



Short communication

Novel synthesis of PtRu/multi-walled carbon nanotube catalyst via a microwave-assisted imidazolium ionic liquid method for methanol oxidation

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ABSTRACT

A facile and fast microwave-assisted ionic liquid method has been developed to prepare PtRu nanoparticles onto multi-walled carbon nanotubes (MWCNTs). This novel method has some advantages, such as the high electrocatalytic activity of the catalysts for the methanol oxidation, simple preparation procedures, and recycle of the ionic liquids. Transmission electron micrograph shows that PtRu nanoparticles with diameter of 2–5 nm are uniformly deposited along the length of the MWCNTs (PtRu/MWCNTs). The structure and nature of the resulting PtRu/MWCNT catalysts are also characterized by X-ray diffraction. Electrochemical measurements show that the electrocatalytic oxidation of methanol shows very high catalytic efficiency compared with commercial E-TEK Pt/C (20 wt%Pt) catalysts, which is crucial for anode electrocatalysis in direct methanol fuel cells.

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1. Introduction

The direct methanol fuel cells (DMFCs) have received considerable attention for applications in transportation, portable electronics, and residential power sources, due to their high energy density, relatively low operating temperatures, zero or low emission of pollutants, and minimal corrosion problems. There is increasing interest in developing direct methanol fuel cells as a future power source for small portable electronic devices [1,2]. Pt and Pt alloys are catalytically active in room temperature electro-oxidation reactions of interest to fuel cell applications. It is well known that the catalytic activity of the metal is strongly dependent on the particle shape, size and size distribution [3]. A variety of methods are available for the preparation of Pt and Pt alloy nanoparticles: chemical reduction [3–5], sonication [6,7], γ -ray radiolysis [8], UV irradiation [9,10], thermal decomposition [11,12], vapor deposition [13] and electrochemical synthesis [14], and so on. Microwave heating through dielectric losses is fast and simple, uniform, energy efficient, and has been used in preparative chemistry and material synthesis. Recently, there had been more reported successes in using microwave irradiation to prepare high purity nanoparticles with narrow particle size distributions. For example, polymer-stabilized Pt, Ru, Ag and Pd colloids were prepared from the microwave heating of ethylene glycol solutions of dissolved metal salts [15–18].

In this paper, a novel strategy to synthesize PtRu nanoparticles supported on multi-walled carbon nanotubes (MWCNTs) is reported via a microwave-assisted ionic liquid method. PtRu/MWCNT nanocomposites containing 20 wt% of Pt were successfully prepared by microwave irradiation. HRTEM imaging showed a uniform dispersion of spherical PtRu nanoparticles 2.0–4.0 nm in diameter and with a narrow particle size distribution on the MWCNT surface. Laboratory tests showed that these PtRu/MWCNTs catalysts were more electrochemically active in the room-temperature oxidation of liquid methanol than commercially available catalysts.

2. Experimental

2.1. Preparation of PtRu/MWCNT composites

Multi-walled carbon nanotubes (MWCNTs) were obtained from Chemical Engineering Department, Tsinghua University. The MWCNTs were treated by boiling the as-received MWCNTs in HNO₃ for 3 h, rinsed with copious water, dried and ground. In a typical process, a PtRu/MWCNT catalyst with a nominal molar Pt/Ru ratio of 1/1 is prepared as follows. Firstly, 25 mg H₂PtCl₆·6H₂O, 10 mg RuCl₃ and appropriate amounts of MWCNTs were mixed with 25 mL acetone and then 50 mg ascorbic acid was added as reducing agent. The mixture was then added into 30 mL [(BMI)BF₄] [19], stirred and sonicated at the room temperature for 15 min. Acetone was removed at 80 °C for about 30 min. Then 2.5 M NaOH was added to adjust the pH of the solution to about 10. Next, the mixture was heated in a household microwave oven (Midea China KD23B-C, 2.45 GHz, 700 W),

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with 2.45 GHz microwave radiation of 30% power for 20 min and the mixtures were cooled to room temperature. Finally, the black product was separated by centrifugation, washed with acetone and distilled water in sequence and dried at 373 K overnight in a vacuum oven and then the PtRu/MWCNT (20 wt% Pt) catalysts were obtained.

2.2. Measurement

Electrochemical reactivity of the catalysts was measured by cyclic voltammetry (CV) using a three-electrode cell at the CHI660C electrochemical workstation (USA). The working electrode was a gold plate covered with a thin layer of Nafion-impregnated catalyst. As a typical process, about 1 mg of catalyst sample was ultrasonically mixed with Nafion EG solution to form homogeneous ink which was cast on the gold plate. Pt gauze and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. All potentials in this report are quoted versus SCE. CV test was conducted at 50 mV s^{-1} in a solution of 1 M HClO_4 and 1 M CH_3OH , potential ranging from -0.2 to 1.0 V. CO stripping experiments were performed as follows: after purging the solution with N_2 gas for 20 min, gaseous CO was bubbled for 20 min to allow adsorption of CO onto the electro-catalysts while maintaining a constant voltage of 0.1 V versus SCE. Excess CO dissolved in solution was purged out with N_2 for 20 min and CO stripping voltammetry was recorded in 1 M HClO_4 solution at a scan rate of 10 mV s^{-1} . The electrochemical measurements were conducted under 25°C .

The morphology of PtRu/MWCNT composites was investigated using transmission electron microscopy (TEM, JEOL model JEM-1200EX). The X-ray diffraction (XRD) analysis was performed using the Rigaku X-ray diffractometer with $\text{Cu K}\alpha$ radiation source. The 2θ angular regions between 20° and 90° were explored at a scan rate of 6° min^{-1} with step of 0.02° .

3. Results and discussion

3.1. TEM analysis of the PtRu/MWCNT composites

The typical TEM image of the PtRu/MWCNT catalysts is shown in Fig. 1. TEM image of the isolated product revealed round PtRu present at moderately high density and with fairly even, non-

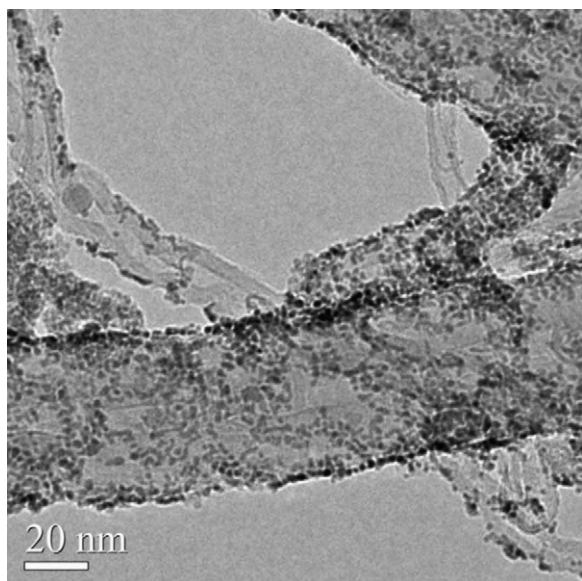


Fig. 1. HRTEM image of PtRu/MWCNT composites.

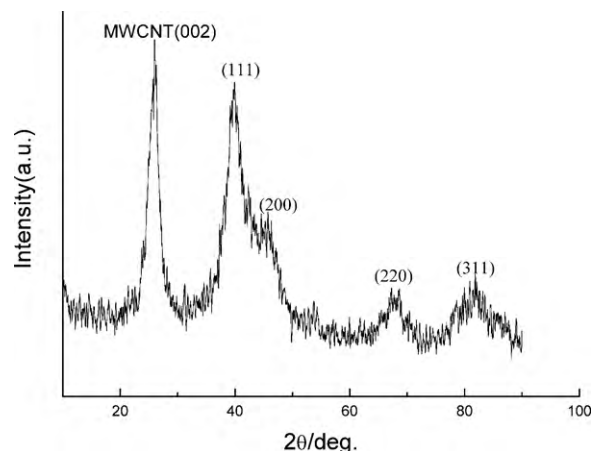


Fig. 2. Powder X-ray diffraction (XRD) pattern of PtRu/MWCNT composites.

ordered distribution along the walls of multi-walled nanotubes. A size distribution obtained from microscopy images indicated that PtRu ranged in diameter from 2.0 to 5.0 nm, with mean diameter of 3.4 nm. The advantage of our method is that size of the resulting PtRu nanoparticles is very small and the distribution is also quite uniform. The formation of small size of PtRu nanoparticles is due to the presence of imidazolium ionic liquid. The complete coating of supramolecular aggregates of imidazolium ionic liquid on PtRu nanoparticles keeps them well separated from each other [20].

3.2. XRD analysis of PtRu/MWCNT composites

Fig. 2 shows the X-ray diffraction patterns obtained from the microwave synthesized PtRu/MWCNTs catalysts. The diffraction peaks at 26.5° can be attributed to the graphite-like structure (002) of the CNTs. The results also show that the PtRu on MWCNT supports has a face centered cubic structure and has major peaks at around 39.7° (1 1 1), 46.2° (2 0 0), 67.4° (2 2 0) and 81.2° (3 1 1). The mean particle size can be estimated to be about 3.4 nm using Scherrer's formula based on the (2 2 0) peak, in good agreement with the results by the TEM image. It is well known that the smaller metal particles exhibit higher electrocatalytic activity because of their higher specific surface area. The sample of microwave synthesized PtRu/MWCNTs with ionic liquid support has a smaller particle size. The results suggest that ionic liquid contributes to the formation of small PtRu particles in the microwave-heated process.

3.3. Electrochemical properties of PtRu/MWCNT composites

The activities of the PtRu/MWCNT catalysts in the electrooxidation of methanol were investigated in a half-cell reaction. For comparison, the catalysts of PtRu/C were also studied under the same experimental conditions. Fig. 3 shows the cyclic voltammograms of the 1.0 M $\text{CH}_3\text{OH} + 1.0 \text{ M HClO}_4$ solution at the PtRu/MWCNT and PtRu/C electrode. For PtRu/C electrode, two oxidation peaks of CH_3OH can be observed. One is located at 0.62 V in the positive scan direction and its peak current density is 6.71 mA cm^{-2} . Another is at 0.42 V in the negative scan direction with 2.33 mA cm^{-2} peak current density. For PtRu/MWCNT electrode, two oxidation peaks of CH_3OH were also observed. Their peak potentials are similar to those at PtRu/C electrode. However, their peak currents are 10.06 and 3.42 mA cm^{-2} , respectively, which are larger than that at the PtRu/C electrode. Therefore, it can be concluded from the above cyclic voltammetric results that the electrocatalytic activity of the PtRu/MWCNT catalyst for the methanol oxidation is better than that of the PtRu/C commercial catalysts.

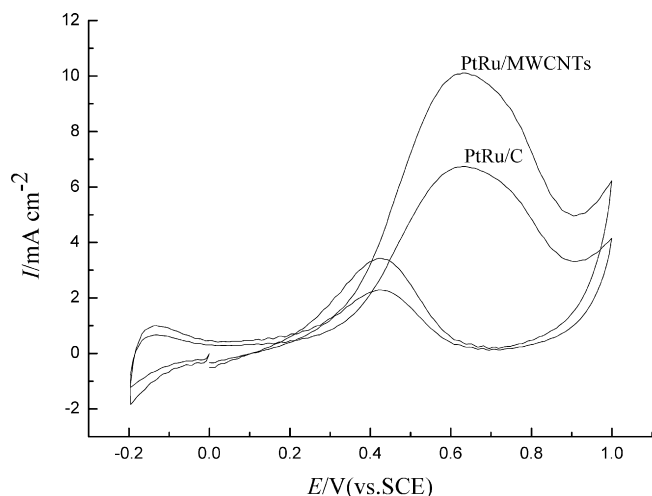


Fig. 3. Cyclic voltammograms of 1 M CH₃OH in 1 M HClO₄ at PtRu/MWCNT and commercial PtRu/C catalysts. Scan rate: 50 mV s⁻¹.

Chronoamperometric technique is an effective method to evaluate the electrocatalytic activity and stability of catalyst materials. Fig. 4 shows the typical current density–time responses of PtRu/MWCNT and PtRu/C catalysts for methanol electro-oxidation. Before the chronoamperometry was performed each time, the electrolyte (1 M HClO₄ + 1 M CH₃OH) was deaerated with N₂ for 30 min. In principle, all of them present a gradual current decay before a steady current status was attained, which was attributed to the formation of some Pt or Ru oxides and/or adsorbed intermediates in methanol electrooxidation reaction. As expected, the methanol oxidation current of PtRu/MWCNT catalysts was evidently higher than that of PtRu/C catalysts. In other words, PtRu/MWCNT catalysts showed superior electrocatalytic performance including higher catalytic activity and better stable life for methanol oxidation than that of PtRu/C catalysts.

CO stripping voltammetry is commonly used to test the catalytic activity of an electrocatalyst for electrochemically oxidizing adsorbed CO on the catalyst. Usually, the lower the onset potential and peak potential for the CO_{ads} electrooxidation, higher is the activity of the catalyst for the electrooxidation of the CO_{ads}. Fig. 5 shows the CO_{ads} stripping scans recorded on electrodes of PtRu/MWCNT and PtRu/C. It is observed that the adsorbed CO on PtRu/MWCNT and PtRu/C had been completely oxidized in a single scan, and no CO oxidation is monitored during the second

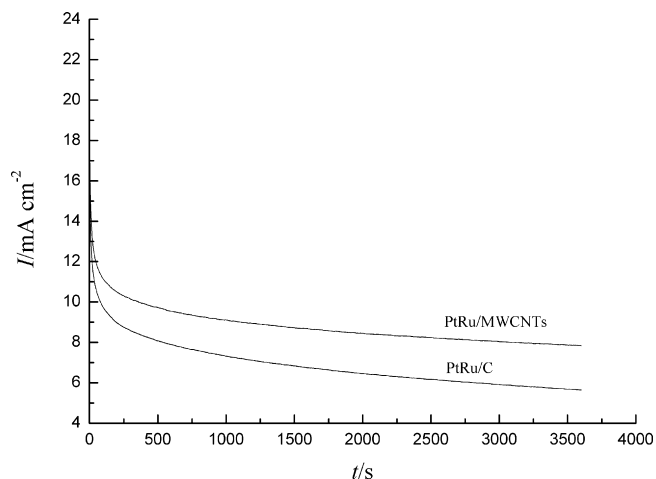


Fig. 4. Chronoamperometry curves for PtRu/MWCNT and PtRu/C in 1 M HClO₄ + 1 M CH₃OH at 0.45 V.

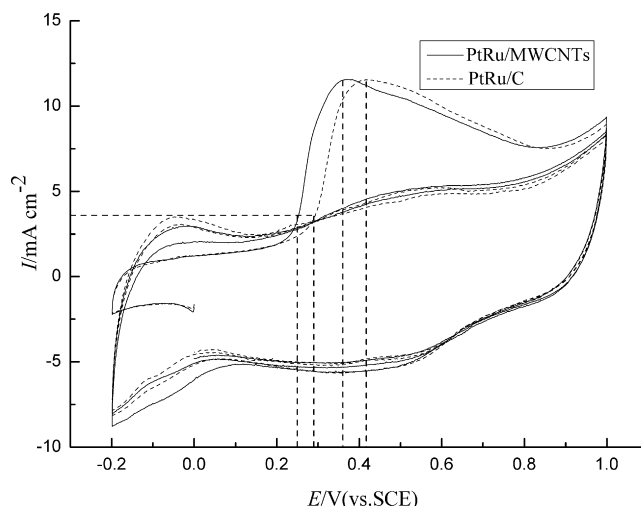


Fig. 5. CO stripping curves for PtRu/MWCNT and PtRu/C in 1 M HClO₄. Scan rate: 20 mV s⁻¹.

scan for the two catalysts. The onset potential for CO_{ads} electro-oxidation on PtRu/MWCNT and PtRu/C is 0.24 and 0.29 V versus SCE, respectively, while the peak potential for CO_{ads} electro-oxidation on PtRu/MWCNT and PtRu/C is 0.37 and 0.41 V versus SCE, respectively, indicating that PtRu/MWCNT catalysts synthesized via a microwave-assisted imidazolium ionic liquid method leads to an enhanced catalytic activity for CO_{ads} oxidation, even higher than that for the commercial PtRu/C catalyst.

From the above results, it can be concluded that the PtRu/MWCNT catalysts prepared using the ionic liquid as the solvent can possess high electrocatalytic activity for the methanol oxidation.

4. Conclusions

In this study, PtRu/MWCNT nanoparticles have been synthesized using a simple and rapid microwave-assisted ionic liquid method. The XRD and TEM showed that the prepared catalysts had narrow particle size distribution. Compared with commercial E-TEK PtRu/C, PtRu/MWCNTs exhibited higher catalytic activity for methanol electro-oxidation at room temperature, and the corresponding CO stripping potential and onset potential shifted to a lower value. The high levels of electrocatalytic activity were mostly due to the formation of the well-dispersed PtRu alloy nanoparticles and the large surface area and structure of the multi-walled carbon nanotubes.

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References

- [1] M.P. Hearsh, G.A. Hards, *Platinum Met. Rev.* 40 (1996) 150–159.
- [2] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangapani, E.S. Smotkin, T.E. Mallouk, *Science* 280 (1998) 1735–1737.
- [3] T.S. Ahmadi, Z.L. Wang, T.C. Green, A. Henglein, M.A. El-Sayed, *Science* 272 (1996) 1924–1926.
- [4] J. Turkevich, G. Kim, *Science* 169 (1970) 873–879.
- [5] K. Esumi, A. Suzuki, A. Yamahira, K. Torigoe, *Langmuir* 16 (2000) 2604–2608.
- [6] W. Huang, X. Tang, Y. Wang, Y. Koltypin, A. Gedanken, *Chem. Commun.* (2000) 1415–1416.
- [7] J.C. Yu, J. Yu, W. Ho, L. Zhang, *Chem. Commun.* (2001) 1942–1943.
- [8] Y. Yin, X. Xu, Z. Zhang, *Chem. Commun.* (1998) 1641–1642.
- [9] K. Mallik, M. Mandal, N. Pradhan, T. Pal, *Nano Lett.* 1 (2001) 319–322.
- [10] Y. Zhou, C.Y. Wang, Y.R. Zhu, Z.Y. Chen, *Chem. Mater.* 11 (1999) 2310–2312.

- [11] K. Soulantica, A. Maisonnat, M.C. Fromen, M.J. Casanove, P. Lecante, B. Chaudret, *Angew. Chem. Int. Ed.* 40 (2001) 448–451.
- [12] K. Esumi, T. Tano, K. Meguro, *Langmuir* 5 (1989) 268–270.
- [13] K.J. Klabunde, Y.X. Li, B.J. Tan, *Chem. Mater.* 3 (1991) 30–39.
- [14] M.T. Reetz, W. Helbig, *J. Am. Chem. Soc.* 116 (1994) 7401–7402.
- [15] W.Y. Yu, W.X. Tu, H.F. Liu, *Langmuir* 15 (1999) 6–9.
- [16] W.X. Tu, H.Y. Liu, *Chem. Mater.* 12 (2000) 564–567.
- [17] W.X. Tu, H.F. Liu, *J. Mater. Chem.* 10 (2000) 2207–2211.
- [18] S. Komarneni, D.S. Li, B. Newalkar, H. Katsuki, A.S. Bhalla, *Langmuir* 18 (2002) 5959–5962.
- [19] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, *Chem. Commun.* (1998) 1765–1766.
- [20] O.P. Khatri, K. Adachi, K. Murase, K.I. Okazaki, T. Torimoto, N. Tanaka, *Langmuir* 24 (2008) 7785–7792.