic acid (HCOOH), formate (HCOO^-) and CO species.

To benchmark CO tolerance performance, current densities I_f/I_b ratio has been used as qualitative indicator of poisoning catalyst tolerance. Lower I_f/I_b value indicates poor methanol oxidation and excessive accumulation of carbonaceous species on catalyst surface. Therefore, a higher I_f/I_b value is indicative of improved CO tolerance [7, 8]. The I_f/I_b ratio was estimated to be 0.98, 1.15 and 1.49 for Pt/CNT , Pt/TiO_2 and $\text{Pt}/\text{CNT}/\text{TiO}_2$, respectively.



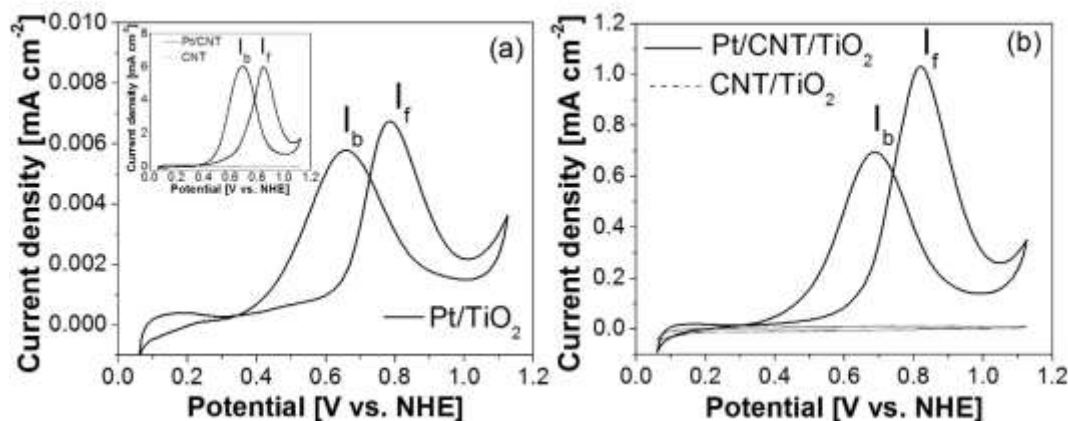


Fig. 3. Cyclic voltammograms of methanol oxidation on (a) Pt/TiO₂, (b) Pt/CNT/TiO₂; inset Pt/CNT. The CV test were performed in a mixture of 0.5 M H₂SO₄ and 0.5 M CH₃OH at scan rate of 0.02 Vs⁻¹, thirty cycle is reported.

These results suggest that the materials prepared with TiO₂ have less carbonaceous accumulation, indicating better oxidation of methanol to carbon dioxide and therefore more tolerant towards CO poisoning. Pt/CNT/TiO₂ must be activated the H₂O in the electrolyte to form hydroxide species on TiO₂ surface and oxidize CO poisoning species, accordingly to bi-functional methanol oxidation mechanism between Pt and Ru [4, 10].

4. Summary and perspectives

The anodic catalyst Pt/CNT/TiO₂ was successfully synthesized without heat treatments, surfactants or additives. The synthesized electrocatalyst was obtained with a narrow pore size distribution and the specific surface area was 193 m² g⁻¹. In the other hand, the Pt/CNT/TiO₂ showed better methanol oxidation and CO tolerance than Pt/CNT. This effect is directly related with the TiO₂ presence in the electrocatalytic system and clearly observed in the cyclic voltammograms. The inclusion of TiO₂ in electrocatalytic systems for methanol oxidation may be provide some insights to improve the electrocatalysts CO tolerance.



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References

- [1] S. Sundarajan, S. I. Allakhverdiev, S. Ramakrishna, Progress and perspectives in micro direct methanol fuel cell. *International Journal of Hydrogen Energy* 2012; 37: 8765-8786.
- [2] L. Li, Y. Xing, Methanol Electro-Oxidation on Pt-Ru Alloy Nanoparticles Supported on Carbon Nanotubes. *Energies* 2009; 2: 789-804.
- [3] E. A. Franceschini, M. M. Bruno, F. J. Williams, F. A. Viva, H. R. Corti, High-Activity Mesoporous Pt/Ru Catalyst for Methanol Oxidation. *Applied Materials & Interfaces* 2013; 5: 10437-10444.
- [4] C. Roth, N. Benker, R. Theissmann, R. J. Nichols, D. J. Schiffrin. Bifunctional electrocatalysis in Pt-Ru nanoparticle systems. *Langmuir* 2008; 24: 2191-2199.
- [5] S. Sharma, B. G. Pollet, Support materials for PEMFC and DMFC electrocatalysts-A review. *J. Power Sources* 2012; 208: 96-119.
- [6] R. Borup, J. Meyers, B. Pivovar, Y. Seung, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J. E. McGrath, M. Inaba, K. Miyake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K. Kimijima, N. Iwashita, Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation. *Chemical Reviews* 2007; 107: 3904-3951.
- [7] B. Yu Xia, S. Ding, H. Bin wu, X. Wang, X. Wen, Hierarchically structure Pt/CNT@TiO₂ nanocatalysts with ultrahigh stability for low-temperature fuel cells. *RSC Advances* 2012; 2: 792-796.
- [8] H. Song, X. Qiu, F. Li, Effect of heat treatment on the performance of TiO₂-Pt/CNT catalysts for methanol electro-oxidation. *Electrochimica Acta* 2008; 53: 3708-3713.
- [9] W. Xiuyu, Z. Jingchang, Z. Hong, Pt-Au/CNT@TiO₂ as a High-Performance Anode Catalyst for Direct Methanol Fuel Cells. *Chinese Journal of Catalysis* 2011; 32: 74-79.
- [10] P. Kolla, A. Smirnova, Methanol oxidation on hybrid catalysts: PtRu/C nanostructures promoted with cerium and titanium oxides. *International Journal of Hydrogen Energy* 2013; 38: 15152-15159.
- [11] A. Aguilar-Elguézabal, W. Antúnez, G. Alonso-Núñez, F. Paraguay Delgado, F. Espinoza, M. Miki-Yoshida, Study of carbon nanotubes synthesis by spray pyrolysis and model of growth. *Diamond & Related Materials* 2006; 15: 1329-1335.
- [12] J. H. Lehman, M. Terrones, E. Mansfield, K. E. Hurts, V. Maunier, Evaluating the characteristics of multiwall carbon nanotubes. *Carbon* 2011; 2581-2602.
- [13] S. Lowell, J. E. Shields, M. A. Thomas, M. Thommes, *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density*, Kluwer Academic Publisher, Netherlands, 2004.

